

Studies in Plant Science, 8



*L.E. Datnoff, G.H. Snyder
and G.H. Korndörfer
(Editors)*



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Silicon in Agriculture

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Preface

Silicon continues to be an anomaly, an under appreciated element, despite decades of research by many scientists. Most plant scientists still view it as not being essential for plant function. Nevertheless, in certain plant species, silicon is absorbed as $\text{Si}(\text{OH})_4$ from soil in large amounts that are higher than that of “essential macronutrients”. For example, the uptake of silicon is about twice that of nitrogen in rice. Although not considered essential for plant growth and development, silicon can benefit plant growth through greater yields (cucumber, rice and sugarcane). Silicon also can be very useful, especially when these plants are under abiotic or biotic stress. Silicon may enhance soil fertility, improve disease and pest resistance, increase photosynthesis, improve plant architecture, regulate evapotranspiration, increase tolerance to toxic elements such as Fe and Mn, and reduce frost damage.

Recognizing that it was time to bring researchers together from around the world to better understand this silicon anomaly and to discuss the role of silicon for promoting plant health and soil productivity, the first international conference on Silicon in Agriculture was organized by the University of Florida and the Federal University of Uberlandia. Over 90 participants representing scientist, growers and producers of silicon fertilizers attended the conference. Sixty-two papers (22 invited oral, 40 volunteered poster) were presented. This book contains the full text of the invited papers and abstracts of the posters. As such, it represents a consolidated summary of our current understanding of silicon in agriculture. In preparing the manuscripts, the authors were asked to summarize their very latest published and unpublished data and knowledge. In particular they were encouraged to speculate on the implications of their knowledge and propose hypotheses for testing and to suggest further areas for research. We hope that this combination of in-depth chapters and abstracts will serve as a reference and guide for silicon researchers in agriculture for years to come.

Although the SI system (Système International d’Unités) for reporting measurements is used by all authors, certain colloquialisms inherent to the various countries involved in the conference appear. Thus, Mg, MT, and T all refer to the metric ton (1000 kg), and TC refers to tons of sugarcane. Concentrations of nutrients in plant tissue may be cited as % or as g kg^{-1} , and the relationship of one measurement to another may be given as X/Y or as $X Y^{-1}$ (e.g. g/kg or g kg^{-1}). Variations in the spelling of English-language words inherent to certain countries also appear (e.g., fertilizer, fertiliser). We hope that rather than causing confusion, the reader will regard these inconsistencies as an interesting aspect of international collaboration.

We could never have brought so many people together from so many countries without the assistance of several dedicated people and sponsors. Drs. Emanuel Epstein and Richard Belanger helped in identifying speakers and participants. Financial and logistical support was generously provided by University of Florida-IFAS, United States Department of Agriculture-Foreign Agricultural Service, Calcium Silicate Corporation, Rhodia, and PQ Corporation.

We also would like to thank Dr. Christopher W. Deren, Ms. Janice Collins and Ms. Brenda

Rutherford for their helpful reviews and Mr. Norman Harrison for helping with preparation of figures. Ms. Collins also was instrumental in collating and formatting the text.

Finally, we would like to thank the conference participants and the authors. It is through their interest, dedication and efforts that the conference and this volume were such a success.

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Chapter 1

Silicon in plants: Facts vs. concepts

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The facts of silicon (Si) in plant life are one thing; the concepts regarding Si in plant physiology are another thing altogether. Most terrestrial plants grow in media dominated by silicates, and the soil solution bathing roots contains Si at concentrations exceeding those of phosphorus (P) by roughly a factor of 100. Plants absorb the element, and their Si content is of the same order of magnitude as that of the macronutrient elements. The general plant physiological literature, however, is nearly devoid of Si. The reason for this marked discrepancy is the conclusion that Si is not an “essential” element because most plants can grow in nutrient solutions lacking Si in their formulation. Such Si-deprived plants are, however, experimental artifacts. They may differ from Si-replete plants in (i) chemical composition; (ii) structural features; (iii) mechanical strength; (iv) various aspects of growth, including yield; (v) enzyme activities; (vi) surface characteristics; (vii) disease resistance; (viii) pest resistance; (ix) metal toxicity resistance; (x) salt tolerance; (xi) water relations; (xii) cold hardiness; and probably additional features. The gap between plant physiological facts and plant physiological concepts must be closed. The facts of Si in plant life will not change; hence it is the concepts regarding the element that need revising.

1.1. INTRODUCTION

The organizers of this conference are to be highly commended for getting so many of us together, who are interested in Si, to exchange information. Two main features of Si in agriculture make this meeting an important event. The first is that, as pointed out recently (Epstein 1994, 1999, 2000), many plant scientists pay little attention to this element because it is not included in the list of elements considered generally essential for plants, i.e., it is not considered a nutrient. That dismissal of the element from consideration is unjustified, being based on an inadequate definition of what constitutes an essential element (Epstein, 1999). The second reason for considering this conference so important in agricultural and crop science is that we, who have indeed invested time and effort in studying biological aspects of Si, have tended to specialize. Some of us study the role that Si plays in bestowing disease resistance on plants; others are interested in phytoliths, those remarkable that form in plant cell walls and elsewhere; still others are impressed by the importance of Si in mitigating metal toxicities. Silicon plays a role in preventing or minimizing lodging of cereal crops, a matter of great interest to agronomists. Both agronomists and horticulturists use Si as a fertilizer for crops on certain soils and report that its

use increases yields and sometimes, quality -- key factors in crop production. This list of the roles that silicon plays in the life of plants is far from complete, as shown below.

We should not chide ourselves too harshly for our tendency to specialize in this or that role of silicon in plant science and agriculture. As already mentioned, silicon is involved in a great number of structural and dynamic aspects of plant life, and its roles are surprisingly diverse; many of them show no obvious relation to each other. That diversity of functions reinforced our tendency to specialization, which as scientists, we are prone to in any departure.

Be that as it may, both the general disregard of silicon in plant physiology and our own tendency to specialize in some aspect of it make this meeting a significant event in plant and crop science. The American humorist Will Rogers said: "Everybody is ignorant, only on different subjects." Through this meeting and its proceedings, a good many agricultural scientists, ourselves included, will be less ignorant about different subjects having to do with this baffling element.

1.2. THE MEDIUM: THE SOLID PHASE

1.2.1. The medium: The solid phase

The medium or substrate of agriculture is soil. Soil in turn is derived from rock, and most rocks and the soils derived from them are silicates and aluminosilicates. The composition of the Earth's crust is given in Table 1.1, after Singer and Munns (1999). For granite rock, the percentage of silica, SiO_2 , is given by Jenny (1980) as 74.51. This exceeds the second highest value, 14.45%, for aluminum oxide, Al_2O_3 , by a factor of 8.7, on a molecular basis. This quantitative dominance of silicon is most pronounced in acid igneous rocks such as granite, but silicon constitutes a large fraction of most rocks (Jenny, 1980).

Rocks weather into particles categorized by their size, into gravels, sands, silts, and clays; clays being particles less than $2\text{ }\mu\text{m}$ in size. The size of the particles making up soil is exceedingly important for the rate at which their silicon goes into solution (King, 1947), and indeed, in the entire complex of reactions termed weathering. This is so not only because purely chemical reaction rates increase with the increase in surface area, important as that is, but even more significant is the fact that the huge surfaces of mineral matter ranging from parent rock to clay form the habitat of an immense number of microorganisms, ranging from 10^3 to 10^9 cells/ cm^3 (Banfield et al., 1999). These authors have used the lichen-mineral microcosm to study microbe-mineral interactions. As lichens grow on rocks, this surface-based system lends itself to detailed

Table 1.1
Elemental Composition of the Crust of the Earth

Element	Mass (%)	Volume (%)
O	47	94
Si	28	1
Al+Fe	13	1
Other	11	4

Reprinted from: Singer and Munns, 1999.

study of the mineral-biological interface without the profound disturbances introduced when the belowground soil-biological interface is investigated (see below, *Roots In Their Medium: Soil*). Figure 1.1 shows four zones, ranging from parent rock to clays with photosynthetic microbial populations.

The lowest stratum or zone, #4, consists of unweathered rock; the next higher zone, #3, has clay minerals and its water contains solutes. In zone #2 microbial life is pronounced, and intimately associated with mineral surfaces and organic constituents such as organic acids and polymers. Finally, the topmost zone, #1, exposed to light, is the habitat of photosynthetic organisms, both free-living and symbiotic such as lichens.

Banfield et al. (1999) demonstrate that microbial populations are an integral agent in an exceedingly dynamic system, which in purely chemical terms, has often been treated as fairly inert. [A good case can be made for the proposition that mineral, siliceous surfaces provided the templates for the assembly of the earliest bio-organic molecules which led to the formation of replicating polymers and the emergence of life on Earth (Smith, 1998, 1999; Parsons et al., 1998; Smith et al., 1999). These prebiotic events on mineral surfaces must have occurred long before the emergence of true living organisms, that is, more than 3.85×10^9 years ago (Holland, 1997) -- a surprisingly short time after the formation of the Earth, about 4.55×10^9 years ago.]

Throughout the weathering process of siliceous parent material, the quantitative dominance of silicates and aluminosilicates is preserved, but not without considerable modification. This is, shown in Figure 1.2, taken from a paper by the organizers of this meeting (Savant et al., 1997a).

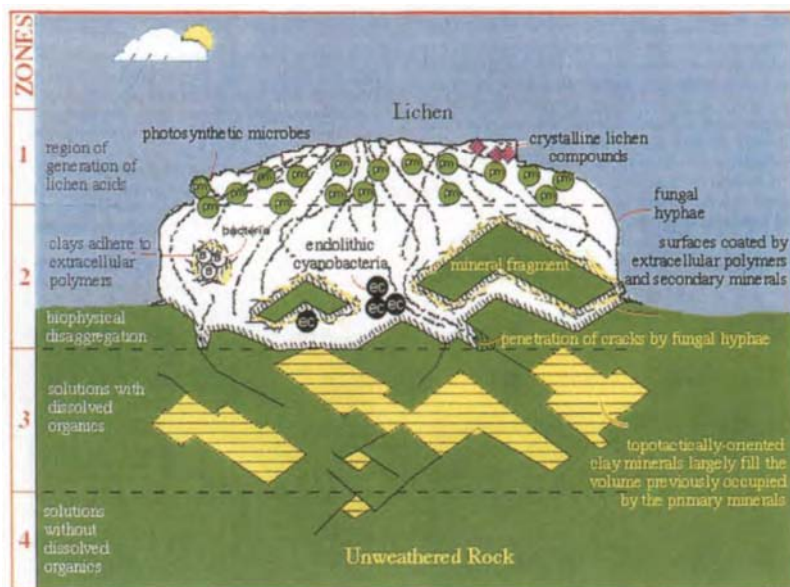


Figure 1.1. Model of four weathering zones of mineral weathering and the impact of microbes. See text for explanation. From Banfield et al. (1999). Reproduced by permission from Proceedings of the National Academy of Sciences, USA. vol. 96, ©1999 by The National Academy of Sciences of the United States of America.

Acid weathering is a progressive desilicification of the soil system. The generally fertile Mollisols of grasslands, with high proportions of silicon, weather progressively as shown in the figure. Highly weathered soils are the Ultisols and Oxisols. They are common in warm to hot, humid areas, where they are subject to intense leaching. They tend to be highly desilicified, acidic, low in essential nutrient elements, and on account of their acidity, high in soluble aluminum. All this said, there are soils in which silicon plays a subordinate role, such as those derived from calcareous parent material, and organic soils.

It is the mineral matrix of soils that is the ultimate reservoir that plant roots draw upon in their absorption of nutrients and other elements. The immediate source however, of these elements is the soil solution. Plants cannot grow without water. Where and when there is water, the solid phase of the soil undergoes solution, ion exchange, complexation, and a host of other interactions with the liquid phase, and with the part of the biosphere that resides there, as already discussed. Thus, the terms soil water and soil solution are synonymous.

1.2.2. The medium: The liquid phase

All soil minerals undergo chemical and biological weathering. These processes vary greatly in their rates, but the net effect is that silicon goes into solution, i.e., it becomes a solute in the soil solution. There is abundant evidence that its chemical form in the soil solution is silicic acid, (H_4SiO_4) (Faure, 1991; Langmuir, 1997). The simplest source of silicic acid is quartz, SiO_2 ,

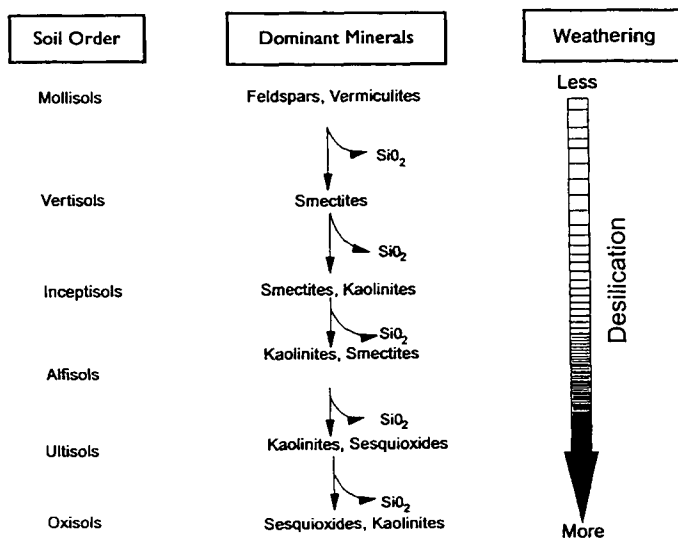


Figure 1.2. Simplified acid weathering sequence in soils. See text for explanation. From Savant et al. (1997a). Reproduced by permission from *Advances in Agronomy* vol. 58, © 1997 Academic Press, Inc.

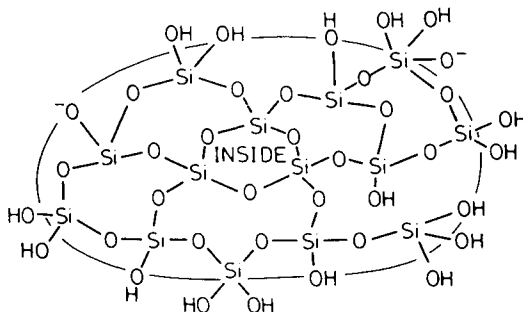


Figure 1.3. Schematic illustration of the nature of amorphous hydrated silica. See text for explanation. From Williams (1986). Reproduced by permission from Silicon biochemistry, © 1986 John Wiley & Sons, Chichester.

which reacts with water to form H_4SiO_4 as shown by the equation:



Quartz is sparingly soluble and therefore, does not control soil solution Si. The equilibrium constant of the above reaction is $K = 10^{-4.01}$. Hence the activity of silicic acid in solution in contact with quartz is less than 0.1 mM. The concentration of silicic acid in most soil solutions is higher than this, as a result of its being derived from aluminosilicates such as feldspars and micas. When the soil solution becomes supersaturated in silicic acid, amorphous rather than crystalline silica is formed. The structure of amorphous hydrated silica is shown in Figure 1.3 (Williams, 1986). The author draws attention to the different numbers of OH groups on different silicons, the absence of structural repeat, and the low surface charge. Amorphous silica is much more reactive than crystalline silica. At equilibrium, the concentration of silicic acid, in contact with amorphous silica is 1.8 mM. For a thorough discussion of the solubility of soil minerals, see Langmuir (1997). Amorphous silica is also formed in many plants in the form of phytoliths ("opal"). This biogenic silica eventually finds its way into the soil.

Actual concentrations of silicic acid in soil solutions are for the most part lower than that 1.8 mM value for several reasons. Both green algae belonging to the Bacillariophyta (the soil diatoms) and plant roots absorb silicic acid. The roots of many plants absorb silicic acid at rates high enough to keep the Si concentration lower than it would be as a function merely of the solubility of the various soil silicates. By and large, the rates of dissolution of soil silicate minerals are low (White and Brantley, 1995). In addition, silicic acid is adsorbed to soil minerals (Beckwith and Reeve, 1963; Bruun Hansen et al., 1994) and Si reacts with various aluminum compounds to form hydroxyaluminosilicates, HAS (Wada, 1989; Exley, 1998), and the concentration of silicic acid in the soil solution is thereby lowered. A survey of the literature suggests that the common range of concentrations of Si in soil solutions is 0.1-0.6 mM, although both lower and higher values may be encountered (Epstein, 1994).

1.3. ROOTS IN THEIR MEDIUM: SOIL

As suggested above, the solid, aqueous, and biological complexity of the soil system is nothing less than mind boggling. Its study is difficult not only on that account; but in addition, because of its inaccessibility. Being dominated by a solid phase, it is a refractory material to deal with; and experimental procedures for its study very often disturb the very materials or processes being investigated (Epstein, 1977, 1990).

Ultimately, the intricate complexity of the belowground ecosystem depends on carbon photosynthetically acquired by plants, much of it being delivered to their roots. Living roots exude organic solutes into soil, and upon their death, become the substrate for the microflora referred to above. Jenny (1980) has visualized the root-soil boundary region (Figure 1.4). The plasmalemma (Pl) is the outer boundary membrane of the cell. It is appressed against the cell wall, composed of cellulose microfibrils (m), zones of pectic gel (p), and the apoplastic space (f) the site of all these components. The apoplastic space is the volume external to the outer cell membrane, that is, the space occupied by the cell wall and intercellular spaces. In roots, part of it is contiguous with the soil solution (ss), as shown in the figure. A virus (V) is shown, as are clay particles (Cl) and a bacterium (B). Not shown in this simplified figure is a host of structures, entities, and their interactions, recently discussed by McCully (1995, 1999).

In addition to roots, a major contributor of photosynthate to soil is the plant shoot. Through leaf fall during the life of plants and their eventual death, their photosynthate in all its forms is delivered to the soil and becomes substrate for its microflora. All consumers of plants, be they herbivores or carnivores, are ultimately products of photosynthetic carbon fixation, and from their excretions and eventual death, their carbon is delivered into the soil, to become grist for the mills of the soil microorganisms, agents of Si mobilization. Direct effects of plants on mineral weathering have been discussed by Kelly et al. (1998); and Markewitz and Richter (1998) have given an account of an investigation of Al and Si cycling in a South Carolina forest ecosystem.

In view of the large importance of soil microorganisms in mineral degradation discussed above,

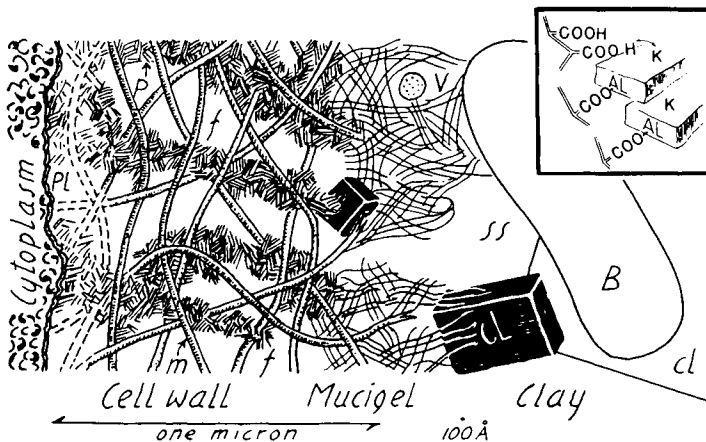


Figure 1.4. The root-soil interface. Note the scale. See text for explanation. From Jenny (1980). Reproduced by permission from The Soil Resource, © 1980 Springer-Verlag, New York.

including the solubilization of Si, what all this means is that ultimately it is green plants that supply much of the energy for these transformations, and hence, for the presence in soil solutions of such high concentrations of Si as have been referred to, on the order of 0.5 mM, though quite variable.

The interplay between silicate minerals and the biosphere, driven ultimately by the photosynthesis of green plants, amounts to a Si cycle (Figure 1.5). This author believes that an analysis of the biogeochemical cycle of Si suggests that the biosphere may face a deficiency of Si available for its functioning. Indeed, Savant et al. (1997b) have argued specifically that depletion of soil Si available for absorption may be a cause of declining rice yields. But not to lose sight of the grand picture, Exley (1998) reminds us that the world's oceans, which are sinks for Si, are a part of the biogeochemical Si cycle; see also Smetacek (1999).

1.4. SILICON TRANSPORT AND BIOCHEMISTRY

For the nutrition of mankind, wheat (*Triticum aestivum*) and rice (*Oryza sativa*) are the premier crops, and other grains such as barley (*Hordeum vulgare*) and oats (*Avena sativa*) make large contributions. These cereal crops are Si accumulators, and may suffer a variety of ills when the supply of soil Si available for absorption is low. The absorption of Si by these and other crops

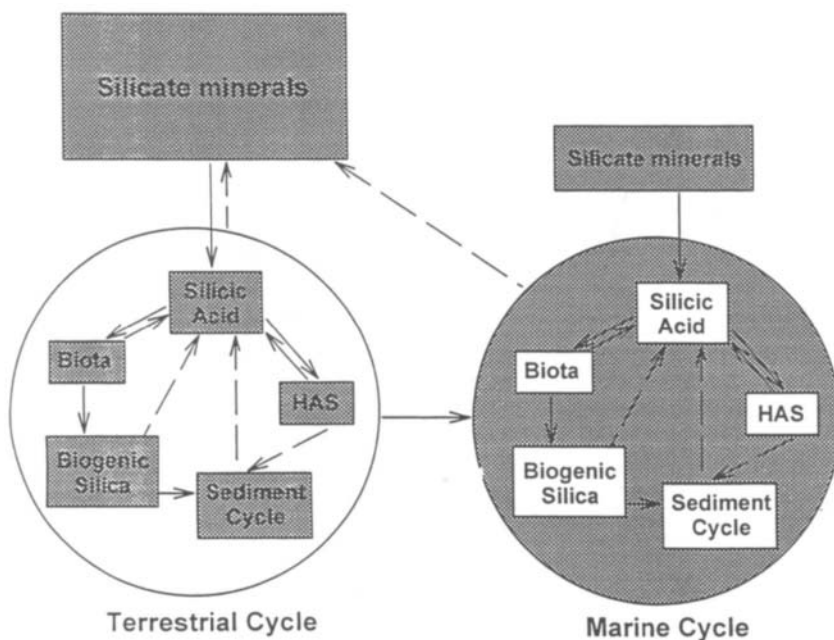


Figure 1.5. The biogeochemical cycles of silicon. From Exley (1998). HAS: hydroxy-aluminosilicates. Reproduced by permission from the Journal of Inorganic Biochemistry vol. 69, © 1998 Elsevier Science, Inc.

should therefore be a matter of intense interest, as is the case for such elements as phosphorus, potassium, and indeed, all elements accorded the status of nutrients.

Nevertheless, Jones and Handreck (1967), in their groundbreaking review, could not report definitive evidence concerning the physiology of Si transport by any species, nor of Si biochemistry. Progress had been made by the time Raven (1983) reviewed the subject. As this author is a contributor to the present proceedings, the subject will be discussed here but briefly. By 1983, the date of Raven's review, there was available a wealth of information on the physiology of the transport of plant nutrient and other ions (Bloom and Taylor, 2000). There did not, however, exist a body of knowledge about the transport of Si even remotely commensurate with what was then already known about ion transport. The reason for this discrepancy in knowledge was not that Si exists in solution, in the usual range of pH values, as silicic acid, which is not an ion but a neutral solute. On the contrary, the review by Tanner and Caspari (1996) presents ample evidence that sophisticated knowledge about the transport of neutral organic solutes including sugars was developing along with that concerning ions.

No, the reason for the paucity of knowledge concerning the absorption of Si by higher plants was the general disinterest in the element by plant physiologists already mentioned in the introduction (Epstein, 1994, 1999). The element was mainly studied in the context of agriculture, especially its role in minimizing damage to crops from disease organisms and pests. But while study of the absorption of Si has not kept pace with transport studies in general, neither has it been dormant. As for Si biochemistry, it has been a vexing problem (Epstein, 1999), but as will be seen, progress is being made.

Barber and Shone (1966), in experiments with solution cultures, found that at an external Si concentration of 0.07 mM, bean plants, *Phaseolus vulgaris* 'The Prince,' absorbed the element to the extent that the concentration of it in the xylem sap (measured as the exudate of detopped plants) greatly exceeded that of the external solution. The results indicated that the plants absorbed Si against the concentration gradient.

The same conclusion was reached by Jarvis (1987) in experiments with perennial ryegrass, *Lolium perenne* L. 'S23' and wheat, *Triticum aestivum* L. 'Sappo.' Jarvis used the depletion of Si from the culture solution to measure its absorption by plants, a common technique. He found that absorption of Si greatly exceeded the value to be expected if Si were absorbed in tandem with the flux of water into and through the plants. [The concept of Si moving passively into at least certain plants, along with the water, recurs in the literature. Jarvis cites earlier investigations by authors who supported or questioned that proposition; for critical discussions, see Raven (1983) and that author's contribution to these proceedings.]

In her Master's Thesis, Stookey (1995) reports on her experiments on Si uptake by rice, *Oryza sativa* 'M102,' and some additional ones on cucumber, *Cucumis sativus* 'Corona.' As in the earlier studies discussed above, Si transport by rice was not found to be accountable by transpirational water flux. Inhibitory conditions such as hypoxia and low temperatures, as well as exposure of the roots to KCN, greatly diminished the rate of Si uptake; all these findings being consistent with the hypothesis of a metabolically active system of Si transport. Kinetic studies suggested that system to have a low affinity for Si, the K_m value being 0.587 mM.

The absorption of Si by wheat plants, *Triticum aestivum* L. 'Yecora Rojo,' was investigated by Rafi and Epstein (1999). Using the depletion technique, they found rates of Si absorption, from solutions initially at 0.5 mM, on the order of 2.7 μmol per gram fresh weight roots per hour -- rates that are comparable to those for phosphate, potassium, and nitrate, as found by various investigators. Given time, the depletion of the solution of Si proceeded until it could no longer

be detected (less than 1 μM). An active transport of Si is to be inferred, with a high affinity for the element.

As observed often in earlier investigations, translocation of Si to the shoots of the plants was rapid. In the leaves, trichomes were notable sites of Si accumulation, with marked effects on their stiffness (Rafi et al., 1997). Reports exist in the literature that mechanical strength and surface properties of plants are influenced by Si; but the investigation just cited is the first one in which such an effect has been quantified in physical terms (the friction force).

In its absorption and transport, Si often interacts with the absorption and transport of other elements. In an agricultural context, those interactions in which Si interferes with the absorption or partitioning within the plant of elements present in the soil at concentrations high enough to be damaging to the plants are particularly noteworthy.

Toxicities of Al and other metal ions in the soil solution, common in highly leached, acidic, and desilicified soils, are often mitigated by Si; and experimental work with solution cultures has shown the same effect (Corrales et al., 1997; Cocker et al., 1998).

Salinity is another instance of potentially damaging ions (sodium (Na), chloride), and evidence indicates that Si may retard or minimize Na uptake by plants (Liang, 1999; Yeo et al., 1999).

Though beyond the immediate scope of proceedings devoted to Si in agriculture, the transport of Si by diatoms must be mentioned. Its study has advanced much farther than that of Si transport in higher plants. Indeed, Hildebrand et al. (1997, 1998) have characterized a gene family of Si transporters in the diatom, *Cylindrotheca fusiformis*.

If the evidence is valid that both in higher plants and in diatoms, Si is actively transported, then the question whether Si can associate with organic entities has to be answered in the affirmative. It is generally understood that solute transport as discussed above involves the interaction of the solute with membrane constituents such as carriers or channels (Epstein, 1973; Tanner and Caspari, 1996), and for active transport of Si, the same conclusion must hold. That Si-transporter association would be temporary, to be followed by the dissociation of this entity and the release of the Si, almost certainly as silicic acid, H_4SiO_4 , into the trans-membrane compartment.

Another line of investigation has been pursued by plant pathologists. It has long been known that Si plays a role in the defenses plants mount against disease organisms (Jones and Handreck, 1967). Although the sheer incrustation of cell walls with phytoliths (amorphous hydrated silica bodies, or "opal") may indeed play a role as a defense mechanism (Blaich and Grundhöfer, 1998), that is not the whole story. Chérif et al. (1992, 1994), Fawe et al. (1998), and Fawe, Menzies, and Bélanger (1999, private communication) have provided increasingly good evidence that Si elicits the synthesis of low-molecular-weight metabolites with anti-fungal activity, specifically, phytoalexins. Fawe and collaborators relate the phenomenon to a particular type of induced resistance to pathogens, viz. systemic acquired resistance (SAR). Carver et al. (1998) contribute further evidence of a possible role of Si in the resistance of oat plants to attack by a powdery mildew fungus. In the epidermis of Si-deprived plants, phenolic compounds accumulated. Silicon-deprived leaves showed higher activity of phenylalanine ammonia lyase (PAL) than did Si-replete leaves. Silicon deprivation may have been compensated for by the rise in PAL activity, that in turn contributing to the resistance of the plants to the fungus.

There is other evidence for intimate associations or complexations between Si and both carbohydrates and proteins. Harrison and Lu (1994), working with *Phalaris canariensis* (canary grass) and *Equisetum talmateia* (great horsetail), provided evidence for both intrasilicic protein and associations between Si and carbohydrate polymers; the latter apparently playing a role in Si particle formation. These structures and processes were associated with the cell wall. Inanaga

and Okasaka (1995) and Inanaga et al. (1995) investigated the role of Si (and calcium) in cell walls of rice, *Oryza sativa* 'Koshijiwase', with particular reference to complexes between these mineral elements and phenol- or lignin-carbohydrate complexes. They concluded that silica may be instrumental in forming cross-links between lignin and carbohydrate, via complexations with phenolic acids or aromatic rings.

Evidence obtained from diatoms is to the effect that a 200-kDa protein is associated with a silica-based substructure of the cell wall (Kröger et al., 1997). Turning to investigations dealing, not with plants, but sponges (Porifera), Shimizu et al. (1998) discovered silicateins (silica proteins). The most abundant one, silicatein α , resembles the members of the cathepsin L and papain family of proteases. Cha et al. (1999) showed by means of *in vitro* experiments that silicatein filaments and subunits are instrumental in the polymerization of silica and silicones.

Finally, momentarily leaving biology altogether, there is exciting new evidence being presented in these proceedings that stable 5- and 6-coordinated Si complexes involving polyols can readily be produced in aqueous solutions (Kinrade et al., 1999). These authors point out that Si biochemistry had all but been dismissed by some authors. They interpret their own findings of the ease with which stable silicon-polyolate complexes can be obtained in aqueous solution as evidence for the likelihood of roles for Si in biology. The manifold instances of demonstrated or inferred organic and biochemical complexes of Si discussed in this section lend force to that view.

1.5. SILICON IN PLANTS: FACTS VS. CONCEPTS

On account of recent reviews referred to in this essay (Epstein, 1994, 1999), no attempt has been made to review again the entire gamut of topics bearing on the subject of Si in plants. Rather, what has been presented and documented is an argument: Si is a ubiquitous and prominent constituent of plants and their environments, and plays a multitude of roles in plant life and crop performance. The time is at hand for much greater attention to this enigmatic element in plant science than it has received. Invigorated research and development on the role of Si in plant biology will yield handsome returns in knowledge and its application in the field. A mere list, surely incomplete, of plant features, structures and processes, all documented in the literature, shows the significance of the element in the life of plants and the performance of crops.

- Essentiality: diatoms (Bacillariophyta); horsetails or scouring rushes (Equisetaceae).
- Enhancement of growth and yield.
- Promotion of upright stature and resistance to lodging.
- Role in favorable exposure of leaves to light; hence promotion of photosynthesis.
- Effects on surface properties.
- Resistance to disease organisms.
- Resistance to herbivores ranging from phytophagous insects to mammals.
- Resistance to metal toxicities.
- Resistance to salinity stress.
- Reduction of drought stress.
- Protection against temperature extremes.
- Promotion of nodule formation in a legume.

- Effects on enzyme activities.
- Effects on mineral composition.

Silicon is an integral and quantitatively major component of the soil-plant system that exists in nature and in agriculture. These facts will not change. What has to change, then, is the all too common concept that such a ubiquitous and abundant element as Si, with so many important roles in plant life, can be disregarded in plant biological thinking and experimentation.

ACKNOWLEDGMENTS

I thank Lawrence E. Datnoff for asking me to present this paper at the conference on Silicon in Agriculture, the first gathering on what is bound to be an increasingly important subject of research and application in the agricultural, plant biological, and environmental sciences. I benefitted from discussions with my colleagues, W. H. Casey, R. A. Dahlgren, M. J. Singer, R. J. Southard, and R. J. Zasoski, but bear full responsibility for such flaws as remain in this essay. I am grateful to authors who allowed me to use figures from their publications, as noted in the figure legends. The secretarial staff stinted no effort in assisting me with this project. Finally, Peggy helped in many ways, from proofreading to suggestions on style. To all, my thanks.

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Chapter 2

Silicon as a beneficial element for crop plants

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Silicon (Si) has not been proven to be an essential element for higher plants, but its beneficial effects on growth have been reported in a wide variety of crops, including rice, wheat, barley, and cucumber. Si fertilizer is applied to crops in several countries for increased productivity and sustainable production. Plants take up Si in the form of silicic acid, which is transported to the shoot, and after loss of water, it is polymerized as silica gel on the surface of leaves and stems. Evidence is lacking concerning the physiological role of Si in plant metabolism. Since the beneficial effects of this element are apt to be observed in plants which accumulate Si, the silica gel deposited on the plant surface is thought to contribute to the beneficial effects of Si, which may be small under optimized growth conditions, but become obvious under stress conditions. In this review, the effects of Si under biotic stresses (disease and insect damage) and abiotic stresses including climate stresses (typhoon and cool summer damage), water deficiency stress, and mineral stresses (deficiency of P and excess of P, Na, Mn, N and Al) are discussed.

2.1. INTRODUCTION

More than 60 elements are present in plants growing in soils, although their concentrations vary greatly among plant species and soils. These elements have been classified into essential, beneficial, and toxic elements according to their effects on plant growth. Seventeen elements have been proven to be essential for plant growth. These elements are absolutely necessary for the growth of all plant species under any growth conditions. In contrast, beneficial elements are those having positive effects only in some plant species or under specific growth conditions (Marschner, 1995). Therefore, essential elements represent the universality of the nutritional requirement in higher plants, while beneficial elements reflect the diversity of nutritional requirement. Silicon (Si) is a typical beneficial element. The positive effects of Si have been observed in some plant species such as rice, wheat, and barley, but not in all plant species. Furthermore, the beneficial effects of Si are usually expressed more clearly under stressed conditions. Since plants are always exposed to various stresses during growth, Si

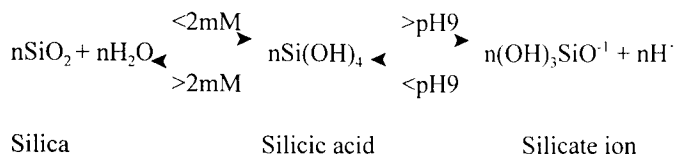


Figure 2.1. Solubility and various forms of silicon

certainly plays an important role in alleviating stresses, ultimately resulting in increased productivity. Since 1955, Si fertilizers have been applied to paddy soils in Japan resulting in a significant increase in rice production (Takahashi et al., 1990). Various Si fertilizers are now widely applied in other countries such as Korea, China, and the USA. In this paper, for better understanding of Si nutrition, we discuss the kinds of crops and the growth conditions requiring Si as a beneficial element.

2.2. CHEMICAL PROPERTY OF SILICON AND SILICIFICATION PROCESS IN PLANTS

Si in soil solution is mainly present in the form of an uncharged monomeric molecule, silicic acid (Si(OH)_4) at a pH below 9.0 (Figure 2.1). At a higher pH (>9.0), silicic acid dissociates into silicate ion ($(\text{OH})_3\text{SiO}^-$). The solubility of silicic acid in water is 2.0 mM at 25°C and polymerization of silicic acid into silica gel, $\text{SiO}_2 \cdot \text{H}_2\text{O}$, occurs when the concentration of silicic acid exceeds 2 mM. The form of Si absorbed by plant roots is silicic acid. After silicic acid is transported to the shoot, it is concentrated due to loss of water and is polymerized to colloidal silicic acid and finally to silica gel with increasing silicic acid concentration. Figure 2.2 shows the various forms of Si in the rice shoot (Ma, 1990). More

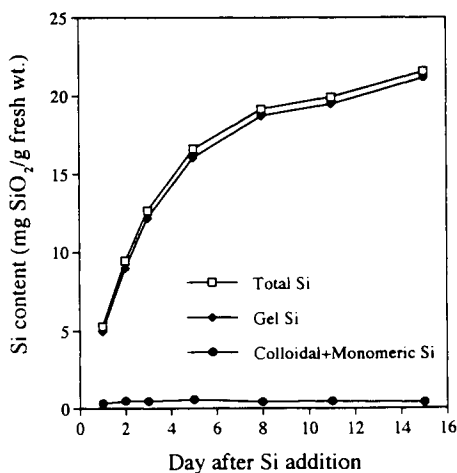


Figure 2.2. Different forms of Si in the shoots of rice cultured in a solution containing 100 ppm SiO_2 as silicic acid.

than 90% of total Si is present in the form of silica gel and the concentration of colloidal plus monomeric Si is kept below 0.3 to 0.5 mg SiO_2/g fresh weight at any sampling time. Similar results were obtained in cucumber leaves although the Si content in cucumber is much lower than that in rice (Ma, unpublished data). Due to undissociation of silicic acid at a physiological pH and polymerization, neither binding to cellular substances nor creation of high osmotic pressure occurs in plants even where SiO_2 is accumulated up to 20% in dry weight.

Si is the only element that does not cause serious injury in excess amounts. Si is deposited as a $2.5\ \mu$ -thick layer in the space immediately beneath the thin ($0.1\ \mu$) cuticle layer, forming a cuticle-Si double layer in the leaf blade of rice (Moshida et al., 1962). There are two types of silicified cells; silica cell and silica body or silica motor cell (Figure 2.3) (Ma, 1990). Silica cells are located on vascular bundles, showing a dumbbell-shape, while silica bodies are in bulliform cells of rice leaves. When the Si content in the rice shoot is below 5% SiO_2 , only silica cells are formed. Silica bodies are formed when the Si content is above 5% SiO_2 and the number of silica bodies increase with increasing Si content in the shoot (Figure 2.4). These facts suggest that the silicification process of cells in rice leaves is from silica cells to silica bodies. In addition to leaf blades, silicified cells are also observed in the epidermis and vascular tissues of stem, leaf sheath, and hull.

No evidence that Si is involved in metabolic processes has been reported previously. Herein, we report that silica gel deposited on the tissue surface may play an important role in alleviating biotic and abiotic stresses, and that accumulation of Si in the shoots is a prerequisite for benefit from Si.

2.3. CHARACTERISTICS OF CROP PLANTS WHICH REQUIRE SILICON AS A BENEFICIAL ELEMENT

2.3.1. Silicon accumulators and nonaccumulators

The Si content in plant shoots varies from 0.1 to 10% Si on a dry weight basis. This large

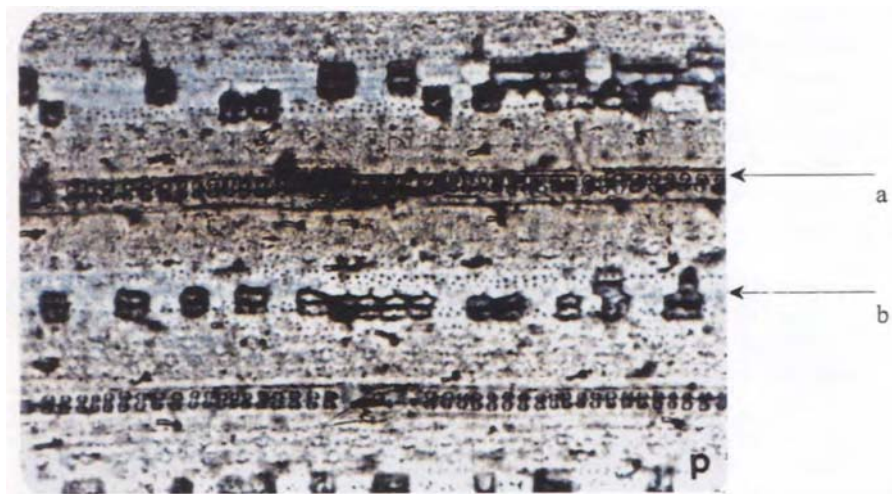


Figure 2.3. Silica cell (a) and silica body (b) in rice leaf blades.

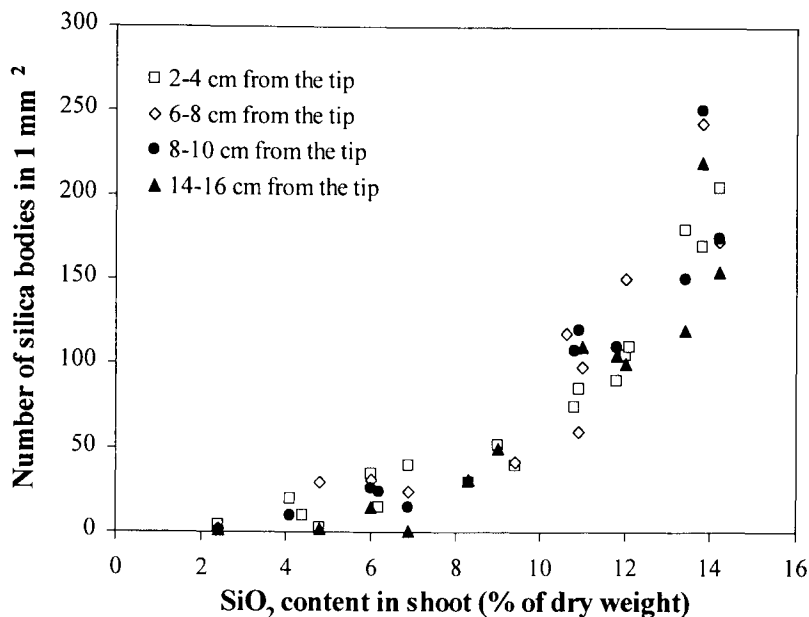


Figure 2.4. Relationship between Si content in the rice shoot and number of silica bodies at different parts of the third leaf blades.

variation results from both plant species and growth environment. We analyzed the mineral content in nearly 500 species ranging from Bryophyta to Angiospermae growing under similar soil conditions. Among the nine elements (Si, Ca, Fe, Mn, P, B, Mg, K, and Al) Si accumulators are tentatively defined as plants which contain higher than 1% Si and show a Si/Ca mol ratio higher than 1. Plants which contain 0.5-1% Si, or higher than 1% Si, but show less than 1 Si/Ca mol ratio are defined as intermediate, and plants which contain less than 0.5% Si, non-Si accumulators. Si accumulators clearly show a characteristic distribution in the phylogenetic system (Table 2.1, Figure 2.5). Si accumulators are distributed in Bryophyta, Lycopsidea, Sphenopsida, 9 families of Pteropsida, Eriocaulales, 7 species of Cyperales, and Graminales, while Si nonaccumulators are distributed in 5 families of Pteropsida, Gymnospermae and 2 species of Cyperales (Table 2.1). Cucurbitales and Urticales show an intermediate type of Si accumulation.

2.3.2. Characteristics of silicon uptake in silicon accumulators and nonaccumulators

The large variation in Si content among plant species is the result of differing abilities of Si uptake. We analyzed Si content in 147 species of Angiosperms grown on the same soil. The average Si content in 147 species was 0.5% (Table 2.2) (Takahashi et al., 1976). Supposing that plants passively uptake Si from a soil solution of 0.35 mM (10 ppm) Si and have a transpiration coefficient of 500, the Si content in these plants can be calculated as 0.5% Si. Based on the Si content, three groups are classified. In group A, the Si content is lower than 0.5% Si, suggesting that these plants take up Si more slowly than water. A rejective uptake seems to be operating in this group. In contrast to group A, the Si content in group C is more

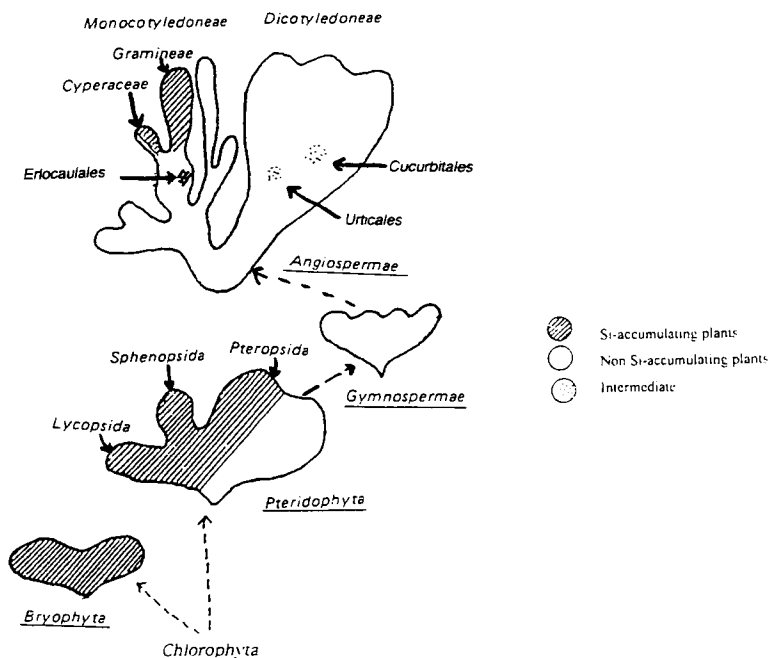


Figure 2.5. Distribution of Si-accumulators in the plant kingdom.

than 3-fold of the criterion value (0.5%), suggesting that these plants take up Si faster than water and an active uptake mechanism is involved. Most of the plants in this group are members of the Gramineae family. Group B has a similar Si content as the criterion value. These results suggest that there are three different modes of Si uptake: rejective, passive, and active uptake, depending on plant species.

A different uptake mode of Si results from the characteristics of roots. In a study with rice and tomato, which are very different in Si content (Figure 2.6B) (Okuda et al., 1962), the Si concentration in the solution decreased from initial 12.6 to 1.8 ppm SiO_2 after a 72-h uptake by rice (Figure 2.6A). However, the Si concentration was increased from 12.6 to 14.4 ppm SiO_2 by tomato. When the roots were cut off, the excised tops of both plants did not change the Si concentration in the solution (Figure 2.6A), implying that Si is taken up passively. The Si concentration in the bleeding sap of rice was ten times higher than that in the external solution (Figure 2.6C), while that in the bleeding sap of tomato was one-tenth of the Si concentration in the external solution. All these results clearly show that rice roots take up Si actively, while tomato roots take up Si rejectively. However, the mechanisms involved in active or rejective uptake are still unknown.

2.3.3 Similarity of silicon and germanium in uptake

One of the problems which hamper Si research is the lack of an available radioisotope for Si. The half time of ^{31}Si is too short (2.62 h) to be used. However, the cognate element of Si,

Table 2.1

Distribution of Si-accumulators in the plant kingdom. A, non-accumulator; B, intermediate; C, accumulator.

Phylum/class/order	No. of species tested	Si%	Ca%	Si/Ca mol ratio	Type of Si accumulation
Bryophyta ^a	2	3.46	1.06	4.73	C
Pteridophyta ^b					
Lycopsidea	2	4.60	0.55	12.0	C
Sphenopsida	2	5.81	2.18	3.99	C
Pteropsida					
9 families	26	2.30	1.18	3.74	C
5 families	25	0.26	1.21	0.32	A
Gymnospermae ^a	12	0.13	1.20	0.24	A
Angiospermae					
Dicotyledoneae					
Cucurbitales ^c	8	2.09	4.40	0.67	B
Urticales ^b	5	1.03	4.64	0.46	B
Monocotyledoneae					
Eriocaulales	1	1.10	0.40	3.96	C
Cyperales ^a					
7 species	7	2.12	0.63	6.66	C
2 species	2	0.21	0.52	0.59	A
Graminales ^d	211	4.73	0.63	13.4	C

Samples were collected from ^aYamashina Institute for Plant Research, Nippon Shinyaku Company, ^bKyoto Prefectural Botanical Garden, ^cExperimental Farm of Okayama University, and ^dExperimental Farm of National Institute of Genetics

Ge, has a radioisotope ⁶⁸Ge, whose half time is 282 days. Therefore, ⁶⁸Ge could be a useful tool for Si research if the behavior of Si and Ge is similar in plants. Research has indicated similarities exist in uptake between Ge and Si. Table 2.3 shows the content of Si and Ge in the shoot of several plants (Takahashi, Syo et al., 1976). Plants with a high Si content had a high Ge content. When the roots of rice are removed, the Ge concentration in the rice shoot is dramatically decreased (Table 2.4), while that of morning glory is increased by removing the roots (Takahashi, Matsumoto et al., 1976). This suggests that Ge uptake is controlled by the

Table 2.2

Mineral content in 147 species of Angiosperm grown on the same soil.

	Si	Ca	Mg	K	P	B
	% of dry weight					ppm
Average of Angiosperm (147) ^a	0.50	1.66	0.24	2.70	0.33	19.2
Group A						
Monocots (40)	0.18	1.78	0.25	3.18	0.34	13.7
Dicots (77)	0.23	1.87	0.27	2.57	0.33	27.7
Average	0.21	1.84	0.26	2.78	0.33	22.9
Group B						
Dicots (8)	0.86	1.76	0.17	2.34	0.44	9.5
Group C						
Monocots (22)	1.87	0.65	0.14	2.39	0.26	3.0

^aAll plant materials were collected from the field of Yamashina Institute for Plant Research, Nippon Shinyaku Company. Number in parentheses indicates number of plant species analyzed.

root, which is similar to Si uptake (Figure 2.6). The results also suggest that, like Si, there are three different modes of Ge uptake; active (rice), passive (kidney bean), and rejective (morning glory). Furthermore, in rice, Ge is concentrated in the bleeding sap (Table 2.5), and Ge uptake is inhibited by DNP, 2, 4-D, and NaCN as is Si (Takahashi, Matsumoto et al., 1976). These facts suggest that plant roots can not distinguish Ge from Si in terms of uptake; and Ge can be used as a substitute for Si in the study of Si uptake. However, Ge taken up is

Table 2.3

Si and Ge contents in various plants sand-cultured with nutrient solution containing 50 ppm Si (as H_4SiO_4) and 5 ppm Ge (as H_4GeO_4). The plants were treated for 3 to 4 weeks.

Plant species	Si (%) ^a	Ge (ppm) ^a
Rice	6.61	3140
Wheat	3.81	1720
Maize	2.23	105
Kidney bean	1.24	860
Tomato	0.11	140
Morning glory	0.11	105

^a dry weight basis

toxic to plants, characterized by brown spots on the leaves. The physiological function of Ge seems to be different from that of Si. Furthermore, Ge is also concentrated in the bleeding sap in rice (Table 2.5), and uptake is inhibited by DNP, 2,4-D, and NaCN, as is Si (Takahashi, Matsumoto et al., 1976). These facts suggest that plant roots are unable to distinguish Ge from Si in terms of uptake, and Ge can be used as a substitute for Si in the study of Si uptake. However, Ge taken up is toxic to plants, which is characterized by brown spots on leaves. The physiological function of Ge seems to be different from that of Si.

2.3.4. Silicon accumulators and beneficial effects

Beneficial effects of Si are usually obvious in crops which actively accumulate Si in their shoots. This is because most of the beneficial effects of Si are expressed through Si deposited on the leaves and stems. A beneficial response can be observed when Si fertilizer is applied to fields of rice, barley, maize, and sugarcane. In solution-cultured cucumber, melon, strawberry and soybean, which take up Si passively, the beneficial effects of Si are also observed if the Si concentration in the solution is high.

2.4. BENEFICIAL EFFECTS OF SILICON UNDER STRESS CONDITIONS

Plants are exposed to various biotic and abiotic stresses in the field. Numerous studies have shown that beneficial effects of Si are slight under optimized growth conditions, but obvious under stress conditions (Epstein, 1994). In this section, the effects of Si under stress conditions are discussed.

2.4.1. Silicon and biotic stress

It is well known that Si applications reduce the severity of fungal diseases such as blast and sheath blight of rice, powdery mildew of barley and wheat, and vermin damage of rice by the plant hopper, in the field. In addition to these plants with active Si uptake mode, Si has also

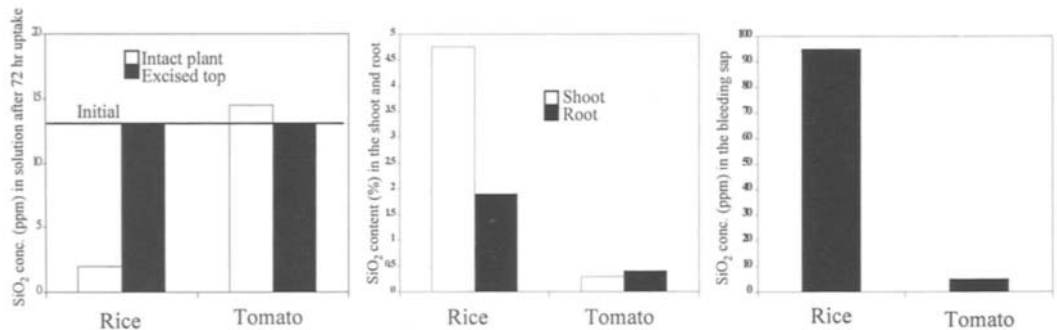


Figure 2.6. Si concentration in the external solution after a 72-h uptake by intact plant and excised top of rice and tomato (A); Si content in the root and shoot of rice and tomato (B); Si concentration in the bleeding sap of rice and tomato after a 5-h uptake (C). Initial external concentration of Si is 12.6 ppm SiO_2 .

Table 2.4

^{68}Ge content in the shoot with or without roots. The roots or cut end of shoots were placed in 10 ml of 5 ppm Ge (H_4GeO_4) containing $0.1 \mu\text{Ci } ^{68}\text{Ge}$ for 20 h at room temperature.

	Content (^{68}Ge cpm/mg fresh weight)		
	With root (A)	Without root (B)	A/B
Rice	2330	90	25.9
Kidney bean	29	23	1.26
Morning glory	4	22	0.18

been reported to prevent powdery mildew of solution-cultured cucumber and musk melon (Table 2.6) (Miyake and Takahashi, 1982a). With increasing Si concentration in the culture solution, the Si content in the cucumber shoot is increased, resulting in resistance to powdery mildew. In recent years, foliar application of Si has been reported to be effective in inhibiting powdery mildew development on cucumber, muskmelon, and grape leaves (Menzies et al., 1992; Bowen et al., 1992). Si applied to leaves may deposit on the surface of leaves and play a similar role as Si taken from the roots. This approach may be useful for the crops with a passive or rejective uptake mode. Si deposited on the tissue surface has been proposed to be responsible for the protective effects of Si against biotic stress. The deposited Si prevents physical penetration by insects and/or makes the plant cell less susceptible to enzymatic degradation by fungal pathogens. Recently, Si application to cucumber has been reported to result in stimulation of chitinase activity and rapid activation of peroxidases and polyphenoloxidases after infection with *Pythium* spp (Cherif et al., 1994). Glycosidically bound phenolics extracted from Si-treated plants when subjected to acid or beta-glucosidase hydrolysis displayed a strong fungistatic activity.

2.4.2. Silicon and abiotic stress

2.4.2.1. Climate stress

Si application reduces injury of rice caused by climate stress such as typhoons, and cool summer damage (low temperature and insufficient sunshine). Damage by typhoon usually

Table 2.5

Ge concentration in the bleeding sap of rice plant. The plants were placed in 100 ml of 5 ppm Ge (H_4GeO_4) solution containing $0.1 \mu\text{Ci } ^{68}\text{Ge}$ for 0-32 h.

Exposure time (hr)	Ge conc. (ppm)		B/A
	External solution (A)	Bleeding sap (B)	
0	5.0	-	-
4	4.4	33	7
24	2.3	106	47
32	1.9	136	71

Table 2.6

Effect of Si on the resistance of cucumber plant to powdery mildew.

	Si supply concentration (SiO ₂ ppm)				
	0	5	20	50	100
Si content in dry leaves (%)	0.04	0.06	0.33	1.02	1.5
Leaf position	Severity of powdery mildew ^a				
1 (top)	●●●	●●	●	●	-
2	●●●●	●●	●●	●	-
3	●●●	●●●●	●●	●	-
4	●	●●●	●●		-
5	●●	●●	●		-

^aNumber of colonies per cm² of leaf area: - = 0; ● <0.1; ●● = 0.2-0.5; ●●● = 1.0; ●●●● >1.0.

results in lodging and sterility. Deposition of Si in rice increases the thickness of the culm wall and the size of the vascular bundle (Table 2.7) (Shimoyama, 1958), preventing lodging. Sterility is related to many factors, including excess water loss from the hull. For normal development of panicles, a high moisture condition within the hull is necessary during ripening. Transpiration from the panicles occurs only from the cuticle of the hull because the hull has no stomata. Si deposited on the hull decreases the transpiration from panicles by about 30% at either milky or maturity stage (Table 2.8) (Ma, 1990), preventing excess water loss. This is the reason why Si application significantly increase the percentage of ripened grain (Ma et al., 1989). Low temperatures during summer usually cause serious damage to rice

Table 2.7

Effect of Si application on the thickness of culm wall and the size of vascular bundle.

Treatment ^a	Culm wall thickness (μ)	Vascular bundle size (100 μ ²)
N	728	202
N+Si	781	239
N+2Si	826	282
3N	638	179
3N+Si	622	171
3N+2Si	659	183

^a N: ammonium sulfate 5 g/pot (3N: 15g/pot), Si: sodium silicate 10 g/pot (2Si: 20 g/pot). Rice cv: Aichi-asahi

Table 2.8

Effect of Si application on transpiration from the panicle at different stages. The excised panicles were placed in an incubator for 1 hr at 30°C with a relative humidity of 30%.

Treatment	Transpiration (mg H ₂ O/g fresh wt./1 h)	
	Milky stage	Maturity stage
+Si	204.00	39.2
-Si	279.00	50.4
+Si/-Si	1.37	1.29

production in Japan. Low temperatures decrease Si uptake by rice and insufficient sunshine lowers the Si:N ratio, which induces blast. Application of Si under such conditions markedly reduces the incidence of blast in rice (Table 2.9) (Ohyama, 1985). The effect of Si is more evident under low light intensity. The Si effect on rice growth (fresh weight) under shaded conditions is larger than that without shading (Table 2.10) (Ma, 1990), but the mechanism responsible for this phenomena is unknown. It has been hypothesized that Si deposited on the leaf epidermal system might act as a "window" to facilitate the transmission of light into photosynthetic mesophyll tissue. However, evidence supporting this hypothesis could not be obtained at this time (Agarie et al., 1996).

2.4.2.2. Water deficiency stress

Si can alleviate water stress by decreasing transpiration. Transpiration of leaves is mediated through the stomata and cuticle. Rice plants have a thin cuticle and the formation of a cuticle-Si double layer significantly decreases cuticular transpiration. As shown in Table 2.11, the transpiration of rice decreases with increasing Si content in the shoot (Ma, 1988). Water stress causes stomata closure which decreases photosynthetic rate. Therefore, Si stimulates the growth of rice more clearly under a water-stressed condition (low humidity) than in a non-stressed condition (high humidity) (Table 2.12) (Ma, 1990).

Table 2.9

Effect of Si application on the degree of infection by blast disease in rice.

N applied (kg/10 ^a)	Degree of infection		Leaf blade (% SiO ₂) ^b		Leaf blade (%N) ^b	
	-Si	+Si ^a	-Si	+Si	-Si	+Si
0	6.4	2.6	6.5	9.4	2.30	2.26
3.6	9.5	1.7	4.5	9.2	2.38	2.14
7.2	16.7	2.6	3.9	7.9	2.40	2.39
10.8	19.3	5.0	3.3	7.8	2.73	2.24

^a calcium silicate applied at 180 kg/10a

^b content at time of full heading

Table 2.10

Effect of Si on the fresh weight of rice shoot with shading (light-interception coefficient of 52%) or without shading for 20 days. Values are means (n=4) with SD in parentheses.

Treatment	No shading (g/pot)	Shading (g/pot)
-Si	3.76(0.27)	1.45 (0.04)
+Si	4.14 (0.10)	2.03 (0.08)
+Si/-Si	1.10	1.40

2.4.2.3. Mineral stress

Mineral stress can be classified into the deficiency of essential elements and the excess of essential and other elements. Many reports have shown the beneficial effects of Si under mineral stress. In this section, the beneficial effects under P deficiency, excess of P, Na, Mn, N and Al are described.

2.4.2.3.1. P deficiency stress

Beneficial effects of Si under P-deficiency stress have been observed in many plants such as rice and barley. According to a long-term field experiment conducted at Rothamsted Experimental Station (Hall and Morison, 1906), the effect of Si on barley yield is larger when P is not supplied. Previously, such beneficial effects of Si were explained as a partial substitute of Si for P or an improvement of P availability in soil. However, later experiments showed that Si can not displace P nor decrease the ability of the soil to adsorb P in a P-deficient soil (Ma and Takahashi, 1990b; Ma and Takahashi, 1991), suggesting that Si does not have any effect on P availability in soil. As stated above, Si is present in the form of silicic acid in soil solution, which does not dissociate at a pH of less than 9. It seems unlikely that interaction between silicic acid and phosphate (anionic form) occurs in the soil. In a solution culture experiment, there was no significant effect of Si on the dry weight of shoot, root, and grain of rice when P was supplied at an adequate level (200 μM) (Table 2.13) (Nagaoka, 1998). However, when the P level is decreased to 12.5 μM , the effects of Si are obvious. P uptake is not enhanced by Si when the P level is low, but the rate of P translocation to panicle is enhanced by Si in rice (Table 2.13). This implies that Si improves internal P utilization. Si

Table 2.11

Effect of Si application on transpiration in rice. The transpiration during 72 h was measured in rice with various Si contents.

% SiO ₂ content	Transpiration (g H ₂ O/g dry wt.)
0.02	200.3
1.59	181.7
10.29	168.0
13.22	154.4

Table 2.12

Effect of Si application on the growth and transpiration rate of rice under two different humidities. Values are means (n=4) with SD in parentheses.

Treatment	Shoot dry weight (g/pot)	Transpiration rate (g H ₂ O/g dry wt.)
Relative humidity at 40% ^a		
+Si	0.91 (0.06)	471.1 (28.7)
-Si	0.73 (0.04)	635.9 (21.4)
+Si/-Si	1.25	0.74
Relative humidity at 90 % ^b		
+Si	4.40 (0.18)	297.6 (3.5)
-Si	4.05 (0.21)	323.3 (8.5)
+Si/-Si	1.09	0.92

^a grown for 10 days

^b grown for 30 days

has been reported to decrease the uptake of Mn and Fe, resulting in a higher ratio of P/Mn and P/Fe when the P supply is low (Table 2.14) (Ma and Takahashi, 1990a). These facts suggest that the beneficial effect of Si on the growth under P deficiency stress results from decreased Mn and Fe uptake, and thus, increased P availability in P-deficient plants.

Table 2.13

Effect of Si supply on the growth and yield of rice under P-deficiency stress.

		P concentration (M)			
		200	50	25	12.5
Shoot dry weight (g)	-Si	80.3	68.6	46.9	29.6
	+Si	79.1	70.8	53.1	35.0
Root dry weight (g)	-Si	9.3	9.9	9.1	7.9
	+Si	9.4	7.8	6.8	5.5
Grain dry weight (g)	-Si	20.8	18.7	15.1	9.1
	+Si	21.7	22.4	23.4	12.9
P uptake (mg/plant)	-Si	176.2	53.9	29.0	18.4
	+Si	161.5	53.1	32.9	20.0
Rate of P translocation to panicle (%)	-Si	31.0	46.0	37.0	35.0
	+Si	29.0	56.0	54.0	50.0

Table 2.14

The P/Fe and P/Mn ratios in rice shoots grown on nutrient solution containing P at various concentrations with or without Si (100 ppm SiO_2). Values are the means \pm SD (n=3).

P level (mM)	P/Fe		P/Mn	
	-Si	+Si	-Si	+Si
0.014	12 \pm 1	17 \pm 1	3 \pm 1	9 \pm 1
0.21	59 \pm 7	57 \pm 5	13 \pm 2	19 \pm 2
0.70	113 \pm 20	80 \pm 8	23 \pm 2	29 \pm 2

2.4.2.3.2. P excess stress

Si decreases P uptake when P supply is high. This phenomenon has been observed in rice (Ma and Takahashi, 1990) and some non Si-accumulators such as tomato (Miyake and Takahashi, 1978), cucumber (Miyake and Takahashi, 1982b), soybean (Miyake and Takahashi, 1985), and strawberry (Miyake and Takahashi, 1986). In rice, the content of organic-P is not affected by Si, but that of inorganic-P is significantly decreased by Si when P is supplied at a high concentration (0.7 mM) (Figure 2.7) (Ma and Takahashi, 1990b). Excess internal inorganic P has a negative effect on growth by causing inactivation of metals such as zinc; inhibiting enzyme activity, and creating abnormal osmotic pressure in the cell. Therefore, P-excess stress can be alleviated by Si-induced decrease of P uptake.

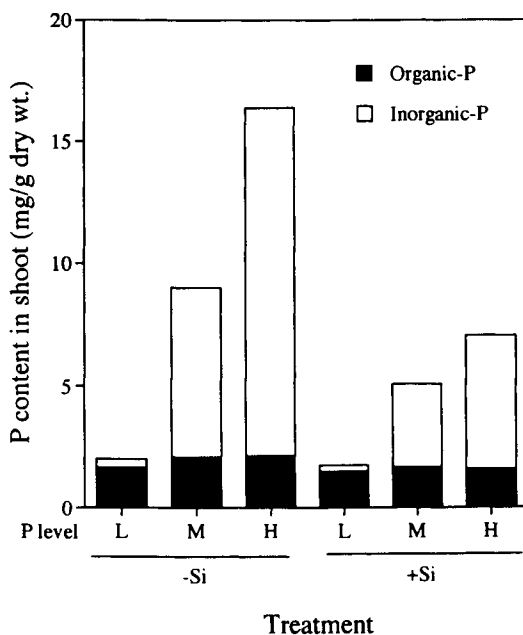


Figure 2.7. Content of organic- and inorganic-P in the shoots of rice plants supplied with 0.014 (L), 0.21 (M), and 0.7 mM P (H) in the presence and absence of Si (1.67 mM Si as silicic acid).

2.4.2.3.3. Salt stress

Si has a beneficial effect in rice under salt stress (Figure 2.8) (Matoh et al., 1986). In this experiment, NaCl was added to the culture solution at an increment of 25 mM every 3 days to reach a final value of 100 mM and then cultured for about 3 weeks in the presence or absence of 25 ppm SiO_2 as silicic acid. Shoot and root growth of rice is inhibited by 60% by the exposure to 100 mM NaCl for three weeks, but the addition of Si significantly alleviates the salt-induced injury (Figure 2.8). The Na concentration in the shoot is decreased to about half by the presence of Si. Translocation of Na to the shoot is partially related to the transpiration, while Si decreases transpiration as discussed above (Table 2.11). These findings suggest that the beneficial effect of Si under salt stress results from decreased transpiration; decreased Na influx to the plants.

2.4.2.3.4. Mn excess stress

Si has been reported to have an alleviative effect on Mn toxicity in water-cultured rice (Okuda and Takahashi, 1962), barley (Williams and Vlamis, 1957; Horiguchi and Morita, 1987), bean (Horst and Marschner, 1978), and pumpkin (Iwasaki and Matsumura, 1999). Three different mechanisms seem to be involved depending on plant species. In rice, Si reduces Mn uptake by promoting the Mn-oxidizing power of the roots (Okuda and Takahashi, 1962). In barley (Williams and Vlamis, 1957) and bean (Marschner, 1978), Si does not reduce Mn uptake, but causes homogenous distribution of Mn in the leaf blade. Although the mechanism for this homogenous distribution is still unknown, Horst et al. (1999) found that Si led to lower apoplasmic Mn concentration in cowpea and suggest that Si modifies the cation binding properties of cell walls. Recently, the third mechanism was postulated based on the results with pumpkin (Iwasaki and Matsumura, 1999). Cucumber in Japan has been produced by grafting onto pumpkin stocks. Grafting on the bloom-type stocks which produce a white powder of silica (blooms) on the fruit surface has been replaced by grafting on the bloomless-type stocks, because cucumber fruits with blooms are not preferred by consumers in Japan. However, occurrence of Mn toxicity in cucumber was increased by using bloomless-type stocks and this has been attributed to rejective uptake of Si by the pumpkin stock (Iwasaki and Matsumura, 1999; Yamanaka and Sakata, 1993; Yamanaka and Sakata, 1994). Table 2.15

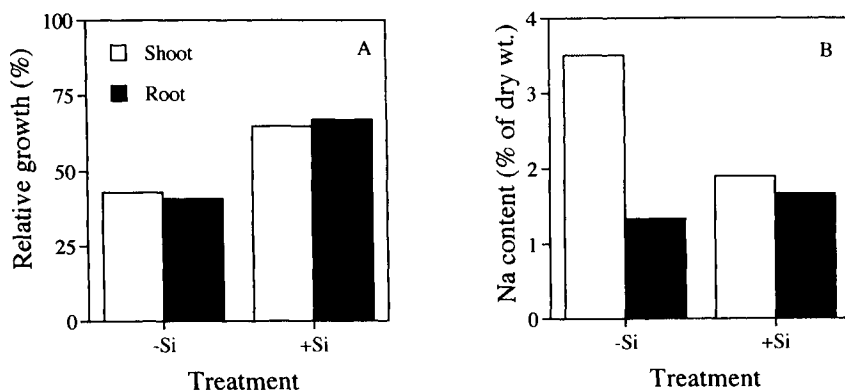


Figure 2.8. Effect of Si on salt-induced reduction of growth (A) and Na content (B) of the shoot and root of rice plants.

shows the effect of Si and Mn on growth, and the uptake of Si and Mn in bloom-type (cv. Shintosa) and bloomless-type (cv. Super unryu) cultivars of pumpkin stocks (Iwasaki, unpublished data). Exposure to high Mn (125 μM) significantly inhibited the growth of the root and shoot in both cultivars in the absence of Si. However, in the presence of Si (1.67 mM as silicic acid), high Mn did not inhibit the growth of Shintosa, but decreased the shoot dry weight by 40% in Super unryu (Table 2.15). Si did not affect Mn uptake of either cultivar, but Shintosa took up much more Si than Super unryu. Electron probe X-ray microanalysis on the leaf of Shintosa without Si supply showed that Mn was accumulated around the necrotic lesion between veins and around the base of the trichomes. However, in the presence of Si, both Mn and Si were accumulated only at the base of trichomes and the accumulation of Mn was confined to that region more distinctly than that in the absence of Si (Iwasaki and Matsumura, 1999). These results indicate that the alleviative effect of Si on Mn toxicity in Shintosa is due to the ability of this cultivar to better accumulate Si and translocate it to the shoots. This in turn may cause localized accumulation of Mn together with Si in a metabolically inactive form at the base of trichomes. However, further studies will be needed to clarify whether the localized accumulation of Mn and Si at the trichomes is the reason or the consequence of the alleviative effect of Si on Mn toxicity.

2.4.2.3.5. N excess stress

In Japan, dense plantings and high N applications are usually adopted to maximize yield

Table 2.15

Growth and the content of Si and Mn in two pumpkin cultivars (Iwasaki, unpublished data). The plants were cultured in a nutrient solution containing 10 or 125 μM Mn in the presence and absence of 1.67 mM Si for 2 weeks.

Mn conc. (μM)	-Si				+Si			
	10		125		10		125	
	Shoot	Root	Shoot	Root	Shoot	Root	Shoot	Root
Shintosa								
Dry weight (g/pot)	26.8	4.0	10.8	1.4	31.3	4.2	29.3	4.8
Content (mg/plant)								
Si	23.6	1.3	10.1	1.1	167.6	6.0	163.4	5.8
Mn	4.5	0.6	19.0	2.1	4.6	0.5	27.6	3.7
Super unryu								
Dry weight (g/pot)	29.6	3.1	10.4	1.0	30.9	2.5	19.7	1.8
Content (mg/plant)								
Si	38.9	1.1	16.8	0.8	45.8	8.9	24.7	6.1
Mn	4.9	0.4	19.2	2.9	4.3	0.3	25.7	2.1

Table 2.16

Relationship between Si and N supply and leaf erectness in rice plants (cv. IR8) at flowering stage.

	Si supply (mg SiO ₂ L ⁻¹ as sodium silicate)		
	0	40	200
N supply (mg L ⁻¹)	Angle ^a		
5	23	16	11
20	53	40	19
200	77	69	22

^a Angle between the culm and the tip of the leaf.

potential of rice. Under such cultural conditions, leaf erectness is an important factor affecting light interception. As shown in Table 2.16 (Yoshida et al., 1969), leaf erectness decreases with increasing N application, but Si application increases leaf erectness, decreasing mutual shading caused by dense planting and high N application. Excess N also increases susceptibility to diseases such as blast disease in rice (Table 2.9), but Si decreases the occurrence of blast disease in rice with high N fertilizer applications. These beneficial effects also are attributed to the Si deposited on the leaves.

2.4.2.3.6. Al stress

Al toxicity is a major factor limiting crop production in acid soils. Ionic Al inhibits root growth and nutrient uptake. An alleviative effect of Si on Al toxicity has been reported in many crops including maize, cotton, rice, teosinte, sorghum, and wheat (Cocker et al., 1998).

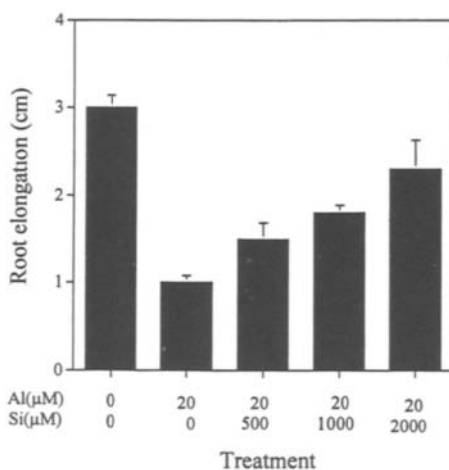


Figure 2.9. Effect of Si on Al-induced inhibition of root elongation in maize. Roots were exposed to 20 μM AlCl₃ for 20 h in the presence of various concentrations of silicic acid.

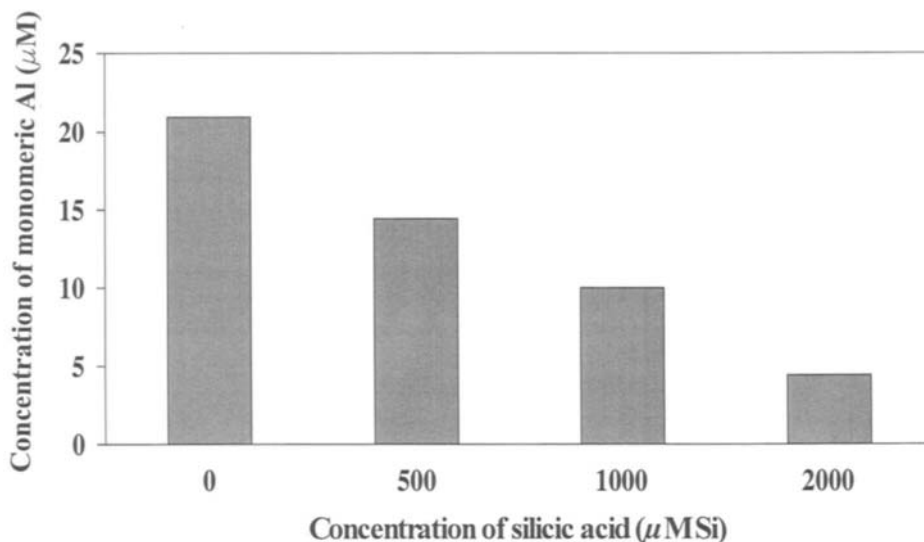


Figure 2.10. Effect of various silicic acid concentrations on the concentration of toxic Al^{3+} .

In an experiment with maize, the addition of silicic acid significantly alleviated Al-induced inhibition of root elongation (Figure 2.9) (Ma et al., 1998). The alleviative effect is more apparent with increasing Si concentration. The concentration of toxic Al^{3+} is found to be decreased by the addition of silicic acid (Figure 2.10). These results suggest that interaction between Si and Al occurs in solution, probably by the formation of Al-Si complexes, a non-toxic form. However, interaction between Al and Si within the plant has also been suggested (Cocker et al., 1998).

2.5. CONCLUSION

The beneficial effects of Si on crops are summarized in Figure 2.11. Most effects of Si are expressed through silica gel, which is deposited on leaves and stems of plants, and some effects are through interaction between silicic acid and other elements such as Al. Currently, there is no evidence showing the involvement of Si in plant metabolism. Therefore, in contrast to essential elements, the function of Si in plants is probably mechanical rather than physiological. This characteristic of Si function explains why Si effects are easily observed in plants that accumulate Si to a certain extent and why Si effects are more obvious under biotic or abiotic stress. With the changes occurring in the global environment, the role of Si will become more and more important for better and sustainable production of crops. Beneficial effects also are observed in some crops which do not accumulate Si. For example, tomato is a typical plant with a rejective mode of Si uptake. The growth of tomato in the nutrient solution without Si is rather normal during the vegetative growth stage, but abnormal at the flowering

stage, showing symptoms such as curling of newly developed leaves (Miyaki and Takahashi, 1978). Pollen fertility also is decreased by Si-deficiency, resulting in drastic reduction in fruit yield. However, the mechanism responsible for such Si effect is unknown. It is argued that Si promotes growth by improving the imbalances of nutrients, especially P. Si decreases P uptake in rice, tomato, cucumber, soybean, and strawberry, as previously discussed. Decreased P uptake may improve internal availability of Zn and other metals. In fact, symptoms of Si deficiency in cucumber are rectified by raising the Zn concentration in the nutrient solution (Marschner et al, 1990). The role of Si in balancing nutrients should be further elucidated in future. The mode of Si uptake varies from rejective to active depending on species of plant being studied, but the mechanisms regulating Si uptake is still unknown. In the future, more attention should be paid to the active uptake of Si in rice. Si is taken up in the

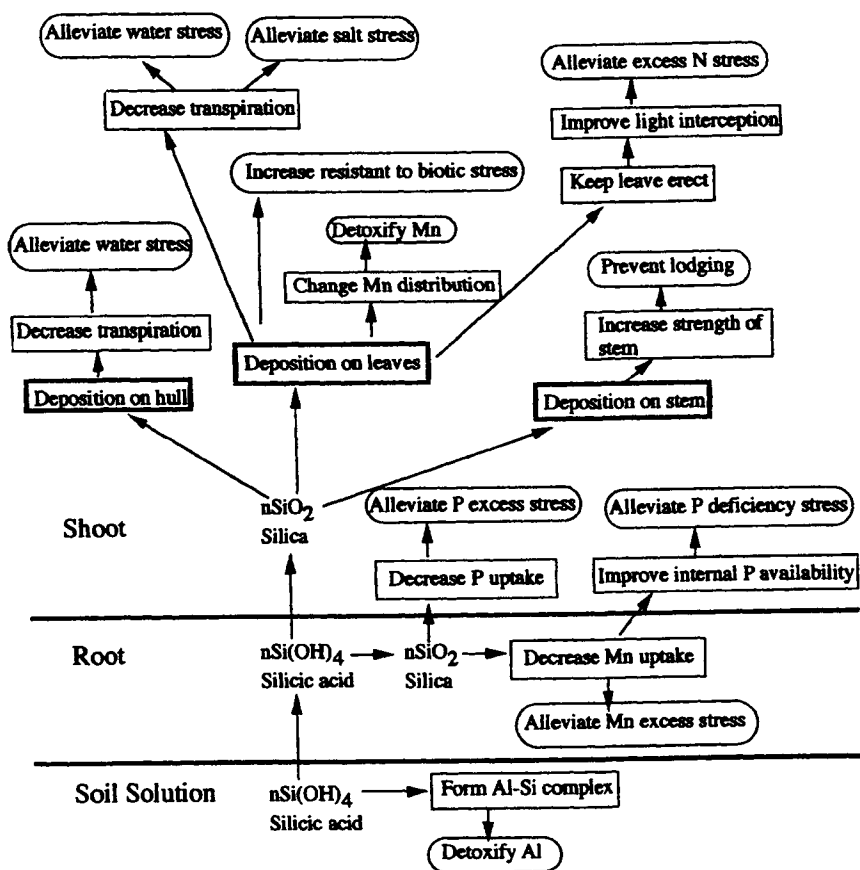


Figure 2.11. Beneficial effects of Si on crop growth in relation to biotic and abiotic stresses.

form of silicic acid, an uncharged form, and its uptake is energy-dependent (Okuda and Takahashi, 1962). The rice plant is supposed to have a transporter for silicic acid. Isolation and cloning of this transporter will enhance our understanding of different Si modes of uptake in plants.

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Chapter 3

Silicon transport at the cell and tissue level

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The predominant silicon (Si) compound in the soil solution is silicic acid, and the baseline condition for Si transport into and within a plant with no membrane channels or transporters which can move Si compounds is the movement of silicic acid across membranes by dissolving in the lipid phase of the membrane ('lipid solution' transport). Based on the best current estimates of 'lipid solution' permeability of membranes to silicic acid ($\sim 10^{-10}$ m s⁻¹), even the lowest Si contents in plants cannot be explained in terms of the soil solution silicic acid concentration and the lipid solution mechanism, and a component of silicic acid entry coupled to transpiratory water uptake is required. For *Oryza* (rice) and, under some conditions, *Hordeum* (barley), and *Phaseolus* (bean), active influx of silicic acid is needed to account for the observed silica content. Further work is needed as to the mechanism of active transport of silicic acid following the lead of the characterization of Na⁺-coupled transport in a diatom, and on how silicic acid is coupled to water transport (involving aquaporins?), and on the phloem mobility of silicic acid.

3.1. INTRODUCTION

The most significant interactions of silicic acid with organisms involve the entry of silicic acid into cells and, for multicellular organisms, into the aqueous intercellular spaces of the organism. This paper examines the transport possibilities at the cellular and the tissue level on the basis of reductionist approaches, and then attempts to interpret the observed data on silicon transport in terrestrial plants in terms of the known mechanisms (cf. Jones and Handreck, 1967; Raven, 1983; Marschner, 1995; Epstein, 1999). An evolutionary approach is adopted throughout.

3.2. SILICIC ACID TRANSPORT AT THE CELL LEVEL

3.2.1. Passive transport of silicic acid across membranes

The 'default condition' for solute transport across cell membranes is that the solute crosses the membrane by diffusion across the lipid component of the membrane. In the case of a neutral (uncharged) solute like silicic acid, such a lipid solution flux occurs from the side of the membrane on which the silicic acid concentration is higher to the side of the membrane on which the silicic acid concentration is lower by the solute dissolving across the membrane,

and emerging into the aqueous solution on the low-concentration side (Raven, 1983). For ionized solutes, the electrical potential difference across the membrane must also be considered. However, since the pK_{a1} of silicic acid is 9.82 at 25 C, this uncharged form is the only molecular species likely to cross the membrane by lipid solution under ecologically or agriculturally important conditions, especially in view of the much lower permeability by lipid solution of ions relative to the corresponding uncharged species (Raven, 1983).

Raven (1983) has computed the lipid solution permeability to silicic acid for the inner mitochondrial membrane using the data of Johnson and Volcani (1978), and for the plasmalemma using the model proposed by Stein (1967). The estimate for the sterol-free inner mitochondrial membrane is 10^{-9} m s^{-1} , while that for the sterol-containing plasmalemma is $10^{-10} \text{ m s}^{-1}$. The difference between the two estimates is in the direction expected from the difference in fluidity of the two membranes, and the magnitude of the difference is also

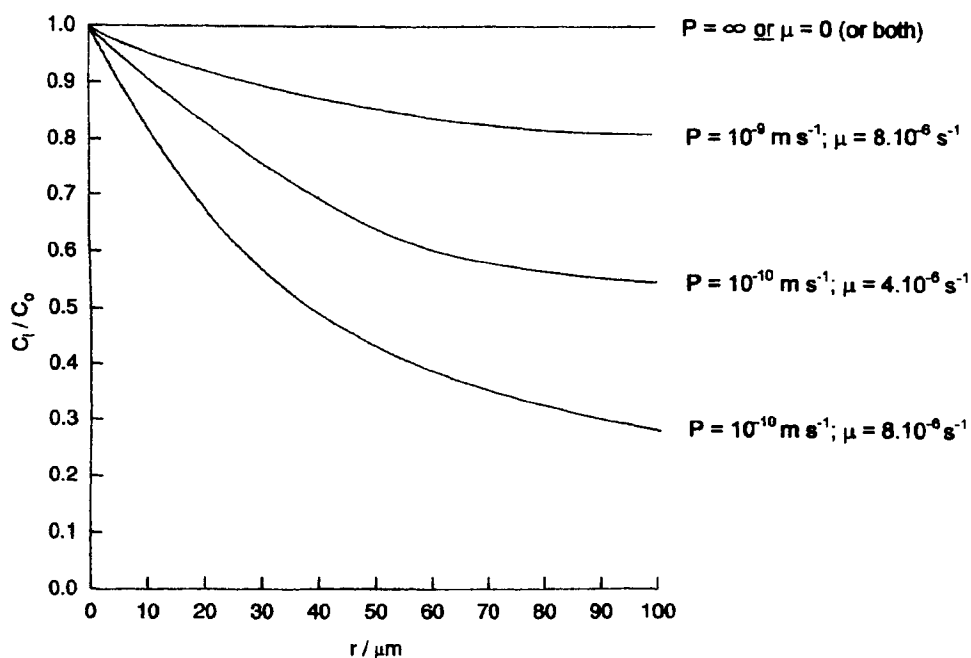


Figure 3.1. Calculated ratio of internal (C_i , mol m^{-3}) to external (C_o , mol Si(OH)_4) concentration as a function of cell size for spherical cells (radius r , μm) for a variety of permeability coefficients (P ; m s^{-1}) for Si(OH)_4 at the plasmalemma and of specific growth rates, μ (increment of cell material (existing cell material) $^{-1} \text{ s}^{-1}$). The assumption made is that the Si(OH)_4 enters by lipid-solution diffusion through the lipid parts of the membrane, or through aquaporin-like channels, with the flux (J ; mol m^{-2} plasmalemma area s^{-1}) given by $P \times (C_o - C_i)$.

reasonable, especially in view of the approximations made in the estimates. Before considering the impact of these permeability coefficients on the extent to which a growing cell would maintain the intracellular silicic acid concentration equal to that in the growth medium, it is helpful to also consider the possibility that silicic acid can cross membranes in response to a concentration difference *via* proteinaceous channels. One possibility involves aquaporins, a family of membrane proteins which facilitate water fluxes. Some members of the aquaporin family facilitate fluxes of certain low M_r solutes as well as that of water (Tyerman et al., 1998). An example is the work of Gerbeau et al. (1999), which shows that a plant tonoplast aquaporin can cause a many fold increase in the membrane permeability to erythritol, an uncharged organic molecule which, like silicic acid, has four hydroxyl groups, but has a rather higher M_r (122 for erythritol; 96 for silicic acid). Thus, although the permeation of silicic acid through aquaporins does not seem to have been tested, it is likely that the silicic acid permeability coefficient of membranes could be increased many fold by the presence of the appropriate aquaporin(s) at their normal density(ies) in the membrane (Raven, 1984a; Gerbeau et al., 1999).

Raven (1983) performed calculations on the extent to which a nanoplanktonic diatom cell of 5 μm equivalent spherical diameter maintains silicic acid in its intracellular solution in equilibrium with the external solution during growth with a generation time of 24 h (specific growth rate of $8.10^{-6} \text{ m s}^{-1}$) and a plasmalemma permeability coefficient for silicic acid of $10^{-10} \text{ m s}^{-1}$. The results of this computation are presented in Figure 3.1, together with computations for a lower specific growth rate (generation time of 48 h) and for a ten-fold higher silicic acid permeability coefficient, equivalent to a more endomembrane-like lipid composition or to the presence of proteinaceous channels which permit the passage of silicic acid. Figure 3.1 also shows the effect of changing cell radius on the extent of equilibration.

The computed steady-state intracellular silicic acid concentrations in growing cells, based on lipid solution entry, can be very significantly lower than in the medium for large (100 μm radius) cells growing with a generation time of 24 h. While a 24 h generation time is appropriate for root meristem cells, 100 μm radius is much larger than a typical root meristem cell, and the typical situation would be that the growing meristem cells would be close to equilibrium with extracellular silicic acid *via* lipid-solution entry, provided diffusion through the apoplast from the soil solution to the growing root meristem cells is adequate. Cell expansion behind the meristem would also occur with only relatively small drawdown of silicic acid in the growing cells, even with only lipid-solution entry of silicic acid. Certainly non-growing root cells basipetal to the growing zone would be very close to silicic acid equilibrium with the soil solution, although this would be slowed if the outer part of the root apoplast has a low permeability to silicic acid (Peterson and Cholewa, 1998). Raven (1983) notes that lipid-solution flux across the plasmalemma is inadequate to support $\text{Si}(\text{OH})_4$ fluxes from the rooting medium to the root xylem even when this transport is active, the Si content of plants are low, and no $\text{Si}(\text{OH})_4$ moves apoplastically.

Turning to silicic acid transport across intracellular membranes, we have seen that the intracellular membranes may have higher lipid-solution permeability than the plasmalemma as a result of lower sterol content; and the tonoplast may have more aquaporins (possibly capable of transporting silicic acid) than the plasmalemma (Gerbeau et al., 1999; Tyerman et al., 1999). This, together with the high surface area per unit volume of most intracellular compartments than of the whole protoplast and plasmalemma, means that equilibration of silicic acid between the cytosol and other membrane-bounded compartments is at least as fast

as the equilibration of silicic acid between the apoplasm and the cytosol when entry of silicic acid across the plasmalemma is by (facilitated) diffusion. Bhattacharya and Volcani (1983) and Hildebrand, Dahlin, and Volcani (1998) discuss the means by which silicic acid is transported within cells of diatoms; since these organisms have active silicic acid influx at the plasmalemma, these intracellular transport processes occur at high (supersaturated) silicic acid concentrations. It is likely that these intracellular transmembrane fluxes are facilitated and passive.

3.2.2. Active transport of silicic acid across membranes

The active transport of Si(OH)_4 can be recognized at the cell (or multicellular) level by the demonstration of Si(OH)_4 movement from a lower to a higher concentration. In some cases the occurrence of active Si(OH)_4 transport is deduced from the occurrence of intracellular SiO_2 deposition in cells growing in a medium with Si(OH)_4 at lower than saturated concentrations. Two caveats must be made in interpreting these SiO_2 deposition data. One is that the occurrence of transpiration can concentrate Si(OH)_4 at sites where the Si(OH)_4 flux is restricted relative to that of water; this necessarily occurs at transpirational termini since Si(OH)_4 has a negligible vapor pressure at normal leaf temperatures. A naive interpretation of transpiratory Si(OH)_4 transport (see later) would have Si(OH)_4 in the transpiration stream at the same concentration as in the soil solution; under these conditions the Si(OH)_4 concentration at transpirational termini will exceed saturation levels throughout the shoot apoplasmic water and, probably, intracellular water if the ratio of the water lost in transpiration to that retained in the growing plant exceeds the ratio of the saturated concentration of Si(OH)_4 to the Si(OH)_4 concentration in the soil solution. In this case no active transport of Si(OH)_4 across cell membranes is needed to achieve saturation of the Si(OH)_4 solution within the plant. The other caveat applicable to, for example, diatoms is that the cellular compartment in which SiO_2 is precipitated need not necessarily be the one into which Si(OH)_4 is concentrated by active transport, since Si(OH)_4 could equilibrate from a compartment into which Si(OH)_4 is actively transported, but which contains substances which restrict SiO_2 precipitation from a supersaturated Si(OH)_4 solution, into a compartment with no constraints on SiO_2 precipitation or, indeed, with templates encouraging such precipitation (Vrieling, Gieskes, and Beler, 1999).

Another problem with assessing the occurrence of active transport comes from assessing the concentration of monosilicic acid in the compartment from which Si(OH)_4 may be transported and in the compartment to which Si(OH)_4 may be transported. Differences in pH between the compartments cause differences in distribution of measured Si between silicic acid and silicate(s); however, since the pK_{a1} of silicic acid is 9.82, this is only important at very high pH values. Furthermore, polymerisation of monosilicic acid can complicate the interpretation of measurements of soluble Si. Finally, Kinrade et al. (1999) showed that Si(OH)_4 can give high yields of stable polyolates containing five- or six-coordinated silicon in solutions of appropriate aliphatic polyols. The coordinating polyols must have at least four hydroxyl groups, two of which must be in the *threo* configuration; coordination to Si is via hydroxyl oxygen in the chain or either side of the *threo* pair. This complexation provides a further species of Si in solution other than as monosilicic acid, and belatedly brings Si into line with its diagonal partner B in the Periodic Table (see Raven, 1980). However, the appropriate aliphatic polyols are not present in appreciable quantities in the main Si(OH)_4 -accumulating higher plants or, indeed, diatoms. It is important to note that these

considerations of speciation of soluble Si also apply to the definition of passive transport.

Active influx of silicic acid across the plasmalemma requires a membrane-spanning integral membrane protein with a binding site or sites for silicic acid, as well as a mechanism which couples the silicic acid influx to some exergonic reaction which permits silicic acid to be moved from a low concentration in the apoplasm to a higher concentration in the cytosol. Examples are known of primary active transport, in which the exergonic driving reaction is a biochemical reaction, e.g. ATP hydrolysis, and of secondary active transport, where the exergonic driving reaction is a biophysical reaction, e.g. the exergonic influx of H^+ or Na^+ (Raven, 1983, 1984a, 1988). In the case of silicic acid, the only characterized active transport reaction system is the Na^+ -coupled active silicic acid transporter at the plasmalemma of diatoms (Hildebrand et al., 1997, 1998).

Hildebrand et al. (1997, 1998) have characterized the SIT gene family from a number of diatoms, the centric marine photosynthetic *Stephanopyxis turris* and *Thalassiosira pseudonana*, the pennate photosynthetic marine *Cylindrotheca fusiformis* and *Phaeodactylum tricorutum*, the pennate marine heterotrophic *Nitzschia alba*, and the freshwater pennate photosynthetic *Navicula pelliculosa*. All of these diatoms, including *Phaeodactylum tricorutum* with a minimal silicon requirement, express multiple SIT homologues. The *Cylindrotheca fusiformis* SIT1 gene, expressed in *Xenopus laevis* oocytes via the mRNA derived from the SIT1 clone, catalyzes the uptake of radioactive germanic acid (an analogue of silicic acid) in a manner which is competitively inhibited by silicic acid (Hildebrand et al., 1997). The uptake was, as in the intact diatom cells, inhibited by the absence of sodium in the bathing medium and the presence of the sulphhydryl blocker N-ethyl maleimide (Hildebrand et al., 1997, 1998). Targeting of the products of this gene to the plasmalemma in *Xenopus* oocytes suggests that at least SIT1 codes for a plasmalemma transporter. It is possible that some other members of the SIT family occur in intracellular membranes (Hildebrand et al., 1998), although currently available data on targeting sequences do not give definitive evidence for this.

What relevance does this have to active transport of silicic acid in higher plants and, especially, agriculturally important plants? Phylogenetically, the diatoms (Bacillariophyceae) are distant from the higher plants (Medlin et al., 1997; Goillou et al., 1999), and independent evolutionary origins of the active transport of silicic acid in the Heterokontophyta (where the class Bacillariophyceae is to be found) and the Streptophyta (the clade containing charophycean green algae and their descendants, the embryophytes or higher plants) is likely. The Streptophyta evolved in freshwater and the embryophytes originated on land, with secondarily marine members, whereas the diatoms evolved in the sea and later invaded freshwaters. The marine diatoms accord with the paradigm that primarily marine eukaryotes use Na^+ as the driving ion for secondary active transport from their aqueous environment as far as silicic acid (and, probably, several other nutrient solutes) is concerned, while streptophytes generally use H^+ as the driving ion for secondary active transport at the plasmalemma (Raven, 1984a, 1988). However, it is possible that freshwater diatoms, and higher plants with active silicic acid transport at the plasmalemma, can also use Na^+ as the driving ion for active silicic acid transport. Freshwater and terrestrial photosynthetic organisms maintain an inwardly-directed driving force on Na^+ as well as for H^+ , although the electrochemical potential difference for Na^+ is commonly less than that for H^+ (Raven, 1984a, 1988). Walker and Smith and their colleagues have described Na^+ -coupled secondary active transport of K^+ , $H_2PO_4^-$ and urea in freshwater characean algae, although Cl^- influx is H^+ -

coupled (Walker, Reid, and Smith, 1993; Reid et al., 2000). In this case the involvement of Na^+ cotransport may relate to the occurrence of acid and alkaline zones on the macroalgal surface which are involved in HCO_3^- use; the alkaline zones have no H^+ electrochemical potential difference across the plasmalemma so that only half of the plasmalemma surface is available for H^+ -coupled secondary active transport, whereas the whole surface area is available for Na^+ -coupled cotransport. For higher plants, the evidence for Na^+ cotransport influx of nutrient solutes is less clear cut (Maathuis and Amtmann, 1999). It is not clear what the energy source (Na^+ ? H^+ ?) is for the active silicic acid influx in freshwater diatoms such as the *Navicula pelliculosa* which was shown by Hildebrand et al. (1998) to have members of the SIT gene family. In view of the work of Walker et al. (1983) and Reid et al. (2000) on freshwater charophycean algae, it is clear that Na^+ cotransport is a possibility for silicic acid active influx in freshwater diatoms.

There seems to be very little evidence as to the nature of active transport of silicic acid in higher plants. A cotransport (secondary active transport) mechanism rather than direct biochemical energization of silicic acid entry is likely on comparative biochemical grounds. The stimulation of plasmalemma H^+ ATPase activity in *Hordeum vulgare* by growth in the presence of $\text{Si}(\text{OH})_4$ (Liang, 1999) could perhaps be interpreted in terms of the involvement of the H^+ ATPase in energizing secondary active influx of $\text{Si}(\text{OH})_4$. Liang (1999) examined the interaction of Si supply (0 vs 1 mol^{-3} $\text{Si}(\text{OH})_4$) and salinisation (0 vs 120 mol m^{-3} NaCl) on H^+ ATPase activity in two barley cultivars, and found that a salt-sensitive cultivar had a higher H^+ ATPase activity with Si than without Si both with and without salinisation, while the salt-tolerant cultivar shows Si stimulation of activity only under high-salt conditions. In both cultivars the ATPase activity is reduced by salinisation, while the H^+ ATPase activity is higher under all growth conditions in the salt-sensitive cultivar. The Si stimulation of the H^+ ATPase in three of the four cultivar-salinisation combinations could indicate a greater demand for H^+ extrusion in the presence of $\text{Si}(\text{OH})_4$ as a result of H^+ entry during $\text{H}^+:\text{Si}(\text{OH})_4$ cotransport. However, the data are also consistent with $\text{Na}^+:\text{Si}(\text{OH})_4$ cotransport, linked to the H^+ ATPase-catalysed active H^+ efflux by a Na^+ (efflux) H^+ (influx) antiporter. Further work is clearly needed to determine if these tenuous lines of reasoning have any validity.

A final point about active transport of $\text{Si}(\text{OH})_4$ is that the mechanisms, which were discussed earlier whereby $\text{Si}(\text{OH})_4$ can cross membranes in response to a concentration difference of $\text{Si}(\text{OH})_4$ between the two sides of the membrane, act to short-circuit any active $\text{Si}(\text{OH})_4$. The extent of such cycling is not known; presumably this is largely a result of the expense of the appropriate radioactive isotopes of Si, the expense of the purified stable isotopes of Si, the relative insensitivity of mass spectrometry as an assay method, and concerns about the utility of germanium (with an accessible radioactive isotope) in such compartmental flux analysis (Cheeseman, 1986).

3.3. SILICIC ACID TRANSPORT AT THE TISSUE LEVEL

3.3.1. Pathways and mechanisms involved

Movement of silicic acid through plant tissues can involve the apoplast (i.e. cell walls, and water-filled intercellular spaces, including the lumen of the dead conducting cells of the xylem) and the symplast (i.e. the cytosol, including the cytosolic sleeve of the plasmodesmata, and conducting cells of phloem, i.e. the contents of sieve cells, sieve tube

elements, and the sieve pores connecting adjacent conducting cells). Transport in cell walls, and intercellular spaces other than xylem cell lumen, and in cytosol, including plasmodesmata cytosol sleeves, but excluding the long-distance conducting cells of the phloem, involves diffusion and mass flow (driven by the transpiration stream or root pressure in the apoplast, and by cytoplasmic streaming in the symplast). However, Canny (1995) cites evidence suggesting negligible mass flow of water in cell walls. In the long-distance conducting cells of the (apoplastic) xylem and the (symplastic) phloem, essentially all of the solute transport occurs by mass flow.

3.3.2. Transport from root medium to the xylem

Dealing now with short-evidence transport (≤ 1 mm) in which apoplastic and symplastic transport involves diffusion and mass flow, we initially consider the transport of silicic acid from the soil solution to the xylem (Jones and Handreck, 1967; Raven, 1983; Marschner, 1995; Epstein, 1999). Here the apoplastic pathway involves the cell walls of the root epidermis, exodermis (where present), cortex, endodermis (where present) and pericycle. The symplastic pathway from root medium to xylem comprises all living cells within the roots, since all of the cells are interconnected by plasmodesmata, which are apparently all functional in transport.

The apoplastic pathway is available for transport of water-soluble chemicals such as Si(OH)_4 from the root medium to the xylem provided the water-filled spaces in the cell walls are not partially occluded, or replaced, by lipophilic (e.g. suberin) compounds such as are found in fully developed endodermis (between pericycle and cortex) and exodermis (usually the hypodermal layer = outer cortex layer) (Peterson and Cholewa, 1998). The water-filled spaces in unsuberized cell walls have a molecular exclusion limit of $M_r \cdot^3 \geq 17,000$ (Raven, 1984a; Peterson and Cholewa, 1998), so that Si(OH)_4 would clearly be able to penetrate these water-filled spaces. However, the diffusion coefficient for solutes in cell walls, expressed on a total wall volume basis rather than a volume of cell wall water basis, is at least several fold lower than the diffusion coefficient in free solution, thanks to the facts (1) that only about half of the wall volume consists of water, not all of which is available as a solvent (i.e. some is bound to cell wall macromolecules) (2) that the water-filled channels follow a tortuous path and (3) that solutes may interact (e.g. by hydrogen bonding) with the walls of the pores (Raven, 1984a; Canny and Huang, 1994).

Mass flow of water, and of such solutes as Si(OH)_4 , through the root apoplast, is also possible although the small effective diameter of the aqueous pores in the cell walls means the conductivity of this pathway for radial water flow is very low compared with that of the xylem for axial flow. It is important to understand that Si(OH)_4 transport through the root apoplast from the soil solution to the xylem cannot produce a higher Si(OH)_4 concentration in the xylem sap than occurs outside the root, regardless of whether the flux is by diffusion or by mass flow (Raven, 1983). Furthermore, this pathway has the potential to return to the soil, by diffusion, some of the Si(OH)_4 which any active transport mechanism involving the symplast has delivered to the xylem. Thus, while active transport maintains Si(OH)_4 at a higher concentration in the xylem sap during steady-state transpiration or root pressure flow than in the medium, diffusion would tend to lower the xylem sap concentration. Any such diffusive loss of Si(OH)_4 would be countered during transpiration (and during xylem solution flow related to root pressure) by the mass flow of water in the other direction.

The symplastic pathway involves the uptake of Si(OH)_4 from the soil solution and/or

cortical apoplast, radial transfer of the solute through plasmodesmata toward the xylem, and efflux of Si(OH)_4 from the symplasm to the apoplast in the pericycle. If such a process is to lead to a higher steady-state Si(OH)_4 concentration in the xylem sap than in the soil solution, then either the transmembrane flux into the symplasm, or that from the symplasm into the apoplast, or both of these fluxes, must be by active transport.

However, it is not necessary for such a symplasmic flux to involve active transport of Si(OH)_4 across the plasmalemma if there is no evidence for active transport from the medium to the xylem sap; either lipid-solution diffusion or diffusion through aquaporin-like pores could be involved. As with apoplastic transport, both diffusion and mass flow can be involved. Thus the flux of silicic acid through the symplasm could involve either diffusion around individual cells and through plasmodesmata, cyclosis (cytoplasmic streaming) around individual cells and diffusion through plasmodesmata or a net radial water flux through the cytosol and plasmodesmata, or a mixture of two or all three of these.

The relative importance of the symplasmic pathway is increased if the apoplastic pathway is impeded by suberin deposits which (as encrustations) decrease the fraction of the cell walls, which is available for apoplastic fluxes, and may (as adcrustations) cover the outer surface of the wall. Such deposits also restrict leakage to the root medium of solutes, which have been concentrated in the xylem sap by active transport involving the symplasm.

Suberin deposits are most commonly thought of in the context of the endodermis, forming a partial or essentially complete apoplastic barrier to fluxes between cortex and pericycle in the more mature parts of the root, but the hypodermal (= outer layer of cortex) exodermis is also significant in many plants (Peterson and Cholewa, 1998). While root epidermal cells, and root hairs, are also suberized, the suberin is diffuse (i.e. not forming a continuous barrier within the wall) so that it does not form a complete barrier to transport of water or solutes (Peterson and Cholewa, 1998).

A suberized endodermis in the more mature parts of roots, at least before initiation of cambial activity, is universal among the extant vascular plants which have been investigated, with the exception of the ten *Lycopodium* species examined (Damus et al., 1997). The absence of an endodermis in *Lycopodium* roots is not characteristic of all lycophytes, since Damus et al. (1997) also examined *Selaginella* spp., and found not only an endodermis but also an exodermis in the roots. Furthermore, an endodermis is found in stems of *Lycopodium* (Eames, 1936; Bierhorst, 1971; Gifford and Foster, 1988). Raven (1984b, 1994; Edwards, Abbot and Raven, 1997) commented on the relatively late (Lower Carboniferous, 350 million years ago) evolution of the endodermis; the absence of an observable endodermis in fossils such as those from the Rhynie Chert (395 million years old) with their exquisite anatomical preservation is clearly not due to poor preservation since this structure is visible in less well preserved but younger fossils. Grubb (1961) had previously investigated the functional significance of the absence of an endodermis around the hydroid (xylem analogue) in gametophytes of the moss *Polytrichum*.

The absence of an endodermis (or exodermis) in *Lycopodium* roots means that there is a pathway for apoplastic solute movement from the root medium into the xylem, as shown by movement of the tracer berberine sulphate (Damus et al., 1997). Further investigation is needed of extant endodermis-less roots to determine how they transport solutes with (in the present context) emphasis on silicic acid. The functional investigation undertaken by Damus et al. (1997) also demonstrates the absence of apoplast-blocking materials other than suberin in the apoplast of *Lycopodium* roots; such materials include polymerized silicic acid and

silica (Yeo et al., 1999). In any case, the outermost site of silica position in roots is generally the endodermis (Yeo et al., 1999).

Turning to the exodermis, this barrier to radial apoplastic transport is less frequently observed in roots than is the endodermis (Peterson and Cholewa, 1998). However, when present it is clearly an effective barrier to movement of a range of solutes and of water (Petersen and Cholewa, 1998; Gierth, Stelzer, and Lehman, 1999), so that the exodermis would surely impose great restrictions on apoplastic Si(OH)_4 fluxes.

In starting to see how these generalized perceptions of root functioning relate to the transport of silicic acid, it is clear that all of the best characterized Si-accumulating vascular plants such as *Equisetum*, and some members of the Cyperaceae and Poaceae (Timmel, 1964; Jones and Handreck, 1967; Kaufman et al., 1981; Raven, 1983) have a well developed endodermis. These organisms have a higher Si content than can be accounted for by transpiratory water loss, assuming that Si(OH)_4 enters with water in the same ratio as Si(OH)_4 and H_2O occur in the root medium. This means that active transport of Si(OH)_4 from the root medium to the xylem sap will not be short-circuited by diffusive back flow as much as would be the case in organisms without an endodermis. This active transport into the xylem has been shown in some members of the Poaceae (and, perhaps rather surprisingly in view of its taxonomic position, the legume *Phaseolus*) (Raven, 1983) but, apparently no measurements have been made on the Cyperaceae or on *Equisetum*, which have high SiO_2 concentrations in their tissues.

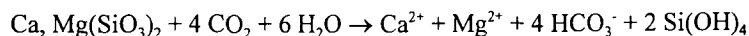
Turning to those vascular plants with no obvious active transport of Si(OH)_4 into the xylem during growth, such organisms are characterized by Si contents which can be explained by Si(OH)_4 uptake during growth in proportion to the H_2O uptake, or with less Si(OH)_4 uptake than H_2O uptake, relative to the ratio of Si(OH)_4 to H_2O in the medium (Raven, 1983).

In some cases (*Phaseolus*, *Hordeum*) the xylem sap can have higher Si(OH)_4 than in the medium, demonstrating that there is active transport of silicic acid across the root, despite the finding that overall the Si(OH)_4 entry during growth in relation to H_2O uptake is equal to (*Hordeum*) or less than (*Phaseolus*), the $\text{Si(OH)}_4\text{:H}_2\text{O}$ ratio in the soil solution. It is likely that the mode of Si(OH)_4 entry to the xylem of the detopped plants used to measure xylem sap concentration is by active transport involving the symplasm, while the growing, transpiring plant has an additional pathway for water *via* the symplasm and/or the apoplasm with a reflection coefficient for silicic acid which is greater than zero, i.e. the $\text{Si(OH)}_4\text{:H}_2\text{O}$ ratio transported across the root in the transpiration flow is less than that in the soil solution. This suggestion, with a reflection coefficient near one for the legumes (i.e. very little Si(OH)_4 enters with H_2O relative to the $\text{Si(OH)}_4\text{:}$ ratio in the medium) and lower for the dryland grasses, can account for the observed Si content in the dry matter of plants, granted the Si(OH)_4 concentration in soils and the water loss per unit dry matter gain. However, it is odd that the mix of active transport of Si(OH)_4 into the xylem (with little or no H_2O moving with the Si(OH)_4 , i.e. a negative reflection coefficient), and the Si(OH)_4 flux with transpirational H_2O with a reflection coefficient near-zero (but positive) for the grasses, yields an effective overall reflection coefficient of zero (Raven, 1983), such that the Si content of dryland cereals has been used as an indicator of the transpirational water cost of their growth (Jones and Handreck, 1967; Hutton and Norrish, 1974). The natural abundance of stable carbon isotopes has also been used in this way (e.g. Condon et al., 1987). While the stable isotope method can be used for any crop (indeed, any transpiring plant), the actual water cost requires knowledge of the water vapor content gradient from leaf to atmosphere; this is not the case for Si

measurements in dryland cereals. However, it is necessary to reiterate that this useful correlation between Si content and water cost of growth in dryland cereals is, as yet, incompletely explained in terms of why the effective reflection coefficient for silicic acid uptake in these grasses is zero. Furthermore, Mayland et al. (1993) found that Si content was not as good a predictor of water use than was ash content or the carbon isotope ratio in a pasture grass.

Finally, in this consideration of silicic acid transport from the soil solution to the solution flowing to the transpiring surface, we return to those plants which lack any obvious apoplastic barrier (endodermis, exodermis) to silicic acid movement. Such organisms include ectohydric bryophytes, in which the water movement to the site of evaporation is mainly external to the plant, and in which there can by definition be no barrier to solute movement with the water flow (Raven, 1984b). This category of plants also includes the endohydric bryophytes (e.g. those like the moss *Polytrichum*, with hydroids as the analogue of xylem) and the vascular plant *Lycopodium*, as well as the earliest fossil vascular plants (Grubb, 1961; Raven, 1984b; Damus et al., 1997). It is of interest that bryophytes and lycopsids (which include *Lycopodium*) are among the plants listed by Takahashi, Tanaka and Miyake (1981) as Si accumulated; the absence of an apoplastic barrier to silicic acid movement from the soil solution to the photosynthetic structures accounts for this. However, more work is needed to determine quantitative relationships between plant Si content on a dry matter gain, and the silicic acid concentration in soil water before the absence of an apoplastic barrier to flow of soil solution to transpirational termini is an adequate explanation of the Si content of these plants. Furthermore, we need to know how the absence of an apoplastic barrier impacts on the accumulation or exclusion of other solutes.

It is possible to envisage a positive feedback of the early embryophytic vegetation on land on their silicic acid supply. Thus, the endodermis-less below-ground axes of the earliest vascular plants (not properly termed roots: Raven, 1984b) would have been exposed to Si(OH)_4 generated by the weathering which was accelerated by their production of CO_2 (from carbohydrates moved down from above-ground axes) according to a very generalized equation:



Such reactions had an important role in the draw-down of CO_2 during the Devonian period when there was a great expansion of terrestrial vegetation (Berner, 1998).

3.4. Transport of xylem-delivered Si(OH)_4 in the shoot

Turning to tissue-level transport of Si(OH)_4 in the shoot following delivery in the xylem, the available data do not permit many unequivocal statements. Even for plants with low Si contents such as legumes, it is not clear if lipid-solution diffusion into cells is sufficient to maintain equilibrium with apoplastic concentrations at transpirational termini as Si(OH)_4 is left by evaporating water (cf. Aston and Jones, 1976). Raven (1983) notes that lipid-solution Si(OH)_4 transport is inadequate to account for all of the root transport of Si(OH)_4 to the xylem even in low-Si organisms like most legumes if Si(OH)_4 transport is through the symplasm by a non-active process. Presumably, the occurrence of Si outside the endodermis in the aerial

axes of *Equisetum*, and outside the mestome sheath in grass leaves, requires symplasmic transport through the sheath (Canny, 1994).

Another approach to the extent of redistribution of xylem-borne silicic acid comes from measurements of the distribution of SiO_2 and of dry matter in the shoots of plants. This is shown for *Avena* at maturity in Table VI of Jones and Handreck (1967). Similar distributions were found for *Hordeum*, *Secale* and *Triticum* (Jones and Handreck, 1967). If we assume that no movement of Si occurs in the phloem (see Raven, 1983 who suggests that there is some such movement), then the occurrence of SiO_2 in tissues in the shoot reflects the extent of transpiration in that tissue. For *Avena*, the inflorescence contains 41.3% of the total shoot SiO_2 and 39.2% of the dry matter. This suggests that all of the carbon which is in the inflorescence at maturity could have been fixed there, assuming the same water loss per unit carbon fixed in photosynthesis and the same fraction of that carbon is lost in respiration occurs in the inflorescence as occurs in the other photosynthetic structures (leaf blade, leaf sheath, culm). The caryopsis had 23.7% of the total shoot dry matter but only 0.5% of the total shoot SiO_2 , which is consistent with almost all of the organic carbon in the mature caryopsis being imported from the glumes with essentially none of the glumes SiO_2 . Furthermore, the data are consistent with none of the organic carbon in the inflorescence being imported from elsewhere in the shoot. Clearly further data are needed to test these suggestions on SiO_2 deposition as a marker, *via* water costs of carbon fixation and maximization of carbon fixed per unit water lost, of sites of carbon fixation. Photosynthesis, respiration and water vapor loss measurements are clearly needed. Natural abundance $^{13}\text{C}/^{12}\text{C}$ as an indicator of the water cost of carbon fixation is difficult to apply in inflorescences with large fractional carbon retranslocation (cf. Araus et al., 1993). Furthermore, Jones and Handreck (1967) point out that the very Si-rich wetland cereal *Oryza* has a very different pattern of SiO_2 and dry matter deposition in shoots at maturity than do the four less Si-rich dryland cereals.

Further work is needed on the occurrence of $\text{Si}(\text{OH})_4$ transport in the phloem, and especially the possibility that the small quantity of Si (relative to many other solutes) transported in the phloem is a result not of intrinsic difficulties in moving Si, but that most of the Si delivered to phloem loading sites in photosynthetic tissues are irreversibly precipitated as SiO_2 , thereby limiting the quantity of $\text{Si}(\text{OH})_4$ available for export (see Raven, 1983).

3.5. CONCLUSION

Our understanding of silicic acid transport at the cell and tissue level in higher plants is deficient relative to our knowledge of the transport of the solutes, which contribute other major plant constituents, and also relative to our knowledge of silicic acid transport in diatoms. Among the areas on which more knowledge is needed are the following: (1) the mechanism(s) of active and passive transport across the plasmalemma; (2) the role of symplasmic and apoplasmic fluxes and of the endodermis and exodermis in transporting silicic acid from the root medium into the xylem, and the mechanisms underlying the occurrence of plants which accumulate quantities of SiO_2 less than, equal to, or more than the amounts they would contain if they took up the silicic acid in their transpiration stream at the concentration found in the rooting medium; (3) the mechanisms of distribution of silicic acid in the shoot in relation to transpirational termini, and the role of transport in the phloem.

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Chapter 4

A primer on the aqueous chemistry of silicon

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A fundamental understanding of aqueous silicate chemistry is a prerequisite to unraveling silicon's (Si) role in living systems. Owing primarily to the advent of ²⁹Si nuclear magnetic resonance (NMR) spectroscopy, the depth of that understanding has increased dramatically over the past two decades. By comparison, details of the biochemistry of Si are sparse. Although several proteins and amino acids believed to be associated with silicates have been isolated, no organosilicon compounds have so far been identified under physiological conditions. Nevertheless, hypervalent Si complexes have very recently been shown to form in the presence of aliphatic polyols and polyol acids, such as mannitol and saccharic acid, respectively. Such simple aliphatic hydrocarbons may play a crucial role in the uptake, transport, and deposition of Si in nature. The objective of this paper is to provide an overview of the speciation, equilibria, and chemical exchange kinetics of Si in aqueous environments, along with an examination of applicable methods of chemical analysis.

4.1. INTRODUCTION

Silicates - compounds comprised of Si and oxygen - play a fundamental role in natural systems. These two elements alone make up 75% of the mass of the Earth's crust, while metals capable of fitting into atomic frameworks of Si and oxygen make up another 22.5%. Silicates are ubiquitous in the hydrosphere and, thus, in the biosphere as well. There is now abundant evidence to suggest that Si is crucial to the healthy growth of many plants (Raven, 1983; Epstein, 1994). Silicon can significantly increase crop yield, decrease susceptibility to certain diseases, and increase resistance to both biotic and abiotic stress (Rafi et al., 1997; Savant et al., 1997). Epstein (1999) has suggested that Si be termed a "quasi-essential element" in that it fits the criteria of essentiality in some, though not all, plants. "The evidence is overwhelming," he states, "that in the real world of plant life, Si matters."

But how exactly are the beneficial effects of Si conferred upon the plant? While there is general agreement that Si is taken up as 'silicic acid' by the root system of higher plants and deposited as amorphous opaline silica in cell walls, the actual chemistry underlying this process remains a mystery. Almost twenty years ago, Simpson and Volcani (1982) observed "the most striking aspect of [silica] polymerization in biological systems is that the process produces opal at low temperatures with apparent ease and efficiency, whereas under non-

living conditions, its formation requires substantial heat. How siliceous organisms accomplish this is still unknown.” The prominent role Si plays in affecting the response of plants to pathogens indicates that it is biochemically active. This implies that it reacts directly with the carbon-based constituents of living matter. Yet, no such interactions have ever been detected under physiological conditions. Appropriating from Churchill, Epstein (1999) puts it aptly: “The biochemistry of Si is a riddle wrapped in a mystery inside an enigma.”

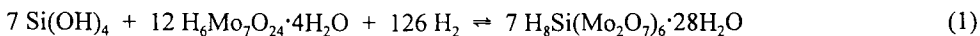
Indeed, the chemistry of aqueous Si can be extraordinarily complex (Iler, 1979). Dissolved silicate species range from simple monomeric and dimeric molecules – favored at higher pH, lower silica concentrations, or higher temperatures – to oligomeric cages containing up to 9 Si centers. Much larger species are not observed as discrete molecules, apparently nucleating the formation of freely dispersed colloidal silicates or, at higher Si concentrations, silicate gels. In this article, we present an overview of aqueous Si chemistry, especially in the context of determining Si’s role *in planta*.

4.2. EXPERIMENTAL TECHNIQUES

Owing to the industrial and geochemical importance of silicates, a plethora of different analytical techniques has emerged over the past century to elucidate the concentration and solution chemistry of Si. Early work consisted of measuring macroscopic properties such as turbidity (light scattering) (Debye and Nauman, 1948, 1951; Greenberg and Sinclair, 1955; Audsley and Aveston, 1962), viscosity (Iler, 1953; Audsley and Aveston, 1962), gel time (Iler, 1953; Audsley and Aveston, 1962), freezing point depression (Iler, 1953), conductivity (Lagerstrom, 1959), pH (Lagerstrom, 1959), and ultracentrifugation time (Audsley and Aveston, 1962). These physical methods yielded the bulk of the data in the forties, fifties, and sixties (Vail, 1952; Eitel, 1954; Iler, 1955), but provided little information on the structure or dynamics of aqueous silicate species.

4.2.1. Chemical methods

Silicomolybdic acid conversion (Strickland, 1952; Alexander, 1954; Thilo et al., 1965; Bennet and Reed, 1971; Hoebbel and Wieker, 1973; Iler, 1979, 1980; Zini et al., 1980), an ingenious approach first reported by Jolles and Neurath (1898), relies on the premise that only monosilicic acid, but no higher polymers, can react directly with acidified ammonium heptamolybdate to form the yellow silicomolybdic acid complex (reaction 1) which can be detected spectrophotometrically at 410 nm.



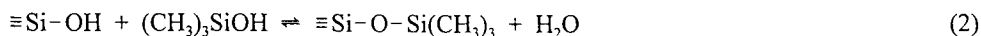
The method is accurate for silica concentrations in the 1000 to 1 ppm range, and the lower threshold can be extended to 0.1 ppm by reducing the yellow silicomolybdic acid to molybdenum blue and/or blue silicomolybdic acid. As with all other chemical methods of analysis, the underlying assumption here is that by rapidly diluting (to < 1% SiO₂) and acidifying (to pH 1-2) an alkaline solution at low temperature, the rearrangement of the polysilicate anions is minimal, and therefore, the constituents of the acidified solution accurately reflect those of the parent solution. Recent work has demonstrated that this assumption is not always valid, as discussed below. Because the non-monomeric forms of

silicic acid must first depolymerize to monomer in the acidic analyte solution, the rate of color development can be correlated with the extent of polymerization. Resulting rate data have been variously interpreted in terms of the relative amounts of monomeric, oligomeric, and polymeric silica, the average number of Si atoms per polymeric species, and the average size of colloid particles. The reader should be cautioned, however, that these correlations are qualitative at best, and frequently misleading, being derived from model silicate dissolution studies. Silicomolybdic acid methods are quite incapable, of course, of determining the structures of individual silicate ions and simply reflect the average degree of polymerization of the solution.

The separation and characterization of low molecular weight silicate oligomers was first accomplished by paper chromatography. Having locked in (supposedly) the equilibrium distribution of silicate species present in alkaline solution through rapid acidification, Baumann (1956), employed a mixture of isopropanol and acetic acid as the moving phase to resolve the monomer, dimer, and some higher species. The chromatogram was developed with an ammonium molybdate spray. Hoebbel and Wieker (1969) resolved a somewhat larger range of species using dioxane and trichloroacetic acid as the moving phase. Analogous studies were later carried out using gel permeation chromatography (Tarutani, 1970). A range of chromatographic techniques have also been used to resolve and characterize trimethylsilylated silicate ions (see below).

Ion chromatography is employed to separate the weakly ionized silicic acid from other ionic species (Potts et al., 1986; Kumagai, 1992; Sakai et al., 1995; Fujiwara et al., 1996). Here, the detection limit of inorganic Si in highly dilute aqueous media such as groundwater or polished laboratory water is reportedly ≤ 1 ppb. Post-column analysis is most often by photometric detection of the silicomolybdic complex (Potts et al., 1986; Kumagai, 1992), or by detection of the chemiluminescence from silicate-catalyzed oxidation of luminal (Sakai et al., 1995; Fujiwara et al., 1996).

The first direct evidence of the structure of silicate anions in alkaline solution was provided by Lentz (1964). He pioneered the technique of trimethylsilylation in which, following rapid acidification, labile $\equiv\text{Si}-\text{OH}$ groups are converted into relatively unreactive organosilyl derivatives, thus permitting their isolation and characterization by standard means. He observed that several different trimethylsilyl derivatives are obtained upon trimethylsilylating a sodium silicate solution, implying the simultaneous existence of a number of low molecular weight silicate anions in dynamic equilibrium. This discovery challenged the prevailing view which held that silicate species are entirely monomeric in such solutions (Vail, 1952; Eitel, 1954; Iler, 1955). His technique, along with later variants (Goetz and Masson, 1970; Dent-Glasser and Sharma, 1974; Hoebbel et al., 1976; Tamas et al., 1976; Bent-Glasser et al., 1977; Garzo et al., 1978), is based on the reaction (2) of trimethylsilanol (or possibly trimethylsilylchloride [Dent-Glasser and Sharma, 1974]) with silicic acids to form stable, end blocked siloxanes.



In the case of monosilicic acid, the final product is stable $\text{Si}(\text{OSi}(\text{CH}_3)_3)_4$. Low molecular weight derivatives, containing up to about 8 Si atoms in the parent molecule, can be characterized using gas (Garzo and Hoebbel, 1976) or thin layer (Hoebbel and Wieker, 1974) chromatography, often in conjunction with mass spectrometry (Wu et al., 1970). Analysis of higher polymers is possible by gel-permeation chromatography along with carbon-hydrogen

analysis (Dent-Glasser et al., 1977). The technique is the subject of a comprehensive review (Calhoun and Masson, 1981).

As noted, each of the chemical methods of speciation entails a preliminary acidification stage. Early work suggested that silicate anions in neutral or alkaline solutions would be unaffected by rapid acidification, and consequently, could be converted directly and quantitatively into the corresponding silicic acids, the acidified solutions accurately reflecting the original anion distribution. Later studies have shown that this is not the case. Oligomeric species reach equilibrium very rapidly (Dent-Glasser and Lachowski, 1980a), and will undergo substantial and systematic rearrangement upon acidification. For example, Calhoun, Masson, and Jansen (1980) showed that the linear tetrameric anion readily undergoes cyclisation during trimethylsilylation to give the cyclic tetramer, and the technique was modified to prevent this (Dent-Glasser and Lachowski, 1980b; Hoebbel, Goetz et al., 1984). Calhoun and Masson (1980) also showed that the ion exchange resin commonly used in trimethylsilylation reactions was responsible for catalyzing a variety of 'side reactions'. Specifically, the concentration of linear trimer was exaggerated at the expense of that of the monomer, and, significantly, the cyclic trimer (Garzo et al., 1978; Shimono et al., 1980). Moreover, Garzo et al. (1980) showed that the double three-ring species, or prismatic hexamer, is also prone to cleavage of its trimeric rings, and is rapidly converted under acid conditions into a bizarre array of structures containing tetrameric rings. Garzo et al. (1984) noted that the double four-ring polyanion, or cubic octamer, is also susceptible to acid-induced rearrangement, although to a lesser extent than the prismatic hexamer. Indeed, many of the first silicate anion structures proposed in the literature are now known to be acid induced modifications which bear little resemblance to the parent anion. Unfortunately, much effort has been expended in the structural determination of these by-products (Hoebbel and Wiekler, 1974b; Hoebbel et al., 1976; Dent-Glasser et al., 1977, 1979).

4.2.2. Potentiometry

Sjöberg and coworkers (1981, 1985a,b; Svensson et al., 1986), conducted several detailed potentiometric studies of aqueous silicates. They determined the pK_a 's of $\text{Si}(\text{OH})_4$ and $\text{Si}(\text{OH})_3\text{O}^-$ to be 9.47 and 12.65, respectively, at 298 K and ionic strength 0.6 mol L^{-1} , with various values for the oligomeric species (e.g., 10.25 for $(\text{HO})_3\text{SiOSi}(\text{OH})_2\text{O}^-$). The average charge per Si atom in alkaline solutions up to pH 12.2 is -0.98 ± 0.04 . Thus, in such solutions, each Si center will tend to be singly deprotonated. In the solutions studies, the average charge per Si varied from -2 to -0.5.

4.2.3. Spectroscopic studies

X-ray scattering is useful for determining the size and abundance of small colloidal particles, but is of no use for characterizing aqueous silicates (Himmel et al., 1990; Wijnen et al., 1994; DeMoor et al., 1999). Atomic absorption (AA) spectroscopy and, more recently, inductively coupled plasma atomic emission spectroscopy (ICP-AES) and inductively coupled plasma mass spectroscopy (ICP-MS) are extremely powerful techniques for rapidly determining total dissolved silicon down to ppb levels (Bowman and Wills, 1967; Lewis-Russ et al., 1991; Hopp, 1993; Hioki et al., 1996), although they are unable to shed any light on solute speciation. In contrast, vibrational and NMR methods are non-invasive and, in principle, can be used to determine the structures of silicate anions in solution.

The first Raman analysis of aqueous silicates was by Fortnum and Edwards (1956) who

concluded that Si is coordinated to four oxygens in the monomeric silicate species. Specifically, species such as $\text{Si}(\text{OH})_6$ and SiO_3^{2-} are absent. These findings were confirmed by Freund (1973) who, in addition, was able to monitor the protonation of the monomeric SiO_4^{4-} anion as a function of pH. Along with later workers (Marinangeli et al., 1978; Guth et al., 1980; Alvarez and Sparks, 1985), he showed that the monomer is a relatively minor component of low alkalinity solutions (which are dominated by numerous polymeric species that are indistinguishable by Raman spectroscopy), that silicate equilibria are attained rapidly, and that they are independent of solution history. Dutta and Shieh (1985) employed Raman spectroscopy to determine the average degree of polymerization in solution, and showed that it increases with the concentration of alkali-metal cations. Like Raman, infrared (IR) spectroscopy yields a composite spectrum of broad absorption bands and has primarily served only to distinguish between monomer (absorption at 950 cm^{-1}) and a generic polymer (1120 cm^{-1}) (Beard, 1973; Marinangeli et al., 1978; Farmer et al., 1979; Groenen et al., 1987; Marley et al., 1989; Roggendorf et al., 1996). However, by closely correlating IR spectra with ^{29}Si NMR analysis (see below) for a wide range of solution compositions, Bass and Turner (1997) recently assigned a number of band components to different silicate structure types (e.g., $\equiv\text{SiOSiO}_3^{3-}$ groups, cyclic or acyclic $(\equiv\text{SiO})_2\text{SiO}_2^{2-}$ groups, $(\equiv\text{SiO})_3\text{SiO}^-$ groups, etc.). Thus, vibrational spectroscopy methods can provide qualitative information on the distribution of silicate anions and degree of polymerization under circumstances in which other techniques are hampered, such as in colloidal or heterogeneous systems (Farmer et al., 1979; Guth et al., 1980; Dutta and Shieh, 1985; Groenen et al., 1987) and in very dilute solutions (Alvarez and Sparks, 1985).

The first ^{29}Si NMR spectra of aqueous silicate solutions appeared in 1973 and showed four distinct spectral regions, indicating that in theory at least ^{29}Si NMR was capable of differentiating between various types of silicate structural units (Jancke et al., 1973; Marsmann, 1973). Later work indicated that by increasing sample purity and external magnetic field strength very highly resolved spectra could be obtained from concentrated alkaline (Engelhardt et al., 1974, 1975; Gould et al., 1974; Marsmann, 1974; Harris and Newman, 1977) and acidic (Engelhardt et al., 1977; Harris et al., 1980b) silicate solutions. By 1980, it was clear that a single silicate solution can contain many different types of silicate anion in dynamic equilibrium, although there was no way of reliably assigning NMR signals to individual anion structures. This was because: 1) Si-29 is a 'rare spin' (natural abundance of 4.7%) and thus NMR spectra show no spin-spin scalar coupling, yielding only a single signal for each chemically distinct site and making it impossible even to correlate signals arising from sites within the same molecule; 2) rapid exchange of the hydroxy protons removes all evidence of ^1H - ^{29}Si scalar coupling; and 3) silicate solutions often contain many structurally similar silicate anions in dynamic equilibrium, leading to complex spectra comprised of a series of closely spaced and often overlapping signals. Owing to such limitations, the assignment of resonances to individual chemical sites in silicate anions was originally a matter of speculation based mainly upon ^{29}Si chemical shift and relative intensity considerations. However, unambiguous structural assignments were made possible in the early 1980s through the combined use of (i) high magnetic field strengths and (ii) samples isotopically enriched in ^{29}Si . Here, ^{29}Si - ^{29}Si coupling provided direct evidence on intramolecular connectivities (Harris et al., 1981, 1982, 1984a; Harris and Knight, 1983a, b; Knight, 1988). Using one- and two-dimensional peak correlation techniques, eighteen silicate anions so far have been identified with a high degree of certainty, and a further four structures

assigned rather more tentatively (Kinrade and Swaddle, 1988a; Knight, 1988).

Isotopic enrichment is, however, only an effective assignment tool for silicate anions which contain two or more inequivalent chemical sites. Species which contain only a single Si environment, such as symmetric rings and cages, still yield only one NMR peak (Harris, Jones, et al., 1980; Knight, Kirkpatrick, and Oldfield, 1989). Nonetheless, it is sometimes possible to identify such species by lifting the chemical shift degeneracy within the molecule via replacement of one or more of the Si sites with chemically similar metals such as germanium (Knight et al., 1986a, 1987), aluminum (Engelhardt et al., 1982; Hoebbel et al., 1982b; Dent-Glasser and Harvey, 1984; Engelhardt and Michel, 1987; Kinrade and Swaddle, 1989; Swaddle et al., 1994), or tin (Kinrade et al., 1996).

4.3. THE CHEMISTRY OF SILICATE SOLUTIONS

By combining the results from chemical, physical and spectroscopic analyses, it is now possible to paint a reasonably detailed picture of Si chemistry for a range of aqueous environments.

4.3.1. Nomenclature and conventions

Alkaline silicate solutions are classified according to three parameters: 1) the concentration of Si; 2) the ratio of Si to basic oxide; and 3) the nature of the basic oxide. The Si to basic oxide ratio is used to represent the degree of alkalinity and may be expressed in several ways. Most commonly it is given as either the *mole* or *weight* fraction $\text{SiO}_2:\text{M}_2\text{O}$, designated respectively as R_M or R_W , where M is (typically) the alkali-metal counter ion. Alternatively, the composition may be described in terms of the ratio of total hydroxide concentration to Si concentration, $[\text{OH}^-]:[\text{Si}]$. Thus, a solution prepared from equal molar proportions of silica and sodium hydroxide is characterized by $[\text{OH}^-]:[\text{Si}] = 1.0$, $R_M = 2 / ([\text{OH}^-]:[\text{Si}]) = 2.0$, and $R_W = R_M \times (\text{molar mass } \text{SiO}_2) / (\text{molar mass } \text{M}_2\text{O}) = 1.9$. Table 4.1 lists the solution compositions commonly used in industry, together with their traditional names. These colloquial names, it is important to note, imply *nothing* about solute speciation. The chemistry of industrially important silicate solutions is the subject of an extensive review (Barby et al., 1977).

In aqueous solution, Si is almost always four-coordinated by oxygen with more or less tetrahedral symmetry. When siloxane bridges ($\equiv\text{Si}-\text{O}-\text{Si}\equiv$) occur, the tetrahedra may be visualized as sharing corners. In solution, neither edges nor faces of SiO_4 tetrahedra are ever shared. Double bonds to oxygen are unknown, as are Si-Si bonds. Thus, species of the type $\text{O}=\text{Si}=\text{O}$ or $\text{O}=\text{SiO}_2$ do not exist. Very recently, five-fold and six-fold coordination by oxygen has also been reported in solution (Kinrade et al., 1999a), as noted below in the section on Si biochemistry. Four-coordinated Si centers are denoted 'Q sites', five-coordinated centers 'P sites' and six-coordinated centers 'H sites' (for 'quadrifunctional', 'pentafunctional' and 'hexafunctional', respectively) (Kinrade et al., 1999a). The number of siloxane bonds attached to the Si center under consideration is denoted by a superscript. Thus, the simplest species, the tetrahedral monomer SiO_4^{4-} , would be represented as Q^0 , and the linear trimeric anion as $\text{Q}^1\text{Q}^2\text{Q}^1$. Because exact information on the center under consideration is denoted by a superscript. Thus, the simplest species, the tetrahedral monomer SiO_4^{4-} , would be represented as Q^0 , and the linear trimeric anion as $\text{Q}^1\text{Q}^2\text{Q}^1$. Because exact information on the protonation state of individual species is usually unavailable, the extent of ionization of any anion is not

Table 4.1

Compositions and traditional names of some common sodium silicate solutions.

Oxide molar ratio	R_M	$[\text{OH}^-]:[\text{SiO}_2]$	Traditional name
$\text{SiO}_2 : 2 \text{Na}_2\text{O}$	0.50	4 : 1	orthosilicate
$2 \text{SiO}_2 : 3 \text{Na}_2\text{O}$	0.67	3 : 1	sesquisilicate
$\text{SiO}_2 : \text{Na}_2\text{O}$	1.00	2 : 1	metasilicate
$2 \text{SiO}_2 : \text{Na}_2\text{O}$	2.00	1 : 1	di or alkaline silicate
$3.4 \text{SiO}_2 : \text{Na}_2\text{O}$	3.40	0.6 : 1	neutral silicate

represented. The terms ‘*n*-mer’ or ‘*n*-ring’ are used in reference to species containing *n* silicon sites, such as the cyclic trimer, or ‘three-ring’, Q_3^2 .

4.3.2. Solubility and speciation.

Silica (SiO_2) is only sparingly soluble in water at neutral pH, with reported solubilities at 298 K ranging from 5 ppm ($8 \times 10^{-5} \text{ mol L}^{-1}$) to 11 ppm for quartz (Rimstidt, 1997) and 100-130 ppm for amorphous silica (McKeague and Cline, 1963; Iler, 1979). Although at low pH, silica solubility increases slightly (Andersson et al., 1982), the increase is dramatic above pH values of *ca.* 9.5, and silica concentrations of several mol L^{-1} are feasible at very high pH. The chemistry of silica in solution is thus critically dependent upon pH.

A useful starting point in understanding the solution chemistry of silicates is with the help of the solubility diagram shown in Figure 4.1. Here the heavy line represents the solubility of amorphous silica. In the region below and to the right of this, silicate anions are in true solution. That is, the components of the solution are molecular, and its composition is stable with time. In very dilute and very alkaline solutions the dominant anion will be the monomer. The degree of polymerization, and thus the number and type of silicate anions present, increases as Si concentration is increased, as pH is decreased or as temperature is decreased.

The structures of the silicate anions identified in solution are shown in Figure 4.2. These species are extremely labile (see below) and equilibria are re-established within seconds in low alkalinity solutions following a change in solution composition. In the ‘instability region’, however, solutions are metastable with respect to the eventual precipitation of amorphous silica (Andersson et al., 1982). Silicate species here are no longer small labile molecules, but tend to be large particles of colloidal dimensions. These systems sometimes react slowly to changes in composition such as dilution or acidification, often taking months or years to reach equilibrium. In the region of true solution, silicate anions are governed by the dictates of polymer chemistry. They exist in dynamic equilibrium with one another. As noted above, the exact distribution of anions is critically dependent upon pH, concentration and temperature. Thus, two interdependent sets of equilibria govern solution behavior (Andersson et al., 1982). These are acid-base equilibria



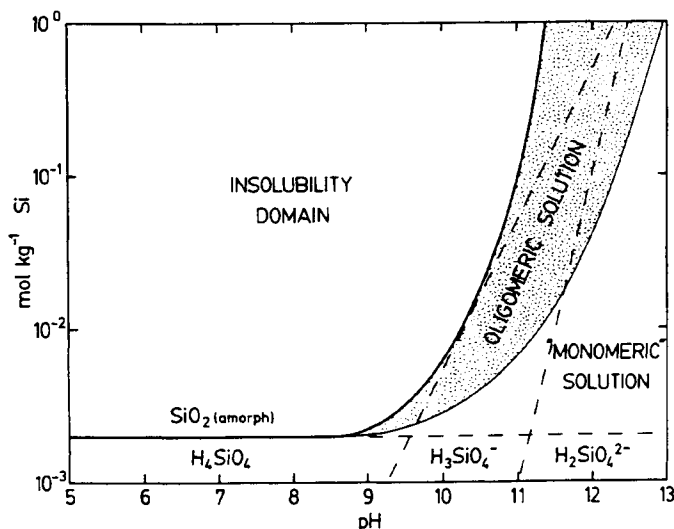
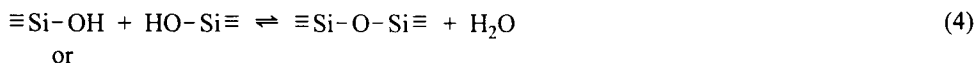


Figure 4.1. Stability diagram for soluble silicates at 298 K (after Ref. 104). The heavy solid line is the solubility curve for amorphous silica, while the dashed lines are calculated from the first and second pK_a 's of silicic acid.⁵³ The shaded region corresponds to solutions with a preponderance of oligomers. There is *no* distinct boundary, however, between oligomeric and monomeric systems. The silicate monomer is always in equilibrium with higher species.

and polymerization-depolymerization equilibria.



For any given cation, these equilibria alone define which anions will be present in solution. The source of the Si has no effect on speciation, although it can affect the rate at which the equilibrium is established. The nature of the cation(s) present, however, can influence the distribution of silicate anions, as can the presence of additives to the solution.

Since the solubility of silica in near neutral solution lies between *ca.* 5 to 130 ppm, most naturally occurring solutions contain silica concentrations within this range and, indeed, silicate concentrations at least this high are virtually unavoidable in nature. In cases of extreme alkalinity, such as in alkaline lakes where the pH may reach 9.5 or more, the solubility of silica will of course be much greater. However, due to the relatively low Si concentrations in groundwater the constituent species originally were thought to be entirely monomeric (Stumm and Morgan, 1981). Cary et al. (1982) showed that this is not the case. In neutral solutions containing 97.1 ppm silica ($1.62 \times 10^{-3} \text{ mol L}^{-1}$) at room temperature, they observed using ^{29}Si NMR that 6% of the silica in solution exists as the dimer, $\text{H}_6\text{Si}_2\text{O}_7 (\text{Q}^1_2)$. Meinhold et al. (1985) confirmed this observation in a near neutral solution that contained *ca.*

$5.5 \times 10^{-3} \text{ mol L}^{-1}$ silica. There is clearly no 'monomeric boundary' in solution. The monomer will always be in equilibrium with some amount of dimer, and also higher species. The presence of the dimer and even higher oligomers in dilute solution has also been indicated by Raman spectroscopy (Dutta and Shieh, 1985) and trimethylsilylation studies (Shimono et al., 1983; Rothbaum and Rohde, 1979). There is no doubt, however, that the *dominant* silicate molecule dissolved in groundwater is monomeric $\text{Si}(\text{OH})_4$. Typical electrolyte levels in groundwater have little apparent effect on silicate speciation (Iler, 1979). The speciation of Si in groundwater is dealt with in a recent review (Robards et al., 1994).

Concentrated solutions. As the concentration of silica in solution increases, so does the extent and range of polymerization at any given pH. High-field ^{29}Si NMR spectra of moderately concentrated (*ca.* 1 mol L^{-1} in SiO_2) alkaline silicate solutions reveal a dynamic equilibrium of over 25 different species. Harris and Knight (1983a,b), using high-field NMR along with isotopically enriched materials, provided the first definitive evidence of the structure of these anions, identifying eighteen with varying degrees of certainty. Knight and coworkers later employed two-dimensional NMR techniques (Knight, 1988) and germanium substitution (Knight et al., 1986, 1987) to confirm all the previous assignments and to tentatively identify three more species. Kinrade and Swaddle (1988a) proposed one more structure based on a variety of NMR parameters. All twenty two structures are illustrated in Figure 4.2. Two empirical observations may be made. First, the anions appear to be as highly condensed as possible. Accordingly, there is no evidence of long chains (the longest being the linear tetramer, the concentration of which is always lower than that of the linear trimer), isolated rings containing more than four Si, nor indeed any large, open framework structures (containing six-rings or larger). Compact cage-like structures are favored as polymerization progresses, the largest positively identified structures containing only nine Si sites. Second, the three-ring is a very common structural feature. This is contrary to the traditional view of silicate structures (Iler, 1979; Dent-Glasser and Lachowski, 1980), which holds that four-rings and structures based upon them are to be expected. That view, however, is based upon the results of trimethylsilylation analysis, which is now known to selectively break down cyclic trimeric species during its acidification stage (Garzo et al., 1980). Indeed, in acidic solutions, three-rings are unknown, as shown by ^{29}Si NMR studies of tetraalkoxysilane hydrolysis under acidic conditions (Harris et al., 1980b; Engelhardt et al., 1977a; Hoebbel et al., 1979; Artaki et al., 1986). The spectra here are similar to those obtained under alkali conditions, with the exception that there appears to be no signals from structures containing three-rings. Consequently, trimethylsilylation studies are likely to be considerably more accurate for acidic solutions than for alkaline solutions (Artaki et al., 1986). Dent-Glasser (1980, pers. comun.) has proposed an electrostatic model to rationalize the pH dependence of the three- and four-rings, showing that the three-ring is stabilized with respect to the four-ring when the non-bridging oxygens are deprotonated as they would be in alkaline solution. This situation arises because the non-bridging oxygens are further apart in the cyclic trimer than in the cyclic tetramer, while the opposite is true for the silicon atoms. As pH is lowered, protonation increases and the repulsion between oxygen atoms is decreased, while Si-Si repulsion remains unaffected. Eventually, the cyclic tetramer becomes the more stable configuration.

Andersson and coworkers (1982) conclude, "the labile species in true equilibrium could thus be equated with species based on rings of three tetrahedra, whereas colloidal species are based on rings of four or more. This would be consistent with what is known of crystalline silicates: rings of three tetrahedra are only very rarely encountered in extended structures such

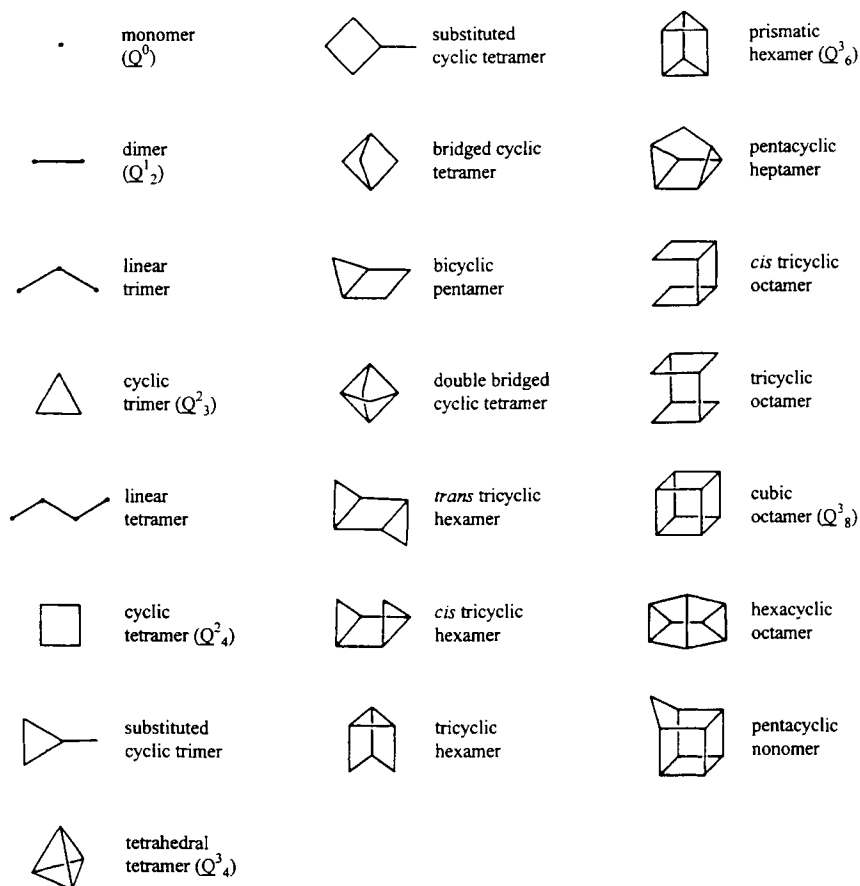


Figure 4.2. The twenty-two aqueous silicate species identified to date from ^{29}Si NMR analysis. Each line in the stick figures represents a $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ siloxane linkage.

as networks, and have so far never been found in frameworks.” In keeping with this, ^{29}Si NMR studies have shown that as silicate solutions become more acidic, the ratio of cyclic trimer to cyclic tetramer decreases dramatically (Knight, 1982; Haines, 1984).

The predilection for forming anions containing three-rings shown by alkaline silicate solutions has some far reaching implications in terms of our understanding of the molecular mechanism by which crystalline silicates form from solution. As Andersson et al. note, the three-ring is rare in extended mineral structures and unknown in molecular frameworks such as zeolites. This observation would suggest that such structures do not form by the sequential addition of pre-existing building blocks or “secondary building units”, (Meier, 1968; originally proposed by Barrer et al., 1959) because building units of appropriate structure are actually quite rare in solution. Knight (1990) has argued that such a view of zeolite formation is therefore misleading, since the idea that logical zeolite precursor structures actually exist as discrete entities in solution tends, unwittingly, to guide NMR assignment protocol.

Henry (1997), using the silicate anion structures in Figure 4.2 as his basis set, has recently proposed a semi-empirical partial charge model to account for the chemical properties of silicates.

As solutions become more concentrated yet, the complexity and quantity of anion structures increases so dramatically that NMR signals tend to overlap and assignment of signals to individual anions becomes impossible. Harris et al. (1993) have shown that it is nevertheless feasible to extract quantitative information on the types of silicate structural units present by ^{29}Si NMR, and has noted the formation of Q^4 units in very concentrated ($> 5 \text{ mol kg}^{-1} \text{ SiO}_2$) potassium and sodium silicate solutions. These are presumed to arise from colloidal particles.

4.3.3. Chemical exchange between anions.

The rate and pathways by which silicate anions interconvert have been extensively studied. In the mid 1980s, controversy arose concerning the origin of ^{29}Si spectral line broadening that occurs as the temperature of silicate solutions is increased (Engelhardt and Hoebbel, 1984; Harris et al., 1984b; Creswell et al., 1984; Griffiths et al., 1986). Engelhardt and Hoebbel (1984) speculated that the broadening is due to chemical exchange of SiO_4 between the different silicate anions. Harris and coworkers initially made the same suggestion (1984b), but later reported contradictory findings based on spin-saturation-transfer experiments performed using high alkalinity solutions (Greswell et al., 1984).

Detailed kinetic line shape analysis by Kinrade and Swaddle (1988b) showed that temperature-dependent ^{29}Si line broadening observed for solutions with $[\text{OH}^-]:[\text{Si}] = 1:1$ (conditions under which each SiO_4 center has a -1 charge) line broadening is indeed due to Si-Si chemical exchange if care is taken to exclude adventitious paramagnetic contaminants. Evidently the neutral monomer $\text{Si}(\text{OH})_4$ is the common vehicle of Si exchange. The intermolecular exchange lifetime τ for the large majority of species is merely 0.39 s at 298 K. Fitting the temperature dependence of τ to the Eyring equation

$$\tau^{-1} = (k_{\text{B}}T/h) \exp[(\Delta S^\ddagger/R) - (\Delta H^\ddagger/RT)] \quad (6)$$

Kinrade and Swaddle obtained an enthalpy of activation $\Delta H^\ddagger = 50.0 \text{ kJ mol}^{-1}$ and an entropy of activation $\Delta S^\ddagger = -69 \text{ J K}^{-1}$ for the polymerization process controlling spin-site lifetimes in solutions with $[\text{OH}^-]:[\text{Si}] = 1:1$. For hydrolysis of the silicate dimer, $\Delta H^\ddagger = 51.0 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -51.8 \text{ J K}^{-1}$, and the first order rate constant $k_{298 \text{ K}} = 14 \text{ s}^{-1}$. Resonances corresponding to the acyclic trimer and acyclic tetramer broaden to a greater extent than all the others due to rapid intramolecular cyclization (Kinrade and Swaddle, 1988b; Knight et al., 1988). These kinetic data, all obtained through ^{29}Si NMR, were later corroborated by dynamic ^{17}O NMR measurements (Kinrade, 1996; Knight et al., 1989).

At higher $[\text{OH}^-]:[\text{Si}]$ ratios silicate centers become further deprotonated, dramatically retarding Si-Si exchange – with site lifetimes increasing about 100-fold as $[\text{OH}^-]:[\text{Si}]$ goes from 1:1 to 4.5:1 – and decreasing both the extent and uniformity of temperature-dependent line broadening (Kinrade and Swaddle, 1988b). Therefore, exchange rates can be difficult to determine by line shape analysis. Also, paramagnetic relaxation makes a proportionally greater contribution to broadening at higher pH values. Vallazza et al. (1998) used the selective inversion-recovery (SIR) technique at elevated temperatures to monitor ^{29}Si - ^{29}Si exchange between the monomer, dimer and cyclic trimer in solutions with $2.8 \text{ mol kg}^{-1} \text{ Si}$ and $[\text{OH}^-]:[\text{Si}] = 4.7:1$. They determined actual rate constants for dimer formation, giving $k_{363 \text{ K}} =$

$0.13 \text{ kg mol}^{-1} \text{ s}^{-1}$, $\Delta H^\ddagger = 67.4 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -78 \text{ J K}^{-1}$, and for dimer hydrolysis, giving $k_{363 \text{ K}} = 1.4 \text{ s}^{-1}$, $\Delta H^\ddagger = 64.7 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -66 \text{ J K}^{-1}$.

In addition, Bahlmann et al. (1997) have measured self-diffusion coefficients of silicate anions in concentrated solution, ranging from $5.8 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ for Q^4 centers to $1.9 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for Q^1 centers. These provide the upper limits to chemical exchange.

4.3.4. Effect of cations on silicate speciation and kinetics.

Early ^{29}Si NMR studies indicated that varying the alkali-metal ions in silicate solutions had little effect on speciation or on the overall extent of polymerization (Harris and Knight, 1982). Later observations, however, suggest that silicate-cation ion-pairing promotes silicate condensation by weakening the electrostatic repulsion between silicate anions (Kinrade and Pole, 1992). Yet, because strongly paired cations will resist subsequent formation of a siloxane bond, the extent of polymerization increases slightly in the order $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$, *i.e.*, with increasing size of hydrated ion. Electrostrictive water-structuring apparently causes additional polymerization in the case of Li^+ . Moreover, M^+ cations stabilize certain large polyanions with open frameworks that, without the support of silicate- M^+ ion-pairing, quickly rearrange into more compact structures (Kinrade and Pole, 1992). In contrast, silicate condensation kinetics are negligibly affected by the concentration and nature of alkali-metal cation in solution (Knight, unpub.).

Silicate solutions may also be prepared with organic bases with dissociation constants greater than *ca.* 1×10^{-3} (Merrill and Spencer, 1951). In this case, though, the effect on speciation can be very pronounced. Silicon-29 NMR spectroscopy has been used to investigate the components of silicate solutions prepared with tetramethyl- (Lippmaa et al., 1978; Harris and Knight, 1982; Hoebbel et al., 1982a; Engelhardt and Hoebbel, 1983; Engelhardt and Raemacher, 1984; Knight et al., 1986a,b), tetraethyl- (Hoebbel et al., 1980; Harris and Knight, 1982), tetrapropyl- (Harris and Knight, 1982; Cavell et al., 1982; Boxhoorn et al., 1983), and tetrabutyl- (Harris and Knight, 1982; Hoebbel et al., 1984) ammonium hydroxide, trimethyl- and triethyl-(2)-hydroxyethylammonium hydroxide (Schlenkrichet et al., 1984a,b, 1990), triethyl-(2)-hydroxypropylammonium hydroxide (Ziemans et al., 1984), benzyltrimethyl-ammonium hydroxide (Knight, n.d.), *n*-(2)-hydroxyethyl- and *n*-(2) hydroxypropylpyridinium hydroxide (Rademacher et al., 1984), choline (Kinrade et al., 1998a), and benzyltrimethylammonium methoxide (Knight, unpub.) As opposed to the multitude of small anions found in the alkali-metal silicate solutions, concentrated tetramethylammonium silicate solutions are dominated by the cubic octamer (Q^3_8), and, to a lesser extent, the prismatic hexamer (Q^3_6) (Kinrade et al., 1998a,b). (Refer to Figure 4.2.) Similar control over speciation is exhibited by other quaternary ammonium ions, however the extent decreases systematically with the number and size of alkyl- or aryl substituents (Kinrade et al., 1998a,b). When all four groups are C4 or bigger, the effect disappears completely (Harris and Knight, 1982). What causes these particular polyanions to be favored? Kinrade et al. (1998a,b) provide convincing evidence to suggest that cage-like species, having numerous anionic sites which project in several directions, become surrounded by ion-paired tetraalkylammonium cations. The hydrophobic hydration spheres on the cations merge, decreasing solvent mobility in the immediate vicinity of the silicate anion, and thereby impede hydrolysis. The formation of such 'clathrated polyanions' explains why freshly prepared tetraalkylammonium silicate solutions can require as much as a week to attain equilibrium conditions (Knight et al., 1986b).

However, it is important to note that it is only the relative distribution of silicate structures

that is dependent upon the organic cation. Tetraalkylammonium silicate solutions contain the same array of species as do alkali-metal silicate solutions, with approximately the same relative concentrations, except that the cubic octamer and prismatic hexamer are notably favored. Indeed, one cation may favor an individual silicate anion structure over others, but there are no examples of species that are *unique* to a given cation. Furthermore, the cumulative weight of evidence tends to indicate that, for solutions of intermediate concentrations and pH values, there is not an unlimited range of silicate anion types possible. The structures of all the major anions observed in a wide variety of alkali-metal and organic base silicate solutions have already been determined and reported, and are shown in Figure 4.2. Of course, as noted earlier, very concentrated solutions can contain a great number of anion structures of colloidal or near-colloidal dimensions. However, the species shown in Figure 4.2 are ubiquitous and consistent, and represent the twenty two simplest species observed in any solution regardless of the cation.

4.4. SILICON BIOCHEMISTRY

As Epstein has noted (1999), some plants cannot live without Si, an observation that implies a direct biochemical function for silicates. However, there have been very few reports of direct chemical interaction occurring between aqueous silicates and organic species. Indeed, well-defined instances of formal Si-O-C bonds occurring in aqueous solution are so rare that their very existence has been questioned (Birchall, 1995). Yet simple organisms such as diatoms actively isolate, transport and deposit silica on a massive scale, and thus must form stable organo-silicate complexes under aqueous conditions.

One aspect of recent work has focused on the biochemical activity of naturally occurring proteins associated with silica in plants. Hildebrand et al. (1993) cloned and characterized the cDNA encoding the first silicic acid transporter protein ever identified, and more recently (1998) cloned a family of genes that code for such proteins. They noted that the protein forms a sodium-dependent transmembrane ion channel that mediates the transport of silicic acid. This could help to account for the uptake of silicic acid from groundwater. Kroger et al. (1994, 1997) have cloned cDNA's that encode two families of proteins known to contribute to the organic sheath surrounding the silica walls in diatoms. These proteins contain regular arrays of hydroxyl rich regions, which may attract and organize silicate species (Swift and Wheeler, 1992; Harrison, 1996), eventually forming opaline silica, as originally suggested by Hecky et al. (1973). Morse and colleagues (Shimizu et al., 1998; Cha et al., 1999) recently identified three similar protein subunits which they termed 'silicateins'. Cloning and characterizing the cDNA's responsible for encoding silicatein- α (the most common subunit), Morse notes that it is "highly homologous to members of the cathepsin L subfamily of papain-like proteases, suggesting a possible catalytic mechanism for its control of silicification" (Shimizu et al., 1998). Interestingly, silicatein contains "tandem arrays of multiple hydroxyl" (Shimizu et al., 1998). Perry and Lu (1992) have shown that hydroxyl-rich polysaccharides are capable of affecting silica polymerization. Thus, it seems that hydroxy groups may play a key role in biosilicification. Indeed, Morse and co-workers (Cha et al., 1999; Zhou et al., 1999) recently suggested a detailed reaction mechanism involving the hydroxy group of serine-26 and the imidazole side chain of histidine-165 for the silicatein-a mediated hydrolysis of tetraethoxysilane at neutral pH *in vitro*. Furthermore, a set of polycationic peptides, 'silaffins', have been isolated from diatom cell walls by Kroger et al.

(1999). These have been shown to increase markedly the rate of condensation of silicic acid. Here again, a high proportion of hydroxy amino acids are present. Thus, although specific reaction mechanisms and structures remain unknown, the role of hydroxy containing substrates is beginning to appear to be critical in the natural chemistry of silicates.

Although evidence is now accumulating concerning the role and structure of the proteins associated with silica in plants, there is still little hard information available about the chemistry involved, and the fact remains that no organosilicon complex has ever been detected under physiological conditions.

There are in fact very few reported examples of any type of formal organo-silicate

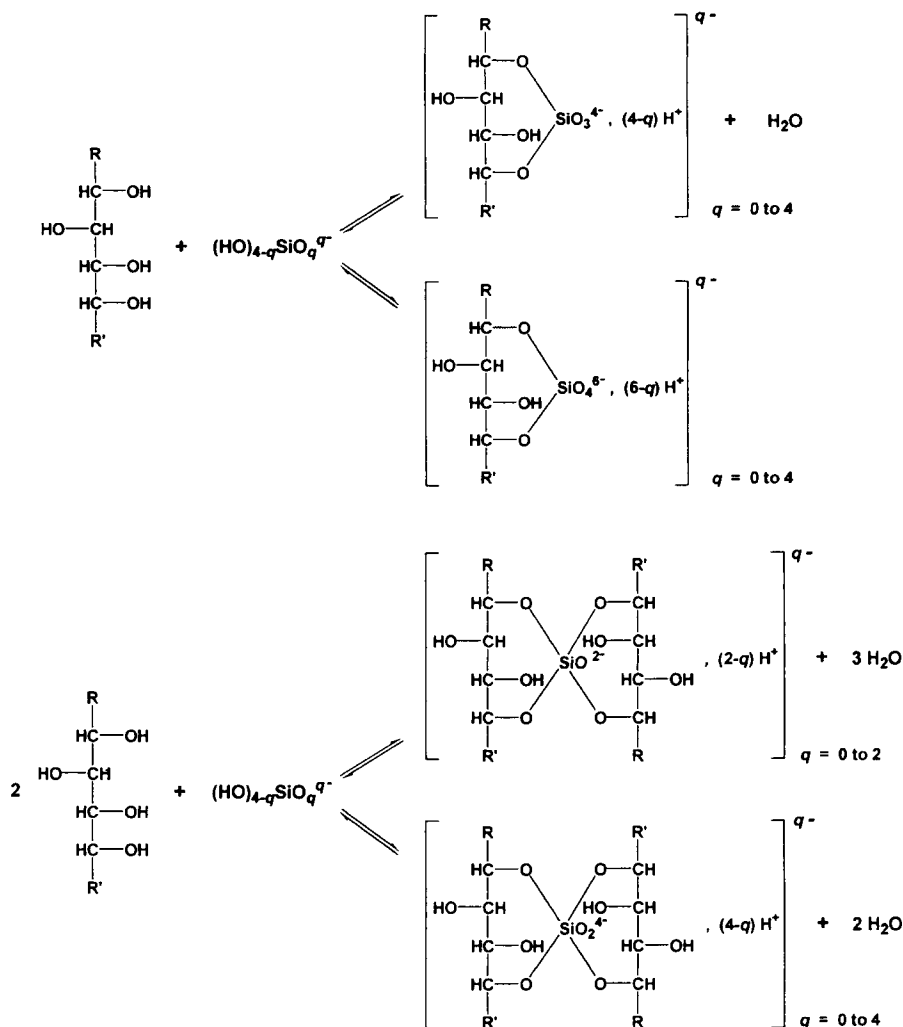


Figure 4.3. Reaction schemes for the formation of five- and six-coordinated silicon polyolate complexes, where R and R' represent polyol chain ends.

compounds in nature. Up until 1999, the only documented cases were that of the six coordinate complexes formed when silicon is chelated by catechol, 2-hydroxypyridine N-oxide, tropolone or their respective analogues (Gardner and Katrizky, 1957; Weiss and Harvey, 1964; Sjoberg, 1985b; Evans et al., 1992; Sedeh et al., 1992). Very recently however, Kinrade and colleagues (1999b) have shown that stable alkoxy substituted silicate anions are readily formed when aliphatic mono- or polyhydroxy alcohols are added to alkaline silicate solutions. Moreover, high concentrations of five- and six-coordinated Si complexes, as shown in Figure 3, result from the addition of certain aliphatic polyhydroxy molecules ('polyols' such as threitol, xylitol, and sorbitol) to alkaline silicate solutions (Kinrade et al., 1999a). These only occur, however, if the polyol contains four or more hydroxy groups, two of which are in *threo* configuration. Silicon coordinates to the hydroxy oxygens on the two carbons at either side of the *threo* hydroxy pair. Indeed, at this conference, we have disclosed as yet unpublished data showing that polyols which contain terminal carboxylate groups show even greater affinity for silicates, and form 5-coordinate silico-polyolate complexes even at neutral pH. This is the first reported example of an organosilicon complex self assembling under biologically relevant conditions, and may perhaps be one of the loose ends required to start unraveling the so far intractable field of silicon biochemistry. Silicon-29 NMR spectroscopy seems ideally suited to such a task, modern instruments being capable of detecting silicon containing compounds down to 150 ng mL^{-1} (150 ppb) in favorable circumstances (Knight and Kinrade, 1999), implying that even the low concentrations of organosilicon compounds thought to exist in natural systems may now be directly amenable to NMR analysis.

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Chapter 5

Silicon Deposition in Higher Plants

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Silicification is reported in the Pteridophyta and the Spermatophyta, including gymnosperms and angiosperms. Dicotyledon families containing Si accumulators of considerable agricultural significance include the Fabaceae, Cucurbitaceae and Asteraceae. Among the monocotyledons, the Cyperaceae and Poaceae (Gramineae) are pre-eminent. Silica deposits, commonly called phytoliths, occur in cell walls, cell lumens or in extracellular locations. These deposits frequently possess a characteristic morphology revealing their tissue and taxonomic origin. Silicification occurs in roots and the shoot including leaves, culms and in grasses, most heavily in the inflorescence. Deposits occur in epidermal, strengthening, storage and vascular tissues. Biogenic silica structure is affected by ambient physico-chemical conditions mediated by tissue maturation, pH, ionic concentrations and cell wall structure, as illustrated by the results of a developmental study of silicification in wheat seedlings. Silicified tissues provide support and protection and may also sequester toxic metals, as illustrated by our recent work on the codeposition of aluminum with silicon in cereals and conifers. Some phytoliths have been implicated as carcinogens. Phytoliths are being increasingly used in archaeology as many retain their morphology in sediments.

5.1. RANGE OF PLANT GROUPS

Solid silica, $\text{SiO}_2 \cdot n\text{H}_2\text{O}$, is deposited by higher plant tissues following the root uptake of soil water containing monosilicic acid, H_4SiO_4 . Terms applied include plant opal, opaline silica and silica gel. The widely used term, phytolith, is reserved for silicified structures, produced in higher plant tissue (Piperno, 1988). Although phytoliths vary as to their tissue location, those produced within families reveal a consistent similarity of form. From the early investigations by de Saussure (1804), phytolith formation has been described for the Pteridophyta, including the horsetails (Equisitaceae) and the spikemosses (Selaginellaceae) (Dengler and Lin, 1980) for the Spermatophyta (seed-bearing plants), including the divisions Coniferophyta (gymnosperms) and Magnoliophyta (angiosperms), the latter subdivided into the Magnoliopsida (the dicotyledons) and the Liliopsida (the monocotyledons).

Piperno (1988) investigated over 1000 species of New World tropical plants representing

70 dicotyledon families, recording the frequency of various phytolith types produced by individual plant organs. Economically significant dicots, which form silica deposits, include arrowroot, *Maranta arundinacea*, avocado, *Persea americana*, banana, *Musa paradisiaca*, pineapple, *Ananas comosus*, and squash, *Cucurbita*. The following families are consistent accumulators of identifiable phytoliths: Poaceae or Gramineae (grasses) and Cyperaceae (sedges) among the monocotyledons and the Ulmaceae (elm), Fabaceae (bean), Cucurbitaceae (squash) and Asteraceae (sunflower) among the dicotyledons (Mulholland and Rapp Jr., 1992). The examples described in this paper do not constitute a comprehensive, but rather, a selective review of representative studies, primarily of cereals and grasses. A broader range of plant groups is treated in previous reviews (Jones and Handreck, 1969; Kaufman et al., 1981; Parry et al., 1984; Piperno, 1988; Sangster and Hodson, 1986). Following decay-in-place mechanisms in the detritus, the plant phytoliths become incorporated into the upper soil horizon, where, as predicted by Dr. F. Smithson (University of Wales), "they might provide information about the former vegetation" (Smithson, 1956). Subsequently, depending upon soil conditions, dissolution transforms amorphous silica back into monomeric silicic acid, thus completing the biogeochemical cycle of Si.

5.2. PHYTOLITH MORPHOLOGY AND PLANT ORGANS

Following uptake and transport, root and shoot tissues are exposed to monomeric silicic acid. Silicification is governed by cell development and tissue maturation. Deposition generally does not occur in juvenile organs during the cell expansion stage, the exception being in the specialized silica cells, which may be silicified even in juvenile leaves, not yet differentiated into sheath and blade (Parry and Smithson, 1964). In mature organs, however, silica deposition may occur in cells of tissues associated with protection, storage, support and strengthening.

5.2.1. Range of deposition sites

Three loci of silicification are recognized: (i) the cell wall; (ii) the cell lumen, either wholly or partially infilled with silica and (iii) the intercellular spaces in root or shoot tissues or in an extracellular (cuticular) layer (Sangster and Hodson, 1986; Piperno, 1988). Phytolith shape is determined by taxonomic affinities. The most distinctive phytoliths arise from characteristic epidermal cells, including the silica cells or idioblasts, the hairs or trichomes and the stomatal complex. Other distinctive types may originate from the hypodermis and the mesophyll, as well as sclerenchyma, endodermal and vascular cells (Piperno, 1988).

5.2.2. Silica in archaeology and food science

The presence of identifiable soil phytoliths offers the possibility of detecting ancient agricultural systems and their cultigens (ethnobotany) or of determining ancient vegetational composition (palaeoecology). Following separation from the soil, phytoliths are identified by means of microscopic examination (Piperno, 1988). Computer-assisted image analysis is also employed to examine three-dimensional structure (Rovner and Russ, 1992). Identification involves comparison with modern phytolith assemblages (Twiss et al., 1969) in conjunction with regional phytolith keys, such as the survey of the grass phytoliths of the central U.S. by Brown (1984) which defines, illustrates and tabulates phytolith shapes by species, genus and

tribe. These deposits are characteristic primarily of the grass shoot, including the leaf (sheath and lamina), and culm (Piperno, 1988; Mulholland et al., 1992). The phytoliths of floral bracts are highly diagnostic allowing for discrimination between species at archaeological sites. Inflorescence papilla phytoliths can be used to distinguish between barley (*Hordeum vulgare*) and wheat (*Triticum aestivum*), and between different wheat species and cultivars (Tubb et al., 1993). The papillae of bread wheat (*Triticum aestivum*) can be distinguished from those of barley (*Hordeum vulgare*) as they are larger and have more pits. Within the genus *Triticum*, pit number and papilla diameter increase as the ploidy level increases from AA to AABB, and again from AABB to AABBDD. This type of approach has been developed much further using image analysis and statistical analysis to compare the phytoliths of wheat species (Ball et al., 1996). This type of work holds great promise for the future.

Bread wheat has the genome AABBDD, while durum wheat (*Triticum durum*) is AABB. The grain of durum wheat is ideal for the making of pasta, and bread wheat grain makes pasta of inferior quality. Adulteration of durum with bread wheat is difficult to prove, particularly in cooked pasta products. A method for the detection of adulteration of pasta samples with bread wheat using inflorescence papillae was developed (Hodson et al., 1999). Papillae of mean diameter over 20 μm mostly originate from *T. aestivum*, while papillae of mean diameter below 15 μm mostly originate from *T. durum*. Phytoliths were then extracted from pasta samples. All of the samples investigated contained phytoliths, and microhairs were common. Inflorescence papillae were rare, but some were located in all samples. All of the papillae isolated were of similar dimensions to those seen in *T. durum* inflorescence bracts, and no evidence of adulteration was found. This method has the potential to be developed into a standard adulteration test.

Silicification in graminoid roots is confined to the endodermis during maturation. However, in older roots, the cell walls of virtually all tissues - epidermal, cortical and vascular, may become silicified (Sangster, 1978). The graminoid rhizome (tribe Andropogoneae) exhibits up to four concentric zones of silicification involving variously the epidermis (a major deposition site), cortical air canals, perivascular cells (bundle sheaths, endodermal) and vascular tissues (Sangster, 1985). These underground graminoid phytoliths appear to lack the distinctive characteristics required to qualify them as diagnostic tools for phytolith analysis (Parry et al., 1984; Sangster and Hodson, 1986; Piperno, 1988; Sangster and Hodson, 1992). Of the few Old World dicotyledon domesticates tested, some produce genus-specific phytoliths (e.g. *Cucurbita* sp.) while others (e.g. manioc, *Manihot esculenta*; cotton, *Gossypium barbadense*) do not. Most New World root and tuber domesticates are in the latter category (Piperno, 1988). As the information base increases, so too does the usefulness of the phytolith analysis technique.

5.3. FACTORS AFFECTING SILICIFICATION

Silica deposition is influenced by the age, type and location of tissues, as well as by root uptake and transpiration. Relevant soil factors would include silica, nutrient and water content, pH and soil type. The impact of atmospheric on climatic factors is not completely understood (Jones and Handreck, 1969; Hodson and Parry, 1982; Lanning and Eleuterius, 1985; Sangster and Hodson, 1986).

5.3.1 Silica distribution in the mature plant

The total silica content of cereals increased in all parts of the shoot with increasing age which was attributed to continuous deposition in the plant tops (Jones and Handreck, 1969). The significance of tissue and organ location was shown by the consistent increases of total plant silica, starting in the roots of cereals through the leaf sheaths to the leaf blades. In rice, the corresponding figures, on a dry matter basis for root, leaf sheath and blade, were 2.07, 12.3 and 13.4% SiO_2 , respectively (Yoshida et al., 1962). The highest silica levels generally occur in the inflorescence bracts (Jones and Handreck, 1969). In rice, solid silica gel constituted 90% of the total silicon, and soluble or colloidal forms, the rest. Silica gel was compartmentalized between the cell lumens and cell walls and as an extracellular layer under the cuticle. This cuticle-silica layer was the heaviest silica deposition site in the rice leaf and inflorescence husk (Yoshida et al., 1962). The basic silica distribution pattern was unaffected by varying the monosilicic acid content of the soil solution over the range of 7 to 67 ppm SiO_2 (Jones and Handreck, 1969).

Between-leaf variation of silica content occurs in wheat and barley, where the upper leaves contain more silica than do the lower. The uppermost, or flag leaf of the oat plant contains the highest silica concentration. In addition, in oats, silica distribution along a single leaf is non-uniform, following a hyperbolic curve, the concentration being highest at the apex and lowest at the base of the blade (Handreck and Jones, 1968; Jones and Handreck, 1969). Silicified bulliform cells along the leaf blade exhibited a maximum apical frequency followed by a decreasing basipetal gradient in rice and Bermuda grass (Sangster and Parry, 1969), and two moorland grasses (Parry and Smithson, 1964). Assemblages of phytoliths from (i) different leaf parts and (ii) cultivars of corn (maize) varied significantly (Mulholland et al., 1988). This within-leaf distribution pattern is attributable to the basipetal developmental sequence of tissue maturation exhibited by the graminoid leaf (Sangster and Parry, 1969), while the between-leaf differences reflect differential leaf growth rates during shoot ontogeny (Sangster, 1970a). In growing leaves, cellular expansion and a basipetal senescence gradient may severely limit the availability of silica deposition sites (Sangster and Parry, 1969). However, in senescing leaves, where cytodifferentiation and tissue maturation cease to be limiting factors, in the grass *Sieglingia* (*Danthonia*) *decumbens* virtually all leaf cell types became potential repositories for silica; whereas, in younger leaves, intracellular deposition was confined to silica cells and abaxial long cells. Also, in senescing leaves, deposition shifted to the other (adaxial) leaf surface, to epidermal cells other than silica cells (e.g. bulliform cells), as well as to sub-epidermal tissues (Sangster, 1970b). Similarly, the walls of most cells of the mature oat plant eventually become silicified. Non-uniform distribution of silica has been interpreted as indicating that silica is carried passively in the transpiration stream and deposited most heavily where the water loss is greatest (Jones and Handreck, 1969).

In subterranean organs, the extent of silicification also is determined by developmental anatomy. Along the gradient of tissue maturation in roots, silica deposits are confined to the older, basal portion, being absent from the extending tip region. In growing rhizomes, silica deposition is very restricted, as in the apical epidermis, but in older organs, it becomes increasingly non-specific (Parry et al., 1984; Sangster, 1985; Sangster and Hodson, 1986).

Other significant factors are: (i) the soil silica content; (ii) root uptake rates; (iii) the transpiration rate; (iv) the soil nutrient level. The concentration of monosilicic acid in soils is influenced by the pH and the presence of iron and aluminum oxides. Species can be divided

into Si - accumulators, such as wheat and ryegrass (*Lolium*) (Jarvis, 1987) or Si – excluders, such as crimson clover (*Trifolium incarnatum*) which metabolically excludes monosilicic acid (Jones and Handreck, 1969). The transpiration rate may greatly influence the amount of monosilicic acid translocated to the shoot. Finally, soil fertilization with either nitrogen or phosphorus decreased the silica content of barley and wheat (Jones and Handreck, 1969).

5.3.2. Leaf silica distribution patterns

Silica deposition differs between the abaxial (lower) and the adaxial (upper) leaf surfaces. In mature leaves of *Sieglingia decumbens*, deposition is restricted to specialized epidermal cells above the veins or at the leaf margins, thus leaving the considerable areas between the veins (intercostal) largely deposit-free on both surfaces. Especially on the adaxial surface, deposits in cell lumens could interfere with light transmission to the mesophyll chlorenchyma, while internal wall silicification might affect permeability and transport. It is only in senescent leaves that deposits appear in the intercostal zones (Sangster, 1970b). Similarly in barley, Hayward and Parry (1973) found that the total Si content was greatest in the abaxial leaf surface. In the adaxial surface, Si was confined to the trichomes, sclerenchyma and silica cells along veins, thus avoiding the photosynthetic areas. Even at the leaf apex (oldest), no silica was detected in the intercostal zones of the adaxial surface.

The pulvinus, located at the base of the leaf sheath (Pooideae) or the culm internode (Panicoideae), possesses starch statoliths. The lower side of the pulvinus grows by cell wall elongation in response to horizontal displacement of the shoots (geotropism). Pulvini of all grasses examined preferentially exclude, or accumulate very little silica; whereas, the regions of the shoot immediately above and below accumulate large quantities of silica (Dayanandan et al., 1977). Although epidermal cork cells generally are deposit-free, they may be sporadically silicified in older leaves and inflorescence bracts. In the intercostal zones of the leaf sheath and culms, cork cells frequently are paired with silica cells (Parry and Smithson, 1966; Blackman, 1969). Mechanisms by which tissues avoid silica deposition remain to be elucidated.

5.3.3. Silica detection

Earlier investigations employed tissue ashing and clearing by strong oxidants or acids, followed by the use of histochemical dyes such as toluidine blue or phenol, prior to mounting in a medium of differing refractive index so that the silica is visible under the microscope (Blackman, 1968). Quantitative estimations were made gravimetrically by ashing or by the colorimetric measurement of a blue silico-molybdate complex, as used to measure free (soluble) and deposited silica fractions during the leaf ontogeny of rye (*Secale cereale*) (Blackman, 1968; Sangster, 1970b; Kaufman et al., 1985).

Optical techniques were utilized by Drs. D. Wynn Parry and F. Smithson, University of Wales, Bangor, N. Wales (1958, 1964, 1966) in their pioneering survey of opal phytoliths in British grasses and cereals, especially phase-contrast and polarization, which increase the contrast by using the sequence of colors (Newton's scale) in thin films caused by various birefringent tissues, thus rendering the silica bodies more visible.

Kaufman et al. (1985) applied industrial methods to stain silica gel which exhibits surface absorption of numerous organics. Staining procedures for plant silica were devised using methyl red, crystal violet lactone, and silver amine chromate. By removing interfering components from the silica and surrounding tissues, these chemical tests were rendered

specific for silica, based upon the reactivity of the silanol groups (-Si-OH) of silica bodies (Dayanandan et al., 1983; Kaufman et al., 1985). The tests were then utilized to quantitatively determine the relative densities of silica bodies, bulliform cells, trichomes and long epidermal cells in adaxial (upper) and abaxial (lower) epidermi of leaves of various C₃ and C₄ grasses. The C₄ grasses, typical of warmer regions, have higher frequencies of bulliform cells, silica cells and long epidermal cells, whereas the C₃ grasses (minimum July mean of 20°C) have higher frequencies of trichomes. For both categories, the adaxial epidermis has 1.5 times more silica cells per unit area of leaf surface, than does the abaxial (Kaufman et al., 1985; Lanning and Eleuterius, 1989).

5.4. CHARACTERISTIC SILICATES OF VARIOUS PLANT ORGANS

Quantitative determinations of silica in bulked plant tissue samples using gravimetric techniques may obscure highly localized and irregular silica deposition. Electron-probe microanalysis (EPM) in combination with the scanning electron microscope (SEM) can be used to detect such distributions yielding analyses which are quantitative except at the lower concentrations because of the high background in the X-ray spectrum due to bremsstrahlung radiation. Lower detection limits are high, varying from 0.2 to 2%, depending on the element. Because of its much lower background radiation, the scanning proton microprobe overcomes this problem (Mazzolini et al., 1985).

5.4.1. Hazardous silica fibers

Using optical microscopy, it was shown that the dust arising from the storage and handling of wheat grains contained fiber-shaped, acicular fragments of silica, derived largely from the inflorescence bracts. Because of their respirable size, and their hardness, specific gravity and shape, these silica particles were believed to cause broncho-pulmonary ailments (Baker, 1961). EPM studies of the inflorescence bracts of barley and rice revealed that the elongated sclerenchyma fibers and trichomes were silicified (Hayward and Parry, 1973; Soni and Parry, 1973). Inhalation of the airborne dust produced by the burning of sugarcane (*Saccharum officinarum*) leaves during harvesting also was implicated in pulmonary diseases. In a study of ashed sugarcane leaves (Trinidad), Newman (1983) demonstrated the presence of acicular biogenic silica, especially hypoderm fibers, 0.85 μm in diameter and 10-300 μm long, within the carcinogenic size range for asbestos fiber. In a later study of sugarcane harvesting in Florida, similarly-sized silica fibers of leaf origin, were found, at concentrations as high as 300,000 fibers m^{-3} of air (Boeniger et al., 1988).

Oral ingestion of plant silica phytoliths also has been implicated as a cause of human and animal health problems. Siliceous uroliths can occur in human kidneys because silicic acid is freely diffusible in tissue fluids. It is suggested that high fiber diets could be a major source of silicon uptake (Parry et al., 1984). Urolithiasis in grazing sheep was an economic problem in western Australia where mortalities in individual flocks occasionally reached 30%. Renal calculi formation was found to be related to urinary silica concentration and wheat diet (Nottle and Armstrong, 1966). Another potential problem for ruminants is presented by the ingestion of the fern, bracken (*Pteridium aquilinum*), which contains silica in the epidermis walls and in elongated sclerenchyma fibers (Parry et al., 1985).

5.4.2. Silica and human cancer

Plant silica has been implicated in the aetiology of human esophageal cancer in the three geographic areas of highest incidence (O'Neill et al., 1986). Although many interacting variables are suspected, the investigative focus has been upon local dietary components (Parry et al., 1984). In the S. African region, certain foods are contaminated with silicified leaf hairs, up to 650 μm long, derived from weedy dicots, especially *Sonchus oleraceus* and *Bidens pilosus* (Parry et al., 1984; Parry et al., 1986). In northern China, foxtail millet (*Setaria italica*) is a dietary component whose inflorescence bracts may contain up to 20% silica dry weight. Studies revealed heavy deposition in epidermal papillae, in a layer external to the outer aleurone walls of the caryopsis, in bristles subtending the inflorescence bracts and in unicellular macrohairs covering the inflorescence branches (Hodson et al., 1982; Parry et al., 1984). In Iran, O'Neill et al. (1980) found that the local bread contained fine siliceous hairs originating from several grasses of genus *Phalaris*. Flour samples contained up to 3000 hairs per gram, which experimentally, were found to stimulate the proliferation of mouse fibroblast cells by 100-fold. These acicular fibers, up to 250 μm long, fall within a critical size range for carcinogenic activity (Bhatt et al., 1984). Subsequent examination of four *Phalaris* species which contaminate the cereal crops of the Middle East indicated that the macrohairs and the friable sheets formed by the silicification of the abaxial epidermis of the inflorescence bracts were the main source of sharp, elongated siliceous fibers. Developmentally, silicification of the macrohairs and epidermal long cells of the lemma was initiated immediately following panicle emergence (Sangster, Hodson, and Parry, 1983; Sangster, Hodson, Parry, and Rees, 1983).

Although much indirect evidence has been gathered in support of the plant silica-cancer hypothesis, it is still not known how plant silica interacts with animal tissues to produce cancers. One of the key species thought to be involved in carcinogenesis in NE Iran, is *Phalaris canariensis* (Sangster, Hodson, and Parry, 1983). More recent studies have focused on an attempt to locate plant silica fibers, isolated from the inflorescence of the grass *P. canariensis*, in animal tissues by labeling the fibers with fluorescent dyes. Rhodamine or FITC were covalently linked to acid-extracted fibers and using confocal microscopy, these were observed in thick sections of mouse skin tissue (Hodson et al., 1994). With the retirement of Dr. C. H. O'Neill (Imperial Cancer Research Fund, London, UK), much of the drive to investigate this topic has evaporated. A recent review (McLaughlin et al., 1997) concluded, "In summary, the overall evidence from existing studies indicates that amorphous silicas are unlikely to be carcinogenic in humans. However, the limitations in previous studies preclude definitive conclusions." However, the irritant nature of the *P. canariensis* macrohairs has long been recognized, and this has led crop breeders at the University of Saskatchewan in Canada to develop a glabrous variant, which has no hairs on its inflorescence bracts (Putnam et al., 1996). This group saw the elimination of these plant trichomes as an important goal. The hypothesis that plant silica could be involved in human cancer now has a lot of evidence to support it, but if this work is to be taken forward, it will require cancer scientists to show renewed interest.

5.4.3. Anatomical studies

A transmission electron microscope (TEM) coupled with energy-dispersive X-ray (EDX) microanalysis was used (Perry et al., 1984) to follow silicification in the walls of the lemma macrohairs of *P. canariensis*. Silica was deposited in sheet-like and globular arrangements,

indicating that different structural morphologies of silica are initiated at precise time intervals during wall development. A study of the macrohair lumen, using a scanning proton microprobe, indicated that during these wall events, the vacuolar content of potassium, phosphorus, sulphur and chlorine steadily declined. This result was regarded as indicative of a controlled silicification process (Perry et al., 1984). A further study measured ionic contents of fresh lemmas of *P. canariensis* by chemical analysis and also obtained TEM-EDX microanalyses of lemmas prepared by the freeze substitution method, which immobilizes the soluble ions so as to precisely determine their subcellular location. Ionic levels and water content of the lemmas declined immediately following panicle emergence. Soluble silicon moved primarily via the macrohair walls where potassium and chlorine ions also accumulated (Hodson and Bell, 1986).

The mature inflorescence of wheat was investigated using SEM-EDX microanalysis. Various patterns of silicified papillae, silica cells and prickles, interspersed with sinuous-walled long cells, were characteristic of the epidermis of the lemma and glume. However, the majority of long siliceous fibers originated from the apex and margins of the palea (bract). The entire outer wall system of the epidermal complex of both the glume and lemma was silicified with the greatest Si concentration in the trichomes. Deposition was greatest in the outer (abaxial) surface of the bracts (Hodson and Sangster, 1988b; 1989b). Backscattered electron imaging was found to be useful in revealing the epidermal silica distribution pattern of the wheat bracts (Hodson and Sangster, 1989b) and for other members of the Poaceae (Brandendurg et al., 1985).

In the epicarp trichomes (brush hairs) of wheat, most Si is deposited as a thin (100 μm) outer wall layer at the tips, shortly after inflorescence emergence, and similarly for these hairs in barley, oats and rye. Hair silicification for wheat is determined by an interaction between genotype and climate (Bennett and Parry, 1981; Perry et al., 1984; Sangster and Hodson, 1986).

5.4.4. Developmental studies using the cryo-SEM

Frozen hydrated sections taken from the root, culm, leaf and inflorescence of wheat were examined by EDX on the cryostage of an SEM. This technique not only prevents loss but also minimizes the redistribution of soluble ions. In the root, soluble Si was located in the lumina of the central metaxylem and in the radial walls of the xylem parenchyma and pericycle cells, representing a possible Si pathway between the peripheral metaxylem vessels and the endodermis. Silica is distributed throughout the culm, but after emergence, the peripheral localization of Si intensifies in outer epidermal walls. In the flag leaf at the time of inflorescence emergence, soluble Si was almost entirely confined to the abaxial epidermal cell vacuoles and walls. Calcium ions were confined to vacuoles of the adaxial epidermis. In older leaves, these two elements were present in both epidermi. In the juvenile awn at two weeks before the inflorescence emerges, Si is already deposited in the walls of epidermal prickles and papillae and is beginning to accumulate in the long cell protoplasm. This finding challenges the concept linking silica deposition solely to evapotranspiration (Jones and Handreck, 1969; Hodson and Sangster, 1988a; 1989a; 1990).

In seminal roots of sorghum (*Sorghum bicolor*), Si was detected in the protoplasts and walls of most tissues at low levels. High levels occurred only in the endodermal walls, which exhibit a Si gradient, decreasing acropetally. Potassium and chloride ions were consistently present around silica wall deposition sites. A subsequent study of the seminal root of sorghum

revealed two biomineralization sites: the endodermis walls and atypically, the outer epidermal wall where both Si and Al were deposited (Sangster and Parry, 1976a; Hodson and Sangster, 1989c; 1993).

5.5. RECENT STUDIES

5.5.1. Silicon deposition in the wheat seedling

In a previous review (Sangster and Hodson, 1992), it was evident that the endodermal cell walls were the most important site for silica deposition in roots. Previous work has shown that this is the case in wheat roots (Bennett, 1982; Hodson and Sangster, 1989b). However, little is known of the timing of deposition or its mechanism. We investigated the early stages of Si deposition in the wheat (*Triticum aestivum* cv. Beaver) seedling, concentrating particularly on the roots (Tubb, 1995). Seeds were germinated on filter paper moistened with distilled water in petri dishes in a growth cabinet with a photoperiod of 18 hours at 23°C, and a dark period of 6 hours at 15°C. After 4 days germination, the seedlings were transferred to nutrient solutions in plastic water culture containers. The macronutrient and micronutrient concentrations followed previous formulations (Hewitt, 1966; Van der Vorm, 1980). Silica was added in the form of sodium metasilicate ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$) at a concentration of 0.5 mM and all nutrient solutions were set at $\text{pH } 5.2 \pm 0.1$. The plants were grown in the growth cabinet under the same conditions as stated above until they were harvested, up to 10 days after being transferred to the containers.

Total and soluble silica in the roots and shoots was determined by molybdate spectrophotometric analysis. For light microscopy, 15 μm wax-embedded sections were either stained with safranin to stain all the cell walls or ashed and then stained with toluidine blue to reveal silicified cells (Tubb, 1995). The percentage of endodermal cells which were silicified could then be calculated for different regions of the root at different periods of time in silica nutrient solution.

Partitioning of soluble and deposited silica within the wheat seedling was observed over a period of ten days. Figure 5.1 shows which pool Si moved into in four successive two-day periods. Soluble Si was always present at levels much lower than deposited Si, and tended to decrease in time. Early in this period, silica was deposited in the root, but as the experiment proceeded, almost all deposition was in the shoot. This implies that most of the sites for deposition in the root were filled within the first few days of exposure to Si in the nutrient solution, and that thereafter, silica was almost entirely transported to the shoot, where it was rapidly deposited. After 24 hours in the silica solution, there was slight silicification of the walls of endodermal cells in the basal part of the root (Figure 5.2). The percentage silicification of a root region increased with increasing time in silica solution. After 10 days in 0.5 mM silica solution, over 80% of the endodermal cells in the base of the root had silicified inner tangential walls. The percentage of silicified cells decreased towards the apex where very few cells were silicified. The concentration of silica in the root, measured in mMoles/g DWT, decreased over the time the plant was exposed to the silica solution, falling from 4.1 mMoles/g DWT to 1.8 mMoles/g DWT over 10 days. However, the quantity of silica per root system increased with increasing time (Figure 5.3), suggesting that the root is extending rapidly and therefore, producing a dilution effect on the quantity of silica/g DWT. The percentage of silicified cells in the endodermis in the basal part of the root is compared to the quantity of silica per root system, and it can be seen that there is a reasonable relationship

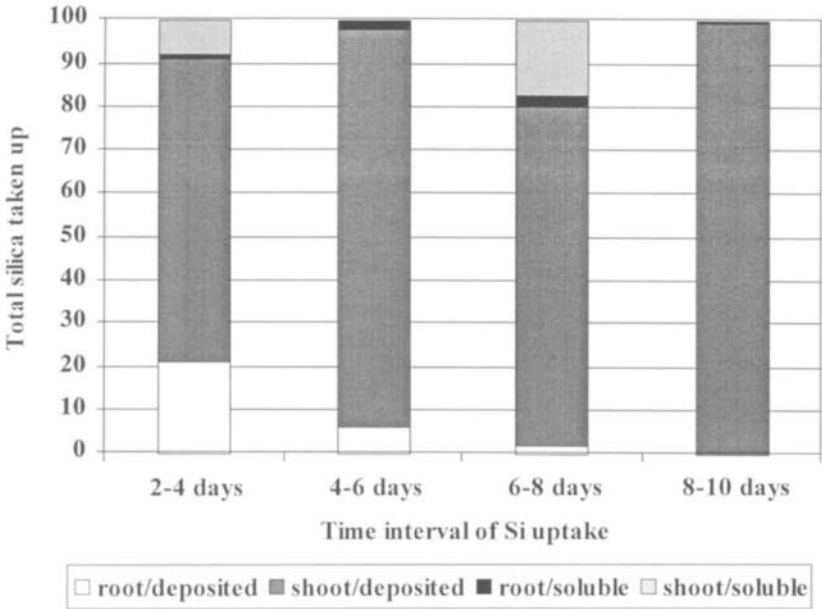


Figure 5.1. Partitioning of soluble and deposited silica in the wheat seedling.

between the two parameters. It is thus clear that silicification of the endodermal cell walls in wheat occurs quite rapidly, within two days of exposure to Si in the culture solution. It seems that once the endodermal sites are silicified, most Si is then transported to the shoot. The factors controlling deposition in the endodermis, and the reasons that the endodermal walls are the only site of root silicification, are still unclear. One possibility might be differences between the composition of the organic matrix of the cell walls of the endodermis and that of the surrounding cells. Recent work has characterized the chemical composition of endodermal cell walls isolated from seven monocotyledonous and three dicotyledonous plant species (Schreiber et al., 1999). Endodermal cell walls of roots contain varying amounts of suberin, lignin, cell wall proteins, and carbohydrates, depending on the species. Although analysis of the chemical composition of these walls has been achieved, whether this has any significance to endodermal silicification is still unknown.

5.5.2. Sequestration of toxic metals

Although elements other than Si have been fairly frequently detected in phytoliths using microanalysis, they have often been considered as incidental, or possibly involved in the deposition mechanism. Indeed, Perry and Keeling-Tucker (1998) wrote, "In most silicifying systems (where it has been measured) although cations may play a role in the genesis of the mineral phase, they are essentially actively excluded from the final material." However, recent evidence has suggested that this is not the case for aluminum and a number of heavy metals.

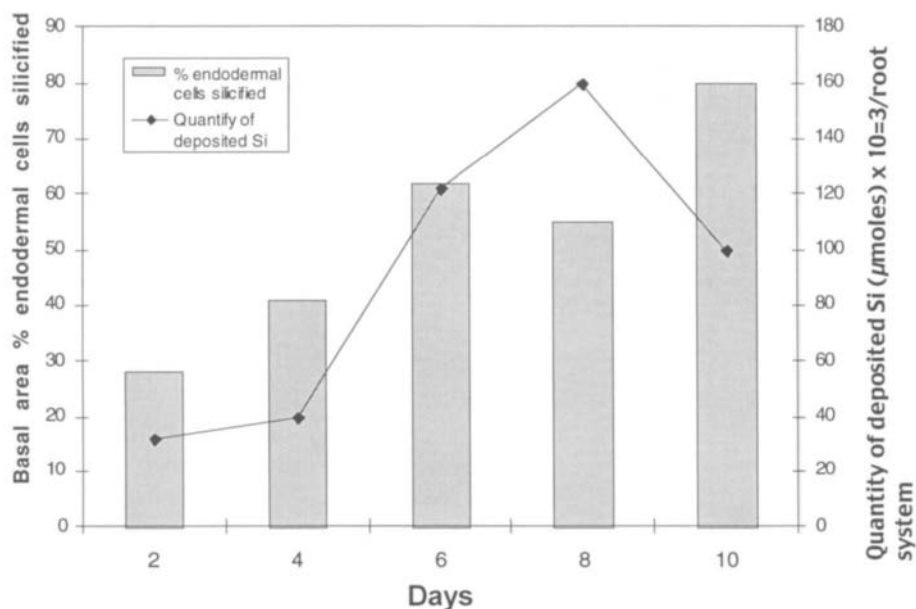


Figure 5.2. Percentage of silicified endodermal cells in wheat seedling roots.

and that codeposition with Si may represent an important mechanism for dealing with potentially toxic elements.

Neumann and his coworkers in Germany have recently produced a series of publications showing heavy metals collocated with silicon. Moreover, use of electron energy loss spectroscopy (EELS) has enabled them, for the first time, to investigate the chemical structure of the deposits they observed. In EELS, a spectrometer is used to separate inelastically scattered electrons from each other on the basis of their different energies. An electron energy loss spectrum for all of the elements in the sample can be then produced. Energy loss near edge structures (ELNES) in the spectra gives information concerning crystal chemistry, coordination numbers and distances (Lichtenberger and Neumann, 1997). Thus, one of the advantages of EELS is that compounds can be determined. Deposits of tin silicate have been found in the intercellular spaces of the leaf parenchyma of the metal tolerant plants, *Silene cucubalus*, *Thlaspi coerulescens* and *Viola calaminaria* (Neumann et al., 1997). Zinc has also reported to be co-precipitated as zinc silicate in the leaf epidermal cell walls of the zinc tolerant plant, *Minuartia verna* (Neumann et al., 1997). It is clear from the above that heavy metals are colocalized with silicon, and that this may be a resistance mechanism. However, as yet none of this work has been matched with experiments showing that Si can ameliorate heavy metal toxicity.

Silicon can act as a powerful ameliorator of aluminum toxicity in biological systems (Birchall, 1995), and in a number of cases inclusion of silicon in nutrient media has been shown to ameliorate some of the deleterious effects of aluminum on the growth of higher plants: sorghum (Galvez et al., 1987; Hodson and Sangster, 1993); teosinte (Barcelo et al.

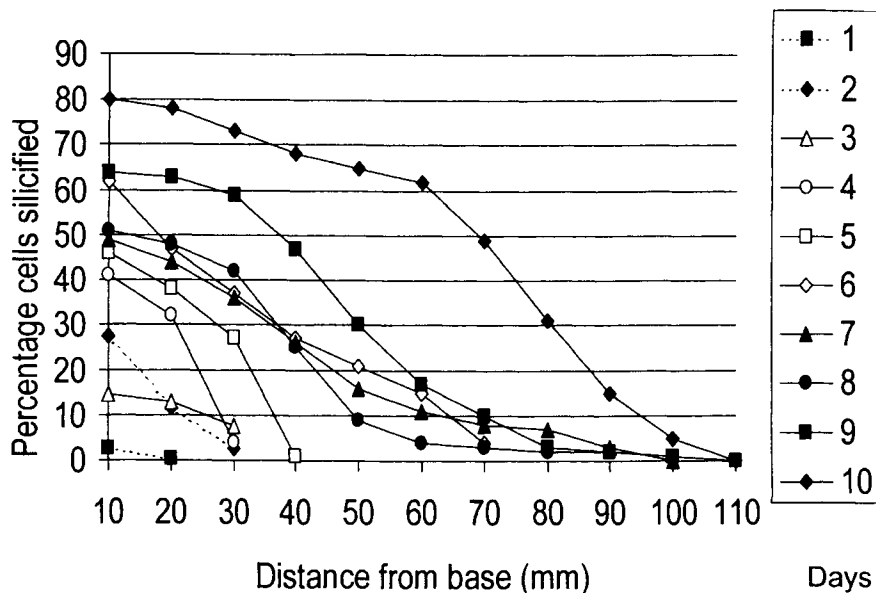


Figure 5.3. Endodermal silicification and total deposited Si in wheat seedling roots.

1993); soybean (Baylis et al., 1994); barley (Hammond et al., 1995); corn (Corrales et al., 1997; Ma et al., 1997); wheat (Cocker et al., 1997; Cocker et al., 1998b); and rice (Rahman et al., 1998). The pH at which the investigations are carried out seems to be critical and the examples in the literature where no amelioration was found (Hodson and Evans, 1995) may reflect this. Thus, a difference of only 0.4 of a pH unit made the difference between whether amelioration was observed in wheat (Cocker et al., 1998a). One mechanism for amelioration of Al toxicity may be coprecipitation with Si. The early data concerning Al/Si codeposition in plants has been reviewed (Hodson and Evans, 1995). We have updated this for higher plants in general (Cocker et al., 1998a), and more specifically for the gymnosperms (Hodson and Sangster, 1999; Sangster and Hodson, 1999). Table 1 shows the range of species and locations where Al/Si codeposition has been found using microanalysis. Evidently codeposition is a widespread phenomenon phylogenetically, with examples from the sedges, gymnosperms, monocotyledons, and dicotyledons. It also seems to occur in a wide range of plant organs, although it has not been detected in seeds so far. In the cereals, codeposition appears to be mostly confined to the roots; but this is not too surprising, as little Al is usually transported to the shoot in these plants. In the gymnosperms and Al accumulators (e.g. tea), Al/Si codeposition is not uncommon in the leaves, particularly in the epidermis. We have recently added white pine (*Pinus strobus*), tamarack (*Larix laricina*), and balsam fir (*Abies balsamea*) to the list of species in which Al/Si codeposition has been detected (Hodson and Sangster, 1999). As more evidence becomes available, it appears that the earlier assertion that high Al accumulation and high Si accumulation by plants are mutually exclusive (Hodson and Evans, 1995) may need revision.

X-ray microanalysis can only tell us that Al and Si are colocalized, but does not indicate the chemical nature of the deposits. A comparison of the chemistry and surface properties of pine and beech phytoliths has been conducted (Bartoli, 1985). The conclusion was that in pine

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5.5.3. Other techniques

Silica phytoliths were observed *in situ* in living maize (*Zea mays*) leaves by means of x-ray contact microradiography using a laser-produced plasma x-ray source: High resolution holographic images were produced which indicated that the first-formed deposits appeared in the dumb-bell shaped silica cells (Cheng and Kim, 1989). Another study used EDX microanalysis in conjunction with an environmental scanning electron microscope to observe unfixed, hydrated, living roots of rice; comparing both lowland and upland cultivars. As with sorghum (Sangster and Parry, 1976), rice roots exhibited an axial gradient of Si. The two upland rice cultivars had a higher endodermal Si content than did the lowland cv., which was ascribed to a higher drought resistance required in the upland environment. No correlation was found between the extent of leaf epidermal silicification and environment (Lux et al., 1999).

Silica microfossils occurring in palaeosols, ceramics, tool surfaces, tooth tartar and coprolites, can provide significant archaeobotanical information. Currently, there is an increasing emphasis upon intra-plant variation. For example, the silicification of large sheets of articulated epidermal cells, such as long cells of cereals, has been noted in archaeological material from sites in the Middle East. The extent of this form of deposition is believed to be largely "environmentally sensitive". The proximity of a deposit relative to the water transported by the xylem should influence the hydration form of the phytoliths and their silica microstructure. Intra-specific variations in epidermal sheet phytolith size should reflect the water regimes, whether irrigated or dryland, under which the plants were grown (Perry, 1989; Powers-Jones et al., 1997). In a different approach to the problem of intra-specific variation, Ball et al. (1993) subjected the morphometric data obtained through computer-assisted image

analysis of the epidermal phytoliths of einkorn wheat (*Triticum monococcum*) to discriminant analysis, providing the means to accurately identify all phytolith types as to their source in the plant, based upon size and shape differences. Another study showed that variation in phytolith morphology in maize leaves was not related significantly to geographic location (Mulholland et al., 1988). However, environmental factors may account for the wide variation of deposits among senescent leaves in which more tissue sites are available (Blackman, 1968).

5.6. PHYTOLITH STRUCTURE AND DEPOSITION MECHANISMS

In addition to herbaceous phanerogams, intracellular silica inclusions occur in secondary wood (xylem) tissues of 32 dicotyledon families of arboreal taxa as well as in woody arboreal monocots, including the palms (Sangster and Parry, 1981; Piperno, 1998).

Earlier investigators favored a passive mechanism (not requiring metabolic energy) for silica deposition based upon concentration and evapotranspiration (Jones and Handreck, 1969). Other workers studying deposition in highly localized sites, e.g. the endodermis wall, adduced that an active (requiring metabolic energy) mechanism must be involved. Both mechanisms have been discussed previously (Blackman, 1969; Sangster, 1970a; Kaufman et al., 1981). There is often confusion between transport to deposition sites and the deposition process itself. Reduction in transpiration rate has been shown to decrease silica deposition (Sangster and Hodson, 1986), but these effects are presumably primarily on transport of Si to deposition sites. Factors thought to influence the deposition process include the organic wall matrix (Perry et al., 1987) and mineral ions present at the deposition site, including K and Cl in *Phalaris* macrohairs (Hodson and Bell, 1986) and Ca in wheat and sorghum (Hodson and Sangster, 1989a; Hodson and Sangster, 1989b).

5.6.1. Deposition in the cell lumen

Silica cells arise from the protoderm (young epidermis) files of the graminoid shoot, where some short cells divide, giving rise to a pair, the apical cell becoming the silica cell and the basal cell, the cork cell: the pair being known as a cork-silica cell (CSC) pair. Silica cells experience premature protoplasmic disintegration. As quickly as 36 hr afterwards (Blackman, 1969), the cell lumen becomes filled by a mass of solid hydrated amorphous silica, noncrystalline, and isotropic with 13.5% bound water, known as silica gel (Kaufman et al., 1981). Optical microscopy studies (Blackman, 1969) indicated that deposition was initiated in a zone next to the cell wall and then proceeded inwards trapping cytoplasmic debris in the form of vesicles at the center of the deposit. Prior to biomineralization, pH and enzyme localization tests indicated no change. Subsequent TEM studies of epidermal cells of the grass *Lolium temulentum* (Lawton, 1980) and of the leaf tips of barley (Bennett, 1982) confirmed the inward growth of the silica cell deposit. Young silica cells possess a large nucleus, occupying 70% of cell volume, a large quantity of rough endoplasmic reticulum and many mitochondria, suggesting a high activity within the cell. Cork cells with suberized walls, which may remain unsilicified, may be involved in the metabolism of the silica cell; the two are connected by plasmodesmata and to the surrounding cells (Lawton, 1980). Based upon TEM studies of CSC pair differentiation in the internodal epidermis of oats and of the epidermal system of rice (*Oryza* sp.), silica deposits are composed of rods about 2.5 μm in length and 0.4 μm in width as the basic units. These silica rods in turn consist of silica particles in the 1-2 nm range. This basic ultrastructure was the same for all cell lumen deposits

of the rice epidermis. Lumens became filled with electron-dense fibrils around which silica polymerized, but the fibrillar material later disintegrated (Kaufman et al., 1970; Kaufman et al., 1985).

Kaufman et al. (1981) proposed a "passive model" whereby soluble silica moves upwards with the transpiration stream while being excluded by membranes of expanding cells. In senescent cells, membrane barriers are removed and polymerization thresholds are reached aided by water loss, such as might occur through the unusually thin periclinal walls of silica cells (Lawton, 1980; Hodson et al., 1985). The "active model" proposes a membrane surface to which silica is attracted by ionic forces to form a silica layer which becomes thicker as monomeric silicic acid is deposited from supersaturated solutions, produced not by an evaporative process, but by soluble chelates of Si which are concentrated by physiological processes utilizing metabolic energy at highly localized sites. Both mechanisms could operate in the same plant, the passive, accounting for deposition in epidermal cell lumens and the active, for highly localized deposition events, such as in trichome walls (Kaufman et al., 1981). Oliver et al. (1995) mixed organic molecules and silica with acidified water in beakers. In a few hours, dense silica structures (spheroids, discoids, gyroids), whose shapes were controlled by acidity, concentration and temperature, self-assembled on the surface of organic molecules, without metabolic input. Powers-Jones et al. (1997) argue that silica cells are actively silicified, as a genetically-fixed plant function, because they routinely accumulate silica irrespective of the ambient hydrological conditions, in contrast to environmentally-sensitive deposition in senescent tissue. Conical and discoid phytoliths which do not fill the cell lumen are formed in epidermal cells of members of the Cyperaceae, e.g. *Cyperus alternifolius* (Soni et al., 1972) and in rows of silica cells along the vascular bundles, containing silica bodies called stegmata, of members of the Orchidaceae (Moller and Rasmussen, 1984). If, as reported, these phytoliths are formed inside living protoplasts (in contrast to idioblasts), then some measure of metabolic control probably is exercised.

5.6.2. Extracellular deposition

In roots of purple moor-grass, *Molinia caerulea*, silica deposits were confined to the intercellular spaces (ICS) between the cortex cells. Initially, silica spheres line the outer walls of the ICS. These spheres coalesce into rod-shaped structures, similar to those described for the silica cells of the shoot epidermis. Further deposits develop inwards until the solid silica mass fills the ICS. Prior to phytolith formation, the ICS contained electron-dense, fibrillar debris, possibly representing degraded cytoplasmic material, possibly of lysigenous origin (Montgomery and Parry, 1979; Sangster and Parry, 1981). The same passive model may be adequate to account for deposition here as well as in the silica cell lumen.

An extracellular silica layer, where the preponderance of leaf silica occurs in the rice leaf, as a cuticle-Si double layer (Yoshida et al., 1962), may result from a more actively controlled deposition process. Extrusion of soluble Si through ectodesmata of the outer walls of epidermal cells, especially silica cells, may occur, spreading over the leaf surface (Soni and Parry, 1973; Lawton, 1980). In johnsongrass, *Sorghum halepense*, CSC pairs extrude filaments of wax paste $> 100 \mu\text{m}$ long, which solidifies into an amorphous wax cuticle. EDX microanalysis indicates that the wax filaments have a high Si content. Wax precursors arise in the cork cell protoplast, but the filaments appear to originate from the walls of the silica cells, which presumably supply the Si (McWhorter and Paul, 1989). Tabasheer, an opaline silica mass in the hollow stem of bamboo (*Bambusa* sp.) is another example of *extracellular* silica. It also contains small quantities of alkaline earths, alkalis and Al (Jones et al., 1966;

Klinowski et al., 1998). While the accretion of silica on the deposit may be passive, the internal mobilization and interior secretion of silica could be active.

5.6.3. Deposition in plant cell walls

Silica deposits may occur as (i) a layer lining inner surfaces of cell walls, or (ii) rows of nodular aggregates projecting into the cell lumen or (iii) layers inside the wall lamellae. Differences between cultivars and ecotypes figure prominently (Jones and Handreck, 1969; Sangster and Parry, 1976b; Sangster, 1978; Sangster and Parry, 1981). Certain plant tissues accumulate silica in cell walls at an early stage of their ontogeny. Extensive ultrastructural studies of these deposits in the root endodermis and the shoot trichomes have been undertaken (Sangster and Parry, 1981; Hodson et al., 1984; Sangster and Hodson, 1986; Hodson and Sangster, 1989c).

5.6.4. Ultrastructure of wall deposits

In sorghum and other members of the tribe Andropogoneae, deposits in the root endodermis occur as nodular-shaped “silica aggregates” which project into the cell lumen, while being incorporated basally within the cellulosic lamellae of the tertiary-state, thickened inner tangential wall (ITW). In sugarcane, silica aggregates additionally occur on the radial walls and Si extends in successive layers to the middle lamella at the endodermal-pericycle boundary. The endodermal silica aggregates extend in serial files along the endodermal cell axis in the upper root (Sangster and Parry, 1976b; Parry and Kelso, 1977; Bennet and Parry, 1981; Sangster and Parry, 1981; Hodson and Sangster, 1989c.) Deposition begins at the ITW interface, immediately exterior to the plasmalemma, on the primary wall, and continues during secondary-wall thickening in the form of “primary spherical units” (PSU) which are about 100 μm in diameter. Subsequent close-order packing of the PSU results in larger sub-units or lenses of silica oriented as are the wall microfibrils. As more lenses are deposited, in step with each successive wall layer, they coalesce to form the silica aggregate whose tip continues to advance until wall thickening ceases (Sangster and Parry, 1976b; Sangster and Parry, 1981).

Silicification of the macrohairs of the inflorescence of *Phalaris canariensis* commences for the glume, before, and for the lemma, immediately after, panicle emergence. A thin layer of electron-opaque siliceous material appears at the outer boundary of the hair wall while the cytoplasm is rich in mitochondria. After about two weeks, the thickened wall is entirely silicified to the hair base while the cytoplasm becomes degraded. Silica ultrastructure varies during secondary wall-thickening, depending upon the particular carbohydrate being synthesized. A sequence of three forms of silica-sheet, globular, and fibrillar, was created by different arrays of silica particles 100 μm in diameter. These forms were associated with peaks in the synthesis of the wall polymers arabinoxylan, cellulose, and β -glucans. Trichomes of the dicots nettle (*Urtica dioica*) and marijuana (*Cannabis sativa*) also are heavily silicified, especially in the distal portion, while the base contains calcium deposits (Dayanandan and Kaufman, 1976; Hodson et al., 1984; Perry, Mann, and Williams, 1984; Perry, Mann, Williams, Watt, Grime, and Takacs, 1984; Perry et al., 1987).

5.6.5. Deposition mechanisms

Biogenic silica is assigned the general formula $[\text{SiO}_n \cdot \text{OH}_{(4-2n)}]_m$, where n is < 2 and m is very large, indicating a variable state of hydration. Each Si is tetrahedrally coordinated and individual SiO_4 units are connected by Si – O – Si bonds of varying bond angle (Robinson and

Sullivan, 1987). Silicic acid may form spherical particles, 1-3 μm in diam., in colloidal suspension. Further polymerization results in growth in particle (PSU) size in basic (pH 7-10) solution; while in acid solutions, small particles may aggregate into 3-D networks, forming gels. Silicic acid characteristically polymerizes into spherical particles which exhibit low surface areas, exposing a minimum of uncondensed SiOH groups (Bennet, 1982).

In the case of random silicification in senescent cell lumens or ICS, the production of suitable organic matrices may be the only aspect requiring metabolic input or genetic control. Otherwise, silica appears to possess the capacity for self-assembly without energetic input. However, in actively Si-accumulating tissues – endodermis, trichomes, and the aleurone layer (Hodson and Parry, 1982), Si may be involved in more complex interactions suggesting a high degree of specific cellular control (Perry, Mann, and Williams, 1984; Perry, Mann, Williams, Watt, Grime, and Takacs, 1984; Perry et al., 1987). Wall silicification in the root endodermis occurs in close proximity to a protoplast containing abundant organelles – mitochondria, ribosomes and polysomes (Sangster and Parry, 1976). Presumably, these cells are able to selectively accumulate and concentrate soluble silica while preventing polymerization prior to transporting it across the plasmalemma/cell wall (i.e. symplast/apoplast) boundary into the thickening wall, where silicification must be synchronized with successive bursts of wall polymer production. In diatoms, an elaborate, metabolically-driven system has been elucidated to account for silicification of the outer wall (Robinson and Sullivan, 1987). In reviews of higher plant silica (Jones and Handreck, 1969; Sangster and Hodson, 1986; Piperno, 1988; Epstein, 1999), there is a dearth of information regarding Si pathways culminating in wall deposition. Epstein (1999) describes recent studies asserting Si-aromatic ring associations with lignin and carbohydrate in rice cell walls. Using cold plasma ashing, silica in rice husks was found as fibrous micelles similar to microfibrils. Although evidence for organosilicon compounds is lacking, silica was tightly bound to pectin and hemicelluloses (de Lhoneux et al., 1988), as was also the case in stomatal walls of sugarcane (Sakai and Thom, 1979). Silica deposition in cell walls of dicotyledon trichomes was delayed until callose, a β 1,3 polyglucan was synthesized. High transpiration from the trichome walls was presumed (Waterkeyn et al., 1982); however, for oats, very little cuticular water loss occurred from epidermal cells, including trichomes, except above the stomatal complex (Aston and Jones, 1976). Other secondary wall polymers reported to be somehow linked to silicification include polyphenols, suberin and lignin (Sangster, 1978). Delaying cell senescence, preventing silica polymerization or interfering with environmental factors such as humidity, have all been shown to affect silicification (Parry et al., 1984; Hodson et al., 1985; Sangster and Hodson, 1986), but may have impacted more on Si transport. The structural involvement of Si with the wall polymers remains unclear, as does the role of other elements detected in phytoliths, including metals and calcium, which is frequently codeposited with Si in the root endodermis and the shoot trichomes. Divalent ions (e.g. Ca^{2+}) are reputed to facilitate silicification (Arimura and Kanno, 1966; Bennet and Parry, 1981; McWhorter and Paul, 1989). In concluding their 1972 paper, Kaufman et al. (1970) posed several questions: (i) Considering the divergent morphogenesis of the cork-silica cell pairs, what causes the nuclear breakdown of the silica cell? (ii) By what mechanism does the silica cell accumulate soluble silica? At this time, the validity of these questions remains undiminished. Also, in many respects, our understanding of how other internal and external factors affect silica deposition remains largely conjectural.

5.7. FUNCTIONS OF PLANT SILICA

The major functions which have been reviewed previously (Viehoever and Prusky, 1938; Jones and Handreck, 1969; Sangster and Hodson, 1986) can be categorized as structural, physiological and protective. Structural functions include compression-resistance in cell walls, emphasized by Raven (1983), which adds shearing resistance during soil penetration (Hansen et al., 1976). Increased shoot rigidity improves light interception, reduces lodging due to climatic factors and increases seed retention by inflorescence bracts (Sangster and Hodson, 1986). Physiological functions include reduction of evapo-transpiration, increasing of the root oxygen supply by strengthening air-canal walls, interactions with phosphorus and the amelioration of metal toxicity (e.g. Mn) (Jones and Handreck, 1969; Hodson and Evans, 1995). Protective functions include resistance to pathogens, insects, molluscs, and grazing by herbivores. Silicified inflorescence bracts protect the embryo. Overall, silica aids in promoting normal growth, development, and yields. The protective function relates to the evolution of grass-herbivore interactions. Phytolith complexity is greatest in those grasses (Panicoideae) which have had the longest history of vertebrate grazing (Herrera, 1985).

Recent studies concerning silica have focused on its employment in sustainable rice production (Savant et al., 1997), on silicon-mediated accumulation of flavenoid phytoalexins in cucumber (Fawe et al., 1998) and on the role of soluble Si in disease management in greenhouse systems (Bélanger et al., 1995). Grape (*Vitis* sp.) cultivars active in producing callose and silica deposits are more mildew resistant (Blaich and Wind, 1989). Silicon content varies between different genotypes of rice and sugarcane (Deren et al., 1992; Deren et al., 1993). Moore (1984) found that cultivars of ryegrass, which were more resistant to dipterous stem-boring larvae, had a higher content of silica, with a more irregular distribution of phytoliths and recommended breeding for these traits.

Kaufman et al. (1985) speculated that epidermal silica bodies and silicified trichomes might facilitate light transmission to the photosynthetic tissue, by functioning as "windows" and "light pipes", respectively. Test results using photo-sensors were negative, so they abandoned their "window-hypothesis". This conclusion was supported by a subsequent evaluation using the rice leaf epidermis, which showed that the light energy use efficiency and quantum yield of Si-treated leaves was in fact less than that for leaves not containing silica bodies (Agarie et al., 1996). Kaufman et al. (1985) also proposed that phytoliths composed of silica gel, with its water of hydration, could regulate temperature by cooling the leaf during drought. Silica gel could also serve as a store of cations (Kaufman et al., 1985). Wallace (1993) further suggested that Si could help regulate cation-anion balance, thereby facilitating greater tolerance towards Al and Fe. Plant phytoliths have been used in forensic science to identify soils (Marumo, 1986) and to detect traces of marijuana using characteristic Si and Ca structures in trichomes of ashed leaves (Dayanandan and Kaufman, 1976). Rice husks (15% silica by wt.) could provide high purity Si for solar cells (Amick, 1982). Epstein (1994) emphasized that organosilicon matrices have important applications in materials science. In this regard, macromolecular assemblages in which protein is intimately associated with biogenic silica have been extracted from hairs of canarygrass (*Phalaris*), branches of horsetail (*Equisetum*) and leaves of common reed (*Phragmites*). It is proposed (Harrison, 1996) that the protinaceous and other organic phases extracted from the macromolecules may have different roles to play in the regulation of silica polymerization and precipitation in plant cell walls.

5.7.1. Future considerations

There are several areas of science in which the study of Si compounds is increasing. The use of phytolith analysis in ethnobotany and archaeology has been described. In a study of epidermal leaf phytoliths of 17 *Oryza* species, Whang et al. (1998) found that even within a single leaf, silica bodies were not uniform, those of the midrib varying both as to size and shape from those of other veins. Morphological variability is believed to be caused by water conduction and its influence upon silica availability as well as by genetic (developmental) factors. These variations in the means and range of size values of phytolith populations can be treated statistically. A recent controversy (Piperno et al., 1999; Rovner, 1999) is centered upon the acceptance of size changes in archaeological samples of squash phytoliths, from 10,000 to 7,000 years B.P. (before present), as evidence justifying major revisions of the time and place of agricultural origins in South America. Phytolith size issues must be resolved to avoid undermining confidence in this technique. J. D. Birchall (1995) concluded that the major role of Si in biology was to interact with metal ions, especially with Al, of particular significance in acidic precipitation zones. The increasing importance of silica in studies of crop protection and increased yields has been detailed elsewhere. Epstein (1994) has argued that Si as a major mineral constituent of plants has not received the attention it is due in experimental plant biology. Therefore, one might reasonably conclude that the future looks promising for higher plant silica research.

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Chapter 6

Silicon in horticultural crops grown in soilless culture

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A lack of knowledge about the role of silicon (Si) in horticultural crops became apparent with the change to soilless growing media in the glasshouse industry in the Netherlands. It was found that in these systems the Si contents in plant tissue were significantly lower in comparison with crops grown in soil. Investigations were carried out on the effects of Si application in soilless culture. With cucumber (*Cucumis sativus*), melon (*Cucumis melo*), courgette (*Solanum melongena*), strawberry (*Fragaria ananassa*), bean (*Phaseolus vulgaris*), and rose (*Rosa*), the Si contents were increased as a result of the addition of Si into the root environment. However, the uptake was almost negligible in tomato (*Lycopersicon esculentum*), sweet pepper (*Capsicum frutescens* cv. 'grossu'), lettuce (*Lactuca sativa*), gerbera (*Gerbera* sp.), and carnation (*Dianthus caryophyllus*). Results showed that cucumber, rose, and courgette could benefit from enhanced Si concentration in the root environment, since total yield was increased and powdery mildew was suppressed. Despite a minor uptake of Si in lettuce, it was found that Si uptake affected the Mn distribution, thereby, alleviating Mn toxicity in the plant. Initially, severe problems with blocking of the irrigation system occurred due to instability of Si sources. These were solved by the introduction of potassium metasilicate. The use of Si colloids was found to be less effective.

6.1. INTRODUCTION

The role of Si in the nutrition of plant species used in horticulture has not been well investigated in comparison to agricultural crops like rice (Iler, 1979). Some authors have demonstrated the relevant uptake of this element for some plant species used in horticulture, such as cucumbers (Wagner, 1940; Miyake and Takahashi, 1983), strawberry (Lanning, 1960), and tomato (Miyake and Takahashi, 1978). Horst and Marschner (1979) found application of Si in bean alleviated Mn toxicity. However, there was no evidence that crops could benefit from Si application. This could likely be explained by the broad availability of Si in the root environment of those soils used for growing horticultural crops under glass (Lindsay, 1979). So, the interest in Si application to support growth and development of soil-grown horticultural crops has been very limited. This was altered with the changeover in the glasshouse industry to soilless culture, which occurred in the Netherlands and other glasshouse areas around the world in the early 1980's. The principal substrate used was rockwool. Although this medium contained 47 % SiO₂, the quantity available for the plant is negligible. The main reason is the decrease in rooting volume, from over 500 L m⁻² for crops

Table 6.1

Range of silicon contents (mmol Si kg⁻¹ d.m.) found in young leaves of horticultural crops grown in soil and soilless media, and supplied with only ambient silicon in the root environment.

Crop	Growing medium			
	Soil		Soilless ¹	
	Min	Max	Min	Max
Tomato ¹ (<i>Lycopersicon esculentum</i>)	13	17	11	13
Cucumber ¹ (<i>Cucumis sativus</i>)	280	440	39	127
Sweet pepper ¹ (<i>Capsicum frutescens</i>)	12	22	15	17
Melon ¹ (<i>Cucumis melo</i>)	22	378	not determined	
Gherkin ¹ (<i>Cucumis anguria</i>)	128	370	not determined	
Courgette ¹ (<i>Solanum melongena</i>)	220	220	69	130
Bean ¹ (<i>Phaseolus vulgaris</i>)	224	-	not determined	
Lettuce ² (<i>Lactuca sativa</i>)	12	-	5	5
Strawberry ³ (<i>Fragaria ananassa</i>)	130	-	25	48
Gerbera ¹ (<i>Gerbera</i> sp.)	10	-	12	22
Carnation ¹ (<i>Dianthus caryophyllus</i>)	17	-	not determined	
Rose ¹ (<i>Rosa</i> sp.)	30	130	7	36
Heath aster ¹ (<i>Aster ericoïdes</i>)	280	-	40	40

¹Rockwool, ²Nutrient Film Technique, ³Peat substrate

in soil to merely 10 L m⁻² for rockwool. In addition, the small portion of the solid phase in these substrates is only 3% in volume (Voogt, 1989). The need for research on the role of Si in horticultural crops became apparent after the publication of Miyake and Takahashi (1978 and 1983) who concluded that omission of Si in the nutrient solution for tomato and cucumber in water culture led to deficiency symptoms. Irrespective of the discussion on whether Si is an essential nutrient for higher plants (Epstein, 1994), investigations were started on the role of Si for crops grown in soilless culture.

In this paper, an overview is presented of the work conducted during the last 15 years on Si application in soilless culture. The presence of Si in the plant tissue of various crops, indicating a potential role of Si, was first investigated. Various experiments were conducted to investigate the beneficial effects with cucumbers, beans, courgettes, roses, and strawberries. An important part of the research concentrated on finding Si compounds applicable to the nutrient supply system currently used in commercial practice. Some of the results reported herein have been published before in Dutch growers' magazines.

6.2. SILICON CONTENT IN HORTICULTURAL CROPS

A survey was made of the Si content in various crops grown in soil and in soilless-growing media. Since the glasshouse industry in the Netherlands is situated mainly in areas with marine clay soils which contain considerable quantities of clay minerals, it is plausible that the availability of Si in these soils is practically unlimited (Lindsay, 1979). Starting from this assumption, it is possible that the Si content in the tissue of crops grown in soil can be used as an indicator for the accumulation rate of Si by these crops. Plant samples were collected from crops at commercial holdings, growing in either soil or soilless culture (mainly rockwool). The Si content in the plant tissue varied considerably among crops (Table 6.1). The results indicated that some species absorb little Si, (tomato, gerbera, lettuce), while others accumulate relatively large quantities in their leaves (cucumber, bean). The results found for soil-grown cucumber were comparable with the results found by Wagner (1940). For bean, the data published by Horst and Marschner (1978) were 1.5 times higher than we found. For the other crops, no relevant data could be found in the literature. The Si content in the tissue samples of soilless-grown crops was remarkably lower than that in the same species grown in soil. The broad variation in the Si content found in the various crops may be caused by difference in availability of Si in the root environment, the age of the sampled leaves, or crop age. The results of this investigation demonstrated that for cucumber and other Si-accumulating crops, the availability of Si in soilless systems is limited. However, the clear differences among Si content in crops grown in media with and without ambient Si is not proof of the essentiality of Si for these crops (Epstein, 1994). Many authors have suggested that Si accumulation in higher plants is only a result of non-selective passive transport in the transpiration stream (Jones and Handreck, 1967). In general, Si cannot be considered as essential for higher plants (Epstein, 1994). Nevertheless, the experimental work from Miyake and Takahashi (1978 and 1983) referred to previously, made studying Si application with soilless-grown cucumber worthwhile. This starting point was justified by the results published by Adatia and Besford (1986) and Vaughan and O'Neill (1989).

6.3. SILICON IN NUTRIENT SOLUTIONS

6.3.1. Accessibility of silicon sources

The study of Si application in soilless culture needed to be conducted with appropriate Si sources, i.e. soluble. According to Iler (1979), water-soluble Si compounds could be distinguished in different groups. First of all, there is monosilicic acid, H_4SiO_4 or $\text{Si}(\text{OH})_4$. In this form, saturation is reached at 100 - 200 ppm of SiO_2 , which is 1.7 - 3.3 mmol Si L^{-1} . Monosilicic acid can be supplied as a metasilicate with the cations of K, Na, or Li as counter ion, dissolved in water. These compounds contain high concentrations of OH^- and will increase the pH in the nutrient solution. Another group of silicates is the oligomers, like the dimer $\text{Si}_2\text{O}_7\text{H}_6$, the trimer $\text{Si}_3\text{O}_{10}\text{H}_8$, etc. These oligomers are easily formed if the concentration of $\text{Si}(\text{OH})_4$ increases. Waterglass (as sodium or potassium) is a mixture of monosilicic acid and several oligomers, mixed with NaOH or KOH. With increasing concentration, the oligomers polymerize rapidly, initially forming polysilicic acids of low molecular weight. Below a molecular weight of 100,000, this Si form is called polysilicic acid. Above this arbitrary weight, these are called silica sols, with particle sizes larger than 5 nm. Depending on pH and salt concentration, the properties of the particles of polysilicates differ: from

amorphous silica at low pH, a gel with increasing concentration, to stable colloids, with spherical particles at high pH and without salts. Silica sols are available varying in particle size, with mainly Na as the cation. Information about the availability of Si in commercially-available sources was obtained by a series of tests with a variety of Si sources and Si compounds. For this purpose, cucumber seedlings were grown in aerated containers with 15 L nutrient solution. The Si compounds were added to a concentration of 1 mmol Si L⁻¹. After 4 weeks development, the plants were harvested and the amount of dry matter Si was determined. The uptake was greater with sodium-, potassium- and lithium silicate compounds which dissolve as the monosilicic acid (Si(OH)₄) in water (Table 6.2). The uptake with waterglass was at the same order, despite it being an oligomer, with only a small percentage of monosilicic acid. With the polysilicates, the uptake was dramatically lower and decreased clearly with particle size. Colloidal silica, or polysilicate with a particle size of 20 nm provided little Si to the plants.

Next to differences in uptake of the various Si forms, it became clear that for determination of Si in nutrient solutions, the analytical method is rather important. With the Atomic Absorption Spectrophotometry (AAS) method, the analytical results were in good agreement with the amount of Si added as Si compound to the nutrient solution. The same was found with the colorimetric method (molybdate complexation) for the monomer Si sources. However, with the polysilicates, the concentrations found by the colorimetric method were much lower and decreased with increasing particle size, comparable with the decrease in uptake (Table 6.2). This suggests that the colorimetric analytical method is a useful instrument to distinguish Si availability. This makes sense since the colorimetric method is based on the identification of Si(OH)₄ groups (de Bes, 1986), which is most likely the only form absorbed by plant roots (Iler, 1979; Epstein, 1994). In colloidal silica, free Si(OH)₄ groups are only present at the colloid surface, which are naturally smaller in number with increasing particle size. At glasshouse holdings where well water is the main water source, substantial Si concentrations might be present in the irrigation water (Table 6.2). Tissue samples of soilless-grown crops (cucumber) derived from these holdings showed enhanced Si contents (Figure 6.1). Trials in which Si-containing well water was compared with Si supplied as potassium silicate (Table 6.2) resulted in comparable Si contents. So, for the application of Si in the nutrient solution, the concentration of Si in the well water should be considered.

6.3.2. Silicon release from growing media

The investigation of Si content in crops discussed previously determined that Si availability in soilless-growing media is limited. The release from some growing media: new and used, (one year used for growing cucumber), and under different pH regimes was evaluated. The materials were rinsed with three times the water capacity of the materials using the standard nutrient solution for cucumber, containing only ambient Si concentrations. The pH treatments were 4.0, 5.5, and 7.5. The materials were saturated with the nutrient solutions for 6 months, during which the pH was kept more or less constant and the solution was not refreshed. Each treatment was re-saturated with the leachate regularly. Less Si was released from glasswool, perlite, pumice stone and peat than from rockwool. Mixing peat with rice hulls, however, did increase the Si availability significantly (Table 6.3). The Si concentration of the nutrient solution from rockwool was higher at the low pH treatments. Used slabs released more Si, especially at low pH. Notwithstanding the Si found in the root environment in this investigation, the quantity of Si released by the different growing media is poor in relation to

Table 6.2

Effect of different silicon sources, i.e., well water and chemical compounds differing in form and particle size, on the silicon content in young laminae of cucumber plants and on the silicon concentration in the nutrient solution as analysed by atomic absorption spectrophotometry (AAS) and by the colorimetric method.

Si source/compound	Particle Size	Si content mmol kg ⁻¹ dry matter	Water analysis Colorimetric	Si mmol L ⁻¹ AAS
Rainwater	-	60	5	5
Well water	-	210	28	31
Rainwater + monomer Si(OH) ₄	-	245	32	35
Li ₂ SiO ₃ + monomer Si(OH) ₄	-	308	95	102
Na ₂ SiO ₃ + monomer Si(OH) ₄	-	392	112	120
K ₂ SiO ₃ + monomer Si(OH) ₄	-	368	105	98
Waterglass + oligomer	-	420	89	95
Silica sol + colloidal silica	10nm	177	35	118
Silica sol + colloidal silica	15nm	75	18	105
Silica sol + colloidal silica	20nm	45	12	95

the potential uptake even in used rockwool slabs with low pH. The total available quantity of Si is less than 5 % of the total demand of a long-term cucumber crop (Voogt, 1989).

6.3.3. Silicon in nutrient solutions

As the quantity of Si in growing media is limited, supply of Si to crops which absorb greater quantities of Si could be necessary. Si application in soilless culture is only appropriate if it could be supplemented to the nutrient solution system (Voogt, 1989a). However, the specific behaviour of many Si compounds makes it impossible to add these to the concentrated fertilizer solutions which are commonly used. The monomer Si compounds are only stable in their original formulations (Iler, 1979). If mixed with electrolytes in concentrated form, like in fertilizer solutions, they rapidly precipitate.

Colloidal Si compounds, however, are stable in concentrated salt solutions and could be added in the concentrated fertilizer solution. Since water and nutrients are supplied exclusively by trickle irrigation, stable Si sources are essential in order to avoid clogging of the irrigation nozzles. Unfortunately, soluble Si polymerizes rapidly if the concentration of Si increases above 2 mmol L⁻¹ (Iler, 1979). In contrast, large molecules of polysilicates in the form of colloids, are very stable. but unfortunately, have shown to be less accessible to the plant. In experiments in which different Si sources were used, it appeared that some Si compounds were quite unstable, and caused severe clogging of the irrigation system. The instability of Si sources can be illustrated by the change in water delivery and the variation coefficient of the trickle nozzles of the irrigation system in one of the experiments (Table 6.4).

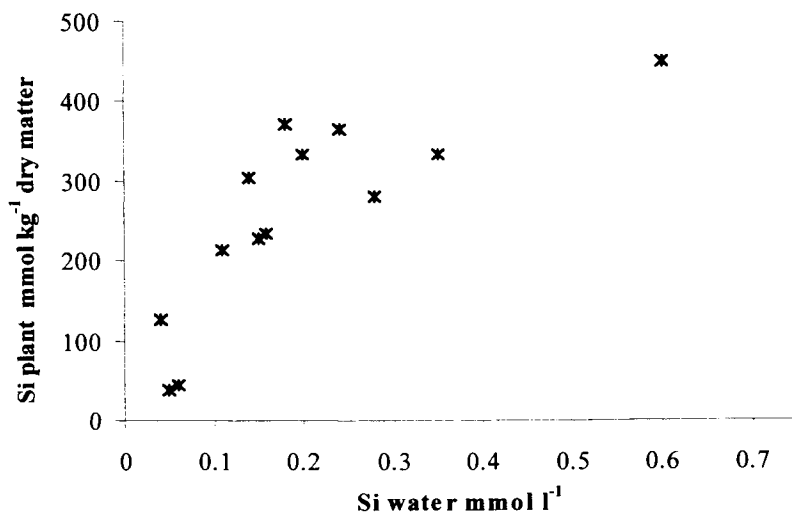


Figure 6.1. Relation between the Si concentration in well-water, used for irrigation, and the Si content in the young full-grown leaves of cucumber, grown in rockwool.

With waterglass, the water delivery was reduced and the variation coefficients of the emitters dramatically increased, indicating severe clogging, despite regular upkeep and cleaning of the drip lines. Moreover, the number of necessary cleanings of the irrigation system was much higher as compared to the control treatment. Even with colloidal Si, at high concentrations, more clogging was observed. The treatments with Si as monomer $\text{Si}(\text{OH})_4$ showed no clogging problems.

Monomer Si compounds are available in many configurations, differing in cation type and ratio of cation to Si (Iler, 1979). The applicability of several Si compounds was examined. Lithium silicate (mole ratio $\text{Li}:\text{Si} = 1.81$), was very stable in nutrient solutions. No precipitation was observed in a stagnant solution with $1.5 \text{ mmol Si L}^{-1}$. Lithium silicate however, proved to be toxic to cucumber, producing severe chlorosis in young leaves, which turned into severe necrosis later on. Sodium metasilicate, (mole ratio $\text{Na}:\text{Si} = 2.0$) was as stable as lithium silicate. This Si source is not appropriate, however, since the Na quantity introduced with Si is much higher than the uptake by the plant (Voogt and Sonneveld, 1997), and will accumulate in the root environment beyond acceptable limits. Potassium silicate solutions with several configurations, with $\text{K}:\text{Si}$ mole ratios varying from 1.2 to 2.0, were also tested. The configurations with low $\text{K}:\text{Si}$ ratio were less stable, showing precipitation in stagnant nutrient solutions and gel forming in the stock solution. The one with a mole ratio of 2.0 performed best. A complication with this Si compound is it is strongly basic, a mixture of KOH and H_4SiO_4 . For the neutralization of KOH , addition of an equivalent amount of acid in the nutrient solution is necessary. The problem was solved by adding HNO_3 to the nutrient solution, and at the same time reducing equivalent quantities of KNO_3 from the fertilizer formulation. This corrected for the extra K input involved with potassium silicate.

Table 6.3

Increase of Si in the nutrient solution, as released from several growing media, after 6 months of immersion in three times the water volume at saturation with a standard nutrient solution.

Growing medium		Si concentration mmol L ⁻¹
Rockwool new slab		0.7
Rockwool used slab		1.1
Glasswool new slab		0.2
Peat substrate		0.3
Peat substrate + 50 % rice hulls		1.1
Perlite		0.05
Pumice		0.15
Rockwool new slab.	high pH (7.5)	0.4
Rockwool new slab.	low pH n(4.0)	1.4
Rockwool used slab.	high pH (7.5)	0.75
Rockwool used slab.	low pH (4.0)	1.9

6.4. EFFECTS OF SILICON APPLICATION ON CROPS

6.4.1. Silicon with cucumber

During a period of 9 years, a number of Si experiments have been conducted with cucumbers. The information presented herein is a summary of these results published from Dutch Growers' magazines (Voogt, 1989a; Voogt, 1989b; Voogt, 1990; Voogt and Kreuzer, 1989; Voogt and van Elderen, 1991; Voogt, 1992; Voogt and Bloemhard, 1992). The data in Table 6.5 are a summary of yield data for cucumber crops (six experiments) with and without Si application. In the first experiment with cucumber, no response of the treatments on growth or development of the crop could be observed and the Si content in plant tissue were only slightly enhanced by the Si applications (Voogt and Sonneveld, 1984). No increase in soluble Si was found in either the nutrient solution or in the root environment, using the colorimetric analytical procedure (de Bes, 1986). It appeared that the Si source used in this experiment (silicon colloid solution) was inaccessible to the plant. This is plausible, since the release of monomer Si(OH)_4 from colloidal silicon is rather poor (Iler, 1979). In the second experiment, the response of the +Si treatment was negatively affected by water shortage in these plots, as a result of the severe clogging of the system caused by the instability of the Si source, i.e., potassium waterglass. In follow-up experiments, precautions were taken to prevent clogging.

Except for the first two experiments, a significant positive response in yield was found as an overall effect of Si application. In all experiments, the number of fruits increased with the Si application. The average fruit weight increased as well, except during the fourth experiment. The yield increase from the Si application differed from 6 to 16 % for number of fruits and from 11 to 33 % for the total yield among the different experiments. Adatia and Besford

Table 6.4

Effect of Si form on clogging of the trickle irrigation system in a long-term trial with rockwool grown cucumber. Average water delivery ($\text{L m}^{-2}\text{hr}^{-1}$) and variation coefficient (V.C.) of the trickle nozzles after 6 months and the number of necessary cleanings.

Treatment		Average water delivery $\text{L m}^{-2}\text{hr}^{-1}$	V.C.	Total cleanings
No silicon		1.6	9.3	4
Potassium waterglass	1.5 mM	1.1	17.3	11
Potassium metasilicate	1.5 mM	1.5	6.6	5
Silica sol	1.5 mM	1.5	8.4	4
Silica sol	3.0 mM	1.5	140	5

(1986) observed increased chlorophyll content and rubisco activity in cucumber leaves as a result of Si application. This increased photosynthetic capacity was probably due to a more effective light interception by the silicon-treated plants. This reason might explain why yields increased in our trials. Moreover, the Si supply which reduced the powdery mildew incidence in many of the trials could have increased yield as well. In an effort to determine an optimum Si concentration in the nutrient solution and in the root environment, a trial was conducted with a range of concentrations, from zero to four mmol Si L^{-1} (Table 6.6). The maximum yield response was reached at a concentration of $0.5 \text{ mmol Si L}^{-1}$, both in the nutrient solution and in the root environment. Further increase in Si concentrations did not affect the yield

Table 6.5

Effect of Si on the yield of cucumber, as found in six consecutive experiments with and without application of Si using different Si sources and with different cropping periods, P value for the total yield (kg m^{-2}).

Experiment	Yield						P	Si		Remarks
	-Si			+Si				Source	Supply (mmol L ⁻¹)	
	Fruits (m ⁻²)	Kg (m ⁻²)	Fruit wt (g)	Fruits (m ⁻²)	Kg (m ⁻²)	Fruit wt (g)				
1	85	326	384	87	334	384	ns	Silica sol	15	poor Si uptake
2	73	289	369	73	294	403	ns	waterglass	15	Severe clogging
3	88	334	380	93	394	424	<0.05	waterglass	15	clogging
4	74	324	438	85	361	425	<0.05	waterglass	10	clogging
5	56	318	568	64	368	575	<0.05	K ₂ SiO ₃	10	
6	18	82	456	21	109	519	<0.05	K ₂ SiO ₃	75	short autumn crop, severe mildew

Table 6.6

Effect of Si supply on Si concentrations in the root environment (RE), on yield (fruits m^{-2} , kg m^{-2} , fruit weight) and on tissue content of cucumber grown in rockwool.

	Supply (mmol L^{-2})	Root environment (mmol L^{-1})	Yield		Fruit wt (g)	% 1 st class	Tissue content (mmol kg^{-1} d.m.)		
			Fruits (m^{-2})	(Kg m^{-2})			Young laminae	Old laminae	Fruits
1	0	0.04	75 ^a	33.4 ^a	444 ^a	97 ^a	84	244	20
2	0.5	0.47	89 ^b	40.1 ^b	448 ^a	94 ^a	347	665	55
3	1	0.95	87 ^b	39.4 ^b	455 ^a	95 ^a	544	1114	78
4	2	1.71	88 ^b	39.6 ^b	450 ^a	95 ^a	691	1419	118
5	4	2.37	86 ^b	38.4 ^b	448 ^a	95 ^a	776	1421	110

Yield components in each column followed by the same letter are not significantly different according to Duncan's multiple range test at $P < 0.05$.

significantly. Many authors have mentioned the effect of Si on enhancement of resistance against powdery mildew (Menzie's et al., 1991; Samuels et al., 1991; Belanger, 1995). In all our experiments, the incidence of powdery mildew was monitored by visual assessment of the incidence of colonies on the laminae. In some of them, a reduction in incidence of mildew was found with the + Si treatments (Table 6.7). Especially in experiment 6, the incidence of powdery mildew was severe; because the disease was not controlled with fungicides, while in the other experiments fungicides were applied routinely. The reduction in mildew incidence in this case was quite clear for the + Si treatments. This result probably helps explain the strong

Table 6.7

Effect of silicon application on the incidence of powdery mildew in cucumber. Infection was rated and indexed from 0 (no mildew colonies) to 10 (completely covered with colonies).

Experiment	-Si mildew index	+Si mildew index	Remarks
1	not observed		
2	not observed		
3	6	4	
4	7	5	
5	5	5	
6	10	4	no fungicide treatment

Table 6.8

Appearance of bloom on the epidermis of cucumber fruits during the first and second half of the growing period, visually judged with an index of 0 (no bloom) to 10 (severe bloom), as affected by continuous or changing Si supply, with cucumber grown in rockwool.

Si supply (mmol L ⁻¹)	Bloom index	
	First half	Second half
0	0	0
0.75 continuously	3	2
1.5 continuously	10	10
1.5 4 weeks, then 0.75	10	2
1.5 8 weeks, then 0.75	10	4

yield response of cucumber to Si in this experiment. Fruit quality assessments were made during all experiments. No significant differences could be observed between Si treatments, either in external quality parameters as fruit shape and fruit color or shelf life. However, in all experiments, fruits from the +Si treatments had a dull appearance associated with wax on the epidermis. This so-called *bloom*, which is a common phenomenon with soil-grown cucumbers, increased in intensity with increasing Si supply. Fruits with severe bloom are easily affected by fingerprints during the handling process and lower the grade of the fruit. In an experiment with treatments of 0.75 and 1.5 mmol Si L⁻¹ supplied continuously, as well as changing these concentrations during the crop growing season, the bloom incidence appeared to be suppressed to an acceptable level with 0.75 mmol Si L⁻¹ (Table 6.8). In another experiment, bloom did not appear when the Si concentration in the nutrient supply was 0.5 mmol L⁻¹. Currently, the processes involved in the formation of this bloom and what role silicon plays is not very clear (Samuels et al., 1993). The experimental results with Si application were confirmed by tests in

Table 6.9

Effect of Si supply (zero and 1.0 mmol L⁻¹) on the yield (kg m⁻² and fruit weight) at two commercial greenhouses with rockwool-grown cucumber in two successive years.

Grower	Crop	-Si		+Si		<i>P</i> (yield)	<i>P</i> (Fruit wt)
		kg m ⁻²	Fruit wt	kg m ⁻²	Fruit wt		
1	1st year	58.8	485	62.2	492	0.05	0.05
1	2nd year	67.8	510	70.9	505	0.05	ns
2	1st crop	28.2	520	28.5	544	ns	0.05
2	2nd crop	26.6	498	27.6	485	0.05	ns
2	3rd crop	10.9	-	11.3	-	ns	-

Table 6.10

Effect of Si application on yield and Si content in young leaves with bean, courgette, and strawberry grown in soilless systems.

Crop	Treatments (mmol Si L ⁻¹)		Total yield (kg m ⁻²)		Tissue content (mmol Si kg ⁻¹)	Dry matter
	-Si	+Si	-Si	+Si	-Si	+Si
Bean ¹	0	1.5	1.4	1.4	19	360
Courgette ¹	0	1	10.4	11.6	120	480
Strawberry ²	0	1	2.8	2.7	17	418

¹ Rockwool

² Water culture

commercial glasshouses (Table 6.9). At two locations, experiments were conducted involving four replications of a treatment with Si supplied as K₂SiO₃, and compared with four replications supplied with the standard nutrient solution, randomly arranged in a section of the greenhouse. Growth, crop development, and yield were monitored. At the first location, the experiment was conducted over two years, with long-term cucumber consecutive short crops grown. At the first location, there was a significant yield in crops in both years. At the second location, the experiment lasted one year and three three consecutive short crops were grown. At the first location, there was a significant yield increase (5%) in both years. At the second location, the yield was greater with the + Si treatments, but was not significantly different from the control. Possibly, the cropping periods at the second location were too short (12 - 15 weeks) to profit from Si supply. In the first year, powdery mildew incidence was 15% lower at the first location, compared with the control crop. At the second location, powdery mildew was not observed at all.

6.4.2. Silicon with courgette, roses, strawberry and bean.

The previous results on the Si content in other horticultural crops (Table 6.1), also led to Si experiments with crops other than cucumber. Courgette, rose, strawberry, and French bean were tested. Courgette was grown in polyurethane foam slabs, strawberry in water culture, and roses and French bean in rockwool. In all trials, treatments with amendment of 1 mmol Si L⁻¹ (as K₂SiO₃) and without Si in the nutrient solutions were performed. With French bean and strawberry, no differences in yield were observed (Table 6.10). Courgette and roses, however, responded positively to additional Si. With courgette, nearly 10 % higher yield was obtained with Si amendment. With strawberry, a clear reduction was observed in the incidence of powdery mildew. However, with this crop, the fruit quality was negatively affected. After it was found that the Si uptake by rose was significant, a more detailed survey was conducted on the Si content in rose plants, grown under different conditions. It was found that the differences in Si content of the plants grown in soil- and soilless culture were not as great as with cucumber. Indeed, the highest Si content of soilless roses were higher than the lowest of the soil crops (Table 6.1). This is probably connected with the fact that a rose crop is grown over a long period (up to six years) and over time more Si is released (Table 6.3). Moreover,

Table 6.11

Effect of Si supply on Si concentration in the root environment (R.E.), yield (stems m^{-2} , stem g and kg m^{-2}) and the Si content in the tissue of rose 'Madelon', grown in rockwool at a common location, during an 11 months trial.

Si concentration			Yield			Si content laminae ($\text{mmol kg}^{-1} \text{ d.m.}$)	
	Supply	R.E.	Stem (m^{-2})	Stem wt (g)	kg m^{-2}	Young	Old
- Si	0.02	0.06	144	40	5.8	32	69
+Si	0.7	1.6	159	38	6	108	220

the pH in the root environment is usually lower in rose crops periodically (Voogt and Sonneveld, 1997). Nevertheless, an experiment was arranged at a commercial rose producer to investigate the effect of Si applications. The greenhouse, with an existing 4 month old rose crop, c.v. 'Madelon' had 8 compartments. In all compartments, a standard nutrient solution (de Kreij et al., 1997) was supplied. In four of them, Si was supplemented as K_2SiO_3 . In each of the compartments, a random section of 5 m^2 was used for yield observations. The yield response was significant, but rather small (Table 6.11). The total number of stems was increased, but the average stem weight was somewhat reduced, because of shorter stems. The differences in yield appeared only after 3 months, and it took 6 months before the observed yield differences were statistically significant. The incidence of powdery mildew was monitored, but the observations were hindered because the grower routinely applied fungicides.

6.4.3. Silicon with lettuce

The growth of lettuce in soilless culture, (nutrient film technique systems (nft) in particular) is often plagued by the occurrence of manganese (Mn) toxicity, even if Mn is omitted from the nutrient solution (Vlamis and Williams, 1973). Williams and Vlamis (1957) and Lewin and Reiman (1969) reported that Si plays a role in manganese distribution in barley plants and alleviated occurrence of Mn-toxicity. Later on, Horst and Marschner (1978) obtained similar results with beans. We conducted an experiment to determine whether silicon supplied in the nutrient solution could reduce the incidence of manganese toxicity in lettuce. Lettuce plants were grown in nft and the supply of Mn and Si were experimental factors, in combination with the pH in the recycling water. Mn was supplied in concentrations of 0 and 20 $\mu\text{mol L}^{-1}$, and Si in concentrations of 0 and 1.5 mmol L^{-1} . The pH treatments were in the range of 5 – 5.5 and 6 – 6.5 respectively, as target values in the recycling nutrient solutions. Neither the supply of Si nor Mn affected the growth, development, or the head weight. However, severe Mn toxicity symptoms developed in the heads in the final weeks of the growing period with all treatments showing the specific brown spots in the margins of the older leaves. With the + Si treatments, the symptoms were much less than in the other treatments (Table 6.12). The Mn supply had no effect on the incidence of the toxicity, although the Mn content was to some extent suppressed by the omission of Mn from the nutrient solution. There was also no clear response of pH on Mn toxicity nor on Mn uptake. Despite the clear effect of Si supply on reduction of Mn toxicity, the Si uptake of lettuce was poor; the Si content of the plants were only slightly increased in comparison with the zero Si treatments. The Mn content in the plant were slightly suppressed by the Si supply, but still at levels in the same order of magnitude

Table 6.12

The effect Mn supply (0 and 20 $\mu\text{mol L}^{-1}$), pH of the recycling nutrient solution and Si supply (0 and 1.5 mmol L^{-1}) on the incidence of manganese toxicity, manganese and Si uptake with lettuce grown in nutrient film technique.

	Treatment			Toxicity index ¹	Tissue content	
	Mn ($\mu\text{mol L}^{-1}$)	pH	Si (mmol L^{-1})		Mn (mmol kg^{-1} d.m.)	Si (mmol kg^{-1} d.m.)
1	yes	6.5	0	0.7	1.6	12
2	no	5.5	0	0.8	1.1	8
3	yes	6.5	0	0.7	1.6	7
4	no	5.5	0	0.5	1.1	8
5	yes	6.5	1.5	0.1	1.1	19
6	no	5.5	1.5	0.1	1	14

as the zero Mn treatments, which definitely had toxicity symptoms. These results were in agreement with Horst and Marschner (1978), who found a corresponding increase in manganese tolerance in beans affected by Si application. They found localized distribution of Mn in laminae in the absence of Si, characterized by a spot-like accumulation. It seems that Si prevents the accumulation of MnO_2 to large aggregates which is mainly the cause of brown spots which resemble Mn toxicity (Marschner, 1986). Memon et al., (1981) demonstrated that Mn normally accumulates in the cell wall of epidermal and mesophyl tissue and thus is isolated from the active sites of metabolism. This appears to make the plant tolerant. In the absence of Si, this specific distribution is disturbed; however, the controlling mechanism and the role of Si is yet unknown.

6.5. DYNAMICS IN SILICON UPTAKE

The mechanistic aspects of uptake and transport of Si is still under discussion (Epstein, 1994). Like Jones and Handreck (1967), many authors assume that the monomer Si(OH)_4 is absorbed passively and follows the movement of water. However, other workers showed relations with plant metabolism (Barber and Shone, 1965). Our investigations were not focussed on plant physiology, but some of the observations could be useful in the discussion. An investigation was conducted with cucumber plants grown for 2 months in a closed water-culture system, to establish a complete mineral balance. The plants were allowed to deplete the available nutrient solution almost completely. From the initial available nutrient solution, 96 % of the water was absorbed, and 93% of the Si. The Si concentration was 0.9 mmol L^{-1} at the start of the experiment and 1.2 eventually in the solution remaining at the end of the experiment. From the water uptake and the mineral quantities determined in the plant, it could be calculated that the uptake concentration, i.e. total nutrient uptake/water uptake was 0.95

mmol L⁻¹ water absorbed. This corresponded with the average concentration in the root environment. Another indication for Si uptake by mass flow is from the experiment with different silicon concentrations in Table 6.6. This was a closed growing system, with treatments of 0.5 and 1.0 mmol Si L⁻¹. The concentrations in the root environment were generally equal to the concentrations in the nutrient solution supplied (Table 6.6). This also indicated that the influx concentration corresponds with the concentration in the root environment. With the higher levels in this trial, less Si was found in the root environment, probably caused by polymerization and precipitation (Iler, 1979). According to Iler (1979), a maximum concentration of 3 mmol L⁻¹ can be expected in a nutrient solution. In contrast with the supposed uptake by mass-flow, throughout the growing period of cucumber, the Si concentration in the root environment tended to decrease. This depletion can only be explained by precipitation, which is unlikely at these low concentrations (Iler, 1979), or by active uptake. Active uptake of Si is as yet unknown (Epstein, 1994), so this requires further research. With roses, the concentration in the root environment was on average higher than the concentration supplied (Table 6.11), which indicates that the absorption rate is much lower than the concentration in the root environment. During a long term trial of cucumber, the progress in silicon content in the plant was followed, by sampling specific leaves at several heights on the plant in a two week cycle. During the growth of cucumbers, silicon accumulates in the leaves, and consequently the highest Si concentration in the plant was found in old laminae (Figure 6.2). The total Si content seems to be maximized at 1400-1500 mmol kg⁻¹. With increasing light intensity during the development of the crop from winter into spring and summer, this maximum level is reached more rapidly than earlier in the season. This could be

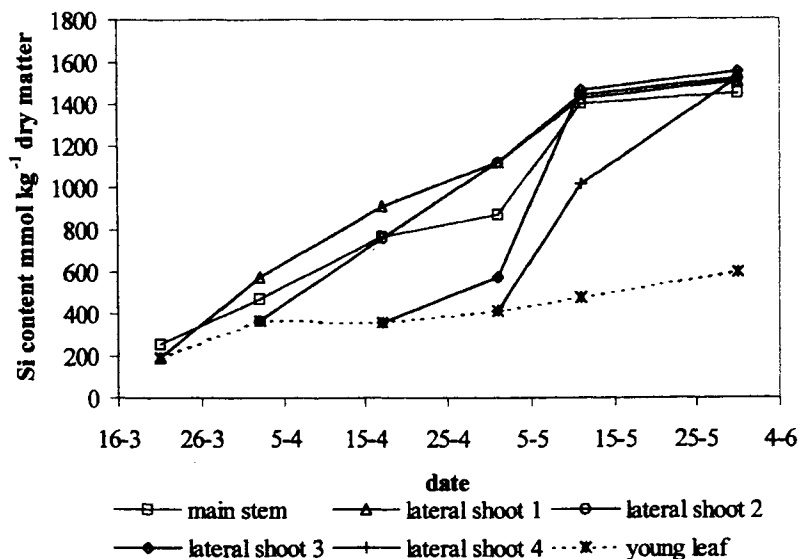


Figure 6.2. Progress of the Si content in cucumber laminae from the main stem and four lateral shoots and from young fully-grown laminae, sampled every two weeks in ten weeks of a cucumber crop.

simply explained by the transpiration rates. The content in young fully-grown leaves also increased during the spring and summer which is also likely due to greater transpiration.

6.6. CONCLUSION

The availability of Si in soilless culture is more restricted than in a soil environment, which results in a lower Si content in soilless-grown crops. Although the essentiality of Si has not been proven, there are several horticultural crops which absorb Si in significant quantities: cucumber, courgette, melon, gherkin, bean, strawberry, and rose. Cucumbers, courgette, and rose have been shown to benefit from an additional Si supply to the crop. Yield increases, and in the case of cucumber and rose, powdery mildew was reduced. This effect on mildew was also found for strawberry, however without any yield increase. In lettuce, the Mn distribution was influenced by additional Si uptake so that Mn toxicity was strongly suppressed. The form of Si which is supplied is important. Si colloids (silica sol solutions) are absorbed poorly and oligomer silicic acid (like waterglass solutions) can cause clogging of the irrigation system. Monosilicic acid (like in metasilicate) performed the best. However, Li_2SiO_3 was toxic to cucumber and Na_2SiO_3 contains too much Na for long term use, which leaves K_2SiO_3 as the only suitable form for application in nutrient solution systems. The appearance of bloom on cucumber fruits is a negative effect of Si supply, but could be diminished by supplying not more than 0.75 mmol L^{-1} .

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Chapter 7

Effect of silicon on plant growth and crop yield

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Integrated management of six macronutrients: nitrogen (N), phosphorus (P), potassium (K), sulfur (S), calcium (Ca), and magnesium (Mg) as well as the seven micronutrients iron (Fe), manganese (Mn), zinc (Zn), boron (B), copper (Cu), molybdenum (Mo), and chloride (Cl) are the ones that most agronomists only consider as essential for sustainable crop yields. However, under special crop/soil agriculture conditions there are some “non-essential” elements, like silicon (Si) that will enhance crop yield by promoting several desirable plant physiological processes.

Due to the desilication process, Si in the soil is continuously lost as a result of leaching process. Subtropical and tropical soils are generally low in plant-available Si and would benefit from Si fertilization. Silicon content in some regions might be limited to sustainable crop production. The need for proper Si management to increase yield and sustain crop productivity appears to be necessary in temperate as well in tropical countries. In addition, Si diminution in the soil can occur in intensive cultivation practices and continuous monoculture of high-yielding cultivars. As a result, these soils are generally low in plant-available Si (Juo and Sanchez, 1986; Foy, 1992). Rice and sugarcane grown in rotation on organic and sandy soils have shown positive agronomic responses to pre-plant applications of calcium silicate slag (Anderson, 1991).

7.1. GENERAL ASPECTS OF SILICON IN SOILS

Soils are considered to be formed as a result of the interaction among parent material, climate and living organisms as influenced by relief and time. Soils are interpreted also as a result of several processes that can be grouped into additions, transformations, removals, and translocations. Most chemical transformations are related to the silicate minerals. These Si-rich minerals vary with the duration and intensity of many specific processes related to the soil forming factors. Under conditions of high rainfall weathering, the less resistant silicates release silica that in most conditions is rapidly leached to the nearby streams. The proper management of highly weathered soils must be based on the understanding of their nature and properties. According to Fox (1980), a soil fertility program needs to take into consideration the return nutrients exported by the harvest as well as depletion by leaching.

7.2. SILICON AND RICE

Since 1955, Japanese farmers have increased and sustained average rice yields up to 6 t ha^{-1} (IRRI, 1993). This could be due to adoption of a balanced integrated nutrient management that includes Si fertilization. Silicate slag application at an optimum rate of $1.5\text{--}3.0 \text{ t ha}^{-1}$ is now widely used in degraded paddy fields in Japan (Kono, 1969; Takahashi and Miyake, 1977). Yield increases of 10% are common when Si is added and at times exceed 30% when leaf blast is severe (Yoshida, 1981). Rice grain quality is also affected by Si application. The percentage of perfect grain in brown rice and in milled rice hull where Si n was applied increased by 7.5% and 3.5% respectively, as compared with the NPK application (without Si) (Kang et al., 1997).

More than 100,000 Mg of calcium silicate are used annually in Florida to provide Si for rice and sugarcane. Growers often apply calcium silicate at the rates of 4.5 Mg ha^{-1} (2 tons per acre), although higher rates, up to approximately 6 Mg ha^{-1} , have been shown beneficial for increasing rice grain yield (Snyder et al., 1986; Anderson et al., 1987).

Korndörfer et al. (1999), working on wet-land rice and 28 field experiments grown in the Everglades Agricultural Area (Histosol), throughout a 5-year period (1992-1996) concluded that in 19 out of 28 field experiments, Si had a positive effect on yield (Table 7.2). When considering only sites with Si response, the average increase yield was 1007 kg ha^{-1} . Based on the calibration study, the authors established three categories for the soil test - low (L), medium (M), and high (H). The lower third ($< 75 \%$ RY) of the response zone was arbitrarily called the low category and corresponded with the range of Si in the soil from 0 to 6.4 mg L^{-1} (Figure 7.1). The upper zone ($75 - 95 \%$ RY) was called medium and corresponded to those soils with Si content between 6.5 and 24.0 mg L^{-1} . The high category was any soil tested above 24.0 mg L^{-1} ($\text{RY} > 95 \%$). The equation describing the curve was: $\text{RY} (\%) = 54.9 + 46.32 [1 - \text{EXP}(-0.088X)]$; ($R^2 = 0.24^{**}$). The relatively poor fit of this model (Figure 7.1) suggested that factors such as cultivar variation, insect damage, lodging, and other biotic and abiotic stresses

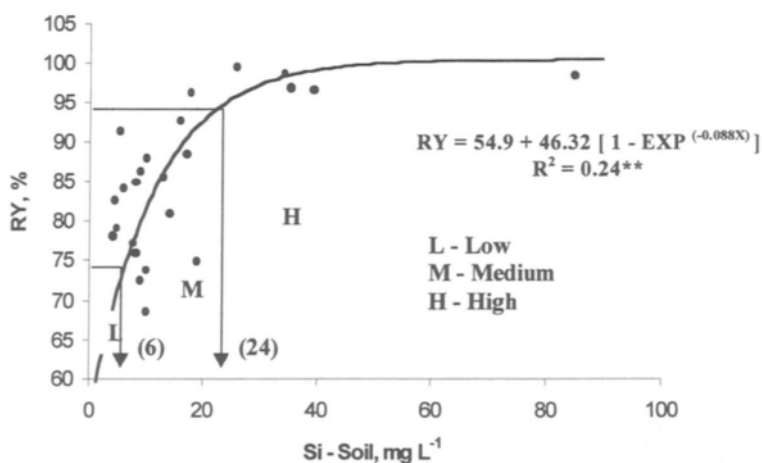


Figure 7.1. Calibration of soil test Si to relative yield (RY) for rice grown in the EAA, Histosol.

Table 7.1

Si in the soil (before planting) and tissue (at harvesting), predicted check and maximum yield by the model, yield increase, and relative yield.

Experiment Site	Soil Si (before planting) mg dm ³	Tissue Si (check treatment) g kg ⁻¹	Predicted Check Yield kg ha ⁻¹	Predicted Maximum Yield kg ha ⁻¹	Predicted Yield Increase ⁽¹⁾ kg ha ⁻¹	Relative Yield ⁽²⁾ %
1992						
C.F.- 715	85.0	39.00	7030	7141	---	98
Brida	19.0	16.00	3800	4802	1002	74
New Farm - 12	14.0	17.00	4966	5926	960	81
Baker	9.0	29.00	4843	5526	683	86
Shawano	6	27.00	5280	6138	850	84
1993						
31ABE	8.0	22.58	4947	6110	1163	76
18CDE	9.0	23.00	4223	5360	1137	73
67-1-4	8.0	md	7015	8152	1000	84
15-ABW	5.0	24.50	4853	5853	665	79
1994						
10ABW	10	16.71	5608	6273	1132	88
33BNS	10.0	18.00	4280	5412	734	74
L6SE2	18.0	29	4712	4907	---	96
1995						
2-52-CDW	4.0	md	3377	4111	1625	78
13-54S	md ⁽³⁾	26.17	5773	5835	---	99
1996						
29DNS	26.0	31.40	6473	6476	---	100
29ANS	10.0	15.60	5216	6841	1625	69
4-H-21-EW	13.0	28.14	5947	6857	910	85
F.9-17N	17.0	md	6485	7240	755	88
N.H. 1-4N-5	20.7	26.50	2804	2804	---	100
N.H. 1-4N-6	39.5	26.50	2976	3072	---	97
N.H. 1-1W-8	11.2	18.55	3733	4986	1253	66
N.H. 1-1W-9	35.5	32.27	5335	5478	---	97
C.F.48-EF-9N	5.3	21.83	7380	8059	679	91
S.F. 2-E-7	md	24.17	5117	6179	1062	79
S.F. 2-E-8	4.5	22.00	5159	6026	867	83
48CG32W	7.6	23.29	4401	5439	1038	76
N.H. 2-20E-4	16.0	36.83	5307	5577	---	93
N.H. 2-20E-3	34.5	37.00	5575	5630	---	99

⁽¹⁾ Predicted Increase Yield = Maximum Yield - Check Yield

⁽²⁾ Rel. Yield (%) = $1 - [\text{Predicted Maximum Yield} - \text{Predicted Check Yield} / \text{Predicted Check Yield}]$

⁽³⁾ md = missing data

probably had an important impact on yield. According to the same authors, lower Si concentrations in the straw were associated with lower relative yield. Si in the straw concentration in the EAA were grouped and associated with one of the three classes: low Si in the straw concentration ranging from 0 to 17 ($< 75\%$ RY); medium concentration, 17 to 34 ($75 - 95\%$ RY), and high concentration exceeding 34 g kg^{-1} ($> 95\%$ RY) (Figure 7.2). The amount of calcium silicate needed to correct Si deficiency in the soil and to obtain optimum rice yield were 7.5, 5.6, and 0 Mg ha^{-1} for low ($< 6 \text{ mg L}^{-1}$), medium (6 to 24 mg L^{-1}), and high ($> 24 \text{ mg L}^{-1}$) level of Si in the soil, respectively. However, 5.6, 4.3, and 0 kg ha^{-1} of calcium silicate were needed for the low, medium, and high level of Si in the straw, respectively (Table 7.2).

It has been suggested that rice straw should contain approximately 30 g kg^{-1} of Si (dry weight basis) for optimum production (Snyder et al., 1986). In the absence of adequate Si, diseases such as brown spot are often severe, giving the standing rice an overall brownish appearance.

7.3. SILICON AND SUGARCANE

Sugarcane strongly responds to Si applications. Ross et al. (1974) reported the removal of 408 kg ha^{-1} of total Si from soil by a sugarcane crop (tops + millable cane) yielding 74 t Si per ha^{-1} . The removal of Si from soil could be more important in intensively cultivated areas. As a result of an Si export of this magnitude, a temporary depletion of bio-available Si in soils could also be a possible factor of declining yields of ratoon crops. In other words, there may be an apparent need for consideration of Si nutrient management in developing appropriate integrated nutrient management systems for sustainable sugarcane production, especially in certain ecoregions having Si-deficient weathered soils and organic soils. Several reports in the literature suggest that Si nutrition has a definite agronomic role in sugarcane crop cultivation, especially on weathered tropical soils such as Oxisols, Ultisols, Entisols, and Histosols (organic soils).

Silicon may be involved in cell elongation and/or cell division. In a field study, plant crop height was quadratically related to the rate of Si applied, while plant crop stem diameter was linearly related (Elawad et al., 1982). Gascho (1978) reported that application of TVA slag

Table 7.2

Calcium silicate recommendation for rice grown on Histosol (EAA) based on the Si soil test and Si in the straw.

Si soil test	Soil class category	CaSiO ₃ recommended
mg L^{-1}		Mg ha^{-1}
< 6	Low	7.5
6- 24	Medium	5.6
> 24	High	0
Si in the straw	Si-straw category	CaSiO ₃ recommended
g kg^{-1}		Mg ha^{-1}
< 17	Low	5.6
17 - 34	Medium	4.3
> 34	High	0

and Na silicate to greenhouse-grown sugarcane increased plant height. Plucknett (1971) indicated that some of the effects of Si on sugarcane were longer stalks with larger diameters and increased number of suckers. These observations on cane and observations for other crops suggest a possible role of Si in cell elongation and/or cell division (Elawad et al., 1982). Ayres (1966) determined that only 15% of the total plant Si is present in sugarcane stalks at 14 months. The leaf sheaths on the best cane-growing soils contained about 2.5 percent Si. Using the sixth leaf sheath, Halais (1967) suggested critical levels of 1.25 percent of Si and 125 mg kg⁻¹ of Mn. If the Si level were below this value, Si responses could be expected.

Research work, largely conducted in Hawaii, Mauritius, and Florida, demonstrated the use of silicate slag as a source of Si for sugarcane. Yield responses were great enough that sugarcane grown in the Everglades (South Florida) is routinely fertilized with calcium silicate when soil tests indicate the need. However, Si fertilization requires large quantities of slag (generally 5 Mg ha⁻¹), making it quite costly (Alvarez et al., 1988). Yields of cane and sugar in Hawaii have been increased 10-50% on soils low in Si, and many sugar plantations regularly apply calcium silicate in responsive fields (Ayres, 1966; Clements, 1965; Fox et al., 1967). Increased yields of sugarcane fields have been reported in Mauritius (Ross, 1974) (Table 7.4) and Puerto Rico (Samuels, 1969). While in South Africa (Preez, 1970) and Brazil (Franco and Korndörfer, 1995), several sources of silicate were found to increase sugarcane yields in pots.

Sugarcane is a Si-accumulator plant (Table 7.3). The Si form which sugarcane usually absorbs has no electric charge (H₄SiO₄) and is not very mobile in the plant. Because the uptake of undissociated H₄SiO₄ may be nonselective and energetically passive, and its transport from root to shoot is in the transpiration stream in the xylem, the assumption has sometimes been made that the movement of Si follows that of water (Jones and Handreck, 1965). The silicic acid is deposited mainly in the walls of epidermal cells, where it is integrated firmly into the structural matter and contributes substantially to the strength of the stem.

Better Si-accumulating cultivars may have the advantage of requiring lower rates of Si fertilizer or less frequent applications. A relatively narrow base of sugarcane germplasm demonstrated significant variability for Si content in leaf tissue (Deren et al., 1993). Korndörfer et al. (1998) also found that sugarcane cultivars have different capacities to accumulate Si in the leaves. The Si levels in the leaf were of 0.76, 1.04, and 1.14 g kg⁻¹

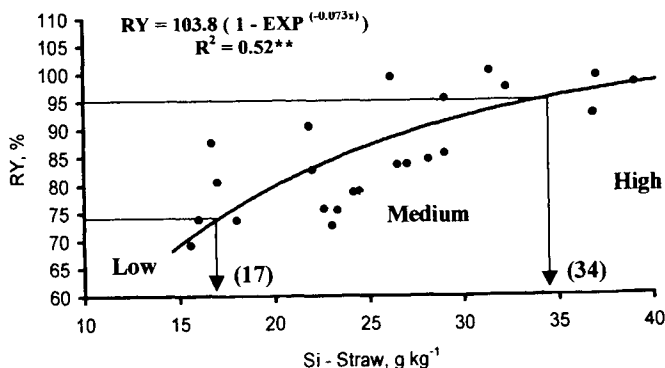


Figure 7.2. Relationship between Si in the straw at harvest and relative yield (RY) for rice grown in the EAA.

Table 7.3

Effect of wollastonite in an Oxisol on the Si content in the plant and soil, and Si accumulation by the aerial part of the sugarcane plant.

Si applied kg ha ⁻¹	Si in the tissue %	Si accumulated g pot ⁻¹	Si in the soil mg dm ⁻³
0	0.70	0.36	14
116	0.89	0.43	17
231	1.41	0.68	19
462	1.77	0.74	30
924	1.93	1.03	46

respectively for the cultivars: RB72454, SP79-1011, and SP71-6163.

In Brazil, on sandy soils, sugarcane has shown consistent response to Si fertilization mainly. The increase yield, using cement and calcium silicate on soils with low Si content, ranged from 7 to 12% (Table 7.5). The benefits of Si fertilization are generally observed in sugarcane grown on Si-deficient soils such as weathered tropical soils and Histosols. Ayres (1966) obtained increases in tonnage of sugarcane to 18 % in cane and 22 % in sugar for plant cane crop following the application of 6.2 t ha⁻¹ of electric furnace slag to aluminous humic ferruginous Latosols in Hawaii. The beneficial effect of the slag lasted on low Si soils for four years, and the first ratoon crop also produced about 20 % more cane and sugar. In Mauritius, calcium silicate slag applied at 7.1 t ha⁻¹ to low Si soils (less than 77 mg dm⁻³ Si extractable with modified Truog's extractant) at planting gave annual cane increases that were economically profitable over a 6-year cycle. A net return from the application of calcium silicate could be expected if the total Si level in the third leaf lamina was below 0.67 % of Si or if the acid-soluble soil Si was below 77 mg dm⁻³ Si (Ross et al., 1974) (Table 7.4).

Based on the results of a 3-year study, Gascho and Andreis (1974) concluded that Si is beneficial and probably essential for sugarcane grown on the organic and quartz sand soils of Florida. For TVA calcium silicate slag applied at 4.9 to 11.6 t ha⁻¹ to muck and sand soils, Gascho (1979) observed significant positive response at all seven muck locations and two out of four sand locations. The economic analysis of the results of these field tests showed the profitability of Si management under the given field conditions (Alvarez and Gascho, 1979). In the early days, in the same area, the addition of calcium silicate slag (obtained from El SIGLO Corporation, Columbia, Tennessee) at 6.7 t ha⁻¹ the yields of five inter-specific

Table 7.4

Effects of calcium silicate on cane yields average of 2 cultivars.

Treatments	Plant cane		Ratoon				
	----- t ha ⁻¹ -----						
	1968	1969	1970	1971	1972	1973	Means
Control	400	784	538	711	611	552	599
7.1 t calcium silicate	63.5	922	621	839	728	685	738
14.2 t calcium silicate	685	962	645	905	768	720	781

Table 7.5

Effect of calcium silicate on sugarcane yield cultivated on sandy soil in Brazil.

Calcium silicate kg ha ⁻¹	Barreiro Farm ----- t ha ⁻¹ -----	Amoreira Farm
0	145	128
700	153	134
1400	154	136
2800	163	137
5600	161	135

hybrids of sugarcane were increased by an averages of 17.2 % and 21.8 % during 1989 and 1990, respectively (Raid et al., 1992). Anderson et al. (1986 and 1987) observed that a single application of silicate slag to Terra Ceia muck in the Everglades (Florida) prior to planting of rice increased production of rice and sugarcane in rotation, but to a lesser extent than the slag applied prior to cane planting. In an investigation to determine multi-year response of sugarcane (cv. CP72-1020), the application of 20 t ha⁻¹ of slag (100% passing through 40 mesh screen) increased cumulative cane yield as much as 39 % and sugar yield as much as 50 % over the three crop years (Anderson, 1991).

In Mauritius, Ross et al. (1974) observed that there was a marked increase in sugarcane yield with calcium silicate application throughout the cycle (Table 7.4). Preez (1970) also has reported positive yield responses of sugarcane to applied silicate materials in southern African soils.

Silicon plays the role of a beneficial nutrient in sugarcane by improving cane plant growth. Application of TVA and Florida calcium silicate slag (up to 20 t ha⁻¹) to sugarcane (cv. CP 63-588) grown in a Pahokee muck soil increased plant height, stem diameter, number of millable stalks, and cane and sugar yields in both plant and ratoon crops (Elawad et al., 1982). This suggested that Si improved the photosynthetic efficiency of individual plants as well as of the whole stand. The application of 15 t ha⁻¹ of slag increased cane and sugar yields by 68 % and 79 % in the plant crop, and 125 % and 129 % in the ratoon crop. Similar results have been reported in Taiwan (Shiue, 1973), Australia (Hurney, 1973) and Puerto Rico (Samuels, 1969). In most of the above reports, the increases in cane and sugar yields associated with the application of silicate materials have been attributed to increased number of millable stalks and increased plant size, not to Pol reading.

In field trials at two non-irrigated sites in south Africa conducted during 1983-1985 on fine-textured acid soil (pH 4.5), steel slag from Japan was applied at a rate of 1-3 t ha⁻¹ before planting cane. The results of the trials indicated an increase in cane and sugar yields in the plant and ratoon crop (Allorerung, 1989).

In Hawaii, based on the economic evaluation of field experiments conducted during 1976 to 1982, the calcium silicate recommendations for sugarcane have been set based on soil and plant Si indexes:

- (1) For fields not fertilized with CaSiO₃ for two or more consecutive crops, apply 4.48 t ha⁻¹ CaSiO₃ to the current crop, if soil Si levels are at or below the critical level of 112 kg ha⁻¹.
- (2) For fields to which CaSiO₃ was applied to one or both of the preceding crops (plant cane and ratoon), apply 2.24 t ha⁻¹ CaSiO₃ to the current crop if the soil Si levels are at

or below the critical level of 78 kg ha⁻¹. Thereafter, apply 2.5 t ha⁻¹ to each succeeding crop, if soil Si levels fall below 78 kg ha⁻¹.

- (3) The critical levels for the "Crop Log" sheath Si (0.7 %) and the Mn/SiO₂ ratio = 75 established by Clements (1965) remain the same: if sheath Si levels of "Crop Log" samples are less than 0.7 % or the sheath Mn/SiO₂ ratios are above 75, apply 2.5 t ha⁻¹ of CaSiO₃ to the current crop (Hagihara and Bosshart, 1985).

In Florida, finely ground slag has been recommended under the following specified conditions (Kidder and Gascho, 1977):

- The land in question must be located more than five km from Lake Okeechobee.
- Soil pH must be less than 8.
- Leaves of sugarcane grown on the soil in question must have shown heavy freckling symptoms.
- Calcium silicate slag used as the soil amendment must be ground finer than 60 mesh.
- Slag must be applied broadcast and disked into the soil prior to planting the cane.

When the slag is applied to sandy soils with Mg test levels below 120 (according to Everglades Research and Education Center, laboratory test), concurrent Mg fertilization at the rate of 40 kg Mg ha⁻¹ at planting is suggested as a precaution (Kidder and Gascho, 1977).

7.4. SILICON AND OTHER CROPS

According to Clark et al. (1990), the relatively high leaf concentration of Si in pearl millet and sorghum may have contributed to its ability to yield well on acid soil (Colombia, South America). The chemical properties of the relatively acid soil were: 60% Al saturation; pH 4.0 (1 water: 1 soil); 7.9% organic matter; 4.0 cmol_c kg⁻¹ Al (Table 7.6).

Khan and Roy (1964) showed a marked effect of silicate on growth and yield of jute plant (*Corchorus capsularis*). Optical measurement of fiber cell dimension of jute showed a greater cell elongation, fineness, and elongation/fineness ration due to silicate treatment (Table 7.7).

Table 7.6

Silicon accumulation in plants (sorghum and Pearl millet) and yield.

	Plant	
	Sorghum	Pearl millet
	Range	
Grain yield (kg ha ⁻¹)	325 - 3600	1980 - 3460
N (g kg ⁻¹)	12.3 - 20.2	14.8 - 22.4
K (g kg ⁻¹)	4.5 - 15.4	2.8 - 8.6
Si (g kg ⁻¹)	8.1 - 18.8	27.9 - 43.4
Al (μg g ⁻¹)	429 - 1855	160 - 653

Table 7.7

Growth characteristics of jute plant with and without silicate (average of 116 kg ha⁻¹ of Si as sodium silicate).

Treatment	Plant height (cm)	Green matter (g plant ⁻¹)	Cell elongation (μ m)	Cell fineness (μ m)	Elongation: fineness ratio
Check	115	58.7	2409	173	140
Silicate	126	69.4	2840	164	174

Foliar sprays with potassium silicate showed increased chlorophyll content and plant growth (Wang and Galletta, 1998). Plants with Si significantly produced more dry matter, as measured by aerial and root weight, than the controls (Table 7.8). The enhanced growth was evident even at a low Si concentration (4.25 mM). The increase in strawberry plant growth by Si may be related to enhanced tissue elasticity and symplastic water volume, which were associated with cell expansion and plant growth (Emadian and Newton, 1989). Potassium silicate treatments also induced metabolic changes such as increases in citric acid and malic acid level, and decreases in fructose, glucose, and sucrose contents. These results suggest that Si has beneficial effects on strawberry plant metabolism. Since strawberry plants are classified as Si non-accumulators, Si has been regarded as unnecessary for their healthy growth. However, Miyake and Takahashi (1978) observed Si deficiency symptoms in the tomato plant, which is also a non-accumulator of Si.

Strawberry plants were grown in solutions containing 50 mg L⁻¹ SiO₂ and lacking Si (Si-free plants) for about 10 weeks (Miyake and Takahashi, 1986). Treatments were divided into three series: plants continuously subject to 50 mg L⁻¹ SiO₂ treatment (referred to as + Si + Si); plants subjected to the 50 mg L⁻¹ SiO₂ treatment after initial Si-free treatment (referred to as - Si + Si); and plants continuously deprived of SiO₂ (referred to as - Si - Si). During strawberry growth, no abnormal symptom caused by the silicon-free treatment was observed; however, at harvest, the total amount of fruits produced was much higher in the plants with the + Si + Si and the - Si + Si treatments than in the plants with the - Si - Si treatment. The total amount

Table 7.8.

Growth enhanced by Si treatment in strawberry plants (means of four replications).

Si*	g dry matter plant ⁻¹					Chlorophyll content**
	Leaves	Petiole	Crowns	Roots	Whole plant	μ g chl a+b/cm ⁻²
mM						
0	1.55	1.37	0.48	0.45	3.85	40.20
4.25	2.10	1.37	0.67	0.53	4.67	57.34
8.50	2.13	1.39	0.69	0.50	4.71	63.95
12.75	2.24	1.38	0.67	0.56	4.85	62.76
1700	2.35	1.40	0.68	0.59	5.02	64.23

* Foliar spray with K silicate

** Chlorophyll content: Leaf disk of 1.0 cm diameter were extracted with 30% acetone. Chlorophyll content of leaf disc was determined using spectrophotometric method.

Table 7.9

Effect of silicon supply on the growth and yield of strawberry plants (2 plants per plot).

	Treatment		
	+ Si + Si*	- Si + Si	- Si - Si
	----- fresh matter - g -----		
Total yield			
- Number	91.5	77.7	67.5
- Fruit -weight	675.5	618.5	521.4
Useful yield ^a			
- Number	53.5	47.2	40.7
- Fruit -weight	528.7	516.7	422.3
Si content (%)			
- Leaves	57	0.45	0.03
- Crown	0.01	0.02	0.01
- Roots	0.03	0.03	0.00

^a total value with a fruit-weight of 6g or above

* plants continuously subject to 50 mg L⁻¹ SiO₂ treatment (referred to as + Si + Si); plants subjected to the 50 mg L⁻¹ SiO₂ treatment after initial silicon-free treatment (referred to as + Si + Si); and plants continuously deprived of (referred to as - Si - Si).

of fruit produced by the plants grown with Si application (+ Si + Si) was much higher than that of the plants receiving Si after initial Si-free treatment (- Si + Si). The total yield of useful fruit was also much higher in the plants with the + Si + Si and the - Si + Si treatments than in the plants in which Si had been omitted (- Si - Si). The total yield of useful fruit of the + Si + Si plants was much higher than that of the - Si - Si plants (Table 7.9).

Si deficiency appeared in the tomato plant at the reproductive stage when cultivated on low Si levels solution culture (Miyake and Takahashi, 1978). It was observed in the first bud flowering stage. This suggests the possibility that reproductive growth might be affected by silicon treatment (Table 7.10). Moreover, tomato plants raised in a Si-free culture bore few fruit. The authors also observed that growth and fruiting were quite normal when 100 mg L⁻¹ of SiO₂ was applied, but upon receiving Si-free treatment, the plant was able to bloom, but produced no fruit (Table 7.11). Field experiments were conducted in alluvial soils for 3 years to evaluate the effect of silicate fertilizers on the growth of cucumber plants. Application of silicate fertilizer promoted the growth and yield of cucumber plants, and also reduced damage caused by wilt disease (Miyake and Takahashi, 1983). At the end of the experiment, the total

Table 7.10

Effects of Si deficiency on tomato pollen fertility.

Treatment - SiO ₂ (mg L ⁻¹)	Growth stage	Fertility ratio - %
0	Before bloom	82
0	In bloom	64
100	Before bloom	93
100	In bloom	91

Table 7.11

Effect of Si on the growth of tomato plants.

Treatment	Top-length (cm)	Root-length (cm)	Top-wt dry matter (g)	Root-wt (dry matter) (g)	Number of leaves	Number of fruits	Fruit-wt (fresh matter) (g)
+ Si + Si*	108	63	46.2	6.7	19	4	168
+ Si - Si	53	54	37.9	7.4	13	3	70
- Si + Si	88	59	32.5	3.7	27	0	0
- Si - Si	45	55	24.3	3.5	10	0	0

* 100 + 100 mg L⁻¹ SiO₂

amount of fruit produced was higher in the plants with Si application than in the plants in which Si application had been omitted (Table 7.12). The difference in fruit yield between plants with and without Si application increased due to the presence of a larger number of wilted plants when Si application had been omitted than when Si had been supplied. The Si content in the leaves of plants with Si application increased considerably to values ranging from 1.3 to 1.9 % Si, while the content remained low at levels of 0.7-1.0% Si in the leaves of plants without Si application. The silicon concentrations in the stems were lower than in the leaves. The available-Si content increased markedly, 44-116 mg of Si/100g soil in the treatments with Si application, while they remained at 20-22 mg of Si/100g in the treatments where Si application had been omitted.

7.5. IN CONCLUSION

- Silicon fertilization may increase and sustain crop productivity on different crops.
- Silicon may affect positively not only accumulator plants but also non-accumulator Si plants.

Table 7.12

Effect of calcium and potassium silicate supply on yield of field-grown cucumber plants, incidence of *Fusarium* wilt disease, content of Si in plants and available Si in the soil.

Treatment	Sol. Si ^a kg ha ⁻¹	Fruit yield ^b t ha ⁻¹	Wilted Plants ^c %	Si-Leaves ----- % -----	Si-Stems ----- % -----	Available Si-soil ^d mg/100g
Ca-Si	327	143	20	1.3	0.5	44
Ca-Si	654	135	15	1.5	0.4	78
K-Si	327	139	11	1.3	0.4	54
K-Si	654	155	0	1.9	0.4	116
Control 1	0	121	37	0.7	0.2	20
Control 2	0	121	62	1.0	0.2	22

^a 0.5 N HCl soluble Si^b yield to the end of harvesting^c estimated at harvest stage^d pH 4 ammonium acetate buffer solution soluble Si

c) Based on the economic approach. Si should be part of the fertilizer management of many different crops.

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Chapter 8

Plant genotype, silicon concentration, and silicon-related responses

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The silicon (Si) concentration in plants can affect their health and productivity. Several experiments evaluated the variability of Si concentration in an array of rice (*Oryza sativa*) and sugarcane (*Saccharum officinarum*) genotypes grown under Si-limiting conditions. In all tests, significant variation for Si concentration among genotypes was identified, and ranking of genotypes over environments was fairly stable. *Indica* rices appeared to be less efficient at acquiring Si than *japonicas*. There were significant negative correlations between Si concentration and plant disease development. Silicon did not increase leaf photosynthesis but did increase sexual fertility and grain set.

8.1. INTRODUCTION

Improved plant growth in response to Si fertilization is well-documented. In many agronomic plants, the most obvious result is increased yield, but many factors affecting yield are themselves enhanced by the addition of Si especially when it is low in availability. Reviews by Epstein (1994), Gascho (1977), Elawad and Green (1979) and others have listed several factors affecting plant growth and health that are improved by Si, including: disease resistance, insect and nematode resistance, soil-nutrient availability (particularly phosphorus (P)), nutrient balance within the plant (nitrogen (N), P, zinc (Zn), manganese (Mn)), improved photosynthesis, reduced transpiration, and improved reproductive fertility.

In south Florida, sugarcane and rice are grown on organic soils (Histosols) of the Everglades and sand soils on adjacent lands. Extensive areas in each soil type are low in plant-available Si. Following work begun by Gascho and Andries (1974), sugarcane and rice now are fertilized routinely with calcium silicate slag (Snyder et al., 1986; Anderson et al., 1987). As Si became a more prominent component of Florida cropping systems, research on various aspects of Si nutrition and plant growth was undertaken. The purpose of this paper is to review research in Florida and relevant efforts elsewhere on the variability of plant genotype for plant-tissue Si concentration and the interaction with various plant responses.

The reason for interest in genotypic variability for Si concentration can be best illustrated by the example of plant response to disease. Quite simply, in virtually every crop species, genotypes (cultivars) have different levels of disease resistance. Indeed, developing disease-resistant cultivars is the main objective of many breeding programs. It is also well documented that Si contributes to reduced disease development (Datnoff et al., 1991; Osuna-

Canisalez et al., 1991). Hence, the logical question follows: is the variation among cultivars for disease response related to genotypic variability for Si concentration in the plant? Are more disease-resistant varieties inherently higher in Si concentration? Of course, this line of thought is not limited to disease response. It can be extended to other Si-influenced attributes as well, such as insect or nematode resistance. From a broader perspective, cultivars could be screened or bred for general adaptation to low-Si environments. Such an effort depends on genetic variability of potential germplasm sources. Genetic variability is the "raw material" of plant breeding, and its existence and nature must first be established before exploitation of a trait can be considered.

8.2. BRIEF REVIEW OF RESEARCH ON PLANT GENOTYPIC VARIABILITY FOR SILICON CONCENTRATION

Because Si is associated with such a broad array of plant responses, genotypic variation for Si concentration has been evaluated in crop cultivars without being specifically related to a particular trait (disease, nutrient concentration, etc.). Yuan and Cheng (1977) grew *indica* and *japonica* rice cultivars in nutrient solution containing a fixed (100 ppm) Si concentration. Total plant Si concentrations ranged from 117 mg g⁻¹ to 171 mg g⁻¹, demonstrating that some genotypes are better at accumulating Si than others. Studies of the actual genetics of Si concentration are few. Majumder et al. (1985) created a 7-parent diallel cross to investigate the inheritance of Si uptake in rice. Genotypes ranged in leaf Si concentration from 11 to 70 mg g⁻¹ at 60 days and 32 to 85 mg g⁻¹ at harvest. Variation was largely additive and some heterosis was observed.

As mentioned above, disease resistance is a major component of most crop breeding programs that include rice. Genetic variability of Si concentration and its relationship to disease reaction have been the subjects of several studies. Authors frequently found that genotypes with greater disease resistance did, in fact, have greater Si concentrations. Blast (*Pyricularia oryzae*) is a severe rice disease world-wide, and has been the subject of studies of the interaction of disease and Si. In Russia, Aleshin et al. (1987) found that the blast resistance of cultivars was related to the silicon dioxide content in the leaves. Silicon fertilization of rice in the Philippines reduced blast severity (Osuna-Cansalez et al., 1991). Research in India (Rabindra et al., 1981) also found that irrigated rice varieties with greater Si content were lower in both leaf and neck blast. Upland rice, which is grown in a non-flooded, aerobic environment, also is responsive to Si. In the uplands of Colombia, Seebold (1998) found that a cultivar's inherent disease resistance could be enhanced with Si fertilization. Further research on a diverse array of upland rice genotypes in Colombia by Winslow et al. (1997) found a high negative correlation ($r = -0.91$) between Si concentration and husk discoloration (*Bipolaris oryzae* and other organisms). Genotypic differences in Si concentration were associated with ecotype (subspecies). Tropical *japonica* rice types had 93% greater Si concentration than *indica* ecotypes. It was hypothesized that the *japonicas* evolved in the Si-deficient uplands and had developed mechanisms to attain greater Si concentrations, whereas *indicas* evolved in lowlands where Si was more available. Under African upland conditions, Winslow (1992) decreased blast and husk discoloration (*Bipolaris oryzae* and other organisms) with Si in both *indica* and *japonica* cultivars. However, the variation in blast severity was not correlated to Si concentration, whereas there was a significant negative linear correlation between husk discoloration and Si concentration. The

significant negative linear correlation between husk discoloration and Si concentration. The lack of cultivar variation in the blast reaction was attributed to the variability in the blast pathogen, which has many host-specific races. Because of host-pathogen specificity, field evaluations for blast can be difficult or misleading without the assurance that appropriate races are present. The association between blast and Si concentration of rice genotypes has also been reported by Tanaka (1965) and Suzuki (1965).

Some research has gone beyond simply quantifying reactions to Si and investigated the actual mechanisms responsible for observed responses. Yoshida et al. (1962) reported that soluble Si is deposited as a gel under the cuticle of the plant cells, forming the "double layer" of cuticle and Si. This double layer acts as a physical barrier to pathogens and pests, and likely contributes to resistance against disease, insects and nematodes as well as reducing transpiration (Isuzika, 1971). The *indica* and *japonica* rice genotypes evaluated by Yuan and Cheng (1977) had cell wall Si content that ranged from 180 to 211 mg g⁻¹, which were greater than the concentrations in the whole plant. Although these genotypes were not subjected to pests or pathogens, the fact that their cell wall Si concentration varied raises the possibility that this could be a genotype-dependent mechanism for resistance. Garrity et al. (1984) screened rice genotypes for silicon layer thickness with the idea that the trait may be a means of selecting for reduced transpiration and increased reproductive fertility. Si layer thickness ranged from 4.2 µm to 17.7 µm among varieties, leading them to conclude that this trait could be screened for in rice breeding populations.

Varietal resistance to nematodes and insects also has been associated with Si concentration. Swain and Prasad (1991) quantified the Si concentration in roots of rice varieties and found that those genotypes with greatest concentration of Si had greater resistance to root-knot nematodes (*Meloidogyne* spp) and that Si increased with plant age. Similar results were observed regarding the Asiatic rice borer (*Chilo suppressalis*) by Patanakamjorn and Pathak (1967) and Djamin and Pathak (1967). There was a strong negative correlation between Si concentration and borer damage. In fact, rice plants with high concentrations of Si actually wore away the mandibles of the borers. The authors suggested that choosing varieties with high Si concentration would be a better strategy than amending the soil with Si.

8.3. FLORIDA STUDIES OF SILICON CONCENTRATION IN RICE AND SUGARCANE VARIETIES

In Florida, sugarcane and rice are grown on two extremely different soil types, organic soils and sand soils. Si fertilizer is readily available and is applied as a standard practice on rice and sugarcane fields on both soil types. Although the calcium-silicate slag used as Si source is relatively inexpensive per unit of weight, the amount usually applied is 2 Mg ha⁻¹, making it one of the more costly crop amendments. Various strategies have been considered to reduce Si fertilizer costs, including the identification or development of cultivars that can grow well under Si-limiting conditions.

8.3.1. Sugarcane

The sugarcane breeding program at Canal Point (CP), Florida has an excellent record of producing cultivars for Florida, which in turn are grown in many other countries besides the US. Although the genetic base of the CP program is limited (Deren, 1995) there is sufficient exploitable variation to consistently release improved cultivars.

In 1990, a study was made of the variability of Si content in elite clones that had been advanced in the CP breeding program (Deren et al., 1993). There were two objectives: to observe if clones varied for Si concentration for use as a selection criterion in breeding, and to screen clones to see if entries varied for their ability to accumulate Si when it was limiting.

A total of fifty-two genotypes were evaluated in two tests at each of four field locations which were low in native Si. In the Stage III test, forty clones had a broad range of genotypes and included germplasm from wild sugarcane relatives (*Saccharum spontaneum*, *Erianthus arundinaceus*, *Miscanthus sinensis* and *M. erectus*) and foreign breeding programs. Since sugarcane relatives often are disease resistant, there was a possibility that they could have had higher Si concentrations. Results of the experiment showed that Stage III genotypes did vary significantly for Si concentration, ranging from 6.4 to 10.2 mg g⁻¹. However, there was no trend for wild relatives to have greater Si concentrations.

The remaining 12 clones were from breeding Stage IV, and were all closely related. As a result, their mean Si concentrations were of a narrower range (6.1 to 7.8 g kg⁻¹) but still expressed significant variation. Although Si concentrations were not evaluated in relation to other traits, the variability observed suggested the possibility of breeding and selecting genotypes for greater Si accumulation.

It was noteworthy that the popular commercial variety, CP 72-1210, was included in both the Stage III and Stage IV tests. At almost all locations in both tests, CP 72-1210 had the greatest Si concentration of all clones, indicating its ability to acquire Si was consistent (stable) across environments.

8.3.2. Rice

Rice is much more affected by Si fertilization and has been the subject of more research than sugarcane, particularly in relation to disease. Datnoff et al. (1997) summarized the role of Si for managing rice diseases in Florida. In addition to disease suppression, Si has been studied in Florida for its effect on yield components, nutrient concentration and balance, and photosynthesis, as well as simple genotypic variability for Si concentration.

8.3.2.1 Genotypic Variability

Most of the rice grown in US is of the *japonica* type (Mackill, 1995). Mid-south varieties are tropical *japonicas* suited to the humid, warm environment of Arkansas, Louisiana, Mississippi, Missouri, Texas, and Florida. California varieties are temperate *japonicas* bred for a cool, dry climate. Despite the narrow genetic base of US rice cultivars (Dilday, 1990), the mid-South and California breeding populations are fairly distinct. Variation for plant-tissue Si concentration among US rice was evaluated in the greenhouse and in the field (Deren et al., 1992). In the greenhouse study, a group of 10 cultivars were evaluated, which included 8 mid-South tropical *japonicas*, an *indica*, and a temperate *japonica* from California. The varieties were planted in a low-Si soil and 2 levels of Si fertilization (2 Mg ha⁻¹ and 5 Mg ha⁻¹) were compared to an unfertilized control. Si concentration in plant tissue increased as expected with increasing rate of fertilization, but within each Si treatment and the control, cultivars varied for Si concentration (Table 8.1). The temperate *japonica* had the greatest concentration in all treatments, indicating some genotypes accumulate greater amounts of Si whether the element is limiting or in excess. By contrast, the single *indica* entry had consistently low Si. Thus, genotypes appeared to be fairly stable in their relative ranking for Si

Table 8.1

Silicon concentration (%) of greenhouse-grown rice cultivars and their relative ranking in three environments with various Si fertility.

Cultivar±	Si Treatment		
	Control	2 Mg/ha ⁻¹	5 Mg/ha ⁻¹
A301	0.40 (2)*	1.46 (1)	3.00 (1)
Rico	0.32 (3)	1.32 (4)	2.23 (8)
Gulfmont	0.31 (5)	1.37 (3)	2.64 (4)
Jasmine 85	0.27 (8)	1.01 (9)	2.10 (10)

*Relative ranking within Si treatments. ±Rico and Gulfmont tropical *japonicas* and Jasmine 85 is an *indica* adapted from Deren et al., 1992.

was observed in rice cultivars in Africa and South America (Winslow, 1992; Winslow et al., 1997).

In field experiments, 18 genotypes were evaluated at 3 locations with high, adequate, and low native Si (116, 40, and 5 mg Si L⁻¹ soil, respectively) (Table 8.2). The low fertility site was amended with 1 Mg Si ha⁻¹. As in the greenhouse experiment, genotypes varied significantly for Si concentration, ranging from 4.1 to 6.0%. The *indica*, Jasmine 85, was the lowest in Si concentration at all locations. When cultivars were ranked by Si concentration, they were quite consistent (stable) across all locations. This stability indicates some genotypes are relatively more efficient at obtaining Si, regardless of the Si status of the environment.

Further evaluation was made of these rice genotypes to relate plant growth and disease responses to Si concentration (Deren et al., 1994). Two low-Si field sites each had plots that were fertilized with 2 Mg Si ha⁻¹ which were compared to unfertilized control plots. All plots were then evaluated for plant tissue Si concentration, brown spot disease severity, panicles per m², 1000 seed weight, and grains per panicle. The purpose was to investigate the relationship between plant responses associated with yield and plant tissue Si concentration under both Si-limiting and Si-enriched environments. Seed weight and panicles per m² were little changed by Si fertility, but brown spot decreased by about 40% and grains per panicle (sexual fertility) increased by about 15% with Si. Obviously, disease affects yield, so the increased seed set logically is a consequence of lowered brown spot severity.

Genotypes varied for Si concentration in both Si environments, with concentration increasing up to 150% with Si fertilization. At both locations there was a significant ($P < 0.01$) negative linear correlation between severity of brown spot and Si concentration in the Si-deficient control plots. This was similar to what Winslow (1992) found for husk discoloration in African upland rice. From the standpoint of breeding, the correlation of Si concentration with the severity of brown spot is encouraging. However, the strength of the correlation is diminished by the fact that the two cultivars with the greatest Si concentrations also had high disease ratings. Clearly, disease resistance is controlled by an array of genetic factors, and while a cultivar's ability to accumulate Si certainly can enhance resistance, increasing Si concentration does not necessarily confer it.

8.3.2.2. Photosynthesis, Biomass partitioning

Silicon has been associated with several other factors affecting plant growth, including photosynthesis, nutrient balance, and reproductive fertility. Because these factors can be

Table 8.2

Silicon concentration (%) and relative ranking of rice cultivars grown at three locations with different Si fertility.

Si Percentage				
	Watson±	EREC	M&M	Mean
Rico	6.00 (1)*	4.98 (2)	5.17 (1)	5.38 (1)
Gulfmont	5.68 (5)	4.90 (5)	5.01 (3)	5.19 (2)
Jasmine 85	5.14 (17)	4.12 (18)	4.17 (18)	4.48 (18)
L202	4.98 (18)	4.20 (15)	4.72 (13)	4.63 (17)

*Relative ranking within locations.

±Native Si (mg Si L⁻¹ soil) was 116 for Watson, 40 for EREC, and 5 for M&M, which was later fertilized with 1 Mg Si ha⁻¹.

confounded or influenced by disease, an experiment was designed to study them in a disease-controlled environment (Deren, 1996a, b; Deren, 1997).

Two rice cultivars, Lemont and Edomen, were grown in a screenhouse containing lysimeters filled with a low-Si organic soil. Lemont is a US tropical *japonica*, and Edomen is a temperate *japonica* from Japan. Half of the lysimeters were fertilized with 5 Mg Si ha⁻¹ and the other half were an unfertilized control. Variables analyzed were partitioning of biomass, yield components, leaf photosynthesis (CER), and concentrations of Si, N, and P in plant tissue. All plants were sprayed regularly with fungicide to control disease.

Cultivars differed significantly for many response variables in both the Si and control treatments, yet their responses were parallel within each treatment. Thus, treatment effects can be generalized for both cultivars (Table 8.3). Biomass partitioning into total leaf and root weights were not significantly different in the Si treatment compared to control. However, with Si fertilization, flag leaves, which "feed" the panicle, and culms increased in weight by 35 and 32%, respectively,. The greatest change in biomass was in grain yield, which increased by about 75%. In the analysis of yield components contributing to grain yield, panicle number, and 1000-seed weight increased by 16% and 7% respectively, with Si fertilization. However, yield components related to sexual fertility were much more benefitted by the addition of Si. Grain number per panicle increased by 46%. The number of infertile florets in the control treatment was 54% greater than in the Si treatment. Hence, the greatest contribution Si made to increasing yield was increasing the grain number through improving reproductive fertility.

Table 8.3

Biomass partitioning of Si-fertilized rice.

	Control	Si	% Change
Grain	23.0*	40	75
Culm	19.0	25	32
Flag Leaf	2	2.7	35
Lower Leaves	6.6	7.5	NS
Root	10.4	11.3	NS
Total	69.0	92	33

*Grams per plot.

Table 8.4

Yield components of Si-fertilized rice.

Yield Component	Control	Si	% Change
Panicle Number	10.7*	12.4	16
Wt. 1000 Seed	23.0	24.6	7
Grains per panicle	91.0	133	46

*Grams per plot.

Grain number per panicle increased by 46%. The number of infertile florets in the control treatment was 54% greater than in the Si treatment. Hence, the greatest contribution Si made to increasing yield was in increasing the grain number through improving reproductive fertility.

The references to Si improving photosynthesis have often been speculative and relate to plant architecture, particularly leaf angle. Si-fertilized rice often has more erect leaves, and it is assumed that more erect leaves allow for greater canopy photosynthesis, but this has not been substantiated. In quantifying individual leaf photosynthesis (CER), we found no trend for Si-fertilized plants to have greater photosynthetic rate. Edomen had slightly greater leaf photosynthesis than Lemont in both the control and Si treatments. But for both cultivars, CER was consistently lower in the Si treatment and declined throughout the growing season (Figure 8.1). The question then arises that if the control treatment had greater CER, what was the fate of the captured carbon? It did not get fixed as biomass. It could have been lost through night respiration. In Florida, night temperatures are high and it is suspected that low

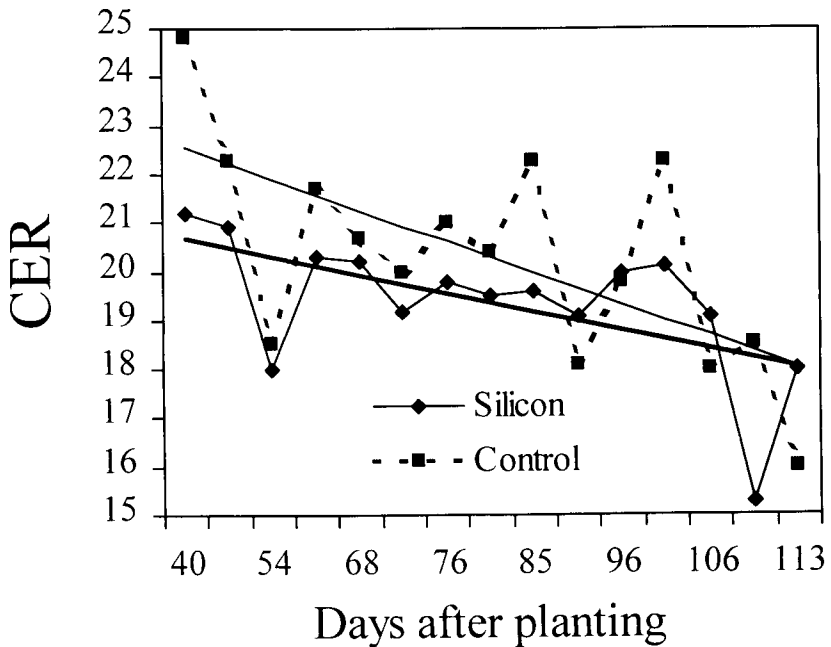


Figure 8.1. Photosynthesis of Si-fertilized rice.

yields there may be due partly to loss of C through night respiration. These results also raise the question of why Si-enriched plants would have a lower CER. Reflection or impedance of light penetration to the chloroplasts may occur in the presence of the silicon-cuticle double layer described by Yoshida et al. (1962).

Maturation of plants in the Si-fertilized treatment was about one week earlier than the control. Earlier maturity may be due to changes in N:P in the plant resulting from Si fertilization (Deren, 1997). Phosphorus concentration was significantly greater ($P < 0.01$) in leaves, flag leaves, culm and roots when plants were fertilized with Si. By contrast, all plant parts were significantly lower in N concentration. Hence, the N:P ratio was reduced in all plant parts with additional Si. A high ratio of N:P can delay the onset of reproduction (Salisbury and Ross, 1992). By contrast, the lowered ratio observed with Si fertilization appeared to promote earlier maturity.

8.4. CONCLUSION

Even small, closely-related populations of sugarcane and rice genotypes showed significant variation for Si concentration. The relative ranking of genotypes for Si concentration was fairly stable over a range of environments with varying Si availability. Although greater Si concentration was associated with reduced disease severity, there were exceptions to this trend, obviously because disease resistance is conferred by traits other than Si concentration. Selecting for Si concentration would not be prudent as a breeding strategy for disease resistance alone. However, given the other attributes associated with Si fertilization, plant breeding programs would be justified in the introgression of germplasm that has a greater ability to accumulate Si.

Silicon does not increase leaf photosynthesis in rice, despite that it is responsible for greater biomass accumulation, particularly grain yield. Earlier maturity observed in Si-fertilized rice was probably due to the reduced ratio of N:P within the plant.

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Chapter 9

Silicon and disease resistance in dicotyledons

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Silicon (Si) has been exploited for its prophylactic properties against plant disease for hundreds of years. Its role as a disease-preventing product has been well documented, but the mechanisms by which it exerts its beneficial properties *in planta* remain poorly understood. For a long time, the observation of a systematic accumulation of silica in cell walls and appositions occurring at pathogen penetration sites led to the conclusion that this parietal strengthening was responsible for the increased resistance of plants to diseases. However, recent evidence suggests that Si. would rather play an active role in reinforcing plant disease resistance by stimulating the expression of its natural defense reactions. Incidentally, in the cucumber (*Cucumis sativus*)-powdery mildew (*Sphaerotheca fuliginea*) system, this latter mechanism appears to be predominant, if not exclusive. A better understanding of this rather unique property of Si. could be exploited to optimize its use in agriculture and to help decipher how plants can be naturally stimulated to protect themselves against pathogens.

9.1. INTRODUCTION

The beneficial effects of Si. have been demonstrated on different dicot species with the most convincing results coming from soilless cultures in greenhouses (for review, see Voogt, this book). If consistent proof of beneficial effects on yield have been hard to obtain, most experiments have reported positive effects in terms of disease control. For instance, positive effects have been demonstrated against powdery mildew on cucumber (Wagner, 1940; Miyake and Takahashi, 1983; Adatia and Besford, 1986; Menzies et al., 1991a), muskmelon (*Cucumis melo* var. *reticulatus*), zucchini squash (*Curcubita pepo*) (Menzies et al., 1992), rose (*Rosa*), and strawberry (*Fragaria ananassa*) (see Voogt, this book) and pythium root rots on cucumber (Chérif et al., 1992; 1994a). For other diseases on other crops, Bélanger et al. (1995) gives a more comprehensive listing. In dicots, the most significant body of work has

been conducted using cucumber. Reports of beneficial effects have been made by scientists from different countries, e.g. Canada, United Kingdom, The Netherlands, Japan, Australia, Brazil, and the United States. Accordingly, cucumber has become the model of choice for understanding how Si. confers plant protection against pathogens.

9.1.1 Silicon in *planta*, background

Today, Si. still represents an element apart in plant physiology, behaving with essential features in certain species, while being at the most considered as beneficial for others. Epstein has provided by far the most exhaustive reviews on the anomaly of Si. in plant biology (Epstein, 1994; 1999; this book). Silicon is absorbed by plants as uncharged silicic acid ($\text{Si}(\text{OH})_4$) present in the soil solution or in the case of soilless culture, in the nutrient solution. Following the transpiration stream, it then moves forwards from roots to leaves by the apoplast to essentially polymerize in the extracellular spaces and in walls of epidermal cells, at sites of strong evapotranspiration. Once polymerized, silicic acid is no longer available as a subsequent source of Si for any other part of the plant. Thus, at any time, a plant only contains 1 % of the $\text{Si}(\text{OH})_4$ it absorbs under a soluble form, while the rest is continuously transformed into insoluble polymers (Jones and Handreck, 1965; Lewin and Reimann, 1969). Higher plants differ widely in their capacity to absorb Si. Jones and Handreck (1967) have divided them in two groups depending on their content of polymerized Si (% of dry weight). On one hand are the accumulators, including wetland grasses, Equisetaceae and Cyperaceae (10-15 %), and on the other hand are non-accumulators, including the other grasses (1-3 %) and dicots (< 0.5 %).

Silicon, under the form of $\text{Si}(\text{OH})_4$, possesses strong affinities for organic polyhydroxyl compounds, such as *ortho*-diphenols, which participate in the synthesis of lignin. This characteristic partly explains its tendency to accumulate in cell walls in maturation or during a pathogen attack, two situations which correspond to a radical change in the constitution of the cell wall, with the apposition of lignin (Jones and Handreck, 1967; Marschner, 1986; Perry et al., 1987; Inanaga and Okasaka, 1995; Inanaga et al., 1995). Once polymerized, Si participates in the rigidification of cell walls with lignin, a process which is confined to the periphery of the plant where evapotranspiration occurs.

9.2. MODE OF ACTION OF SILICON IN DISEASE RESISTANCE: RE-EVALUATION OF THE MECHANICAL BARRIER HYPOTHESIS

Physical barriers, constitutive or induced, are thought to play an important role in plant disease resistance (Vance et al., 1980; Aist, 1983; Nicholson and Hammerschmidt, 1992; Raid et al., 1992). Considering its intrinsic characteristics and its behavior in plants, it was logically proposed that Si plays a role as a mechanical barrier restricting the penetration of fungi in both monocots and dicots. This, in turn, would explain its positive effect on plant disease resistance. Indeed, the primary sites of Si polymerization (cell walls of leaves and xylem vessels) correspond to the privileged infection routes of pathogens.

This hypothesis was first tested in monocots where studies concentrated on trying to establish a link between the accumulation of polymerized Si at the sites of pathogen penetration and a reduction of the incidence of diseases following Si fertilization (see Ishiguro, this book). In dicots, polymerization of Si in walls of epidermal cells following

fungal infections was also detected (Heath, 1981; Kunoh and Ishikazi, 1975), which extends the concept of physical barrier played by Si to non-accumulator plants.

In the case of dicots, most of the results followed from studies conducted on cucumber (for a review, see Bélanger et al., 1995; 1998), which became the model species to study the role of Si in dicot disease resistance. In controlled conditions of culture and infection, Menzies et al. (1991a) showed a reduction of powdery mildew caused by *Sphaerotheca fuliginea* on cucumber following the addition of Si in the nutrient solution. They found that there was a saturable effect of Si in the nutrient solution with the optimum concentration being at 100 ppm (1.7 mM). Higher concentrations of Si in the nutrient solution did not result in greater disease suppression. This observed resistance was expressed by a decrease of leaf colonization and of parasitic fitness of the pathogen. The synchronism observed between the accumulation of Si in cucumber leaves and the decreased receptivity of the plant to the fungus led the authors to correlate the increase in resistance with the reinforcement of cell walls by Si to build an efficient physical barrier. These conclusions were supported by studies made with scanning electron microscopy coupled with an energy dispersive X-ray analysis of minerals in infected cucumber tissues (Samuels et al., 1991a) and with light microscopy and transmission electron microscopy (see Menzies et al., this book; Samuels et al., 1994). The presence of high Si surrounding colonies correlated with lower fungal growth, but only in the early stages of fungal development (first 72 hours after inoculation). However, following an exhaustive analysis of the infection process of cucumber by powdery mildew, Menzies et al. (1991b) noted a radical change in the expression of the defense responses of infected epidermal cells of Si-fertilized cucumber plants. The initiation time of an accumulation of phenolic-like compounds in infected cells was considerably reduced and the number of cells reacting to the pathogen was greater. Moreover, while the percentage of cell penetration of the fungus remained the same, the number of haustoria and of conidiophores produced decreased drastically. It appeared that Si accumulation was subsequent to appearance of phenolic compounds in the host cell. These observations challenged the hypothesis that insoluble Si present in papillae and in cell walls in close contact with the parasite conferred resistance as a physical barrier to fungal penetration.

Another revealing observation was made by Samuels et al. (1991b). In experiments in which plants were alternately fed with 100 and 0 ppm Si nutrient solutions, the protective effects against powdery mildew were lost when Si feeding ceased. At that time, even though cucumber leaves contained high levels of polymerized Si, disease suppression could not be obtained. This was further proof that the deposited Si in the leaves did not participate in the reduction of disease. This new information led Samuels et al. (1991b) to conclude that Si is needed in its soluble, mobile form at the time of infection for resistance to powdery mildew to occur.

9.3. SILICON: AN ACTIVE ROLE?

Pursuant to the concept that Si would not act as a physical barrier to pathogens in dicots, the possibility that Si played an active role had to be established. The opportunity for exploring this new theory first came with the pathosystem cucumber-*Pythium* spp. Silicon applied at a saturable concentration of 100 ppm in the nutrient solution was also found to provide resistance to *Pythium ultimum* and *P. aphanidermatum* in cucumber (Chérif and Bélanger, 1992; Chérif et al., 1994a). As in the case of the foliar interaction described by Menzies et al.,

(1991b), the plants reacted more promptly to the infection by *P. ultimum* and the number of infected cells accumulating an electron-dense, phenolic-like material was far greater. Unlike a physical barrier to the proliferation of the fungus, the accumulated material displayed strong antifungal properties (Chérif et al., 1992b). This material hindered the propagation of the parasite into the vascular system (Chérif et al., 1992b). Noteworthy, none of these deposits, nor the cell walls at sites of penetration of the fungus, contained any trace of Si (Chérif et al., 1992a) as determined by SEM and scanning X-ray analysis. This excluded the possibility of Si functioning as a mechanical strengthener of cell walls to limit the progress of *P. ultimum*, and corroborated the observation of the association of phenolic-like material associated with powdery mildew haustoria made by Menzies et al., (1991b). The fact that it did not appear that there was a direct effect of Si on disease reduction led to the hypothesis that soluble Si was somehow involved in inducing plant defense reactions. This phenomenon, also referred to as induced systemic resistance (ISR), implies that there is an active resistance of the plant based on specific mechanisms. How Si was involved in ISR and what were the mechanisms it triggered in cucumber remained unknown. Chérif et al. (1992a; 1992b) provided the first elements of the answer to these questions. From the literature, it is known that the main defense mechanisms of cucumber are the formation of papillae, the production of hydrolytic enzymes such as chitinases, a controlled cell death also known as hypersensitive response, and the production of phenolics, which would be part of the lignification process, since there has never been a report of phytoalexins in cucumber (Hammerschmit and Kuc, 1982; Siegrist, 1994).

Papillae were obviously not involved in the defense response of Si-treated cucumbers against *Pythium*. Wurms et al. (1999) recently demonstrated that papillae do not play a role in fending off powdery mildew in cucumber treated with compounds known to induce resistance.

In the case of PR proteins, Chérif et al. (1994b) were able to show an enhancement of the activity of chitinases in infected root tissues from cucumber fertilized with Si. While some authors will routinely use PR proteins as an indicator of ISR, chitinases could obviously not be part of effective defense responses to *Pythium* spp., since the cell walls of these fungi do not contain chitin. Further, work with powdery mildew could not corroborate the direct role of chitinases in degradation of the fungus. Indeed, in plants treated with resistance-inducing compounds, the integrity of the cell wall of dead powdery mildew hyphae and haustoria was maintained as demonstrated with gold-labeling of chitin (Wurms et al., 1999).

With regards to hypersensitive response, cell death was never observed as a form of resistance to *P. ultimum* (Chérif et al., 1992b) and powdery mildew (Menzies et al., 1991b; Wurms et al. 1999).

This left the option of phenolics being involved, which was first suggested by Menzies et al (1991b) and Chérif et al. (1992a). Incidentally, analysis of the phenolic contents of Si-treated plant tissue challenged with *P. ultimum* showed a marked increase in the concentration of antifungal phenolic compounds. This suggested that cucumber produced phytoalexins as a defense mechanism, a mechanism that was once thought to be absent in cucurbits (Hammerschmit and Kuc, 1982). However, Daayf et al. (1997) provided conclusive proof that cucumber did produce phytoalexins that were instrumental in reducing powdery mildew infection. Interestingly, in cucumber, these molecules seemed to be present at the time of infection in the plant principally under the form of inactive glycosylated precursors. The antifungal activity was only detected following an acidic hydrolysis of the root extracts.

Conclusive evidence that Si plays an active role in ISR was provided when the interaction between cucumber and powdery mildew was further analyzed at a biochemical level (Fawe et al., 1998). The detection and analysis of antifungal compounds in infected cucumber leaves led to the determination of the nature and to the estimation of the effect of Si amendment on its appearance and accumulation (Fawe et al., 1998). Some of these metabolites, identified as flavonoids and phenolic acids, were specifically and strongly induced in a pattern typical of phytoalexins. As previously reported (Chérif et al., 1994b; Daayf et al., 1997), the fungitoxicity of these phenolics was only apparent after an acid hydrolysis of the leaf extracts. Shortly thereafter, Benhamou and Bélanger (1998) suggested that the release of aglycones in the plant was regulated by the pathogen itself. Indeed, they showed that only conjugated phenolics in close proximity of the fungal structures were converted to their active state, presumably by β -glucosidases produced by the fungus. In turn, these aglycones promptly induced fungal cell death.

Thus, from those results obtained from two very different pathosystems, Si likely plays an active role in disease resistance by being able to stimulate the defense mechanisms, namely phytoalexins, of cucumber in reply to fungal attack.

9.4. A NEW MODEL FOR THE MODE OF ACTION OF SILICON

An interesting hypothesis is that silicon could represent a natural activator of plant disease resistance. If indeed silicon is playing an active role in inducing resistance in cucumber, it could be an inducer of a particular type of ISR, called SAR (systemic acquired resistance), which is strictly dependent on the accumulation of an inducing compound, such as salicylic acid, locally or at the site of infection, and systemically to be activated. An important difference between silicon and known plant activators of SAR is the quick loss of silicon mediated resistance (SiMR) when silicon is depleted from the nutrient solution (Samuels et al., 1991b), while SAR is characterized by a long-lasting effect (Dalisay and Kuc, 1995; Kuc and Richmond, 1977). However, this effect could be the result of the properties of silicon *in planta* in which it is required in a soluble state to effectively stimulate disease resistance (Samuels et al., 1991b), but is continuously transformed to polymerized forms. Recently, it was proposed that the efficacy of a chemical to condition SAR could be related to its resistance to degradation/modification, leading to its continuous presence under its active form in the treated plant (Kauss et al., 1993). By analogy, polymerization of silicon leads to its inactivation as an inducer of resistance and explains the necessity of an uninterrupted feeding. This could also explain why the prophylactic properties of silicon are more subtle and often not as spectacular as the ones displayed by more stable molecules such as dichloroisonicotinic acid (DCIA) or benzothiadiazole derivatives (BTH).

A particular substance can act at different levels in a signal transduction pathway implicated in plant disease resistance. Among others, it can act as a modulator influencing the amplitude of expression of defense responses. Salicylic acid, methyl jasmonate and other compounds able to induce SAR belong to this category of modulators (Fauth et al., 1996; Graham and Graham, 1996; Kauss, 1994; Siegrist et al., 1994). Kauss (1994) has defined this phenomenon as potentiation. It would play an essential role in the development of SAR. Its molecular basis is still unknown (Zhu et al., 1996).

Table 9.1

Comparison of SAR activators and silicon properties in stimulating resistance.

Activators of SAR ^a (SA, DCIA, ...)	Silicon (as Si(OH) ₄)
Saturable effect. In tobacco plants: threshold level=10µM; maximum≈1 mM (Mur et al., 1996).	Saturable effect. In cucumber plants: threshold level≈20 ppm (0.34 mM); maximum=100 ppm (1.7 mM) (Chérif et al., 1992a; Menzies et al., 1991a; Miyake and Takahashi, 1983)
Activation effect time-dependent. In tobacco plants, maximum of SAR expression after 7 days (Mur et al., 1996); in cell/tissue cultures, 1 day of incubation with the activator (parsley: Kauss et al., 1994; cucumber: Siegrist et al., 1994; Fauth et al., 1996).	In cucumber, acquisition of silicon-induced resistance in 1 day (Samuels et al., 1991b). Minimum and maximum of expression not determined.
Activation effect dependent on protein synthesis (Fauth et al., 1996).	Never tested.
No visible sign of defense responses stimulation before infection takes place in entire plants (cucumber: Hammerschmidt and Yang-Cashman, 1995; tobacco: Mur et al., 1996) or before an elicitor is added in the solution in cell cultures (parsley: Kauss et al., 1994; cucumber: Siegrist et al., 1994; Fauth et al., 1996). An exception is the pre-infectional appearance of PR-proteins (Ward et al., 1991).	Idem in cucumber plants (Chérif et al., 1992b, 1994; Fawe et al., 1998; Menzies et al., 1991b). Pre-infectional induction of PR-proteins detected by Shneider and Ullrich (1994) but not by Chérif et al. (1994).

^aSA:salicylic acid; DCIA: dichloroisonicotinic acid; PR proteins: pathogenesis-related proteins

The effect of silicon on disease resistance expression is similar to this potentiation process. Indeed, its stimulating properties on plant resistance is only visible once infection occurs and is characterized by a precocious and amplified expression of defense reactions (Chérif et al., 1992a; 1994; Fawe et al., 1998; Menzies et al., 1991b). Thus, silicon could be assimilated to a modulator similar to SAR-inducing compounds. Another argument in favor of this role is the absence of the emergence of an habituation state of the plant cell following a continuous feeding with the element. This habituation state generally appears with molecules used by the cell as secondary messengers in signal transduction pathways (Ca²⁺..). As the messenger accumulates, the cell progressively becomes insensitive to it (Gillroy and Trewavas, 1990). In this respect, Table 9.1 summarizes and compares characteristics of SAR activators and silicon. Several interesting analogies appear from this comparison like the saturable property of both induced-resistances, or the strict post-infectional expression of defense responses (except for PR proteins). Thus, it becomes clear (that Si MR could function in similar ways as SAR in plants. Exhaustive studies of the accumulation of PR proteins known to appear in cucumber following SAR induction (pre- and post-infectional) as well as the determination of the possible dependence of Si MR expression on protein synthesis notably, could clarify the link between SiMR and SAR.

9.5. CONCLUSION

The results of recent research demonstrate that the role of soluble Si in cucumber-pathogen interactions appears to be an active one, presumably as a signal for inducing defense reactions. In cucumber, these defense reactions are of a phenolic nature and were specifically and strongly induced in a pattern typical of phytoalexins. There is a saturable limit to the amount of Si that can induce the defense response in cucumber and the Si needs to be in a soluble form constantly in the plant to be actively involved in inducing resistance.

Considering the work on the role of Si in plant disease resistance, one can still wonder if Si acts similarly in accumulator monocots and in non-accumulator dicots. Indeed, the resistance of sensitive barley to *Erysiphe* obtained with Si amendment is expressed by a decrease of the pathogen penetration (Carver et al., 1987), which speaks for a role as a passive mechanical protection. On the other hand, Si-induced resistance in cucumber is translated into a rapid and extended expression of its natural defense reactions, whatever the plant-pathogen interaction analyzed (Menzies et al., 1991; Chérif et al., 1992a, b, 1994; Fawe et al., 1998). Whether this difference reflects reality or is only dependent on the ways dicots and monocots have been studied remains to be established. The reaction of monocots to Si treatment has mainly been analyzed using a microscopical approach. Following the results obtained in cucumber with a biochemical approach, it would be of importance to analyze the effect of Si on the defense reactions known to occur naturally in the monocots studied; and then be able to discern if the passive mechanical protection offered by Si polymerization in cell walls is the only means by which Si acts in this group. In dicots, there is a need to study the influence of Si on disease resistance of other species to determine if Si plays a similar role. At this level of knowledge, a genetic approach would certainly be an interesting next step to a deeper understanding of its mechanism of action in cucumber resistance.

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Chapter 10

The use of silicon for integrated disease management: reducing fungicide applications and enhancing host plant resistance

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Silicon can reduce levels of several important diseases of rice, including blast, brown spot, sheath blight, leaf scald and grain discoloration. Levels of control are equal to that achieved by fungicides for diseases such as blast and brown spot. Hence, the number of fungicide applications and rates can be reduced significantly. Residual activity of silicon was effective for disease control in the second year crop and was comparable to a first year silicon application or a full rate of a fungicide. Silicon enhanced performance of partially-resistant cultivars so that they were comparable to highly resistant cultivars for both blast and sheath blight. These findings suggest that silicon could be employed in integrated disease management systems for reducing fungicide use and enhancing host plant resistance for the control of important rice diseases worldwide.

10.1. INTRODUCTION

Silicon (Si) is the second most abundant element in the earth's crust after oxygen (Elawad and Green, 1979; Epstein, 1994; Jones and Handreck, 1967; Savant et al., 1997). Most soils contain considerable quantities of this element, but repeated cropping can reduce the levels of plant-available Si to the point that supplemental Si fertilization is required for maximum production. However, some soils contain little plant-available Si in their native state. Low-Si soils are typically highly weathered, leached, acidic and low in base saturation. Highly weathered soils such as Oxisols and Ultisols can be quite low in soluble Si. Highly-organic Histosols that contain little mineral matter also may contain little Si. In addition, soils comprised mainly of quartz sand (SiO_2), such as sandy Entisols, also may be very low in plant-available Si. These conditions are found in many crop producing areas of the world.

Silicon is considered a plant nutrient "anomaly" because it is presumably not essential for plant growth and development (Epstein, 1994). However, soluble Si has enhanced the growth, development, and yield of several plant species including rice (*Oryza sativa* L.), sugarcane (*Saccharum officinarum* L.), and most other cereals and several dicotyledons (Belanger et al., 1995; Elawad and Green, 1979; Jones and Handreck, 1967; Savant et al., 1997; Savant et al., 1999). Silicon is absorbed as Si(OH)_4 by rice from soil in large amounts that are several fold higher than those of other essential macronutrients. For example, Si accumulation is about 108% greater in comparison to N in rice. In general, a rice crop producing a total grain yield of 5,000 kg ha⁻¹ will remove from 230 to 470 kg Si ha⁻¹ from the soil (Savant et al., 1997).

Silicon amendments have proved effective in controlling several important plant diseases, especially in rice (Ou, 1985). In the years 1920 to 1940, pioneering work by Japanese researchers first indicated that Si was effective in controlling rice diseases (Ishiguro, 2000; Kozaka, 1965; Suzuki, 1935). These studies demonstrated that applications of 1.5 to 2.0 tons ha⁻¹ of various Si sources to Si-deficient paddy soils dramatically reduced the incidence and severity of blast, caused by *Magnaportha grisea*, and other rice diseases such as brown spot (*Cochliobolus miyabeanus*), sheath blight (*Thanatephorus cucumeris*), leaf scald (*Monographella albescentis*), and grain discoloration (species of *Fusarium*, *Bipolaris*, and others). Since the first reports by the Japanese, many researchers in other countries also have investigated the use of Si for controlling rice diseases (Aleshin et al., 1987; Correa-Victoria et al., 1994; Chung et al., 1989; Datnoff et al., 1997; Datnoff et al., 1992; Datnoff et al., 1991; Hooda and Srivastava, 1996; Kumbhar et al., 1995; Lee et al., 1981; Lian, 1976; Nanda and Gangopadhyay, 1984; Ohata et al., 1972; Okuda and Takahashi, 1964; Osuna-Canizalez et al., 1991; Takahashi, 1967; Volk et al., 1958; Wang et al., 1980; Yamauchi and Winslow, 1989).

Despite all the past research on Si for disease reduction and increased yields, little effort has been given to the idea of using this element as a tool in Integrated Disease Management. Silicon has been demonstrated to control several important diseases as effectively as fungicides (Datnoff and Snyder, 1994; Datnoff et al., 1997; Kithani et al., 1960; Mathi et al., 1977). Therefore, crop production inputs such as fungicides might be better managed by using Si. The number of applications or rates of application might be reduced or eliminated altogether. Host plant resistance also might be better managed. Resistant cultivars are notorious for becoming susceptible to diseases such as blast within a short time after commercial release due to the emergence of pathogenic races (Seebold, 1998). Cultivars that are partially resistant can be environmentally sensitive or fail in areas with greater disease intensity. Silicon might enhance this lost resistance or partial resistance to the same level as complete genetic resistance. All the above could be accomplished without compromising grain quality and yield. This Integrated Disease Management strategy has been demonstrated experimentally in both irrigated and upland rice. This paper will provide an overview on the application of Si and its interaction with fungicides and host plant resistance for managing major rice diseases.

10.2. INTERACTION OF SILICON AND FUNGICIDES

Kitani et al. (1960) probably were the first scientists ever to demonstrate the influence of silicon and fungicides alone and in combination for controlling rice blast. In their study, Si applied as calcium silicate reduced neck blast severity almost as effectively as a mercuric fungicide, 12% vs. 10% and 11.2% vs. 7.4%, respectively, depending on the level of N also applied (Table 10.1). Silicon alone was associated with a gain in grain weight over the control, 37% (50 kg N/ha) to 40% (75 kg N/ha). The mercuric fungicide led to weight increases of 28% to 34%, respectively, for the two different N treatments. Combined Si/fungicide treatments were the most effective for reduction of neck blast severity (below 3%) and increased grain weight (40% to 48%). Hashimoto and Hirano (1976) conducted similar studies on neck blast development, but included other factors such as rice cultivars and nitrogen. They demonstrated that calcium silicate alone reduced rice blast 13%, fungicide alone (Hinosan), 22% and the fungicide + calcium silicate, 27% in comparison to the non-

amended control. They concluded that the fungicide effect in reducing blast was supplemented by the addition of calcium silicate.

Mathi et al. (1977) conducted similar experiments for sheath blight development. In this study, they evaluated Si applied as sodium silicate alone and in combination with two fungicides, Hinosan and Dithane 45. All treatments were effective in reducing sheath blight intensity (SBI) and increasing yields in comparison to the control; Si (SBI=48% and yield=4.6%), Dithane (SBI=68% and yield=9.5%), Hinosan (SBI=99% and yield = 16.8%), Dithane + Si (SBI=84% and yield=13.1%) and Hinosan + Si (SBI=118% and yield=37.2%). Again, the combination of Si and a fungicide were the best treatment for dramatically reducing disease. The increase in grain yield was synergistic when the fungicide Hinosan was used in combination with Si.

In Florida, an evaluation of Si fertilization in combination with benomyl or propiconazole was undertaken to determine if Si could control diseases such as blast or brown spot as effectively as a fungicide (Datnoff and Snyder, 1994; Datnoff et al., 1997). A rice crop was treated with Si at 0 and 2 Mg Si ha⁻¹ and benomyl at 0 and 1.68 kg ha⁻¹ and propiconazole at 0 and 0.44 L ha⁻¹. Fungicide sprays were applied at 2.1 x 10⁵ Pa with a CO₂ backpack sprayer equipped with three Cone-Jet nozzle tips on a hand-held boom at panicle differentiation, boot, heading and heading + 14 days. Blast incidence was 73% in the non-Si, non-fungicide control plots and 27% in the benomyl treated plots. Where Si was applied, blast incidence was 36% in the non-fungicide plots and 13% in the benomyl treated plots. The same degree of disease control was generally obtained when either the benomyl or Si were applied individually. Brown spot responses were similar to those observed with blast. Brown spot severity and disease progress were reduced more by Si alone than propiconazole. For both diseases, the greatest reduction in disease development was obtained by integrating Si fertilization with fungicides. Thus, Si provided control for two economically important diseases to a greater degree than U. S. registered fungicides.

From the aforementioned studies, it can be concluded that the combination of Si and a fungicide was the most effective treatment for reducing several important rice diseases while increasing yields in Japan, India and the US. In most of these studies, Si appears to be able to control disease as effectively as a fungicide, suggesting that Si may help in reducing fungicide applications and rates.

10.2.1. Silicon and number of fungicide applications or rates

Because Si can control several rice diseases to the same general degree as a fungicide, it is possible that Si might help reduce the number of fungicide applications or the rate of active ingredient. Seebold (1998) and Seebold et al. (1995; 1998b) tested these hypotheses in field experiments of upland rice in the savannahs of Colombia. Si was applied as wollastonite at 400 kg Si ha⁻¹ and the rice cultivar Oryzica Sabana 6 was seeded at 80 kg ha⁻¹. Treatments included a nontreated control, Si applied alone, and Si plus fungicides (edifenfos at 1L ha⁻¹ and tricyclazole at 300 g ha⁻¹) applied at the following growth stages: tillering (T), panicle initiation (PI), booting (B), 1% panicle emergence (1%), 50% panicle emergence (50%), PI, B, 1%, and 50%; B, 1% and 50%; 1% and 50%; B and 1%; PI and 1%; T (Figure 10.1). Neck blast incidence was significantly reduced using either Si alone or Si plus fungicides in comparison to the nontreated control (Figure 10.1). Silicon alone significantly reduced neck blast incidence by 40%. Si + one fungicide reduced neck blast 75 to 90% while Si + two applications reduced neck blast 76 to 94%. Si + three to five applications reduced neck blast

Table 10.1

Influence of calcium silicate and mercuric fungicide alone and in combination at two different nitrogen levels on % neck blast incidence and grain yield.

	% Neck Blast		Grain Weight (g/2.9m ²)	
	50 N kg/ha	75 N kg/ha	50 N kg/ha	75 N kg/ha
Si*	12	11.2	1398.7	1415.7
Fu**	10.1	7.4	1302	1357.3
Si + Fu	1.7	2.5	1425	1504.7
Control	26.5	42.5	1018	1012.7

Adapted from Kitani et al. 1960.

*Calcium silicate applied at 2.25 t/ha.

**Mercuric fungicide = phenyl mercuric acetate : calcium carbonate mixture (1:5) applied at 40 kg/ha.

94 to 98%. Therefore, one application of the fungicide in combination with Si was as effective as two, with somewhat better results with 3 to 5 applications. No significant differences in yield were observed among Si alone or Si plus fungicide applications, regardless of timing, with all treatments significantly increasing yield in comparison to the control.

In another experiment, Si was incorporated prior to seeding at 0 and 1000 kg ha⁻¹ (Seebold, 1998; Seebold et al., 1998b). Two foliar applications of edifenfos were applied at 0, 10, 25, and 100% of recommended rates. Ratings of leaf blast for Si alone and Si plus edifenfos at various rates were 54-75% lower than in the nontreated control (Table 10.2). For neck blast, Si alone and Si plus edifenfos and tricyclazole at various rates were 28-66% lower in comparisons to the nontreated control. The greatest leaf and neck blast reductions were observed where Si plus the full rate of fungicide had been applied. Si + lower rates of fungicides (10% and 25%) were able to reduce leaf and neck blast as effectively as a full rate of the fungicide. Silicon alone was just as effective as the fungicides alone or the fungicides + Si for reducing leaf blast. However, Si alone reduced neck blast incidence only 28%.

Fungicides improved yields ranging from 22 to 28% over the control. Interestingly, Si alone improved yields by 51%, and this increase was significantly greater than the fungicide contribution. The effect of Si on reducing a disease such as blast unquestionably contributed to an increase in yield, but Si also has been shown to increase yields in the absence of disease (Ou, 1985). Increase in grain yield can be attributed to an increase in the number of grains per panicle (Deren et al., 1994). Spikelet fertility also has been associated with Si concentration in rice (Savant et al., 1997). Therefore, Si alone could improve grain yields of rice cultivars without further genetic improvements.

10.2.2. Residual silicon effect and fungicides

In 1995 and 1996, Si was incorporated prior to seeding at 0 and 1000 kg ha⁻¹ (Seebold, 1998; Seebold et al., 1998b). Plots that were treated in 1995 (residual Si) were compared to plots receiving a fresh or current year application of Si in 1996 to study the residual effect.

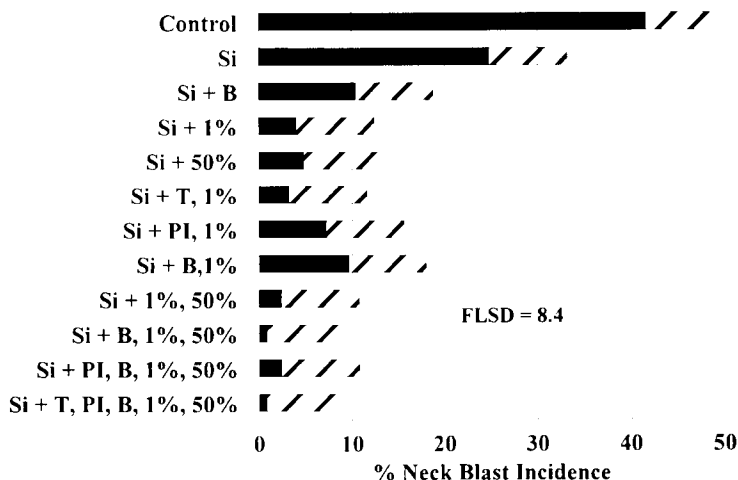


Figure 10.1. Effect of silicon and fungicide timings on neck blast incidence. Fungicides timings are tillering (T), panicle initiation (PI), booting (B), 1% heading (1%), 50% heading (50%) and various combinations. Stripe Bars represent FLSD value ($P=0.05$). Reproduced by permission from *Advances in Rice Blast Research*, D. Tharreau, et. al. Eds., Kluwer Academic Press, The Netherlands.

Two foliar applications of edifenfos, sprayed at 20 and 35 days after planting, were made and followed by three applications of tricyclazole. Leaf blast was evaluated as percent area of individual leaves and neck blast was rated as percent incidence of 100 panicles.

In both 1995 and 1996, ratings of leaf blast for Si alone (residual and fresh applications) and Si plus edifenfos (residual and fresh applications) were 50-68% lower than in comparison to the nontreated control (Table 10.3). The greatest reductions in leaf blast were observed where Si plus fungicide had been applied. The one year residual Si application was as effective as a fresh application and these treatments were not significantly different. for leaf blast control in comparison to edifenfos alone or in combination with a one year residual. Silicon alone reduced leaf blast to the same level as the edifenfos applied with Si in 1995. In 1996, ratings of leaf blast for Si alone were significantly lower (35%) than for the full rate of fungicide. Incidence of neck blast was reduced 28 to 66% with applications of Si and Si plus tricyclazole (Table 10.3). A one year residual application of Si applied in 1995 was as effective as a fresh application in 1996 in reducing neck blast incidence. However, these treatments were not as effective as fungicide applied alone or in combination with Si. Tricyclazole alone or in combination with Si provided the best reductions in neck blast incidence.

Silicon alone and in combination with tricyclazole applied in 1995 or in 1996 increased yields 28 to 51% over the nontreated control (Table 10.3). The 1995 residual Si application was as effective in increasing yields and not significantly different from tricyclazole alone or tricyclazole applied in combination with Si applied in 1995 or 1996.

Silicon can control diseases as effectively as fungicides. Si apparently can help to reduce the number of fungicides applied in a growing season. The use of Si plus reduced rates of fungicides are as effective as full rates of fungicides alone. These results suggest that the

Table 10.2

Effects of silicon and fungicides alone and in combination on AUDPC for leaf blast, % neck blast incidence and rough rice yields.

Si ^a kg ha ⁻¹	Fungicide ^b Rate (%)	AUDPC for Leaf blast	Blast Incidence (%)	Yield kg ha ⁻¹
0	0	4.3 a ^c	72 a	2284 d
0	10	1.8 cd	26 c	2769 cd
0	25	2.9 b	20 cd	2777 cd
0	100	2.7 b	12 ef	2932 bc
1000	0	1.6 cd	44 b	3445 a
1000	10	1.4 d	18 de	3373 ab
1000	25	2.2 bc	15 de	3682 a
1000	100	1.4 d	6 f	3380 ab

^aSilicon applied as calcium silicate at 5 t/ha = 1000 kg Si ha⁻¹.

^bFungicides applied as 10, 25 and 100 % of recommended rate. Edifenfos applied for leaf blast and tricyclazole applied for neck blast.

^cMeans followed by same letter are not significantly different based on Fisher's LSD.

number of fungicide applications and their rates may be reduced. A one year residual application also is effective for reducing leaf and neck blast and maintaining rice yields. Since Si alone enhanced yields more effectively than fungicides alone, fungicides might be eliminated altogether. Consequently, growers may save either initial or additional application costs for either fungicides or Si while providing positive environmental benefits.

10.3. SILICON AND HOST PLANT RESISTANCE

As previously mentioned, Japanese researchers first indicated that Si was effective in augmenting resistance of susceptible cultivars to blast and several other important rice diseases. However, the role of Si in reducing plant diseases is not clearly understood. In the case of rice blast or brown spot, Si may act to block fungal penetration through synthesis in the host of organic-Si complexes or formation of a physical barrier of hydrated silica beneath the cuticle of the epidermis (Ishigoro, 2000). Silicon also may play a role in pathogenesis-induced host defenses as well (Fawe et al., 2000). Regardless of the mechanism (s) involved in resistance, Si provides effective disease control.

Kozaka (1965) probably had the first comprehensive English translation on the effects of Si on host plant resistance in rice. He cited the works of several Japanese scientists dating from 1917 to 1959. General observations were Si-treated rice plants had fewer blast infections, a large number of silicated epidermal cells, and increased resistance to blast by the application of Si. He also mentioned that a high correlation existed between Si in the plant and disease

Table 10.3

Comparisons made in 1996 of area under disease progress curve (AUDPC) for leaf blast, neck blast and yields from rice treated with silicon (Si) in 1995 (residual) with either fresh Si applications in 1996, fungicide^a alone or in combination with Si.

Comparison ^b	AUDPC for Leaf blast	Neck Blast (%)	Yield (kg ha ⁻¹)
Residual Si - 1995 application (1000 kg ha ⁻¹) vs.	2.2	43	3042
Non-treated Control 1996	4.3 (0.0001) ^c	72 (0.0001)	2284 (0.0004)
Fresh Si - 1996 application	2.0 (0.08)	44 (0.60)	3444 (0.04)
Fungicides alone 1996	2.7 (0.08)	12 (0.0001)	2932 (0.57)
Residual (1995 Si application) + fungicides 1996	1.8 (0.37)	9 (0.0001)	3101 (0.77)
Fresh Si (1996 application) + fungicides 1996	1.4 (0.01)	6 (0.0001)	3380 (0.09)

^aFungicides = edifenfos applied for leaf blast and tricyclazole applied for neck blast.

^bComparisons are made between AUDPC for leaf blast, % neck blast and yield from 1995 residual plots with treatments in 1996.

^cNumber in parentheses are P values from comparison between AUDPC for leaf blast, % neck blast and yield for residual Si application in 1995 and 1996 treatments. Means are considered to be significantly different if $P \leq 0.05$ based on t-tests of two means in each comparison.

resistance within a given rice cultivar, but this same relationship may not exist between different rice cultivars. Deren et al. (1994) and Winslow (1992) have made similar observations for this disease and several others. Nevertheless, Kozaka (1965) provided data suggesting that susceptible cultivars amended with Si could provide disease protection approaching that of non-amended resistant cultivars (Figure 10.2).

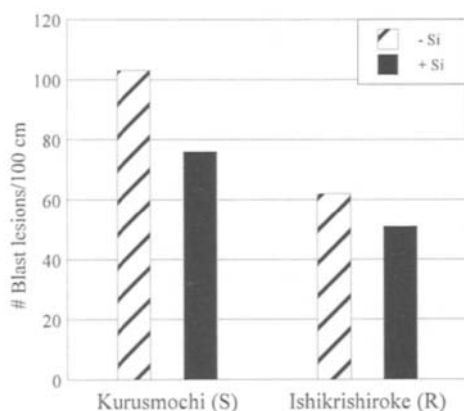
Kim and Lee (1982) investigated the effects of Si soil amendments on the susceptibility of several rice cultivars to neck blast development in Korea. They used several cultivars that were either Tongil or Japonica types. Their study revealed that the Tongil types were the most susceptible to neck blast because the incidence ranged from 37 to 79% in the controls vs 4.6 to 6.3% for the Japonicas. The Tongil types had the best disease reduction response to Si amendments, 56 to 60% reduction in comparison to 6 to 46% for the Japonica types. Yield increases among all the cultivars due to Si amendments ranged from 9 to 22%. Interestingly, the cultivar Akibare, which might be considered the most resistant to rice blast in this study, had yield increases of 10% over the non-amended control even though its resistance was little improved with the addition of Si. This suggests that cultivars that have complete genetic resistance to blast or any other disease might still have their yields augmented without further

genetic improvements by using Si. It may be that rice cultivars that have lost resistance to a disease such as blast, but with good to excellent agronomic traits, might be redeployed simply by using Si fertilization or amendments for disease management.

10.3.1 Silicon enhancement of partial blast resistance

Seebold (1998) and Seebold et al. (2000) conducted an extensive study on the interaction of Si rates with differing levels of blast resistance. In this study, blast resistant, Oryzica Llanos 5 (OL-5), partially resistant, Linea 2 (L2), and susceptible, Oryzica 1 (O1), cultivars of rice were planted in soil amended with Si at 0, 500, or 1000 kg ha⁻¹. Although disease intensity was low (>1 to 6%), leaf blast was reduced by Si at the highest rate by 50 and 73% on L2 and O1, respectively, as compared to the control (Figure 10.3). The level of resistance to leaf blast in L2 amended with 500 or 1000 kg/ha Si was augmented to the same level of OL-5 without Si. Similar results were obtained by Osuna-Canizalez et al., 1991. They conducted experiments with nutrient solutions of Si and three IR cultivars varying in levels of blast resistance. IR36 and IR50 were lowland cultivars, and IR36 contained a higher level of partial resistance to blast than IR50. IAC165 was an upland cultivar with almost complete resistance to the race of *M. grisea* used in this study. They demonstrated significant reductions in number of lesions cm⁻² (30 to 35 for IR50 and IR36 non-amended versus 2 to 4 amended with Si). The resistance of these two cultivars was greatly improved with the addition of Si. In addition, the level of resistance of these two cultivars amended with Si was equivalent to that of IAC165 without Si fertilization.

Seebold (1998) also investigated neck blast incidence in blast resistant OL-5, partially resistant, L-2, and susceptible, O1, cultivars of rice. Neck blast incidence was significantly different among the cultivars for each rate of Si. Silicon rate reduced the incidence of neck blast for L2 and O1. No appreciable changes were recorded for OL-5. For L2 and O1, neck blast incidence decreased by 37 and 28%, respectively, as the rate of Si increased from 0 to 1000 kg ha⁻¹. L2 and O1 had higher blast incidence at 500 or 1000 kg of Si ha as compared



Adapted from Kozaka, 1965

Figure 10.2. Influence of silicon on # of lesions developing on Japanese cultivars resistant and susceptible to blast.

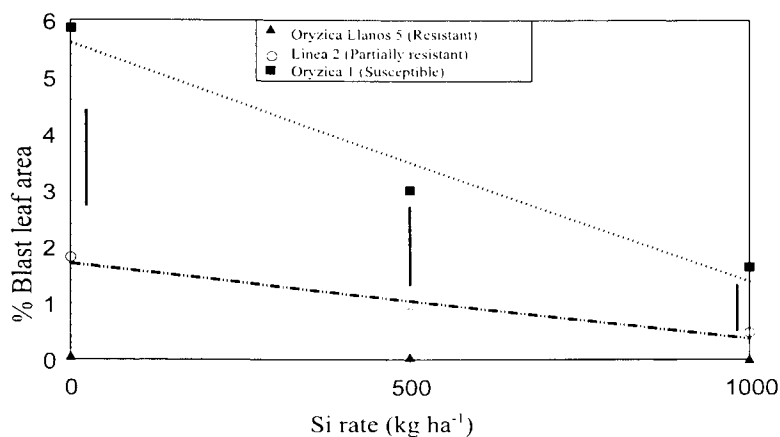


Figure 10.3. Relationship between leaf blast severity and Si applied at 0, 500 and 1000 kg ha⁻¹ to resistant, partially resistant and susceptible rice cultivars. Vertical bars represent FLSD values ($P \leq 0.05$).

to the non-amended blast resistant cultivar OL-5. However, the addition of 1000 kg of Si ha reduced the incidence of neck blast on O1 as effectively as partially resistant L2 without Si. Rough rice yields of O1 amended with 500 and 1000 kg ha⁻¹ Si did not differ from either the non-amended OL-5 or L2. When the rate of Si was increased from 0 to 1000 kg ha⁻¹, yields increased by 20% for both OL5 and L2.

10.3.2. Silicon enhancement of sheath blight resistance

Rodrigues et al. (1998) studied the effects of Si on differing levels of resistance to sheath blight of rice. The rice cultivars used were Jasmine and LSBR-5 (high level of partial resistance), Drew and Kaybonnet (moderately susceptible), and Lemont and Labelle (susceptible). Silicon significantly reduced AUDPC for lesion development and final disease severity for sheath blight on all the rice cultivars (Figure 10.4). As expected, sheath blight development generally was lower on Jasmine and LSBR-5 compared to either the moderately susceptible or susceptible cultivars. Differences were greater when these cultivars with high partial resistance were grown in Si-amended soil. The moderately susceptible cultivars, Drew and Kaybonnet, when grown in soil amended with silicon, had AUDPC (310.4 and 230.6, respectively) and final disease severity (2.6 and 2.8) values that were not significantly different from resistant Jasmine and LSBR-5 (AUDPC=345.8 and 348.9; final disease severity = 2.9 and 3.2) grown in non-amended soil.

10.4. CONCLUSION

Silicon fertilization of rice, especially where natural soil levels of Si are deemed less than optimum, offers promising results with respect to disease control and improved yields.

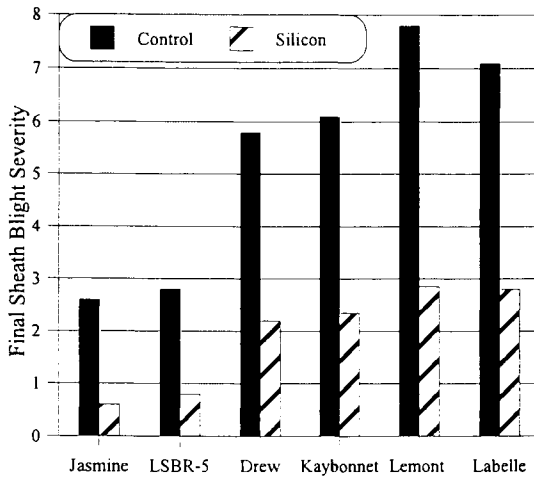


Figure 10.4. The effect of silicon and cultivar resistance on final sheath blight severity.

Silicon has the potential to control several economically important diseases threatening one crop, whereas some fungicides do not have as broad a spectrum of activity. Silicon can control diseases such as blast to the same general degree as a fungicide and reduce the amount and frequency of fungicides needed, reducing costs, and providing positive environmental benefits. Silicon sources have residual activity that persists over time, raising the possibility that applications are not necessary on an annual basis. Silicon reduces susceptibility in rice to many fungal diseases. Cultivars that have lost resistance to a disease such as blast and have good to excellent agronomic traits might again be useful commercially simply by using Si fertilization or amendments. In addition, cultivars that have high levels of genetic resistance to blast or other diseases might still show yield increases due to Si effect on agronomic traits. Therefore, Si sources and their management practices should be developed and practiced in Integrated Disease Management programs.

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Chapter 11

Methods for silicon analysis in plants, soils, and fertilizers

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The classical method for determining total silicon (Si) content of various materials has been conversion of insoluble silicates into sodium silicate through high temperature fusion with sodium hydroxide, or other sodic bases. The Si can then be determined by a variety of methods, including gravimetric, colorimetric, and absorption/emission spectrometry. Silicon also has been determined gravimetrically in plant tissue as the residue after acid digestion. We have developed a simple, inexpensive, and rapid method for solubilizing Si in plant tissue that facilitates analysis of a large number of samples. When analyzing soils and fertilizers, a method for gauging the plant-available Si, rather than total Si, generally is desired. A number of soil-test methods have been developed. Some require extended incubation periods, field-moist soil, or other procedures that inhibit adoption by routine soil-testing laboratories. Silicon extracted by acetic acid has been correlated to Si uptake by rice (*Oryza sativa* L.) and rice grain yield. Using this method, the Everglades Soil Testing Laboratory analyses nearly five thousand samples annually. Since Si fertilizer sources differ in Si content and Si solubility, analytical methods have been developed for predicting their relative ability to provide plant-available Si. We use a column leaching method based on Si elution in Tris buffer (pH 7) for the evaluation of potential Si soil amendments. However, greenhouse and field evaluations are essential for making final determinations.

11.1. INTRODUCTION

Although the compound SiO_2 was isolated from various plant tissues in the late 18th century, the pure element Si was first isolated by Berzelius in 1823. He obtained it by combining potassium fluorosilicate with potassium (Urry, 1983), i.e., $\text{K}_2\text{SiF}_6 + 4\text{K}_{\text{metal}} = 6\text{KF} + \text{Si}_{\text{metal}}$. Many procedures for determining the Si content of a wide variety of materials have been developed since that time. Nevertheless, although there are a few compendia of methods for examining mineral silicates, i.e., Jackson et al. (1986), there are virtually none that also review methods for chemically and physically analyzing plant materials for Si, and for determining total as well as plant-available Si in soils and fertilizers. An attempt is made to provide such comprehensive information on Si analysis in this paper. However, procedures are not presented in detail when they can be referenced in English-language journal publications that are widely available.

11.2. TOTAL ANALYSIS

11.2.1. Gravimetric methods.

The earliest procedures used to analyze various materials for Si were based on gravimetric methods utilizing chemistry that produced either losses or increases in weight. Typical weight loss methods utilize HF to evolve Si as SiF_4 gas. Robinson (1945) used this principle to analyze for Si in soils, after first bringing Si into solution by fusion. For determining Si in an organic matrix, such as plant tissue, the organic matter can be removed by oxidation at 550 C. After solubilizing non-Si elements in 6M HCl, the sample is filtered through ashless paper that retains the Si precipitate. The paper is ignited and weighed. Then HF is used to evolve the Si, so that the weight loss is assumed to be Si.

Yoshida et al. (1976) determined Si gravimetrically in rice straw in conjunction with the analysis of other elements. After chemical oxidation of the organic matter and acid dissolution of all remaining components of the straw except for Si, the remaining residue was assumed to be SiO_2 (termed "crude silica"), which was removed by filtration. The dried precipitate was transferred to a weighing vessel, and the increase in weight was assumed to be SiO_2 .

Although requiring only relatively common and simple laboratory equipment, the gravimetric methods for determining Si in plant tissue, nevertheless, are time consuming and laborious, especially if only an analysis for Si is required. Elliott et al. (1988) described a "rapid" gravimetric procedure for the determination of Si in plant tissue that reduced analysis time and handling of individual samples through the use of fritted glass Gooche crucibles. The plant material is destroyed by heat and chemical additions, and the SiO_2 residue is weighed directly in the crucible as the increase in weight over the crucible alone.

11.2.2. Spectrometric methods

The development of modern spectrographic techniques has led to the general replacement of gravimetric methods in favor of more rapid techniques that are suitable for handling large numbers of samples. Solubilization of Si-containing materials is a prerequisite for using most of these methods.

11.2.2.1. Silicon solubilization for spectrometric analysis

Silicon, in a wide variety of substances, can be solubilized by fusion with such strongly-alkaline chemicals as Na_2CO_3 , NaOH, LiBO_2 , or LiB_4O_7 . Sodium hydroxide is a good choice because sample decomposition is relatively rapid and can be performed in inexpensive Ni crucibles at relatively low temperatures (Kilmer, 1965). After cooling, the flux is dissolved in acid, and Si in the resulting solution can be determined by a variety of spectrometric procedures.

Silicon, in a wide variety of substances, can also be solubilized by closed system digestion (CSD) techniques that require less attention to individual samples than fusion methods, and therefore, are well-suited to the processing of large numbers of samples. For a typical CSD dissolution technique, the sample is digested with aqua regia (HNO_3/HCl) in a sealed TFE-fluorocarbon-lined digestion vessel (sometimes termed a "digestion bomb") that is heated in an ordinary drying oven at 100 to 110 C for two hours (Jones and Dreher, 1996). After cooling, H_3BO_3 is added and the sample is reheated below the boiling point for 10 to 15 min. to aid in the dissolution of any resulting precipitate.

Elliott and Snyder (1991) developed an autoclave induced digestion (AID) procedure for solubilizing Si in rice straw, which only requires NaOH and H_2O_2 as reagents, unsealed

polyethylene tubes, and an autoclave as specialized equipment. The AID procedure is well adapted to handling batches of 40 or more samples at a time. The procedure uses the autoclave to develop pressure, rather than developing pressure in sealed digestion vessels. Bell and Simmons (1997) found no significant difference between Si analyses of a National Institutes Standards Technology (NIST) pine needle standard (no. 1575) by a variety of methods and that by the AID procedure. Recognizing the unavailability of NIST standards for Si, they used the AID procedure to determine Si in several other NIST plant sample standards as well.

Nonozamsky et al. (1984) also described a "rapid" technique for extracting Si from plant tissue. By their method, ground plant material was shaken overnight at room temperature in a solution of HCl and HF, and remaining plant debris was removed by filtration. Methods for preventing formation of less soluble fluorosilicates were discussed.

11.2.2.2. Spectrometric analysis of dissolved silicon

Although dissolved Si can be determined by atomic absorption spectrometry (AAS) using a nitrous oxide-acetylene flame (Eaton et al., 1995) or by inductively coupled atomic plasma spectrometry (ICP, ICAP) (Jones and Dreher, 1996), it is probably most often determined by either manual or automated colorimetry because of the lower cost of the instrumentation, and the lower detection limits.

Silicon is determined colorimetrically (light absorption spectrometry) either by the yellow silicomolybdic acid procedure or by the blue silicomolybdous acid procedure. The latter generally is preferred because of its greater sensitivity. The two methods are similar, except that the blue color is developed through the addition of a reducing solution. The sample containing dissolved Si is reacted with ammonium molybdate (Kilmer, 1965; Hallmark et al., 1982). Tartaric acid is added to minimize interference by P in the form of a phosphomolybdate complex. After reduction with a solution containing sodium sulfite, sodium bisulfite, and 1-amino-2-naphthol-4-sulfonic acid, the intensity of the blue color that develops is measured at 650 m μ . This method will detect as little as 0.02 mg Si L⁻¹ (Bunting, 1944). Both the yellow silicomolybdic acid method and the blue silicomolybdous acid procedure are presented in Standard Methods (Eaton et al., 1995) as method 4500-Si D and 4500-Si E, respectively. The latter can be conducted with automated colorimetry analytical instruments (Method 4500-Si F in Eaton et al., 1995), which is useful for large sample numbers.

11.2.2.3. Non-destructive spectrometric methods for determining total silicon

Several modern techniques have been used to determine the total Si content of soils, plants, and fertilizers without pre-analysis solubilization of the matrix. X-ray fluorescence spectroscopy (XRFS), which also is known as X-ray emission spectrography or X-ray spectrochemical analysis, assesses the presence and concentration of Si in soil and plant materials by measuring the characteristic secondary radiation emitted from a sample that has been excited with an x-ray source (Karathanasis and Hajek, 1996). Although certain limitations exist, excellent equipment has been developed in recent years, making it possible to rapidly analyze a great variety of samples.

Near infra-red spectroscopy (NIRS) also has been used to non-destructively determine Si in various materials. There is a sound chemistry basis for using this method for determining the content of water and nitrogen in samples, but for other elements and constituents the basis is less clear. Statistical associations between NIRS spectra of standard samples and unknowns can be constructed when a large data base exists for the matrix, but the correlations between

standards and the content of constituents in unknowns that have been analyzed by classical methods generally are lower than would be accepted in classical analytical chemistry. Nevertheless, because of the rapidity and simplicity of the analysis, and the relatively low cost of the equipment and improvements in the ease of operation, NIRS is becoming widely adapted for many analytical purposes, and such expansion in usage can be expected to continue. J. H. Meyer of the South African Sugar Experiment Station has been a leader in the use of both XRFs and NIRS for the analysis of Si in sugarcane leaves (Wood et al., 1985; Meyer, 1998).

11.3. CHEMICAL FORMS OF SILICON

11.3.1. Silicon in solution

Silicon can exist both as monosilicic acid and as polysilicic acid in soil solutions and soil extracts. The ammonium molybdate procedure reacts only with monosilicic acid, and therefore does not determine Si in the polysilicic acid form. Since plants are only able to absorb Si in the monosilicic acid form, it often is preferable that only this specie be measured in soil solutions and extracts. Atomic absorption spectropy and ICAP measure total Si, including monosilicic acid, polysilicic acid, and soluble organosilicon compounds. Alternatively, polysilicic acid polymers can be broken up with ultrasonification, or over time (weeks) with NaOH, and then can be determined colorimetrically. Monosilicic acid may be present both as orthosilicic acid and as metasilicic acid, but the former probably dominates in aqueous solutions. Metasilicate is more prevalent in crystalline minerals, such as wollastonite (calcium metasilicate). It should be possible to use IR spectrometry to differentiate between the two Si forms, since metasilicic acid has an oxygen-silicon double bond, whereas with orthosilicic acid all oxygens have a single bond to Si.

11.3.2. Silicon in organic compounds

Inanaga et al. (1995) provided evidence that Si in rice can exist in association with organic compounds. After suitable preparation, plant tissue was extracted with dimethylsulfoxide, and lignin-carbohydrate complexes that were analyzed for Si were precipitated with ethanol.

Organosilicon compounds can be isolated from soil solutions and extracts by selective adsorption on activated charcoal, which does not adsorb mono and polysilicic acids (Panov et al., 1989). The adsorbed organosilicon compounds then can be isolated by filtration, and the Si released by treating with NaOH and ultrasonification (Matychenkov and Snyder, 1996). ²⁹Si nuclear magnetic resonance (NMR) spectroscopy has been used to examine the structure of organosilicate coordination complexes (Kinrade et al., 1999).

11.4. PHYSICAL FORMS OF SILICON

A number of researchers have been interested in elucidating the physical forms of Si, particularly in plant tissue epidermal cells and in cell walls, but also in soils. Analysis of phytoliths, which are microscopic mineral particles, often containing Si, that are deposited within and around the cells of certain plants (Rovner, 1983), has been used to study paleosols, paleovegetation, for paleoenvironmental reconstruction, and for archaeological interpretation.

Analysis of the physical form of Si-containing phytoliths (silicophytoliths, opal phytoliths) can be used for plant identification (Ollendorf et al., 1988). A variety of silicon depositional patterns have been observed in plants, which are closely related to certain epidermal structures (Lanning and Eleuterius, 1987).

The petrological microscope has been used to examine silicified cells (Parry and Smithson, 1958; Lanning et al., 1980). Microscopic examination is made easier by partially or totally destroying the plant tissue, either with heat or chemically (Jones and Milne, 1963), or by a combination of both. The scanning electron microscope (SEM) also is used to observe Si deposits in plants after ashing tissue by heat, or chemically. Backscattered SEM images of silica bodies in leaf epidermal cells have been obtained after sonicating tissue in hexane-chloroform to remove epicuticular wax and sputter coating with gold (Whang et al., 1998). Bright dot maps of the distribution of Si in plant tissue can be obtained by combining SEM with energy-dispersive X-ray (EDX) analysis (Lanning and Eleuterius, 1987; Terrell and Wergin, 1981). Combinations of light microscopy of thin sections and SEM/EDX have been used to locate Si deposits in various ultrastructures of plants (Hodson and Parry, 1982).

Other physical analyses that have been conducted to study Si in plants include differential thermal analysis, specific gravity, refractive index, and measurement of surface area (Jones and Milne, 1963).

11.5. ASSESSMENT OF PLANT-AVAILABLE SILICON IN SOILS

Sufficient reports of improved crop yields and other benefits to Si applications have been documented in the scientific literature to suggest that Si fertilization should be considered for commercial production of rice, sugarcane (*Saccharum* sp.), and perhaps other crops. However, because of the expenses associated with Si fertilization, soil tests are needed to identify soils containing insufficient plant-available Si for optimum production. A number of Si soil tests have been investigated, with varying degrees of reliability, practicality, and commercial acceptance.

Khalid and Silva (1978) used a modified Neubauer (Stewart, 1932) biological extraction procedure to gauge the Si-supplying capacity of soils. One hundred rice seedlings were grown in 50 g of soil for 10 weeks, and Si was determined in the top growth plant tissue. Obviously, this procedure is not suitable for routine soil testing because of, among other things, the time required to complete the analysis.

Almost all soil test methods that have gained acceptance for routine use by laboratories that service commercial growers utilize an extracting solution to remove the nutrients of interest from the soil in some proportion that can be correlated with plant uptake and/or crop yield. After evaluating a variety of chemicals as extractants for Si, Imaizumi and Yoshida (1958) proposed the use of a M sodium acetate buffer (pH 4.0) for gauging plant-available Si in soils. The paper, which was written in Japanese and published in bulletin form, has been widely cited, but the details of the method are almost never given and, therefore, will be presented here. The buffer is made by diluting 49.2 ml acetic acid and 14.8 g anhydrous sodium acetate to 1 liter, and adjusting to pH 4.0 with acetic acid or sodium acetate (K. Nonaka, personal communication). Ten g of air-dried soil are placed in a 200 ml flask with 100 ml of the sodium acetate buffer. The flask is placed in a water bath for 5 hours at 40 C and shaken "occasionally". After filtering, Si in the filtrate is determined by the silicomolybdate blue

method, sometimes with modifications, has been used in Japan, Taiwan, and Korea (Lian, 1976), in China (Liang et al., 1994), India (Nayer et al., 1977), Malaysia and Thailand (Kawaguchi, 1966), and in Sri Lanka (Takijima et al., 1970). No doubt, it has been used in other countries as well, especially in conjunction with rice production. Nevertheless, in several reports (Takahashi, 1981; Takahashi and Nonaka, 1986; Nonaka and Takahashi, 1990), it was concluded that for soils previously fertilized with calcium silicate, the acetate buffer method is "too strong", i.e., it dissolves some nonavailable Si from the residual calcium silicate fertilizer. To overcome this problem, Nonaka and Takahashi (1988, 1990) developed a method for measuring water-soluble Si in rice soil that involves flooded soil incubation. By this method, a 10 g dry soil sample (air-dried and < 2 mm) is submerged in a 100 ml cylindrical bottle (about 4.5 cm i.d.) with 60 ml water and incubated at 40 °C for a week, after which time the supernatant is analyzed for Si content. However, the researchers considered the 2-week period between sampling and reporting of results to be a serious disadvantage for commercial use.

Sumida (1992) developed two additional incubation methods. One requires 4 weeks of incubation at 30 °C, and the other requires an unstated period of incubation of soil in a series of Si solutions of varying concentration. Because of the time requirement and complexity of these methods, neither appear suitable for use in a routine soil testing laboratory.

A number of extractants other than acetate buffer have been used in procedures that are suitable for routine soil testing. Hesse (1971) reported that H. F. Birch in East Africa found that soil fertility, as shown by yield, was significantly related to the water-soluble Si content of soils, and suggested that determinations of water-soluble Si would be very valuable in soil fertility investigations. However, no specific procedure for a Si soil test utilizing a water extract was given, which is unfortunate because Hesse also reported that J. A. McKeague found that the concentration of Si in water extracts varied with the contact time, pH, and temperature. Khalid et al. (1978) used a water extract (3 g soil, 30 ml water, 4 hours shaking) and a phosphate extract to gauge plant-available Si. For the latter test, 3 g soil was shaken for 4 hours with 30 ml 0.1 M acetic acid containing 50 mg P L⁻¹ as Ca(H₂PO₄)₂ and adjusted to pH 3.5 with NH₄OH. It was assumed that the water extract measured the "intensity factor", and the phosphate buffer measured the "capacity factor". Multiple extractions were employed with the latter extract.

Naoto Kato (National Institute Agro-Environmental Sci., Tsukuba, Japan, 1999, personal communication) also has proposed a phosphate buffer method for measuring plant-available Si in which 5 g soil is shaken for 24 hours at 40 °C with 50 ml of 0.04 M phosphate buffer (pH 6.2) solution (made by titrating 0.04M Na₂HPO₄ with 0.04 M NaH₂PO₄ to pH 6.2). After centrifugation and filtration, the Si concentration in the supernatant is measured colorimetrically. Kato reports that his proposed method is better for evaluating the Si availability to rice in paddy soils than the traditional acetate buffer method because the proposed method does not overestimate Si availability in soils that have been fertilized with Si. Apparently the buffer does not excessively solubilize residual calcium silicate, but the PO₄³⁻ displaces adsorbed SiO₃²⁻.

Haysom and Chapman proposed the use of 0.01 M CaCl₂ for extracting plant-available Si from soils. Two g soil is shaken for 16 hours with 20 ml extractant in a 50 ml Nalgene tube using an end-over-end shaker. After centrifuging at 2000 rpm for 10 minutes, the supernatant is analyzed for Si. Values of 10 mg Si 100 g⁻¹ soil or less are considered to have insufficient Si for maximum sugarcane production. They also evaluated 0.5 M NH₄OAc and 0.005 M H₂SO₄.

as extractants for Si. These reagents were well correlated with cane yield, but Si extracted with CaCl_2 had the best correlation ($r=0.903$).

Citric acid has been used by Acquaye and Tinsley (1964) as an extractant for Si. One g soil was shaken with 50 ml extractant for 2 hours. After standing overnight, the sample was shaken for another hour, and Si determined in the supernatant.

It has been proposed that Si availability in soils can be determined on the basis of examining the ratio of Si to Al in acetic acid-ammonium acetate buffer solutions, or in 0.2 M HCl extracts, with additional consideration of Si/Fe and $\text{Al}/(\text{Si}+\text{Al}+\text{Fe})$ ratios, but not solely by the amount of Si extracted (Kawaguchi and Matsuo, 1958; Kawaguchi et al., 1958). However, this method does not appear to have gained much acceptance.

The University of Florida Everglades Research and Education Center, Belle Glade, provides a Si soil test for farmers growing rice on organic and sand soils in South Florida. Although developed and calibrated for rice, sugarcane growers also use the analysis. In this test, 25 ml 0.5 M acetic acid is added to 10 ml soil in a 75 ml test tube. After standing overnight, the mixture is tumbled for 2 hours on an end-over-end shaker. Following filtration, the filtrate is analyzed for Si colorimetrically, and expressed as mg Si L^{-1} soil. In a recent (presently unpublished) paper, Korndorfer and Snyder established Si soil test ranges of low ($< 7 \text{ mg Si}$), medium ($7 - 24 \text{ mg}$) and high (> 24). Nearly 6,000 soil samples were analyzed in 1999 by the soil test laboratory to determine the need for Si fertilization on rice and sugarcane, and requests for this analysis have grown nearly exponentially since 1994.

The fact that many extracts have been used for determining plant-available Si suggests that no one extract has been found that works equally well on all soils. Research is warranted when using any of the established extracts in a new soil area for which correlations with plant response have not been conducted. Furthermore, since air drying soil reduces the content of monosilicic acid, the plant-available Si form, because of adsorption to mineral surfaces, polymerization, and dehydration (Matychenkov and Snyder, 1996), that common precursor to soil analysis deserves examination.

11.6. ASSESSMENT OF PLANT-AVAILABLE SILICON IN FERTILIZERS

Although plant residues can be used for Si fertilization, most Si fertilization, both experimentally and commercially, is done with mineral Si sources, and most of these are calcium silicates. The calcium silicates range from fairly pure, naturally-occurring minerals, such as wollastonite, to industrial by-products from steel making or from the electric furnace production of phosphorus. Products from both processes commonly are termed "slag", although the term has been applied to a variety of materials and therefore, provides little information about the chemistry and physical properties of the material other than that it is inorganic.

The earliest wide-spread commercial fertilization of a crop, rice, with Si occurred in Japan. In that country, Si extraction with 0.5 M HCl at 30 C for 1 hour is the "official" method of gauging Si availability in slags (NIAES, 1987). However, many researchers in Japan have expressed the opinion that this method is of little value for predicting Si uptake by rice (K. Nonaka, H. Sumida, and N. Kato, personal communication), and several research reports support this contention (Takahashi, 1981; Kato and Owa, 1997). The pH 4.0 acetate buffer method of Imaizumi and Yoshida (1958) also has been proposed for gauging Si availability in slags (NIAES, 1987), even though, as has been previously stated, the method has been found

unsuitable for evaluating plant-available Si in soils that have been fertilized with calcium silicate slags, and Kato and Owa (1997) demonstrated that this method is poor.

Simple water extraction of Si in slags also has been used for estimating plant-availability. However, Kato and Owa (1997), after investigating the dissolution process of slags in flooded rice soils, modified the water extraction method to account for their findings. They pointed out that flooded rice soils generally are in the pH range of 6 - 7, and dissolved Ca is adsorbed by the rice. In the laboratory, dissolution of calcium silicate in water increases both pH and Ca concentration of the solution phase, both of which repress further calcium silicate dissolution. Therefore, these researchers developed a procedure using a weakly acidic cation exchange H-resin in the water to both moderate pH and adsorb Ca. Their procedure also is designed to prevent polymerized Si from forming. To do this, they keep the concentration of monosilicic acid below 100 mg Si L⁻¹ by selecting an appropriate ratio of slag to water. Specifically, by their procedure, 0.2 g slag and 0.5 g of weakly acidic cation exchange resin (Amberlite IRC-50) in the H form are put into a 500 ml plastic bottle. After adding 400 ml distilled water, the bottle is immediately shaken for a while by hand and then by a reciprocal shaker (100 rpm) at 25 C for 96 hours. After filtration, the Si concentration in the solution is measured colorimetrically.

The author (Snyder), C. L. Elliott, and their colleagues utilized the dissolution principles elucidated by Kato and Owa (1997) in developing a "column" technique to rank mineral Si sources for plant availability. This method maintains neutral solution pH and low Ca concentration in the vicinity of the Si source, and sufficiently low dissolved Si concentration to minimize polymerization. Three g of Si source are mixed with 5.0 g medium density polyethylene and placed in a 20 ml plastic syringe. Glass wool above and below the mix is used to retain the mixture in the center of the syringe. A stopper fitted with a glass tube is inserted in place of the syringe plunger. A peristaltic pump is used to pass 0.1 M TRIS buffer (pH 7) upward through the syringe (the "column") at the rate of 1 ml min⁻¹. The total quantity of water passed through the column in each of 2 successive 24 h periods is analyzed for Si. The data are presented as Si dissolved g⁻¹ Si source in each 24 hour period. A similar analysis of finely ground wollastinite is included with each analysis of candidate Si sources to serve as a reference.

We use laboratory analysis to identify promising mineral Si sources, and to reject those that appear unsuitable. However, greenhouse and field studies ultimately are required to provide absolute confidence about the Si supplying ability of the sources. For the greenhouse studies, rice is grown in pots containing a low-Si organic soil amended with various rates of candidate Si sources, including a wollastinite standard material and/or a calcium silicate slag that has been used commercially for about 10 years in south Florida. The rice is grown to maturity. The grain is harvested, but the most reliable criteria of Si availability is considered to be the concentration of Si in the "straw", which in this case is all of the top growth other than the grain. In field trials utilizing rice, both grain yield and the Si concentration of true straw, i.e., that cut by a combine, are used to evaluate the Si-supplying ability of the Si sources.

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Chapter 12

Silicon sources for agriculture

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Characteristics of an acceptable silicon (Si) source are: a high content of soluble-Si, physical properties conducive to mechanized application, ready availability, and low cost. Since Si is the second most abundant element in the earth's crust, finding sources of Si is easy. But, Si is always combined with other elements and most sources are insoluble. Responses of crops to soluble-Si applications in sands (largely SiO_2) provide an example of the insolubility of one source. Slags, by-products from the processing of iron and alloy industries, have been utilized quite extensively. Their concentrations and solubility of Si and their contents of other elements vary widely. For a given source, solubility is indirectly related to particle size. A few sources are soluble, but too costly for general use. Potassium silicate is used in nutriculture for disease control in some high value crops. Sodium silicate and silica gel have also been used to supply Si in research and high value crops. Calcium silicates have emerged as the most important sources for soil applications. Of those, calcium *meta*-silicate (wollastonite, CaSiO_3) has been the most effective source in many locations with low concentrations of soluble-Si in soils. Such a material, supplied as a slag by-product from the high temperature electric furnace production of elemental P, is applied extensively to Everglades mucks and associated sands planted to sugarcane and rice. Thermo-phosphate, a commercial fertilizer used in Brazil to supply P, Ca, and Mg, also supplies soluble-Si due to high temperature manufacturing process effects on its magnesium silicate ingredient.

12.1. SILICON IN NATURE

Silicon, atomic number 14, molecular weight 28.0855, has 4 outer valence electrons and oxidation states of +2, +4, and -4. Its melting point is 1410°C and boiling point is 2355°C . It is not attacked by acids, except for hydrofluoric acid. In the periodic chart, Si is surrounded by near neighbors B, C, N, O, P, and S (sulfur). It is interesting to note all those neighbors are recognized as 'essential elements' while Si is recognized to only be 'beneficial' for some plant species, because the criteria for proof as an essential element have not been met. Silicon is present in the sun, in stars, and in meteorites. Oxygen is the most prevalent element in the earth's crust and Si is the second most prevalent, comprising 25.7% by weight. It is not found free in nature, but is always combined, predominantly as oxides or silicates. Single crystals can be prepared for solid-state and semi-conductor devices. Silicon compounds are used in many applications useful to man, including polymeric products (silicones) and glass.

Hopefully, their usefulness in agriculture will be enhanced by this conference and proceedings.

12.2. CHARACTERISTICS NEEDED IN SOURCES FOR AGRICULTURE

Many sources have been evaluated for use in agriculture. A recent review of Si sources for rice production has been published (Savant et al., 1997). Certain characteristics can be listed for a Si source for agriculture. Every source will fall short of ideal in some characteristics. The goal is to find the best source for a given situation and location.

12.2.1. Solubility

The purpose of application of a Si source is to provide soluble Si to plants; therefore a good source must have much of its Si readily soluble in the soil solution. This characteristic is likely both the most important and the one most difficult to fulfill. A low solubility material is easily dismissed as a potential source. Because Si is always combined with other elements and most natural sources are insoluble, finding a soluble source that also has other good characteristics is not easy. Responses of crops to soluble-Si applications in sands (largely SiO₂) provide an example of the insolubility of one source that comprises much of the crust of the earth. The total number of Si-bearing materials is great, but the list of sources with soluble Si is very short.

12.2.2. Availability

A candidate source must be obtainable within a reasonable distance from the point of application in order to avoid costs that are greater than potential benefits. At the present time agriculture has very limited choices in soluble Si sources.

12.2.3. Physical properties

Materials must be in a suitable condition for uniform broadcast application with lime and/or fertilizer spreaders. In most cases byproduct materials will have to be ground and screened to acceptable particle sizes. Extractable Si increases as particle size decreases, but the difficulty of uniformly and accurately spreading a material increases with fineness of the material. In order to obtain rapid dissolution, most sources are finely ground. No literature was found to guide the manufacturer in a proper particle size distribution that will provide some rapid release of Si and also provide for residual Si solution. Research and development of best physical properties, such as has been done for limestone and silicate laws similar to those for sale of limestone, could be of benefit in the application technology for silicates.

12.2.4. Contaminants

Some sources have levels of heavy metals, associated with their origin or processing. The high rates needed to supply adequate silicon may result in heavy metal concentrations greater than allowed and believed safe. In some instances, soils could become useless for agriculture due to binding of metals in the soil with little hope of removal by any economically feasible method. Alternatively, some sources contain essential nutrients that enhance their value, if they are needed. Notably, a major problem with the electric furnace calcium silicate slag byproduct from elemental P production has been its contamination with radon. That contamination is always related to the location of the rock phosphate raw material.

12.2.5. Economics

In the final analysis, the cost:benefit ratio of a source will determine its usage. Once the potential for profit from Si application is determined, farmers will look for the source supplying soluble Si at the least cost. However, consideration of all of the above mentioned characteristics should be included in selection.

12.3. SOURCES

Plant residues are used as Si sources both intentionally and incidentally. Obviously, Si application is not a prominent idea in most agriculturist's minds as they incorporate residues. Some residues, notably rice (*Oryza sativa*, L.) hulls and sugarcane (*Saccharum* spp.) bagasse have considerable Si concentrations. Their applications at high rates supply Si, but the demand for Si fertilization exceeds that which can be supplied by crop residues.

Most of the planned Si application is with byproducts. High processing temperatures often release Si from tightly bound states and as a result the solubility increases. It is apparent from the results obtained in comparisons that the manufacturing process of the product makes considerable difference in Si solubility and therefore, the value of the byproduct.

Calcium silicate slag (mostly CaSiO_3) is a byproduct of the production of elemental P by reduction of phosphate rock with coke in electric arc furnaces. A major problem in the early development is related to the radon activity of some calcium silicate slags. That content is dependent on the location of the phosphate rock mines. The first research applications in Hawaii (Table 12.1) and Florida (Table 12.2) utilized slag from a Tennessee Valley Authority (TVA) plant at Muscle Shoals, AL (Ayres, 1966; Gascho and Andreis, 1974; Gascho and Freeman, 1970). The value of the applications to Hawaiian and Everglades sugarcane fields was established in the studies, but distance from the byproduct was an economic consideration for Hawaii. The TVA soon thereafter suspended any shipment from their source due to a perceived radon problem in home construction where the slag was utilized as a building material. Therefore, the material was also unavailable in Florida. The Hawaiian Cement Company investigated several possibilities as a replacement for TVA slag and developed a calcium silicate source by mixing cement with coral sand (Table 12.3; Clements et al., 1968). Later HSPA (1982) developed mini-granulated calcium silicate by binding fine (100-200 mesh particles) with 2 % sodium oxide. The effectiveness of the mini-granulated source has been confirmed by Medina-Gonzales et al., (1988) and the mini-granulation improved handling and application uniformity of fine materials (Jakeway, 1983). Because of the added cost of granulation, it is not likely that the mini-granulated material will have a significant impact on the Si market for agriculture.

Following further research demonstrating the value of the calcium silicate slag for rice production in the Everglades (Snyder et al., 1986) and finding a source with lower radon activities, the calcium silicate slag business has flourished in the Everglades Agricultural Area. The main source now used in Florida is processed in Tennessee and used as a Si source for rice and sugarcane in the high organic mucks of the Everglades and in some associated sands in south Florida. In addition to its Si content (211 g kg^{-1}), it contains about 5, 330, 3, 90, and 2 g kg^{-1} P, Ca, Mg, Al, and Mn, respectively (Snyder et al., 1986). Presently, about 100 thousand MG ha^{-1} are applied each year. Due the size and the potential of the market, several companies are interested in developing markets for agriculture. As new calcium silicate

sources are developed, their content of heavy metals must be evaluated in addition to evaluations of their abilities to supply Si and their radon activities.

Even though calcium silicate slag will likely dominate the market in south Florida, it may not be the Si source of choice everywhere due to logistics, economics and the availability of other sources. Portland cement and cement kiln dust (9 to 23 % Si) have been used effectively (Elawad et al., 1982; Queensland Bureau of Sugar Expt. Stns. 1978), but the economics generally precluded any widespread usage. Likewise, sodium silicate (water glass) is effective for both soil applications (Elawad et al., 1982) and as foliar sprays (McAvoy and Bible, 1996), but it is uneconomical for the rates needed for soil application. Potassium silicates are used in nutrient solutions for tomatoes and cucumbers for control of *Pythium* diseases (Adiatia and Besford, 1986). They are too expensive for soil applications at rates suitable for supplying 'Si nutrition'. Wollastonite or pseudowollastonite (calcium *meta*-silicate, CaSiO_3) contains approximately 330 mg Ca kg^{-1} , the material has produced good results in research, but widespread application is not a possibility due to economics. Slags that are byproducts of the iron and alloy industries have been used for producing rice in Japan. There are many kinds of such by-product slags including blast furnace slags, silico-manganese slags, ferronickel slags, stainless steel slags, manganese slags, and converter slags. The annual consumption of silicon fertilizer supplied as slags for rice in Japan has been as great as 325,000 tons/year (Naoto, K., personal communication). The main slag used in Japan has been blast furnace slag followed by the silico-manganese slag. Slags are variable in composition, but generally have high concentrations of total Si. In most, only a small proportion of the total Si is easily solubilized. Therefore, high rates of application may be required, eliminating application at points distant from the steel mill and increasing the total costs of application. Basic slags often contain significant quantities of Fe and Zn and those must be considered in terms of needs and potential toxicity and environmental problems.

Magnesium silicate (magnesium *meta*-silicate, MgSiO_3) contains approximately 240 g kg^{-1} , though its solubility is low. Other products that have been researched, but generally eliminated as important sources, include di-calcium ortho-silicate (Medina-Gonzales et al., 1988), mini-granulated calcium meta-silicate, mill furnace ashes, and volcanic cinders.

Recently, Japanese rice farmers have employed the use of a calcium silicate hydrate, a waste byproduct of the building industry having Si solubility greater than slags from the iron and alloy mills. Also, silica gel is being tested and used in some nursery beds in Japan (Naoto, K., personal communication).

Thermo-phosphate is manufactured and sold in central Brazil for phosphorus fertilization. It is made from a mixture of rock phosphate and magnesium silicate during the elimination of fluorine by heat. In this process, rock phosphate is enriched with magnesium silicate, melted in an electric furnace, and then submitted to thermal shock by spraying with water. After evaporation of the water, the material is ground. Although its total Si content is relatively low in comparison to basic- and calcium silicate-slugs, the proportion soluble is high. That fact, and its concentration of 80 g P kg^{-1} , 200 g Ca kg^{-1} , and 90 g Mg kg^{-1} may make it an attractive and relatively available source for purchase in Brazil or other locales where the fertilizer material is produced and sold.

12.4. COMPARISONS OF SOURCES

Early considerations of the sources of Si were made in Hawaii at the Hawaiian Sugar Planters' Association (HSPA) and the Hawaii Agricultural Experiment Station. Their first efforts were made to improve growth and yield of sugarcane on low pH aluminous humic ferruginous Latosols (Ayres, 1966). Field studies led to the suspicion that Si was involved in otherwise unexplainable responses to various slag materials when no Si was present in the irrigation water. In pot tests, Ayres (1966) found that TVA electric furnace slag, blast furnace slag, and purified calcium *meta*-silicate all increased dry weight of cane and Si uptake (Table 12.1). Since all plots were fertilized adequately with calcium, Ayres concluded from the experiment that Si was the constituent of the materials that was the effective growth stimulant. The blast furnace slag, as well as, the electric furnace slag obviously supplied soluble Si. In other experiments (see below), slags other than electric furnace have not always provided soluble Si. There is a wide variance in the solubility of slags and each should be evaluated for soluble Si prior to any determination of its value as an amendment for supplying Si.

Table 12.1

Effect of siliceous materials on yield of sugarcane and mineral element uptake in pots of two aluminous humic ferruginous Latosols.*

SiO ₂ (g)	Waialua Agricultural Co., Manana Family**		Grove Farm Co., Haiku Family†	
	Dry Weight (g)	Si Uptake (mg)	Dry Weight (g)	Si Uptake (mg)
Control				
0	530	100	485	40
Electric furnace slag				
6	685	470	675	230
12	635	520	800	740
18	790	855	875	940
Blast furnace slag				
6	685	310	760	275
12	620	360	850	695
18	670	540	930	1110
Purified CaSiO ₃				
6	660	360	545	270
12	725	795	540	460

*From Ayres (1966)

**Values for control are means of 6 replicates; for treatments, 2 replicates.

† Values are means for 3 replicates, except at maximum slag rates where means are of 2 replicates.

Upon reports of improved growth of sugarcane in Hawaii using slags, Bair (1966) began analysis of leaf Si in sugarcane, field corn, and St. Augustine grass in Florida. Because of the low concentrations found in the samples, a comparison of sources was made (Table 12.2). Fuller's earth provided the highest concentration of total Si, but similar to assorted limes, colloidal phosphate, and rock phosphate: essentially none of the total Si was soluble in 0.5 N ammonium acetate (pH 4.8). Open hearth slags provided significant concentrations of soluble Si, but less than one-half of the concentration of soluble Si in electric furnace (TVA) slag.

Meanwhile in Hawaii, a search was made for Si sources that could be obtained locally, eliminating the high cost of transportation of the materials from the mainland. Quantities of several calcium silicates were obtained by the Hawaiian Cement Company and evaluated against TVA slag and a product they proposed made from coral sand and cement (Clements, 1968). All of the calcium silicates provided soluble Si to sudan grass (Table 12.3) and most provided more Si than the TVA slag. The results suggest that CaSiO_3 is the most desirable form. Most of the subsequent application of Si in Hawaii has been with the Hawaiian silicate source.

Upon confirming the freckling leaf blade symptoms of inadequate Si in some sugarcane fields in the Everglades, research began to determine the potential for response and suitable sources for application (Gascho and Freeman, 1970). Calcitic and dolomitic limes were included in an initial pot study, as well as, TVA slag and two basic slags (Table 12.4). Dry weight of cane in the test increased in a linear fashion with increased leaf Si concentration ($R^2 = 0.95$). Calcite and dolomite provided no significant increase in either leaf Si concentration or cane weight above the values where nothing was applied. The two basic slags appeared to be approximately equal in their significant increases in both leaf Si concentration and cane dry weight, but TVA slag application resulted in leaf Si concentrations double of those determined for the other slags. It also increased soil pH approximately the same amount as

Table 12.2

Total and soluble silicon content of some soil amendments.*

Material	Local	Si	
		Total (%)	Soluble (%)**
Slag-electric furnace	Alabama	18.2	3.96
Slag-open hearth (ground)	Alabama	6.9	1.72
Slag-open hearth	Alabama	2	1.66
Hi-cal silicate limestone	Florida	0.2	0.016
Hi-cal silicate limestone	Florida	3.4	0.026
Dolomite	Florida	0.4	0.023
Dolomite	Florida	4.5	0.023
Rock phosphate	Florida	3.6	0.025
Colloidal phosphate	Florida	10.8	0.023
Fuller's earth	Georgia	35.1	0.023

*From Bair (1966)

** 0.5 N ammonium acetate, pH 4.8.

Table 12.3
Silica analysis of sudan grass (% SiO₂)*.

Mineral	Predominant chemical	MG ha ⁻¹				
		0	4.5	9	18	36
Wollastonite	CaSiO ₃	0.28	2.19	5.13	6.4
Rankinite	Ca ₃ Si ₂ O ₇	0.28	2.31	4.21	4.56	6.89
Larnite	Ca ₂ SiO ₄	0.28	3.16	2.94	5.75	6.06
Anorthite	CaAl ₂ Si ₂ O ₈	0.28	0.4	0.8	0.82
Gehlenite	Ca ₂ Al ₂ SiO ₇	0.28	1.38	2.32	2.6
TVA slag	CaSiO ₃ + Gehlenite	0.28	1.45	1.85	2.08	2.82
Hawaiian silicate	CaSiO ₃	0.28	2.49	3.42	3.28	4.25

*From Clements et al. (1968).

dolomite. Measurements of soluble Si in the soil 9 months following application indicated an increase in 0.5 N ammonium acetate (pH 4.8) extractable Si due to sources that agrees well with increases in leaf Si concentrations and cane weights. The study provided evidence of the importance of Si for some of Florida's sugarcane. Furthermore, TVA slag appeared to be effective and the best material available at that time.

Subsequently, economically important responses to TVA slag were determined in Florida fields with low concentrations of soluble Si in soils (Gascho and Andreis, 1974). Following the TVA decision to stop shipment of their slag due to the "radon scare", a new evaluation was made to determine if other sources of Si were effective and feasible for application to Florida's sugarcane. In a pot experiment, Elawad et al. (1985) found sodium silicate an effective source, but too expensive. In the field, Elawad et al. (1982) evaluated the effects of TVA slag, a Florida electric furnace slag and cement for plant and first ratoon sugarcane (Table 12.5). Both Florida slag and Portland cement were as effective in producing cane and sugar yields as TVA slag. Unfortunately, the Florida slag had radon activity as great as TVA slag and cement was difficult to spread due to fine particle size and it was also too expensive for agricultural application. Later, following additional research indicating great responses of rice yields due to TVA slag applications (Snyder et al., 1986) and further indications of responses in a rice-sugarcane rotation in the Everglades (Anderson et al., 1987; Alvarez et al., 1988), a calcium silicate source was found that provides soluble Si and has acceptably low levels of radon.

Solubility of a source can be determined in the laboratory to provide the first estimate of the potential value of a source. Estimates of solubilities of sources have been obtained in several studies. One potential measurement of the Si availability may be attained by extraction with a weak acid as done to evaluate P and K in fertilizers. The Fertimtsui Co. (Minas Gerais, Brazil) used 0.1 M citric acid extraction to evaluate solubility of Si sources. Calcium silicate slag (Tennessee source that is marketed in Florida) has 70 % of its total Si soluble in citric acid (Table 12.6; Gascho and Korndorfer, 1998). One basic slag produced in Brazil (basic slag 2) had a low concentration of total Si, but a high proportion was soluble. Application of high

amounts of such a slag would possibly provide adequate Si, but such application would not be economically feasible, unless the field was close to the origin of the slag. The other basic slag (slag 1) and magnesium silicates appeared to be worthless for supplying Si. Thermo-phosphate has a total Si concentration of 10.8 %, but nearly all appears to be soluble in the citric acid extractant. The data demonstrate the importance of analysis for both total and soluble Si and the importance of the high temperature processes involved in both the calcium silicate and thermo-phosphate sources for releasing Si from a bound state. Additionally, the data indicate the potential for a Brazilian manufactured fertilizer to provide Si along with P and Mg.

Snyder (1991) found that 0.5 M acetic acid was the superior extractant for evaluating the Si status of the soils of the Everglades. As for other elements, it is not likely that a universal Si extractant will be recognized to be superior for all soils and conditions. Another more involved measurement is to determine the release of Si to an extractant following incubation of a soil-source mixture. Medina-Gonzales et al. (1988) devised such a test to evaluate two sources and two particle sizes of sources that were available in Hawaii. Following 60 d incubation in plastic bags with soil near field capacity, they evaluated Si release by extraction with water and 0.5 M ammonium acetate, by water displacement from a the saturated soil, and by Si uptake by sugarcane roots. They found that Si was more available from Wollastonite (CaSiO_3) than from Ca_2SiO_4 and a fine particle size generally enhanced the release of Si, for both sources. Datnoff et al. (1992) also found that finely divided ($100\% < 0.15\text{mm}$) calcium silicate slag was more effective in suppressing blast and brown spot diseases of rice than a standard grade ($90\% < 2.36\text{ mm}$) which was more effective than pellets of calcium silicate ($100\% > 1\text{mm}$ and $< 3.35\text{mm}$). Emphasis in selection of materials has been placed on fine particle size for quickly supplying Si. No studies were found that determined the potential of providing a longer-term release of Si by mixtures of particle sizes or by other means. Gascho and Korndorfer (1998) evaluated five sources of Si believed to have some potential to supply Si to plants in the Cerrado of Brazil. They used the plastic bag incubation test of Medina-

Table 12.4

Effects of lime and slag on sugarcane leaf Si, cane dry weight, soil pH and Si*

Material	Leaf Si (g kg ⁻¹)	Dry weight (g pot ⁻¹)	Soil pH	Soil Si (mg kg ⁻¹)
None	1.36	621	5.09	6
Calcite	1.85	650	6.61	7
Dolomite	1.56	624	6.03	7
TVA slag	7.48	803	6.12	31
Fairfield basic slag	3.89	729	5.78	18
Wylam basic slag	3.28	669	5.8	14

*from Gascho and Freeman (1970). Experiment conducted in pots of Everglades peat. Values are means of rates of 11, 22, and 44 MG ha⁻¹ for the lime and slag amendments. Soil pH (water) and soluble Si (pH 4.85 0.5 N ammonium acetate) determined from soil samples collected 9 mo. following application of amendments.

Table 12.5

Sugarcane and sugar yields as affected by source*.

Source	Plant cane		1 st ratoon	
	Cane (MG ha ⁻¹)	Sugar (MG ha ⁻¹)	Cane (MG ha ⁻¹)	Sugar (MG ha ⁻¹)
none	93	9.2	63	4.8
TVA slag	134	13	95	7.3
FL slag	141	13.9	112	8.8
Cement	136	13.9	105	8.1

*from Elawad et al. (1982), study conducted on Pahokee muck, yields are means of 11, 22, 33, and 44 MG ha⁻¹ rates of application for slags and cement.

Gonzales et al. (1988) and Si uptake of rice in a multi-rate greenhouse experiment. Incubation of 1000 mg Si kg⁻¹ as thermo-phosphate with all soils resulted in much greater soluble-Si increase, above a no Si control, than incubation of the other sources (Table 12.7).

There was no significant interaction between soil and Si source. Averaged over four soils included in the study, calcium silicate slag provided a soluble-Si increase which was 46 % of that recorded for thermo-phosphate while wollastonite provided 34 % of that provided by thermo-phosphate. Incubation of the soils with basic slag and Mg silicate did not result in a significant increase in soluble-Si in the soil. Application of thermo-phosphate, at rates much lower than the 1000 mg Si kg⁻¹ in this study, should provide adequate soluble soil Si as well as P and Mg.

Table 12.6

Total and citric acid soluble silicon in Si sources.*

Source	Total Si (%)	Si-soluble by 2% Citric Acid (%)	Soluble/Total
Calcium Silicate Slag**	21.1	14.8	0.7
Basic Slag 1	39.1	0.05	0
Basic Slag 2	8.5	6.9	0.82
Magnesium Silicate-course	27.8	Trace	0
Magnesium Silicate-fine	27.7	Trace	0
Thermo-phosphate	10.8	10.4	0.96

*From Gascho and Korndorfer (1999)

**Elemental P Electric Furnace by-product (Monsanto Calcium Silicate Corp.)

Table 12.7

Increased 0.5 M acetic acid-extractable Si from four soils following incubation with 1000 mg Si kg⁻¹ from five Si sources*

Soils:	LV(mg kg ⁻¹)	LE (mg kg ⁻¹)	LR (mg kg ⁻¹)	AQ (mg kg ⁻¹)	Mean
Cal. Sil. Slag	115 b	163 b	107 b	266 b*	163 B †
Wollastonite	78 b	116 b	117 b	157 c	117 B
Basic slag	1 c	1 c	0 c	3 d	1 C
Mg Silicate	6 c	3 c	4 c	4 d	4 C
Thermo-Phos	253 a	272 a	284 a	586 a	349 A
Mean	91 B	111 B	103 B	203 A ‡	

* Si applied at 1000 mg kg⁻¹ of total Si.

† Interaction means within a column followed by a common lower-case letter are not significantly different by LSD (P = 0.05).

‡ Soil or source means followed by a common upper-case letter are not significantly different by LSD (P = 0.05).

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Chapter 13

The relationship between silicon and soil physical and chemical properties

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Soil minerals and organic matter control physical and chemical soil properties. Silicon (Si) is a basic mineral formatting element. The aim of our investigation was to obtain information about the effect of Si fertilization on physical and chemical soil properties. Silicon fertilization has been reported to result in increased soil exchange capacity, improved water and air regimes, transformation of P-containing minerals and formation of aluminosilicates and heavy metal silicates. All these effects are caused by the change in soil mineral composition that results from silicate addition (Si fertilizers) and/or formation of new clay minerals, which are characterized by high biogeochemical activity. They have large surface area and are able to adsorb water, phosphates, potassium (K), nitrogen (N), aluminum (Al), and heavy metals. Adsorption may occur as chemisorptions or physical sorption. Cations (Al, heavy metals) usually are chemisorbed on Si-rich surface and lose their mobility. Phosphates and N are weakly adsorbed and remain in plant-available form. Amorphous silica, montmorillonite, and vermiculite represent the newly-formed minerals. These minerals affect the soil composition, and physical and chemical properties. The amounts of amorphous silica, monosilicic acids, and polysilicic acids in the soil are closely related to each other. Monosilicic acids regulate chemical properties of the soil solution. Polysilicic acids have an effect on soil physical properties.

13.1. INTRODUCTION

Soils generally contain from 5 to 40% Si. Soil Si compounds usually are in the form of silicon dioxide and various aluminosilicates. Quartz, together with crystalline kinds of silicates (feldspar, plagioclase, orthoclase), secondary or clay Si-rich minerals (kaolin, vermiculite, smectite) and amorphous silica form the skeleton of the soil (Orlov, 1985). Numerous physical-chemical soil properties are influenced by minerals. Both mineral composition and organic matter are responsible for soil fertility.

In addition to solid Si compounds, soils contain soluble and weakly adsorbed Si substances. There are three main groups of soluble Si compounds - monosilicic acids, polysilicic acids and organosilicon compounds. However, modern investigations demonstrate that Si complexes with heavy metals, Al, Fe, and organic compounds are present in soil solution and in natural waters as well. Our investigations indicate the need to separate low and high molecular weight polysilicic acid. An analysis of our data and literature data suggest a classification system for Si substances in the soil (Figure 13.1).

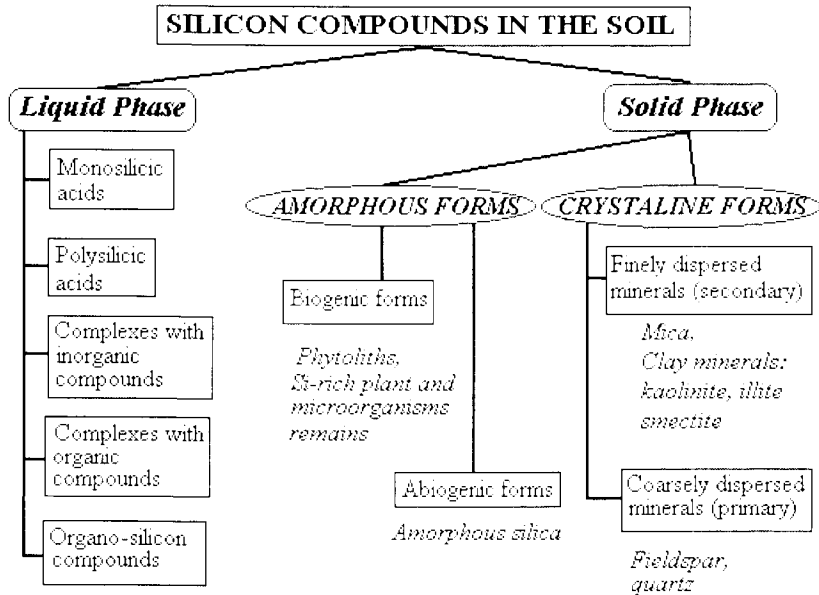


Figure 13.1. The classification of silicon compounds in the soil.

13.2. SILICIC ACIDS IN SOIL

13.2.1. Monosilicic acids

Monosilicic acid contains one atom of silicon. Orthosilicic acid (H_4SiO_4), $K = -9.85$ and its anion (H_3SiO^+) are the most widely distributed varieties of monosilicic acids. Metasilicic acid (H_2SiO_3) seldom occurs in natural waters (Babyshkin et al., 1972). The same standard methods are used for determining ortho- and meta-silicic acids, making it methodologically difficult to separate ortho- and meta-silicic acids. In the soil solution, only orthosilicic acids are presumed to be determined and are called monosilicic acids.

13.2.1.1. Interaction between silicon and phosphorus

Most investigations of monosilicic acids on soil properties concern their interaction with phosphates. Hall and Morrison (1906) presented a hypothesis about the possibility of an exchange reaction between silicate-ions and phosphate-ions due to Si fertilization. Later, it was determined that various Si fertilizers (amorphous dioxide of Si, silica-gel, silicates of calcium, K, or sodium) can increase the quantity of mobile phosphates in the soil (Gladkova, 1982; Matichenkov and Ammosova, 1996; O'Reilly and Sims, 1995; Singh and Sarkar, 1992).

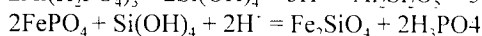
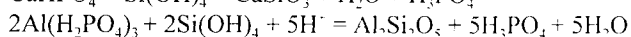
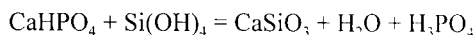
Thermodynamic calculations showed that the reaction of displacing phosphate-anion by silicate-anion from slightly soluble phosphates and formation of the corresponding silicates is possible (Matichenkov and Ammosova, 1996). The model and field experiments have completely confirmed this suggestion (Table 13.1, Figure 13.2).

Table 13.1

The effect of silicon substances on phosphate solubility.

Silicon-rich substances	CaHPO ₄		Ca ₃ (PO ₄) ₂		Al(H ₂ PO ₄) ₃		FePO ₄	
	P mg/l	pH	P mg/l	pH	P mg/l	pH	P mg/l	pH
H ₂ O	0.061	7.21	0.029	6.89	0.1124	2.23	0.1632	3.83
Super fine silica								
300 m ² /g	0.0730	6.98	0.0288	6.89	0.1124	2.23	0.1632	3.83
30 m ² /g	0.0624	7.18	0.0309	6.91	0.1893	2.30	0.1618	4.04
Quartz	0.0646	7.14	0.0256	6.98	-	-	0.1682	3.88
Calcium silicate slag	0.2564	5.55	0.0310	6.60	0.2067	2.21	0.1982	3.8

The literature and our data suggest the following stages of this process (Lindsay, 1979; Matichenkov and Ammosova, 1996). First, an increase in concentration of monosilicic acids is observed in the soil solution, along with their adsorption on slightly soluble phosphates of calcium, Al, ferric, and magnesium. The next phase is an exchange of phosphate-anion by silicate-anion:



These reactions are followed by desorption of phosphate-anion leading to increasing phosphorus in the soil solution. A new equilibrium between silicate and phosphate-anions is established. A portion of the newly-formed mobile phosphates can be adsorbed on new

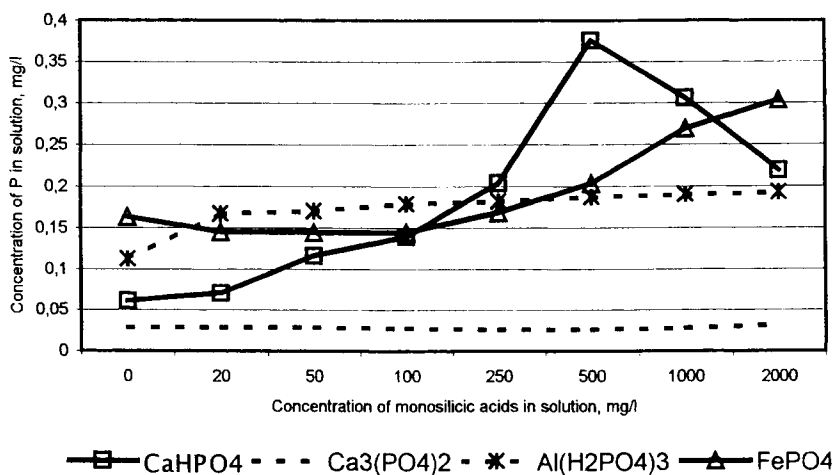


Figure 13.2. Effect of monosilicic acids on solubility of phosphates.

surfaces. On the other hand, applied Si fertilizers usually have good adsorption capacity. Our experiments were conducted with chemically pure substances (amorphous fine SiO_2 , CaCO_3 , and CaSiO_3) and with industrial by-products: slag (by-product from the electric production of phosphorus, Calcium Silicate Corp., TN) and Recmix Slag (product of processing steel slag, PRO-CHEM Chemical Company, FL).

Triplicate material samples were mixed with P-bearing solutions (prepared from KH_2PO_4) and shaken for 24 hours. The following concentrations of P were used: 0.5, 2, and 10 mg P L^{-1} . The samples were centrifuged and orthophosphate was determined by the standard method with a spectrophotometer at a wavelength of 880 nm.

The Si-rich materials varied in their capacity to adsorb P from the solution (Table 13.2). Amorphous silica significantly ($P < 0.05$) adsorbed P only from the solution with the highest concentration of P. There was no significant adsorption from the solutions with a P concentration of 0.5 and 2 mg P L^{-1} (Table 13.2). Other types of Si-rich materials adsorbed P from all P-bearing solutions. The most effective adsorption of P was observed on Recmix P from all P-bearing solutions. The most effective adsorption of P was observed on Recmix (Table 13.2). CaCO_3 adsorbed P from solutions with 2 and 10 mg P L^{-1} as well.

Leaching of P was modeled in a column experiment. The cultivated Spodosol was mixed with Si-rich materials at 10 Mg ha^{-1} . The plastic column had a volume of 60 cm^3 and a diameter of 2 cm. The P bearing solution with a concentration of 10 mg P L^{-1} was added to the column at 6-8 ml hr^{-1} , using a peristaltic pump. A total of 450 ml solution was applied to each column. The percolate was collected at 20 ml intervals. A minimum of 2 replications of columns and triplicate analyses of each liquid sample was conducted.

At the conclusion of the leaching period, the soils were air-dried and ground. Triplicate soil and sand samples were analyzed for mobile (water-extractable) and plant-available (acid extractable) P by standard colorimetric methods. The column experiment demonstrated that

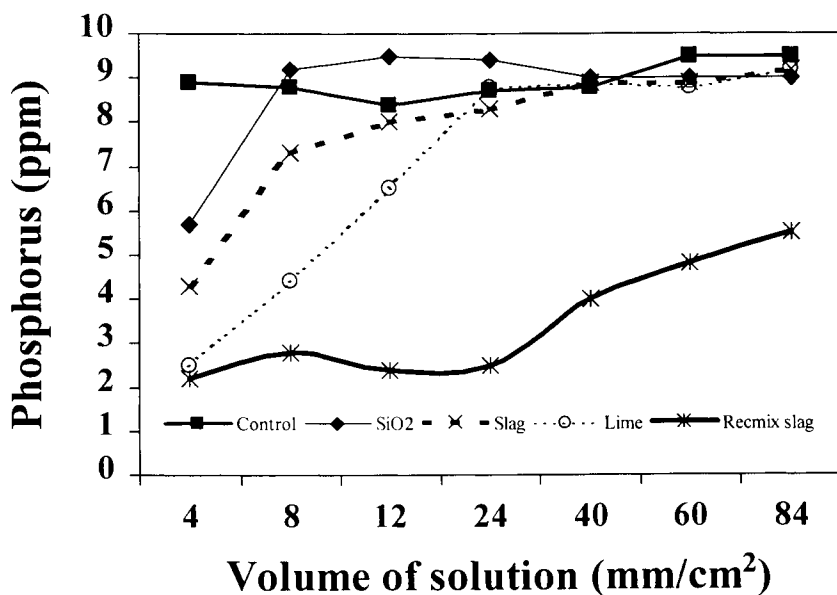


Figure 13.3. Phosphorus in percolated solution after irrigating a cultivated Spodosol with a P-bearing solution.

Table 13.2

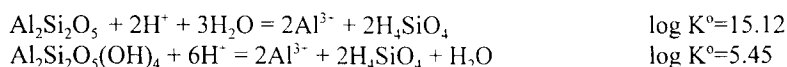
Phosphorus in supernatant after shaking with silicon materials and centrifugation.

Silicon Material	P in supernatants (mg P L ⁻¹)		
	0.500	2.000	10.000
Original Solution	0.500	2.000	10.000
Amorphous SiO ₂	0.482	1.920	4.820
CaCO ₃	0.430	1.600	3.020
CaSiO ₃	0.243	0.485	0.940
Slag	0.390	0.430	0.670
Recmix Slag	0.025	0.018	0.110
LSD ₀₅	0.060	0.080	0.100

application of Si-rich material could decrease P leaching by 40-70% (Figure 13.3). Phosphorus was adsorbed by applied silicon-rich substances. The data demonstrated that adsorbed P remained in a plant-available form (Table 13.3).

13.2.1.2. Interaction between silicon and aluminum

In 1917, a study was started in the USA on the effect of Si on Al toxicity in the soil. This, and other laboratory and field experiments, has shown that the use of Si substances for reducing aluminium toxicity is very effective (Haak and Siman, 1992; Myhr and Erstad, 1996). It is possible to postulate five different mechanisms of Al toxicity reduction by Si-rich compounds. Firstly, monosilicic acids can increase soil pH (Lindsay, 1979). Secondly, monosilicic acids can be adsorbed on aluminium hydroxides, impairing their mobility (Panov et al., 1982). Thirdly, soluble monosilicic acid can form slightly soluble substances with ions of Al (Horigushi, 1988; Lumsdon and Farmer, 1995):



Another possibility for Al toxicity reduction by Si-rich compounds can be strong adsorption of mobile Al on silica surfaces. (Schulthess and Tokunda, 1996). Fifthly, mobile silicon compounds can increase plant tolerance to Al (Rahman et al, 1998). All of these mechanisms may work simultaneously, with certain ones prevailing under various soil conditions.

13.2.1.3. Interaction between silicon and heavy metals

Silicon compounds are shown to affect heavy metal behavior in the soil. Monosilicic acids are able to combine with heavy metals (Cd, Pb, Zn, Hg, and others) in soluble complex compounds (Schindler et. al., 1976) and poorly soluble heavy metal silicates (Lindsay, 1979). Low concentration of monosilicic acids in the solution leads to formation of complexes of a heavy metal with a silicic acid anion. As the result of this reaction, the content of heavy metals increases if the concentration of monosilicic acids in the soil solution slightly increases (Bocharnikova et. al. 1995; Schindler et. al., 1976). This is connected with a change in the equilibrium between soluble and solid forms of heavy metals in the soil.

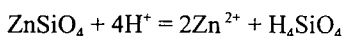
At the same time, a high concentration of monosilicic acids may cause full precipitation of

Table 13.3

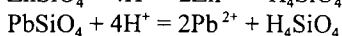
The content of water and acid extractable P from a cultivated Spodosol before and after irrigation with a P-bearing solution.

Variant	Before irrigation		After irrigation with a P-bearing solution	
	P water extractable	P acid extractable	P water extractable	P acid extractable
Control	5.9	51.1	8.6	84.3
SiO ₂	6.1	52.3	9.4	87.3
CaSiO ₃	6.0	51.4	8.4	94.2
Slag	5.8	54.2	9.7	99.7
Recmix Slag	5.7	51.6	9.8	104.5
Lime	5.7	51.2	7.5	80.4
LSD ₀₅	0.8	6.1	0.8	6.1

heavy metals with a poor formation of soluble silicates (Cherepanov et al., 1994; Lindsay, 1979).



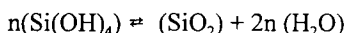
$$\log K_o = 13.15$$



$$\log K_o = 18.45$$

13.2.2. Polysilicic acids

Polysilicic acids are an integral component of the soil solution. Polysilicic acid has two or more atoms of Si and does not form a yellow color complex with ammonium molybdate. These compounds can have different forms: chains, branches and spheres (Iler, 1979). The mechanism of polysilicic acid formation is not clearly understood. Silicic acid polymerization is assigned to the type of condensable polymerization (Dracheva, 1975; Iler, 1979).



In the soil, polysilicic acids mainly affect physical properties. Polysilicic acids are capable of linking soil particles. Soil structure formation takes place through the creation of silica bridges between particles (Norton et al., 1984). With increasing polysilicic acids, the degree of soil aggregation, water-holding capacity, exchange capacity and buffering capacity of a light soil increases. Soil compaction by machinery increased the polysilicic acid content (Matichenkov et al., 1996). Our investigation showed that polysilicic acids influence the mineral formation processes (Figure 13.4).

In addition to silicic acids, soil solutions and other natural waters contain organosilicon compounds (Fotiev, 1971; Matichenkov and Snyder, 1996). It is possible that Si plays an important role in specific matter formation.

13.3. EFFECT OF SOLID PARTICLES

Silicon substances usually exhibit very good adsorption ability (amorphous fine silica, calcium silicates, Si-rich clay minerals). Silicon fertilization reduced leaching of K and other

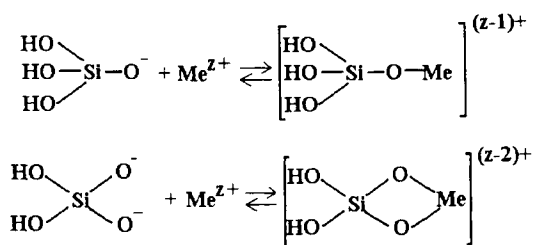


Figure 13.4. Influence of polysilicic acids on mineral formation, where Me is any heavy metal.

mobile nutrients from the surface soil horizon (Tokunaga, 1991). At present, this principle is the basis for some slow-release fertilizers (Komissarov and Panfilova, 1987; Volker et al., 1985). Our study of various textures (sand, clay-sand, sand-clay, and clay) demonstrated that treatment with Si-rich materials (10 Mg ha⁻¹) and one-month incubation under normal conditions resulted in increased water-holding capacity (Table 13.4).

13.4. SILICON FERTILIZATION

Based on information gathered from the literature on Si removal by different agricultural plants (Bazilevich et al., 1975; Reimers, 1990; Savant et al., 1997) and FAO data on world crop production (FAO Internet Database, 1998), it was calculated that 210-224 million tons of plant-available Si are removed from the soil annually. This results in acceleration of mineral weathering, depolymerization of polysilicic acids, change of P, Al, heavy metals, Fe, and Mn behavior, degradation of soil humic compounds, increased erosion, decreased microbial population, and decreased plant Si nutrition. We believe that Si fertilization is needed on all soils, except for unique soils with an abnormally high level of Si, such as recent volcanic soils, or soil formed in zones with an extremely accumulative type of geomorphology. Si fertilizers generally are Si-rich inorganic substances that increase the content of plant-available Si compounds (monosilicic acids) in the soil. Due to their large surface area, they increase the soil adsorption capacity. In addition to increasing the adsorption surface area and the content of monosilicic acids in the soil, treatment with Si fertilizer increases the amount of

Table 13.4

The change of soil water holding capacity following application of Si-rich industrial by-products.

Texture	Sand	Clay-sand	Sand-clay	Clay
Variant	W ^o %	W ^o %	W ^o %	W ^o %
Control	15.7	27.3	42.0	87.2
Amorphous silica	20.3	29.9	44.8	76.9
Slag	26.7	35.2	42.3	67.2
Cement dust	31.5	48.7	77.4	84.3

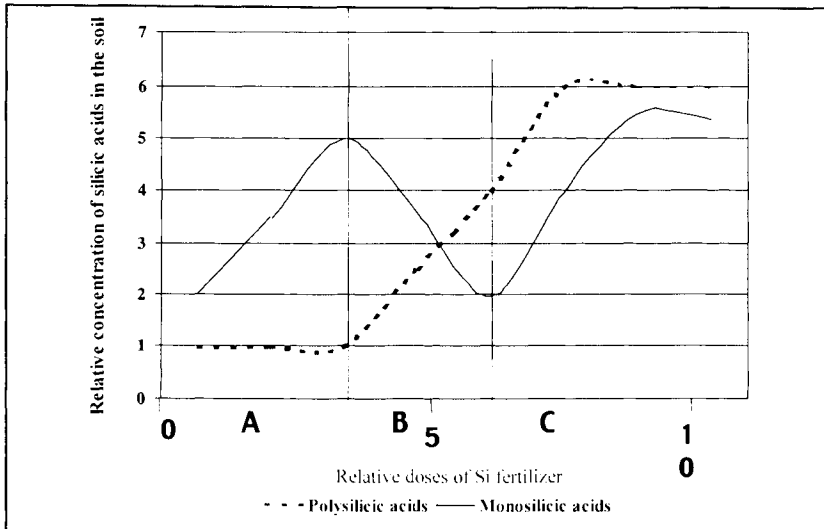


Figure 13.4. The schematic change in soluble Si compounds in soil under gradually increasing doses of Si fertilizer.

polysilicic acids. The content of monosilicic acids and polysilicic acids depends nonlinearly on the rate of Si fertilization (Figure 13.4). It is possible to identify three phases on the basis of changes in monosilicic acid and polysilicic acid concentrations.

Phase «A» represents an increase in monosilicic acid concentration in the soil solution under low doses of Si fertilizer. A further increase in Si leads to such a concentration of monosilicic acids in the soil solution that a synthesis of polysilicic acids begins. This is phase «B». During this phase, monosilicic acids that are formed are spent on the synthesis of polysilicic acids. As a result, the concentration of monosilicic acids falls and the effect from Si fertilizer decreases or disappears completely. Hereafter, an increase in the dose of Si fertilizer results in an increasing concentration of monosilicic acids, which is enough to cause both further synthesis of polysilicic acids and an increase in monosilicic acid concentration in the soil solution. This is phase «C». Further increases in the dose of Si fertilizer lead to new soil Si status, characterized by a high concentration of both mono- and polysilicic acids.

The following direct effects of Si fertilizers on soil properties have been observed:

1. Optimization of phosphate fertilizer efficiency due to transformation of slightly soluble phosphates into plant-available forms and a reduction of phosphate leaching out of the arable horizon.
2. Increase in K fertilizer efficiency.
3. Decrease in Al toxicity.
4. Change in heavy metal mobility in the soil.

5. Initiation of soil mineral formation process.
6. Improvement in adsorption properties and water-air regime of the soil.

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Chapter 14

The economics of silicon for integrated management and sustainable production of rice and sugarcane

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Despite the prolific research conducted in crop production and other aspects of silicon (Si) application, little is known about the potential economic benefits of its use in agriculture. Although some physical benefits obtained are impressive, the relative high cost of the material could make Si application unprofitable in some areas of the world. The purpose of this chapter is to show an economic analysis of two crops and one rotation: rice (*Oryza sativa*), sugarcane (*Saccharum officinarum*), and a rice-sugarcane rotation. The first case demonstrates the potential economic benefits taking into account the research conducted and the areas where rice is grown or could be grown. The second case does the same for sugarcane. The last case pertains to a specific rice-sugarcane rotation in Florida. These three cases seem to indicate that Si has a tremendous potential for increasing farm revenue.

14.1. INTRODUCTION

The overall beneficial effects of Si fertilization have been documented for different plant species in prolific literature. They include yield increases, and improved disease, insect, and fertility management, in addition to other benefits. Because of these effects, the title of this chapter portrays Si as an alternative for integrated management and sustainable crop production. Rice and sugarcane are used as case studies because of their world importance and the abundance of scientific literature. Despite the benefits derived from its application, Si is considered extremely expensive in most areas of the world. The objective of this chapter is to investigate the possibility that the numerous benefits obtained from Si applications could outweigh the costs of the material and applications in most rice and sugarcane producing regions of the world.

The first part of this chapter describes some of the research conducted on rice with the numerical results of the benefits obtained in field experiments along with the corresponding economic analysis. The second part, for sugarcane, follows the procedures of the first one. Finally, a rice-sugarcane rotation in the Everglades Agricultural Area (EAA) in Florida is used as a special case. Although the three parts of this chapter use a yield and cost-price structure that reflects Florida's EAA in the United States, it is changed in the case of rice to reflect conditions in other regions of the world.

14.2. RICE

14.2.1. A general review of the relevant literature

Rice is an important staple food that is produced throughout most of the world, accounting for more than 22% of global caloric intake (Wailes et al., 1997). Total utilization of rice is projected to increase from 376 million metric tons (MT) in 1996 to 435 MT by 2010 (Wailes et al., 1997).

There are several different types of ecosystems or growing environments for rice production throughout the world, including upland and lowland. Soils limiting in Si from parts of Asia, Africa, and Central and South America could be a major constraint to optimal rice production (Savant et al., 1997a; 1997b).

Some soils cropped to rice in the tropics have been shown to be particularly poor in plant-available Si. These soils are classified in the order of sandy Entisols, Oxisols and Ultisols (Soils and Rice, 1978; Brady, 1992). Histosols (organic soils) also belong in that group (Snyder et al., 1986). Oxisols and Ultisols account for 34% of the area of major soil orders in the tropics, including Africa, America, and Asia (Sanchez, 1976), which translates into about 1,666 million hectares.

Research conducted on Oxisols, Ultisols, Histosols, and others has shown Si to be a functional element for either flooded or upland rice (Okuda and Takahashi, 1964; Jones and Handreck, 1967; Lian, 1976). The benefits include dramatic increases in rice yields, prevention of Fe and Mn toxicity, and better uptake of P. Furthermore, Savant et al. (1997b) have conducted an extensive review of the literature documenting the positive impact of Si applications on rice yields under subtropical to tropical conditions, while Lian (1976) and Elawad and Green (1979) have done so for temperate countries of the world.

The phenomenon of yield decline in different rice ecosystems from many parts of the world has been reported to be associated with decreases in the effective N supply from soil (Savant et al., 1997a). Depletion of plant-available Si in soils where rice is grown could be a possible limiting factor contributing to declining or stagnating yields (Savant et al., 1997a; 1997b). Research conducted in 16 provinces of China (where rice is the most common grain crop) during 1979-99 showed yield increases from zero to 400%, depending on the severity of Si deficiency (Wang et al., 2000). The situation in China is particularly important because of its large land area in Asia, where most of the rice is grown, that is being treated with Si, and the potential for other areas. Thus, it is clear that Si applications have beneficial impacts on rice yields in many areas of the world. The use of Si may reduce the level of previous fertilization regimes which results in reduced costs and beneficial effects to the environment.

Another important beneficial effect which also impacts on yields relates to disease management. The overwhelming evidence seems to indicate that Si reduces the severity of several economically important diseases such as blast (*Magnaporthe grisea*), brown spot (*Cochliobolus miyabeanus*), scald (*Monographella albescentis*), sheath blight (*Thanatephorus cucumeris*) and stem rot (*Magnaporthe salvanii*) (Volk et al., 1958; Takahashi, 1967; Ohata et al., 1972; Elawad and Green, 1979; Lee et al., 1981; Kim and Lee, 1982; Nanda and Gangopadhyay, 1984; Ou, 1985; Aleshin et al., 1987; Yamauchi and Winslow, 1987; Datnoff et al., 1990; Datnoff et al., 1991; Osuna-Canizalez et al., 1991; Seebold et al., 1995; Datnoff et al., 1997; Seebold et al., 1997 and Seebold et al., 1998). It has also been demonstrated that disease tends to decrease with increasing concentrations of Si in the plant tissue (Datnoff et al., 1990, 1991; Osuna-Canizalez et al., 1991). Similar observations have been made for many insect pests (Savant et al., 1997b). In this era of serious environmental concerns, Si

applications appear to be an available option for disease management by reducing fungicide use and, therefore, potential environmental threats to agricultural land and water (Datnoff et al., 1997; Seebold et al., 1995, 1997, 1998).

Intertwined with the disease-related benefits are those resulting from reductions in grain discoloration. Research conducted in this area includes the studies by Yamauchi and Winslow (1987); Winslow (1992) and Correa-Victoria et al. (1994).

A review of the literature reveals that improving the Si concentration of rice plants results in the suppression of several economically important arthropod pests, such as stem borer (*Chilo suppressalis*), brown planthopper (*Nilaparvata lugens*), green leafhopper (*Nephotettix bipunctatus cincticeps*), white-backed planthopper (*Sogetella furcifer*), leaf spider (*Tetranychus spp.*), and mites (Savant et al., 1997b, p. 173).

Research has shown that silicon fertilization increased the P content of the rice straw and grain when P was not even applied (IRRI, 1965; 1966). Phosphate fertilizer efficiency has increased when applied along with Si (IARI, 1988). In the case of lime fertility management, data have shown that silicon applications on acid soils increase the pH, thus reducing or eliminating the need for liming applications (L.E. Datnoff and F.J. Correa-Victoria, 1999, unpublished data).

There are several other advantages from Si applications. For example, silicon sources have residual effects that persist over time. Thus, yearly applications may not be needed. In addition, the residual effect might reduce subsequent applications considerably after the first treatment (Datnoff et al., 1997). Economically feasible Si applications in a rice-sugarcane rotation in the Everglades Agricultural Area (EAA) of southern Florida have resulted in not only increased rice yields but also increased sugar yields from cane grown immediately after rice (Alvarez et al., 1988).

This prolific research on such a variety of issues has not included any economic analysis. Perhaps for that reason, despite all the potential beneficial effects, most Si sources are considered expensive. The objective of this section is to conduct a simple benefit/cost analysis (partial budgeting) to investigate the possibility that the numerous benefits obtained from Si applications could outweigh the costs of the material and application in some regions of the world. Here we describe numerical results of some of the field experiments reported above in the different research areas along with the corresponding economic analyses. We analyze yields first, and then we portray different scenarios combining the remaining potential benefits. Although the base yield and price-cost structure used reflects Florida's EAA in the United States, results from variations of both are also investigated since the base case is not entirely typical of other rice-producing regions of the world.

14.2.2. Benefits and costs

In order to quantify benefits and costs for the base case from a wide range of data resulting from the field studies above, it is necessary to make some preliminary general assumptions. They include: 1) Application rate: 2.5 ton/ha of calcium silicate slag (standard silicon grade from Calcium Silicate Corporation, Inc., Columbia, TN), with a 20% Si content or 500 kg/ha of elemental silica, at a cost of \$48/ton including application, with a length of effectiveness of two years. 2) Average yield: 5,000 kg/ha without Si application. Costs and prices were obtained in Florida from a rice mill in the EAA and dealers servicing the local producers in early 1998. Once an upper limit is obtained from these assumptions, a sensitivity analysis will be conducted to reflect lower benefits in other regions of the world.

Table 14.1

Assumptions and resulting economic benefits from yield increases due to silicon applications in the base case and two alternate cases.

Assumptions	Base case	Alternate case 1	Alternate case 2
Average yield without silicon (kg/ha)	5000	2500	7500
Application rate (ton/ha)	2.5	2	3
Yield increase (%)	12	30	8
Silicon cost (\$/ton)	48	48	48
Extra production cost (\$/kg)	0.0046	0.005	0.005
Price of rice (\$/kg)	0.24	0.15	0.15
Interest rate for discounting income (%)	8	12	16
Extra net revenue (\$/ha/year)	73.54	52.32	6.43

14.2.2.1. Impact on rice yields

The review of the literature conducted by Savant et al. (1997b) found several levels of yield increases. One experiment reported increases from 10% to 30%. In another study, yields were raised by more than 500 kg/ha. Other results ranged from 4.6% to 20.7% increase, and a 48% boost was reported in another study.

A 12% increase in yields translates into 600 kg/ha. If the price of U.S. No. 2 rough rice is \$0.24/kg, the extra gross revenue amounts to \$144/ha. Silicon cost is \$120/ha; the cost of harvesting and hauling the extra rice produced is \$0.0046/kg or \$2.76/ha ($\$0.0046 \times 600$). Subsequently, the first year extra net revenue amounts to \$21.24/ha ($\$144 - \$120 - \2.76).

Calculation of the extra net revenue for the second year requires the use of the present value formula: $\$1(1+i)^{-n} = \$1(1+0.08)^{-1.5} = 0.891$; where i = interest rate (8%) for discounting income, and n = number of years (1.5) until income is received; or $(\$144 - \$2.76) \times 0.891 = \$125.84$ /ha. Thus, the average extra net revenue per year amounts to \$73.54/ha (Table 14.1). This figure appears to be an upper limit because of the associated economic conditions prevalent in the United States.

We now change some of the assumptions for two alternate cases: In alternate case 1, average yields are 2,500 kg/ha, and potential yield increases are set at 30% after application of Si at a rate of 2.0 ton/ha. Because of high variability, which depends on the availability of local sources, the cost of the material remains the same. Extra production costs are somewhat higher (\$0.005/kg), as well as the interest rate for discounting income (12%). The price of rice is set at \$0.15/kg, or 9 cents lower than in the base case. The average annual extra net revenue in this case amounts to \$ 52.32/ha (Table 14.1).

Alternate case 2 intends to portray the case of much higher yields in some areas. The initial yield level is set at 7,500 kg/ha, which needs to increase the application rate to 3.0 ton/ha to achieve an 8% increase in yields. The cost of Si, the extra cost of production, and the price of rice remain as in the alternate case 1, but the interest rate for discounting income is increased

to 16% to reflect higher interest rates in some countries. The extra net revenue per year amounts to only \$6.43 (Table 14.1).

The three cases show different results. They lead to different implications that will be discussed in the last section of this paper.

14.2.2.2. Other benefits and costs combined: the base case

This section duplicates what was done with yield increases, but combines all other potential benefits from Si applications. In addition to the base case, alternative cases 1 and 2 are also discussed (Table 14.2).

14.2.2.2.1. Controlling blast and other diseases

It has been demonstrated that Si may eliminate the need for fungicides in managing rice diseases. Following the same price-cost structure defined above for the base case, the savings from two applications of fungicide per year, including cost of material and application, are \$79/ha. The second year savings are \$70.39 ($\79×0.891). Thus, average annual savings are \$74.69/ha (Table 14.2).

14.2.2.2.2. Potential grain discoloration

Research has shown that Si application, in addition to producing a healthier plant, also provides better grain appearance. In Florida, it is widely recognized that Si improves the quality of the rice grain, which translates into better grain milling and an increase in its white color (Anonymous, 1997).

In countries with strict grades and standards, this result provides a definite market advantage to producers. The penalty for moving from U.S. No. 2 to U.S. No. 3 rice as a result of grain discoloration in the United States is \$0.011/kg at the reference price. If the quality increases from No. 3 to No. 2 due to the Si application, the 5,600 kg/ha previously estimated generate an added annual net income of \$61.60/ha (Table 14.2).

14.2.2.2.3. Insect management

Silicon has the ability to considerably reduce several economically important insect pests. This can lead to a reduction in insecticide applications. For example, if the cost of one application is \$10.50/ha, and they are reduced from three to one per crop (Savant et al., 1979b), total savings amount to \$21/ha (Table 14.2).

14.2.2.3. Fertility management

14.2.2.3.1. Reducing phosphorus applications

In upland conditions, P applications may be reduced every year. For example, if 25 kg/ha need to be applied instead of 50 kg/ha, and the cost of P_2O_5 , including application, is \$0.51/kg, total annual savings per crop amount to \$12.75/ha (Table 14.2).

14.2.2.3.2. Eliminating lime applications

In acid soils where the application of Si eliminates or reduces the need for liming, more savings can be obtained. Assume the cost of applying dolomitic lime to one hectare at \$5.25, and 3.60 mt/ha were applied at a cost of \$26.67 mt before using Si. If liming is completely suppressed, the annual savings amount to \$101.81/ha (Table 14.2).

Table 14.2

Potential benefits, other than yield increases, due to silicon applications in the base case and two alternate cases.

	Base case	Alternate case 1	Alternate case 2
Potential benefits	\$ /ha/year		
Controlling blast and other diseases	74.69	37.34	0
Reducing grain discoloration	61.6	30.8	30.8
Insect management	21	10.5	10.5
Reducing phosphorus applications	12.75	6.37	8.92
Eliminating lime applications	101.81	50.9	0
Extra net revenue	271.85	135.91	50.22

14.2.2.4. Other benefits and costs combined: the alternate cases

The results from the basic case changed dramatically when we changed the assumptions in the two alternate cases. In alternate case 1, we just divided by two the potential benefits in the base case. This reflects the same cost-price structure used in the base case but was done to account for those potential benefits at half the scale. Alternate case 2 leaves intact the results concerning grain discoloration and insect management in alternate case 1. It also assumes that P applications are only 7% of the base case. In addition, it assumes no fungicide and lime applications. These assumptions intend to portray the Asian situation, where most of the rice is actually grown. The resulting extra net revenues per year in alternate case 1 are \$135.91, and \$50.22 in alternate case 2.

14.2.2.5. Other benefits and costs not considered

Several other benefits from silicon applications have been documented in the introduction of this paper. Some of them are difficult to quantify. Others may be the result of inter-related factors that, if quantified, could lead to double-counting. For those reasons, they are not included here in the numerical description of the benefits and costs. They should be, however, taken into considerations when evaluating the tradeoff between the benefits from silicon application and the high cost of the material.

14.2.2.6. Total benefits

Table 14.1 provides a range of net benefits from yield increases, while Table 14.2 does that from other benefits resulting from silicon applications. Comparing the two extremes in both tables gives an idea of the potential magnitude of those benefits. The highest figures in both tables represent the base case. They amount to extra net revenues of \$345.39/ha/year. The lowest figures in both tables portray alternate case 2 and add up to additional net revenues \$56.65/ha/year due to Si applications.

14.2.3. Discussion

These results, despite their limitations, are important when analyzed within the context of world rice parameters derived from the Arkansas Global Rice Model's projections for 1996-2010 (Table 14.3). The first observation is that, throughout the study period, total rice utilization will continue to grow at very slow rates which, if compared with population growth and previous growth rates, may indicate a decrease in the consumption of this crop.

A second observation relates to total world savings resulting from Si applications. The upper limit of the results is \$345.39 per hectare. If that figure is assumed a world average, then total world savings from Si applications would have amounted to \$51.3 billion in the 1996 crop season. The savings in 2010 could approach \$52.4 billion. If the lower limit of the results (\$56.65/ha) is used in the calculations, the former figures would change to \$8.4 billion in the 1996 crop season, and to almost \$8.6 billion in the 2010 crop. The figure in the middle of the range (\$188.23 per hectare) would translate into \$27.9 billion and \$28.5 billion for the 1996 and 2010 crops, respectively. We believe the latter figures to be more realistic.

No price effects were considered in the previous calculations. The explanation of their importance is a simple one. Partial budgeting applied to a global aggregation is generally inappropriate since, for example, a 15% global increase in world rice yields and production will be expected to result in at least a 10% decrease in world rice prices, assuming a price flexibility (defined as a percent change in price for a percent change in quantity supplied) of 0.67. This situation, however, does not apply when one assumes no increases in production, but a reduction in land area devoted to rice from the yield increases assumed, as explained later in this section.

Finally, rice yields during the 1996-2010 period are projected to increase at an annual average rate of 0.93%. The International Rice Research Institute is constantly emphasizing the importance of increasing yields in their research program, recognizing the expenses involved in breeding new varieties (IRRI, 1993a; 1993b; 1994; 1997). The literature reviewed, however, has suggested yield increases in the order of between 10% and 48% from Si applications which should be of some help to expensive breeding programs.

Wailes et al.(1997) made two important statements relevant to this study. First, "the growth in world rice production necessary to satisfy the projected consumption levels over the next

Table 14.3

World rice total utilization, area harvested, yield, and total production, 1996 and projected 2010, and growth rates for 1976-95, 1990-95, and projected 1996-2010.

Item	Year		Growth rate per year (%)		
	1996	2010	1996-2010	1990-1995	1976-1995
Total utilization (million mt)	376	435	1.05	1.09	2.27
Area harvested (million ha)	148.5	151.6	0.15	0.17	0.23
Rice yield (mt/ha)	2.52	2.87	0.93	0.68	2.04
Total production (million mt)	375	436	1.08	0.84	2.28

Source: Developed from Wailes et al. (1997, pp. 2, 3, 4).

15 years (1996-2010) will mainly come from yield increases, as it has for the past 20 years." This projection translates to rice occupying the same amount of land, because production increases through land expansions at the same yield levels seem to have been unattainable in the past decades and will continue to be so in the future. Second, "to the extent that yield growth exceeds the 0.93 percent growth rate, less land resources will be needed to accommodate the consumption projections." Silicon applications are known to increase rice yields under a variety of conditions. Looking at the projections in Table 14.3, average world yields are expected to reach only 2.87 mt/ha in 2010. If one assumes only an additional 0.5 mt/ha from Si applications for the entire period, the resulting total yield increase of 3.37 mt/ha would only need 129.4 million hectares to produce the required 436 million metric tons to match consumption requirements in 2010. This would represent a saving of 22.2 million hectares of land harvested annually that could be devoted to the production of other crops. For the developing world, this would represent a significant achievement. Land, in these countries, goes mostly to satisfy the most important requirement of the population's diet. Additional land could be used for the production of non-traditional crops for exports to generate foreign exchange earnings.

It is difficult to apply the cost of Si, including application, in other countries of the world, and relate them to the benefits described above, including the monetary savings and the use of available land for the production of other crops. When all benefits are considered, it is reasonable to believe that they outweigh the cost of Si, including application, in some rice-producing countries of the world.

14.3. SUGARCANE

14.3.1. A general review of the relevant literature

Sugarcane is an important crop throughout the tropical and semitropical regions of the world. For many countries in the developing world, it is the main source of foreign exchange.

Most of the literature related to the use of Si on sugarcane deals with nutritional aspects and resulting impacts on yields. Savant et al. (1999) have conducted an extensive review of the literature. They found positive responses in Florida, Hawaii, Mauritius, Puerto Rico, South Africa and Brazil. Research conducted in Florida, and subsequent commercial applications, has shown different response rates. In general, good responses were found by Gascho and Andreis (1974), and Gascho (1979), the latter showing economic profitability (Alvarez and Gascho, 1979). Elawad et al. (1982), Anderson (1991), and Raid et al. (1992) among others, have shown similar results in sugarcane monocultures. In Hawaii, Clements (1965a), Ayres (1966), and Fox et al. (1967) have found positive responses of sugarcane yields to Si application, as well as Ross et al. (1974) in Mauritius, and Samuels (1969) in Puerto Rico. In South Africa, Preez (1970) and Moberly (1974), among others, have obtained similar results. Other countries, where fewer reports have been published, include, Indonesia, Malaysia, Taiwan, and Australia.

As it is in the case with rice, in addition to increased yields, other benefits in several aspects of sugarcane culture are attributed to Si fertilization. They include disease control, pest control, mineral toxicity alleviation, freezing alleviation, water use efficiency, and reduction in lodging and improvement in erectness. Some of these effects, however, may not render themselves to quantification, thus hindering performing an economic analysis.

In terms of disease control, researchers have found the beneficial effects of Si applications corrects a leaf disorder called freckling, thus avoiding decreases in yield (Clements, 1965b; Ayres, 1966; Fox et al., 1967; and Wong et al., 1972). Takahashi (1996) demonstrated that Si deposited in the epidermal tissue mechanically deters hyphal invasion. Raid et al. (1992) noticed decreases in severities of ringspot, but not of rust, in sugarcane hybrids.

There are not many reports on pest control. Elawad et al. (1985) noticed increased resistance to stem borer when Si was applied, while Rao (1967) did so for shoot borers. Other researchers have shown that applying Si to the regular fertilization regime decreases the incidence and damage of stalk and other borers.

Applying soluble silicates to some areas of the sugarcane plant results in the alleviation of toxicity (Clements, 1965b). Other researchers have also reported, and explained, the previous finding.

In addition to the use of cold-tolerant varieties and the performance of certain cultural practices, Si applications appear to reduce damage caused by freezing in subtropical areas. Ulloa and Anderson (1992) found that in Florida, while Rozeff (1992) did so in Texas.

Improved Si nutrition may reduce excessive leaf transpiration (Cheong et al., 1972), and thus, contribute to water use efficiency. Lewin and Reimann (1969) quantified the results which Okuda and Takahashi (1965) had previously outlined.

Although related to rice, the reduction in lodging and improvement in erectness reported by Takahashi and Miyake (1982), and by Balastra et al. (1989), are believed to be true for sugarcane also.

As in the rice case, none of the results mentioned above for sugarcane included an economic analysis. The next sections do that.

14.3.2. Benefits and costs

The sugarcane case also makes some assumptions in order to quantify benefits and costs. They are: 1) The example pertains to a producer of administration cane (sugarcane grown by a corporation or cooperative members for use in their own mills), and not to an independent producer. 2) Application rate: 5 Mg/ha of a calcium silicate source (standard Si grade) at a cost of \$48/ton, including application, with a length of effectiveness of two years. 3) Yield: 90 net Mg/ha (or 107.61 kg of sugar per Mg, assuming 14.27% sucrose in normal juice) for the plant cane crop, and 80 net Mg/ha (same sugar assumption) for the first stubble crop. Costs and prices were obtained in Florida from several sugarcane growers in the EAA and dealers servicing the local producers in early 1998.

14.3.2.1. Impact on sugarcane yields

The review of the literature conducted by Savant et al. (1999) unveiled several levels of yield increases due to Si applications. Some of them included 10% to 50%; 5% to 35%; 18% in cane, and 22% in sugar in plant cane; 20% in sugarcane and sugar; 17% and 22%.

A 10% yield increase in the plant cane and stubble cane crops translates into 9 net Mg of sugarcane per ha (968.41 kg of sugar), and 8 net Mg of sugarcane per ha (860.88 kg of sugar), respectively. If the average market price of sugar received by the mill is set at \$485/Mg, then the extra gross revenue for the plant cane crop amounts to \$469.68. Silicon cost is \$240/ha. Additional costs include mechanically harvesting the extra sugarcane produced (at \$6/Mg of sugarcane), and milling it (at \$132.30/Mg of raw sugar produced, or \$0.1323/kg). These costs amount to \$54/ha, and \$128.12/ha. Then, the plant cane crop's extra net revenue amounts to \$47.68/ha (\$469.68 - \$240 - \$54 - \$128.12). Since revenues are not received until after 1.5

years, net revenues need to be discounted to their net present value using the formula $\$1(1+i)^{-n} = \$1(1+0.08)^{-1.5} = 0.891$; where i = interest rate (8%) for discounting income, and n = number of years (1.5) until income is received; or $\$47.68 \times 0.891 = \$42.48/\text{ha}$.

For the first stubble crop, the 10% increase in yield represents an additional 860.88 kg of sugar/ha, which translates into a gross revenue of \$417.53/ha. No Si cost is involved in this case. The cost of mechanically harvesting the sugarcane, and milling the extra sugarcane produced are \$48/ha, and \$113.89/ha, respectively. Then, net revenue for the first stubble crop amounts to \$255.64. As in the plant cane crop, the calculation of the extra net revenue for the first stubble crop requires the use of the present value formula: $\$1(1+i)^{-n} = \$1(1+0.08)^{-2.5} = 0.825$; where $i = 8\%$, and $n = 2.5$ years; or $\$255.64 \times 0.825 = \$210.90/\text{ha}$. The total extra net discounted revenue per year amounts to both revenues divided by two, or \$126.69/ha/crop.

14.3.2.2. Disease control

The findings about the decrease in percent freckling in the sugarcane plant due to Si applications do not contain the negative impact on yields to be able to quantify its positive effect. The same occurs with hyphal invasion. No quantification was found for yield reductions due to rust damage or in ringspot (Raid et al., 1992).

14.3.2.3. Insect control

Several species of sugarcane borers were found to cause less damage to the sugarcane plant due to Si applications. As in the previous case, no quantification was done in the different studies reviewed. This could have been an important contributor to net revenues in our analysis because these insects are known to reduce yields considerably.

14.3.2.4. Toxicity alleviation

As expected, the impact of Si on alleviating toxicities is very difficult to measure. Thus, no figures were found in the literature.

14.3.2.5. Freezing alleviation

Cold tolerance due to silicate fertilization was also not properly quantified. This could have been another important contributor to net revenue because of the heavy losses produced by freezes in the semitropical areas such as Florida, where most of the freezing experiments have been conducted.

14.3.2.6. Water use efficiency

Although this parameter was measured in a few studies, none of them explain what they mean in terms of positive impact on yields or other characteristics of the plant that leads to economic quantification.

14.3.2.7. Lodging reduction and erectness improvement

No figures on the results of the experiments are available.

14.3.2.8. Other benefits and costs

Another important benefit of Si application is its role in the synthesis, storage, and retention of sucrose in the sugarcane plant. This is an important parameter to measure in future research. In addition, an extra cost would be the mill role wear attributed to silicates in sugarcane arriving at the mill.

14.3.2.9. Total benefits

Because of the lack of quantification of the above benefits in the experiments, yield increases are the only cause when measuring total benefits. As stated above, they amount to \$127/ha/crop.

14.3.3. Discussion

The high discounted net returns computed for sugarcane are the result of two facts. First, the high price received by sugar producers in the United States relative to the so-called world market price, makes a very positive impact on the return to the Si investment. Second, the assumption of a producer of administration cane, instead of an independent grower, results in higher returns because of the economic benefits from grinding his own sugarcane. Despite the conservative assumptions, it is obvious that applying a calcium silicate source to sugarcane does pay in Florida, since the returns obtained more than outweigh the cost of the material.

Other countries of the world may not face the same cost-price structure assumed in this example. The response of sugarcane to Si, however, has been proven to be so high in several soil types that it seems safe to state that applying Si to sugarcane would be an income-rewarding enterprise in most sugarcane-producing areas of the world.

As in the case of rice, land area devoted to sugarcane production can be liberated to produce other crops. This is particularly important in both sugarcane and rice since both industries are facing stagnant or decreasing consumption.

14.4. A RICE-SUGARCANE ROTATION IN THE EAA

The two prior sections have demonstrated that applications of Si may be economically feasible in most areas of the world where these two crops are grown in a monoculture production system. But what about in a rice-sugarcane rotation? The problem of when, if ever, to apply Si becomes an economic one for three reasons. First, both rice and sugarcane respond to pre-plant applications of Si, with residual effects in the rice-sugarcane rotation. Secondly, there are unequal gross and net returns per hectare for each crop. Finally, material and application costs are very high. Furthermore, the material application has a direct impact on the timing of the investment and the expected returns it generates in the future. Prices of the commodities are different, as are the harvest and post-harvest costs associated with the extra production generated from the Si application.

This section presents an economic analysis of the two Si applications (rice and sugarcane) in the three production systems of the EAA: "before rice," "before sugarcane," and "before rice-sugarcane". For comparison purposes, the data and corresponding analyses have not been modified or updated from the original version of Alvarez et al. (1988). The methodology is just an example of how to use economic theory to approach the problem of when to apply a fertilizer in a given rotation practice.

14.4.1. Methodology

The equations relating used in this chapter Si application to rice and sugar yields were developed by Anderson et al. (1987). The structural form of the response functions estimated for rice and sugar was:

$$Y = a + b_1 S + b_2 S^2 + e,$$

where Y = yield of rice or sugar expressed as metric tons per hectare; S = rate of calcium silicate application in metric tons per hectare; and e = random error.

The conditions for maximum yields require that the marginal physical product (the addition to product resulting from the addition of one unit of the input), derived from the response function, be equal to zero and that the second derivative be negative. Second-order conditions are satisfied in all the equations. Solving for S in the equation of the first-order condition gives the rate of S that maximizes yields of rice or sugar. Plugging that rate into the response function gives the maximum physical output.

Economic optimum conditions are derived from a profit equation. In general,

$$\pi = P_Y * Y(S) - C_S * S,$$

where π = profits;

P_Y = price of rice or sugar;

$Y(S)$ = the relevant response function;

C_S = cost of the calcium silicate including application; and

S = rate of calcium silicate applied.

Profits are maximized when marginal costs equal marginal revenue (or price in this case), provided the second-order condition of profit maximization holds. This procedure, with the necessary changes, was used in each of the three cases resulting from the two application times in the rotation.

14.4.1.1. Before rice

The “before rice” case analyzed the effect of silicon on rice yields only, when the Si was applied prior to rice planting. The equations of the first and ratoon crops were combined into one giving the equation

$$Y = 7.069 + 0.3627 S - 0.00884 S^2.$$

The linear coefficients in the first- and ratoon-crop equations were statistically significant at $P = 0.0026$ and $P = 0.0238$, respectively, while the quadratic terms were significant at $P = 0.0679$ and $P = 0.2477$, respectively. The coefficients of determination were 0.79 and 0.71 for the first- and ratoon crops equations, respectively.

The profit equation described above was used to calculate the economic optimal rate of calcium silicate. This value was plugged into the response function, giving the maximum economic yield utilized in the profit equation using the corresponding input costs and product price.

The resulting profit figure, however, was preliminary. It was necessary to perform the following computations:

- (a) The extra rice produced was calculated by subtracting the intercept (yield with no Si) from the maximum economic yield.
- (b) The extra quantity of rice produced was multiplied by the additional cost of harvesting, hauling, and drying, adjusted from wet to dry weight.

(c) The additional cost of the extra rice was subtracted from the preliminary profit figure, resulting in the net profit from the Si application. Since those revenues are received in less than a year, the Si was treated as another input and no discounting was done.

(d) Revenues from the “no Si” case were calculated by multiplying the intercept times the price of rice.

(e) The comparison was made by subtracting the “no Si” case figure obtained in (d) from the net profits due to Si computed in (c). The difference was the net effect of Si on rice profits.

The price of U.S. No. 2 rough rice was set at \$220.45 per Mg (\$0.22045 per kg). The cost of the calcium silicate was \$41.89/mt, which included application costs. The additional cost of harvesting, hauling, and drying the extra rice produced was estimated at \$44.09 per Mg, which was then multiplied by 1.106 to convert it from wet to dry weight, resulting in \$48.50 per Mg.

14.4.1.2. Before sugarcane

This alternative consisted of analyzing the effect of the calcium silicate on sugar yields only, when the material was applied prior to sugarcane plantings. The equation showed statistical significance at $P < 0.01$ in both the linear and quadratic terms and a coefficient of determination of 0.65:

$$Y = 11.8 + 0.493 S - 0.017 S^2.$$

The first part of the analysis was identical to the ones described in the “before rice” case. Since the revenues from the sugarcane crop, however, are not received within a year of the Si application, the additional revenues and costs were discounted using a present value approach:

(a) The additional cost from harvesting, and milling the extra sugarcane was discounted at 10% for 1.5 years.

(b) The discounted figure was subtracted from the preliminary profits.

(c) The extra revenue was calculated by multiplying the extra sugar produced by the price of sugar.

(d) The extra revenue figure was discounted at 10% for 1.5 years.

(e) The discounted revenue figure was subtracted from the extra revenue obtained in (c).

(f) The figure obtained in (e) was subtracted from the one calculated in (b).

(g) Revenues from the “no Si” case were calculated by multiplying the intercept (yield with no Si) times the price of sugar. Although sugar revenues in both cases are received at the same time, discounting is only performed in the Si case to reflect the opportunity cost of money of the additional investment.

(h) The comparison was made by subtracting the “no Si” case figure obtained in (g) from the net profits due to the Si calculated in (f). The difference, as in the previous case, was the net effect of the Si application on sugar profits.

The average market price of sugar received by the independent sugarcane producer was \$179.23/Mg, equivalent to an average market price of \$441/Mg received by the mill. The cost of harvesting and hauling the extra sugar produced was assumed to be \$99.21/Mg, equivalent to \$11.85/gross Mg of sugarcane. For both computations, equations in Alvarez and Rohrmann (1984) were used assuming a 5% trash content per gross ton and a 14.25% sucrose content in normal juice. As before, the cost of calcium silicate was \$41.89 per mt applied.

14.4.1.3. Before rice-sugarcane

This case combined the effect of the Si on both the rice and sugarcane yields when the material was applied prior to rice planting. The “before rice” equation was used with the equation showing sugarcane yield responses after the rice culture:

$$Y = 11.8 + 0.371 S - 0.012 S^2.$$

Statistical significance was shown at $P < 0.01$ and $P = 0.0159$ for the linear and quadratic coefficients, respectively, and the model R^2 was 0.70.

The profit equation used to analyze this case was:

$$\pi = [P_r * Y_r(S)] + [(P_s * Y_s(S)) * (1 + i)^{-n}] - (C_s * S) - [Y_r(S) * AC_r] - [(Y_s(S) * AC_s) * (1 + i)^{-n}]$$

where P_r = price of rice;

$Y_r(S)$ = response function for the “before rice” case;

P_s = price of sugar;

$Y_s(S)$ = response function for sugar when the material is applied prior to rice planting;

$(1 + i)^{-n}$ = present value formula;

C_s = cost of calcium silicate, including application;

S = rate of calcium silicate application;

AC_r = additional cost of the extra rice produced; and

AC_s = additional cost of the extra sugar produced.

These variables were expressed in the same units used in the two previous cases. After taking the first partial derivative with respect to the Si variable, the two response functions plugged into the equation did not include the intercepts. Since the intercepts represent the yield with no Si, the result obtained was the profit figure from the extra production generated by the Si application. Solving for S provided the equation for the optimal rate of calcium silicate:

$$S^* = \{C_s + 0.3627AC_r + [0.371AC_s * (1 + i)^{-n}] - 0.3627P_r - [0.371P_s * (1 + i)^{-n}]\} / \{0.01768AC_r + [0.024AC_s * (1 + i)^{-n}] - 0.01768P_r - [0.024P_s * (1 + i)^{-n}]\}$$

The costs, prices, and discount factor used before were substituted into this equation and the resulting optimal rate of calcium silicate was plugged into the profit function.

14.4.2. Results and discussion

Agronomic and economic responses are shown in Table 14.4. The most significant finding is that, with the costs and prices used in this example, the calcium silicate should be applied in the rotation in order to obtain the highest extra profit. About additional \$227/ha are received in this case. Applying the calcium silicate before the rice in a monoculture system results in extra profits of about \$56/ha.

The “before cane” alternative teaches us two lessons. First, with the prices and costs assumed, it is not economically feasible for growers of independent cane despite the positive responses found in the EAA. The relatively high cost of the material in relation to the price received at the farm level restricts the economic use of Si in this system. The positive

Table 14.4

Agronomic (Mg/ha) and economic (\$/ha) responses of the equations relating rice and sugar yields to time and rate of application of calcium silicate.

Application time	Agronomic maximum		Economic optimum		
	Si	Yield	Si*	Yield	Profit
Before rice*	20.51	10.8	9.77	9.77	55.62
Before sugarcane ⁺	14.5	15.37	7.63 [#]	14.56	-128.15
Before rice-cane ¹	-----	-----	9.82	-----	226.93

* The analysis of the effect on rice yields only when the Si was applied prior to rice planting.

⁺ The analysis of the effect on sugar yields only when the Si was applied to sugarcane planting.

[#] In this case the economic optimum is zero. No fertilizer should be applied.

¹ The analysis of the effect on both rice and sugar yields when the Si was applied prior to rice planting.

response of sugarcane, however, is still present in the rotation and may be estimated as the difference between the "before rice-cane" and the "before rice" alternatives. We have left this example intact since 1987 to show what can happen in many countries of the world. As seen in sections 14.3.2. and 14.3.2.1., the assumption of administration cane, and a higher price received for sugar, made Si applications economically feasible in a monoculture system. Second, the use of Si in the EAA, however, generates extra profits for producers of administration cane and, for that reason, the application of calcium silicate by these firms has been growing for several years in the EAA.

In addition to the extra revenue, producers will also benefit from having to perform an additional cultural practice during the busiest time of the season. Perhaps more important are the other benefits described in previous sections of this chapter, and other chapters of this book, whose economic computations are a challenge for further research in this startling area of agriculture of which, perhaps, scientists have only begun to scratch the surface.

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Chapter 15

Silicon research down under: Past, present, and future

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Ninety-five percent of Australia's sugarcane is grown on the narrow coastal plain that stretches along the east coast of Queensland with rainfall ranging from 700 to 4500 mm. The most northern part of this area has a unique combination of landforms and climate (very high annual rainfall) that give rise to a specific range of soils. These soils have been under sugarcane production for up to 130 years, and apart from low levels of soluble soil Si resulting from natural weathering and leaching processes, there is evidence of declining Si levels following long-term sugarcane production. Although significant responses attributed to Si were observed in studies in the early 1970's following the application of cement, these studies were confounded by the influence of associated cations (eg. calcium) accompanying the Si source. Recent research has identified specific Si responses and delineated soils having sub-optimal levels of Si. Future research will focus on developing response functions on a range of soil types identified as Si responsive, and on assessment of the efficacy of silicate containing materials.

15.1. INTRODUCTION

In discussing Si research in Australia, we have confined ourselves to the sugar industry. This is in part due to the crop having an inherently high requirement for Si and that this industry makes a significant contribution (\$4.7 billion per year, Australian Sugar Industry Handbook, 1999) to the overall economy of Australia. However, the pioneering work of Jones, Milne and Handreck on Si in a range of soils, plants, and animals had a significant international impact (Jones and Handreck, 1963; Jones and Milne, 1963; Jones et al., 1963; Jones and Handreck, 1965; Jones and Handreck, 1967). These broad-based studies highlighted the uptake and distribution of Si in oats and wheat, and the morphological characteristics of silicified structures within these species. In addition, the studies showed the close relationship between the amount of water transpired by these cereals and Si content in selected plant components. During the same period, Beckwith and Reeve (1963a and 1963b) undertook detailed studies on the sorption and release of monosilicic acid from soils. Jones and Handreck (1963) also highlighted the importance of the effects of iron and aluminium oxides on the concentration of Si in solution.

15.2. THE AUSTRALIAN SUGAR INDUSTRY: LOCATION, SOILS AND CLIMATE

Most of Australia's sugarcane is grown on the narrow coastal strip that extends from Grafton (30° S, 153° E), in the northern part of New South Wales, to Mossman (16° S, 145° E) in far north Queensland. There is a small industry in the Ord River area in Western Australia, but this comprises approximately one percent of Australia's total production. Of the rest, New South Wales accounts for six percent and southern Queensland, 14%, leaving approximately 80% of sugarcane production north of the Tropic of Capricorn. Of this, 29% of the production is in the central area (Mackay), 32% in the Burdekin and Herbert districts, and 18% in north Queensland (Tully to Mossman) (Australian Sugar Industry Handbook, 1999). The distribution of mountain ranges along the east coast of Queensland has resulted in large river systems that frequently run parallel to the ranges to the west before cutting through to the sea. As a consequence, these rivers have built up large alluvial plains on the coastal lowlands (Hughes, 1980). It is on these coastal plains where most of the cane is grown.

In the southern growing region, rainfall is lower than in the north and the landscape has a moderate relief, with some hilly areas of basaltic metamorphic and granitic rocks and sediments. In addition, large sand dune systems dominate the coastal fringe. Texture-contrast podzolic soils are often dominant nearer the coastal fringe, while basaltic krasnozems and black earths can be locally prominent.

The most northern sugarcane region occupies Australia's only high-rainfall and humid tropical environment. The mean annual rainfall ranges from 1500 mm in most areas, to an upper limit of 4500 mm between Tully and Babinda in the north. The landscape is predominantly high mountains of acid igneous and metamorphic rocks, hilly basalt plateaux, and narrow coastal plains. The parent materials (metamorphic, granite, and acid and basic volcanic), together with the alluvium derived from them, are the main factors controlling the distribution of soils. Soil differentiation is affected strongly by the rainfall gradient from south to north (Hubble and Isbell, 1983).

Coarse grained granite and basic volcanic rocks are the dominant parent material in the northern landscape. The soils are generally deep with clay content gradually increasing with depth. As rainfall increases, soils tend towards being acidic in reaction with low inherent cation exchange capacities. Red earths are the major soils of the upper piedmont slopes and fans derived from acid rocks, while yellow siliceous sands and yellow earths dominate the lower, flatter parts of these fans. The soils formed from metamorphic parent materials are moderately deep, medium textured, structured, red or yellow loams. In contrast, the basaltic landscape is characterized by the uniform coverage of very deep, dark red, strongly structured clay soils whose chemical and mineralogical properties are closely related to rainfall and leaching intensity (Hubble and Isbell, 1983; Murtha and Smith, 1994).

Most of the soils on the narrow coastal plain are derived from alluvium, and can contain a mixture of all three major parent materials in their catchments. Except when parent material is entirely basaltic, soil distribution is largely a function of drainage. In general there is a close relationship between the landform element and soil formation. There are also small areas of beach ridges that occur adjacent to the coast, with siliceous sands on the younger and podzols on the older ridges (Hubble and Isbell, 1983; Murtha and Smith, 1994).

15.3. HISTORIC SILICON RESEARCH IN THE AUSTRALIAN SUGAR INDUSTRY

Early research on Si nutrition of sugarcane (*Saccharum officinarum*) was undertaken in the central region and on the wet tropical coast of north Queensland (Hurney, 1973; Haysom and Chapman, 1975). These studies indicated a response to Si additions in several cases when cement was used as the Si source, but the effect was strongly dependent on soil type. Further, the experiments did not clearly separate whether responses were due to Si or Ca.

The field studies carried out in the wet tropics were established as factorial experiments with cement and superphosphate as the Si and P source, respectively. Although the treatments were designed to investigate a possible relationship between Si and P, there was neither response to P or any P by Si interaction. However, yield responses to cement were recorded on a soil classified as a 'brown volcanic clay loam'. These responses were attributed to Si. Further, soil types classified as 'red loams' exhibited clear responses to cement additions at eight months, but these responses were not evident at harvest (12 months), possibly due to yield losses from lodging. On a third soil type, an 'old alluvial silty clay loam', no yield responses to amendments were observed.

On all soils, there was a corresponding increase of leaf Si levels (top visible dewlap leaf blade) with increasing rates of cement. However, there was no correlation between extractable ($0.005\text{ M H}_2\text{SO}_4$) soil and tissue Si levels. Responses on the first two soils were attributed to Si rather than Ca, as the Ca levels in the leaf were not altered by the treatments, despite increased pH and soil Ca (Hurney, 1973). Even at the highest rate of cement application, the percent Si in the leaf was approximately 0.6%, which is sub-optimal when compared to published critical levels (Wong You Cheong and Halais, 1970). It was suggested that the application rates were insufficient to fully realize the potential yield benefits.

During the early 1970s, Haysom and Chapman (1975) carried out a series of field trials in the central region on soils that were deemed to be responsive to Si additions. Rather than assessing a range of calcium silicate rates, lime and cement were compared at a single application rate (4 Mg/ha) in these studies. In all cases, significant yield increases were observed following the addition of lime and cement, with the latter treatment resulting in the highest yields. However, as for the work of Hurney (1973), attributing the observed responses in these studies directly to Si must be approached with caution as they may well have been confounded by the concomitant alleviation of a Ca insufficiency and an increase in soil pH. This is evidenced by the fact that cement was subsequently advocated as a liming product.

Studies by Ridge et al. (1980) demonstrated that the use of liming products, particularly to supply both Ca and Mg, was necessary to sustain soil fertility and productivity in north Queensland. They reported on a number of liming trials in tropical north Queensland that used different liming products, including cement; and although cement treatments resulted in the highest cane yields, they attributed this to its greater reactivity and Mg content. Despite this, cement was not recommended as a liming material in preference to calcitic or dolomitic lime because of its higher cost. However, several years later, Kingston et al. (1996) reviewed a number of liming trials across the cane industry with respect to the overall economics of liming materials, and concluded that on 60% of north Queensland sites, maximum economic returns were achieved through the addition of cement. In this respect, it is interesting to speculate that the benefit of using cement may have been in part due to its Si content as well as its ability to supply other nutrients and alter soil pH.

Recent studies in the wet tropics of north Queensland using silicated materials have substantiated the potential role of Si in increasing sugarcane yields (Rudd and Berthelsen,

1998). On a highly weathered sand, increases in sugar yields of 38% and 13% were recorded for treatments receiving calcium silicate slag and cement, respectively. Sugar yields were strongly correlated ($r^2 = 0.86$) with increases in percent Si in the leaf, which in turn, was reflected in changes in extractable soil Si following the various treatments.

Maclean (1976) reported on studies that evaluated filter mud and a filter mud-fly ash mix. In all cases, the filter mud-fly ash mix out-yielded filter mud treatments. The results were surprising as it was considered that the filter mud contained adequate nutrients for the plant crop. However, one of the constituents of fly ash is fine Si particles (approximately 40%) coated with carbon. Possibly, these particles could have improved soil structure and increased levels of soluble Si. Since an examination of undisturbed soil cores showed that there was no improvement in the physical properties (bulk density or porosity) due to treatments, it is plausible that the observed yield benefits were due in part to improved Si nutrition. Recent studies by Kingston (1999) have quantified significant increases in yield in the presence of fly ash, and this supports the above argument. In addition, Kingston (1999) observed increases in leaf and soil Si concentrations in response to applications of fly ash, and that both were well correlated with cane yield.

15.4. RECENT AND CURRENT RESEARCH INITIATIVES

Over the past decade, the sugar content of millable cane has progressively declined in certain districts of the wet tropics. The causal factors associated with this decline are still unknown. However, studies undertaken by Rudd and Berthelsen (1998) have demonstrated significant increases in sugar content with the addition of silicate based materials in the wet tropics, and this has resulted in a resurgence of research on this element. Current ongoing activities include:

- 1) the assessment of the Si status of soils that are deemed to be most at risk of having sub-optimal Si levels in the wet tropics;
- 2) quantification of both the 'intensity' and 'capacity' factors of soil Si, their relationship to other soil properties, and through the comparison of a number of different extractants, establishing an analytical method that can be used to predict responsive soils;
- 3) examination of the effects of long-term sugarcane monoculture on soil Si status, and the effect of breaking this monoculture with crop rotations;
- 4) attempts to directly attribute a response from the addition of silicate materials to Si through pot trial work.

15.4.1. Assessment of the soil silicon status

In an effort to identify soils predisposed to Si deficiency, a study to assess plant-available Si levels of sugarcane-growing soils in the wet tropics is currently being undertaken (Berthelsen et al., 1999). This region has a uniform climate and rainfall (> 3500 mm) and contains soils of basaltic, granitic, and metamorphic origins, including poorly and well-drained alluvial soils formed from these different parent materials, in addition to soils formed on old beach ridges.

Silicon analysis was undertaken on a representative range of soils from the area that included archival soil samples collected when the area was initially surveyed and mapped. Readily available soil Si, as extracted with 0.01 M CaCl₂, ranged from 1.8 to 34.8 mg/kg. This assessment clearly indicated that there was a considerable range of extractable Si. However, the majority of the soils within the region would be classified as having sub-optimal to

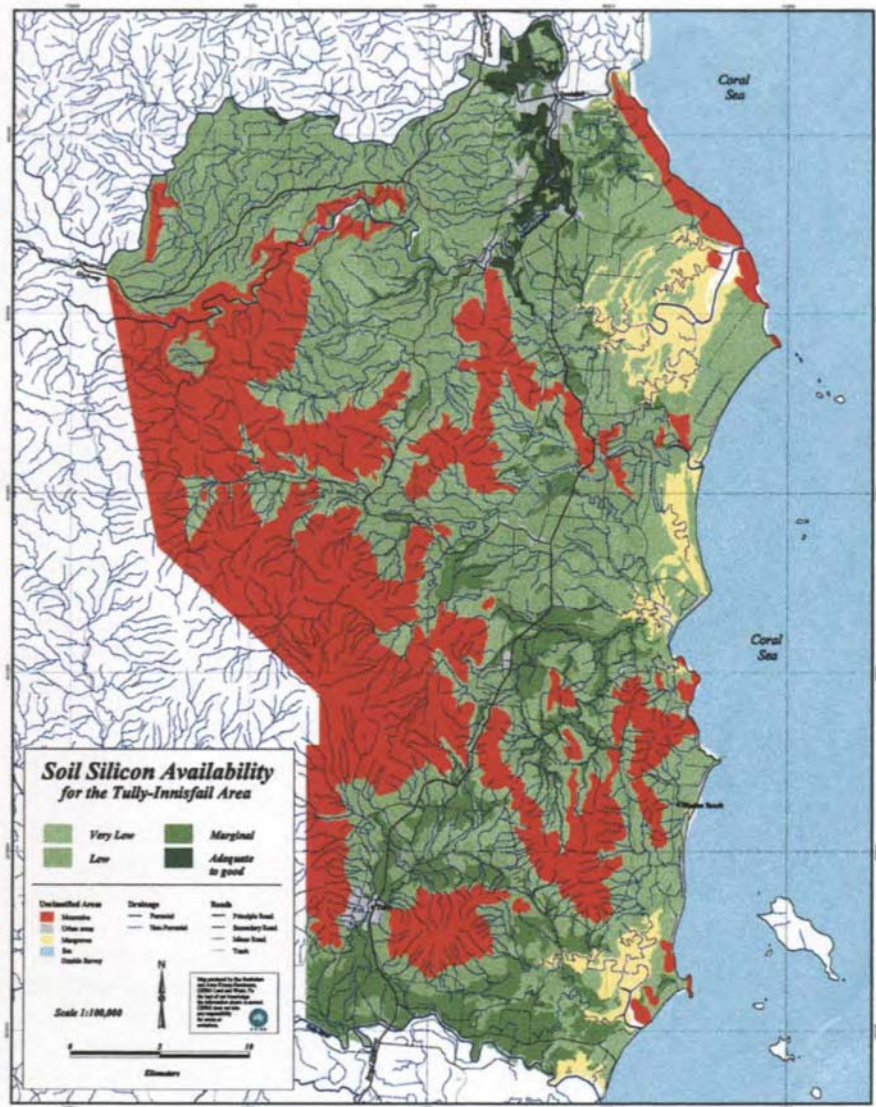


Figure 15.1. Map of the readily soluble soil Si levels for the soils in the Tully-Innisfail region in North Queensland.

marginal levels of Si for sugarcane production according to the critical value of 10 mg/kg, as defined for a CaCl_2 extract by Haysom and Chapman (1975). The basalt-derived soils have a variable range of Si levels (4.2-25.5 mg/kg), and this appears to be related to soil/landscape age. Alluvial soils have the greatest variability (2.6-34.8 mg/kg), due to a number of factors including drainage and the parent material from which they were derived. In contrast, soil

derived from beach ridge, metamorphic, and granitic parent material all have sub-optimal levels of available Si.

A Si status map for this area (Figure 15.1) has been constructed using the data collected from this assessment. For each of the soil associations mapped by Murtha (1986), a soil Si level was assigned, based on the dominant soil series present in the mapping unit. In the case of alluvial soils, cognisance was taken of the dominant geology of the surrounding area from which these soils were derived, before assigning a Si level.

The Si status map clearly delineates those soils that have sub-optimal Si levels. To further examine the significance of this to the cane industry, the ratings were incorporated into existing land suitability classes. Forty percent of the land resource in this area is classified as suitable for cane production with no or few limitations. However, 67% of this cane growing area has low levels (<10 mg/kg Si), and 28% has marginal levels (10-20 mg/kg Si). In total, 95% of the land that is most suitable for sugarcane production has inherent levels of available soil Si that could limit production if the critical levels used here are reliable indicators.

The identification of soils that have sub-optimal Si levels has not only highlighted the extent and agronomic significance of low plant available Si levels, but has also enabled a more targeted approach to further experimental work in developing management strategies to correct such situations. It is interesting to note that areas now being mapped as low in soil Si are also the same areas where a condition first known as Northern Poor Root Syndrome (NPRS) was identified. NPRS, as outlined by Egan et al. (1984), consists of poor root growth and fungal root rots that can have a major impact on crop production, and is attributed to a number of biological and non-biological factors, including fungal pathogens, nematodes, and nutritional disorders (eg. Ca and Mg deficiencies and micro-nutrient toxicities). As adequate Si nutrition is reported to provide protection from many of these situations, it is possible that sub-optimal soil Si levels in this area could have aggravated the conditions causing the symptoms involved in NPRS.

15.4.2. Comparison of analytical methods for determining soil silicon

The early studies of Hurney (1973), Haysom and Chapman (1975), and Ridge et al. (1980) primarily focussed on quantifying agronomic growth responses to Si-based materials. However, scant attention was paid to evaluating soil extractants for their ability to identify sub-optimal soil Si levels. Haysom and Chapman (1975) evaluated three soil extractants (0.01 M CaCl_2 , 0.5 M NH_4OAc , and 0.005 M H_2SO_4) for their ability to predict cane yield. Although levels of soil Si determined by all three extractants were well correlated with yield, 0.01 M CaCl_2 resulted in the most significant correlation coefficient ($r = 0.903$).

Soils collected during the aforementioned mapping exercise have been used to compare analytical methods that could be used to predict sub-optimal levels of soil Si. Six methods currently used to assess soil Si were selected for evaluation (Table 15.1).

When considering the various components that make up the Si pool in the soil, the following classification of the six extractants was made:

- dilute calcium chloride measured the easily soluble Si component;
- ammonium acetate, acetic acid and phosphate acetate estimated both the soluble and some exchangeable Si;
- citric acid and dilute sulfuric acid extractants provided an estimate of the potential pool of Si by measuring soluble, exchangeable and specifically adsorbed Si.

The correlation between the different extractants was significant, with correlation coefficients ranging from 0.81 to 0.93 for all the extractants, when compared to the readily

Table 15.1

Extractants and methodology used to determine available soil Si.

Extractant (gms soil:mls extracting soln.)	Method	Reference
0.01 M CaCl_2 (1:10)	continuous shaking for 16 hrs	Haysom and Chapman, 1975
0.5 M NH_4OAc (1: 20) (pH 4.5-4.8)	continuous shaking for 1 hr.	Fox et al., 1967; Wong You Cheong & Halais, 1970
0.5 M Acetic acid (1:10)	1 hr shake, rest 15 minutes. decant, rest 12 hours	Snyder, 1991
Phosphate acetate (1:10)(pH 3.5) [500ppm P as $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and 0.1 M $(\text{H},\text{NH}_4)\text{OAc}$]	continuous shaking for 4 hrs.	Fox et al., 1967
0.1 M Citric acid (1:50)	2 hr shake, rest O/N, 1 hr shake	Acquaye and Tinsley, 1964
0.005 M H_2SO_4 (1:200)	continuous shaking for 16 hrs	Hurney, 1973

soluble soil Si extracted with 0.01 M CaCl_2 . Si extracted with a dilute salt, in this case CaCl_2 , was found to be a reliable estimate of the Si present in the soil solution. The quantity of Si extracted by the other extractants relative to CaCl_2 was, 1, 1.5, 3, 12, and 16 times greater for the NH_4OAc , acetic acid, phosphate acetate, dilute sulfuric, and citric acids, respectively. Considering the relative amounts of Si solubilized by each extractant, the different extractants appear to be able to differentiate between:

- A - the 'readily available Si' (0.01 M CaCl_2);
- B - the 'more slowly available Si' (0.01M NH_4OAc and 0.5 M acetic acid);
- C - the 'slightly available' (phosphate acetate);
- D - the more 'insoluble and structural forms of Si' (0.1M citric acid and 0.005M H_2SO_4).

It is possible that no single measure is adequate to determine plant-available Si. However, if a single measure is required, 0.01 M CaCl_2 extractable Si is considered to be the most suitable. It would appear that the 'intensity' and 'capacity' factors associated with a soil are closely linked. Consequently, it is unlikely that readily available Si will be of a high 'intensity' in the soil solution unless there is sufficient 'capacity'. As 0.01 M CaCl_2 extractable Si represents the Si available in the soil solution, it also reflects the effects of the sorption/desorption reactions that control solubility, thus giving a true measure of current availability.

15.4.3. Effect of long-term sugarcane monoculture on the soil silicon status

The Si status map presented in Figure 15.1 is based on data collected predominantly from undisturbed rainforest sites. These data therefore represent the inherent capacity of the soil to supply Si but not their current capacity following a considerable period of agricultural activity. A decline in soil Si concentration with continued cane production has been observed and quantified in a 'paired sites' study (Berthelsen, 1997).

Table 15.2

Comparison of soil chemical analyses from the 0 to 10 cm depth increment, from a rainforest and an adjacent long-term sugarcane production system, on an alluvial silty loam (Typic Troporthent).

Soil chemical property	'Rainforest' site	'Sugarcane' site
Si (0.01M CaCl ₂), mg/kg	13.1	5.3
Si (citric acid), mg/kg	331.9	176.2
pH (CaCl ₂)	5.05	4.67
Ca, cmol (+) /kg	6.8	1.3
Mg, cmol (+) /kg	2	0.24
K, cmol (+) /kg	0.31	0.19
H+Al, cmol (+) /kg	0.18	0.45
Organic carbon,	2.3	0.93
P (0.005M H ₂ SO ₄), mg/kg	22.7	116.8
ISS (*104)	484	140

Selected soil chemical properties from a paired 'rainforest' and adjacent 'sugarcane' site are presented in Table 15.2. These sites are on an alluvial silty loam (Typic Troporthent), and the 'sugarcane' site has been under continual sugarcane production for over 30 years. There is clear evidence of a considerable decline in extractable soil Si and exchangeable bases resulting from crop export and also perturbation of the soil profile following various agronomic practices such as cultivation, burning and fertilizer additions. An index of silica saturation (ISS), as described by Herbillon et al. (1977), simultaneously takes into account the potentially soluble and sorbed Si in the soil. Although they used this index to evaluate the effects of weathering in a tropical environment, the ISS results for these two sites indicate that continual cane production has altered the soil charge properties, significantly reducing the ability for the soil to retain plant available soil Si.

It can be concluded that the long-term production of sugarcane will result in depletion of plant available soil Si. Similarly, Savant et al. (1977) suggested that depletion of plant available Si in soils used for rice production might be a limiting factor contributing to declining yields. They suggested that crop rotations using non-Si accumulator crops may allow soil Si equilibrium concentrations to re-establish, and thus naturally replenish plant available levels of Si.

Long-term crop rotation experiments established by the Sugar Yield Decline Joint Venture initiative (Garside et al., 1999) provided an opportunity to evaluate the effect of various crop rotations and fallow periods on the Si status of the following sugarcane crop. At all of these sites, cropping histories of either continual cane production, or rotations, including a mixed pasture of *Brachiara decumbens* and forage peanut (*Arachis pintoi*), break crops, using

Table 15.3

Soil Si (0.01M CaCl₂ extractable, at 0-10 cm), plant Si levels (whole leaf and tops) and yield from control (continuous cane) treatments from Sugar Yield Decline Crop Rotation trials.

Site	Extractable soil Si (mg/kg)	Plant % Si at 256 DAP	Sugar yield (t/ha)	Biomass (t/ha)
Tully	5.5	0.35	7.7	16.7
Ingham	14.5	0.83	8.1	20.5
Mackay	15.9	0.87	8.8	23.2

predominantly legume crops of peanuts (*Arachis hypogaea*) and soybeans (*Glycine max* L. Merrill), and a bare fallow treatment were established. These treatments were imposed for various periods ranging from six months to three and a half years, after which sugarcane was replanted. Plant samples were collected at 256 days after planting (DAP) and percent Si was determined on the combined leaf and tops material. The Si data from the three experiments are presented in Tables 15.3 and 15.4 (Berthelsen et al., 1999).

At all sites, the Si content of the plant tissue is clearly controlled by the levels in the soil. As the same sugarcane variety (Q117) was used at all the sites, there is no confounding effect due to varietal differences in uptake. The soil at Tully is a well-drained coarse sandy soil with low available Si (0.01 M CaCl₂ extractable) throughout the profile, increasing from 6 mg/kg at the surface to 9 mg/kg at 90 cm. In contrast, the sites at Ingham and Mackay were established on heavier alluvial soils, with a sandy clay loam surface overlying a medium clay subsoil. The available Si at both sites ranged from 15 mg/kg at the surface, increasing to >30 mg/kg at 50 cm. The data in Table 15.3 illustrates the close association between soil Si levels, plant uptake and yield, with lower soil Si levels at the Tully site associated with reduced plant Si and biomass. Data from leaf samples collected at 256 DAP (Table 15.4) indicate that over all sites, there were significantly higher Si concentrations in the leaf and tops and significantly higher contents in the stalks following the 'break' treatments when compared to continuous cane (Berthelsen et al., 1999).

Table 15.4

Plant Si levels at 256 DAP, and yield data at harvest, for the major cropping treatments, combined for the three Sugar Yield Decline Crop Rotation sites at Tully, Ingham, and Mackay (Berthelsen et al., 1999).

Cropping History	% Si leaf + tops	% Si stalk	Sugar yield (t/ha)	Biomass (t/ha)
continuous cane	0.68	0.17	5.49	13.31
barefallow	0.85	0.17	9	21.71
crop	0.79	0.16	8.85	21.81
pasture	0.88	0.17	8.44	22.11
LSD 5%	0.15	n.s.	1.62	3.83

These differences may be associated with improved plant and root health resulting from the break from cane, thus allowing better access to, and utilization of, soil Si reserves. In addition, the results indicate that the ability of sugarcane to accumulate Si is enhanced following a 'break' from continual sugarcane. Although the reasons for the substantial yield improvement following these breaks are likely to be many and varied, it seems plausible that Si may be directly and/or indirectly involved.

15.4.4. Determining a response to silicon

As previously discussed, a major limitation associated with previous research undertaken on silicate materials is the confounding effects associated with changes in the chemical properties of soils with the application of materials containing Ca and Mg and their influence on soil pH. In an effort to address this issue, a series of greenhouse pot studies were undertaken to quantify a Si response and to delineate soils that are most responsive to prophylactic applications of silicated materials. A study was undertaken on a krasnozem (soil taxonomy, Acrudox) with an inherently low extractable Si content. Treatments were designed to include two rates of calcium silicate (2.9 and 5.8 t/ha), a control treatment, and extra treatments that would add Ca without the addition of Si (using lime), and another, that would adjust pH without the addition of Ca (using NaOH). A significant response in plant height to Si additions was observed within one week of transplanting the sugarcane sett. This initial response continued through harvest 6 weeks later. At harvest, soils from each treatment were analysed for pH, Si, and basic and acidic cations. Plant height and biomass were strongly correlated with both soil solution and 0.01M CaCl_2 extractable Si levels. There was no correlation of crop growth with Ca addition or increase in soil pH (Table 15.5). A second pot study was established using three distinctly different soils. While two of the soils were selected from soil types identified as having sub-optimal soil Si levels, the third was from an inherently fertile alluvial soil with a high extractable soil Si. The soils were from sugarcane

Table 15.5
Treatments, plant and soil data (replicate means).

Time (wks)	Treatments (t/ha)						
	Control	CaCO ₃		CaSiO ₃		NaOH	LSD 5%
	0	2.5	5	2.9	5.8	2	
Plant height (mm)							
1	243	235	252	265	279	248	34
4	709	684	670	719	801	743	89
Selected soil data at harvest							
pH (1:5 water)	5	5.7	6.3	5.1	5.3	5.6	
Ca (cmol+)/kg)	1.24	3.25	5.37	1.55	1.98	1.21	0.11
Si (mg/kg)	14.5	9.2	7.8	17	18.8	15.2	2.3

fields that had been under continual production for several years. Details of selected soil properties are in Table 15.6.

To ensure that responses were not due to deficient levels of any other nutrient, basal nutrients were added to all soils according to standard recommendations. Three rates of Si were applied, equivalent to 600, 1200 and 2400 kg Si/ha, using silicic acid, calcium silicate and potassium silicate. Two control treatments, with and without basal nutrient additions, and with no added Si, were also included. The experiment was harvested after three months and plant weights at harvest were strongly correlated ($r^2 = 0.88$) with extractable soil Si regardless of soil type and initial level of available soil Si (Figure 15.2).

It can be difficult to design an experiment using silicate based materials and avoid the concomitant effects due to the other nutrient elements, and the different solubilities of Si in the material. However, the results presented from these two pot trials demonstrate yield responses in sugarcane that appear to be due to the Si content of the amendment rather than other contributing factors, and a clear association between plant available soil Si content and sugarcane yield.

15.5. FUTURE RESEARCH

The importance of Si in sugarcane nutrition has been an active area of research for several decades. From the initial research of D'Hotman de Villiers (1961) in the early 1960s, there has been a significant amount of research into the role of Si in sugarcane production systems.

Table 15.6

Details of selected soil properties of the three soils used in a greenhouse study.

Soil series	Innisfail	Mission	Maria
Soil type	alluvial, light clay	reddish brown, clay loam	black sandy loam
Soil taxonomy	Oxic, Dystropept	Typic. Haplorthox	Haplustult
Parent material	basaltic	metamorphic	beach ridge
Si (0.01M CaCl ₂), mg/kg	24	4	1.5
Si (citric), mg/kg	316	54	88
pH (1:5, water)	5	4.9	7.7
Ca, cmol(+)/kg	3.2	0.66	13
Mg, cmol(+)/kg	1	0.15	1.3
K, cmol(+)/kg	0.35	0.11	0.06
H+Al, cmol(+)/kg	0.51	0.62	0.05
Organic carbon, %	1.6	1.3	1.9
ISS (*104)	618	137	10

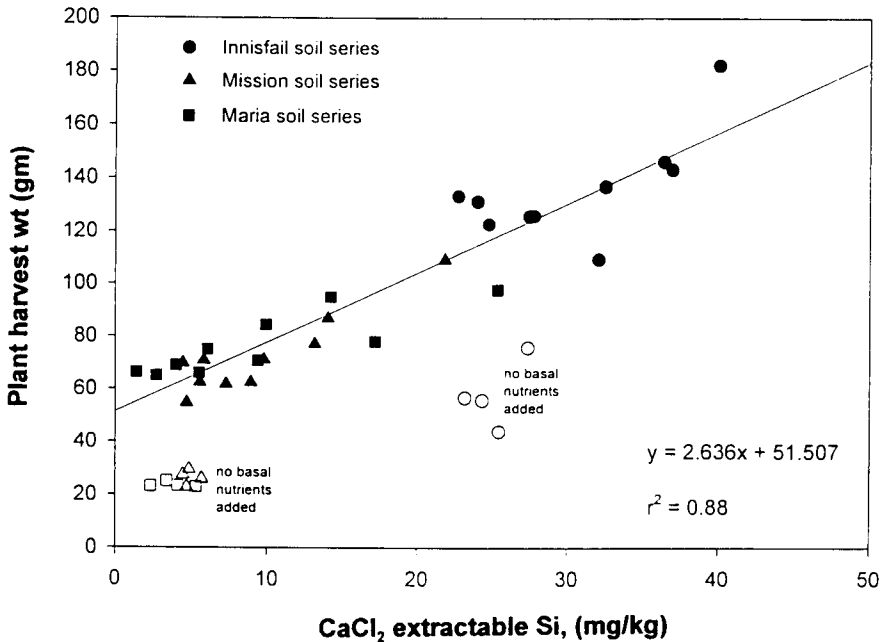


Figure 15.2. Responses to Si additions on three soil types.

Whilst it may not assume the importance of macronutrients such as N and P, it is becoming increasingly evident that within the humid tropics of Australia Si may contribute to declining yields observed in the production of sugarcane. Of importance to the sugar industry is the maintenance of productivity. In this respect, future research in the Australian sugar industry will focus on the identification of soils predisposed to sub-optimal Si levels. Concomitant with the identification of these soils, a series of field-based studies have been initiated to determine response surfaces to Si additions on soils identified as having sub-optimal levels. In addition, field-based studies to evaluate different commercial sources of Si have been established. This will enhance our ability to diagnose potential Si problems and make appropriate recommendations for its remediation.

Over the past two decades, the Australian sugar industry has moved from a burnt cane harvesting system to green cane trash blanketing. As sugarcane accumulates large amounts of Si (>1.5%) in its tops in the form of spicules, these siliceous bodies are released unaltered to the soil. These phytoliths are relatively insoluble and tend to accumulate in soil surface horizons. A possible consequence of moving to a green cane trash blanketing system may result in the 'locking up' of Si in these insoluble forms which would otherwise not occur in a burnt situation. It is suggested that further research into the bioavailability of Si in the trash of sugarcane should be undertaken. Finally, there is considerable interest in the use of silicate materials as a means of controlling root feeding insects of sugarcane. Studies are currently being undertaken to assess this aspect.

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Chapter 16

Past, present and future research of the role of silicon for sugarcane in southern Africa

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The results are summarized of a number of glasshouse and field experiments conducted since 1970, in which the relative efficiencies of calcium metasilicate slag and calcium carbonate were compared. In four out of the five field trials, significant responses, ranging from 9 to 24 tons cane/ha, were obtained in both the calcium silicate slag and lime treatments. On average, the silicon-based treatments were 5% better than the lime treatments. In one trial where the ameliorants were incorporated to a depth of 65 cm, calcium silicate increased yield significantly ($P>0.01$), whilst the response to lime did not attain a level of statistical significance. All ameliorants caused a reduction in exchangeable Al in the soil and a reduction in manganese uptake. With treatments containing silica, the increased yields were associated with an increase in the silica concentration in the plant. Current research is focused on the association between silicon assimilation and host-plant resistance to the stalk borer *Eldana saccharina* Walker (Lepidoptera: Pyralidae). Recent evidence from a large scale pot trial in which sugarcane was treated with calcium silicate and artificially infested with *E. saccharina* at 9.5 months showed significant reductions of 33.7% in borer damage and 19.8% in borer mass. Scanning of leaf samples by near infra-red spectrometry (NIRS) suggests that up to 60% of the variation in *E. saccharina* resistance could be accounted for by the leaf silicon ($R=0.60$) content.

16.1. INTRODUCTION

For many years silicon deficiency in crops was relatively unknown and this element was widely regarded as non-essential for plant growth, despite the fact that it is often present in the highest concentration among inorganic constituents. In sugarcane, silicon varies from 0.5 to 1.0% in stalks and older leaf sheaths to between 1.0 and 2.0% in cane leaves (Anderson et al., 1991).

The discovery that applications of silica may benefit cane growth was initially made in 1937 in Mauritius by a young researcher named D'Hotman De Villiers, during experimental efforts to rejuvenate highly weathered sugarcane soils by applying finely crushed basalt. In carefully conducted trials, cumulative yield responses of between 30 to 60 tc/ha were obtained over five crops to which crushed basalt was applied at rates varying from 200 to 400 t/ha. Subsequent studies based on soil and leaf analysis confirmed that it was the soluble silica in the basalt that caused the favorable yield increases.

Since this initial discovery, the application of silicate materials to soils low in soluble Si has resulted in significant responses in both cane and sugar yields in several countries, including Hawaii (Clements, 1967), Mauritius (Wong You Cheong and Halais, 1970), South Africa (Du Preez, 1970), Puerto Rico (Samuels, 1969), Florida (Gascho, 1976), Brazil and Australia (Haysom and Chapman, 1975). The observed responses to Si have been attributed to a number of factors including prevention of aluminum and manganese toxicities, improved water use efficiency, protection from insect and fungal disease damage, improved P nutrition, improved structural strength, and improved photosynthesis through better use of sunlight (Anderson et al., 1991).

Several possibilities may account for the increased frequency of silicon deficiency:

- Declining soil fertility under a system of monocropping. Sugarcane is a gross feeder of nutrients and the production of large tonnages of cane over many years on the same soil has resulted in a net export of soil nutrients in the form of molasses and filter cake. As very few countries recycle these by-products back to the fields, the capacity of the soil to supply silicon and other nutrients is greatly diminished.
- Introduction of higher yield-potential varieties which tend to have higher silicon requirements.
- Silicon deficiency could have existed but may not have been sufficiently severe to produce visible symptoms.
- Concentrated fertilizers with fewer silicon impurities are being more widely used.

The objectives of this paper are threefold:

- To review the results of past trial work in South Africa, with special reference to quantifying the yield responses to corrective applications of silicate materials in pot and field trials and to summarize soil and leaf results of past nutrient surveys to assess the silicon status of sugarcane.
- To highlight current research focused on the association between silicon assimilation and host-plant resistance to the stalk borer *Eldana saccharina* Walker (Lepidoptera: Pyralidae).
- To report on genotypic differences in foliar silicon content as determined by near infrared reflectance and the correlation with cane yield.

Table 16.1

Analysis of the humic Nomanci Oxisol sandy loam sampled from areas with and without wattle ash near Eston in the midlands of Natal.

Soil property	With wattle ash	Without wattle ash	Difference*
% Clay	22	19	NS
% Organic matter	5.5	5.6	NS
pH (water)	5.5	4.5	S
S-value (meq %)	5.9	2.3	S
CEC (meq %)	7.4	7.4	NS
% Base saturation	74	31	S
P (ppm)	22	18	NS
Si (ppm)	38	16	S
Al (ppm)	22	230	S

*NS = non-significant at 5% level; S = significant at 5% level

16.2. SILICON DEFICIENCY IN THE SOUTH AFRICAN SUGAR INDUSTRY

In South Africa, sugarcane is grown on about 400,000 ha under a wide range of climatic and soil conditions. The group of grey sandy soils, also known as Entisols, are the most extensive and account for 60% of the total area under cane (Beater, 1957). The red soils, known as Oxisols, comprise the second largest group (19%), followed by the black Vertisols (13%) and brown humic Ultisol soils (8%).

For many years, Si deficiency was relatively unknown in the South African sugar industry, but in 1967 Si deficiency, together with Al toxicity, were first identified as potential growth-limiting factors in the highly weathered Oxisol soils of the newly developed cane areas of the Natal Midlands (Bishop, 1967).

16.2.1 Wattle brush ash investigation

Sugarcane planted in fields where wattle trees have previously been grown frequently exhibit a very marked 'tramline effect'. The superior growth of cane along these lines is associated with the windrows of wattle brush which are burnt prior to land preparation. The reasons for this effect were investigated by Meyer (1970) in a field survey and through glasshouse experimentation. Analyses of soils containing wattle ash showed highly significant reductions in acidity and labile Al and increases in the amounts of exchangeable Ca, Mg, P, Si, and K. Examination of the associated sugarcane third leaf analytical data showed similar increases in nutrient levels, particularly in regard to P and K. The data in Tables 16.1 and 16.2 illustrate these effects at a site that was sampled in the Eston area.

It has been found to be of great value to test proposed treatments by means of glasshouse pot trials before embarking on long-term and expensive field experimentation. Results of pot experiments using an humic oxisol clay loam (Balgowan form) showed that the greatest responses in cane growth were obtained from the addition of wattle ash, lime or the Si treatment (see Table 16.3). A heavy application of Al salts caused a marked depression in yield and induced severe P deficiency symptoms. This negative response was more marked in the Balgowan soil series, which inherently contains large amounts of exchangeable Al.

Table 16.2

Analysis of cane leaf samples from areas with and without wattle ash.

Plant composition	Eston		Difference
	With ash	Without ash	
% N	2.3	2.26	NS
% P	0.18	0.12	S
% K	1.63	1.21	S
% Ca	0.33	0.54	S
% Mg	0.55	0.7	S
% Si	0.95	0.55	S
Fe (ppm)	230	350	NS
Al (ppm)	220	280	NS
Mn (ppm)	66	80	NS
Zn (ppm)	18	21	NS

Table 16.3

Cane yield, grown in an humic Oxisol clay loam (Balgowan form), in relation to selected treatments.

Selected treatments	Code	Yield tops + stalk G	% Diff relative to c	Root yield (g)
Control (N & K)	A	8.1	-36	1.7
Supers (single)	C	12.8	0	2.5
Sterilization	D	8.2	-36	1.2
Ash	I	19.2	+ 48	4.2
Lime	H	15.2	+ 19	2.9
Aluminium	O	4.2	-66	0.4
Al and Ash	M	11.5	-10	1.2
Silicon	L	15	+ 17	3.1
LSD (P = 9.05)		1.06	-	1.3

The main reason for yield improvement following application of either wattle brush ash appeared to have been due to a reduction in the amount of exchangeable Al, and utilization of P and Si at the higher soil pH values.

Further investigations on soils from fields under wattle, and from adjoining areas not under wattle, indicated that continued wattle production had a strong acidifying effect on the soil. This effect, under certain conditions, will cause a loss of plant available Ca, Mg, K, and Si from the soil and raise the exchangeable Al index from a level considered to be well below the critical value for sugarcane to levels that are dangerously high. The implication is that growers can anticipate an Al toxicity problem.

16.2.2. Further pot trial studies

A second pot trial with sugarcane that followed the exploratory wattle brush trial focused on comparing the relative efficiencies of limestone and various sources of Si on acid soils from the Natal midlands (Du Preez, 1970). The amendments that were applied as replicated treatments, at levels equivalent to 4, 5, 9, and 18 metric tons per hectare to a topsoil of a clay Oxisol (Balgowan form, site A) were as follows:

- Silene F (pure calcium metasilicate CaSiO_3).
- Amcor slag (a blast furnace slag).
- Sodium metasilicate (Na_2SiO_3).
- Hawaiian slag (a metasilicate slag from the same source as that used by Clements (1967)).
- Portland cement.
- Calcium carbonate (CaCO_3).

Two other soils were included from different localities, a second clay Oxisol (Balgowan form, site B) and a sandy clay loam Litosol (Glenrosa form). This time only Hawaiian metasilicate slag and calcium carbonate were applied. The levels of application and the basic dressing were the same as above. The main outcomes of the trial may be summarised as follows:

- All sources of silica except sodium silicate gave significant yield responses as indicated in Figure 16.1 and Table 16.4.
- The highest yields on the Balgowan soil were obtained with cement at 9 metric tons per hectare and Amcor slag at 18 metric tons per hectare. Both these yields were significantly better than the highest yield obtained from the addition of calcium carbonate.
- The maximum yields from the metasilicate treatments were also consistently better than those from the calcium carbonate treatments on the other two soils, the differences being far greater on the more acid Balgowan clay soils than on the less acid Glenrosa sandy clay loam.
- The greater effectiveness of the silica treatments was associated with an increase in the silicon concentration in the plant. This was probably the reason for the depression in yield observed.
- All treatments caused a substantial reduction in exchangeable Al in the soil by raising pH values, the exchangeable aluminum being strongly pH-dependent.
- A depression in yield was observed at the highest level of calcium carbonate application on both the Glenrosa and the Balgowan soil. The highest level of cement on the Balgowan (A) sample also caused a depression in yield. This depression is unlikely to be a pH effect, because the metasilicate slag, calcium carbonate and cement brought about similar pH increases on each soil as shown Table 16.4. The sodium silicate caused an alkaline soil condition due to the large amounts of sodium added to the soil.
- The maximum or highest yield for each treatment on the Balgowan samples was obtained at soil pH levels between pH 5.0 and pH 5.4 and at pH 6.2 on the Glenrosa sample. It is unlikely, however, that the increases in yield were due only to the change in pH, as large yield differences were obtained from treatments having a similar effect on pH.

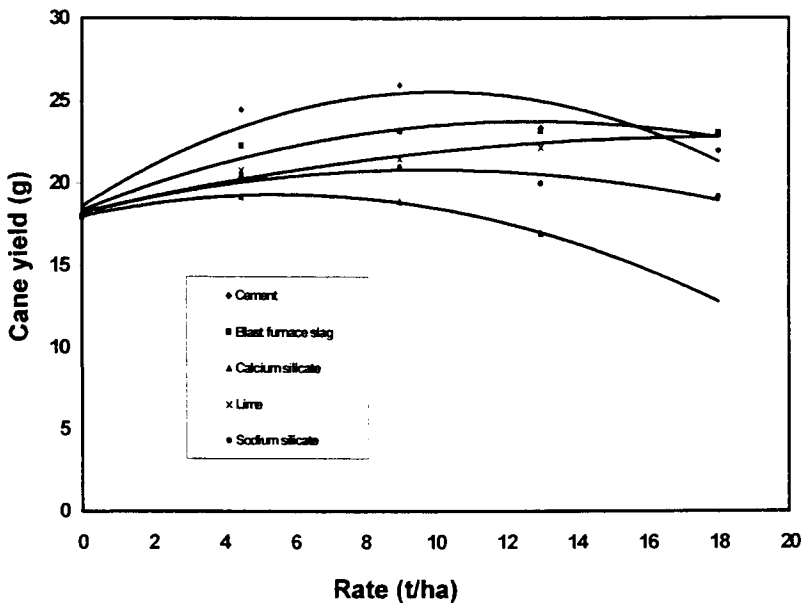


Figure 16.1. Yield responses from different sources of silicon.

Table 16.4

Yields, pH and nutrient uptake for the different soils and treatments.

Soil sample	Amendment	Level (tons/ha)	Dry matter (g)	Soil pH (H ₂ O)	Silicon (%)	Mn in tops (ppm)	Mn:Si ratio
Balgowan (A)	Control	0	19.7	4.67	0.46	360	0.079
	CaSiO ₃	4.5	20.6	4.73	0.59	278	0.047
		9	22	4.84	0.69	283	0.041
		18	23.4	5.03	0.89	223	0.025
	Blast furnace slag	4.5	22.4	5.13	0.93	363	0.039
		9	23.3	5.33	1.05	283	0.027
		18	24.8	5.57	1.31	170	0.013
	Cement	4.5	24.3	5.06	0.65	246	0.038
		9	24.5	5.37	0.81	163	0.02
		18	21.9	5.83	1.12	56	0.005
	Metasilicate slag	4.5	22	5	0.71	270	0.038
		9	23.2	5.27	0.87	166	0.019
		18	23.3	5.63	1.15	69	0.006
Balgowan (B)	CaCO ₃	4.5	20.6	5.13	0.41	307	0.075
		9	21.1	5.43	0.33	197	0.059
		18	19.1	5.82	0.30	67	0.022
	Control	0	13.6	4.49	0.55	338	0.061
	Metasilicate slag	4.5	17.3	5	0.96	230	0.024
		9	18.5	5.1	0.98	128	0.013
		18	18.4	5.45	1.42	57	0.004
	CaCO ₃	4.5	15.8	4.87	0.49	183	0.037
		9	15.9	5.13	0.35	117	0.033
		18	16.3	5.62	0.35	67	0.019
Glenrosa (Trevanian)	Control	0	11.4	4.63	0.39	428	0.116
	Metasilicate slag	4.5	13.4	5.58	0.77	93	0.012
		9	14.4	6.25	1.47	59	0.004
		18	14.5	7.17	1.53	46	0.003
	CaCO ₃	4.5	13.4	5.85	0.32	90	0.028
		9	13.6	6.72	0.32	85	0.026
		18	11.5	7.27	0.29	67	0.023

There were no significant treatment differences in the concentrations of Fe, Cu, Z, and B in the plants. A linear relation between uptake and yield was observed for all four of these elements, which indicated that none of them were deficient and that they were therefore not responsible for the yield differences.

- Calcium metasilicate at all levels increased the uptake of P by the plant. However, the addition of calcium carbonate reduced the amount of phosphorus taken up by the plant.
- The amount of Mg taken up by the plant was increased with the cement and the Amcor slag on all three soils. The treatments with cement, Amcor slag, and metasilicate slag were also the treatments from which the highest yields were obtained. Even though the levels of Mg

in these soils were at least twice the critical level of 25 ppm, it is possible that the increased yields were partly due to increased availability of Mg.

- The concentration of Mn in the plant and the amount of Mn taken up by the plant was reduced considerably by all treatments. All treatments also caused a marked reduction in the Mn to silica ratio. This was greater in the silicate than in the calcium carbonate treatments, the silicate treatments reducing the Mn concentration while increasing the silica concentration. However, the calcium carbonate treatments reduced both the Mn and silica concentrations.
- With the exception of the highest level of metasilicate slag application on the Balgowan (B) soil and the highest level of cement on the Balgowan (A), all the silicate treatments showed an increase in yield with increasing silica concentration in the plant, while the calcium carbonate treatments had the opposite effect (see Figure 16.2).
- The results of this trial closely supported the findings of Ayres (1966) that slag is more beneficial than coral stone (calcium carbonate) even though both neutralize soil acidity and diminish the solubility of Mn. Of the various Si carriers, cement proved to be the most effective in terms of yield but not on a cost basis.
- Du Preez (1970) concluded that the main factors probably responsible for the yield increases were decreased levels of Alum and Mn, and increased levels of silica in the soil. The calcium carbonate and silicate treatments decreased exchangeable Al and Mn to the same extent, and both had the same effect on pH. He considered that the increased yields could not only be due to the elimination of toxic amounts of Al and Mn, but that there is a level of soil Si below which optimum yields cannot be obtained.
- Silicate slag appears to be superior to lime because it gives higher yields and because the consequences of over-application are less harmful.

16.2.3 Past field experiments

In South Africa a total of 14 crops from six trials have been harvested to compare the effectiveness of various forms of calcium silicate slag with lime. Results of some of these experiments have been reported by Moberly and Meyer (1975) and additional results have since become available. Some of the sites on which the trials were conducted were previously under wattle while the other sites had a history of moderate to poor cane yields. Apart from dolomitic and agricultural lime, other materials such as Slagsil, Hulsar lime, Amcor slag and Hawaiian calcium metasilicate were used in a number of experiments. The chemical analyses of some of these materials and brief comments are given below.

- Amcor slag contained 37% SiO_2 , 18% Al_2O_3 , 20% CaO , and 20% MgO . It is a coarse, steel furnace residue from Amcor, Newcastle.
- Calcium metasilicate contained 49% SiO_2 , 2% Al_2O_3 , and 44% CaO . It is a fine by-product of the cement industry, imported from Hawaii.
- Slagsil contained 35% SiO_2 , 15% $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$, and 41% CaO . It is a fine material from the Slagment Co., believed to originate from Amcor.
- Hulsar lime contained 1.4% SiO_2 , 82% CaCO_3 , and 1.2% MgO . It is a fine material from the Hulett's Refinery and is known as 'filter cake'.
- Agricultural lime, the lowest analysis of which contained 46% CaCO_3 and the highest 82% CaCO_3 with varying quantities of MgO .

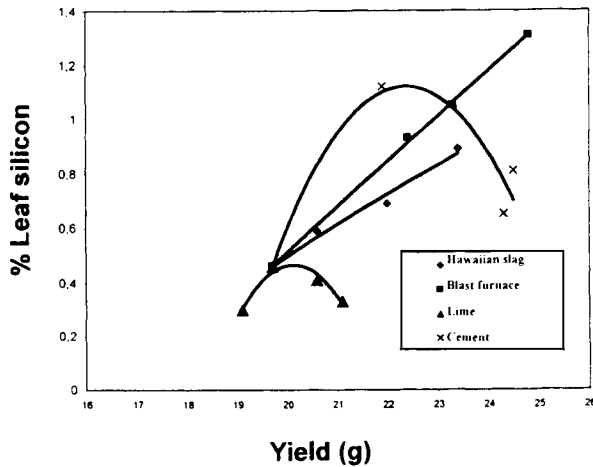


Figure 16.2. Relation between leaf silicon and yield.

In most of the experiments, the ameliorants were applied to the plots only a matter of days prior to planting. To ensure reasonably uniform application of ameliorants, each treated plot was subdivided into six approximately equal parts and a measured quantity of material was broadcast over each subdivision. With the exception of two sites where ameliorants were ploughed down to a depth of 60 cm, disc harrows or rotary hoes were used to incorporate ameliorants to depths of 10 to 25 cm. The responses obtained to the various sources of silicon and lime, expressed as the percentage increase in tons cane/ha over the yield obtained in the unameliorated control treatment, are summarized in Table 16.5.

The main outcomes of these field trial investigations were as follows:

- Of the 14 crops harvested, responses to Si treatment were significant ($p=0.05$) in nine instances compared with the six responses that were significant with lime treatment.
- In the three trials where different levels of ameliorants were tested, significant responses to calcium silicate were obtained in the plant crop in the two trials at sites 1 and 2. However, at site 1, there was no response above the 5.6 t/ha calcium silicate treatment in any of the three crops (see Figure 16.3).
- In the same trial at site 1, Hulsar lime, dolomitic lime, and Amcor slag were also compared at a rate of 5.6 t/ha (see Table 16.6). Hulsar and dolomitic lime were equally effective on all three crops. The Amcor slag, a much coarser material than either of the lime materials, increased yield over control significantly in all three crops, but produced yields consistently (although not statistically significantly) lower than did the two forms of lime.
- At Site 5 on the Balgovan soil, the Hawaiian calcium metasilicate and agricultural lime were compared at 5.6 t/ha, while the Hawaiian calcium metasilicate was compared with Slagment at 11.2 t/ha (see Table 16.7). The response to ameliorants was relatively small and attained a level of statistical significance (<0.05) only in the case of the silicate materials. There was no statistical evidence that the higher level of the Hawaiian silicate was superior than the South African product Slagment.

Table 16.5

A summary of yield responses obtained from the application of calcium silicate and agricultural lime in various field experiments.

Site	Locality	Ameliorant	Soil form	Pre-treatment soil analysis (0-25 cm)				% change in yield		
				pH (water)	Ca (ppm)	EAI (meq %)	Clay	Plant (%)	1st ratoon	2nd ratoon
1	Townhill	Hawaiian silicate (5.6 and 11.2 t/ha) and Amcor slag (5.6 t/ha)	Clovelly	4.8	104	215	53	+27**	+16*	+35**
		Dolomitic lime (5.6 t/ha)						+26**	+18*	+29**
2	Seven Oaks	Hawaiian silicate (5.6 and 11.2 t ha ⁻¹) and slagsil (11.2 t/ha)	Clovelly	4.2	120	2.57	61	+13*	-	-
		Agricultural lime (5.6 t/ha)						4	-	-
3	Seven Oaks	Slagsil (20 t/ha/60 cm)	Clovelly	4.6	270	1.93	45	+15*	+32**	+53**
		Lime (20 t/ha/60 cm)						6	-16*	+47**
4	Upper Tongaat	Hawaiian silicate (5.6 and 11.2 t ha ⁻¹)	Inanda	4.8	360	0.33	22	1	-	-
		Agricultural lime (5.6 t ha ⁻¹)							Nil	
5	Mowbray	Slagsil (1 t/ha in furrow)	Griffin	4.6	10	2.6	19	+16*	6	+16*
		Hulsar lime (6.6 t/ha/20 cm and 20 t/ha/60 cm)						+16*	7	8
6	Kranskop	Calcium silicate (2 t/ha lime) vs dolomitic lime (2 t/ha)	Hutton	5	207	2.3	45	7	8.5	7.6

**Statistically significant, $P < 0.01$; *Statistically significant, $P < 0.05$

- Of particular interest is the comparison between lime and the silicate materials in the two Seven Oaks experiments on the Clovelly soil. In the one case, where the ameliorants were both applied to a depth of approximately 65 cm, Slagsil increased yield significantly ($P > 0.01$) for the first two crops, whereas the response to lime did not attain a level of statistical significance (Table 16.8). The superiority of Slagsil over lime was approximately 11%. In the second experiment where the ameliorants were applied to a conventional depth of about 25 cm, responses were small but the trend was again in favour of Slagsil by approximately 5%. There was no evidence of the siliceous materials being more active than limestone as a soil ameliorant and, similar to the finding from the pot trial, there was a strong likelihood that Si was beneficial as a nutrient.

Table 16.6

Yields in t/ha obtained from plots treated with Hulsar lime, dolomitic lime, and Amcor slag applied at 5.6 t/ha to a Clovelly form soil.

	Control	Hulsar lime	Dolomitic lime	Amcor slag	SE treatment means
Plant	78	101	104	96	± 4.23
1st ratoon	67	82	82	78	± 3.48
2nd ratoon	51	74	75	66	± 4.99

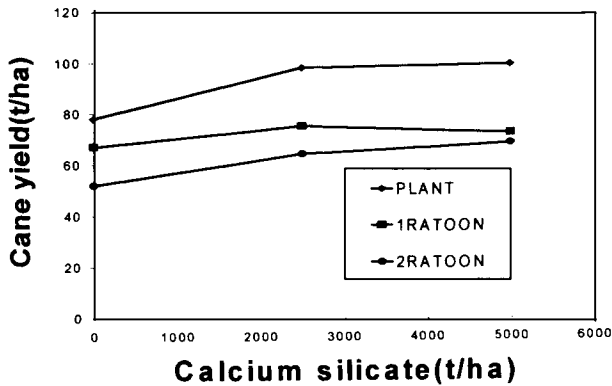


Figure 16.3. Sugar cane yield response to silicon.

- At site 4 on the Trevanian soil, Amcor slag was also compared with agricultural lime, but no response was obtained to treatment with either material.
- The imported Brazilian variety CB36/14 and the Natal variety NCo376 were included in the experiments at sites 2 and 3. Results from the plant crop indicated that CB36/14 was slightly more sensitive than NCo376 to treatment with slagsil and lime. These results are shown in Table 16.9.
- Soil sampling to a depth of 20-25 cm was carried out with a Mount Edgecombe sampler before treatments were applied, and thereafter, at the start of each ratoon crop. At that time, the soil properties that were monitored included pH, exchangeable bases, P, and exchangeable Al. Unfortunately, no tests were carried out to measure plant-available Si in soils.
- In general, the pH of treated soils tended to increase gradually with time. The effect of the various ameliorating materials on soil pH was naturally a function of fineness and purity. In this regard, only the Amcor silica slag material did not perform as well as the standard liming materials. However, in the other trials, both the slagsil and imported Hawaiian slag generally performed as well as the standard lime treatments in raising pH. In the same trial (site 2), the Hawaiian slag at both the low and high rates was more effective in increasing the plant available Ca levels than the other ameliorants.

Table 16.7

Yields in tc/ha obtained from plots treated with Hawaiian calcium metasilicate, agricultural lime and slagment applied to a Balgowan series soil.

	Control	Agric lime (5.6 t/ha)	Hawaiian silicate (5.6 t/ha)	Hawaiian silicate (11.2 t/ha)	Slagment (11.2 t/ha)
Plant crop	91	95	98*	103*	102*

SE treatment mean \pm 3.6; CV% 8.9.

Table 16.8

Residual effectiveness of a silicon treatment versus limestone incorporated to a depth of 60 cm (tc/ha).

Crop stage	Control	Extra P	Lime	Slagsil
Plant	116	128	123	133**
1 st Ratoon	97	113	113	128**
2 nd Ratoon	47	70**	69**	72**
3 rd Ratoon	97	113	115*	114*
4 th Ratoon	46	59*	60*	59*
Average	81	97	96	101

**Statistically significant, $P < 0.01$; *Statistically significant, $P < 0.05$.

16.3. CURRENT RESEARCH INITIATIVES

16.3.1. Evaluating the influence of silicon treatment on the resistance of sugarcane to the stalk borer *Eldana saccharina* Walker (Lepidoptera: Pyralidae)

There is increasing evidence from the literature that in a wide range of crops, nutrients, such as nitrogen (N) and Si, play important roles in susceptibility and resistance to stalk borer damage. In 1982, it was shown by local researchers that excessive N usage increased the incidence of eldana damage in sugarcane (Atkinson and Nuss, 1989), and recommendations for N were subsequently modified. Studies conducted in Nigeria on the maize borer *Sesamia calamistis* have shown that increasing N doses significantly increased larval survival from 18 to 37%, while increasing the silica supply reduced larval survival from 26 to 4% (Setamou et al., 1993). As *E. saccharina* is still endemic in the South African sugar industry, there is a need to investigate whether the Si content of sugarcane is linked to borer resistance.

A replicated split-plot trial, using six commercial varieties of sugarcane planted in pots containing river sand, was established in a shade house. Two treatment levels of calcium silicate (2500 and 5000 kg/ha equivalent to 425 and 850 kg/ha of pure Si, respectively) were applied at planting and again at six months. Controls received no calcium silicate. Leachate and leaf samples taken from all treatments confirmed that Si levels in the growing medium and the plant itself were in accordance with applied treatment levels. The plants were artificially infested with *E. saccharina* at 9.5 months and the trial was harvested six weeks

Table 16.9

Varietal response to lime and slagsil as % increase over unlimed control on Griffin and Clovelly form soils.

	Variety	Lime	Slagsil	Mean
Site 1	NCo376	-6	+2	-2
	CB36/14	+9	+16	+13
Site 2	NCo376	+13	-	+13
	CB36/14	+17	-	+17

Table 16.10

Effect of applied silicon on resistance of sugarcane to *Eldana saccharina*.

Calcium silicate rate (t/ha)	Average stalk yield (g)	Stalk length damaged (cm)	Number internodes bored	Total borer numbers	Total borer mass (g)
Control	1035	114	112	110	115
2.50	1203	100	100	98	93
5.0	1220	87	88	92	92
CV%	22	48	37	39	45
LSD(p=0.05)	132	19	15	16	18
F value	4.6	7.7	10.4	5.1	6.0

later to record *E. saccharina* numbers and mass (borer performance) and borer damage. Some of the preliminary results have been reported (Keeping and Meyer, 1999) and since then further results have become available (Table 16.10).

The main outcomes from this trial may be summarised as follows:

- There was a significant overall response of 16% in stalk production to the first level of calcium silicate. Additional calcium silicate treatment at the high rate resulted in no further yield benefit.
- Variety N11, which is known to be highly susceptible to *E. saccharina*, was the only variety that showed a linear response in stalk yield to the intermediate and high rates of calcium silicate. Of the other two susceptible varieties, NCo376 showed a significant response to the intermediate level of Si, whereas the response from N16 was not significant. Of the three varieties that are more tolerant to the borer, a significant response to the 2.5 t/ha calcium silicate treatment was obtained for varieties N17 and N21. Variety N12 showed no yield benefit from treatment with calcium silicate.
- Silicon treatment resulted in a significant reduction in both borer performance and borer damage (F value=5.1; $p<0.05$). In general, borer mass was reduced by about 19% and borer damage by 33% between the controls and the 5 t/ha treatment level. Values for the 2.5 t/ha treatment were intermediate between controls and the higher treatment. When resistant and susceptible varieties were combined in the analysis, the interaction between variety and silicon treatment became significant (F=3.6; $p<0.05$). The two susceptible varieties (N11 and N16) and the intermediate resistance variety (N17) showed the greatest effect of resistance from silicon treatment (Figure 16.4).
- All varieties showed a positive response in silicon uptake with silicon treatment. On average, the intermediate Si treatment doubled the stalk Si content from 0.16 to 0.33%. Thereafter, additional Si resulted in a curvilinear increase from 0.33 to 0.38%. In general the more susceptible varieties showed the highest Si uptake. (Figure 16.5).
- The length of stalk damage was inversely correlated with the Si content of the cane stalk (4th order polynomial $R^2=0.47$). The most susceptible variety (N11) showed the greatest benefit in terms of reduced stalk damage from Si treatment and this coincided with the largest percentage increase in Si content in the stalk. In contrast, the more resistant varieties such as N21 showed the lowest rate of increase in Si content in the stalk (Figure 16.6).

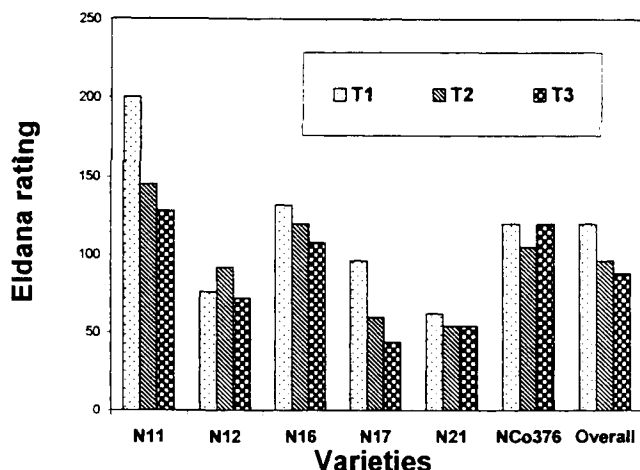


Figure 16.4. Effect of calcium silicate treatment in reducing eldana damage.

- Results indicate that calcium silicate application in the field may achieve a substantial increase in resistance of sugarcane to *E. saccharina* attack, along with improved sucrose yields.

16.4. POSSIBLE REASONS FOR INCREASED SILICON DEFICIENCY IN THE SUGAR INDUSTRY

Our nutrient information retrieval system, based on historical soil analyses done by the Fertiliser Advisory Service of the sugar industry, has indicated that soil acidification has greatly increased in the coastal cane areas. This has come about mainly through shorter cane cycles during the past two decades (1979-99), which has had the effect of increasing the intensity of cropping and nitrogen usage compared with the previous two decades (1959-79). Under increasing levels of soil acidification, Si availability and uptake by the plant may be impaired, and it is possible that a lack of Si will reduce stalk hardness and increase susceptibility to borer. In a recent assessment of 230 leaf samples from 12 regional variety trials, covering 15 cane varieties, both ash and Si content of TVD leaf samples were negatively correlated with *E. saccharina* resistance ratings ($R=-0.61$ and -0.63). Under a system of continuous cane monocropping without rotation, sugarcane has the potential to remove substantial amounts of Si from the soil. A 100 t/ha crop of cane can remove up to 300 kg/ha of Si, while an excess of 500 kg/ha Si can be removed under very high yielding conditions (Anderson, 1991). Monosilicic acid is rapidly utilised by sugarcane and, unless it is replenished, plant-available Si will become depleted. The visual symptoms of Si deficiency in sugarcane appear as minute white circular leaf spots on older leaves. Leaves may senesce prematurely and tillering may be poor.

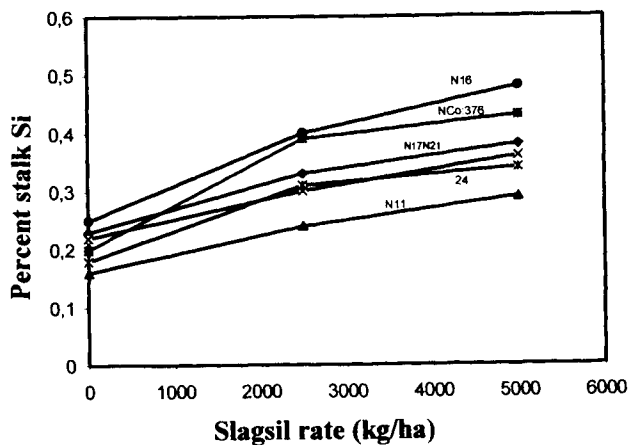


Figure 16.5. Effect of silicon treatment on stalk silicon content.

16.5. METHODS OF SOIL AND LEAF ANALYSIS USED AT THE EXPERIMENT STATION

In the South African sugar industry, 0.5 N ammonium acetate extractant adjusted to pH 4.8 (Ayres, 1967) was used in early investigations (Bishop, 1967), but in recent years the modified Truog 0.02 N sulphuric acid (Fox et al., 1967) has been found to correlate better with leaf Si analyses. In a previous survey of the Si status of soils in the sugar industry, it was found that

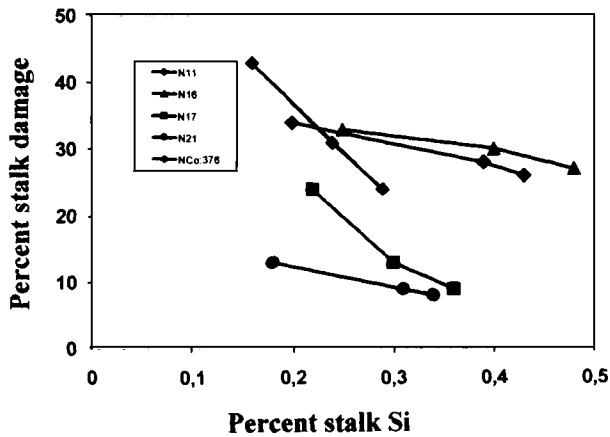


Figure 16.6. Stalk damage in relation to stalk silicon content.

Si extracted from soils with the modified Truog method were moderately well correlated with clay content (Figure 16.7). In general, the results tend to suggest that Si can build up in soils with more than 30% clay. Mollisol and Vertisol soils containing 2:1 lattice clays were found to be the best supplied with Si, usually in excess of 50 ppm extractable Si.

Foliar diagnosis has been used to great advantage in determining the nutrient status of sugarcane and is widely accepted as a means of improving the effectiveness of fertilizer use. With the introduction of X-ray fluorescence and near infra-red reflectance NIR (Wood et al., 1985), leaf analysis has become more accessible as a diagnostic tool. It compares favourably with soil analysis in correlating with fertilizer responses and provides a useful check on the uptake of fertilizers already applied. For diagnostic purposes, a threshold value of 0.70% has been adopted for Si. Investigations with the Diagnosis and Recommendation Integrated System (DRIS) (Meyer, 1981), in which nutrient indices derived from ratios between nutrients, rather than nutrient percentages in the leaf, have indicated that this system can help to expedite corrective fertilizer treatment of the crop that has been sampled. Since nutrient ratios vary less than nutrient percentages as the crop ages, diagnosis on irrigated cane can be made at two months, compared to four months with the conventional approach. Of interest, is that ratios containing Si as a nutrient show the best correlation with cane yield. The K:Si is especially significant in identifying high yielding cane.

16.6. NEAR INFRA-RED REFLECTANCE

Near infra-red reflectance (NIR) analysis is a technique in which sugar industries worldwide are showing increasing interest. Its potential applications are to soil fertility, cane nutrition, cane quality testing (Meyer, 1996), and the possibility of screening for resistance to certain pests and

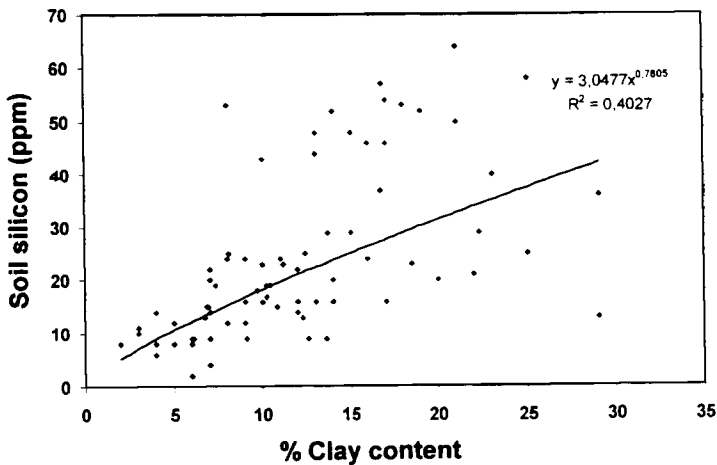


Figure 16.7. Soil extractable silicon versus clay content.

diseases (Rutherford et al., 1993). NIR has the potential to detect key constituents such as starches, sugar, cellulose, lignin, proteins, water, amides and also certain constituents linked with S, Mg, Ca, and K. As part of a project to evaluate the merit of NIR scanning of cane leaves for assessing crop performance, 400 top visible dewlap leaf samples collected from 20 regional variety trials scattered throughout the cane regions, were used to determine possible relationships between yield parameters, leaf composition and NIR reflectance measurements. Results from irrigated trials at Pongola showed that NIR absorption spectra of leaf samples from 4-5 month old cane, in the 2238 to 2500 μm range, were positively correlated with cane yield ($r = 0.91$) and negatively correlated with pol% ($r = 0.82$) at 12 months. Accuracy of the calibration equations was tested on five independent data sets and, although the correlation coefficients for validation were lower (0.60 to 0.86), the results were sufficiently promising to continue this field of study.

Photosynthetic rates were measured on 70 leaf samples from one of the variety trials using a portable infra-red gas analyser (Inman-Bamber, 1995). The samples were then scanned by NIR, both in the fresh and dried state, in the 1100 to 2400 μm region. Step-wise regression analysis showed that photosynthetic rate and internal CO_2 determined concentrations were highly correlated with NIR absorption values ($R > 0.95$). The wavelengths that were selected for the calibration equation (2139 μm , 2100 μm , and 2190 μm) were consistent with the third overtone stretching vibrations of C-O, O-H, and C-H bonds associated with carbohydrate compounds as well as second overtone N-H bending modes found in proteins. Various investigators have also demonstrated positive correlations between leaf photosynthetic rate, chlorophyll, and soluble protein content (Dornhoff and Shibles, 1976). Leaf photosynthesis in various crops has also been positively correlated with leaf greenness, as non-destructively measured by a hand held portable chlorophyll meter (SPAD-502) (Ma et al., 1995). Examination of the NIR data showed that 30% of the variation in photosynthetic rate could be accounted for by variation in leaf N. Photosynthetic response to increasing light intensity is strongly dependent on leaf N (Ludlow et al., 1991). Surprisingly, the other element that accounted for a significant variation (37%) in photosynthesis was leaf Si content. It has been shown, under normal light, that silica deposited in silica cells and stomatal guard cells could serve as 'windows' allowing more light to pass through the epidermal to the photosynthetic mesophyll tissue (Lau et al., 1978), thus enabling higher rates of photosynthesis and more tillers per plant. This could partly account for the significant relationship that was obtained between cane yield and leaf ash content in the Pongola data set ($r = 0.68$), as silica comprises about 70% of the ash in sugarcane.

Leaf NIR scanning is also under investigation as a means of predicting host *E. saccharina*, mosaic, and smut resistance in cane. Preliminary results using 230 leaf samples from trials on 12 commercial varieties suggest that up to 60% of the variation in *E. saccharina* resistance could be accounted for by absorption of constituents in the NIR region. Further investigation into likely cause and effect relationships suggests that some of the resistance was linked to leaf Si ($R = 0.60$) and N content ($R = 0.39$).

16.7. CONCLUSIONS AND FUTURE RESEARCH

The results of the early glasshouse and field experiments agree very closely with the findings of Clements (1967) and Ayres (1966). Ayres mentioned that slag is more beneficial than coral stone (calcium carbonate) even though both neutralize soil acidity and diminish the solubility of Mn and Al. He concluded that there is a level of soil silica below which optimum yields cannot be

obtained. The main factors probably responsible for the yield increases are decreased levels of Al and Mn, and increased levels of silica in the soil. The calcium carbonate and silicate treatments decreased exchangeable Al and Mn to the same extent, and both had the same effect on pH. It is considered therefore, that the increased yields cannot be due only to elimination of toxic amounts of Al and Mn. Silicate slag appears to be superior to lime because it gives higher yields and because the consequences of over-application are less harmful.

Even though the function of silica in the plant is still not clear, there can be little doubt that Si plays a beneficial role in sugarcane. Future research will focus on field studies to quantify the yield response to calcium silicate applied to sandy soils of the Cartef and Glenrosa forms, to evaluate the role of Si in reducing the effects of moisture stress using the newly constructed rain shelter facility and to confirm the linkage with reduced *eldana* infestation in field trials. There is also a need to evaluate the biochemical role of Si in improving sucrose production.

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Chapter 17

Review of research in Japan on the roles of silicon in conferring resistance against rice blast

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In 1917, Onodera first showed that rice (*Oryza sativa* L.) plants affected by blast tended to contain less silicon than healthy ones. This was probably the first report that suggested an effect of silicon on blast resistance. Since then, many researchers have demonstrated that applying silicon to the soil causes higher silicon levels in rice and, as a consequence, an increase in blast resistance. Several hypotheses to explain this phenomenon were proposed up to 1950. Most importantly, the fact that silicon is mainly localized in the leaf surface supports the hypothesis that the silicon layer may act as a physical barrier against blast fungus penetration. However, this cause-effect relationship has not yet been fully accepted. Application of silicon to commercial rice paddy fields became popular after the effectiveness of readily available silicate slag on blast was demonstrated in 1952. The use of silicate slag reached a peak in the early 1970s. However, the amount of research has declined since the 1960s because the interest of most blast researchers has changed to investigating other blast countermeasures such as fungicides and host plant resistance.

17.1. INTRODUCTION

Rice blast, caused by the fungus *Magnaporthe grisea* (Hebert) Barr (the anamorphic state is *Pyricularia grisea* (Cooke) Saccardo) (Rossman et al., 1990) is one of the most serious threats to rice production in Japan, as well as most of the other rice production areas in the world (Ou, 1985). The disease has often caused severe quantitative and qualitative yield losses in Japan. Historically, rice has been the main diet of the Japanese, and rice production has been an important part of the domestic economy. Hence, research on rice and rice production has been emphasized in agricultural science. Research on rice blast also has attracted much attention in plant pathology.

Since Japan changed from the feudal system in 1868, the government has aggressively pursued the introduction of science and technology from western countries. For example, during the 1870s, many foreign agricultural scientists were invited to Japan to teach their respective disciplines to Japanese students. In the mid 1880s, these students became professors and started to provide lectures in plant pathology at their universities. In the late 1890s, the first scientific papers about rice blast were published (Shirai, 1896; Hori, 1898). Of course, most of the literature was written in English or German. However, most of the scientific papers written by the early Japanese researchers were published in Japanese, and this tendency has continued until recently. Consequently, few foreigner researchers could obtain information from this Japanese literature. Japanese agricultural scientists also considered their studies on rice production to be only a domestic issue, and did not foresee a need to publish information overseas.

Much of the scientific literature written in Japanese contains valuable information worth publishing overseas. In other words, this literature should have received critical discussion among international scientific societies. It is typical that research on the role of silicon in enhancing resistance of rice to blast has been mainly discussed among Japanese researchers. Now that this research has attracted considerable worldwide attention, Japanese researchers have the responsibility to introduce and review the advances made in this area in Japan. In this article, I will review the important literature published in Japan dealing with silicon and rice blast.

17.2. RICE BLAST

In Japan, rice blast has been recognized since the late 17th century. Matsumoto (cited by Ono (1928) noted that the first description of rice blast disease in Japan was in 1680. In 1896, Shirai identified the causal fungus as *P. oryzae* Cavara, although the specific name has since been debated (Asuyama, 1965; Rossman et al., 1990). The causal fungus is airborne and can infect all the aerial parts of the rice plant (*Oryza sativa* L.), such as leaves, neck, nodes, and panicles. Conidia of the fungus land on rice plants and germinate when the relative humidity on the rice surface is high. Appressorium forms at the end of germ tubes following conidial germination. The appressorium, an organ of the fungus, strongly adheres to the surface of the rice epidermis. Matsuura (1928) and Sueda (1928) independently found that the fungus penetrates through appressoria into the rice epidermis, and not into stomata or open wounds of the epidermis.

17.3. RECOGNITION OF THE ROLE OF SILICON IN RICE RESISTANCE

Hori (1898) enumerated several conditions that might cause severe outbreaks of blast, such as

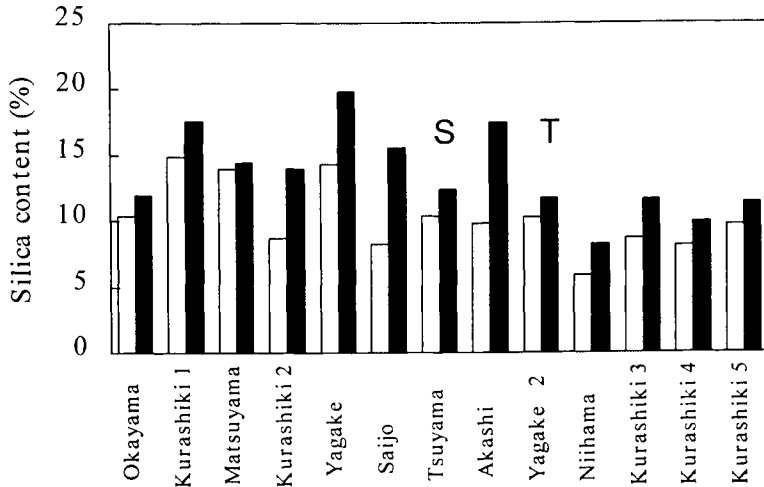


Figure 17.1. Comparison of silica content (per dry weight) from healthy and blast infected rice plants, collected from various regions. White bar: diseased plants; black bar: healthy plants; S: cultivar 'Shotoku'; T: cultivar, 'Tsurachima-bozu'. Cultivar of other fields was 'Sinriki'.

excess plant N content, and cloudy and wet weather conditions. However, he did not refer to Si. Probably, the first researcher who suggested Si in relation to rice blast was Isenosuke Onodera (1888-1953), a plant nutrient chemist. He graduated from the Imperial College of Agriculture and Forestry, Morioka (the present Iwate University) in 1910. He then visited Königsberg University in Germany and Cambridge Agricultural University in England from 1910-1915. Afterwards, he was appointed as a researcher at the Ohara Institute of Agricultural Research (the present Research Institute for Bioresources, Okayama University). In 1917, he published a milestone paper entitled 'Chemical studies on rice blast disease'. For this study, he collected rice plants from 13 different regions in western Japan. Then, he compared the chemical composition of the rice plants infected with blast with that of healthy ones grown in the same paddy field. Three different cultivars were included in the samples, with rice plants in each field sampled, consisting of one cultivar (Figure 17.1). The diseased rice plants always contained less silica than the healthy ones obtained from the same field. Thus, the natural silica content found in these plants depended on the paddy field in which they had been grown. However, this result did not necessarily mean that blast infection was reduced by the silica content of the rice plants, or that plants with less silica content were more susceptible. It just showed a relationship between silica content and susceptibility. Actually, the original objective of this paper was to merely assess the effect of blast infection on nutrient acquisition in the rice plant. He did not intend to explore the role of Si in blast resistance of the rice plant. Still, the result certainly stimulated research on the role of Si.

In 1922, Miyake and Adachi (1922) compared silica contents of two rice cultivars. They examined a susceptible cultivar, 'Akage' and a resistant cultivar, 'Bozu' at three different growth stages. Silica content of Akage at heading, flowering, and milky dough stages were 1.68, 2.27, and 2.92 % (per fresh weight), respectively, and that of Bozu were 1.93, 2.53, and 3.32%, respectively. Obviously, Bozu contained more silica than Akage did at these growth stages. Consequently, they proposed a possibility that more resistant rice cultivars tended to contain more silica.

Kawashima (1927) first demonstrated with pot experiments that application of silica to rice plants increased resistance to blast, as well as increased silica content of rice plants. He applied different amounts of silica gel or solid silica to the soil where rice plants were grown. Then, he evaluated the severity of panicle blast occurrence, and measured silica content of the plants. The results showed that the silica content of the straw and husks were proportional to the amount of silica applied, and that the severity of panicle blast was inversely proportional to the amount of the silica in plants (Figure 17.2). Ito and Hayashi (1931) and Miyake and Ikeda (1932) also showed that the application of silica increased resistance to blast. Inokari and Kubota (1930) demonstrated that application of silica to peat land paddy fields reduced incidence of blast, too.

17.4. HYPOTHESES TO EXPLAIN HOW SILICON CONFERS RICE RESISTANCE

During the 1920s and 1930s, severe rice blast epidemics frequently occurred at the same time cool weather was damaging rice production. These yield losses triggered serious social problems, which may have contributed indirectly to the rise of totalitarianism and militarism in Japan. Then, the Japanese Ministry of Agriculture and Forestry decided to establish a government grant for research on rice blast at two imperial universities and four local agricultural experiment stations. Until 1945 (the end of World War II), most of the work on rice blast was conducted under this project.

Until the early 1930s, there was a general consensus that Si played a role in resistance to blast

and that application of silica to rice plants increased resistance. Since then, the main thrust of the research has shifted to investigating the mechanism of the resistance that Si confers. Researchers have suggested several hypotheses. These can be classified into two types: 1) Si might contribute to mechanical resistance against fungal penetration. 2) Si might change the physiological characteristics of rice plants.

17.4.1. Morphological aspects of the mechanical barrier hypotheses

Ito and Hayashi (1932) suggested that application of silica gel to rice increased the number of silicified cells on the epidermis, thus, increasing the resistance to blast. Consequently, blast resistance and silicified cell density on the epidermis were correlated. Many researchers tried to test their hypothesis concerning whether some of the morphological and anatomical characteristics of rice related to Si nutrition could confer resistance to blast.

Since Hemmi and Suzuki (1933) introduced the ash figure method (1920), Hemmi and his colleagues also tested the same hypothesis using this method. The ash figure method was originally developed for botanical taxonomy. A plant specimen is burnt and the ash is observed with a microscope. Silica opal in silicified cells is well preserved in the ash, and the species or the conditions that the plant was grown in can be identified.

Suzuki (Suzuki, 1934; Suzuki, 1935a; Suzuki, 1935b; Suzuki, 1937) compared the number of silicified cells per unit leaf area of rice plants grown at different soil moisture levels and different amounts of applied N and silica. At that time, it was already known that rice plants grown at low soil moisture (Hemmi and Abe, 1932), and with high N application (Miyazaki, 1928; Bokura, 1930) were more susceptible to blast, and that silica application increased the resistance (Kawashima, 1927; Inokari and Kubota, 1930; Ito and Hayashi, 1931; Miyake and Ikeda, 1932). He confirmed these results by showing that rice plants with a high density of silicified cells always

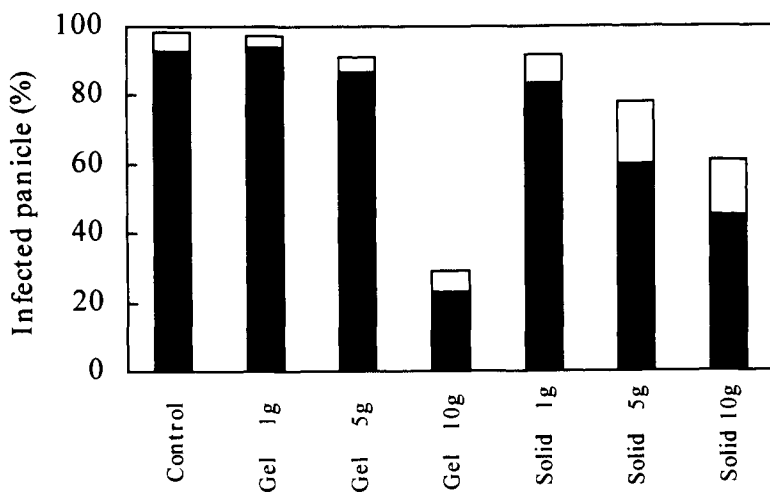


Figure 17.2. Effect of silica rates on panicle blast incidence. (1, 5, and 10g/pot). Each pot contains 4kg sandy soil. Black bars: heavily infected panicles; blank bars: slightly infected panicles; Gel: silica gel; Solid: solid silicate.

had more resistance than those with fewer silicified cells. Thus, he concluded that an increase in the number of silicified cells per unit leaf area was closely related to the resistance of rice plants to blast.

Hemmi et al. (1941) showed that silica application to rice plants increased not only resistance to blast, but also the density of silicified cells on the epidermis. Akai (1938) and Hemmi (1942) compared the morphology and blast resistance of rice plants grown under conventional field conditions with those cultivated using integrated disease management practices. This management included an earlier transplanting date and drying the field later. They showed that rice plants grown using this strategy had a higher density of silicified cells on the epidermis and were more resistant to blast. Akai (1938) and Hemmi (1942) then compared the morphology and blast resistance of rice grown as seedlings in wet nursery beds with those grown in arid nursery beds. They showed that plants grown in wet nursery beds possessed more silicified cells per unit leaf area and were more resistant to blast than those grown in dry nursery beds. Hemmi (1942) asserted that silicification of epidermal cells, including motor cells, must be one of the causes of increased resistance to blast. Akai (1938, 1939) also stated that silicification of the epidermal cells can change the susceptibility of rice plants to this disease, or must at least be a part of this effect. Akai (1959) later reviewed his studies. However, Kawamura (1942) criticized these conclusions as only speculative. He stated that even though morphological and anatomical characteristics, such as the number of silicified cells on the epidermis, existed, it did not necessarily follow that this was the mechanism that conferred resistance to blast. Sakamo (1937) also disapproved of their conclusion for the same reason.

On the other hand, Yoshii (1919) showed that most infections occurred in motor cells. Ito and Shimada (1927) observed that the appressoria could be formed on various types of epidermal cells, such as motor cells, long cells, short cells, and guard cells, and the penetration could occur through these cells in almost the same way. However, they also observed that most fungal penetrations, followed by lesion formation, occurred at motor cells and only a few occurred at long and short cells next to guard cells. Adding to that, Suzuki (1940) found that no appressoria were formed on silicified cells, consequently, no penetration occurred at the silicified cells. These observations somewhat filled the gap that Kawamura (1942) indicated. However, even if penetration did not occur at the silicified cells, the increase in the proportion of silicified motor cells does not quantitatively explain the increase of resistance to this disease.

17.4.2. Physical aspects of the mechanical barrier hypotheses

Several other researchers introduced more reductionistic approaches to explain the mechanical barrier idea. They formed a hypothesis that more resistant plants have more mechanical resistance to penetration. Another hypothesis was that application of silica to rice plants would increase mechanical resistance of the epidermis against fungal penetration, and consequently, could also increase the resistance to blast.

At that time, several researchers tried to relate disease resistance of potato (*Solanum tuberosum*) against *Pythium debaryanum* (Hawkins and Harvey, 1919) or *Berberis* spp. against *Puccinia graminis* (Melander and Craigie, 1927) to puncture resistance of the host plant epidermis. They measured the puncture resistance by a Jolly balance. A Jolly balance consists of a hung spring, a fine needle attached to the spring facing downward, and a stand on which a plant specimen is placed. After the tip of the needle is touched to the surface of a leaf specimen, the spring is gradually pushed until the surface is punctured, and the pressure is measured.

Several researchers in Japan, almost simultaneously, but independently, introduced the Jolly balance to test their hypotheses, and obtained somewhat conflicting results. Ikata et al. (1931)

measured the puncture resistance of different cultivars and those with different fertilizer application treatments. They tested whether or not more resistant rice plants have more mechanical resistance to penetration but did not measure silica content in the plants. They observed considerable variation of susceptibility between the plants. However, they found no clear correlation between the puncture resistance and blast resistance. Later, Sakamoto (1968) noted that the tips of the glass needles they used were around 100 μm in diameter and might be too large.

On the other hand, Sakamoto (1968) tested another hypothesis that application of silica to rice would increase mechanical resistance of the epidermis against fungal penetration, and consequently could increase the resistance to blast. He intensively conducted a series of experiments during 1937-1939, and his results were circulated to a limited number of researchers as internal reports. Publication of his research was delayed until 1968 when he was 60 years old. Sakamoto used a modified Jolly balance with a fine steel needle, whose tip was a conic trapezoid shape with a diameter of about 30 μm . After each measurement by the Jolly balance, he microscopically observed the punctured cell, and evaluated the degree of silicification of the cell as well as determining the cell type (as motor, long, short, or guard cell). He repeated this measurement on various parts of the leaves, and also on different cultivars, leaf positions, and plants with different amounts of silica. Figure 17.3 shows the results of his experiments on the second uppermost leaves of non-silicified motor cells, where fungal penetration, followed by infection, easily occurs. The results showed that the puncture resistance of epidermal cells (Figure 17.3, A) and resistance to blast (Figure 17.3, C) increased with the amount of silica applied to the plants. Hence, there was a correlation between puncture resistance and blast resistance (Figure 17.3, D). This result strongly suggested that Si application increased puncture resistance of the epidermis, and this increase might contribute to the resistance to blast fungus penetration of the epidermal cells. This result strongly supported the mechanical barrier hypothesis.

However, this was only partial evidence and did not necessarily mean that a cause and effect relationship existed between high puncture resistance of rice epidermal cells (especially on non-silicified motor cells of the upper leaves) and resistance of rice plants to fungal penetration. Actually, Sakamoto (1968) later criticized a shortcoming in his own results. He suggested that additional experiments must be conducted to show how much pressure the penetration pegs of blast fungus could apply at their point of penetration and how much puncture resistance could prevent this penetration, in order to deduce if the higher puncture resistance of the epidermis could confer resistance to blast penetration.

In his results, there was another apparent correlation between silicified cell density and blast resistance, as many other researchers have demonstrated (Ito and Hayashi, 1931; Suzuki, 1934; Suzuki, 1935a; Suzuki, 1935b; Suzuki, 1937; Hemmi et al., 1941; Hemmi, 1942; Akai, 1938; Akai, 1939). However, he did adopt a hypothesis that the silicified motor cells might play a major role in resistance of rice plants to blast. This is the same reason that Kawamura (1942) criticized studies that intended to relate morphological properties of rice plants and blast resistance.

On the other hand, Yoshii (1941a; 1941b; 1941c) disagreed with the results that Sakamoto demonstrated. He measured puncture resistance of rice epidermis using a Jolly balance of a different specification from that used by Sakamoto (1968). He showed (1941a) that silica application increased both silica content of the rice plants and resistance to blast. However, he demonstrated that the puncture resistance of rice plants was not proportional to the amount of silica applied. Yosii (1941b) designed a factorial experiment combining silica application (2.6t/ha silica gel) with nitrogen application treatments. He evaluated the severity of blast, silica content in the rice leaves, and puncture resistance of the leaf epidermis (Table 17.1). In this experiment, silica application increased blast resistance and silica content of rice leaves. Also, rice plants with higher

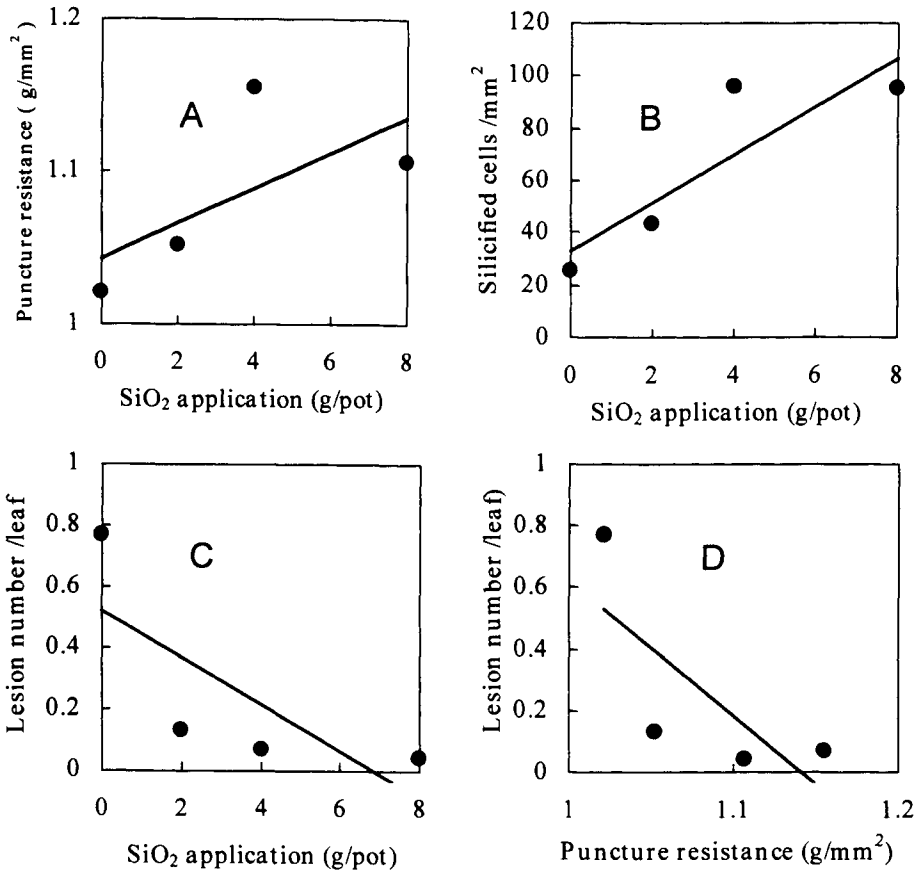


Figure 17.3. Effect of silicon rates on puncture resistance of non-silicified motor cells, density of silicified cells and rice blast susceptibility. The second upper-most leaves of 'Bozu' were tested.

silica contents showed higher puncture resistance within each silica application treatment. However, the puncture resistances of rice plants with silica application were lower than those without silica application, at least within each N application level. Disease occurrence in rice plants with silica, however, was always less severe than that without silica. He concluded an interaction existed between N and silica, and the puncture resistance would not always be proportional to Si content in the rice plants.

While the argument between Hemmi (Hemmi et al., 1941; Hemmi, 1942) and Akai (1938, 1939) versus Sakamoto (1968) and Kawamura (1942) was based on the differences of their scientific philosophy, the debate between Sakamoto and Yoshii was based on the differences of data they obtained. Later, Sakamoto (1968) noted that the method that Yoshii employed might be somewhat rough and lacked reliability. Unfortunately, the aggravation of World War II suppressed their research funding.

Table 17.1.

Effect of silica and nitrogen application on severity of blast, silica content in rice leaves, and puncture resistance of the leaf epidermis. The evaluation and sample collection were conducted on 27 August, 1938 at flag leaf stage. The values for puncture resistance were an average of 20 replications.

Nitrogen (kg/ha)	Disease severity		Silica content (%)		Puncture resistance (g/mm ²)	
	SiO ₂	Non	SiO ₂	Non	SiO ₂	Non
187.5	**	****	6.71	3.74	719.88	938.3
150	**	****	8.69	4.71		
112.5	**	**	8.9	5.97	916.07	960.54
75	0	0	9.7	6.07		
36.5	0	0	10.93	8.46	941.71	1055.23

17.4.3. An hypotheses emphasizing the physiological roles of silicon

Even though the hypothesis that Si nutrition plays a role as a component of mechanical resistance to fungal penetration is the most plausible one to this researcher, several researchers have explored other possibilities. Since silica application might increase the efficiency of photosynthesis, changes in the amount of biomass and nutrients might also occur. Thus, the effect of silica has to be considered along with its effects on other nutrients, such as N, which plays an important role in blast resistance. For example, the results of Yoshii (1941b) (Table 17.2) suggested that silica could influence some of the physiological characteristics of rice, such as N content.

Akimoto (1939) proposed to use the SiO₂/N ratio to indicate susceptibility of rice plants. That is, rice plants with a higher SiO₂/N ratio should be less susceptible than those with a lower SiO₂/N ratio. Because this ratio could explain blast susceptibility relatively well, several researchers interested in disease forecasting have used this ratio as an index to describe rice susceptibility for blast (Yobayashi, 1963). However, the significance of this ratio on the mechanism of blast resistance is not clear.

17.4.4. Could silica explain cultivar resistance for blast?

Generally, it is agreed that rice plants with higher silica content are more resistant than those with a lower content, at least within the same cultivar. Until the 1930s, many researchers considered that this relationship could be extrapolated into cultivar differences for blast resistance. Miyake and Adachi (1922) first showed that a resistant rice cultivar, Bozu, contained more Si than a susceptible cultivar, Akage.

While they referred to only two cultivars, Suzuki (1934, 1935a, 1937) compared several morphological and anatomical characteristics of the rice leaf epidermis of more than 8 cultivars with varying degrees of blast resistance. He showed a correlation between some characteristics, such as the density of a silicified cell in a leaf epidermis, and resistance to blast.

Akimoto (1939) compared the uptake rates of SiO₂, N, and the SiO₂/N of 15 cultivars per unit periods using hydroponic experiments. The cultivars included 13 lowland and two upland rice

Table 17. 2

Blast resistance, leaf epidermal puncture resistance, and silicon and nitrogen content of various rice cultivars grown in hydroponic culture.

Cultivar	Disease severity ^a	SiO ₂ (%) ^b	Total N (%) ^b	SiO ₂ /N
Kamairazu	*****	2.75	4.35	0.63
Asahi	*****	2.46	3.9	0.63
Ban-Jinriki	****	2.68	4.21	0.64
Aikoku	**	2.74	4.28	0.64
Shinju #1	**	2.42	3.9	0.62
Sensho	0	2.28	4.45	0.51
Kameji	**	2.35	3.86	0.61
Guinbozu	***	2.42	4.31	0.56

^a Disease severity was assessed 10 days after inoculation.

^bPercent dry weight of leaf blade.

cultivars. He noticed the more blast resistant cultivar, such as Rikuu #132 and Mubo-Aikoku, had higher uptake rates of SiO₂ than those of the more susceptible ones such as Kamenoo #1.

However, Hashioka (1942) showed that the density of silicified cells in the rice leaf epidermis was not always proportional to cultivar resistance for blast, based on the comparison of resistant Taiwan rice with susceptible Formosan rice. Ikata et al. (1931) demonstrated that the puncture resistance of five cultivars measured with a Jolly balance was not proportional to cultivar resistance for blast, although they did not measure silica content in this experiment. In this study the cultivar Kameji had the highest puncture resistance followed by Sensho, Kyushu #8, Omati, and Sohachi, while Sensho had the highest blast resistance followed by Kameji, Sohachi, Kyushu #8 and Omachi. Yoshii (1941) compared blast resistance, puncture resistance, measured with a Jolly balance, SiO₂ content, and total nitrogen of eight cultivars, as well as those tested for SiO₂/N (Table 17.2). He concluded that the cultivar resistance of rice to blast was not correlated with these physical and chemical properties of the plant.

The discussion of Yoshii (1941) cited above seemed to be decisive for many younger plant pathologists at that time, especially those who were concerned with the dynamic physiological functions of cell protoplasm on host resistance expression. Around 1940, Sakamoto also seemed to change and began to develop his concerns concerning the physiological aspects of resistance to blast. He (1968) expressed that the difference in cultivar resistance to blast seemed to depend on the function of host cell protoplasm. However, it may be necessary to review their results (Ikata et al., 1931; Hashioka, 1942; Yoshii, 1937) again. Most of the cultivars tested were those selected from conventional cultivars. Kiyosawa et al. (1979a, 1979b) showed that these cultivars would possess no race specific resistant genes. On the other hand, Sensho and Sinju #1 were cross bred with a Chinese upland rice strain (Iwatsuki, 1937) to introduce non-race-specific resistant genes. Thus, the cultivars they compared may be only a mixture from different origins. These facts meant that their results did not necessarily deny the existence of a genetic correlation between silica

content and resistance for blast.

17.5. INTRODUCTION OF SILICATE SLAG TO RICE PRODUCTION

Before the 1940s, there were many studies to show that silica application to rice plants could increase resistance of rice to blast, as described above. However, there was no suitable source of silica for practical use. Suzuki and Shigematsu (1952) introduced the use of silicate slag as a control measure for rice blast. He first used the silicate slag from a blast furnace in Korea in 1944. He applied 0.2-1.6 t/ha of silicate slag (calcium silicate, 60% SiO_2) to the soil. Unfortunately, he examined only the density of silicified cells in the rice epidermis and did not evaluate disease severity. However, this stimulated many experiments to confirm the effect of silicate slag for blast control.

For example, Nakagawa and Kobayashi (1956), Kitani et al. (1960), and Ishida and Shiraishi (1971) demonstrated that calcium silicate, from silicate slag, controlled occurrences of blast considerably. On the other hand, Ichikawa and Kuroiwa (1959) suggested that calcium silicate applications did not show significant control of blast. However, Kitani et al. (1960) suggested their results could be due to the soil already containing adequate levels of plant-available Si and, as a consequence, would not respond to Si application. Since rice plants contained around 14% silica, Ichikawa and Kuroiwa (1959) suggested that the effect of calcium silica application on blast control might depend on soil conditions.

Kitani et al. (1960) demonstrated that the combination of calcium silicate with fungicide application showed an additive effect. Hashimoto and Hirano (1976) designed factorial experiments that included calcium silicate application, N fertilizer level, fungicide application, and rice cultivars. They showed that application of calcium silicate (2t/ha) was effective for controlling blast in susceptible cultivars and/or high N level. and, in these cases, calcium silicate application supplemented the effect of fungicide application.

Although these field experiments were actively conducted from 1950 to 1970 and the practice of using calcium silicate was widely disseminated, research to understand the mechanism of how Si could confer blast resistance almost completely declined after the end of World War II. We suppose there are several reasons for this decline. Introduction of effective fungicides and highly resistant genetic resources for blast resistance might have discouraged plant pathologists from investigating this issue. The most plausible mechanical barrier hypothesis may not be attractive to plant pathologists whose interests were in molecular biology.

17.6. STILL A MECHANICAL BARRIER HYPOTHESIS?

Yoshida et al. (1962a, 1962b, 1962c) and Yoshida (1965) demonstrated that Si absorbed from rice roots moved through the transpiration stream and became deposited in the epidermal tissues of transpiratory organs. The Si formed a cuticle-silica double layer at the surface of the epidermis, and excessive silica might collect in silicified cells. This suggested that the silicified cells may be only an indicator to show that rice has absorbed a considerable amount of Si. He suggested that what confers resistance to penetration by the blast fungus should be the cuticle-silica double layer and not the silicified cells.

However, most plant pathologists still hesitate to accept this mechanical barrier hypothesis. The

fact that the blast fungus could penetrate into the epidermis using enzymatic activity can not be excluded. Also, the mechanism which allows the cuticle-silica double layer to confer enough resistance to prevent mechanical penetration has not yet been quantitatively explained from a viewpoint of material mechanics.

Recently, Howard (1994) demonstrated that the blast fungus could penetrate into a polyethylene surface from appressorial turgor pressure. De Jong (1997) estimated the pressure up to 8 MPa. Although the possibility that the fungus may also use enzymatic activity for penetration remains (Howard et al., 1991), these recent findings strongly support the mechanical barrier hypothesis.

17.7. CONCLUSIONS AND PERSPECTIVE

Looking back on the history of Si research in Japan, its amazing how many researchers have enthusiastically tried to demonstrate how Si could confer resistance to blast development. These efforts have definitely contributed to a better understanding of the role Si plays.

So far, we are in agreement on several points. Application of Si to rice plants increases blast resistance as follows: rice plants with higher Si content are generally more resistant to blast, if the general genetic background of the plants are the same. Silicon as a component of the cuticle-silica double layer of the epidermis probably confers resistance to penetration by the fungus as a mechanical barrier. The fact that the leaf epidermal cells of rice plants with higher silica content, together with higher blast resistance, had generally higher puncture resistance supports this hypothesis. However, this hypothesis has not yet been proven because quantitative evidence is lacking to support this mechanical barrier hypothesis to date.

Although this mechanical barrier hypothesis seems to be the most plausible explanation, other hypotheses that suggest Si plays a different role in blast resistance cannot be rejected. While testing these hypotheses is an urgent issue at the moment. I do believe a comprehensive understanding of the role that Si nutrition plays in the rice plant is essential to establish better blast management strategies.

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* [J], [JE], or [G] at the end of the reference indicates papers written in Japanese, in Japanese with English summary, and in German, respectively. A journal's name without the corresponding English name are given with their pronunciation followed by their literal meaning in English in the parenthesis.

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Chapter 18

Silicon from rice disease control perspective in Brazil

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Rice blast and grain discoloration are mainly responsible for significant losses in grain yield and quality both in upland and irrigated ecosystems in Brazil. Rice (*Oryza sativa* L.) planting in rotation with soybean in extensive, contiguous areas and high input technology provided a conducive environment to diseases which were hitherto unimportant, such as sheath blight in irrigated rice and take-all in upland rice. Even though varietal resistance constitutes a major component in rice disease management, it should be integrated with long-term benefits of silicon (Si) fertilization. A field study conducted with genotypes showing wide variability for grain discoloration and different rates of SiO₂ showed promising results. Initial greenhouse inoculation tests are encouraging in controlling leaf blast at the vegetative phase with Si. The logical extension of firmly established existing concepts on Si and rice disease management should rely on multidisciplinary approach and inter-institutional collaboration. Extensive on-farm trials at hot spot locations for diseases will compliment the experimental results and increase the speed and efficacy in accomplishing the desired goals.

18.1. INTRODUCTION

Brazil is a major rice producing country in the South American continent, where five million hectares are annually grown under upland and irrigated conditions. Upland rice occupies approximately 70% of the total area, and is planted in extensive areas in the savannas known as Cerrados *Sensu lato*. Irrigated rice is mainly concentrated in the states of Rio Grande de Sul and Santa Catarina. Cerrado vegetation in Brazil represents 21% of the 8.5 million km² area of National territory. The predominant soils (56%) classified as Oxisols (Typic Haplustox) are characterized by a plain or slightly undulated topography with excellent physical properties but with serious limitations in relation to chemical characteristics. The most important limitations in chemical properties include low fertility, elevated levels of acidity, low cation exchange capacity (CEC) and high phosphorus fixation capacity. These limitations are attributed mainly to the advanced degree of weathering of these soils. However, they could be made highly productive with the application of appropriate amendments and fertilizers. Among the amendments that have demonstrated good soil improvement in cerrado soils found mainly in Central Brazil, calcium or magnesium silicate slags have eliminated the problems caused by soil acidity, and furnished adequate quantities of Si to plants.

Silicon oxide (SiO₂) is the most abundant mineral, in tropical soils and constitutes a base

structure for the majority of the clayey soils. In tropical Oxisols, as a result of Si depletion in the soil profile due to weathering, SiO_2 is found in the form of quartz, opal ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) and other insoluble forms that are not available for the plants.

Soils, poor in Si, are also poor in other essential nutrients. Besides the importance of Si in inducing resistance of the rice plant to diseases and insect pests, the application of silicates increases grain yield. This positive effect can be attributed to the corrective action of Si amendments and the increased availability of Si, phosphorous (P), calcium (Ca), and magnesium (Mg) to plants. In Brazil, research on Si has recently been initiated, but the available data is not adequate to make recommendations of fertilization with Si slag.

The necessity of Si fertilization to the rice crop in Brazil has not been widely evaluated as in other countries. The preliminary data on soluble Si analysis in some areas of Central Brazil indicated available Si content in acetic acid 0.5 M varying from 8.8 to 66.4 mg L^{-1} with an average of 31.5 mg L^{-1} (Barbosa Filho, personal communication). However, as the range is wide, it is possible that in some areas Si deficiencies may occur where the response of rice to this element is expected. Thus, it is important that a large number of experiments should be conducted with the objective of studying the effects of Si application on diseases and grain yield. The literature on current and past investigations on Si nutrition of rice in different parts of the world has recently been reviewed by Savant et al. (1997).

18.2. MAJOR RICE DISEASES AND THEIR IMPORTANCE

The economic, social, and political implications of losses in grain yield and quality caused by rice diseases are well recognized. These losses are caused by the interaction of diverse factors such as degree of cultivar resistance, virulence of the pathogen, and climatic and edaphic conditions. In Brazil, both in upland and irrigated rice ecosystems, the major diseases that are directly responsible for yield losses are rice blast, caused by *Pyricularia grisea* (Cooke) Sacc.; grain discoloration, caused by several fungi (*Bipolaris oryzae*, *Phoma sorghina* (Sacc) Boerema, Dorenbosch & Van Kesteren, *Alternaria padwickii* (Ganguly) Ellis, *Sarocladium oryzae* (Sawada) W.Gams, *Curvularia* spp., *Nigrospora* spp., *Dreschlera* spp., *Fusarium* spp., etc.); and leaf scald, caused by *Microdochium oryzae* (Hashioka & Yokogi) Samuels and Hallett. In irrigated rice, sheath blight caused by *Rhizoctonia solani* Kuhn has become endemic in the state of Tocantins.

To integrate disease management practices, it is necessary to have an appreciation of how crop growth, grain yield, and quality are affected by diseases at different growth stages. Disease effects, such as duration and severity of stress, are dependent on nutrition-plant-pathogen interaction. In upland rice, leaf blast at the vegetative phase causes dead tillers and in some cases, total death of plants, besides its negative effect on photosynthesis and respiration. Leaf scald at the booting stage paralyzes growth and development of plants, decreases photosynthetic leaf area, and produces an uneven crop stand, resulting in panicles with differences in maturity, making harvest difficult. Panicle blast appears 7 to 10 days after heading and the effects are direct in reducing filled grains. Grain discoloration starts earlier than panicle blast if the rains coincide with heading and continues until maturity. A similar sequence of occurrence of these diseases is followed in irrigated rice.

Upland rice, in the past, was usually grown for one or two years after clearing the cerrado, using low N levels to reduce the cost of implanting pasture. Now, it is widely cultivated in rotation with soybean or maize in the favorable upland rice growing regions, mainly in the state of Mato Grosso, using high input technology. There is a growing tendency to use high N levels at the time of

planting in an attempt to increase the yield levels of improved rice cultivars in unfavorable upland conditions by supplementary irrigation. Both leaf and panicle blast have been shown to increase with an increase in N level from 15 to 60 kg ha⁻¹, and decrease grain yield in experiments conducted with a widely grown upland rice cultivar IAC 47 (Farias et al., 1982). Moreover, application of N in the furrow at planting increased blast as compared to split applications (Santos et al., 1983). Several cultivars with different degrees of rice blast resistance and superior grain quality have been developed, but the degree of resistance is not complete. The increased use of N and cultivar susceptibility are responsible for significant yield losses. The yield decrease caused by blast in the recently released cultivars ranged from 300 to 3000 kg ha⁻¹ (Prabhu et al., 1995).

Although irrigated rice has been mainly concentrated in the southern states of Brazil, in recent years, its cultivation has been extended to the states of Tocantins and Mato Grosso de Sul, where diseases constitute the major yield constraints. The tropical climate and the problems associated with crop management, due to lack of sufficient water for irrigation, favor high levels of disease incidence, resulting in yield losses which are staggering in dimension. The newly introduced blast resistant cultivars such as Rio Formoso and EPAGRI 108 and 109 broke in a period of one year causing widespread leaf blast epidemics in the state of Tocantins during the 1998/99 growing season (Prabhu and Filippi, 1999). The farmers resorted to fungicide control which amounted to 14% of the total cost of production in the state of Tocantins, where 70,000 ha are annually planted in contiguous areas. The rice and soybean rotation in this state has increased sheath blight incidence to a level that is causing concern to the farmers.

18.3. RICE BLAST

Breeding for blast resistance is the most commonly adopted control strategy. The recently released improved rice cultivars are susceptible to blast, and the susceptibility increases with increase in frequency of matching races to the genes in the host with time. Even though the yield potential of these cultivars is very high and they possess acceptable consumer-preferred grain quality, blast susceptibility is causing concern to the farmer and requires alternative methods of control with no or low additional cost. If severe panicle blast occurs during the grain formation stage, most of the commercial rice cultivars produce none to extremely low yields in farmers' fields.

Silicon fertilization has been shown to induce resistance to blast in rice by several investigators (Suzuki, 1935; Volk et al., 1958; Kozaka, 1965; Silva, 1971; Kim and Lee, 1982; Kim et al., 1986; Aleshin et al., 1987; Yamauchi and Winslow, 1987; Datnoff et al., 1991, 1992; Osuma-Canizales et al., 1991; Winslow, 1992; Correa-Victoria et al., 1994; Kumbhar, 1995; Seebold et al., 1995; Berni et al., 1999; Paéz and Clavijo, 1999). Recent investigations have brought attention to the importance of blast disease control with Si slags. According to Datnoff et al. (1991), rice grown in soils deficient in Si were highly susceptible to blast and the incidence of blast could be decreased by 30% with the application of Si. At Nuncheia in Colombia (Paéz and Clavijo, 1999), blast severity was shown to be more greatly reduced in irrigated rice cultivars with the application of potassium silicate (SiOK) than with magnesium silicate (SiOM) as source. Soil, fertilized alone or in combination with a fungicide, reduced blast incidence and increased yield (Datnoff et al., 1994). The residual effect of Si fertilization on blast control has been shown in field trials conducted in Florida and Colombia (Correa-Victoria et al., 1994; Datnoff and Snyder, 1994). In an examination of 12 genotypes, susceptible for rice blast, from a Si-grain discoloration field trial

under upland conditions in Brazil, both leaf and panicle blast severities were reduced with the application of 800 kg ha^{-1} of SiO_2 (Figures 18.1 and 18.2).

A greenhouse experiment was conducted utilizing five rates of wollastonite (0.1, 0.2, 0.4, 0.8, and 8.0 g kg^{-1} of soil) and two irrigated rice cultivars, Metica 1 and IR 50. Artificial inoculations were made on 21-day old plants using an isolate of *P. grisea* belonging to the race ID-14. The blast severity decreased with increase in doses of wollastonite, resulting in increased growth at the vegetative phase (Figure 18.3). The disease severity significantly reduced from 43% to 9% and 25% to 3% in rice cultivars Metica 1 and IR 50, respectively, at 4.0 g kg^{-1} of soil, in relation to non-amended soil (Figure 18.4).

A preliminary greenhouse experiment was conducted with three slags of iron furnace from COSIPAR (Marabá -PA), VIENA (Açailândia -MA), and SIMARA (Marabá -PA) with the objective of exploring the Brazilian sources of Si slags. The treatments included five rates of these slags (0, 2.0, 4.0, 8.0, and 16.0 g kg^{-1} of soil) and two irrigated rice cultivars, Metica 1 and IR 50. Under controlled greenhouse conditions, inoculations were made on 21-day old plants with a spore suspension of a monosporic isolate previously identified as race ID-14. The results showed a significant decrease in leaf blast severity and increased dry matter with increased application rates. However, the Si slags from COSIPAR and VIENA were superior to SIMARA. The source from COSIPAR suppressed blast severity from 70% to 34%, whereas the source from VIENA reduced blast from 70% to 54%, at the rate of 2.0 g kg^{-1} of soil, corresponding to 2.0 Mg ha^{-1} (Figures 18.5 and 18.6). At the same rate, the dry matter increased from 1.5 g in non-amended soil to 2.6 g and 3.2 g in amended soil for COSIPAR and VIENA, respectively (Berni et al., 1999).

The available knowledge on the mechanism of resistance in the rice plant, in relation to Si on rice blast, has to be reevaluated in order to utilize the relevant information for further research on other rice pathogens, including blast. The earlier studies in Japan on the nature of blast resistance with reference to Si has been reviewed by Suzuki (1965). These studies have contributed more than any others to our understanding of the role of Si in blast resistance. Some major concepts can

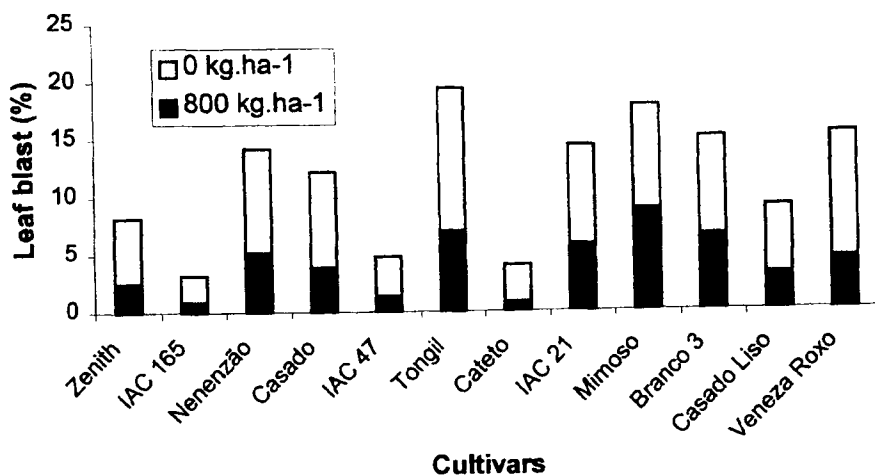


Figure 18.1. Effect of wollastonite at the rate of 800 kg ha^{-1} of SiO_2 on leaf blast in twelve rice cultivars grown under field conditions. Goiânia, Brazil (1994/1995).

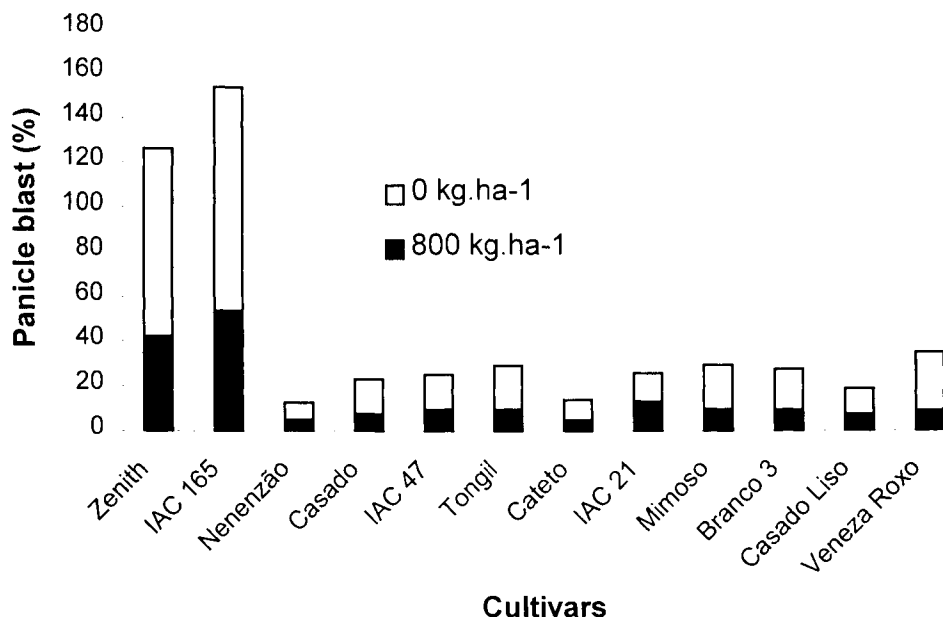


Figure 18.2. Effect of wollastonite at the rate of 800 kg ha⁻¹ of SiO₂, on panicle blast in twelve rice cultivars grown under field conditions. Goiânia, Brazil (1994\1995).

be summarized as follows: The role of silica is mostly mechanical in nature. The penetration rate of the rice blast pathogen is lower in plants with a higher level of silica, due to the mechanical barrier created by an accumulation of silica in the epidermis. Electron microscopic studies revealed the presence of a cuticle and silica double layer in the epidermal cell wall. Varieties resistant to rice blast contain a higher amount of silica than susceptible varieties and the degree of resistance increases in proportion to the amount of silica applied. Heavy nitrogen application decreases silicate accumulation in plants resulting in a decreased number of silicified cells in the uppermost leaves. The percentage of neck blast closely correlates with the number of silicified cells in the uppermost leaves at the heading stage or at the stage five days before heading. The number of silicated cells per unit area is largest in the lower leaves, decreasing towards the upper leaves during the vegetative growth stage. At heading, the number of silicated cells in the upper leaves increases. The age-mediated resistance of the rice plant and leaves seem to be related to silicification of epidermal cells with age (Volk et al., 1958; Prabhu and Filippi, 1993).

All measures that reduce the tissue silica content, such as high doses of N or shading, increase the susceptibility of the plant to rice blast. In japonica upland rice genotypes, the tissue silica content in mature flag leaves is believed to be greater than the irrigated indica rice genotypes (Winslow, 1992). Flooding the soil with water supplies silica in the soluble form, increasing the Si content in the plant and inducing resistance to blast (Winslow, 1992). Nitrogen, as an independent factor, increased both leaf and panicle blast in field experiments conducted under upland conditions in Brazil (Farias et al., 1982). It is not known how much the application of Si affects the availability of N. Several authors have suggested that the effect of N on host susceptibility is due to the amount of phenolic compounds formed, rather than silicification of epidermal cells (Fageria et al., 1991). High K and low N fertilization reduce the severity of panicle blast. While the response

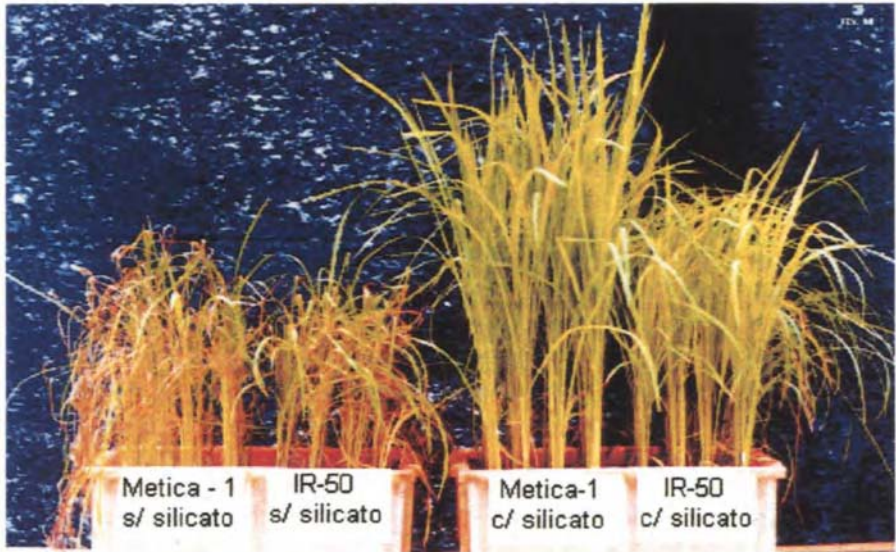


Figure 18.3. Effect of wollastonite applied at the rate of 4.0 g kg^{-1} of soil, on leaf blast severity and growth, in two irrigated rice cultivars, in artificial inoculation tests with an isolate (race ID-14) of *Pyricularia grisea*. Goiânia, Brazil (1998), s=nontreated, c=treated.

of upland rice to K in the absence of N was linear and negative, and curvilinear at N_{30} , there was no response at N_{60} (Prabhu et al., 1999). Unfortunately, little is known about plant nutrient interactions and the magnitude of the defense reaction.

More than 90% of Si is in the form of silica gel, which is mainly localized in the epidermis, vascular bundle, and the sclerenchyma (Suzuki, 1935). Rice plants grown in a Si-free nutrient solution showed an abnormal rate of transpiration. The Si gel layer in the epidermis may serve to control transpiration and to prevent fungal and insect invasion. The susceptibility of rice plants to blast has been known to increase under drought conditions and Si fertilization could possibly increase both drought and blast resistance. Pertinent questions relative to the physiological nature of defense are whether a response requires phenolic compound synthesis or whether some other specific factors are involved. *P. grisea* is a direct-penetrating fungus and the penetration peg enters the plant by perforating the cuticle and underlying cell wall. The defense mechanism that operates during the initial phases of host-pathogen relationships involving tropic responses directly or indirectly has not been investigated.

18.4. GRAIN DISCOLORATION

Grain discoloration ranks second in importance both in irrigated and upland rice in Brazil. There is as yet no fungicide available for effective and economically viable control in Brazil. The causal agent of brown spot, *Bipolaris oryzae* is one of the predominant pathogens associated with grain discoloration. Earlier investigations in other countries have shown effective reduction in disease

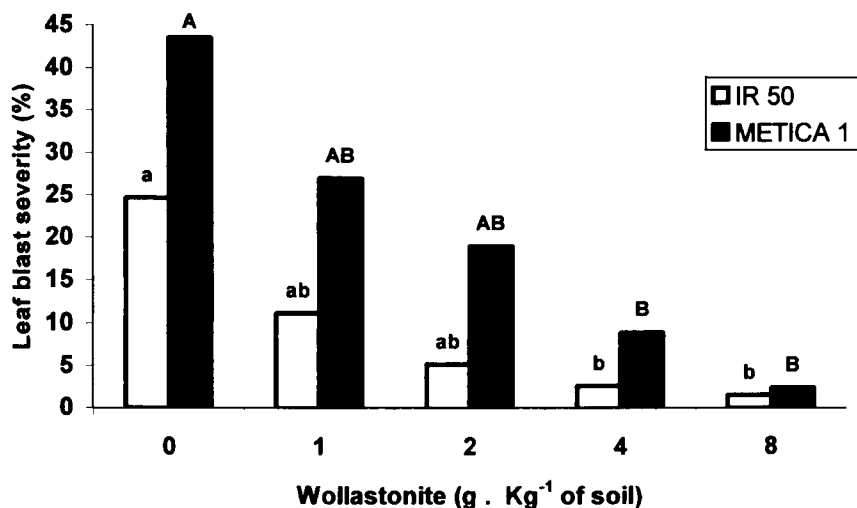


Figure 18.4. Effect of wollastonite on leaf blast severity in artificial inoculation tests with an isolate (race ID-14) of *Pyricularia grisea* (vertical bars followed by the same letter do not differ significantly according to Tukey's test at 5% level) Goiânia, Brazil, 1998.

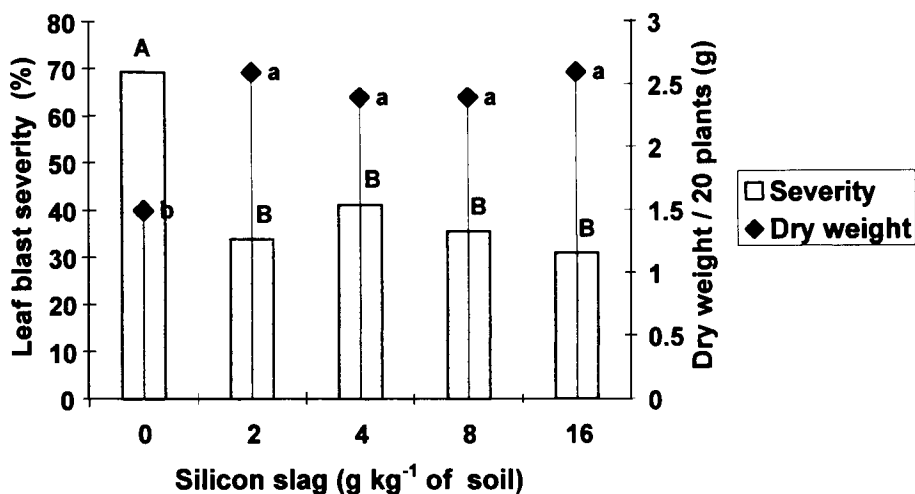


Figure 18.5. Effect of silicon slag from COSIPAR on leaf blast severity and dry weight in artificially inoculated tests with an isolate of *Pyricularia grisea*. (The values represent the mean of two rice cultivars, Metica 1 and IR-50; vertical bars followed by the same letter do not differ significantly according to Tukey's test at 5% level). Goiânia, Brazil, 1999.

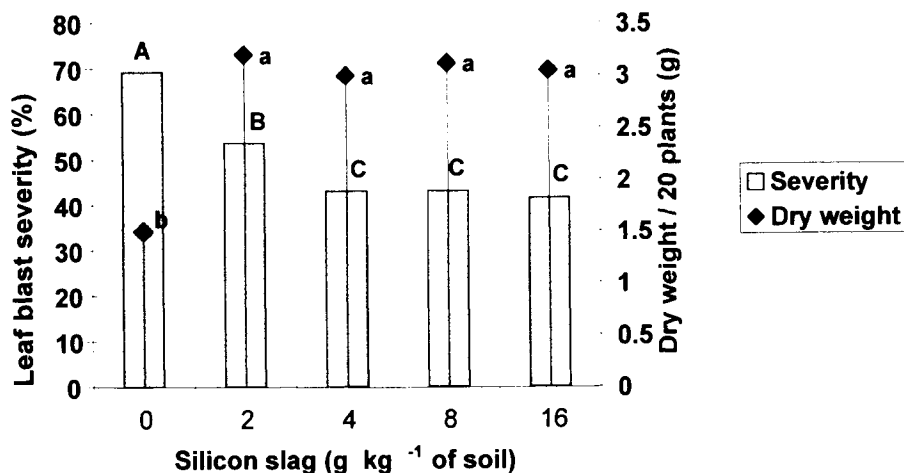


Figure 18.6. Effect of silicon slag from VIENA on leaf blast severity and dry weight in artificially inoculated tests with an isolate of *Pyricularia grisea* (The values represent the mean of two rice cultivars, Metica 1 and IR-50; the vertical bars followed by the same letter do not differ significantly according to Tukey's test at 5% level). Goiânia, Brazil, 1999.

levels with Si (Takahashi, 1967; Ohata et al., 1972; Yamauchi and Winslow, 1987; Datnoff et al., 1992; Lee et al., 1981; Nanda and Gangopadhyay, 1984; Correa-Victoria, 1994). The residual effect of Si fertilization in brown spot suppression has been clearly demonstrated in field experiments conducted at the Everglades Research and Education Center in south Florida (Datnoff et al., 1992). Brown spot was reduced by 14% in the plots with residual Si, compared to an 18% reduction in newly fertilized plots. In West Africa, the application of 18.7 g Si/m² as sodium metasilicate doubled plant Si uptake and significantly reduced the husk discoloration in upland rice grown on highly weathered Ultisols (Winslow, 1992).

In greenhouse studies with four different savanna soils from Brazil, Typic Acrustox-isohyperthermic (Lva), Typic Acrustox-isohyperthermic (LEa) Rhodic Acrustox-isohyperthermic (LRd), and Ustoxic Quartzipsammentic-isohyperthermic (AQa), Si application has been shown to increase total grain weight and decrease grain discoloration associated with fungi such as *Helminthosporium* sp., *Curvularia* sp. and *Fusarium* sp., independent of soil type (Komdorfer et al., 1999).

The knowledge of genotypic differences in relation to Si content and degree of resistance increases the possibilities for developing cultivars with high Si content through appropriate breeding methods. The genetic differences seem to be specific to the part of the plant analyzed. A field experiment with 48 genotypes and five rates of Si (0, 200, 400, 600, and 800 kg ha⁻¹ of SiO₂) was conducted under dry land conditions in Goiania. Wollastonite, a white natural mineral chemically identified as calcium silicate (CaSiO₃), was used as a source of Si. It has the following composition: SiO₂=51.9%; CaO=42.1%; Al₂O₃=1.82%; MgO=1.49%; Fe₂O₃=0.26; Na₂O=0.22; MnO=0.02%; ignition loss (1000°C)=2.18%; density = 2.9 Mg/m³. The predominant field fungi associated with grain discoloration in decreasing order were *Phoma sorghina*, *Bipolaris oryzae*, *Microdochium oryzae*, *Curvularia* sp. and *Nigrospora* sp. Quantitative assessment of grain

Table 18.1

Influence of wollastonite (CaSiO_3) on grain discoloration and silicon content in the grain husk of 48 rice genotypes under upland conditions in Brazil (1994/1995).

Genotypes	Grain discoloration (DSI)			Si content in husk		
	0	$\text{SiO}_2(800\text{kg}\cdot\text{ha}^{-1})$	RDC	0	$\text{SiO}_2(800\text{kg}\cdot\text{ha}^{-1})$	RSC
Araguaia	111	84	75	103	188	182
Arroz de guerra	159	125	78	84	118	140
BG 90-2*	193	198	109	73	111	152
BG 367-4*	199	163	81	62	121	195
Branco três meses	200	178	89	88	172	195
Caiapó	93	116	124	96	155	161
Carajás	130	96	73	109	168	154
Casado	255	176	69	96	148	118
Cajueiro liso	188	180	95	84	175	208
Caqui	230	204	88	103	152	147
Ceysvoni SML*	169	139	81	100	130	130
Chokoto*	197	166	84	94	122	129
CNA 7024	96	60	62	96	147	153
CNA 7449	173	137	79	85	157	184
Colômbia-1	189	161	85	78	122	156
Dawn	220	136	61	62	124	200
Guarani	114	91	79	121	214	176
Iguapé redondo	104	71	68	78	152	194
IAC 21	198	178	89	92	162	176
IAC 47	111	99	89	117	141	120
IAC 165	172	173	100	73	162	221
IR 8*	209	168	80	68	91	133
IR 24*	157	133	84	94	135	143
IR 36*	206	188	91	65	106	163
IR 50*	184	184	100	77	134	174
IRAT 104*	132	151	114	83	112	134
IRAT 127*	193	170	88	88	138	156
IRI 342*	192	188	97	86	171	198
IRI 344*	182	122	67	87	162	186
Kanto 51*	196	188	95	73	118	161
Labelle*	199	166	83	87	129	148
Lebonet*	196	168	85	77	181	235
Metica-1	214	219	102	85	106	124
Milyang 30*	156	128	82	77	147	190
Mimoso	191	190	99	103	125	121
Nenenzão	189	176	93	90	141	156
Pai-Kan-Tão	242	184	76	99	142	143
Pérola	126	97	76	84	155	184
Rio Paraníba	125	119	95	117	181	154

Table 18. 1 – (cont.)

Influence of wollastonite (CaSiO_3) on grain discoloration and silicon content in grain husk of 48 rice genotypes under, upland conditions in Brazil (1994/1995).

Genotypes	Grain discoloration (DSI)			Si content in husk		
	0	SiO_2 (800 kg-ha ⁻¹)	RDC	0	SiO_2 (800 kg-ha ⁻¹)	RSC
Ramtulasi*	206	184	89	114	168	147
Shin 2*	195	132	67	76	123	161
TKM 6*	227	195	85	74	114	154
Tongil *	214	190	88	86	160	190
Três Marias	161	179	111	109	182	166
T S Phoma	262	195	74	160	287	179
Veneza Roxo	214	162	75	144	168	116
Zenith*	152	141	92	58	100	172

DSI= Disease severity index based on a 0-4 scale(0= no symptom; 1= pin head spots; 2= 25% of the grain showing discoloration; 4=> 50% of the grain showing discoloration.).

RDC= Relative disease control in relation to non-amended (0 level).

RSC= Relative silicon content in tissue relation to non-amended (0 level).

*Irrigated rice cultivars.

discoloration severity was made using a scale of 0, 1, 2, and 4. Varietal differences in grain discoloration were evident in plots not amended with Si (Table 18.1). The mean disease severity index (DSI) ranged from 0.93 for cultivar Caiapó to 2.62 for T. S. Phoma. Tall upland varieties of medium duration such as Casado, Tongil, and Veneza Roxo and short duration ones such as Caqui, IAC 21, and Cajueiro liso are widely used as susceptible checks in routine disease resistance evaluations. The disease severity in these varieties showed higher DSI values, indicating a high inoculum pressure. The semi-dwarfs IR 36, IR 8, BG 367-4, IR 36, TKM 6, and Metica 1 showed relatively high disease severity under upland conditions. Silicon amendments at the rate of 800 kg.ha⁻¹ reduced the mean DSI in most of the irrigated and upland rice genotypes tested. The relative disease control (RDC) varied in different genotypes, indicating a differential response of the genotypes to Si. The RDC was higher in genotypes Casado, CNA 7024, Dawn, Iguape Redondo, IRI 344, and Shin 2, independent of the initial disease level in the non-amended plots.

Table 18.2

Grain discoloration and grain weight in relation to silicon fertilization with wollastonite in upland rice cultivars.

Rates SiO_2 (kg ha ⁻¹)	Grain discoloration ¹ (mean score)	Grain weight (g) ²		Grain weight increase (%)
		Filled and unfilled grains	Filled grains	
0	6.2 a	90.1 c	77.9 c	-
200	5.1 b	106.6 b	93.6 b	201
400	4.9 b	111.7 ab	96.8 ab	242
600	4.7 b	115.1 ab	102.9 ab	320
800	4.6 b	123.1 a	109.5 a	405

¹Grain discoloration (0-9 scale- CIAT)

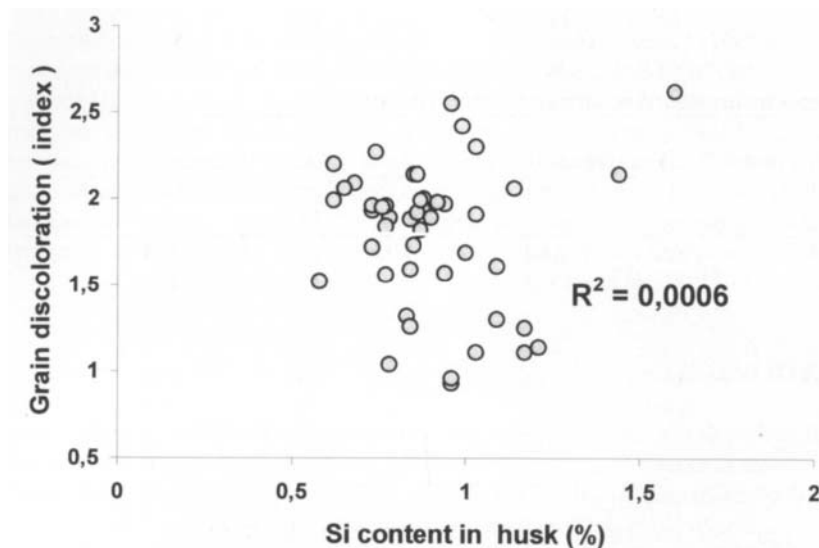


Figure 18.7. Relationship between grain discoloration and Si tissue content in husk of 48 rice genotypes in non-amended plots (each data point indicates a mean value of three replications). Goiânia, Brazil (1994/1995).

The genotypes BG 90-2, Caiapó, IAC 165, IR 50, IRAT 104, Metica -1, and Três Marias did not show any response to Si and may require higher doses. In non-amended plots, the genotypes showed differences in Si tissue content in the husk. While the Si content in the husk increased in all genotypes with Si amendment, the relative Si content (RSC) varied in different genotypes, indicating differences in uptake among genotypes (Table 18.1).

There was no correlation between grain discoloration and Si content in husk from the non-amended plots (Figure 18.7). The grain discoloration on average was reduced by 17.5% resulting in a 20% increase in grain weight with 200 kg ha⁻¹ of SiO₂ (Table 18.2). The relation between grain discoloration and rates of SiO₂ was negative and linear (Figure 18.8). The grain weight increased in a linear fashion with increase in silicon rates (Figure 18.9). These results showed that silicon fertilization may constitute one of the alternatives for integrated disease control of grain discoloration.

18.5. LEAF SCALD

Leaf scald is becoming an economically important disease in both upland and irrigated rice in Brazil. Most of the commercial rice cultivars exhibit different degrees of susceptibility to this disease. The disease is sporadic in nature and is greatly influenced by the rainfall and nutritional status of the soil. Under upland conditions, leaf scald commonly occurs in the first year of planting rice after clearing the cerrado, rice planted in rotation with soybean, and in rice grown with supplementary irrigation. In the state of Tocantins, the factors highly conducive to severe leaf scald development in irrigated rice, are intensive cultivation with high fertilizer inputs and continuous cultivation in rotation with soybean. Several investigators have shown leaf scald to be effectively suppressed by soil amendments with silicon (Elawad and Green, 1979; Yamauchi and Winslow,

1987; Winslow, 1992; Correa-Victoria et al., 1994). In a greenhouse experiment utilizing Oxisol and six levels of SiO_2 (0, 1.0, 2.0, 4.0, and 8.0 g kg^{-1} of soil) thirty day old plants were inoculated on cut leaves with mycelial discs of a single spore isolate of *Microdochium oryzae*, (Bonman et al., 1990). Leaf scald was suppressed with increasing rates of silicon applied in the form of wollastonite (Vansil-10). The relationship between doses of Si and disease severity was negative and quadratic (Figure 18.10). The lesion length was reduced from 0.6 cm to 0.4 cm at the dosage of 2 g kg^{-1} of soil corresponding to approximately 2 Mg ha^{-1} . Leaf scald management with silicon fertilization, both in upland and irrigated rice, could be one of the most feasible alternatives to fungicide control in Brazil and needs further study under field conditions.

18.6. SHEATH BLIGHT

The yield decline due to soil-borne pathogens with intensive cultivation in irrigated rice in the state of Tocantins is expected. The ability of the rice plant to defend against the pathogens is genetically determined, but it can be enhanced in different ways. There are many soil-borne diseases, such as sheath blight, for which resistance sources are not known; or if available, cannot be exploited for practical reasons. In such cases, the possibilities of increasing the resistance of the cultivar by cultural and fertilizer management receives greater impetus. There are number of environmental and cultural conditions that affect plant predisposition to diseases in general and to soil-borne diseases specifically. It was shown many years ago that micronutrients delay symptom expression in different diseases (Huber, 1990). The relationship between Si and nutrient uptake suggest that the resistance can be induced against soil-borne diseases. Reducing the inoculum level in the soil and starving the pathogen could be means of enhancing the effectiveness of the defense

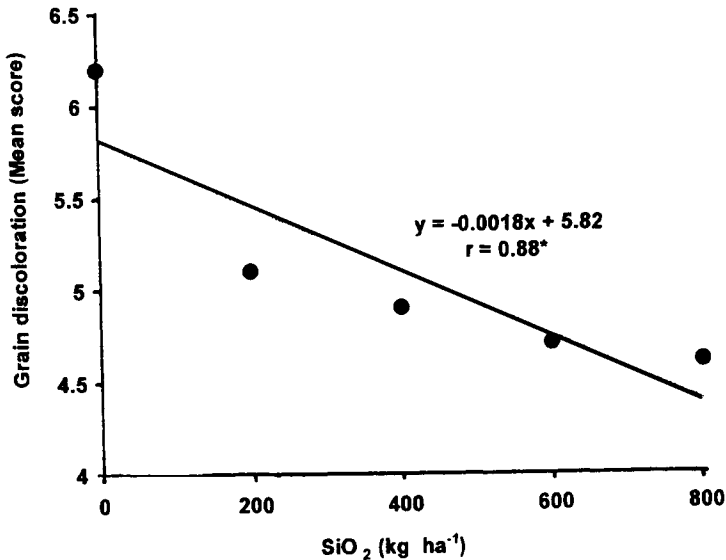


Figure 18.8. Effect of wollastonite on grain discoloration in rice grown under field conditions (each data point represent mean disease score of 48 genotypes). Goiânia, Brazil (1994/1995).

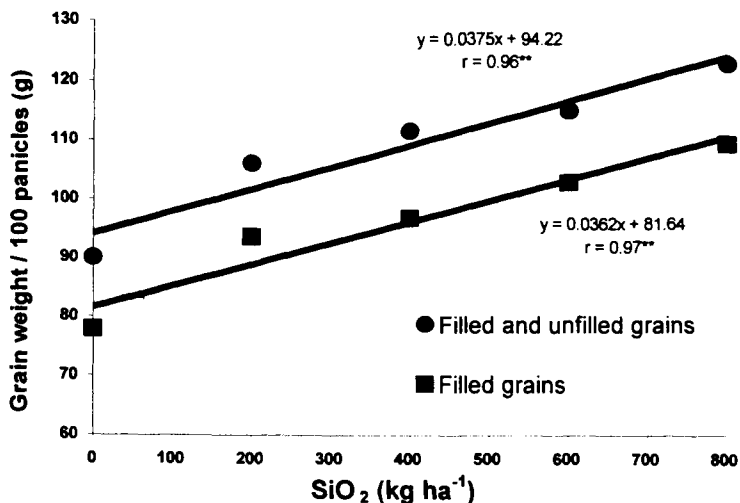


Figure 18.9. Effect of wollastonite on grain weight in rice grown under field conditions (each data point represents mean disease score of 48 genotypes). Goiânia, Brazil (1994/1995).

mechanism. The multiplication of the pathogen and the resulting sheath blight disease levels possibly can be reduced by avoiding the presence of readily available organic matter and by soil fertility management with Si substituting for foliar sprays. Elawad and Green (1979), Datnoff et al. (1997), and Rodrigues et al. (1999) showed that sheath blight severity could be effectively reduced by soil amendments with Si slags. In studies conducted in Brazil, some promising results on sheath blight control, under greenhouse conditions, by Si fertilization have been obtained (Rodrigues et al., personal com.). The effect of calcium silicate (wollastonite) at the rates of 0, 2.0, 4.0, 6.0, and 8.0 Mg·ha⁻¹ on sheath blight development in six irrigated rice cultivars grown on a typic acrustox

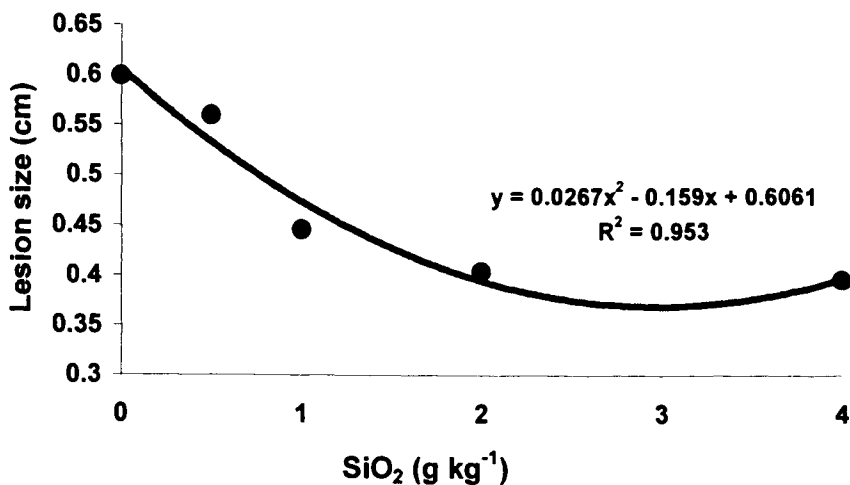


Figure 18.10. Effect of wollastonite doses on lesion extension of leaf scald in upland rice cultivar Caiapó in greenhouse inoculation tests. Goiânia, Brazil (1998).

Table 18.3

Linear regression equations relating relative lesion height (RLH) and silicon rates in rice cultivars inoculated with *Rhizoctonia solani* under green house conditions (Rodrigues et al., unpublished).

Cultivars	Relative lesion height (RLH) ^a
BR-Irga 409	RLH = 76.72 - 2.36x r = 0.96**
Epagri 109	RLH = 79.63 - 2.25x r = 0.67
Metica 1	RLH = 72.69 - 3.13x r = 0.85*
Rio Formoso	RLH = 84.60 - 2.55x r = 0.91**
Javaé	RLH = 75.78 - 3.44x r = 0.75
Cica 8	RLH = 76.82 - 1.72x r = 0.88*

^ar values followed by asterisks * and ** are significant at the probability levels of 5% and 1%, respectively.

(red-yellow Latosol) was examined. Linear regression models described the relationship between the relative lesion height (RLH) and Si rates (Table 18.3). Lesion height decreased with increase in Si rates in all six cultivars. However, the cultivars exhibited differences in the rate of disease decrease. The response to Si application was greater in Metica 1 as compared to CICA 8 (Figure 18.11). The strategy for sheath blight control with Si fertilization has not so far been envisaged and could constitute one of the most economically viable technologies mainly in the state of Tocantins where the conditions are highly favorable for disease development.

18.7. SILICON AND GRAIN YIELD

The positive effects of Si on plant growth and development, as well as on yield, have been shown in Japan (Okuda and Takahashi, 1964). Rice yields increased by more than 30% on Histosols amended with calcium silicate slag (Snyder et al., 1986). The field and greenhouse experiments conducted on Oxisols under upland conditions in Brazil showed positive response to Si in relation to grain yield in the absence of any disease pressure (Barbosa Filho, personal communication). In greenhouse experiments, there was significant response to SiO₂ treatments, application of SiO₂ at the rate of 3 g per pot corresponding to 1 ton per ha. This represented a 22% yield increase in comparison to the control. In a field experiment, the grain yield increased significantly with increased rates of SiO₂. The application of 4000 kg ha⁻¹ of SiO₂ increased yield by 9.4% in relation to the non-treated control. The positive effect of Si was also observed in increasing pH, availability of nutrients in the soil, number of filled grains/panicle, and absorption of Si by the plant. In Brazil, upland rice showed response to SiO₂ on Oxisols, even though the magnitude of response required high doses of silica.

18.8. PROSPECT FOR RICE DISEASE CONTROL

Yield potential of the commercial rice varieties in Brazil is not an actual limitation, but the low yields at the farm level are due to diseases and drought stress. These factors do not permit rice cultivars to fully express their yield potential under upland conditions. However, in upland rice with supplementary irrigation and in favorable rain-fed regions, the yields are relatively high, and the disease control by Si fertilization has a greater prospect than in unfavorable drought prone

areas. The current patterns in agriculture, such as minimum tillage and rice in rotation with soybean and pasture, mitigate and favor disease development under upland conditions. These conditions provide an opportunity for study on Si and disease management. In the state of Tocantins, the yields in irrigated rice have been declining due to rice blast and sheath blight, and the grain quality due to grain discoloration. Improvements of average yields, both in upland and irrigated rice, by Si fertilization with a minimum use of fungicides has an immense future. Long term field experiments should furnish data on yield and yield stability performance under different disease levels.

The most promising short-term approach for disease control is probably the exploration of Brazilian Si sources and the study of their potential effect on principle diseases. These include: a) delay in the disease progress, b) increased growth and development at the vegetative phase, c) Si tissue content in response to Si fertilization, and d) the N/ Si relationship in rice blast, leaf scald, and sheath blight. The effect of Si in varieties with partial resistance is an important aspect that needs to be investigated. The effect of Si on pre-infection phases of disease development, and the combination of pre-infection and post-infection physiological plant response has unlimited prospects for blast control at the vegetative phase. Research to identify these mechanisms and to determine using them as selection criteria is a future, rather than a current possibility. Studies of the effect of Si on rice blast under water stress conditions in upland rice are useful in disease management. The positive effects of Si on drought tolerance will permit the rational use of fungicide input. Insect problems in rice, though increasing, are at the moment less extensive and serious than diseases. The Si effect in controlling both diseases and insects may prove an advantage in integrated pest management. Additional experiments on the defense mechanism should be undertaken by artificial inoculations, on rice blast and other diseases under controlled

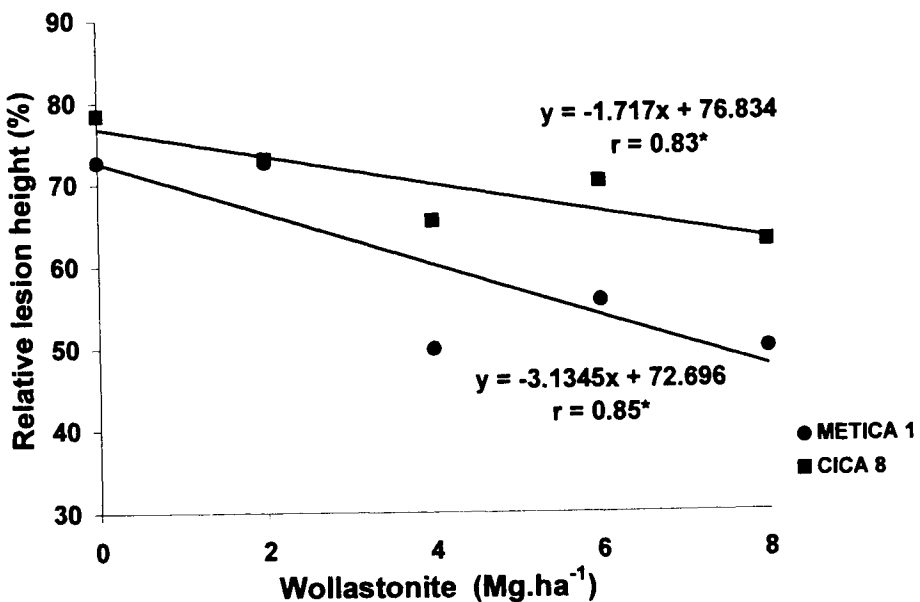


Figure 18.11. Effect of silicon rates on relative lesion height of sheath blight (*Rhizoctonia solani*) in two upland rice cultivars in Brazil. (Rodrigues et al., unpublished)

greenhouse, growth chamber, and laboratory conditions, based on the existing concepts. However, parallel experiments under field conditions should be performed for yield performance and disease control with and without fungicide inputs.

Initially, the field research on Si in relation to disease control should be location specific in hot spot areas for rice diseases and where soil characteristics are adequately known. Nutrient management, with special reference to N and K, is a prerequisite because these nutrients greatly alter disease levels. Crop management practices such as row spacing, planting time, and cropping systems, including crop rotation and minimum tillage, influence disease development and should be taken into consideration. The minimum research team for a given location should consist of a plant pathologist, soil scientist/agronomist, and entomologist. Each member of the team should execute a part of the project in which he has a leading role. The chance of success increases with inter-institutional and international collaboration, not only to exchange information, but in future to establish research networks on important diseases such as rice blast. The network for testing the available Si sources for their relative efficiency in controlling rice blast should be based on a model similar to the one used in the international rice blast nursery for identifying blast resistant sources available in the world germplasm.

The final assessment of progress in disease management by Si fertilization should be judged by the farmer. Major consideration should be given to the cost-benefit ratio in adopting a recommended practice where the participation of a socio-economist is essential. The extensionist has a greater role to play in conducting the trials in farmers' fields, and the data collected would serve as feedback for further research. It is most encouraging that once effective disease control is shown under experimental conditions, a number of farmers in the intensive irrigated rice growing areas in the state of Tocantins are coming forward to fund these trials. The Embrapa Rice and Bean Research Center has reassessed the Si research program, and has put emphasis on disease management of rice cultivars for improvement of grain yield and quality, in both upland and irrigated rice, in the coming years.

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Chapter 19

Effects of silicon fertilization on disease development and yields of rice in Colombia

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The savannas of Colombia contain soils (Oxisols) constrained by silicon (Si) deficiency. Since upland rice production is expanding into this region, field experiments were conducted over two years on three representative soils to determine the extent to which Si deficiency may constrain rice yields and favor disease development. The experiments were complete factorials and included different levels of Si, phosphorus (P) and cultivars. Sources of Si tested included both calcium metasilicate and slag. Lime was applied to equalize lime value and Ca levels across treatments. Silicon significantly reduced all observed rice diseases. Leaf blast severity and neck blast incidence were reduced from about 26% and 53% in non-amended plots to 15% in Si-amended plots. Leaf scald severity was reduced from 42% to 6% in Si-amended plots, while grain discoloration was reduced from 4.2 to 1.0 in Si-amended plots. Si application increased rice yields by about 40% on all three soils. A residual effect was also noted on both, the reduction of disease development and yield increase. By amending these soils with Si, a very effective and potentially sustainable method for upland rice production and management of rice diseases appears available.

19.1. INTRODUCTION

Silicon is one of the most abundant elements in soils, as well as in the ash of plants, especially grasses and cereals (Elawad and Green, 1979). Under a typical irrigated rice crop, Si is present at much higher concentrations in rice tissue than the macronutrients nitrogen (N), potassium (K), and P (Yoshida, 1975). Despite its abundance and importance, Si has received far less attention than K, N, and P, and studies have been particularly lacking for upland rice environments, which may be at highest risk of Si deficiency (Winslow et al., 1997). According to Juo and Sanchez (1986) and Winslow et al. (1997), Si deficiency, acidity, and aluminum (Al) toxicity commonly occur together

reasons for the limited study of Si may be that it is not considered to be among the essential plant nutrients (Epstein, 1994).

The highly acidic, infertile Oxisols, Ultisols, and tropic suborders of Inceptisols which occupy much of the landscape of the savannas of South America are dominated by the end-products of weathering: kaolinite and the oxides and hydrous oxides of iron (Fe) and Al. Weathering has leached the bulk of mineral nutrients from these soils, leaving a cation exchange complex in which Al is the governing cation. Since soil weathering is essentially a process of desilication (Friesen et al., 1994; Savant, Datnoff et al., 1997), low levels of soluble Si may also be expected in highly weathered soils.

The function and mechanism of Si in rice is not fully understood. However, inadequate levels may limit yields and increase crop susceptibility to diseases (Datnoff et al., 1991, 1992, 1997; Savant, Datnoff, et al., 1997; Winslow, 1992). Rice is a known Si-accumulator and benefits from Si nutrition (Yoshida, 1975). In addition, rice response to Si applications has been shown on highly acidic soils in West Africa (Winslow, 1992). Consequently, there is a definitive need to consider Si as an agronomically essential element for increasing and/or sustaining rice production (Savant, Datnoff, et al., 1997).

From several studies, it appears that Si nutrition has direct and indirect beneficial effects on rice growth largely due to different physiological roles (Takahashi and Miyake, 1990; Yoshida, 1975). When blast is severe, yield increases of 10% are common when Si is added, and at times exceed 30% (Yoshida, 1981; Snyder et al., 1986; Datnoff et al., 1991, 1992). Numerous reports in the literature suggest that under intensive rice cultivation, depletion of plant-available Si in soils could also be a possible soil-related factor for declining yields (Savant, Datnoff et al., 1997; Savant, Snyder, et al., 1997). Si has been shown to suppress fungal diseases such as rice blast (*Magnaporthe grisea*, teleomorph; *Pyricularia grisea*, anamorph), brown spot (*Cochliobolus miyabeanus*, teleomorph; *Bipolaris oryzae*, anamorph), leaf scald (*Gerlachia oryzae*), sheath blight (*Rhizoctonia solani*, teleomorph), stem rot (*Sclerotium oryzae*, teleomorph), and a complex of fungal and bacterial pathogens that cause grain discoloration (Datnoff et al., 1991, 1992, 1997; Savant, Datnoff, et al., 1997; Seebold, 1998; Winslow, 1992) both under lowland and upland growing conditions. In field trials, Datnoff et al., (1991 and 1992) reported the reduction in blast ranging from 17% to 30% and in brown spot from 15% to 32% in rice grown on Histosols. Disease severity tended to be reduced with increasing tissue concentration of Si.

Upland rice is widely cultivated on the Brazilian Cerrados and production is rapidly expanding on the Colombian Llanos. However, this potential constraint of Si deficiency has therefore gone unrecognized in this agroecosystem. Consequently, we conducted field experiments on three representative soils on the Llanos of Colombia during 1992 and 1993 to determine: whether upland rice responds to Si applications, whether disease development and subsequent rice yields can be influenced by Si, whether there are cultivar differences in responses to Si, and if there is an interaction of Si with phosphate which is adsorbed on similar mineral surfaces in these soils.

19.2. MATERIAL AND METHODS

Two sets of experiments with four replications were conducted. Experiment 1 evaluated the effect of Si on yields and disease incidence and severity on two rice cultivars at Santa Rosa, Meta Department in Colombia on a piedmont terrain at the base of the eastern side of the Andes

mountains. The soil is an Inceptisol with pH 4.7 and Al saturation of 18%. The crop is dependent on direct rainfall as a water source. In 1992, three weeks before planting, Si was applied as "slag" (a silicate-rich by-product of electric furnace phosphoric acid production: 22% Si, 33% Ca, 0.5% P, 0.1% K, 0.3% Mg, 0.5% Fe) at elemental Si rates of 0, 1, 2, and 3 t/ha. In 1993, plots were split and 1 t/ha Si was applied to one-half of each plot. The rice cultivars, Oryzica 1 and Oryzica Lanos 5, the former susceptible and the latter resistant to rice blast were sown each year.

In 1993, Experiment 2 evaluated the effect of Si and P on yield and disease incidence and severity on two rice cultivars at two acidic upland research sites located on the eastern savanna plains (Llanos) of Colombia: Matazul (Oxisol, pH 4.7 aluminum saturation 79%) and La Florida (sandy Oxisol, pH 5.9, aluminum saturation 67%), Meta Department. Upland rice culture has been recently introduced to this area. The experiments consisted of factorial combinations of three levels of Si (0, 250, and 500) kg/ha as wollastonite which is a native calcium metasilicate (CaSiO_3 , 24% Si, 34.5% Ca), two levels of P (25 and 50 kg/ha as triple superphosphate, TSP) and two rice cultivars (Oryzica Sabana 6 and IAC 165) of apparently contrasting tolerance to Si deficiency. Due to the basic properties of wollastonite, chemically equivalent amounts of calcite lime were applied to the 0 and 250 kg-Si/ha treatments to equalize the lime value and Ca levels across treatments. The total lime value applied to the experiment was equivalent to 2400 kg CaCO_3 /ha. All other nutrients were supplied at adequate levels. In addition to yield, grain quality factors such as coloration and milling quality, and Si tissue concentrations were also determined at harvest. Incidence and severity of diseases were also evaluated.

19.3. RESULTS AND DISCUSSION

19.3.1. Disease response to silicon application

In three different sites of the Colombian Llanos during 1992 and 1993, development of the rice diseases, leaf blast (LB), neck blast (NB), leaf scald (LS), and grain discoloration (GD) were significantly ($P \leq 0.05$) reduced by Si applications to upland rice. All diseases decreased with increasing Si rates, confirming previous reports (Datnoff et al., 1991, 1992, 1997; Deren et al., 1994; Seebold, 1998; Snyder et al., 1986; Winslow, 1992). Leaf blast severity on the cultivar, Oryzica 1, planted in 1992 at Santa Rosa, decreased over the control 62.0 and 69.0% at the lowest and highest Si rates, respectively (Table 19.1). Neck blast incidence was not significantly reduced at any Si rate during the same year and this observation needs further discussion. In 1993, leaf blast severity at the highest Si rate decreased 60.0 and 32.0% over the control for residual 1992 Si effects on the 1993 rice crop, and residual 1992 Si rate receiving 1 t/ha of Si in 1993, respectively (Table 19.1). Neck blast incidence at the highest Si rate decreased 58.0 and 64.0% over the control for residual 1992 Si effects on the 1993 crop, and residual 1992 Si rate receiving 1 t/ha of Si in 1993, respectively (Table 19.1).

Although the application of Si did not apparently suppress neck blast on the 1992 rice crop, it is very important to note that the residual applications of Si were very effective in reducing significantly both leaf and neck blast in 1993. It is possible that in 1992 there was a high blast pressure during panicle formation. The experimental farm at Santa Rosa represents an area of unusually high inoculum pressure (Correa and Zeigler, 1993). Another possibility is that neck blast evaluations were performed too late in 1992, giving opportunity to the pathogen to grow on senescent tissue, and therefore, confound a true infection. This latter affirmation seems to be

Table 19.1

Influence of Si on blast development in rice cultivar, *Oryzica 1*, at Santa Rosa, Colombia.

Silicon (t/ha)		Leaf Blast (%)			Neck blast (%)		
		1993		t/ha Si	1993		t/ha Si
1992	1992	Residual 92	Residual 92+1		1992	Residual 92	Residual 92+1
0	55a	42a	25 bc		25a	60a	47 b
1	21 b	27 b	20 bcd		71a	41 bc	35 cd
2	16 b	20 bcd	20 bcd		57a	33 cd	25 de
3	17 b	17 cd	17 cd		63a	25 de	17 e

following section. In addition, these yields and their differences with the respective controls were comparable to the residual effects on disease development and yields observed in 1993.

Other diseases such as leaf scald and grain discoloration were significantly reduced on the cultivar *Oryzica Llanos 5* planted in the same years at Santa Rosa (Table 19.2). This cultivar was completely resistant to leaf and neck blast during those two years. Although applications of Si at the rate of 1 t/ha were sufficient to influence blast development on cultivar *Oryzica 1*, it seems that more than 1 t/ha of Si was needed to influence the development of leaf scald and grain discoloration on cultivar *Oryzica Llanos 5* (Tables 19.1 and 19.2). Similar effects were observed on yields of the cultivar *Oryzica 1* in both years, and at least in 1992, on cultivar *Oryzica Llanos 5*. Leaf and neck blast, leaf scald, and grain discoloration were also significantly reduced with Si applications to the rice cultivars *Oryzica Sabana 6* and *IAC 165* planted in the Matazul and La Florida sites in 1993 (Tables 19.3 and 19.4). Reduction of disease development at these two sites in the presence of Si was equivalent with no significant differences between the two rates of P used (25 and 50 kg/ha). Influence of Si on the reduction of disease development was higher at the Matazul and La Florida sites compared to Santa Rosa. Responses to Si at the first two sites were observed at Si rates as low as 500 kg/ha compared to more than 1 t/ha used in Santa Rosa. While leaf scald development and grain discoloration were not reduced at Si rates less than 2 t/ha in Santa Rosa (Table 19.2), these diseases were significantly reduced at 500 kg/ha at La Florida (Table 19.4). Differences, however, could have been due to cultivar differences in Si response. Disease development at La Florida tended to be higher at the lower P rate in the absence of Si (Table 19.4). Neck blast incidence significantly decreased from a high of 48-55% in the control to as low as 12-21% with the addition of Si (Table 19.3), while leaf scald and grain discoloration

Table 19.2

Influence of Si on the development of leaf scald and grain discoloration in rice cultivar *Oryzica Llanos 5* at Santa Rosa, Colombia.

Si (t/ha)	Leaf Scald (%)	Grain Discoloration (1-9)	
		1993	1993
		Residual 92	Residual 92 + 1 t/ha Si
1992	1992		
0	23a	3.5a	3.0a
1	22a	3.0a	2.5ab
2	17 b	1.0 b	1.0 b
3	19 b	1.0 b	1.0 b

Table 19.3

Influence of Si and P on neck blast development and yield in rice cultivars Oryzica Sabana 6 and IAC 165 at Matazul, Colombia.

Treatment			O. Sabana 6		IAC 165	
P (kg/ha)	Si (t/ha)	Lime (t/ha)	NB (%)	Yield (t/ha)	NB (%)	Yield (t/ha)
25	0	2.8	48a	2.3a	30a	2.7a
25	0.5	0	12 b	2.9 b	18 b	3.0a
50	0	2.8	55a	2.3a	29a	2.9a
50	0.5	0	21 b	3.4 b	15 b	3.6 b

NB=neck blast

significantly decreased from 28-42% to 6-9% and 4.0-4.5 to 1.0, respectively, with the addition of Si (Table 19.4). If disease reduction of the magnitude discussed here (17-79% reduction range) can be obtained with Si application in this region, it may be valuable to consider the economic, food security, and environmental benefits that an integrated nutrient management system, including the element Si, will have on the sustainability of rice production.

19.3.2. Yield response to silicon application

Rice yields increased significantly ($P \leq 0.05$) with increasing Si rates, confirming previous reports (Datnoff et al., 1991,1992; Deren et al., 1994; Seebold, 1998). Responses to Si were observed up to a rate of 2 t/ha in 1992, and up to 1 t/ha applied fresh in 1993 at Santa Rosa for the cultivar Oryzica 1 grown on an Inceptisol on the Colombian piedmont (Table 19.5). Rice response to slag one year after application at Santa Rosa diminished only slightly in relation to response in the fresh application in the previous year. A supplemental application of 1 t/ha of Si to all treatments in the second year did not produce appreciably greater yields than the applications of one year earlier. Presumably this effect was due to the continuing dissolution of the slag amendment one-year after application. Water-soluble Si levels extracted from residual and freshly tested soils reflected a continuing ability of the slag application to maintain available Si at fixed concentrations over time, keeping a high relationship between available Si and total slag applied in the second year (data not shown). Yield responses were consistent with levels of available Si in soil (data not shown).

Table 19.4

Influence of Si and P on disease development and yield in rice cultivars Oryzica Sabana 6 and IAC 165 at La Florida, Colombia.

Treatment			O. Sabana 6		IAC165		
P (kg/ha)	Si (t/ha)	Lime (t/ha)	LB (%)	Yield (t/ha)	LS (%)	GD (1-9)	Yield (t/ha)
25	0	2.8	27a	2.0a	42a	4.0a	2.6a
25	0.5	0	18 b	2.4a	9 c	1.0 b	3.5 b
50	0	2.8	15 b	2.4a	28 b	4.5a	3.0a
50	0.5	0	11 b	3.1 b	6 c	1.0 b	3.8 b

LB= Leaf Blast; LS= Leaf Scald; GD= Grain discoloration

The greatest yield increases (76%) at the Santa Rosa site occurred in 1992 with Si applications to plots of 3 t/ha. On the 1993 crop, yields at the three Si rates used increased between 33 and 41% over the control for residual 1992 Si effects (Table 19.5). In 1993, yield increases at Santa Rosa were at the level of 48% when 1 t/ha of Si was applied on untreated 1992 plots and up to 56% when the same amount of Si was applied to those plots receiving 3 t/ha of Si in 1992 (Table 19.5). Although there was not a significant effect of Si application on yield in 1992 on the blast resistant cultivar *Oryzica Llanos 5*, yield increases up to 100% over the control were observed for the residual effects of 1992 Si rates of 2 and 3 t/ha in the 1993 rice crop (Table 19.6). Similarly, yield increases of the same level were observed on the 1992 untreated and residual Si rates receiving 1 t/ha of Si in 1993 (Table 19.6). It is very important to note that the residual applications of Si were very effective in increasing the yield of both cultivars at the Santa Rosa site.

Yield responses to wollastonite, a mineral source of Si with solubility comparable to lime, were evident up to 500 kg-Si/ha, the highest rate applied on two more-weathered soils (Oxisols) on the Colombian altillanura. Yields were significantly increased with Si applications to plots of the rice cultivars *Oryzica Sabana 6* and *IAC 165* planted in the Matazul and La Florida sites in 1993 (Tables 19.3 and 19.4). Yield increases at these two sites in the presence of Si tended to be higher at the highest rate of P (50kg/ha) used (Tables 19.3 and 19.4). With the addition of Si, yields increased by 29-48% and 24-27% compared to the control in cultivars *Oryzica Sabana 6* and *IAC 165*, respectively (Tables 19.3 and 19.4). Grain quality was also enhanced in the treatments that received 500 kg of Si compared to the untreated control (Table 19.7). The percentage of unbroken white rice obtained after milling as well as the weight of 1000 grains were increased significantly at this Si level (Table 19.7). A better grain quality reflects an optimum grain filling probably due to the control of several rice diseases.

19.3.3. Cultivar differences in silicon response.

All diseases evaluated in these experiments at the three different sites seemed to have a significant negative correlation with Si and yield as reported by Datnoff et al. (1991 and 1992). In addition, a positive correlation seems to exist between Si and yield. It is logical that reduced disease severities would be partially responsible for increased yield. However, in the absence of disease, as in the case of the blast resistant cultivar *Oryzica Llanos 5*, Si may also increase yield solely as a plant nutrient. Increased yield is then probably a function of both reduced disease and more favorable plant nutrition (Datnoff et al., 1991). Although there were significant differences in absolute yields of the different rice lines sown in each of the experiments, the interaction of variety with Si rate was less clear. At Santa Rosa, *Oryzica Llanos 5* produced both a higher yield and

Table 19.5
Influence of Si on yield of rice cultivar *Oryzica 1* at Santa Rosa, Colombia.

Silicon (t/ha) 1992	Yield (t/ha)		
	1992	1993 Residual 92	1993 Residual 92 + 1t/ha Si
0	2.1a	2.7a	4.0 b
1	3.2ab	3.6 b	4.1 b
2	3.6 b	3.7 b	3.9 b
3	3.7 b	3.8 b	4.2 b

Table 19.6

Influence of Si on yield of rice cultivar Oryzica Llanos 5 at Santa Rosa, Colombia.

Silicon (t/ha)	Yield (t/ha)		
	1992	1993 Residual 92	1993 Residual 92 + 1t/ha Si
0	4.1a	2.3a	4.7 b
1	4.5a	2.2a	4.7 b
2	5.1a	4.6 b	4.7 b
3	5.0a	4.6 b	4.6 b

appeared to have a lower Si requirement At Matazul, the same was apparent for the IAC 165 cultivar compared to Oryzica Sabana 6, but this interaction was not observed on the sandier Oxisol at La Florida (data not shown). The lower level of available Si at La Florida (2.2 ppm compared to 7.1 ppm) may explain this inconsistency, since both cultivars responded up to the 500 kg-Si/ha rate. It is very interesting to note the great response to Si in terms of both disease reduction and yield increase by the two cultivars planted in Matazul and La Florida. Cultivar IAC 165 responded much better than cultivar Oryzica Llanos 5 in terms of disease reduction. Although leaf scald and grain discoloration pressure was higher at La Florida than at Santa Rosa, both diseases were significantly reduced on IAC 165 by the application of 500 kg/ha of Si (Table 19.4), while the same diseases were only reduced on cultivar Oryzica Llanos 5 with applications of 2 t/ha of Si (Table 19.2).

Different rice ecotypes appear to have evolved specialized adaptations to upland and lowland environments. The upland rice grown in South America are japonicas while indica ecotypes are grown in the lowlands of this region (Winslow et al., 1997). The apparent adaptive advantage of japonica rice to the uplands compared to the indica rice may explain the different response to Si observed between the cultivars Oryzica Llanos 5 (indica) and IAC 165 (japonica). Winslow et al. (1997) presented evidence suggesting that adaptation to Si deficiency could be considered as one possibility for the success of the tropical japonica ecotype on weathered upland soils. Adaptation to the uplands should have evolved after selection pressure into rice with more efficient Si uptake (Winslow, 1995; Winslow et al., 1997). Considering the high levels of disease damage commonly observed when lowland-adapted indica cultivars are sown in tropical weathered upland soils, such an adaptation would even be necessary if the rice crop were to be successful in this agro-ecosystem (Winslow, 1992). Upland rice seems to be evolving to become more efficient at Si use, and less Si-dependent (Winslow, 1995).

Table 19.7

Influence of Si and P on two yield components.

Treatment ^a	1000 grain weight (g)	Unbroken white grain after milling (%)
Si ₁ P ₁	24.4	59.8
Si ₁ P ₂	24.1	56.9
Si ₂ P ₁	25.6	69.4

^aSi₁ = No Silicon; Si₂ = 500 kg Si/ha; P₁ = 25 kg P/ha

19.3.4. Interaction of silicon and phosphorus

The efficacy of P has been reported to be enhanced when it is applied along with Si (Savant et al., 1997a). There were no significant differences between the P rates for development of diseases when 500 kg/ha of Si were applied to the plots (Tables 19.3 and 19.4). Since silicate and phosphate are adsorbed by similar mechanisms on oxidic mineral surfaces in soils, large applications of Si can reduce P sorption and increase the availability and effectiveness of P fertilizer applications in soils. It is important, therefore, to be able to distinguish between a direct effect of Si on rice yields and an indirect effect in the soil through improved P nutrition. Such an effect would produce a negative interaction between Si and P on rice yields in that higher Si rates would result in reduced response to P applications. On the contrary, however, a positive interaction of Si and P was observed at both Matazul and La Florida sites (Tables 19.3 and 19.4). Rather than reducing the requirement for P fertilizer, response to TSP was greater at higher than at lower rates of Si. Evidently, these soils are so poor in both Si and P as to require substantial applications of both to achieve the full yield potential of the rice cultivars evaluated in these trials.

19.4. CONCLUSION

These findings, on three diverse and representative soils of the upland savannas in the Colombian Llanos, suggest that Si deficiency is a major constraint, limiting rice yield potential and favoring disease development. Results indicate that Si fertilization may be used to increase rice production of weathered tropical rice soils while enhancing integrated management of several important rice diseases in Colombia, thus probably reducing the reliance on frequent fungicide use.

A wider analysis is required to more fully define the extent and magnitude of this Si-deficiency constraint to rice production on highly-weathered soils. Although rice germplasm is now available which is well adapted to the high levels of soluble aluminum in these soils, low levels of Si may limit their utility.

Among the limited selection of rice lines examined, there was some evidence of cultivar differences in response to requirements for Si. Thus, there may be potential to address this problem through the development of more adapted germplasm.

Si applications to the soils considered in this study enhanced rice response to applied P fertilizer in that yield response to higher P rates were limited by inadequate levels of Si. Si applications have an appreciable residual effectiveness as well as liming value, raising the possibility that Si can replace lime and applications need not be applied annually. However, the high rates required and the availability of this material in relation to the areas in which it is required raise questions of the economic viability of this type of intervention.

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Chapter 20

Plant-Related Silicon Research in Canada

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Research in Canada on the significance of silicon (Si) to higher plants has focused on four main areas: 1) the nature and location of Si deposition in organs and cells of higher plants. 2) the chemistry of Si in biological systems. 3) the role of Si in plant-fungal pathogen interactions and 4) the use of diatomaceous earth and silica aerogels to control insects in post-harvest products. All four provide new and important information which improves our understanding and perhaps, exploitation of Si in agriculture.

20.1. INTRODUCTION

Silicon is one of the most abundant elements on the surface of the earth and is a common, but generally, minor element in the majority of living organisms. Although it is recognized as being physiologically essential for several protists and vertebrates, its biological role in higher plants has not been clearly established (Epstein, 1994, 1999). Silicon is required as a nutrient for normal growth in wetland species of Gramineae, Equisetaceae and some Cyperaceae, but its role is unclear in dicotyledons and other grasses. In dicotyledons and non-accumulator grasses, Si has been suggested to have a positive effect on reproduction, alleviation of metal toxicity and nutrient imbalance, provision of structural rigidity, and increased resistance to fungal diseases.

Research on the role of Si in plant/agriculture systems in Canada has been limited, but generally focused. The four main areas of research include the accumulation of Si in plant structures, the chemistry of Si in biological systems, the role of Si in plant-fungus pathosystems and the use of Si as diatomaceous earth and silica aerogel for the control of insect pests in cereal storage and processing facilities.

20.2. SILICON ACCUMULATION IN PLANT STRUCTURES

Researchers in Canada have played a prominent role in describing the deposition of Si in cells and organs of higher plants. Perhaps the foremost authority in this area is A. Sangster, who in collaboration with colleagues largely in the UK, has worked out the details of Si deposition in members of the grass family (Gramineae or Poaceae).

20.2.1. Roots

Sangster and colleagues have extensively examined Si deposition in roots, and have proposed that the nature and location of Si deposition appears to be based on phylogenetic relationships. For example, in members of the tribe Andropogoneae such as *Sorghum*, *Sorghastrum*, *Miscanthus*, and *Andropogon*, Si deposition is confined to the endodermal cells, primarily occurring as nodular aggregates in the inner tangential wall (Sangster, 1977; Sangster, 1978a; Sangster, 1983a; Sangster and Parry, 1976a, 1976b, 1976c). The endodermal deposition of Si in *Sorghum* roots has been found to form an acropetal gradient, which appears to be related to the initiation of secondary wall thickening (Hodson and Sangster, 1989a; Sangster and Parry, 1976b). In *Sasa* (Bambuseae), however, Si may be deposited in the inner and outer tangential walls and in radial walls of the endodermis (Bennett and Sangster, 1981). Other genera, such as wheat (*Triticum* in the Triticeae), do not show any particular distribution pattern, with Si in the endodermal walls, the central metaxylem lumina, as well as in the peripheral metaxylem, the pericycle, and in the outer parenchyma (Hodson and Sangster, 1989b). Interestingly, *Zea* (Maydeae) does not accumulate Si in adventitious roots at all, even though Si is transported and deposited in the shoot (Bennett and Sangster, 1982).

Several studies have also shown that Si may ameliorate the negative effects of Al on root growth. In *Sorghum*, Hodson and Sangster (1993) found that Si was atypically deposited in the outer tangential wall of the epidermis when aluminum (Al) was present in the root zone. This was also found to be the major site for Al deposition, suggesting some form of sequestration of Al by Si. A similar reduction in Al toxicity by Si was found in wheat (Cocker et al., 1997); and again, Si was accumulated in the epidermal walls only in the presence of Al.

Little work has been conducted on dicot plants in Canada, but in one study, the roots of cucumber plants were not seen to accumulate Si, despite the transport and deposition of Si in the leaves (Chérif et al., 1992a).

20.2.2. Rhizomes

Roots are not the only underground structures to accumulate Si. Sangster (1978b, 1983b, 1985) has shown Si accumulation in rhizomes of three genera of the Andropogoneae (*Miscanthus*, *Sorghastrum* and *Andropogon*). Deposition patterns are not necessarily the same as those found in the roots of the same species. For example, whereas *Andropogon scoparius* shows Si deposition only in rhizome cells which are similar in shape, position and wall thickness to endodermal cells in the root (Sangster, 1978b), *Miscanthus sacchariflorus* rhizomes have three distinct areas of Si accumulation (in the epidermis, parenchyma and central cavity) compared to only one (the endodermis) in the root (Sangster, 1985).

20.2.3. Leaves

Early work by Sangster on the accumulation of Si in leaf tissue used *Sieglingia decumbens* (heath grass) as a model. In this species, Si occurs as opal (phytoliths) in the lumen of specialized

Si cells or epidermal idioblasts in the leaves (Sangster, 1968). Silicon deposition was found to be related to the basipetal maturation gradient found in leaves, and to the Si concentration in the root zone (Sangster, 1970). The transport, influx, and polymerization of Si in these cells appears to be through passive, non-metabolic processes (Sangster and Parry, 1971). In later work, Si deposition has been related to mineral distribution in the leaves of two species. In wheat, Si was found in the abaxial epidermal cells and trichomes of young leaves, and in internal as well as epidermal cells of older leaves (Hodson and Sangster, 1988a). Potassium and chlorine were frequently found at Si deposition sites, but the relationship with Si is unclear.

Relatively fewer studies have been conducted on Si accumulation in the leaves of dicotyledons since they are generally not known to accumulate Si to the same degree as monocotyledons. Even so, some of the information which is available has come from Canada. Cucumber (*Cucumis sativus*) leaves have been found to accumulate Si primarily in trichome bases (Chérif et al., 1992a; Samuels et al., 1991a, 1991b). Samuels et al. (1991a, 1991b) found that when Si-deprived plants were supplied with nutrient solutions containing Si, the element was rapidly deposited in an insoluble polymerized form in the trichome bases. This suggests that trichome bases differ from the surrounding epidermal cells, and that silicification is not necessarily concomitant with cell wall deposition. Si will accumulate in epidermal cells only in the presence of a pathogen, and is confined to those epidermal cells surrounding the point of infection (Samuels et al., 1991a, 1991b).

In gymnosperms, needles of *Picea glauca* (white spruce) were found to accumulate Si in the epidermis, hypodermis, mesophyll, and endodermal cell walls (Hodson and Sangster, 1998). Al was located exclusively in the epidermis, suggesting a relationship with Si as was mentioned previously for the roots of some species.

20.2.4. Reproductive structures

Sangster and colleagues have also examined the distribution of Si in the inflorescence of cereals. In wheat, deposits of Si occur in inflorescence bracts (Hodson and Sangster, 1988b, 1989c; Parry et al., 1984). The outer walls of all the epidermal cells of the glume and lemma awns were found to be silicified. The glume and lemma had similar structures, with silicified short trichomes and papillae on the inner and outer surfaces. The palea were found to have Si deposits in macrohairs. The epicarp hairs of the cereal grain (but no other cells of the caryopsis) were also found to have deposits of Si (Parry et al., 1984).

In *Setaria italica* (foxtail millet), an important food source in Asia, Si was found in the inflorescence bristles which subtend each spikelet, as well as in the unicellular macrohairs which cover the inflorescence axis and branches (Hodson et al., 1982). Given that silicified plant structures may play a role in oesophageal cancer (IARC, 1997), this finding has implications in human nutrition. Sangster and colleagues have also found Si accumulations in the inflorescence bracts of *Phalaris canariensis* (canary grass), a food grain consumed in Iran (Hodson et al., 1985; Sangster et al., 1983).

The mechanism by which Si arrives in the reproductive organs in monocotyledons is unclear. In *P. canariensis*, Si is deposited in macrohairs of the lemma after inflorescence emergence (Sangster et al., 1983), suggesting a passive, transpiration-driven uptake. This hypothesis is supported by bagging experiments to manipulate humidity around the inflorescence (Sangster and Hodson, 1986). Increasing humidity reduced Si accumulation in lemma macrohairs. On the other hand, Si accumulates in glume macrohairs, prickle hairs, and papillae of *P. canariensis* (Sangster et al., 1983) as well as epicarp hairs of wheat grains (Parry et al., 1984) before inflorescence emergence, suggesting an active, metabolic process of Si uptake.

The only other Canadian work to describe Si in reproductive structures deals with fruit. Samuels et al. (1993) showed that when cucumber plants were grown with Si, a bloom developed on the fruit, giving it a dull appearance. Si appeared to induce a change in trichome morphology, from smooth trichomes in the absence of Si to coarse in the presence of Si. The deposition of Si was restricted to trichomes, with none detected in the epidermis.

20.3. THE CHEMISTRY OF SILICON IN BIOLOGICAL SYSTEMS.

The biochemistry of Si in plants is largely an uncharted area (Epstein 1999). The natural occurrence of organo-silicon compounds in plant tissues has not been detected, but there is ample evidence that Si is not biochemically inert. In Canada, recent work at Lakehead University (Thunder Bay, Ontario) by Kinrade and associates has shed some light on possible biochemical modes of uptake and transport of Si *in planta*.

Kinrade and associates studied the effects of alcohols and simple organic cations on the structure of aqueous silicate anions (Kinrade et al. 1999a, 1999b; Knight and Kinrade, 1999). Using ^{29}Si and ^{13}C NMR spectroscopy, they showed that certain aliphatic polyhydroxy molecules, including a number of simple sugars, interact readily with aqueous silicates and increase Si solubility. High concentrations of stable 5- and 6- coordinated Si complexes result if the aliphatic polyol contains four or more adjacent hydroxy groups, with two being in the *threo* configuration. Thus, complexing polyols include threitol, xylitol, sorbitol, and mannitol, but not erythritol. Each of the resulting hypervalent complexes contains only one Si center. Polyols that contain a terminal carboxylate group exhibit still greater reactivity. Thus, 5-coordinated silicon-gluconate species form readily, even at pH 7.0. Their studies demonstrate that stable organo-silicon complexes can form under physiological conditions using common sugar-like molecules and suggest that polyhydroxy containing groups and surfaces may play a key role in isolating silica and silicic acids in nature.

20.4. SILICON ENHANCED RESISTANCE TO FUNGAL PLANT PATHOGENS

20.4.1. Effect of silicon fertilization on disease severity.

The largest Canadian research effort to understanding the influence of Si on plant disease resistance has focused on hydroponically grown, long, English cucumber plants in greenhouses. This work was initiated in the late 1980s at the Pacific Agri-Food Research Centre (PARC, Agassiz) and Laval University, and was largely motivated by the work of Miyake and Takahashi (1983a, 1983b) in Japan and Adatia and Besford (1986) in the United Kingdom. In experiments involving cucumber plants grown in hydroponic nutrient solutions devoid of or supplemented with 100 ppm SiO_2 , Miyake and Takahashi (1983a) and Adatia and Besford (1986) noted that the Si-treated plants remained almost free of powdery mildew, while Si-untreated plants suffered natural outbreaks of the disease. Miyake and Takahashi (1983b) also noted in field experiments that Fusarium wilt was reduced by Si treatment of cucumber plants. Building on this work, researchers at PARC and Laval University started programs to further study this phenomenon and how it might best be used in commercial cucumber greenhouses.

Research at PARC was initially focused on further examining the role of Si fertilization of cucumber in reducing powdery mildew caused by *Sphaerotheca fuliginea* (Schlechtend.:Fr.) Pollacci. At Laval University, the work focused on Pythium root rot caused by *Pythium ultimum*

Trow. In both instances, hydroponically grown cucumber plants were treated with nutrient solutions supplemented with Si over a range of 0 to 200 ppm Si; the Si being added in the form of either soluble sodium or potassium silicate. The cucumber plants were then inoculated with *S. fuliginea* at PARC, Agassiz or *P. ultimum* at Laval University, and monitored for disease development. The results for the two groups demonstrated that Si amendment of the nutrient solutions significantly reduced the negative effects of the diseases. Silicon treatment reduced the area of the leaves covered with colonies of *S. fuliginea* by 98% (Menzies et al., 1991a) and reduced the plant mortality, root decay, and yield losses attributable to *P. ultimum* (Chérif and Bélanger, 1992). At both Laval University and PARC, Agassiz, the concentration of Si in the nutrient solution, giving optimum disease reduction, was found to be 100 ppm. Experimental results also demonstrated that the disease suppressive effect was not influenced by the cations (Na or K) associated with silicate or the change in solution ionic strength caused by addition of the silicate (Menzies et al., 1991a). Only Si influenced the susceptibility of the cucumber plants to the pathogens. A large experiment with cucumber and *S. fuliginea* under conditions similar to commercial greenhouses demonstrated that amending the nutrient solution with 100 ppm Si could delay the development of severe powdery mildew on host leaves (a minimum of 100 colonies per leaf) by 3.5 weeks (Bélanger et al., 1995). Even though powdery mildew could not be completely controlled using silicon amendment in the nutrient solutions, these large-scale experiments, as well as others reviewed by Bélanger et al. (1998), showed that Si could reduce the incidence, and delay the spread of powdery mildew. Overall then, Si has been demonstrated to influence both foliar and root diseases in the same plant species.

The success obtained with reducing the severities of *S. fuliginea* and *P. ultimum* on cucumber led to the exploration of the effects of Si on other pathogens and plants. The detrimental effects of *P. aphanidermatum* on cucumber were also found to be reduced following Si fertilization (Chérif et al., 1994), but the effects were not as dramatic as the Si effects on *P. ultimum* (Chérif and Bélanger, 1992). Treatment of muskmelon and zucchini squash with Si-amended nutrient solutions reduced the infection severities of powdery mildew caused by *S. fuliginea* and *Erysiphe cichoracearum* DC. when inoculated onto leaves (Menzies et al., 1992). Bélanger (unpublished data) also found Si fertilization drastically reduced the severity of powdery mildew on dandelion. Unfortunately, the positive effects of Si fertilization were not universal to all the host-pathogen systems tested. Powdery mildews of grape and tomato were not affected by Si fertilization of the host (Bowen et al., 1992; Ehret and Menzies, unpublished data), and Si had no effect on Fusarium crown and root rot of tomato (Menzies and Ehret, unpublished data), and Pythium root rot of lettuce (Bélanger and Menzies, unpublished data).

20.4.2. Effect of foliar sprays of silicon on disease severity.

The positive results of Si fertilization in reducing the severity of diseases on crops such as hydroponically-grown cucumber led to an exploration of different application methods so that Si could be applied to non-hydroponic crops or to plants unable to transport Si through their vascular systems from roots to foliar parts of the plant. Initial work was conducted on cucumber, muskmelon, and zucchini squash, since a reduction in the severity of diseases through application of Si had already been established for these hosts. Applications of sprays containing 100, 500, 1,000 and 2,000 ppm SiO_2 (applied as soluble potassium silicate) were applied to the leaves of these three hosts one day prior to inoculation with conidia of their respective powdery mildew pathogens. Foliar applications of 500 ppm Si or greater were found to significantly reduce the number of colonies of powdery mildew on the host leaves (Menzies et al., 1992). Foliar

applications of 1,000 ppm Si or greater resulted in a reduction in powdery mildew colonies on the host leaves that was equal to the reduction of colony numbers achieved with Si fertilization at 100 ppm Si. There was no significant reduction in powdery mildew colony numbers with an increase in the amount of Si above 1,000 ppm in the foliar sprays. As in the Si fertilization experiments, the Si appeared to be the active ingredient in the foliar sprays.

Foliar application of Si was also studied in the powdery mildew/grape and powdery mildew/tomato pathosystems. Neither of these plant species are able to transport Si into the shoot from the root. In both systems, the foliar application of 1,000 ppm Si onto the leaves reduced the severity of powdery mildew (Bowen et al., 1992; Ehret and Menzies, unpublished data). Similar to Menzies et al. (1992), Bowen et al. (1992) found that Si appeared to be the active ingredient in the foliar sprays on the grape leaves. Therefore, Canadian groups have demonstrated that foliar sprays of Si will effectively reduce disease infection even in species which are genetically incapable of transporting and utilizing Si from the root zone.

20.4.3. Mode of action

20.4.3.1. Silicon fertilization

Wagner (1940), in Germany, was the first to speculate on the mode of action of Si, supplied as a fertilizer amendment, in reducing the severity of diseases on host plants. Working with powdery mildew, he suggested that the increased silicification of the host cell wall prevented penetration by the pathogen. Consequently, fewer conidia of the pathogen were able to infect Si-treated host plants. Menzies et al. (1991a) did not obtain any data in their experiments that would have contradicted Wagner. Menzies et al. (1991a) found strong negative correlations between the amount of Si in the leaf tissue (percent dry weight) and the area of the leaf covered by colonies, the number of colonies per leaf, the individual colony size, and germination of conidia produced on the leaves. However, further examination, in Canadian labs, of the mode of action of Si in reducing the severity of fungal diseases on plants suggested that the role of Si was more complex.

Samuels et al. (1991a, 1991b) tried to more fully understand the role of Si in disease suppression by examining cucumber leaves infected with *S. fuliginea* using electron microscopy and energy dispersive X-ray analysis. Their studies revealed that along with trichome bases, Si accumulated in regions where the pathogen appeared to be attempting to penetrate the host, i.e. at points along fungal germ tubes or hyphae where the host cell wall had become modified into a region of smooth texture. As colonies of *S. fuliginea* developed from initial points of infection, measurements of total hyphal length per colony showed that colonies on Si-treated plants were significantly smaller than those on control plants. The presence of high Si in plant tissue surrounding the fungal colonies was correlated with less hyphal growth, but the evidence for Si acting solely through increased silicification of host cell walls did not appear to be very strong from these results. As well, if increased silicification of the host cell walls had a major role in disease suppression, it did not appear to be a passive process. Accumulation of detectable Si around conidia of the pathogen occurred after germination and attempted host penetration, and only when the cucumber plant was being actively fed Si. Plants grown in Si-supplemented media and transferred into Si-deficient media contained residual Si in the leaf trichome bases, but failed to display resistance or silicification of host tissue surrounding points of attempted penetration arising from germ tubes or hyphae of *S. fuliginea* (Samuels et al., 1991b). It appears that once Si is deposited in cucumber leaf tissue, it is not remobilized, and the amount of Si deposited in the epidermis prior to stimulation by the pathogen is insufficient to affect the severity of disease caused by pathogens such as *S. fuliginea*.

Light microscopy work by Menzies et al. (1991b) also noted less hyphal growth of colonies of *S. fuliginea* on Si-treated plants, but Si treatment did not affect the number of germinating conidia that formed haustoria. The pathogen was able to infect epidermal host tissue and form haustoria despite the treatment of the host with Si. The effect of the Si was to reduce the number of haustoria per colony over time, rather than prevent colony formation during early colony development. Further electron microscopy work by Samuels et al. (1994) found no apparent differences in the ultrastructure of the haustoria in leaves from Si-treated or untreated plants. However, there were obvious changes to the cell wall of the Si-treated leaves. The cell wall in infected cells and the cells surrounding the trichome bases were electron opaque and often shattered upon sectioning. In infected cells, electron dense deposits were observed within the host cell wall, as well as in the papillae region between the host cell wall and the plasma membrane. The collar, the defense structure produced by the host, which surrounds the haustorial neck, also contained these electron-dense deposits. The presence of Si was confirmed in the cell walls of infected cells, in the deposits between the plasma membrane and cell wall, and around the haustorial neck. No Si was detected in the extra-haustorial membrane, haustoria, fungal mycelium, or uninfected epidermal cells (except for trichome base cells). The cell walls in infected plants from plants not treated with Si were also modified in that they were more electron-dense than uninfected cells, but they did not show the tendency to shatter upon sectioning, and the density was confined to the wall proper. No Si was detected in these leaves.

Chérif et al. (1992a) were also interested in Si movement and location in cucumber plants, but they examined the cucumber-*Pythium ultimum* pathosystem instead. They also found that in uninfected plants, Si deposits were only found in the base cells of trichomes on the hypocotyl or leaf tissue of Si-treated plants. In examining tangential sections of *P. ultimum*-infected roots, there was no detectable Si accumulation in the epidermal, cortical or, stelar tissues of Si-treated or untreated plants. Silicon was not associated with sites of fungal penetration or fungal hyphae. Interestingly, when Chérif et al. (1992a) grew plants in 100 % humidity and inoculated leaf tissue with *P. ultimum*, they did not detect Si at points of fungal penetration.

The results of the electron microscopy and energy dispersive X-ray analysis work of Chérif et al. (1992a) and Samuels et al. (1991b) led both sets of researchers to conclude that the enhanced defense reaction of the cucumber plant to its pathogens (*P. ultimum* and *S. fuliginea*, respectively) appeared to be primarily the result of the Si present in the plant's transpiration stream and not the Si that becomes bound to the host cell wall. This work and further work by Chérif et al. (1992b) and Menzies et al. (1991b) revealed that while the role of silicified cell walls in protecting plants against pathogens may not be completely discarded, it appears that Si acts in cucumber host tissue by affecting signals between the host and pathogen, resulting in a more rapid and extensive activation of the plant defense mechanisms. Further discussion of the role of Si in enhancing plant disease resistance is discussed by Fawe et al. in this book and we would refer you to that chapter.

The association of Si with fungal infection has been noticed and commented on by Canadian researchers studying other pathosystems. Harder et al. (1986) noticed that Si was deposited between wall layers of germinating urediospores of *Puccinia graminis* Pers. f. sp. *tritici* Eriks and E. Henn. They suggested that Si was not involved in the development and germination of the urediospores because Si was observed in only one-half the spores.

Chong and Harder (1980, 1982), using X-ray analysis, examined the ultrastructure of haustorium development of *Puccinia coronata avenae* on oat, and noted an association of Si with the haustorial mother cell and neck ring. In examining the haustorial neck ring, Chong and Harder (1980) noted that there were 2 bands that made up the neck ring: a broad α band that formed closer

to the haustorial mother cell and a narrower β band which formed closer to the haustorium. X-ray analysis showed that Si was a major element in the α band, and iron and phosphorous (possibly in the form of ferric pyrophosphate) were the major elements of the β band. Assuming that the Si was supplied to the fungus through the host, they concluded that deposition or polymerization of Si has to occur at some predetermined location in the haustorial neck wall region to allow the neck ring to form. The neck ring is important to the pathogen because it prevents apoplastic flow of substances along the haustorial neck wall and out of the infected cell, which may favor a more controlled uptake of substances by the fungus through the haustorium (Chong and Harder, 1980; Heath 1976). Chong and Harder (1982) also noted Si deposits in the walls and septa of many haustorial mother cells (HMC) located at or near the centers of the infection colonies. The HMC's were often collapsed and frequently found to be associated with aberrant necrotic haustoria which were common in host cells at the centers of old colonies. They interpreted the necrosis of the haustoria to be an indication of incompatibility, which probably resulted from the production of deleterious cell breakdown products. They concluded that heavy Si deposition in the HMC and septa was a protective mechanism of the fungus and acted as a permeability barrier to prevent or minimize passage of deleterious cell breakdown products to the rest of the pathogen mycelium. They also concluded that Si deposition and/or polymerization must occur through a controlled metabolic deposition of the Si.

Heath and co-workers also noted the association of Si in plant-fungus pathosystems; but what makes their work especially interesting, is that they examined pathogen development on incompatible hosts and non-host plants. Heath (1981) noted the accumulation of high levels of Si in electron-opaque regions of haustorium encasement, necrotic host cytoplasm, and adjacent host cell walls and wall deposits of cowpea (*Vigna sinensis*) infected by an incompatible isolate of the cowpea rust fungus (*Uromyces vignae*). This finding was significant in that it demonstrated, along with earlier work on French bean (Heath, 1979), that the accumulation of Si as a response to infection is not restricted to angiosperms that normally possess silicified cell walls (also noted above with cucumber). Heath (1981) noted that the accumulation of Si was not related to haustorium formation. Heath was uncertain of the significance of Si in the cell walls and necrotic cytoplasm, and suggested that Si accumulation may be an active process or reflect a passive secondary association of Si with phenolic compounds present in the disorganized host cell.

Further work by Heath and co-workers concentrated on the interactions between the cowpea rust fungus and French bean, a non-host. Heath and Stumpf (1986) examined the infection process of the rust fungus on untreated and Si-depleted bean leaves and observed that fungal penetration was stopped earlier on the Si-depleted bean leaves than on the untreated leaves. On the untreated leaves, fungal development apparently ceased while the penetration peg was traversing the haustorial mother cell, often before the peg reached the adjacent silicified wall of the plant. On the Si-depleted leaves, 3 of 10 infection sites had haustoria, but at the remaining sites, development of infection ceased before the development of a penetration peg. They suggested that high levels of wall-associated phenolics in the Si-depleted tissues resulted in a more rapid inhibition of fungal enzymes involved in the formation of the penetration peg. In the untreated tissues, the presence of Si in the plant cell walls acted to: 1) reduce the interchange between the plant and fungus, so lesser amounts of phenolics were produced by the host; 2) restrict the flow of substances to the haustorial mother cell that would normally prevent its premature senescence, and/or 3) acted as a physical barrier to the penetration peg if it reached the cell wall.

Treatment of the leaves of French bean plants with plant growth regulators, intercellular washing fluids, or inhibitors of various cellular processes just prior to inoculation with the cowpea

rust fungus gave further insight into the role of Si in the infection process (Li and Heath, 1990; Perumalla and Heath, 1991). By examining the effects of these different treatments on the deposition of callose, Si and wall-bound autofluorescent materials (thought to be phenolic in nature), these researchers were able to determine how these three wall modifications are related to each other and to successful infection by the fungus. Li and Heath (1990) found that when abscisic acid and gibberellic acid were injected into bean leaves, deposition of Si and autofluorescent materials on mesophyll walls at infection sites was reduced and the incidence of haustoria of the cowpea rust fungus increased. In studies examining corn rust and French bean, similar results were obtained, except the frequency of autofluorescent wall was not reduced. When Li and Heath used intercellular washing fluids from bean rust-infected bean leaves, and other compatible rust-plant interactions to inject French bean leaves prior to inoculation with the cowpea rust fungus, they once again found an increase in the incidence of haustoria produced by the fungus, and a decrease in the deposition of Si in the bean leaves. Perumalla and Heath (1991), using different inhibitors of cellular processes, were able to examine the metabolic relationship between the deposition of callose, phenolic materials and Si, and the relative role each process had in preventing haustorium formation of the cowpea rust fungus on the non-host French bean leaves. They noted that callose deposition was independent of Si deposition and wall autofluorescence is independent of Si deposition. However, Si deposition required the presence of phenolic compounds and possibly hydroxyproline-rich glycoproteins in the plant cell wall. Their data suggested that Si deposition may be the most important of the three responses in preventing haustorium formation in normal plants. They also concluded that Si deposition in French bean was not solely the result of the precipitation of monosilicic acid from the apoplast by phenolic compounds in the cell walls, but required cellular activity.

20.4.3.2. Foliar application.

Much less is known about the activity of foliar-applied Si in host-pathogen interactions. Bowen et al. (1992) used scanning electron microscopy and X-ray analysis to examine grape leaves inoculated with *Uncinula necator* (Schwein) Burrill after either root or leaf applications of soluble Si. The root applications of Si did not reduce the severity of powdery mildew on the leaves, while foliar application of the Si substantially reduced disease development. However, despite the method of Si application to the plant, Si was translocated to the leaves and deposited around the fungal appressoria. On leaves receiving a foliar application of Si, fungal hyphae did not develop on sprayed leaf surface areas when dry Si deposits were present. To test whether Si was an inhibitor of conidial germination or germtube development, conidia of *U. necator* were cultured on agar media to which 0.17 mM Si had been added. Bowen et al. (1992) found that the Si in the agar media weakly promoted conidia germination and germtube development. Interestingly, Samuels et al. (1991a) noted that Si accumulated in germinating conidia of *S. fuliginea* on the surface of Si-treated cucumber leaves (24 hours after inoculation), supposedly being sourced from the cucumber leaf tissue. These germinating conidia had significantly shorter germ tubes than conidia observed on leaves which did not receive Si treatment. At subsequent stages of infection and colonization, Si was detected only in the host cell wall surrounding the hypha and never in fungal structures. However, as noted previously, Si treatment did not appear to affect the number of germinating conidia that formed haustoria (Menzies et al., 1991b). The foliar application of Si may be acting by creating a physical barrier to hyphal penetration or by inducing the accumulation of phenolics and/or other defense mechanisms, but with the data currently available, no conclusions can be made.

20.4.4. Silicon effects on growth and yield in cucumber.

Silicon is well-known to affect plant mineral nutrition, and at least in some cases, may promote growth through this interaction (Marschner et al., 1990). Research around the world has suggested that there is a beneficial effect of Si on cucumber growth and yield (Adatia and Besford, 1986; Bloemhard, 1992; Miyake and Takahashi, 1983; Voogt, 1988, 1990, 1991; Voogt and Kreuzer, 1989). However, these studies do not clearly state whether or not the effects of Si on plant disease were accounted for. In Canada, Straver (1991) examined the effects of Si on growth and yield of cucumber, in which powdery mildew was diligently controlled through the use of fungicides and resistant varieties. Straver found no relationship between Si in the nutrient feed of the cucumber plants and growth of the crop. Since Si appears to alleviate both abiotic and biotic stress (Epstein, 1994), it may be that the effects of Si on plant performance are evident only when some form of stress is imposed. It appears clear that more research is needed in this area, especially with commercially important vegetable crops grown in soilless culture. In these systems, the SiO_2 concentration in the nutrient solutions is usually less than 0.17 mM (10 ppm) (Ehret, unpublished), and can become lower as the plants remove the Si from the nutrient solutions.

20.5. DIATOMACEOUS EARTH AND SILICA AEROGEL FOR THE CONTROL OF INSECT PESTS IN CEREAL STORAGE AND PROCESSING FACILITIES.

The effective management of stored cereals to minimize qualitative and quantitative losses is based on prevention, detection, and control of pest insects, mites, molds, and associated mycotoxins. Canada has a legally defined zero tolerance for pest insects in stored grain for human consumption, which is critical for export markets. Alternative control techniques are needed to the use of chemical pesticides, as consumers are rejecting chemical residues, and the incidence of insecticide resistance is increasing in pest populations. The small number of fumigants and contact insecticides registered for use may become ineffective or be removed from the market because of perceived carcinogenicity to humans or environmental effects, as is happening with the fumigant methyl bromide, an atmospheric ozone depleting chemical. An annual average of 54 million tons of cereal grains and oilseeds were produced in Canada between 1982 and 1991, of which 26.1 million tons per year were wheat. Carryover of wheat for more than 1 year of farm storage averaged 8.7 million tons. In Canada, low level infestation by insects of grain on farms can reach 46% of granaries across a province (Madrid et al., 1990). Canada is the only major grain-exporting nation that stores more than 75% of all grain stocks on the farm rather than in central storage facilities (Moore, 1995). Direct and indirect costs associated with storage insects, mites, and molds probably exceed \$167 million throughout the food-handling chain in Canada (White, personal communication). This has led to research on more consumer and environmentally friendly ways of controlling storage pests.

Inert dusts have been studied as alternatives. They are applied in similar fashions to chemical pesticides and can be effective. In commerce, diatomaceous earth (DE) and silica aerogel are the predominant forms of inert dusts used, both of which are composed of silicon dioxide. The mode of action of silicon dioxide-based inert dusts is generally accepted to be desiccation. Two observations support this conclusion: 1) inert dusts are more effective when the grain moisture content or the relative humidity is low (Fields and Korunic, in press), and 2) insects treated with inert dusts usually have higher rates of water loss (Fields and Muir, 1995; Fields et al., in press). Although DE has been used for centuries to control stored product pests, research in Canada was

initiated to attempt to find ways to use DE at lower concentrations to improve commercial formulations, and to examine the combined effect of high temperature and DE.

20.5.1. Improvement of DE formulations.

Commercial formulations of DE first became widely available in the 1950s. Some of these formulations can be highly effective in protecting stored products from insect damage. In some cases, DE provided better control of insects than malathion, particularly over the long term. However, relatively large amounts of DE were added to grain to provide protection, i.e. 3.5 kg/ton. Since then, improved formulations have reduced the amounts of DE that need be added to stored products to get effective insect control, but these concentrations are still too high (500 to 3600 ppm) to be accepted by the grain industry. The addition of large amounts of DE to grain in storage creates problems because it decreases the bulk density and flowability of the grain (Korunic et al., 1996; Fields, 1998) and leaves visible residues (chalky-white appearance), thereby, reducing the grade of the grain because it is classed as containing foreign material. Diatomaceous earth has also been thought to cause excess wear on machinery, and workers complain because of airborne dust during treatment and movement of grain (Fields et al., in press). Some of these problems could be solved or reduced if the products were used at lower rates.

Korunic and Fields (1995) examined the effects of mixing DE with silica aerogel for the control of stored-product insects. Diatomaceous earth was chosen because it is easy to apply and relatively inexpensive to use, even though it is effective only at high rates; the silica aerogel was chosen because it is highly effective at low rates, but difficult to apply and expensive. In their experiments, they used a number of different types of DE from different parts of the world. This is because the insecticidal properties of DE depend upon the geological origin of the material, some types being 20 times more effective than others (Korunic, 1997; Fields and Korunic, in press). The types of DE's that are most effective in insect control have an SiO_2 content above 80%, a pH below 8.5, and a tapped density below 300 gL^{-1} . The different DE's and silica aerogel were mixed in different proportions by weight. This material was tested by measuring its tapped density and run through laboratory and field bioassay procedures using the rusty grain beetle [*Cryptolestes ferrugineus* (Stephens)], the rice weevil [*Sitophilus oryzae* (Linnaeus)], the lesser grain borer [*Rhyzopertha dominica* (Fabricius)], and the red flour beetle [*Tribolium castaneum* (Herbst)]. They concluded that the efficacy of almost every DE against insects, even with low activity, could be increased by mixing with silica aerogel and the concentration needed to control insects were greatly reduced (Korunic and Fields, 1995). Protect-It™, a formulation containing 10% silica aerogel mixed with DE, is sold in the USA and Canada as a stored grain protectant by Hedley Technologies Inc. It is about 2 fold more effective than other DE-based stored grain protectants.

20.5.2. Diatomaceous earth and heat

Methyl bromide is either used regularly or as an emergency treatment to control insects in the food processing industry. It plays an important role in pest control in these establishments, which is required in meeting food quality and consumer needs. However, because methyl bromide is an ozone depleting substance, it will be unavailable for this use by 2005 in most developing countries. This rapidly approaching deadline has already resulted in some parts of the Canadian milling and processing sectors reducing or eliminating methyl bromide use in favor of heat or other treatments to control pests in food processing facilities (Fields et al., 1997). In Canada, heat treatments to control stored-product insects have been used at Quaker Oats' food processing plant in

Peterborough, Ontario for more than 20 years (Clark, 1996). However, no other Canadian companies are known to rely on heat treatments on a regular basis. Some of the factors that may have prevented the widespread adoption of heat treatments are: the capital investment in heating equipment, the need for more frequent treatments, and concern about heat damage to buildings and equipment. To address some of these concerns, researchers began investigating ways to render heat treatment more effective and less costly.

Since food processing facilities usually have low relative humidities, which are reduced even more during heat treatments, a series of experiments was conducted to determine if DE could be used to increase efficacy and speed of heat treatments (this work was a collaboration between Agriculture and Agri-Food Canada, Hedley Technologies, Vancouver, B.C., and the United States Department of Agriculture, with the cooperation of Quaker Oats of Canada). The DE product used was Protect-It™ (Hedley Technologies, Vancouver, British Columbia, Canada) because it has been shown to perform as well as or better than other commercial DE products (Korunic and Fields, 1995). Laboratory tests were conducted with the red flour beetle (*T. castaneum*) and commercial-scale tests with the confused flour beetle (*T. confusum* Jaquelin du Val). In the laboratory tests, red flour beetles were exposed to no DE or DE at 3 or 7 g/m² and temperatures of 34 or 50°C for periods of 15 or 30 minutes. Some beetles were given flour as food, while others were not fed during the experiments. In general, mortality of the beetles increased as the exposure time to high temperature and DE increased (Fields et al., 1997). After 7 days, almost all beetles exposed to DE were dead for all treatment combinations. The unavailability of food resulted in higher average mortality rates, which was expected, because of starvation and better retention of DE on the cuticle. Insects with food would likely dislodge some DE as they walked through the flour, and food would also be a source of water, reducing the desiccation stress.

Commercial-scale trials were conducted at the Quaker Oats cereal milling and processing facility in Peterborough, Ontario, Canada. Heat treatments are scheduled roughly four times a year at this facility. Heat treatment is preceded by a thorough cleaning of the facility; although cleaning is a daily component of this, and most, Canadian facilities. The treatment normally begins late Friday afternoon, continuing through the night, all day Saturday, and is finished by Sunday morning. The goal is to reach an air temperature at eye level of 50°C and hold that temperature for 24 hours. In this experiment, most areas of the facility reached 50°C after 18 hours from the initiation of heating, although difficult-to-heat areas reached the desired temperature at 30 hours after initiation. The experimental treatments included heat alone, DE alone, heat with DE, and no heat or DE. Dry application of DE resulted in 100% mortality of the confused flour beetles (adults) after 13 to 22 hours at 41°C, compared to no DE treatments that required 32 to 38 hours at 46 to 47°C (Fields et al., 1997). Heat alone did not always result in 100% mortality of the beetles. The authors concluded that DE could make heat sterilization more acceptable to the industry because it would require lower temperatures to obtain control. The use of DE and heat could be a effective alternative to the use of methyl bromide as a fumigant in these types of facilities.

20.6. CONCLUSION

In conclusion, Canadian scientists have been involved in several areas of research pertaining to the role of Si in agriculture. Their input has ranged from the complex chemistry of Si in biological systems to the role of Si as a disease and insect preventing agent to finally the biochemical understanding of the mode of action of Si *in planta*. These contributions have certainly furthered

our knowledge of Si in agriculture, but have probably highlighted even more how little we know about this element and its complex interaction with the plant kingdom.

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Chapter 21

Agricultural utilization of silicon in China

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The first research on potential uses of silicon (Si)-containing industrial by-products as fertilizers and soil amendments in China was carried out in the late 1950s. Silicon fertilization has increased steadily since 1970, and Si fertilizers have been used most often to improve rice production by enhancing resistance to diseases and lodging. Field trial results conducted in recent years have demonstrated that many other crops also have positive responses to Si fertilization. The increased yield from Si fertilization has been attributed mainly to enhanced resistance to diseases, lodging, drought, and other environmental stresses (e.g. salt and elemental toxicity), and optimized crop nutrient balance. It has also been found that applying Si, together with other nutrients such as Zn and Mn as well as N, P, and K, can significantly enhance the beneficial effects of Si.

This paper provides an overview of the soil Si fertility, a history of Si fertilization research and practices in China, and summarizes the research effort to understand the interactions between Si and other elements and improve the efficiency of Si fertilization. This is followed by directions recommended for future research on Si in China.

21.1. INTRODUCTION

Since Sommer (1926) demonstrated the favorable impact of Si on rice growth, numerous studies on the beneficial effects of Si fertilization have been carried out worldwide. In the late 1950s, Chinese scientists began to investigate potential agricultural uses of Si-containing slags, reporting that application of these slags could significantly improve crop growth and yield (Zhu and Chen, 1963). Until the late 1980s, there were no commercial Si fertilizers, and researchers had to manufacture Si fertilizer for their trials. Rice straw and Si-rich clay once were recommended as Si fertilizers (Qin, 1988). Silicon fertilization has been increasingly common in the last two decades, resulting in increasing amounts of commercially produced Si fertilizer. At present, approximately one million tons of Si fertilizer are produced and used annually in China. Most Si fertilizers are produced using steel slag and by-products from phosphorus industries. Work on Si fertilization has mainly been focused on paddy soils and rice production; although, Si fertilizer has also been used to improve yield of upland crops, such as wheat and corn, since the late 1980s. In

many parts of China. Si fertilization has been recommended as a standard practice in crop production.

This paper aims to provide an overview of the past and current research and practices, and make recommendations for future advances of Si fertilization in China.

21.2. SOIL SILICON FERTILITY IN CHINA

Soil-available Si is generally extracted using pH 4.0 HAC-NaAC (sodium acetate) buffer solution in China, expressed as "mg SiO₂/kg". Most researchers use a value within the range of 95-110 mg SiO₂/kg of extractable Si as a critical index to evaluate whether a soil is deficient in Si (Zang and Zhang, 1982; Wu et al., 1996; Li et al., 1999). However, positive yield responses have been achieved in soils with much higher extractable Si, especially in the northern regions of China (Wang, 1993). Although no national database is available, it is apparent from the literature that Si deficiency is common in many paddy soils and some upland soils in China (Zhang and Zang, 1986; Ma, 1990; Ye and Xu, 1995; He and Wang, 1999).

It appears that soil-available Si concentrations in the southern and southeastern regions of China are lower than those in northern and western China. Concentrations of soil-available Si are strongly influenced by soil parent materials, climate conditions, and cultivation history (Ma, 1990; Zang and Zhang, 1982). In southern and southeastern China, strong desilicification and allitic weathering have been the dominant soil formation processes, resulting in many soils containing relatively low available Si. Most light-textured paddy soils are Si deficient, with the available Si concentration being commonly below 80 mg SiO₂/kg. Clayey soils in this region generally have moderate Si supply capacity with an average extractable Si of 120 mg SiO₂/kg. High available Si concentrations (greater than 200 mg SiO₂/kg) can be found in paddy soils developed from alluvium originated from large rivers and lakes, basalt, shale, and other Si-rich parent materials (Zang and Zhang 1982; Fan et al., 1989).

He and Li (1995) analyzed available Si concentrations and distribution in paddy soils developed on different parent materials from various parts of Hubei Province in central China. They showed that concentrations of soil-available Si depended mainly on the parent material. Concentrations of available Si were high in soils developed from limestone and red-purplish carbonated shale; medium from alluvium and lacustrine deposits, and quaternary red clay; and low from granitic gneiss and sandy shale. Silicon concentration was positively correlated with soil pH. The available Si concentrations for the soils with pH<6, pH = 6-6.5, and pH>7 were <100, 166.9, and 229.8-580 mg SiO₂/kg, respectively. He and Li (1995; 1996) concluded that paddy soils in Hubei could be divided into three categories of Si supplying capacity of high, medium, and low, depending on the pH.

Xue and Sun (1991) surveyed the concentrations of soil-available Si in Sichuan Province, in southwestern China. About 2 million ha of paddy soils, equivalent to 44% of total paddy soil area, had an available Si concentration less than 95 mg SiO₂/kg. About 16% of these had an extremely low extractable Si concentration (< 50 mg SiO₂/kg). Hua (1994) analyzed the data from field trials conducted throughout the Sichuan Province in 1984-90 in relation to rice growth and yield. The concentrations of available Si in 270 soil samples ranged from 22 to 450 mg SiO₂/kg, and about two-thirds of paddy soils were below 98 mg SiO₂/kg. Available soil Si was positively correlated with pH, with the degree of correlation varying with soil type.

It has been reported that 55.5% of the paddy soil areas in Guangdong Province of southern China are Si deficient (less than 95 mg SiO₂ kg⁻¹) (Ke et al., 1993). In Guangdong Province, approximately 22.3% of paddy soil are considered as Si sufficient (Ke et al., 1993). In Fujian Province, southeastern China, 95% of paddy soil are Si deficient, with concentrations of available Si ranging from 32 to 90 mg SiO₂ kg⁻¹ (Ye and Xu, 1995). Concentrations of available Si in most paddy soils in Zhejiang Province, in eastern China, are in the range of 87-118 mg SiO₂ kg⁻¹ (Peng et al., 1989). In Jiangsu Province, concentrations of available Si are lower than 100 mg SiO₂ kg⁻¹ in approximately 7 million ha of paddy soil (Lu, 1996). In the southern part of Jiangsu Province, concentrations of available Si in paddy soils only averaged 69 mg SiO₂ kg⁻¹ (Zhang, 1989). Hunan Province is in central China, and the majority of paddy soils there have very low concentrations of available Si (26-73 mg SiO₂ kg⁻¹) (Xiang et al., 1993). Fan et al. (1989) investigated the concentration of available Si in the main types of paddy soils in Jiangxi Province and found that most soils had an available Si of less than 100 mg SiO₂ kg⁻¹. According to a recent survey of the Chinese Academy of Agricultural Sciences, approximately 8.86 million ha, representing 40% of the paddy soil areas in the southern part of China, are Si deficient.

In paddy soils with a long history of rice cultivation in northern and northeastern regions of China, concentrations of available Si in soils vary greatly. In Heilongjiang Province, northeastern China, concentrations of available Si in the paddy soils range from 110 to 500 mg SiO₂ kg⁻¹ (Wu et al., 1992; Wang, 1993). In Jilin Province, concentrations of available Si in some typical paddy soils ranged from 105 to 145 mg SiO₂ kg⁻¹ (Wu et al., 1996). In Liaodong Peninsula, concentrations of available Si in paddy soils had a range of 26-160 mg SiO₂ kg⁻¹, depending on the parent materials of the soils (Zhao and Jiang, 1987). Guan et al. (1995) investigated 70 soil samples from different locations in northeastern China, and found that 70% of the soils tested had concentrations of available Si less than 110 mg SiO₂ kg⁻¹. In the eastern part of Hebei Province in northern China, concentrations of available Si in paddy soils were in the range of 56-82 mg SiO₂ kg⁻¹ (Yu, 1999). These reports indicate that about 50% of paddy soils in the northern part of China are Si-deficient or potentially Si-deficient soils.

The concentrations of available Si in upland soils in northern and northeastern China are not always very high, particularly in highly productive soils (Li et al., 1999). Good yield responses to Si fertilizer have been reported for upland crops, such as wheat and corn, in recent years (Xu et al., 1995). A recent survey conducted by the Chinese Academy of Agricultural Sciences and its collaborators revealed that 8% of soils in Xinji City, Hebei Province, had a concentration of extractable Si lower than 100 mg SiO₂ kg⁻¹, and 80% of the soils were in the range of 100-150 mg SiO₂ kg⁻¹. In the semi-drought region of Jilin Province, the concentrations of plant-available Si ranged from 70 to 120 mg SiO₂ kg⁻¹. The concentrations of available Si ranged from 72 to 258 mg SiO₂ kg⁻¹ in soils from Henan, Shandong, and Hebei Provinces.

21.3. BENEFICIAL EFFECTS OF SILICON ON CROPS

It has been found that an adequate supply of Si in plants helps strengthen cell walls, decreases mutual shading by improving leaf erectness, decreases susceptibility to lodging, decreases the incidence of disease infections, and prevents elemental toxicity in an Si-deficient environment (Qin, 1988; Ma, 1990; Wang et al., 1997; Li et al., 1999; Liang et al., 1999). Reports on the beneficial effect of Si on the growth of rice and other crops in China agree with the findings published by overseas researchers.

21.3.1. Increasing crop resistance to disease, lodging, and drought stress

Leaf erectness is an important factor affecting light interception in dense rice stands and it often decreases with increasing nitrogen supply. Leaf erectness increased by Si fertilization usually counteracts the negative effects of a large nitrogen supply on light interception (Fan et al., 1989; Xie and Zhang, 1992; Wei, 1997). Similarly, Si counteracts the negative effects of a high nitrogen supply on plant stability and lodging susceptibility (Zhao and Jiang, 1987; Ma, 1990; Sheng, 1992; Wu et al., 1992; Lu, 1997).

Application of Si fertilizer can increase the longevity of functional leaves and active roots. It has been reported that even in the ripening stage, the chlorophyll concentrations of treated rice leaves with Si fertilizer were 18.7% larger than that of the control treatment (Zhao and Jiang, 1987; Li, 1993), and dry weight of the active roots in the Si fertilizer treatment was 1.9 times larger than that in the control treatment (Xu, 1993).

Si fertilization can significantly reduce occurrence of blast infection and other diseases in rice (Qin, 1979; 1988; Zang, 1989). Silicification of the epidermis was a major factor in physical resistance of rice to blast, and the degree of resistance increased in proportion to the amount of Si accumulated in the plants (Chen et al., 1985; Chen, 1989). Si fertilizer increased the content plant Si. A close correlation was found between disease susceptibility and the soluble N or amino acid content (Chen, 1989). Shui et al. (1995) studied the effect of Si fertilizer on rice resistance to leaf blast and neck blast in a soil low in available Si. The results indicated that rice resistance to blast was enhanced by Si fertilization, and the disease index of leaf blast and neck blast reduced by 50.5% and 26.8%, respectively. Silicon application reduced concentrations of total-N, protein-N and non-protein-N in the plants. Rows of siliceous cells were observed in the flag leaf of Si-treated plants, but none in the control treatment. Statistical analysis indicated that concentrations of plant Si were negatively correlated with the disease index of both leaf blast and neck blast. Concentrations of total-N and non-protein-N in the plants were positively correlated with the disease index of leaf blast. Similar results were also reported by Zhang et al. (1984). Wang et al. (1994) found that Si fertilization decreased *Helminthosporium* leaf spot of rice plants and rice sheath blight (*Rhizoctonia solani*). Therefore, it is recommended that Si-fertilizer should be applied to fields with high disease incidence (Chen et al., 1985).

Recent studies have indicated that Si fertilizer enhances crop resistance to drought stress (Liao and Zhang, 1996; Li et al., 1999).

21.3.2. Balancing nutrient uptake and preventing elemental toxicity

Silicon may improve plant growth under certain environmental stresses. Liang et al. (1999) conducted a pot experiment to study the effect of sodium silicate on nutrient uptake by wheat exposed to simulated acid rain. It has been reported that added silicate not only inhibited soil acidification and Al activation, but significantly increased the soil-available P concentration and enhanced the uptake of P as well as N and K by wheat, thus stimulating plant growth (Liang et al., 1999).

In a solution culture trial, Yang et al. (1999) studied the effect of Si on Al toxicity to mungbean seedlings, and suggested that Si may ameliorate Al toxicity by affecting plant chlorophyll and soluble protein contents.

Liao et al. (1993; 1994) investigated the effect of application of Si fertilizer on rice orangeing physiological disorder. They found that the application of fertilizer increased the available soil Si, increased the soil water soluble and active Si:Fe ratios, and decreased the incidence of orangeing disorder (related to Fe toxicity and Si deficiency), leading to an increase in grain yields. Electron

probe analysis showed that application of Si decreased accumulation of Fe in the root epidermis and increased Ca and Si concentrations in the root endodermis.

Liang et al. (1996) studied the effects of Si on salinity tolerance of barley. In a solution culture experiment, barley seedlings were exposed to a NaCl solution with or without adding Si. The dry matter yield of the plants grown in solution with the addition of Si was 15-18% greater than that of the plants treated with NaCl alone. The electrolytic leakage percentage was significantly lower in the leaves of barley plants treated with NaCl and Si than in the leaves treated with NaCl alone, which indicated that added Si resulted in a reduction of membrane permeability of salt-stressed barley (*Hordeum vulgare*). It was found that Si could enhance the uptake of K and inhibit the uptake of Na by salt-stressed barley, thus, mitigating the toxicity of salt to barley and increasing salt tolerance of the plants (Liang et al., 1996; Liang, 1999).

Liang (1999) also investigated the effect of Si on enzyme activity and concentrations of Na, K, and Ca in barley plants under salt stress. Compared with the plants treated with salt alone, superoxide dismutase activity in plant leaves and H^+ -ATPase activity in plant roots increased, and malondialdehyde concentration in plant leaves decreased significantly in seedlings treated with salt and Si. The addition of Si was also found to reduce Na but to increase K concentrations in shoots of salt-stressed barley. However, Si addition exhibited little effect on Ca concentrations in shoots of salt-stressed barley. Thus, Si-enhanced salt tolerance is attributed to selective uptake and transport of K and Na by plants. These results suggest that Si could be involved in the metabolic or physiological changes in plants (Liang, 1999).

21.4. CROP RESPONSES TO SILICON FERTILIZATION

21.4.1. Rice

Rice is the most common grain crop produced in China. A healthy growth of rice needs a large amount of Si; and Si may be considered as one of the essential nutrients for rice production. As a result, most work published in China on Si utilization in agriculture is on rice. To date, more than 100 papers on Si fertilization in rice have been published in the last two decades in China. Si fertilization trials have been conducted in all types of paddy soils. Rice yield responses to Si fertilization from some selective field trials range from 0 to 400%, depending on the severity of Si deficiency (Table 21.1). On average, over 10% increases in rice yield have been achieved with Si fertilization nationwide.

The response of rice to Si fertilization is affected by many factors, among which concentration of plant-available Si, soil pH, and N application levels are the most important ones (Li et al., 1999).

Xia et al. (1998) reported that in Jiangsu Province, when concentrations of plant-available Si were between 180 and 240 mg SiO_2 kg^{-1} , rice yield in Si-fertilized treatments was increased by 5-10%. If concentrations of plant-available Si were higher than 240 mg SiO_2 kg^{-1} , the yield increases were less than 5%. Linear regression analysis indicated that when plant-available Si concentrations ranged from 70 to 320 mg SiO_2 kg^{-1} , the yield increase (Y) (%) was significantly negatively correlated with concentration of plant-available Si (X) (Equation 1).

$$Y = 26.107 - 0.088X \quad (r = -0.9133^*, n = 28) \quad (\text{Equation 1})$$

Soil pH generally affects rice responses to Si fertilizer application by its impact on the solubility of

Table 21.1
Rice yield response to Si fertilization.

Trial location (province)	Yield increase (%)	Reference
Zhejiang	18.3-400.0	Qin (1979, 1988)
Zhejiang	0-11.4	He et al. (1980)
Liaoning	7.6-26.8	Zhao and Jiang (1987)
Guangxi, Guangdong, Hunan.	11	Zang (1989)
Hubei, Jiangxi, Zhejiang		
Anhui, Yunnan, Sichuan	5.4-49.7	Hua (1989)
Jiangsu	10.3-56.6	Zhang (1989)
Sichuan	12.5	Xue and Sun (1991)
Heilongjiang	7.8-10.0	Wu et al. (1992)
Jiangsu	5-11.2	Ma et al. (1992; 1993)
Jiangsu	4.6-20.7	Liang et al. (1994)
Jilin	11.0-15.5	Wu et al. (1996)
Henan	16.1-27.9	Zhang (1996)
Hebei	4.4-21.8	Yu (1999)

Si in the fertilizer. While studying the availability of Si in cinder of yellow phosphorus in a pot experiment, Sun et al. (1992) found that the availability of Si in the cinder of phosphorous and Si uptake by rice increased with the soil pH. Similar results were also reported by Zhang and Zang (1986), who found that rice yield increases linearly correlated with soil pH ($r = 0.8904$, $n = 55$), when soil pH values were between 5 and 8.

Nitrogen fertilization levels can influence rice response to Si fertilizer. Ke et al. (1993) reported that an adequate supply of N can enhance rice yield response to Si fertilizer. However, high levels of N can reduce the effect of Si on yield. They concluded that to achieve maximum yield, the best ratio of N:Si for early rice was 1:0.9, or 205.2 kg N/ha plus 187.5 kg Si/ha; and that for late rice, was 1:0.87, or 222.3 kg N/ha plus 193.5 kg Si/ha. To achieve optimum economic return, the best ratio for both early rice and late rice was 1:0.84. Similar interactions between Si and P fertilizers have been also reported (Xu and Chen, 1994).

21.4.2. Sugarcane

Silicon has also been considered an essential nutrient for sugarcane (*Saccharum officinarum*) production. Most sugarcane is exclusively grown in southern and southeastern China, where Si deficiency occurs commonly in most soils (Zhang and Zang, 1982; Ma, 1990; Zhao, 1997). In soils with concentrations of available Si less than 110 mg SiO₂/kg, Si deficient symptoms may be observed in sugarcane crops. Typically, sugarcane suffering from Si deficiency will have twisted leaves and lack of erectness (Ye and Xu, 1995).

When adequate amounts of Si fertilizer (150 kg/ha) were applied to a sugarcane crop in a Si deficient soil, the angle between leaves and stems decreased by 21%, and the number of leaves maintaining a color of green in the ripening stage increased. The height of sugarcane plants increased by 1.2-3.3 cm, circumference of stems by 0.3-0.6 cm, sugar concentrations by 1-2%, yield by 39-50 g/plant, with an increase of sugar output by 8.7-13.8%. When Si fertilizer rates were too high (e.g. higher than 225 kg/ha), sugarcane growth and sugar output decreased (Ye and Xu, 1995). However, Zhao (1997) reported that applying 750 kg of fertilizer (available Si 23%)

increased sugarcane yield by 30 ton/ha, and enhanced sugar output by 8.5%. Similar responses were obtained by applying 450-750 kg/ha of yellow phosphorous slag.

Zhang (1994) investigated the relationship between Si concentration and sugarcane leaf photosynthesis, and found that leaf chlorophyll concentration and photosynthetic rate positively correlated with leaf Si concentration, when Si in the leaf is less than 1.2%. Xue (1997) reported that applying Si to sugarcane could stimulate the transformation of reducing sugar to sucrose, speed up the ripening after harvest, and increase the yield of sugarcane and sugar output. Huang (1997) suggested that application of Si fertilizer could improve sugarcane nutrition balance between N, P, K, and Si and increase yield of both sugarcane and sugar, but over-fertilization with Si had a negative effect to sugarcane production. Huang (1997) found that sugarcane responds to water-soluble Si fertilizer better than fertilizers with Si in citric acid soluble form.

21.4.3. Wheat

Wheat is one of the upland crops that has a positive yield response to Si fertilization. As early as the late 1950s, Zhu and Chen (1963) achieved 6-12% increase of wheat yield after applying steel slag to wheat in Jilin Province. Lu (1997) found that the diameter of the first joint in wheat stems in the Si fertilizer treatment was larger than that of the control treatment, resulting in less susceptibility to lodging. Si fertilizer increased the longevity of functional leaves, and improved their photosynthesis efficiency (Lu, 1997). Bao et al. (1996) found that only about 6-10% of the total Si demand was taken up by wheat before the tillering stage; most Si was taken up after the tillering stage with few differences between varieties. Ma et al. (1993) reported a positive wheat yield response (>5%) to Si fertilizer in calcareous soils with the concentrations of soil-available Si up to 200 mg SiO₂/kg in Jiangsu Province. They concluded that this response may partially be due to the Si in these soils being retained by CaCO₃ and not readily available for take up by roots. Xia et al. (1998) conducted foliar sprays of Si fertilizer 2-3 times from tillering to elongation stages on wheat in calcareous soils and achieved yield increases of 5-10% in six successive years.

Xu et al. (1995) conducted Si fertilizer field trials in Hebei, Shandong, Henan and Jiangsu Provinces, where concentrations of soil-available Si ranged from 72 to 198 mg SiO₂/kg. The average yield increases of wheat were 9.7%. They proposed 170 mg SiO₂/kg as the critical value for wheat, above which no positive response to Si fertilizer would be expected. However, the Chinese Academy of Agricultural Sciences recommended that in northern China, the critical value for a 5% yield increase on wheat was 227 mg SiO₂/kg (Li et al., 1999). He and Wang (1999) suggested that in soils with concentrations of available Si of about 100 mg SiO₂/kg, application of 750-1500 kg Si fertilizer/ha (23.2% available Si) could stimulate wheat growth, increase yield, enhance the uptake of N, P, K, Ca, and Mg, but would decrease the uptake of Zn and Mn slightly. Very high application rates of Si fertilizer may induce toxicity symptoms, including lower tillering ability, fewer tillers forming in the stem, a shorter plant, smaller grain size, and lower yield. He and Wang (1999) recommended that the optimum Si fertilization rates for a wheat crop should be 45-90 kg Na₂SiO₃/ha, or 225-450 kg Si-Ca fertilizer/ha (available Si concentration about 20%).

21.4.4. Corn

Corn is one of the major crops in northern China. Zhu and Chen (1963) conducted field trials on corn in Liaoning Province with steel slag. Yield increases of 8.5-10.2% were reported. Li et al. (1999) conducted eight trials in northern China in 1993 and 1994 on summer corn and reported that Si fertilizer treatments increased yield by 472.5-900 kg/ha. Corn yield in the Si fertilizer treatment was significantly higher than that in the control treatment ($P < 0.001$). Plant tissue

analysis in the elongation stage and late dough stage indicated that Si application greatly increased concentrations of N, P, Zn, and Mn in corn plants. Application of 90 kg/ha Na_2SiO_3 has been considered as an optimum rate for corn (Li et al., 1999). Yuan et al. (1996) suggested that corn yield responses to Si fertilization could be attributed to the increased ear numbers and grain sizes.

Corn response to Si fertilizer may be affected by climate pattern as well as soil-available Si concentration. For example, in 1997, when there was a drought during corn-growing season in Jilin Province, corn yield increased 10% with Si fertilizer, whereas, when no drought occurred in 1998, yield increase in the Si treated area was 5% (Li et al., 1999). This implies that Si fertilization may improve corn growth in dry years by helping the crop counteract drought stress.

21.4.5. Other crops

In recent years, Si fertilizers have been applied to many other crops. Liu (1997) conducted a number of field trials and compared the effect of Si fertilizer and Ca fertilizer on tomato growth and yield. The results indicated that application of Si fertilizer decreased occurrence of disease, increased fruit size, and subsequently increased yield. In addition, Si-Ca fertilization also improved the taste of tomato fruit by increasing sugar concentration. There were no such responses observed if only Ca fertilizer (without Si) was applied. Liang et al. (1993a) reported that, in a solution culture trial, adding 50 μg Si/ml to a nutrient solution increased tomato yield by 62%, but adding 100 μg Si /ml, decreased yield by 30%. In field trials, tomato fruits became ripened four days earlier in the Si fertilizer treatment than in the control treatment (Liang et al., 1993a). Silicon fertilization also increased tomato yield by 31% due to increased fruit numbers and sizes. Silicon fertilization of commercially produced tomatoes achieved significant increases in yield. However, the effect of Si fertilizer on vitamin C and acidity of fruits was not consistent (Liang et al., 1993a).

Application of Si fertilizer has also shown beneficial effect on the growth of tobacco. Li (1997) conducted a number of field trials in seven counties of Yunnan Province, where most tobacco is produced in China. Results from most field trials indicated that Si fertilizer significantly increased tobacco leaf area index, plant resistance to disease, and overall tobacco quality.

Yao (1997) reported that Si fertilization could enhance the value of wild rice by accelerating maturity and increasing stem yield.

Liao and Zhang (1996) found that dressing 75 kg/ha high quality Si fertilizer (water soluble Si concentration >50%) in the budding and blossom stage of cotton, increased numbers of cotton bolls by 3.1-6.0% and cotton yield by 7.6-14.8%. Silicon fertilization also reduced cotton yield losses caused by drought stress.

Reports on apple responses to Si fertilizer have been published by Cai and Qian (1995b) in Henan Province. It was found that Si fertilizer applied at a rate of 15 kg Si fertilizer per tree to soils with concentrations of available Si range from 314 to 404 mg SiO_2/kg and receiving an annual precipitation of 555-600 mm, enhanced health and yield of apple trees. Trees receiving Si fertilizer had stronger shoots, and bigger, thicker, and darker green leaves. Fruits in Si-treated trees became red 3-5 days earlier and ripened about 10 days earlier and overall yield was increased by 10%. Fruits were also bigger with a brighter appearance. Fruit freshness could be kept for a longer period during storage and transportation, which resulted in enhanced market value.

It was reported that application of Si fertilizer to peanuts grown in sandy soils could increase the concentration of chlorophyll in leaves, shoot development, and double pome formation, dry weight of pome, percentage of pome in fruits and yield (Cai and Qian, 1995a).

Si fertilization could increase bamboo yield and quality (Yan, 1982; Hong, 1994; Qiou and Fu, 1987). No significant growth responses to Si fertilization have been observed in pine (*Pinus*) and poplar (*Populus*) trees (Guo et al., 1993; 1995).

21.5. SILICON, SOIL, AND PLANT EXTRACTION METHODS AND THEIR ABILITY TO PREDICT CROP RESPONSE

To make a profit through Si fertilization, it is essential to predict correctly whether a crop will positively respond to Si fertilizer application. To date, concentration of sodium acetate (pH 4) extractable soil Si is most commonly accepted as a measurement of soil Si fertility. However, crop yield in many soils with a high sodium acetate extractable Si may respond to Si fertilizer positively (Liang et al., 1994; Liang et al., 1998; Xia et al., 1998). For example, it has been reported that calcareous paddy soils which have a high concentration of sodium acetate extractable Si were still Si deficient. Therefore, the available Si extracted by this extractant may overestimate the Si-supplying power of the calcareous soils (Liang et al., 1994). Generally, concentrations of soil-available Si increased with the amount of CaCO_3 added and the soil pH (Zang, 1987). This suggests that a new extractant suitable for evaluating the available Si status of calcareous soils should be developed or that the level of available Si in these soils above which Si fertilizer is recommended should be modified, or other alternative methods should be developed.

Liang et al. (1991; 1998) conducted both pot experiments and field trials to investigate the changes in trichloroacetic acid (TCA)-soluble Si in the leaves of rice and to examine the feasibility of using TCA-soluble Si content as an index for diagnosing Si deficiency. The TCA-soluble Si content was significantly higher in the Si-treated plants than in the controls throughout the whole growth period. A close positive correlation was found between TCA-soluble Si and total Si in plants grown in pots ($r = 0.669$). The results obtained in the field trials revealed that the available Si extracted by sodium acetate (pH 4.0) could not predict satisfactorily the response of rice to added Si in calcareous soils. No significant correlation was found between soil-available Si content and rice yield, but TCA-soluble Si in the leaf blades of rice was significantly correlated with both rice yield ($r = 0.57$) and total plant Si ($r = 0.89$). Liang et al. (1998) suggested that the critical value of TCA-soluble Si in the leaves of rice should be 52-57 mg Si/kg, above which no positive response of rice to added Si would be expected.

Zang and Zhang (1982) reported that rice yield could be significantly increased by Si fertilizer if concentration of SiO_2 in straw was less than 10%. Researchers in Hubei Province found that rice yield is highly correlated with Si concentration and Si/N ratios in mature flag leaves (Li et al., 1999). Qin (1988) suggested that rice may respond positively to Si fertilizer if Si concentration in the irrigation water is very low.

21.6. COMBINED APPLICATION OF SILICON AND OTHER NUTRIENTS

Interaction of Si with macro-nutrients, particularly nitrogen, has been well documented in the literature (Qin, 1988; Ma, 1990; Liang et al., 1993b; Wei, 1997). Since the early 1990s, researchers in China have gradually recognized the importance of the beneficial effect of combined application of Si fertilizer and micro-nutrients. In recent years, combined application of Si, Mn, and Zn have been recommended as a standard practice in many regions, especially in northern China (Li et al., 1999).

As large areas of soils are deficient in Mn and Zn as well as Si in many major grain crop-growing regions in China, large-scale field trials were conducted in rice, winter wheat, and corn between 1991 and 1995 in several provinces (Li et al., 1999). All trials had four main treatments, including the control (common practice of local farmers, e.g. NPK fertilizers and manure as basal fertilizer without Si, Mn, and Zn fertilizers), ZnMn ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 15 kg/ha, MnSO_4 30 kg/ha), SiZnMn ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ 45 kg/ha), 2SiZnMn ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ 90 kg/ha). There were 92 field trials on rice carried out in the paddy soils in Hubei, Sichuan, and Jilin Provinces, respectively. Statistical analysis indicated that yields in the treatments of combined application of SiZn, SiMn and SiZnMn were all significantly higher than in the control treatment, and yields of both SiZnMn and 2SiZnMn treatments were significantly higher than that of Si treatment ($P < 0.05$), with the order of $2\text{SiZnMn} > \text{SiZnMn} > \text{SiZn}$ and $\text{SiMn} > \text{Si} > \text{Control}$ (Li et al., 1999).

Field trials on wheat and corn with similar experimental design as for rice trials were performed in Beijing, Hebei, Henan, and Shandong Provinces. Although yield differences between the treatments were not as significant as in rice trials, wheat and corn yields from SiMnZn treatments were usually higher than the control and individual Si, Mn or Zn treatment (Li et al., 1999). In field experiments conducted during 1992-1994, Yan et al. (1996) reported that combined applications of Si, Zn and Mn to wheat and corn increased the average yield of wheat and corn by 11.9% and 15.4% respectively, over the control treatment. Combined application of Zn and Mn also increased wheat and maize yields, but the best yields were obtained with application of Zn, Mn and Si. The yield increases were due to increased 1000-grain weight, the number of grain per ear and the number of ears per unit area.

Shi et al. (1996) reported that a combined application of Si, Zn, and Mg facilitated the uptake of N, K, Zn, and Mg by rice plants and their transportation to the developing grains, increased protein content of the grain, and helped accumulation of starch in the seed. Therefore, combined application of Si, Zn, and Mg enhanced rice yield and quality. Liao et al. (1994) found that in a pot experiment, rice leaf orange disease due to Fe toxicity was reduced by application of Si and/or Mn, with the least toxicity symptoms and best plant growth and yield given by the combined application. Application of Si or Si+Mn decreased the Fe concentration in the soil solution. Wang and Chen (1996) reported that addition of sodium silicate together with selenite increased rice plant height, and content of soluble protein and chlorophyll in leaves. However, these parameters were decreased when the concentration of selenite was increased.

21.7. CONCLUSIONS AND FUTURE DIRECTIONS

As the country with the largest population in the world and a tradition of consuming grain as the main food source, China will continue to adapt new science and technology to enhance the quantity and quality of arable crops. Silicon deficiency is a common problem in many agricultural soils, and Si fertilization plays an increasingly important role in agricultural production. This has been demonstrated by intensive research and numerous trials carried out throughout the country, which has resulted in the establishment of Si fertilizer industry in recent years.

Most data on Si application in China have been obtained from field trials, which implies that these results are practical and acceptable to farmers. Most trials have been conducted on rice, but there is an increasing amount of research in recent years on other crops, such as wheat, corn, sugarcane, etc. Researchers have also paid more attention to combined application of Si and micronutrients (e.g. Zn and Mn). Beneficial effects of Si fertilizer have been attributed to enhanced

resistance of crops to disease, lodging and drought stress, and improved crop nutrient balance. Some studies have been conducted to investigate the metabolic functions of Si in plants, which may lead to a better understanding of the role Si plays in plant physiology. However, considerable variations between factors affecting crop response to Si fertilization, such as soil, climate, property of Si fertilizers, crop cultivars, crop management, etc., make it difficult to compare the trials conducted. More coordinated research on the potential beneficial use of Si fertilizer on other crops as well as rice is required.

Given the importance of Si fertilization in China, we suggest that more attention should be paid to:

1. Understand the significance of Si in plant metabolism, especially the interactions of Si with other nutrients and the mechanisms of improving crop growth under drought stress.
2. Investigate the availability, transformation of Si and its interactions with other factors in soil ecosystems to predict the responses of crops to Si fertilization.
3. Standardize experimental design and procedure to provide farmers with accurate recommendations on Si fertilization.
4. Ensure quality control of Si fertilizer.

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Chapter 22

Past and future advances in silicon research in the Republic of Korea

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During the 1950s, the first field trials of sodium silicate on rice grown in marine deposit soils showed little effect on yield, although furnace slags gave some effect for most paddy soils. However, since 1960, ground wollastonite has been found to be most effective in improving growth of rice under a balanced supply of nitrogen (N), phosphorus (P), and potassium (K) in more than 90% of Korean paddy soils containing less than 130 mg kg of available SiO_2 in the top soil. Intensive studies on models for fertility management of paddy soils based on soil tests, including available silica, were started for sustainable rice production in the 1970s. These approaches and models may also be used for various upland crops of grass species such as maize, wheat, and barley. In the future, the use of those models should also be tested for environmental hazards due to the emission of greenhouse gases, such as nitrous oxide or methane, either from the soil or through the plants. After World War II, the Republic of Korea suffered from a shortage of staple rice grain. Agronomists tried every effort to improve unit area rice production under limited agricultural land area and fertilizer supply. The use of silicon (Si) for increased rice production was started as a measure for increasing food grain production. Since 1977, it has contributed to Korea gaining self-sufficiency in rice production. The use of silicate fertilizer is still a common practice for paddy soil fertility management, having started in the early 1970s with the government-subsidized supply of 400,000 Mg yearly of silicate fertilizer. The Republic of Korea and Japan, having used more than sufficient chemical fertilizers for sufficient rice production in their limited land area for the last several decades, have much experience to share with other countries in the use of Si. This chapter introduces and summarizes Korean experiences of the last several decades and suggests future research aims.

22.1. THE SOURCES OF SILICON USED IN THE REPUBLIC OF KOREA

22.1.1. Sodium silicate

The first use of silicate in 1956 was an attempt to determine the effects of Si on the production of rice grain. However, the use of sodium silicate in rice grown in soil developed under marine deposits, which is usually high in available SiO_2 and low in organic matter content, did not show any significant influences on yield in the field.

22.1.2. Small scale furnace slags and natural wollastonite

The use of furnace slags, byproducts of small-scale iron refineries, gave considerable growth promotion in most paddy soils developed under old alluvium. Since 1960, however, ground wollastonite, occurring in the stratum in limestone areas, has been very effective in growth promotion of rice. Intensive research was started with these materials consisting of rather pure calcium magnesium silicates.

22.1.3. Furnace slags from large scale steel industry

Ground wollastonite was found to be the best source of Si fertilizer. However, it was difficult to mass produce wollastonite due to the labor requirement for refining at limestone mines. An alternative source of Si emerged from the steel industry. Slags produced in factories from the water cooling system could be prilled as an easy way to produce Si fertilizer. Four hundred thousand Mg of Si fertilizers are produced from these slags yearly. In 1974, the government began subsidizing prices for farmers to help the country attain sufficiency in rice production by 1977.

22.2. THE REQUIREMENTS OF SILICON FERTILIZERS

During the United Nations Special Fund Korean Soil Fertility Projects, started in 1963 and lasting for 6 years, extensive field trials were conducted throughout the country on the NPK responses and soil improvement of fields using various amendments, including various types of calcium silicates.

22.2.1. Critical content of available silicon in plow layer soils

During the processing of field trial data of yield, soil, and plant analysis, it was found that application of 2 Mg ha⁻¹ of silicate was of prime importance for rice production. However, the effect decreased as the available SiO₂ content in the soil increased to 130 mg kg⁻¹, and then leveled off, showing the same results as reported in Japan (1958).

22.2.2. Modification of available silicon determination method

The method for determining available Si proposed by Imaizumi & Yoshida (1958) involved extracting 5 g of soil in 50 ml of 1N sodium acetate (pH adjusted to 4.0) for 5 hours at 40° C, and determining Si in the extract by the molybdenum blue method. This time-consuming extraction method was modified and found to be reasonable for use in soil-testing laboratories when extraction time was 90 minutes at 60° C (Park, 1970).

22.2.3. Available silicon content of Korean paddy soils 1960s

During 1967 and 1968, the available Si content of Korean paddy soils, with the use of the modified methods mentioned above, was measured on soil samples taken randomly from 365 sites. The analyses indicated that 94 % of the soil had a Si content less than 130 mg kg⁻¹, ranging from 19-300 with a mean value of 78 or a median of around 70 mg kg⁻¹. The results definitely showed the shortage of a natural supply of available Si in most Korean paddy soils, suggesting Si applications should prove effective.

22.2.4. Requirements of silicon fertilizers for maintaining available silicon

In general, most paddy soils in Korea were found to require 2 Mg ha⁻¹ of ground wollastonite. Tentative wollastonite requirements (WR, Mg ha⁻¹, Model A) for soils of different amounts of

available Si were established under the assumption that (1) 2 Mg ha⁻¹ of wollastonite was the amount needed to increase the available Si from an average content of 78 mg kg⁻¹ to 130 mg kg⁻¹ and (2) the increase of available Si is proportional to the amounts of wollastonite added to the plow layer of soils, which is around 10 cm depth.

Model A: $WR = 4.94 - 0.0385x$, where x = available Si (mg kg⁻¹)

Model (A) has been used since 1970, not only for application rates of wollastonite but also for byproduct silicates. However, some modification may be required for Si fertilizers produced from furnace slags in Korea, which have been found to increase available Si in soil twice as much as wollastonite. Thus, the optimum rate for the currently-used Si sources may be only 1/2 that of Model A over a two-year period, as opposed to the full rate over a four-year period, which was the time period over which wollastonite was found to effectively supply Si. For maintaining available Si in the plow layer soil, the present Si fertilizer requirement SiR, Mg ha⁻¹, could be reasonably estimated from the following modified model (Am).

Model Am: $SiR = (X - x) / (130 - 78) = (X - x) / 52$, where x = available Si (mg kg⁻¹)

22.3. STUDIES ON THE VARIOUS EFFECTS OF SILICON FOR THE GROWTH OF RICE

22.3.1. Pest resistance

Multidisciplinary agronomy teams worked together to evaluate the various effects of Si for growing rice. Resistance to pests such as helminthosporium spot disease, rice blast, and stem borer, etc, was evaluated due to the formation of a protective barrier of Si-cuticle double layers in the epidermal cells. Resistance could be associated with the protective effect of this Si-cuticle layer against NH₄-N volatilization loss from the leaf surface (Park, 1980, 1982.) in addition to the decreased transpiration (Yoshida, 1958) which would reduce the moisture supply for pest growth. The NH₄-N volatilized from the leaf surface, when dissolved in dew or rain water, may serve as nutrients for hatching eggs or growth of spores of those pests.

22.3.2. Enhancement of photosynthesis

Response to Si increases vertical orientation of the active top three leaves, thereby allowing increased rates of carbon assimilation after heading because of a physical increase in leaf area index under more than sufficient solar radiation. For this reason, maturity may also be hastened. In addition, plant N is conserved to keep the leaf active by reducing the loss of NH₄-N from the leaf surface due to the protective barrier of Si-cuticle double layers.

22.3.3. Increased mineral nutrient uptake

Applications of Si have produced increased uptake of mineral nutrients, particularly N and K, due to the increased oxidation power of roots grown under submerged and reduced root spheres. In addition, calcium silicate may eliminate or neutralize various organic acids that are detrimental to nutrient uptake by plant roots and result in nutrient imbalance in the plants due to selective uptake inhibition of nutrients, depending on the kinds of organic acids or sulfides present.

22.3.4. Minimizing effects of various environmental pollutants

Wollastonite minimizes the effects of various injuries of rice growth, such as those from heavy metals (e.g. Pb, Cu), animal husbandry waste water, and gases such as hydrogen fluoride, sulfur dioxide, etc. from industries developed in the 1970s.

22.3.5. Minimizing effects of too low or too high air temperature injury

The growth-enhancing effect of Si are usually observed to a greater degree in low temperature or high elevation areas, compared to those observed in warmer or low elevation areas in Korea. This may be partially because the availability of Si from the soil itself depends on the soil temperature difference due to the air or irrigation water temperature. However, Si also reduces direct plant injury as a result of excessively low or high air temperature as found in Korea and Japan during the growing season.

22.3.6. Minimizing effects of plant absorbed N loss by volatilization or senescence earlier after heading stage of rice

Volatilization loss of $\text{NH}_4\text{-N}$ or ethylene emission from the plants, both of which are known to be associated with early senescence, were reported to be decreased by sufficient supply of Si in growing media. The emission of methane as a chimney effect of rice plants may also be decreased by proper Si supply to the growing media.

22.4. MINERAL NUTRIENT BALANCES IN THE RICE PLANTS

Well-grown rice, which produces more than 10 Mg ha^{-1} of brown rice in Japan, as well as in Korea, absorbs more than $200 \text{ kg ha}^{-1} \text{ N}$, $2 \text{ Mg ha}^{-1} \text{ SiO}_2$, $300 \text{ kg ha}^{-1} \text{ K}_2\text{O}$, but only $75 \text{ kg ha}^{-1} \text{ P}_2\text{O}_5$, and much less amounts of Ca and Mg. This means that mineral nutrient balances are important for the full performance of genetic or biological production potentials of most rice varieties (Park, 1979).

22.5. INTERACTIONS AMONG AVAILABLE NUTRIENTS IN SOIL FOR PLANT UPTAKE

Cation balances, rather than anion balances, are important because a) rice plants take up abundant Si and less P in the form of anions from the soil, and b) iron phosphate is highly available and is a major fraction under submerged soil conditions like paddy soils.

22.5.1. N and other nutrients

The rice plant is known to favor $\text{NH}_4\text{-N}$ uptake and naturally interacts negatively with various other cations in the soil such as K^+ , Ca^{2+} , Mg^{2+} , or Na^+ . The K requirement in rice is rather high in order to keep the $\text{K}_2\text{O/N}$ ratio in the plant optimum throughout the life of the plant. Thus, K activity ratio responsible for K availability from the soil or exchangeable cation ratios such as $\text{K}/((\text{Ca} + \text{Mg})^{1/2} + \text{Na}^+)$ are important factors.

The $\text{K}_2\text{O/N}$ ratio in the plant should be greater than 1.2 even after the heading stage for regular grain filling without causing green wilt, a kind of K deficiency or imbalance, and to retain the optimum balance among K availability and that of N either from soils or fertilizers.

22.5.2. Silicon application and cation balances in the soil

When Si application is required to increase the level of available Si, the cations in the Si sources may be released as soluble forms to increase the cations in soil. This can modify the K activity ratio so as to increase the K fertilizer requirement. This was confirmed by the observation that a good response to K in dry season rice disappeared in the following wet season rice in the same soil in the Philippines.

On the other hand, available Si and available N in soil also need to be in balance to keep the proper SiO_2/N ratio in the plants for development of sufficient thickness of Si-cuticle double layers. These help provide the protective barriers against various environmental hazards and produce efficient photosynthetic plant types with erect leaves.

22.5.3. Sufficient available silicon for the growth of rice

Before the 1970s, in Korea, the optimum level of available Si was found to be $130 \text{ mg SiO}_2 \text{ kg}^{-1}$ air-dry soil in the 10 cm plow layers. This level enhanced growth under the average organic matter content of 26 g kg^{-1} and the fertilizer N dosage of more or less 100 kg ha^{-1} .

However, some researchers found different optimum available-Si levels of 150 up to 180 mg kg^{-1} in soils of different organic matter content or fertilizer N dosages. It was also reported that paddy soils high in organic matter in Japan have a continuous yield response to Si application. This information suggests soils high in N-supplying power, either from soil OM or fertilizers, may modify the optimum levels of available Si. Therefore, it seems better to use these optimum ratios of available SiO_2/OM to eliminate inconsistencies.

The results of N fertilizer response trials conducted in the field with differing amounts of Si as well as of OM, which were prepared by the addition of different levels ($0\text{-}100\text{-}200\text{-}300 \text{ Mg ha}^{-1}$) of fresh soil in the previous year, indicated that the N fertilizer requirements (NR , kg ha^{-1}) were directly proportional to the SiO_2/OM , confirming that the use of optimum levels of SiO_2/OM is much more effective than using only optimum SiO_2 levels. This result, or the following Model (B) serves as the backbone of the N fertilizer requirement Model (1) which is to be discussed later.

Model B: $\text{NR} = (58.8 + 6.47 * \text{SiO}_2/\text{OM})$

22.5.4. Potassium supplying capacity or potassium activity ratios

Si fertilizers usually contain approximately 40% CaO equivalent of Ca and Mg. When the Si is used for increasing available Si in the soil, Ca and Mg in the soil also increased, resulting in a decreased K activity ratio (Kas) in the soil thereby increasing fertilizer K requirements.

A study on the interaction between Si and K fertilizer application was made in field trials using different levels of Si in the main plots, with K fertilizers in sub plots, with the application of optimum N estimated by Model B. The results show more or less linear relationships with both soil factors, i.e. SiO_2/OM and Kas, as shown in regression equations (C) and (D) below.

$$Y = 4.47 + 0.2236 * (\text{SiO}_2/\text{OM}) \quad (\text{C})$$

$$Y = 3.67 + 26.92 * \text{Kas} \quad (\text{D})$$

Y is the paddy yield (Mg ha^{-1}), Kas is the ratio of exchangeable cations (cmol kg^{-1}) or $\text{K}^+ / (\text{Na}^+ + \text{Ca}^{2+} + \text{Mg}^{2+})^{1/2}$. Y, in equations (C) and (D) was the paddy yield obtained from different levels of (SiO_2/OM) and Kas under the application of optimum N estimated by Model B. Both regression equations were equalized to establish relationships between SiO_2/OM and Kas for obtaining paddy

yield, Y under optimum dosage of N estimated by Model B. The K_{as} value obtained from the relation must be the optimum K_{as} at a certain SiO_2/OM level for maximum yield with optimum FN dosage and is termed the "Ideal K activity ratio or K_{ai} " as shown in Model E.

$$K_{ai} = 0.03 + 0.0083 * SiO_2/OM \quad (E)$$

Model E is useful for estimating the K fertilizer requirement to maintain K_{as} equal to K_{ai} ($K_{as}/K_{ai} = 1.0$). K_{as}/K_{ai} , termed the relative K activity ratio, was found as the actual K supplying power of the paddy soils of different SiO_2/OM levels under optimum N supply by Model B.

The importance of the relative K activity ratio was confirmed by the occurrence of K deficiencies or green wilt due to the imbalance of K and N or K/N in the plant which was directly associated with relative K activity ratios rather than K_{as} values or available K content in soil (Figure 22.1).

22.6. PADDY SOIL FERTILITY MANAGEMENT MODELS BASED ON THE MULTI-NUTRIENT FACTOR BALANCE CONCEPT AND SiO_2/OM IN SOIL HAVE BEEN A KEY FACTOR

22.6.1. Multi-nutrient factor balance concept

Available Si content in the plow layer of soils can be a representative chemical or fertility factor of those paddy soils since it has positive correlation coefficients with many physico-chemical factors such as CEC, exchangeable K, Ca, Mg, and Na as well as clay content etc. (Kawaguchi

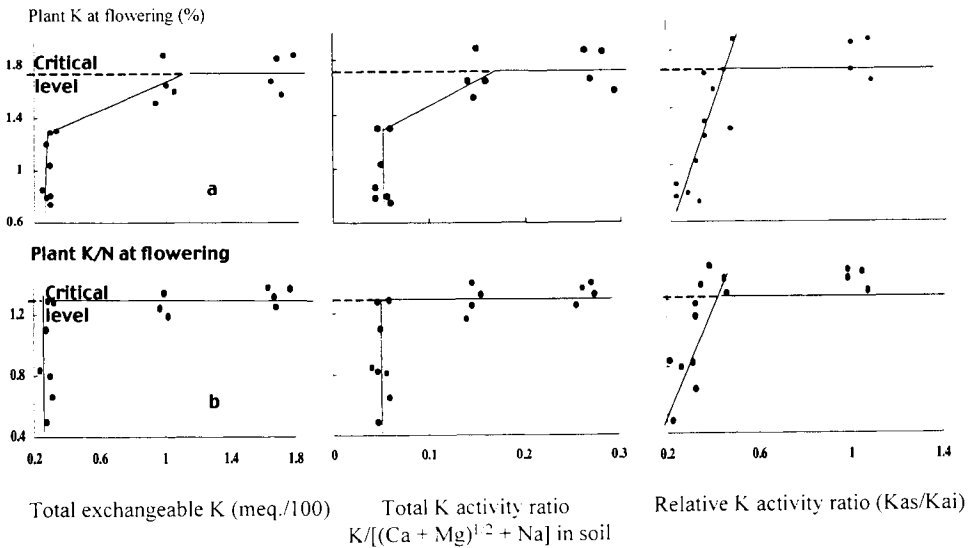


Figure 22.1. Relationships between K supplying status in soil, ie. exchangeable K K activity ratio or relative K activity ratio, and the nutritional status of K in the plant, ie. K concentration (a) or K/N ratio (b) in plant at flowering stage of IR36 in dry season in 1980. Critical levels are the levels for maximum grain yield.

and Kyuma, 1977). The organic matter content may be another important soil factor for the availability of nutrients, such as Si, P, Fe, Mn, Cu, and Zn, besides being the major source of $\text{NH}_4\text{-N}$ from the soil.

However, over-accumulation of OM, or organic C exceeding 1/10 of clay contents, may also lead to production of harmful substances such as organic acids and sulfides, due to heavy reduction under flooded soil conditions.

Because of this existing information, it may be right to use SiO_2/OM as a key factor for fertility evaluation or fertility management of paddy soils under flooded conditions for good production of rice grain (Figure 22.2). Figure 22.2 explains the importance of SiO_2/OM as a key factor in the multi-nutrient factor balance concept (MFBC).

On the other hand, excessively high levels of certain nutrients in soil are usually associated with the inhibition of uptake of other nutrients by plants, leading to deficiencies. For instance, the absorption of NH_4^+ and Mg^{+2} may definitely be inhibited by an excessive supply of K either from soil or fertilizers. The same is true for the uptake of K under excessively high levels of Fe^{+2} or Mn^{+2} , and of Ca^{+2} , Mg^{+1} , or NH_4^+ . This stresses the importance of the MFBC, which is the concept that all the nutrients must be well-balanced for the most economic production of crops. The MFBC was initiated after the worldwide fertilizer crisis due to oil shock in 1973-4. However, this concept is still important at present and may also help prevent environmental hazards due to mismanagement of soil fertility when aiming only at increased grain production.

22.6.2. The optimum levels of key factors for paddy soils

The target available-Si level before 1971 was 130 mg kg^{-1} for the optimum growth of conventional varieties grown with the fertilizer N dosage of around 100 kg ha^{-1} in soils containing

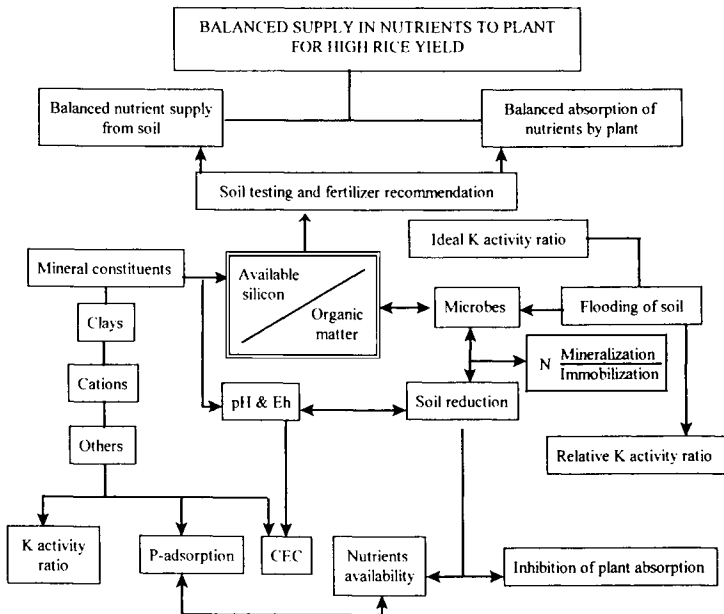


Figure 22.2. Schematic diagram showing the multi-nutrient factor balance concept (MFBC) in the management practices of flooded rice soils.

an average 26 g kg⁻¹ of organic matter. This target gave the present average key factor (i.e. SiO₂/OM) of 5.0. However, the optimum key factor should be modified depending on the N fertilizer responsiveness of new varieties. Thus, it was found that the optimum key factor for N-responsive Japonica varieties was 6.0, but it was 8.0 for the most N responsive high yield varieties of Indica x Japonica hybrids (Park, 1982).

22.6.3. Nitrogen and potassium fertilizer requirement models for rice

Since nutrient balances in rice plants such as Si/N, K/N were found to be important for the production of rice grain, available nutrient balances in the plow layers seemed to be important. Beginning in 1971, these balances were used to establish N K fertilizer requirement models based on the soil analysis data of available Si, OM, and various exchangeable cations.

Those models were expected to be used effectively in the land consolidation areas or old paddy soil areas where 20-30% of plow layer were renewed by the addition of 200-300 Mg ha⁻¹ of fresh or oxidized soil, red in color, with low OM, but high in available Si, CEC, and clay content.

The technique of adding fresh soil with increased doses of manure for exhausted paddy soil started after "Nongsa Jiksal", an old Korean farming textbook, was published in 1429. This technique had been used until the 1970s with an increased fertilizer dosage of 20-30%. However, based on the soil analysis data in the early 1970s, a more scientific fertilizer requirement model was needed, starting with the Model B. After a decade of research efforts, the last models for fertilizer N, Model 1, and fertilizer K, Model 2, were established in 1984.

Model 1: $NRe = (58.8 + 6.47 \times Z^{-1}) * (0.65 + 1.086 * Kas \text{ Kai}^{-1}) * Fv$

Model 2: $KRe = (Kai - Kas) * ((Ca + Mg)^{-2} + Na) * 47.096 * BD$

Table 22.1

Different management practices for paddy soils adopted in the 1996 field trials, and the grain yields obtained by conventional variety (cv) and HYV (hyv).

Practices of fertilizer management	Treatments										Yield	
	Compost		Si		N		P ₂ O ₅		K ₂ O		Paddy	
	cv*	hyv**	cv	hyv	cv	hyv	cv	hyv	cv	hyv	cv	hyv
	-----Mg ha ⁻¹ -----				-----kg ha ⁻¹ -----				--- Mg ha ⁻¹ ---			
LISA 1	0	0	0	0	100	130	0	0	38	38	8.89	9.01
LISA 2	0	0	2.74	2.74	130	130	0	0	38	38	9.12	10.02
Nongto 1	0	0	0	0	125	200	50	50	85	85	8.46	9.8
Nongto 2	0	0	2.74	2.74	125	200	50	50	85	85	9.91	10.3
Nongto 3	10	10	2.74	2.74	125	200	50	50	85	85	9.68	10.32
dito +N	-	0	-	2.74	-	240	-	50	-	85	-	10.08
dito -N	-	0	-	2.74	-	160	-	50	-	85	-	10.11
HY practice	15	15	3.5	3.5	150	180	66	66	135	150	10	10.53
MFBC	0	0	2.12	3.2	136	192	30	30	30	48	9.6	10.64

*conventional japonica variety; **new high yielding variety; ***Multinutrient factor balance concept applied (FN/NRe*SiO₂/OM*Kas/Kal)

Table 22.2

Relationships between paddy yield, "Y", and various soil factors modified by those different soil fertility management practices, "x" s.

Soil factors adjusted (=x)	Regression Equations	%R ²	n	P	x at Y _{max}	Y _{max} (Mg ha ⁻¹)
SiO ₂ /OM	Y=8.59 + 0.203x	57.2	16	.001	(7)	(10.11)
(HYV)	Y=9.02 + 0.174x	71.3	9	.004	(8)	(10.41)
(C V)	Y=8.27 + 0.200x	73.0	7	.014	(6)	(9.47)
Kas/Kai	Y=10.68 - 0.573x	37.2	16	.012	(1)	(10.11)
(HYV)	Y=10.82 - 0.475x	42.0	9	.059 ^{NS}	(1)	(10.25)
(C V)	Y=10.36 - 0.609x	58.9	7	.044	(1)	(9.75)
FN/NRe	Y=5.14 + 10.42x - 5.23x ²	65.4	16	.001	.996	10.33
(HYV)	Y=1.17 + 19.93x - 10.64x ²	76.5	9	.013	.937	10.50
(C V)	Y=3.10 + 40.82 - 32.24x ²	74.0	7	.068 ^{NS}	.633	9.82
MFBC*	Y=7.42 + 0.631x - 0.0342x ²	80.7	16	.000	.80*	8.92
(HYV)	Y=7.15 + 0.828x - 0.0527x ²	92.1	9	.000	7.86	10.40
(C V)	Y=8.09 + 0.248x + 0.0061x ²	74.9	7	.063 ^{NS}	(6.0)	9.60

* Factor MFBC = (FN/NRe)*(SiO₂/OM)*(Kas/Kai); in cases of (FN/NRe)=1.0=(Kas/Kai), the value of MFBC=(SiO₂/OM); Data in () are the optimum value suggested; HYV: new high yielding variety, CV: conventional variety

NRe is Urea N (kg ha⁻¹), KRe is K₂O (kg ha⁻¹). X is the total available Si (mg kg⁻¹). tZ is the total soil organic matter content (g kg⁻¹). Kas is the K activity ratio in soil. Kai is the ideal K activity ratio estimated from the equation E. Fv is the factor for FN uptake efficiency.

The Fv varies depending on the variety or form of fertilizer. For example, a value of 1.0 is used for Indica x Japonica Hybrid or 0.8 for japonica varieties, and 0.5 for sulfur-coated urea or super granule urea, compared to 1.0 for ordinary prilled urea. BD is the bulk density of the plow layer soils (kg m⁻³).

The P fertilizer model, however, may not be needed but it may be necessary to maintain an available P₂O₅ level of around 100 g kg⁻¹ soil, which seems more than sufficient. The importance in the integrated fertility management, however, is the maintenance of the key factor, SiO₂/OM, at a proper level depending on the cultivar used, and then maintaining a relative K activity ratio, Kas/Kai, equal to 1.0, by using model II prior to using model I.

In the 1996 crop season, the use of these models, which have been found to be the best fertility management practices, were compared with several other practices proposed by others, which use higher levels of organic matter, Si, and NPK fertilizers. The results are summarized in Tables 22.1 and 22.2. Much to my surprise, Model I can also be used for other upland crops of grass species

Table 22.3

Regression equations of grain yields and various soil fertility factors (xs) associated with the fertilizer N requirements for grass species.

xs	Regression Equations	%R ²	P	x at Y _{max}	Y _{max} (Mg ha ⁻¹)
For 1977/78 Maize (variety SW 19, n = 99 treatment plots)					
FN kg ha ⁻¹	Y=6.58+2.46*10 ⁻² x - 4.61*10 ⁻³ x ²	32.2	.000	267.000	9.86
FN/NR(e11)	Y=6.57 + 7.41x - 4.01x ²	35.4	.000	.924	9.99
FN/NR(e4)	Y=6.34 + 6.91x - 3.24 x ²	40.6	.000	1.066	10.02
FN/NReMo	Y=6.72 + 8.04x - 5.05 x ²	31.2	.000	.796 (.800*	9.92 9.92**)
For 1977/78 Wheat (variety Jokwang, n = 88 treatment plots)					
FN kg ha ⁻¹	Y=2.38+250*10 ⁻³ x-114*10 ⁻⁶ x ²	11.9	0	110	3.75
FN/NR(e11)	Y=3.40 + 1.11 x - 1.07 x ²	4.9	.119	.519	3.69
FN/NR(e4)	Y=2.10 + 3.64 x - 1.85 x ²	14.3	.001	.984	3.89
FN/NReMo	Y=2.10 + 2.65 x - 0.44 x ²	18.2	.000	3.010 (1.00*	6.09 4.31**)
For 1976/77 Barley (different varieties, n =187 treatment plots)					
FN kg ha ⁻¹	Y=14.3 + 157*10 ⁻⁴ x -566*10 ⁻⁸ x ²	11.5	.000	139.000	2.52
FN/NR(e11)	Y=2.09 + 0.537 x - 0.084 x ²	3.4	.043	3.200	2.95
FN/NR(e4)	Y=1.78 + 1.380 x - 0.632 x ²	5.4	.006	1.090	2.53
FN/NReMo	Y=1.46 + 4.120 x - 3.540 x ²	13.4	.000	.582 (.600*	2.66 2.66**)

1) FN denotes fertilizer N (kg ha⁻¹) applied in each 1 of 1 treatment plots of NPK combinations in 8 to 9 different sites throughout the country.

2) NR(e11) is the FN requirement estimated from FN response equations using 11 NPK combination levels for each site.

3) NR(e 4)is the FN requirement estimated from FN response equations using 4 N levels only in each site.

4) NReMo is the FN requirement estimated by the use of Model 1 from the soil test results of each site.

5) Data in () are the crop factor Fv* may be used for maximum yield** expected by the use of the Model I.

such as maize (with the use of Fv = 0.8), wheat (with the use of Fv = 1.0), and barley (with the use of Fv = 0.6), as shown in both Table 22.3 for grain yield, regardless experimental sites and Table 22.4 for % maximum possible yield of each trial conducted in 1970s.

As shown in Table 22.3, fittings of regression equations are very low probably due to the site effects. However, those relationships show a better fit when single cultivars are used or % maximum possible yield for each site.This may be an indication that varieties used and different experimental sites or micro climatic differences interfere with these relationships, even in the 100,000 km² size of small land areas like in the Republic of Korea.

The SiO₂/OM in soils of upland crop areas is usually too high, containing 300-500 mg kg⁻¹ of available Si with less than 25 g kg⁻¹ of OM in Korea. Further, the use of compost rather than Si for

Table 22.4

Regression equations of % maximum grain yields of each field trial sites and various soil fertility factors (xs) associated with those fertilizer N requirements for grass species.

xs	Regression Equations	%R ²	P	x at %Y _{max}	Y _{max} %
For 1977/78 Maize (variety SW19, n = 99 treatment plots)					
FN kg ha ⁻¹	%Y=60.7 + 2.15 x - .0366 x ²	51.3	.000	294.000	92.3
FN/NR(e11)	%Y=60.6 + 67.9 x - 35.8 x ²	55.0	.000	.948	92.3
FN/NR(e4)	%Y=61.7 + 61.5 x - 31.4 x ²	48.6	.000	.979	91.8
FN/NReMo	%Y=62.7 + 67.8 x - 39.4 x ²	44.7	.000	.860	91.9
				(.800*	91.7**)
For 1977/78 Wheat (variety Jokwang, n = 88 treatment plots)					
FN kg ha ⁻¹	%Y=50.1 + 3.86 x - 0.109 x ²	27.9	.000	107.000	84.3
FN/NR(e11)	%Y=65.1 + 42.1 x - 21.1 x ²	16.4	.000	1.00	86.1
FN/NR(e4)	%Y=46.5 + 80.6 x - 46.4 x ²	46.4	.000	1.10	90.7
FN/NReMo	%Y=48.7 + 75.6 x - 34.6 x ²	36.3	.000	1.09	90
				(1.00*	90.0**)
For 1976/77 Barley (different varieties, n = 187 treatment plots)					
FN kg ha ⁻¹	%Y=44.3 + 4.48 x - .136 x ²	28.6	.000	165.000	73.8
FN/NR(e11)	%Y=59.1 + 54.4 x - 32.2 x ²	16.1	.000	.845	82.1
FN/NR(e4)	%Y=47.9 + 73.2 x - 40.0 x ²	25.8	.000	.915	81.4
FN/NReMo	%Y=46.3 + 133 x - 117 x ²	30.6	.000	.568	84.1
				(.600*	84.0**)

1) FN denotes fertilizer N (kg ha⁻¹) applied in each of 11 treatment plots of NPK combinations in 8 to 9 different sites throughout the country.

2) NR(e11) is the FN requirement estimated from FN response equations using 11 NPK combination levels for each site.

3) NR(e 4) is the FN requirement estimated from FN response equations using 4 N levels only in each site.

4) NReMo is the FN requirement estimated by the use of Model (1) from the soil test results of each site.

5) Data in () are the crop factor Fv* may be used for maximum yield** expected by the use of the Model (1).

maintaining proper SiO₂/OM of less than 10.0, seems to be required for minimizing N fertilizer rates in growing crops of grass species, in general.

22.7. FUTURE RESEARCH NEEDED IN RELATION TO SILICON IN KOREA

In the future, Korean agriculture, like elsewhere in the world, will have to pursue two things, safe food production and environmental protection. For both goals, the use of fertilizers and agricultural chemicals must be at optimum levels for sufficient and safe food production as well as to minimize the environmental hazard due to excessive doses.

These fertilizer requirement models will be very useful based on the multi-nutrient factor balance concept starting with the balance of SiO₂/OM as a key factor. This key factor may also be

important for protection from environmental hazards due to the emission of greenhouse gases such as methane or nitrous oxides, which are known to have 30 and 200 times greater greenhouse effect compared to carbon dioxide. The emission of methane is known to be enhanced by the chimney effects of rice plants, and may be minimized by proper Si uptake to form an Si-cuticle double layer in the plant epidermis as is the case in transpiration loss of water or NH_3 volatilization.

Plants with well balanced nutrients may have a greater capacity to assimilate CO_2 to minimize global CO_2 concentration build up by the emission from other industries. This enhanced carbon assimilation under sufficient Si uptake may also aid resistance to high or low temperatures due to the greenhouse effect or climatic changes.

There may also be a possibility of minimizing genetic modification due to atmospheric deposition or radiation from various sources if the plant is supplied with sufficient Si to protect the plant cells.

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POSTER ABSTRACTS

AUSTRALIA

Silicon is involved in cane yield response to sugar mill waste products

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Sugar mills produce nutrient rich waste products (filter mud and furnace ash). In Australia, these materials are returned to cane fields in nutrient management or soil amelioration plans. Generally, yield responses are attributed to N, P, K, and Ca constituents of the wastes. However, yield responses have also been reported where the above nutrients have been adequately supplied from fertilizer sources. Thus, sugar mill wastes have earned a reputation for "*mysterious capacity*" to ameliorate soils with low natural fertility. How might we explain such responses?

This field experiment, on a gleyed podzolic soil (redoxic hydro sol) involved comparison of sugar mill ash alone and a sugar mill filter mud /ash mixture with supply of nutrients equivalent to the latter, from fertilizers. Data were acquired over two years, for first and second ratoon crops. The following conclusions were obtained: There was a good cane yield response to both sugar mill wastes in first and second ratoon crops; phosphorus, potassium, calcium and trace elements in the wastes did not improve yield; yield benefits of the sugar mill wastes were attributed to reduced bulk density and better nitrogen and silicon nutrition; sugar mill wastes resulted in higher levels of soil and leaf silicon than other treatments; and filter mud/ash increased soil nitrogen supply - ash alone did not. So silicon in ash may have improved nitrogen use efficiency. Silicon may be part of the mysterious benefits of sugar mill wastes.

Soil analysis for predicting sugarcane yield response to silicon

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Silicon is emerging as an important nutrient for sugarcane in Australia and overseas. Large yield responses to Si were recorded in field experiments in north Queensland and Si is involved in response to sugar mill wastes containing ash. Advice for use of Si based amendments is likely to be based on soil analysis.

The following methods were used: Crushed cement building board waste was applied to three soils (euchrozem [volcanic], yellow podzolic & sand [sedimentary]); sugar mill wastes (filter mud /ash mixture and ash) were applied to a gleyed podzolic soil; soil samples from 0 - 25cm zone were assayed for extractable Si in: 0.005 M H_2SO_4 , 0.01 M $CaCl_2$ and 0.5 M Acetic acid at pH 2.5 and also buffered to pH 4.8; leaf samples were assayed for Si; and relative cane yield was calculated for the gley podzolic site. The conclusions were as follows: Soil Si extracted in sulfuric acid and calcium chloride provided useful indices of plant available Si across soil types. Sulfuric acid and pH 2.5 acetic acid extractable Si were most closely related to the yield response on a gleyed podzolic soil. Therefore, 0.005 M sulfuric acid holds promise as the basis of a Si soil test.

Some effects of silicon in potting mixes on growth and protection of plants against fungal diseases

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Cucumbers, snapdragons, and paper daisies were grown in an organic and sand based Control Mix (CON), +Si Mix (SIM = CON + Silicate) and Ricehull Ash Mix (RAM). Molybdate reactive Si in 1:1.5 DTPA extracts of mixes was 2.25-2.55mg/L for CON, 14.1-15.0mg/L for SIM and 11.4-13.6mg/L for RAM. Growth of cucumbers and paper daisies in RAM and SIM was significantly ($P \leq 0.05$) greater than for those grown in CON. Plants grown in RAM accumulated more Si than those grown in SIM, which contained more Si than those from CON. Snapdragons grown in SIM and CON were larger and flowered earlier and than those in RAM. Only bases of snapdragons grown in RAM contained more Si than plants from other mixes, at $P=0.06$.

Incidence and severity of an incidental infection of powdery mildew (*Sphaerotheca fuliginea*) was less for cucumbers grown in RAM at 6 and 10 weeks and SIM at 6 weeks than those grown in CON. Severity of infection of paper daisies by black mould (*Colletotrichum gloeosporioides*) was least when grown in RAM. Commonly used horticultural substrates contain less Si compared with the trial mixes and may contribute to reduced growth and increased susceptibility of potted plants to fungal diseases.

BRAZIL

Response of upland rice to calcium silicate applications

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In Brazil, upland rice is cultivated mainly in Oxisols that are low in soil fertility including low Si in relation to Fe and Al oxide. An experiment was conducted, under greenhouse conditions, with the objective of evaluating the response of rice to SiO_2 . The treatments consisted of six doses of SiO_2 (0.0, 0.75, 1.50, 2.25, 3.00, 3.75 g pot⁻¹ containing 6 kg of soil) in the form of wollastonite, (Vansil-10, 50% of SiO_2) and three rice cultivars (Caiapó, Carajas, and Confiança). The relationship between SiO_2 rates and grain yield was linear and significant ($Y = 3.895 + 0.159x$, $r^2 = 0.638$). The highest grain yield increase of 23%, in relation to control was obtained with the application of 3.0 g pot⁻¹ of SiO_2 corresponding to 1 t ha⁻¹. The cultivar Confiança consistently showed the highest tissue concentration of Si followed by Carajas and Caiapó. The application of SiO_2 also increased the pH and soluble Si in soil. Upland rice responded to SiO_2 applications, but the magnitude of response was greater at the highest calcium silicate dose and varied according to the cultivar.

Use of crushed basaltic scoria as a silicon source for rice

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An experiment has been carried out since June 1999 to study the efficiency of crushed basaltic scoria in supplying available silicon to rice plants. The scoria was mixed to 3 kg samples of a medium-textured Red-Yellow Latosol and a sandy Quartz Sand soil at rates of 0, 70, 140, and 240 t ha⁻¹ and placed in ceramic pots. The soil samples were moistened to 50% of the WHC and incubated for 20 days in the greenhouse. Soluble silicon was extracted from the soil by 0.5 M acetic acid solution and determined by colorimetric method, using ascorbic acid as the reducing agent.

In both soils, the extracted silicon increased linearly with the applied rates of basaltic scoria. For the highest rate applied, silicon content raised from 30 to 58 mg kg⁻¹ (93% increase) in the Red-Yellow Latosol, and from 18 to 35 mg kg⁻¹ (94% increase) in the Quartz Sand.

In continuation, three rice crops will be successively cultivated in the pots. Nutrients will be added in proper amounts, but no extra basalt scoria will be applied. For each crop, both dry matter and grain yields will be evaluated, as well as the amount of silicon absorbed by the plants and the soluble silicon content of the soil.

Silicon and sustainable agriculture in Brazilian cerrado (savannah) soils: One challenging issue for the microbiologists

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In tropical soils, agriculture has been sustained by minimum or no-tillage which have proved to be successful. Thus, a rapid increase in area since the 1990's has stimulated scientists toward the understanding of the contribution of all components and specially the biotic factors involved in the soil quality improvement obtained from his system after the first years of adoption.

Our main goals to determine and quantify the main groups of microorganisms involved in the enhancement of the biological activities after continuous cultivation with the gramineae *Brachiaria* and *Paspalum* or after being cropped with a subsequent crop – soybean. Comparisons were also made with the original non-disturbed savannah soil for plant growth development and nutrient accumulation, including silicon in the plant.

Twenty five (25) cylinders (30 cm diameter, 40 cm depth each) containing a dark red clay soil core collected in core from a chronosequence system of a tropical cerrado soil in Central Brazil, Rio Verde. The study was conducted under greenhouse conditions, using the species of gramineae and the following treatments: 1. Control (undisturbed savannah soil), 2. *Brachiaria* spp., 3. *Panicum maximum*, 4. Minimum tillage with *Brachiaria* spp., 5. Minimum tillage with *Paspalum notatum*.

Bean grown after both gramineae cropping showed to contain high Si concentrations in the shoot. Specially after minimum tillage, an overall enhanced microbial activity was observed, thus promoting a better nutrient availability from the breakdown of organic residues from the gramineae straw. *Brachiaria* spp. had a stronger requirement for N due to its higher growth development. This may be counteracted by adding small amounts of N-fertilizer as starter N, during its vegetative growth. Bean yield, nodulation by *Rhizobium* and mycorrhizal infection were enhanced as well as the number of soil bacteria and fungi in the minimum tillage system, specially after *Paspalum* cropping. We concluded that minimum tillage with such gramineae is capable of improving the soil quality, by altering the microbial activity and nutrient availability to the plants.

A hydroponic survey on silicon, stem canker and root nodulation interactions in soybean [*Glycine max.* (Merril)]

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Stem canker in soybean caused by the fungus *Diaporthe phaseolorum* f. sp. *meridionalis* (Dpm) has been one of the main causes of yield decreases in recent years in Brazil. Among others, genetic resistance is one constraint due to the low genetic variability of the Brazilian soybean germplasm. The breeding program underway in Brazil is now taking into account tolerance to this fungal disease. On the other hand, nitrogen fixation in soybean has been very successful in the savannah tropical soils of Central Brazil, one of the top soybean producers in the world. From recent findings in beans, it seems nitrogen may play an important role on enhancing disease susceptibility when this element is supplied at high levels or is present in rich-N soils. Nodulation ability and disease tolerance are important traits to be evaluated simultaneously when selecting plants in breeding programs.

The effect of silicon on the control of stem canker in nodulated and N-supplied in two commercial soybean lines (Garimpo Comun and EMGOPA 301) was studied under hydroponic conditions. In Study I, Leonard jars containing nutrient solution with a) 3 mM of NH_4NO_3 were inoculated with strain of *Bradyrhizobium japonicum* CB-1809. Nodulation (number, mass, and activity of the nodules) was measured at 42 days after emergence (DAE) in presence or absence of 100 mg/Kg of silicon. In Study II, eight levels of Si (0, 10, 20, 30, 40, 50, 75, and 100 mg/L) supplied as sodium metasilicate in the nutrient solution were tested using Garimpo Comun. The inoculum with fungus *Dpm* was cultured in liquid media and inoculated 10 DAE. Fungal lesions were annotated at 21 DAE. Silicon content in leaves, stems, and roots was compared in all treatments. Interactions among plant-pathogen (fungus) - nodulation (*Bradyrhizobium*) were studied under hydroponic conditions, with and without silicon addition (100 mg L^{-1}) in two commercial cultivars (Garimpo Comun and Emgopa 301). High levels of silicon in the solution (100 mg Si L^{-1}), and consequently, in the soybean tissues, decreased fungal lesions and nodule development and functioning (C_3H_2 reduction), probably due to the induction of defense genes and production of secondary metabolites.

Evaluation of soil extractants for silicon availability in upland rice

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Generally, silicon is not considered an element "essential" for plant growth. However, many workers have shown that silicon improves the growth of rice and other Gramineae species. Therefore, quantification of Si in soils and plant tissue should be an important routine analysis performed in agriculture research laboratories. The suitability of four extraction methods (acetic acid 0.5 mol L^{-1} , buffer pH 4.0, calcium chloride 0.0025 mol L^{-1} and water) for estimating the amount of available Si in soil for upland rice was determined. Four soil types corresponding to the following classes were used: Typic Acrustox-isohyperthermic (LEa), Typic Acrustox-isohyperthermic (LVa), Rhodic Acrustox-isohyperthermic (LRd) and Ustoxic Quartzipsammentic-isohyperthermic (AQa), created in each of the soils by applying calcium silicate. Upland rice was grown to maturity in pots of each soil in the greenhouse. Among the extractants studied, the acetic acid 0.5 mol L^{-1} gave the best estimate for silicon availability in soil. The silicon content found in the leaves was highly correlated with extractable silicon by the acetic acid 0.5 mol L^{-1} method.

Characteristics of an *in situ* opalized vegetative axis in a Brazilian Oxisol and possible plant pathological implications

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Hollow, white siliceous cylinders identified as *in situ* partially opalized branched vegetative axis have been found in an Oxisol in SW Minas Gerais. The main axis was about 4-5 m long and 15 cm diameter with a continuous wall of silicified outermost xylem tissues a few millimeters thick. Bark and more internal tissues were decomposed, and are being studied by SEM, X-ray fluorescence and diffraction, micromorphology, and soil analysis. Organic matter was not preserved, but cell lumina have been replicated, and some cell walls with bordered pits have been permineralized. SEM locally revealed a relict botryoidal texture suggestive of original opal, now converted to low-trydimite. Si was dominant but some Zn and Cu also were detected. "Available" silicon in the adjacent soil increased with depth (3 to 30 ppm), and morphologic studies suggests *Cecropia* sp. Soil, both inside and immediately outside the cylinder, contained numerous biopedotubules with opal fragments. Silicification evidently occurred recently or subsequently. Some *Cecropia* in the region have symptoms reminiscent of citrus blight, common in the area. The tantalizing possibility that silicification may be involved with this disease is currently under study.

Silicon and *Theobroma cacao*

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Witches broom of *Theobroma cacao* is caused by the basidiomycete, *Crinipellis perniciosa*. This disease is endemic to the cocoa producing countries of South and Central America, and the Caribbean Islands. The pathogen infects meristematic tissues, flower cushions, and developing pods. The disease now limits cacao expansion and consolidation in Brazil.

The only effective control measure is through phytosanitation and its adoption depends on the world cocoa price. The long-term solution is through use of resistant cocoa genotypes.

There is limited information regarding the relationship between mineral nutrition and disease development by *C. perniciosa* in *T. cacao*. We herein report for the first time the effect of silicon on cocoa seedling growth, and on the biology of *C. perniciosa*. Germ tube length of basidiospores of *C. perniciosa* was reduced by 250 mg/kg of Si. Mycelial growth rates varied by isolate and the most sensitive isolate of *C. perniciosa* to Si was from Altamira, PA, Brazil. The role of silicon on cocoa growth and disease resistance to *C. perniciosa* will be discussed.

Calcium silicate slag in tropical savanna soil. It's effect on the availability of phosphorus in soil and sugarcane

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The objective was to compare the use of limestone to that of calcium silicate slag (39.9% SiO₂) on the availability of soil phosphorus and in sugarcane on two plantations in two acidic soils in the tropical savanna region. Thus, a pot experiment was performed at the Engineering Faculty of Ilha Solteira/ UNESP. Blocks were randomized, but each one had a factorial design involving 2 levels

of acidic correction (1xNC : 2xNC). saturation was considered on bases equal to 45% (1xNC); two corrective agents (calcitic limestone and calcium silicate slag); and two soils (Quartzose Sand and Dark-Red Latosol). 200mg/dm³ of P was applied together with the corrective agents at the time of the planting of the sugarcane. The soil was analyzed 225 days after the incorporation of these products.

The calcium silicate slag in the dose 1xNC was better than limestone for increasing available P in the soil. For sugarcane, the slag had a linear effect whereas limestone had no effect at both locations. Therefore, the silicon in the slag affected indirectly the P increase of the soil.

Effect of silicon fertilization on rice sheath blight development in Brazil

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Sheath blight (*Rhizoctonia solani* Kühn) is an important disease in intensified rice production systems worldwide. This study examined the effect of calcium metasilicate (wollastonite) at the rates of 0, 2, 4, 6 and 8 Mg ha⁻¹ on sheath blight development. Six rice cultivars were grown on a typic acrustox (red-yellow latosol, 0-20 cm, Ki = 0.74, Si = 9.2 ppm and pH = 4.8). Linear regression models described the relationship between the assessments by highest relative lesion height (HRLH) and severity (scale ranged from 0 to 9) and silicon rates. The HRLH was reduced relative to the control by 24%, 25%, 33%, 20%, 24%, and 32% for the rice cultivars: 'Epagri 109', 'Rio Formoso', 'Javaé', 'Cica-8', 'BR-Irga 409', and 'Metica-1'. Sheath blight severity also decreased by 61%, 57%, 59%, 61%, 62%, and 60% for the rice cultivars 'Epagri 109', 'Rio Formoso', 'Javaé', 'Cica-8', 'BR-Irga 409', and 'Metica-1' in comparison to the control.

Response of six gramineae species to applications of calcium metasilicate

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Despite its abundance and importance, silicon has received far less study than any other nutrient. Silicon concentration of plant varies by soil and plant species. This experiment evaluated the uptake of Si and Ca by six grasses by applying calcium metasilicate (wollastonite) at the rates of 0, 200, 400, 600 and 800 kg SiO₂ ha⁻¹. The grasses were grown on a typic acrustox (red-yellow latosol, 0-20 cm, Ki = 0.74, Si = 9.2 ppm and pH = 4.8). Only Si, not Ca, significantly increased with increasing calcium silicate rates. On average, Ca values ranged from 0.16 to 0.40%. Linear regression models described the relationship between plant tissue silicon concentration and silicon rate. Silicon concentration (%) in the six gramineae species increased relative to the control by 251%, 125%, 100%, 47%, 40%, and 12% for rice, oat, sorghum, corn, wheat, and rye, respectively. Although dry weights of shoots and roots were not significantly different from the non-treated control, plant heights increased significantly.

Influence of silicon fertilization on powdery mildew development in cucumber

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It is long known that silicon enhances the fungal resistance of many plant species. In cucumber, the addition of silicon to hydroponic nutrient solutions has helped to reduced powdery mildew (*Sphaerotheca fuliginea*) development. The effect of silicon on powdery mildew development in cucumber was determined. Silicon was added to a typic acrustox (red-yellow latosol, 0-20 cm, Ki = 0.74, Si = 9.2 ppm and pH = 4.8) as calcium metasilicate (wollastonite) at the rates of 0, 2, 4, 6 and 8 Mg ha⁻¹. Conidia of *Oidium* sp. were collected from infected cucumber plants from fields never treated with fungicides and brushed onto leaves of cucumber plants ('Híbrido Caipira AG370') amended and non-amended with silicon. Silicon was able to reduce the severity of powdery mildew and the number of mildew colonies relative to the control by 30.3%, and 36%, respectively, but these treatments were not significantly different from the non-treated control. Dry weight also was not affected, but leaf area increased significantly.

CANADA

Proof of stable aqueous silicon-sugar complexes

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The importance of silicon in plant physiology has been amply demonstrated. Yet, almost nothing is known of the *chemistry* that plants use to uptake and transport silicon. Indeed, although numerous proteins and naturally occurring ligands have been identified as potential silicon binding substrates, no organosilicon complexes have ever been detected under physiological conditions. Using ²⁹Si NMR spectroscopy, we have shown that certain aliphatic polyhydroxy molecules ("polyols") - including a number of simple sugar molecules - display an extraordinary affinity for aqueous silicate anions, forming stable monomeric polyol-silicon complexes.

The silicon in these complexes can exist in either five- or six-fold coordination by oxygen, a phenomenon previously unknown in aqueous silicon chemistry. Coordinating polyols require at least four adjacent hydroxy groups, two of which must be in *threo* configuration, and coordinate to silicon via hydroxy oxygens at chain positions on either side of the *threo* pair. Such species can reasonably be expected to play a central role in the biochemistry of silicon.

CHINA

Effect of silicon fertilization on crops grown in the yellow river alluvial plain of China

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The effect of a silicon fertilizer, which is made from blast furnace slag, was tested on various plants growing in the Yellow River alluvial plain of China. The results indicated that this silicon fertilizer increased grain production 10-26% for rice, 10-15% for wheat, and 15-25% for peanut. The mechanism for increased yields was based on the original low silicon content in water from the Yellow River, the lack of available silicon in the soil, and the richness of trace elements in the blast-furnace-slag-made silicon fertilizer. Silicon content in water from the Yellow River system was between 0 to 10 mg/L. The concentration of available silicon in the soil ranged from 100 to 300mg/g. Moreover, the relatively high pH value and richness of Ca and Mg observed in the Yellow River alluvial soil probably negatively influenced silicon absorption.

In rural areas of China, agriculture and the farmer are always the pivotal problems in supporting China's economic development and social stability. It is estimated that five million tons of silicon fertilizer would be required per year for agricultural production in the Yellow River alluvial plain. These data suggest that the application and popularization of silicon fertilizer should be enhanced.

Yield response to silicon and combined use of SiZnMn fertilizer in China

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Beneficial effects of silicon application on yield and quality of rice as well as other crops have been achieved in the major grain production areas in China in the past two decades. Generally, critical soil available SiO₂ content is 95 mg/kg, but good response to silicon in rice were found in soils with available content as high as 180mg/kg. In North China, the critical value for winter wheat was 220mg/kg and the same yield increase effect was achieved in summer corn. In Northeast China, significant yield increases were achieved in light chernozem and brown soils in which soil available SiO₂ content ranged 70~140 mg/kg. Field trials demonstrated that, compared with N, P, Zn, and Mn fertilizer use alone or these fertilizers combined with each other, a combined application of SiZnMn could more efficiently increase absorption of N, Zn, Mn, and P by crops, improve water use efficiency and resistance to lodging. Since two or three nutrients often appear deficient in one soil in China, the combined use of SiZnMn proved best. The proper doses of Si fertilizer (calculated as Na₂SiO₃) were not higher than 90 kg/hm² in South and North China.

Silicon induced cadmium tolerance of rice (*Oryza sativa* L.) seedlings

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Cadmium (Cd²⁺) toxicity and the effects of silicon on the cellular and intracellular accumulations and distributions of Cd²⁺ were investigated by conventional electron microscopy and EDX analysis. The silicon-deprived rice plants (-Si) differed greatly in Cd²⁺ distribution in the

cell walls and vacuoles of the leaves and roots in comparison to silicon-amended treatments. Energy dispersive X-ray microanalysis revealed that considerable amounts of Cd could be detected in the cytoplasm, vacuole or cellular organelles in -Si rice plants, while very little was found in +Si ones. From the microchemical and microbiological point of view, cell wall templates mediated the formation of colloidal silica with a high specific adsorption property and this helped to prevent the uptake of Cd^{2+} into the cell.

Effects of silicon on the seedling growth of creeping bentgrass and zoysiagrass

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The effects of silicon on the seedling growth of creeping bentgrass and zoysiagrass grown in a nutrient solution with three concentrations of Si (0, 1.7 mM, and 5.0 mM) were studied in a greenhouse chamber. Silicon promotes rigidity, elasticity, and traffic resistance. It also improves significantly the ability of creeping bentgrass to tolerate heat stress exceeding 45° C during the day and 35° C at night. The silicon-treated seedlings produced more fresh matter over the untreated seedlings. Silicon at 5.0 mM in the solution increased root length, fresh weight of roots and leaves of creeping bentgrass and zoysiagrass. The effects of silicon at 1.7 mM on the root growth of zoysiagrass were not significant. In contrast, silicon at 1.7 mM and 5.0 mM significantly increased growth effects on bentgrass. The treated seedlings increased the uptake of phosphorus and silicon by shoots in comparison to the untreated seedlings as determined by quantitative EDX analysis. Thus, silicon application to turfgrasses seems to be an efficient maintenance practice for improving stress resistance while enhancing agronomic and environmental benefits.

Plant cell wall template-mediated cooperative synthesis of micrometer-sized colloidal silica

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Zoysiagrass (*Zoysia japonica* L.) is widely used in sports turf and golf courses because of its excellent functional qualities, including rigidity, elasticity, resiliency, and disease tolerance. In addition, this turfgrass contains considerable silica deposited in the cell wall and micrometer-sized intercellular spaces of leaf epidermal cells. Thus silicon figures is a major mineral constituent of this turfgrass. Such a deposition would increase the mechanical strength of the plant cell wall, so silicon acts as a compression-resistant element. That in turn may improve the ability of grass to resist traffic and lodging. It is surprising to find a pronounced difference in the roughness of leaf surface physical properties. Silicon deprivation usually results in diminished biological performance. We examined whether different silicon chemical forms affect the morphological characteristics and the cooperative synthesis of hybrid inorganic-organic silicon materials in the turfgrass cell wall template, and we describe intriguing biological strategies to self-assemble colloidal silica through oligosaccharide of zoysiagrass cell wall template and the silica sol-based nanoparticles for the fabrication of the highly ordered silica superlattices.

The biomineral analysis of the intercellular spaces of zoysia showed continuous silica superlattice arrays of organized hexagonal close packed (h.c.p.) which were preferentially deposited on the cell wall templates when applied as the silica sol-based nanoparticles rather than monosilicic acid molecular species. Biomineralized rods are rhombic in outline and virtually of

constant size with major axes averaging $0.6 \mu\text{m}$. The silicon chemical forms of applications for plant absorption and primary building block of mineralization do affect significantly the formation of the superlattice arrays comparable to the random arrays that form without nanoparticles as a control. The composition was estimated by energy dispersive X-ray (EDX) spectra on a scanning electron microscope. The resulting intact rod showed carbon, oxygen, and silicon peaks. The variations of secondary electron peaks in the elemental contents with scanning organic-inorganic interfaces were reflected in commensurate changes. High-resolution image of an individual siliceous domain revealed irregular incoherent fringes in all selected microareas.

INDIA

Recycling of rice plant silicon and potassium for blast management in rice

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Eco-friendly, low-cost input, and agronomically efficient management practices for small resource-poor rice farmers are required in the future. A field trial was conducted during the 1996-97 wet season (southwest monsoon season, June-October) in the tropical region of the Maharashtra State, India. The objective was to evaluate the effect of rice hull ash (RHA) (as a source of silicon) integrated with rice straw (RS) (as source of potassium & silicon) on incidence of blast disease, incited by *Pyricularia oryzae* Cav., and plant growth and yield of rainfed transplanted rice (*Oryza sativa* L., cv. Chhimansal-39). The field trial was a split plot design with three replications. The two main treatments were basal incorporation of RS at 0 and 2.0 t ha^{-1} at transplanting, and the subtreatments were 0, 0.5, 1.0, 1.5, and $2.0 \text{ kg RHA m}^{-2}$ added to the seedbed prior to sowing. Urea briquettes containing diammonium phosphate were applied immediately after controlled transplanting, supplying 56 kg N and 14 kg P ha^{-1} .

The integrated use of RHA at 2.0 kg m^{-2} and RS at 2 t ha^{-1} significantly reduced the severity of leaf blast (24.9%) and incidence of neck blast (29.7%) in comparison to the non-treated control. Grain yield (17.8 q ha^{-1}) also increased over the nontreated control (13.3 q ha^{-1}). Thus, the use of RHA at 1 kg m^{-2} of seedbed combined with RS at 2 t ha^{-1} may be helpful to farmers for reducing blast incidence while increasing the rice yields without the use of fungicides.

Recycling of rice plant silicon and potassium for leaf scald management in rice

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Eco-friendly, low-cost input, and agronomically efficient management practices for small resource-poor rice farmers are required in the future. Three field trials were conducted during the 1995, 1996, and 1997 wet seasons (southwest monsoon seasons, June-October) in the tropical region of the Maharashtra State, India. The objective was to evaluate the effects of rice hull ash (RHA) (as a source of silicon) integrated with rice straw (RS) (as a source of potassium & silicon) on incidence of leaf scald disease incited by *Monographella albescens* (Thum) (*Rhynchosporium oryzae* Hashioka and Yokogi) and plant growth and yield of rainfed transplanted rice (*Oryza sativa* L., cv. Indrayani). The field trials were a split plot design with three replications. The two main treatments were basal incorporation of RS at 0 and 2.0 t ha^{-1} at transplanting, and the subtreatments

were 0, 0.5, 1.0, 1.5, and 2.0 kg RHA m^{-2} added to the seedbed prior to sowing. Urea briquettes containing diammonium phosphate were applied immediately after controlled transplanting, supplying 56 kg N and 14 kg P ha^{-1} .

The integrated use of RHA at 2.0 kg m^{-2} and RS at 2 t ha^{-1} significantly reduced the incidence (34.9%) and severity (29.6%) of the leaf scald compared to the control. The reduction in the incidence and severity of this disease was 29.5% and 25.6%, respectively, over the control. Grain yield (51.2 q ha^{-1}) also increased over the nontreated control (39.1 q ha^{-1}). Thus, the use of RHA at 1 kg m^{-2} of seedbed combined with RS at 2 t ha^{-1} may be helpful to farmers for reducing leaf scald incidence and severity while increasing the rice yields without the use of fungicides.

Calcium silicate slag applied to soil increased yield of rice on Inceptisol of Maharashtra State, India

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Efficient fertilizer management practices are required for farmers to improve low yields of transplanted rice (*Oryza sativa* L.) grown on Inceptisols. A field trial was conducted on an Inceptisol during the 1996-97 Rabi season (December to May) in the tropical region on the west coast of the Maharashtra State, India. The objective was to evaluate the effects of calcium silicate slag (CSS) on plant growth, nutrient uptake, and yield of irrigated transplanted rice (var. RTN-24). The CSS containing 45.0% SiO_2 supplied by Calcium Silicate Corporation, USA was applied at the rate of 0, 2, 4, and 6 t/ha to soil before transplanting. Fertilizers were applied at 60 kg N/ha and 13 kg P/ha either as basal broadcast and incorporated prilled urea and single superphosphate (PU+SSP) or deep placed 2.7 g urea briquettes containing diammonium phosphate (UB-DAP) for every four hills after transplanting with modified 20X20 cm spacing.

For both methods of fertilizers applied, the CSS improved plant growth, nutrient uptake, and yield of rice. However, the CSS, applied along with the deep placement of UB-DAP immediately after transplanting, increased more plant growth, nutrient (N, P, K, Ca, Mg, and Si) uptake and resulted in additional yield increases (1.3 to 1.4 t/ha) than in comparison to the split application of PU+basal SSP. The CSS seemed to reduce the incidence of stem borer in the rice crop. These results suggest the potential use of CSS and deep-placed UB-DAP in enhancing yields of transplanted rice on Inceptisols of Maharashtra State, India.

Effect of calcium silicate slag on plant growth, nutrient uptake and yield of sugarcane on two soils of Maharashtra State, India

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Attempts were made to investigate decreasing or stagnant yields of sugarcane (*Saccharum officinarum* L.) on soils of Maharashtra State, India. Two field trials on a Vertisol (Padegaon, Dist. Pune) and one field trial on Inceptisol (Dapoli, Dist. Ratnagiri) were conducted during 1997-98 to evaluate the effect of calcium silicate slag (CSS) on plant growth, nutrient uptake, yield, and juice quality of two plant sugarcane varieties (CO-86032 and CO-92013). The CCS containing 45.0% SiO_2 was basal-applied to soil at 0, 2, 4, 6, 8, and/ or 10 t/ha. Recommended levels of farmyard manure (FYM) and/ or NPK fertilizers were also applied to the soils.

In all three field trials, the application of CSS in graded levels resulted in significant increases in plant growth, cane yield, and commercial cane sugar. There was improvement in brix, % sucrose, and % purity of juice quality due to the CSS applications on the Vertisol at Padegaon only. The total nutrient (N, P, K, Ca, Mg, and Si) uptake (kg/ha) was increased due to the application of CSS. These results suggest the application of about 6 t/ha CSS to the sugarcane varieties was beneficial under the given agro-climatic conditions. However, more multi-locational trials in different seasons are required to assess the need of calcium silicate fertilizers for improving sugarcane yield in Maharashtra State.

JAPAN

New silicon source for rice cultivation: 1. Characteristic of new silicon source, silica gel

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Silicon is known to be one of the most important elements for growing rice. Many researchers have been studying the effect of silicon on plant growth and development for many years. The effect of silicon on growth and yield of plants grown under field condition may be difficult to determine because silicon fertilizers contain some alkali that may increase soil pH. Furthermore, plant diseases are often observed to be reduced when a silicon fertilizer is applied. These facts indicate that a new silicon source for crop production should be considered. We have developed a new silicon source, silica gel that could substituted for the existing silicon fertilizers used by farmers. The characteristics of this fertilizer are as follows: 1) silica gel is amorphous and has a large surface area, consequently, it is highly soluble in water, 2) milling and sieving can control the particle size of the silica gel, and the pH can range between 3 and 9, and 3) no significant difference in amount of mineralized $\text{NH}_4\text{-N}$ occurred between the treatments with and without silica gel applied to the soil.

New silicon source for rice cultivation: 2. Rooting ability and early growth of wetland rice as affected by silica gel application to the nursery bed

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The early growth of rice is affected by variability among rice seedlings in temperate regions. One of the factors that relates to the variability is silicon content of rice seedlings. The application of silicon to nursery beds of rice is difficult because of its high pH status. The object of this study was to estimate the rooting ability and early growth of rice plants using silica gel. The results obtained were as follows: 1) seedlings treated with silicon had a higher dry weight, a higher dry weight to plant height ratio, and increased content of silica compared to the control, 2) the photosynthetic rates of individual leaves and of the plant canopy of rice seedlings were higher in the silicon treatments. A greater amount of TAC was observed in the seedlings treated with silicon compared to the untreated control, and 3) a greater number of roots and heavier dry weight were found in the silicon-treated plots than in the control.

New silicon source for rice cultivation: 3. Growth and yield of wetland rice with reference to silica gel application

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It is a well-known fact that dry matter production and yield of rice are affected by its silicon content when grown under solution culture. It is difficult to identify the effect of Si on growth and yield of rice grown under field conditions, because the amount of mineralized N increases when a Si source is applied to the field. The objectives of this study were to evaluate the dry matter production and yield of rice grown under field conditions as affected by a new Si fertilizer, silica gel. Results obtained were as follows: 1) Increased rate of Si application enhanced dry weight, amount of N/leaf area (LA), and chlorophyll/LA of rice. 2) Moisture content of the leaf blade and light transmission ratio was greater in Si treated plots in comparison to the non-treated control in the afternoon. These facts suggest that the net assimilation rate of Si treated plots was greater than the non-treated controls. 3) A greater number of grains per unit area, percentage of mature grains and yield of rice were obtained in Si treated plots in comparison to the non-treated control.

New silicon source for rice cultivation: 4. How does silicon influence host resistance to rice blast disease?

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While many researchers have demonstrated that silicon in rice plants plays an important role in the resistance against blast disease, the mechanism is not clearly defined. Based on the work of earlier researchers, we put forward several hypotheses to explain how silicon confers this resistance. One hypothesis was that the absorption of silicon in rice reduces nitrogen uptake, consequently reducing the susceptibility to rice blast. However, our experiments did not support this hypothesis, since applying silica gel to rice did not reduce nitrogen uptake. Another hypothesis was that at least one process of pathogenesis was inhibited in rice plants with higher silicon content. Our results showed no significant differences between high and low silicon concentration on spore germination rates, appressorium formation rates, the size of lesions, and sporulation capacity. Therefore, it is unlikely that these mechanisms are the primary factors of resistance. The remaining possible explanations are that silicon acts as a physical barrier against fungal penetration on the surface of leaves or that silicon promotes some physiological resistance mechanisms within the plant. Consequently, we will test these hypothesis during the early infection phase.

Available silicon in soils extracted with phosphate buffer

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Acetate buffer has been widely used in Japan to evaluate the plant-available silicon status of soils. However, it is known that silicon is extracted in excess when the soil has received silicate slag. We proposed a new method to estimate availability by extraction with 0.02 M-phosphate buffer, pH 6.95 (PB). The procedure was: silicon is extracted from 1 g soil with 10 ml PB in a tube at 40° C for 5 hours, while stirring 5 times during extraction. The silicon extracted with PB

consisted of water-soluble and phosphate extractable fractions; the average ratios of water-soluble silicon of 12 Andosols and 11 non-Andosols were 38% and 53%, respectively.

The result at 4 prefectural agriculture research stations showed that the silicon extracted with PB correlated well with the silicon content of rice plants except for a few soil types. The correlation was not found for the acetate buffer method. The silicon in Andosols tended to be higher than the amount taken up by rice plants and the overestimation was supposed to be due to the difference in the water-soluble ratios.

We concluded the PB method is useful to evaluate the available silicon in soils and is better than the acetate buffer method.

Effects of porous hydrated calcium silicate on silicon nutrition of paddy rice

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Large amounts of porous hydrated calcium silicate (PS) fragment is produced as a industrial waste in the manufacturing process of autoclaved light weight concrete. Silicon is one of the most important elements for rice production, and thus, we investigated the effect of PS as a silicate fertilizer on silicon nutrition of paddy rice. The results obtained are: (1) PS is more effective for supplying silicon to rice plant than most commercial slags that were originally used as silicate fertilizers, (2) PS supplies silicon to rice plants continually from time of transplanting to harvest. (3) Tobermorite, main component of PS, was dissolved by 53 days after rice transplanting under paddy condition, but a silica skeleton remained till harvest time. (4) Application of PS reinforced plant resistance against rice blast disease, and also increased rice grain yield. From the foregoing, PS was determined to be a superior material for silicate fertilization of rice. This work was supported in part by Program of Research for the Future from the Japan Society for Promotion of Science (JSPS-RFTF96LOO604)

KOREA

Influences of silicon on the control of temperature and induction of electronic voltages in rice plant tissues

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Jap. x Ind. hybrid rice variety "Dasanbyeon" was grown in a water culture with silicon and without silicon to investigate the influences of silicon on the control of temperature and induction of electronic voltages in rice plant tissues.

Leaf temperatures of silicon-treated rice measured by infrared imaging radiometer were 22.7° C in 25° C ambient temperature and 30.7° C in 32° C, respectively, which was 1.7° C and 3.1° C higher than those of silicon-free plants, respectively. Leaf temperatures of silicon-treated plants measured by a porometer were 30.8-32.5° C in 30-38° C ambient temperatures, which were 0.7-0.9° C higher than those of silicon-free plant. However, under conditions of high temperature with 43-48° C leaf temperature of silicon-absorbed plant was 0.2-0.4° C lower than that in silicon-free plant.

The difference in electronic voltages between silicon-free and silicon-treated plants was near 6.5 mV. There was a relatively higher difference in unit and electronic induction pattern was also different from each other.

The change in electronic voltages in silicon treated plants was stable, while it was unstable in silicon-free plants. The induction of electronic voltage in leaf blade of rice plants stimulated by hand showed a sensitive response in the silicon-free plant.

RUSSIA

A proposed history of silicon fertilization

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Early agriculturists first used plant ash as a silicon fertilizer. Over two thousand years ago, the Emperor in China mandated the use of barley or rice with manure as a fertilizer by farmers. Vergilian, 70-19 BC, suggested the use of plant ash for improving the fertility of degraded soils of Rome. The first experiment ever conducted using silicon as a fertilizer was by J. Liebig in 1840. His early work helped to promote silicon research in Germany, Great Britain, Japan, Russia and USA. The classic field experiment with silicon was started at the Rothamsted Experiment Station in 1856. Maxwell in 1898 conducted the first soil tests on the content of plant-available (mobile) Si on the Hawaiian Islands. German scientists, Kreuzhage and Wolf (1884) and Grob (1896), explored Si's effect on plant disease resistance. Japanese scientists such as Odonera (1917) and Miyake and Adachi (1922) continued with this idea with rice that resulted in many outstanding discoveries. The Russian chemist D. I. Mendeleev suggested the use of Si fertilizers such as SiO_2 and CaSiO_3 in 1870. The first patent for using silicon-rich slag as fertilizer was obtained in the USA in 1881. The first field experiments using silicon as a by product from the metal industry were conducted by Cowles in 1917. In 1927, V. I. Vernadsky, an academic from Russia, declared that silicon is an important element for all living organisms. Based on past and current scientific research with silicon, these reviews demonstrate the possibility of developing an adequate theoretical base for silicon fertilization and its practical implementation in agriculture.

USA

Silicon use in Louisiana rice: potential improvements in disease management and grain yields

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Sheath blight (*Rhizoctonia solani*) and blast (*Pyricularia grisea*) are major rice diseases in Louisiana, both causing significant losses in grain yield and quality. Field studies were conducted on a Crowley silt loam (1995-1997) and on a Rita muck soil (1995-1996) to determine the effectiveness of silicon soil amendments in reducing the incidence of disease and increasing grain yield of rice. Calcium silicate slag was preplant incorporated at rates of 0, 1120, 2240, 3360, 4480, and 5600 kg/ha. The cultivars Bengal and Cypress were grown in a water-seeded, pinpoint flood cultural system. Grain yield, silicon accumulation in the y-leaf, whole plant, and in the mature rice

straw were determined. Disease ratings for sheath blight, blast, and brown spot (*Bipolaris oryzae*) were determined when significant disease was present.

On the Crowley silt loam soil in 1995 and 1996, grain yield increased 14 and 6%, respectively. Approximately 3360 kg/ha of calcium silicate slag were required to maximize grain yields. The average increase in silicon content over years of the y-leaf, whole plant, and mature rice straw was 30, 34, and 26%, respectively. The incidence of sheath blight was decreased in 1996-1997. Blast was decreased by calcium silicate slag applications in 1995, although the incidence of blast was very low. On the Rita muck in 1995 and 1996, grain yield increased 24 and 9%, respectively. This soil required a higher application rate of calcium silicate slag to maximize grain yields, approximately 4480 kg/ha. The average increase in silicon content over years of the y-leaf and mature rice straw was 46 and 21%, respectively. Whole plant silicon content on the Rita muck was increased 53%. Sheath blight was not affected by increasing rate of calcium silicate slag in 1996, but the incidence of brown spot was significantly reduced.

Applications of calcium silicate slag to a Crowley silt loam and Rita muck soil resulted in rice yield increases and higher accumulation of silicon in the y-leaf, whole plant, and mature rice straw. Grain yield and silicon accumulation responses were higher on the Rita muck. Calcium silicate slag applications had a positive effect on the incidence of blast, sheath blight, and brown spot on both soils. These field studies indicate that silicon soil amendments offer the potential to reduce disease incidence and increase rice grain yield in Louisiana. More research is needed to determine the economic feasibility of calcium silicate slag applications to Louisiana rice soils.

Beneficial effects of silicon on container-grown ornamental plants

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Silicon has been reported as a beneficial element for promoting the growth of monocots, particularly rice and sugarcane. However, limited research has addressed the effects of silicon on container-grown ornamentals. Since most ornamental crops are grown in soilless media where the silicon concentration is minimal, this study was undertaken to determine if silicon could be beneficial to ornamental plant growth. Thirty-seven cultivars from 35 genera of ornamental plants were grown in a soilless medium supplemented with K_2SiO_3 . Afterwards, plant growth and silicon concentration were measured. General results indicated that all of the plants were capable of absorbing silicon through their roots with large amounts found to have been translocated to the shoots, indicating that silicon may play certain roles in plant metabolism. More specifically, the addition of silicon: (1) significantly increased the dry weight of 16 cultivars, and (2) mitigated manganese toxicity. Therefore, silicon could be used as a fertilizer additive for improving the growth and quality of silicon-responsive ornamental plants.

Influence of silicon and host plant resistance on gray leaf spot development in St. Augustinegrass

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This study investigated the effect of silicon on gray leaf spot, caused by *Pyricularia grisea*, in St. Augustinegrass. The experiment was a factorial with 10 replications arranged in a RCB in the greenhouse. Main effects were silicon (14 gm CaSiO_3 / 500 cc soil) and a non-amended control, and sub-effects were four St. Augustinegrass cultivars: Bitterblue, Floratam, FX-10 and Seville. Plants were periodically misted to provide optimum leaf wetness that promoted natural infection by *P. grisea*. Disease severity was rated over a 4 week period by estimating % gray leaf spot on individual leaflets using a Horsfall-Barratt rating scale. Silicon significantly reduced area under the disease progress curves for gray leaf spot between 44% to 78% among all the St. Augustinegrass cultivars. This element also significantly reduced the final disease severity between 2.0% to 38.8%, and final whole plant infection between 2.5% and 50.5%. Plant silicon content in silicon-amended treatments for all cultivars increased between 2.2X to 3.5X over the non-amended controls. Silicon appears to be a good method for reducing gray leaf spot development in St. Augustinegrass.

Plant-available silicon in selected Alfisols and Ultisols of Florida

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Plant-available silicon was measured in soils from 70 locations in Florida. Forty of these were Ultisols including 5 soil series and 30 were Alfisols including 3 soil series. The average soil silicon content in Ultisols ranged from 7 ug/g in the Bonifay soil series to 15 ug/g in the Orangeburg soil series. The average soil silicon content in the Alfisols ranged from 6 ug/g in the Pineda soil series to 15 ug/g in the Winder soil series. One critical minimum concentration of silicon in the soil mentioned in the literature is 19 ug/g. Based on that concentration, corn, Bahia grass, Bermuda grass, pangola grass, chufa, and cucumbers will probably respond to silicon added to the soil.

Effects of fertilization with silicon on the components of resistance to rice blast

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The addition of silicon to silicon-deficient soils is known to reduce the epidemic rate of blast, caused by *Magnaporthe grisea*, in blast-susceptible and partially resistant cultivars of rice. Four cultivars of rice with differential susceptibilities to race IB-49 of *M. grisea* were fertilized with three rates of calcium silicate and inoculated with the pathogen to test the effects of silicon on the components of resistance that influence epidemic rate. The following components of resistance to blast were examined: incubation and latent period, infection efficiency, lesion size, rate of lesion expansion, sporulation per lesion, and diseased leaf area. For each cultivar, the incubation period was significantly lengthened by increased rates of silicon, and the numbers of sporulating lesions, lesion size and rate of expansion, diseased leaf area, and number of spores per lesion were reduced. At the highest rate of silicon (1000 kg ha^{-1}) lesion size and sporulation per lesion were 30-45% lower than for cultivars not treated with silicon. Thus, silicon acts to slow the epidemic rate of blast via reductions in lesion size and spore production per lesion.

Root application of potassium silicate reduce feeding damage to Sargent Crabapple leaf tissues by adult Japanese beetles

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Two-year-old Sargent Crabapple '*Malus sargentii*' seedlings were subjected to 4 continuous days of 100 ml root application of potassium silicate at the rate of 0, 100, 200, and 400 ppm in August, 1998. After three days of post-treatment applications, 3 detached leaves were placed in each of 3 petri dishes along with one adult female Japanese Beetle (*Popilla japonica*) (n=3/concentrations) for 7 days. Root, stem, and leaf tissue Ca, K, Mg, Na, and Si were analyzed using a Coupled Plasma Spectrometer. Potassium silicate at 100 ppm concentration significantly reduced percent leaf tissue eaten by adult Japanese Beetles. The ion leakage of stem tissues of 100 and 200 ppm treated plants were significantly lower than the control and 400 ppm. These lower ion leakage effects were also observed with red-osier dogwood stem tissues at 100 ppm. The results of the tissue analysis indicate that Si and Ca levels were significantly higher in root tissues for 100 ppm treated plants compared to stems and leaves. The K and Mg levels in root tissues were higher for the control and slightly higher for 100 ppm treatments compared to stems and leaves. The Na levels in root tissues were the same for control, 100 and 200 ppm, and significantly lower in 400 ppm treatment. In a companion study, fall webworm larvae were also exposed to the same above concentrations and treatments, however, since there was not a significant effect of potassium silicate on percent leaf tissue eaten by fall webworm larvae (*Paleacrita vernata*), this suggests there may be differences between major groups of leaf-feeding insects.

Lime effect on silicon release from silica fume dust

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The objective of this study was to evaluate lime's effect on silicon release from fume dust, a byproduct dominated by silica from an electric arc furnace. Fume dust was pelletized with 10% Ca(OH)₂ and 10% CaCO₃, respectively. The releases of silicon from lime-pelletized fume dusts were compared with those of pelletized fume dust via a 20-day continuous column leaching, using 10 g sample per column with 1 ml per minute of deionized water buffered to pH 7.0. We calculated leachate silicon ion species using a geochemical model MINTEQA2/PRODEFA2, Version 3.0. We found that leachate silicon concentration of lime-pelletized fume dust varied with leaching time and lime sources. The Ca(OH)₂ has more significant influence than CaCO₃ on silicon release from fume dust; but CaCO₃ has longer residual effect than Ca(OH)₂. The Ca(OH)₂ initially (first 48 hours) reduced silicon release in spite of high leachate pH due to high-soluble Ca level (>100 mg L⁻¹). Maximum silicon concentration occurred when leachate pH ranged from 7.5 to 9 and leachate Ca concentration was lower than 100 mg L⁻¹. Lime affects silicon release from fume dust through its free radicals: Ca²⁺ and OH⁻. The former decreases silicon release by precipitating the free silicate ions from the solution, while the latter increases silicon release from fume dust by forming silicate ions.

VENEZUELA

Silicon applications for blast control of rice on two soils types from Portuguesa, Venezuela

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Blast, caused by *Magnaporthe grisea* (Barr)/ *Pyricularia grisea* (Cooke)Sacc., is an important rice disease in Venezuela. During the 1997 rainy season, a study was done to evaluate the effect of different doses (0, 5, 10, 15, and 20 t/ha) of silica sand (99.64 % SiO₂, granulometry 51 % < 0.075 mm) to control blast in the variety Cimarron. The experiment was a completely randomized factorial (2x5) design with 9 replications conducted on two soils from the state of Portuguesa. The plants were sown in pots and maintained in tubs with water. Leaf blast was reduced using silicon by 81.6, 69.4, 46.9, and 83.7 % in comparison to the control. The injury decreased from grade 7 to 4, 4, 3, and 2. The reduction of blast incidence on the panicle using silicon was 36.5, 42.3, 42.3, and 65.7 % in comparison to the control. The magnitude of the response to silicon was better with the soil from Guanare in comparison to Acarigua. These results demonstrate that blast was controlled with the application of silica sand. Although the residual using silicon needs to be evaluated, the results indicate the possibility of using this material in an integrated blast control program.

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