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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 μm 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).
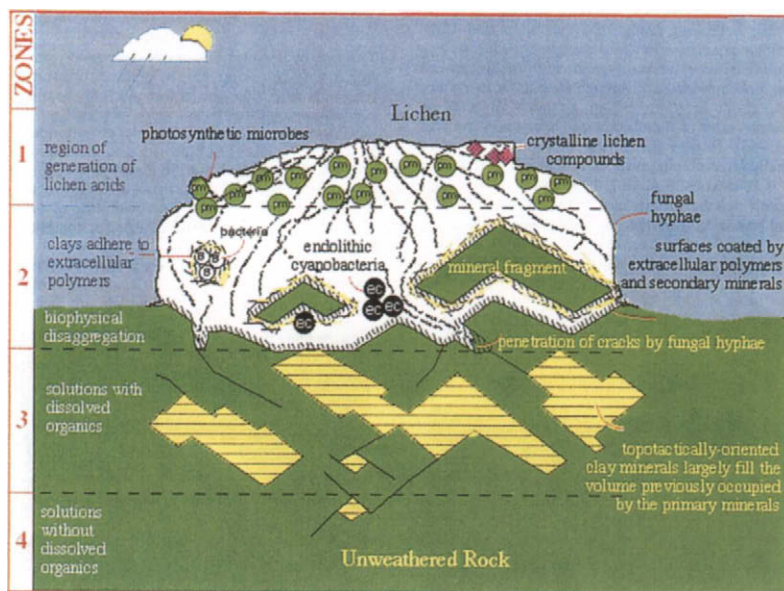

Figure 1.1. Model of four weathering zones of mineral weathering and the impact of microbes. See text for explanation. From Banfield et al. (1999). Reproduced by permission from Proceedings of the National Academy of Sciences, USA. vol. 96, ©1999 by The National Academy of Sciences of the United States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

Acid weathering is a progressive desilification 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,
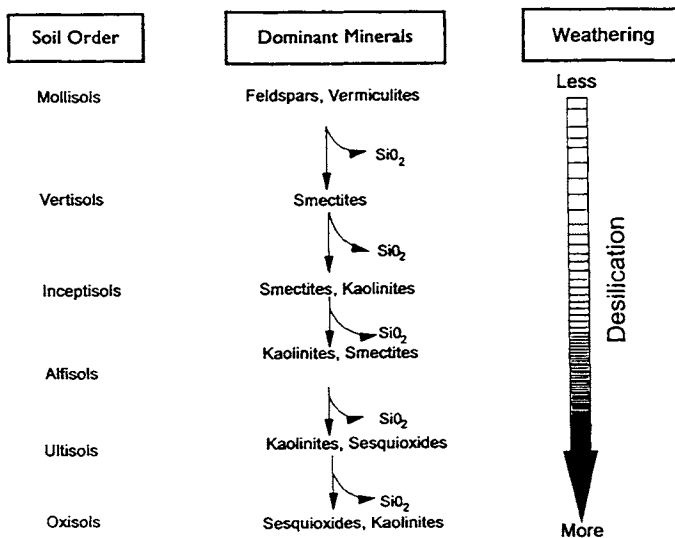

Figure 1.2. Simplified acid weathering sequence in soils. See text for explanation. From Savant et al. (1997a). Reproduced by permission from Advances in Agronomy vol. 58, © 1997 Academic Press, Inc.
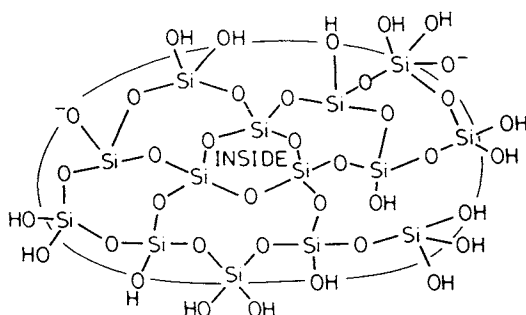
Figure 1.3. Schematic illustration of the nature of amorphous hydrated silica. See text for explanation. From Williams (1986). Reproduced by permission from Silicon biochemistry, © 1986 John Wiley & Sons, Chichester.

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

$$SiO_2 + 2H_2O = H_4SiO_4 . \tag{1}$$

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,
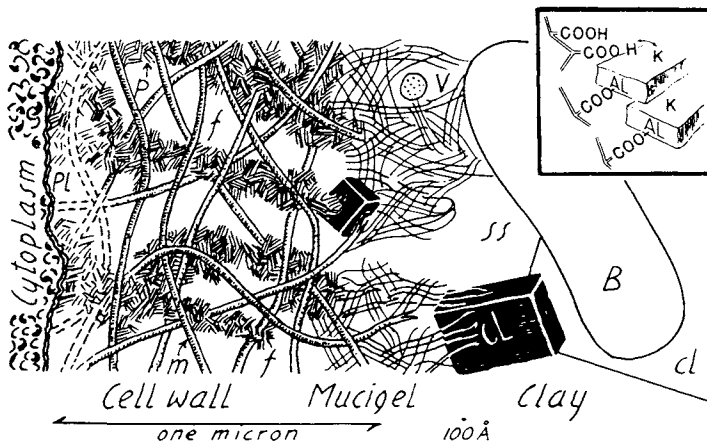

Figure 1.4. The root-soil interface. Note the scale. See text for explanation. From Jenny (1980). Reproduced by permission from The Soil Resource, © 1980 Springer-Verlag, New York.

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
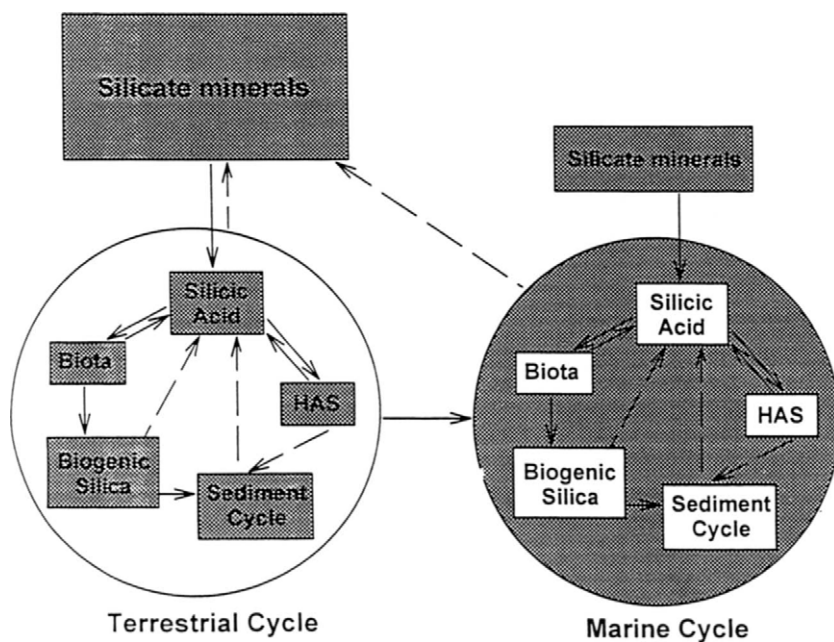

Figure 1.5. The biogeochemical cycles of silicon. From Exley (1998). HAS: hydroxy-aluminosilicates. Reproduced by permission from the Journal of Inorganic Biochemistry vol. 69, © 1998 Elsevier Science, Inc.

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.

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