

CHAPTER ELEVEN

Geomicrobial Interactions with Silicon

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11.1 DISTRIBUTION AND SOME CHEMICAL PROPERTIES OF SILICON

The element silicon is one of the most abundant in the Earth's crust, ranking second only to oxygen. Its estimated crustal abundance is 27.7% (w/w), whereas that of oxygen is 46.6% (Mitchell, 1955). The concentration of silicon in various components of the Earth's surface is listed in Table 11.1.

In nature, silicon occurs generally in the form of silicates, including ferromagnesian silicates (e.g., olivine, pyroxenes, and amphiboles), aluminosilicates (e.g., feldspar, mica, and clays), and silicon dioxide (e.g., amorphous silica, quartz). In general, the silicon in silicate minerals is surrounded by four oxygen atoms in tetrahedral fashion (Kretz, 1972). In most ferromagnesian minerals, iron, magnesium, and/or calcium links single or double chains of silica tetrahedral together, while in aluminosilicates, the aluminum is coordinated

with oxygen in sheets or 3D frameworks, depending on the mineral (see Tan, 1986). In clays, which form during the weathering of primary aluminosilicates, silica tetrahedral sheets and aluminum hydroxide octahedral sheets are layered in different ways depending on the clay type. In montmorillonite-type clays, structural units consisting of single aluminum hydroxide octahedral sheets are sandwiched between silica tetrahedral sheets. The units are interspersed with layers of water molecules of variable thickness into which other polar molecules, including some organic ones, and ions can enter. This variable water layer allows montmorillonite-type clays to swell. The structural units of illite-type clays resemble those of montmorillonite-type clays but differ from them in that Al replaces some of the Si in the silica tetrahedral sheets. These substituting Al atoms impart extra charges, which are neutralized by

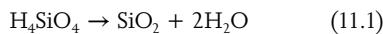
TABLE 11.1
Abundances of silicon on the Earth's surface.

Phases	Concentration	Reference
Granite	336,000 ppm	Bowen (1979)
Basalt	240,000 ppm	Bowen (1979)
Shale	275,000 ppm	Bowen (1979)
Limestone	32,000 ppm	Bowen (1979)
Sandstone	327,000 ppm	Bowen (1979)
Soils	330,000 ppm	Bowen (1979)
Seawater	$3 \cdot 10^3 \mu\text{g L}^{-1}$	Marine Chemistry (1971)
Freshwater	7 ppm	Bowen (1979)

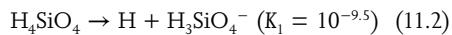
potassium ions between successive silica sheets. The potassium ions act as bridges that prevent the swelling exhibited by montmorillonite in water. In kaolinite clays, structural units consist of silica tetrahedral sheets alternating with aluminum hydroxide octahedral sheets are joined to one another by oxygen bridges (see Toth, 1955).

Silicon–oxygen bonds of siloxane linkages ($\text{Si}–\text{O}–\text{Si}$) in silicate minerals are very strong (their energy of formation ranges from 3110 to 3142 kcal mol⁻¹ or 13,031 to 13,165 kJ mol⁻¹), whereas Al–O bonds are weaker (their energy of formation ranges from 1793 to 1878 kcal mol⁻¹ or 7531 to 7869 kJ mol⁻¹). Bonds between nonframework cations and oxygen are the weakest (energy of formation ranges from 299 to 919 kcal mol⁻¹ or 1252 to 3851 kJ mol⁻¹) (values cited by Tan, 1986). The strength of these bonds determines their susceptibility to weathering. Thus, Si–O bonds are relatively resistant to acid hydrolysis (Karavaiko et al., 1984) unlike Al–O bonds. Bonds between cations and oxygen are readily broken by protonation or cation exchange.

Silicon in solution at pH 2–9 exists in the form of undissociated monosilicic acid (H_4SiO_4), whereas at pH 9 and above, it transforms into silicate anions, such as H_3SiO_4^- (see Hall, 1972). Monosilicic acid polymerizes in solutions supersaturated with respect to amorphous silica, forming oligomers of polysilicic acids (Iler, 1979). This polymerization reaction is favored around neutral pH where silica solubility is lowest (Avakyan et al., 1985). Polymerization of monosilicic acid can be viewed as a removal of water from between adjacent monomers to form a siloxane linkage. Silica can be viewed as an anhydride of silicic acid:



Dissociation constants for silicic acid are as follows (see Anderson, 1972):



Silica can exist in partially hydrated form called metasilicic acid (H_2SiO_3) or in a fully hydrated form called orthosilicic acid (H_4SiO_4). Each of these forms can be polymerized, the ortho acid forming, for instance, $\text{H}_3\text{SiO}_4 \cdot \text{H}_2\text{SiO}_3 \cdot \text{H}_3\text{SiO}_3$ (Latimer and Hildebrand, 1940; Liebau, 1985). The polymers may exhibit colloidal properties, depending on size and other factors. Colloidal particles of silica tend to form at silica supersaturation conditions (Tobler et al., 2009) and are favored by acid conditions (Hall, 1972).

Silica and silicates form an important buffer system in the oceans (Garrels, 1965), together with the $\text{CO}_2/\text{HCO}_3^-/\text{CO}_3^{2-}$ system. The latter is a rapidly reacting system, whereas the system based on reaction with silica and silicates is slow (Garrels, 1965; Sillén, 1967).

Aluminosilicates in the form of clay perform a buffering function in mineral soils. This is because of their ion-exchange capacity, net electronegative charge, and adsorption powers that make them important reservoirs of cations and organic molecules. Montmorillonite exhibits the greatest ion-exchange capacity, illite less, and kaolinite the least (Dommergues and Mangenot, 1970).

11.2 BIOLOGICALLY IMPORTANT PROPERTIES OF SILICON AND ITS COMPOUNDS

Silicon is taken up and concentrated in significant quantities by certain forms of life. These include microbial forms such as diatoms and other chrysophytes; silicoflagellates and some xanthophytes; radiolarians and actinopods; some plants such as horsetails, ferns, grasses, and some flowers and trees; and also some animals such as sponges, insects, and even vertebrates. Some bacteria (Heinen, 1960) and fungi (Holzapfel and Engel, 1954a,b; Heinen, 1960) have also been reported to take up silicon to a limited extent. According to Bowen (1966), diatoms may contain from 1500 to 20,000 ppm silicon, land plants from 200 to 5000 ppm, and marine animals from 120 to 6000 ppm.

Although the function of silicon in higher forms of life, animals and plants, is not presently

apparent, it is clearly structural in some microorganisms such as diatoms, actinopods, and radiolarians. In diatoms, silicon also seems to play a metabolic role in the synthesis of chlorophyll (Werner, 1966, 1967), DNA (Darley and Volcani, 1969; Reeves and Volcani, 1984), and DNA polymerase and thymidylate kinase (Sullivan, 1971; Sullivan and Volcani, 1973).

Silicon compounds in the form of clays (aluminosilicates) may exert an effect on microbes in soil. They may stimulate or inhibit microbial metabolism, depending on the conditions (Weaver and Dugan, 1972; Marshman and Marshall, 1981a,b; see also discussion by Marshall, 1971). These effects of clays are mostly indirect, that is, clays tend to modify the microbial habitat physicochemically, thereby eliciting a physiological response by the microbes (Stotzky, 1986). For beneficial effect, clays may buffer the soil environment and help maintain a favorable pH, thereby promoting growth and metabolism of some microorganisms that might otherwise be slowed or stopped if the pH became unfavorable (Stotzky, 1986). They also help with water retention with the pore spaces behaving as nanoreservoirs for water (Phoenix and Konhauser, 2008). Certain clays have been found to enable some bacteria that were isolated from marine ferromanganese nodules or associated sediments to oxidize Mn²⁺. Intact cells of these organisms can only oxidize Mn²⁺ if it is bound to bentonite (montmorillonite-type clay) or kaolinite (but not illite) that were first pretreated with ferric iron. They cannot oxidize Mn²⁺ that is free in solution (Ehrlich, 1982). Cell-free preparations of these bacteria can oxidize Mn²⁺ bound to bentonite and kaolinite without ferric iron pretreatment, although manganese-oxidizing activity of the cell extracts is greater when clays were pretreated (Ehrlich, 1982). Like intact cells, the cell-free extract cannot oxidize dissolved Mn²⁺ (Ehrlich, 1982). Clays may also enhance the activity of some enzymes such as catalase when the enzymes are bound to their surface (see Stotzky, 1986, p. 404).

By contrast, clays may suppress microbial growth and metabolism by adsorbing organic nutrients, thereby making them less available to microbes. Clays may also adsorb microbial antibiotics and thereby lower the inhibitory activity of these agents (see Stotzky, 1986). In soils, the results may be that an antibiotic producer is outgrown by organisms that in vitro it keeps in check

with the help of the antibiotic it excretes. These effects of clay can be explained, at least in part, by the strength of binding to a negatively charged clay surface and the inability of many microbes to attack adsorbed nutrients, or by the inability of adsorbed antibiotics to inhibit growth of susceptible microbes (see Dashman and Stotzky, 1986). High concentrations of clay may interfere with diffusion of oxygen by increasing the viscosity of a solution, which can have a negative effect on aerobic microbial respiration (see Stotzky, 1986). Clays may also modulate other interactions between different microbes and between microbes and viruses in soil, and they may affect the pathogenicity of these disease-causing soil microbes (see Stotzky, 1986).

Although clay-bound organic molecules may be less available or unavailable to organisms in the bulk phase or even attached to the mineral surface, this cannot be a universal phenomenon. Portions of attached large organic polymers may be attacked by appropriate extracellular enzymes, producing smaller unattached units that can be taken up by microbes. Electrostatically bound organic molecules that are potential nutrients may be dislodged by exchange with protons excreted as acids in the catabolism of some microbes. These processes of remobilization must also apply to mineral sorbents other than clays.

11.3 BIOCONCENTRATION OF SILICON

11.3.1 Diatoms

Diatoms are unicellular eukaryotic microorganisms that take up dissolved silica from both freshwater and seawater. Most live planktonically in the photic zone, and in the oceans, where they contribute nearly 50% of the total primary production (Mann, 1999). It is believed that diatoms first evolved in the early Jurassic (around 185 Ma), based on the oldest fossil evidence, although molecular clock studies suggest that they may be as old as 250 Ma (Kooistra and Medlin, 1996). Today, there are more than 100,000 extant species of living diatoms (e.g., Round and Crawford, 1990).

Diatoms have been most extensively studied with respect to their silica uptake ability (Figure 11.1) (Lewin, 1965; de Vrind-de Jong and de Vrind, 1997). They are unicellular algae enclosed in a wall of silica consisting of two

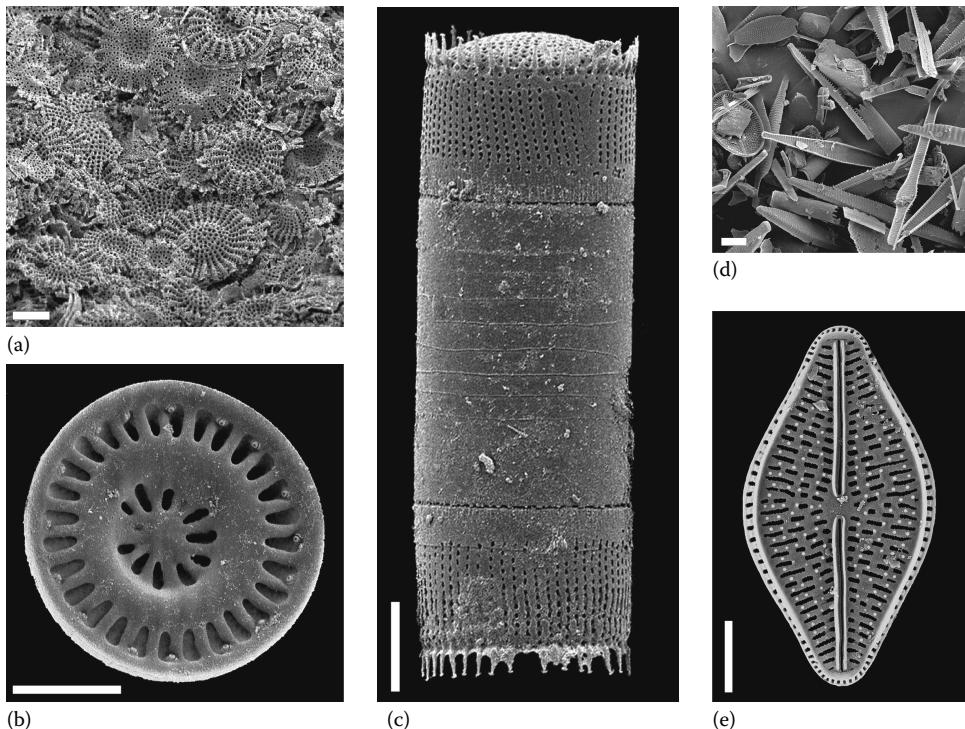


Figure 11.1. An overview of morphological variability in the diatom frustule as viewed in scanning electron microscopy (SEM): Modern and fossil representatives of centric (a–c) and pennate (d, e) genera. (a) Neogene fossil *Cyclostephanos* from British Columbia, Canada, (b) modern *Discostella stelligera* from the Ecuadorian Andes, (c) *Aulacoseira* from the Eocene of north-western Canada, (d) modern periphyton dominated by the araphid genera *Fragilaria* and *Tabellaria*, and (e) the raphid pennate genus *Brachysira*. All scale bars are 5 μm . (Images courtesy of Alex Wolfe.)

valves, an epivalve and a hypovalve, in pillbox arrangement. One or more girdle bands are loosely connected to the epivalve. The valves are usually perforated plates, which may have thickened ribs. Their shape may be pennate or centric. The pores serve as sites of gas and nutrient exchange (see de Vrind-de Jong and de Vrind, 1997). In cell division, each daughter cell receives either the epivalve or hypovalve of the mother cell and synthesizes the other valve *de novo* to fit into the one already present. To prevent excessive reduction in size of the daughter diatoms that receive the hypovalve upon each cell division, a special reproductive step called auxospore formation returns these daughter cells to maximum size. It occurs when a progeny cell that has received a hypovalve has reached minimum size after repeated divisions. Auxospore formation is a sexual reproductive process in which the cells escape from their frustules and increase in size in their zygote membrane, which may become weakly silicified. After a time, the protoplast in

the zygote membrane contracts and forms the typical frustules of the parent cell (Lewin, 1965).

The silica walls of the diatoms consist of hydrated amorphous silica, a polymerized silicic acid (Lewin, 1965). The walls of marine diatoms may contain as much as 96.5% SiO_2 , but only 1.5% Al_2O_3 or Fe_2O_3 and 1.9% water (Rogall, 1939). In clean, dried frustules of freshwater *Navicula pelliculosa*, 9.6% water has been found (Lewin, 1957). Thin parts of diatom frustules reveal a foam-like substructure when viewed under the electron microscope, suggesting silica gel (Helmcke, 1954), which may account for the adsorptive power of such frustules. The silica gel may be viewed as arranged in small spherical particles about 22 μm in diameter (Lewin, 1965). Because of the low solubility of amorphous silica at the pH of most natural waters, frustules of living diatoms do not dissolve readily (Lewin, 1965). At pH 8, however, it has been found that 5% of the silica in the walls of *Thalassiosira nana* and *Nitzschia linearis* dissolves. Moreover, at pH 10, 20% of the silica

in the frustules of *N. linearis* and all of the silica in the frustules of *T. nana* dissolve (Jorgensen, 1955). This silica dissolution may reflect the state of integration of newly assimilated silica in the diatom frustule. Some bacteria naturally associated with diatoms have been shown to accelerate dissolution of silica in frustules (e.g., Bidle and Azam, 2001). Frustules of living diatoms are to some extent protected against dissolution by an organic film, when present, and their rate of dissolution has been shown to exhibit temperature dependence (Katami, 1982). After the death of diatoms, their frustules may dehydrate to form more crystalline SiO₂ that is much less soluble in alkali than that in living diatoms. This may account for the accumulation of diatomaceous ooze.

Rates of silica uptake and incorporation by diatoms can be easily measured with radioactive [⁶⁵Ge]germanic acid as tracer (Azam et al., 1973; Azam, 1974; Chisholm et al., 1978). At low concentration (Ge/Si molar ratio of 0.01), germanium, which is chemically similar to silicon, is apparently incorporated together with silicon into the silicic acid polymer of the frustule. At higher concentrations (Ge/Si molar ratio of 0.1), germanium is toxic to diatoms (Azam et al., 1973). Genetic control of silica transport into diatoms has begun to be studied on a molecular level (see review by Martin-Jézéquel et al., 2000).

Diatoms are able to discriminate between ²⁸Si and ³⁰Si by assimilating the lighter isotope preferentially. The fraction (α) for each of the three diatom species *Skeletonema costatum*, *Thalassiosira weissflogii*, and *Thalassiosira* sp. was 0.9989 ± 0.004 . It was independent of temperature between 12°C and 22°C and thus, independent of growth rate (De La Rocha et al., 1997). This fractionation ability appears to be usable as a signature in identifying biogenic silica (De La Rocha et al., 2000).

Diatoms take up silica in the form of orthosilicate. More highly polymerized forms of silicate are not taken up unless first depolymerized, as by some bacteria (Lauwers and Heinen, 1974). Organic silicates are also not available to them. Ge, C, Sn, Pb, P, As, B, Al, Mg, and Fe do not replace silicon extensively if at all (Lewin, 1965). The concentration of silicon accumulated by a diatom depends to some extent on its concentration in the growth medium and on the rate of cell division (the faster the cells divide, the thinner their frustules). Silicon is essential for cell division, but resting cells in a medium in which silica

is not at a limiting concentration continue to take up silica (Lewin, 1965). Synchronously growing cells of *N. pelliculosa* take up silica at a constant rate during the cell division cycle (Lewin, 1965). Silica uptake appears dependent on energy-yielding processes (Lewin, 1965; Azam and Volcani, 1974; Azam et al., 1974; review by Martin-Jézéquel et al., 2000) and seems to involve intracellular receptor sites (Blank and Sullivan, 1979). Uncoupling of oxidative phosphorylation stops silica uptake by *N. pelliculosa* and *Nitzschia angularis*. Starved cells of *N. pelliculosa* show an enhanced silica uptake rate when fed glucose or lactate in the dark or when returned to the light, where they can photosynthesize (Healy et al., 1967). Respiratory inhibitors prevent Si and Ge uptake by *Nitzschia alba* (Azam and Volcani, 1974; Azam et al., 1974).

Total uptake of phosphorus and carbon is decreased during silica starvation of *N. pelliculosa*. Upon restoration of silica to the medium, the total uptake of phosphorus is again increased (Coombs and Volcani, 1968). Sulphydryl groups (–SH) appear to be involved in silica uptake (Lewin, 1965).

Some progress has been made in understanding how diatoms form their siliceous cell walls (see de Vrind-de Jong and de Vrind, 1997). Valve and girdle-band assembly takes place inside the cell and happens late in the cell cycle during the last part of mitosis. For this assembly, silica is taken into the cell and polymerized in special membrane-bound silica deposition vesicles (SDVs), leading to the formation of the girdle bands and valves. The SDV seems to arise from the Golgi apparatus, a special membrane system within the cell. The endoplasmic reticulum, a membrane network within the cell that is connected to the plasma membrane and the nuclear membrane, may participate in SDV development. The active SDVs are located adjacent to the plasma membrane. The shape of the SDV may be determined by interaction with various cell components such as the plasma membrane, actin filaments, microtubules, and cell organelles. The SDV is believed to help determine the morphology of the valves. Frustule buildup in the SDV appears to start along the future raphe, which appears as a longitudinal slot in each mature pennate frustule. The raphe has a central thickening called a nodule. Completed valves are exocytosed by the cell, that is, they are exported to the cell surface. When the valves are in place at the cell surface of the diatom, the raphe plays a role in its motility. Mature frustules have

glycoprotein associated with them, which may have played a role in silica assembly during valve formation. It may help in determining valve morphology and in the export of assembled valves to the cell surface. For additional information, the reader is referred to de Vrind-de Jong and de Vrind (1997) and references cited therein.

11.3.2 Radiolarians

Radiolarians are silica-secreting, protozoan zooplankton that mostly live planktonically in the surface ocean. The earliest fossil record for radiolaria is at the beginning of the Cambrian period (543 Ma) (Braun et al., 2013), and it is possible that they may even have evolved by the Neoproterozoic (Blair Hedges et al., 2001). Radiolarians have complex morphologies, most are spherical, but other body shapes, such as cones and tetrahedrons, also exist. Their skeletons tend to have spiny protrusions from the central body, which is used to increase their surface area for buoyancy and to capture prey (see Afanasieva et al., 2005). Due to their ornate skeletons, and ancient lineage, radiolarians have been widely used in biostratigraphy and interpreting the sedimentary record (De Wever et al., 2001).

11.3.3 Silicoflagellates

Silicoflagellates are a small group of unicellular algae found throughout the marine photic zone. Their origins extend back to the early Cretaceous (McCartney, 1993). Today, the number of species is believed to vary between only 1 and 3, despite many recognizable forms in the rock record. Their internal silica skeleton is composed of an outer basal ring, with or without radial spines, and a central apical ring to which several supporting struts attach the two (e.g., McCartney and Loper, 1989).

11.3.4 Sponges

Sponges are sessile aquatic animals of the phylum Porifera. They have bodies perforated with channels that allow water to freely circulate through their central cavity. Most sponges have internal skeletons of a material known as spongin (a type of collagen) and/or spicules of calcium carbonate or silica that provide structural support to

the animal and protection against predation (Bergquist, 1978). The type of mineral spicule is dependent upon the environment that the sponge inhabits; calcium carbonate is predominant in warm marine settings, while silica is restricted to colder waters, such as the poles (Barnes, 1982). The glass sponges (or hexactinellid sponges) contain silica spicules that form a scaffolding-like framework. It is believed that the spicule begins with the formation of an organic filament to which silica is secreted (Imsiecke et al., 1995). The earliest known hexactinellid sponges date to the Cambrian (Sperling et al., 2010).

11.4 PASSIVE SILICA BIOMINERALIZATION

A wide variety of ancient and modern hot spring systems are characterized by authigenic silica precipitation. In these systems, the chemical disequilibrium of venting hydrothermal fluids leads to the nucleation and growth of amorphous silica masses and simultaneously the mineralization, and potential fossilization, of many different types of microorganisms. Source waters originating from deep, hot reservoirs commonly contain dissolved silica concentrations significantly higher than the solubility of amorphous silica at 100°C (approximately 400 ppm) (Gunnarsson and Arnórrsson, 2000). Upon discharge of these fluids at the surface, decompressional degassing and boiling, rapid cooling to ambient temperatures, evaporation, and changes in solution pH all work together to cause the solution to rapidly and progressively exceed amorphous silica solubility (Fournier, 1985). Under these conditions, silicic acid dissolved in the monomer form $\text{Si}(\text{OH})_4$ spontaneously polymerizes initially to oligomers (e.g., dimmers, trimers, and tetramers) and then to polymeric species with spherical diameters of 1–5 nm, as the silanol groups ($-\text{Si}-\text{OH}-$) of each oligomer condense and dehydrate to produce the siloxane ($-\text{Si}-\text{O}-\text{Si}-$) cores of larger polymers. The polymers quickly grow in size such that a bimodal composition of monomers and particles of colloidal dimensions (>5 nm) are generated (Crerar et al., 1981, Tobler and Benning, 2013). Depending on the degree of supersaturation, these either remain in suspension, due to the external silanol groups exhibiting a residual negative surface charge due to a low zero point of charge (around pH 2), they coagulate via cation bridging and nucleate homogeneously, or they

nucleate heterogeneously on a solid substrate (Iler, 1979). In the latter case, once the first silica monolayer is deposited, silica itself becomes the reactive substrate.

The precipitation of amorphous silica frequently leads to the formation of hard, siliceous crusts, known as sinters. Individual sinter deposits are architecturally complex because of the intricate lateral and vertical variations in texture, mineralogy, and chemical composition, i.e., geyserite, spicules, columnar and stratiform microstromatolites, oncoids, and coccoid microbial mats (see Konhauser et al., 2004). Moreover, most siliceous sinters have been constructed, to some degree, around microorganisms. Indeed, even geyserite, the microbanded, amorphous silica sinter that forms in the proximity of spring vents and fissures, where temperatures in excess of 73°C were supposedly deemed sterile except for scattered thermophilic microorganisms (Walter, 1976), has now been shown to have surfaces commonly covered with biofilms, while their laminae generally contain silicified microorganisms (e.g., Jones et al., 1997).

Much of the textural variation in siliceous sinters can be attributed to the different types of microorganisms that inhabit different discharge aprons or different parts of an individual apron, primarily in response to differences in water temperature, composition, and acidity (Konhauser et al., 2004). In waters from 75°C to 100°C, life consists of a few dominant chemolithoautotrophic and heterotrophic bacteria and archaea—the more extreme an environment, the fewer the number of taxa and the microbial community may be shaped by the biological properties of just its dominant member. In shallow channels, where flow rates are high, streamers of *Aquifiales* and *Thermus* become mineral encrusted, forming unique fabrics that preserve the original flow directions. On the discharge aprons, where water temperatures have just cooled below the 73°C threshold, thick photosynthetic mats arise, containing species of *Synechococcus* and *Chloroflexus*. In waters cooler than 65°C, filamentous cyanobacteria appear, including species of *Oscillatoria* and *Phormidium*, as well as some purple and green sulfur bacteria. In the most distal parts of the drainage system, where temperatures are <40°C, other cyanobacteria, such as *Spirulina*, *Fischerella*, and *Calothrix*, begin to predominate. Green algae, diatoms, and fungi also become important mat constituents at the lowermost temperature regimes. At similar

temperatures on an individual apron, the determining factor governing species distribution is the composition of the geothermal fluids and gases. For instance, *Calothrix* prefers to grow in alkaline water; fungi dominate areas with acidic waters (pH of <5.0), while *Fischerella* appears to be restricted to waters that contain little or no sulfur. Clearly, there are many more such examples of microbial niches in hot spring settings, and hence, it should not come as a surprise that variations in microbial populations give rise to textural variations in siliceous sinters simply because different microorganisms interact uniquely with the waters in which they are bathed.

When sinters are viewed in detail under the electron microscope, they almost always show microbial cells encrusted in spheroidal grains both extracellularly, on the sheaths or walls of living cells (Figure 11.2a), and intracellularly, within the cytoplasm, presumably after the cells have lysed (Figure 11.2b) (Phoenix et al., 2000). The silicification appears to begin with the attachment of silica colloids, on the order of tens of nanometers in diameter (Schultze-Lam et al., 1995; Konhauser and Ferris, 1996; Phoenix et al., 2000; Konhauser et al., 2001). Those silica particles then grow in size on the cell surface, and eventually coalesce until the individual precipitates are no longer distinguishable. Frequently, entire colonies are cemented together in a siliceous matrix several micrometers thick. The timing and rate of silicification relative to death of the microorganisms governs their preservation as intact cells. When silicification is rapid, cell components can rapidly become encased in a silica matrix, thereby retaining intact morphologies. However, experimental studies have shown that unmineralized cells begin to degrade only a few days after death (Bartley, 1996). As a result, their remnants may become progressively obscured, and just a silicified matrix containing sheath and cell wall material may be left of the original organic framework. These observations suggest that silicification begins when microbial communities are living and continues for some time after their death due to the high reactivity of the newly formed silica.

The role that microorganisms play in their own silicification has been the subject of some debate. Some research has suggested that microorganisms play a passive role (Walter et al., 1972), whereas many other studies suggest that microbial surface ligands serve as favorable nucleation sites for silica

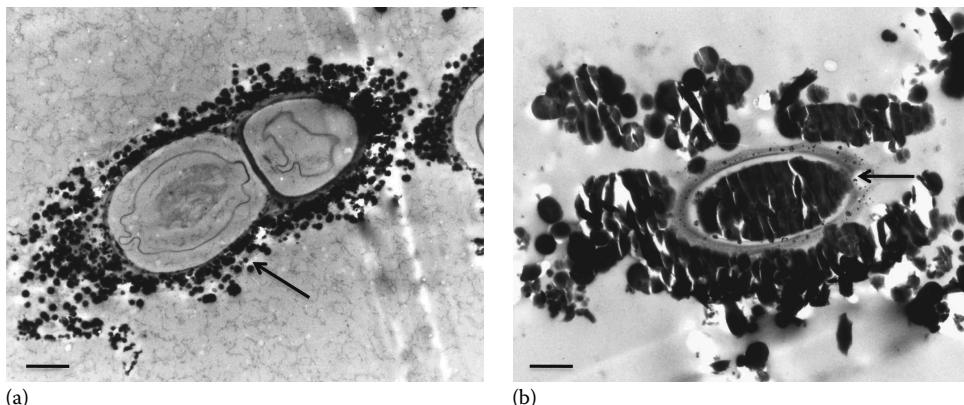


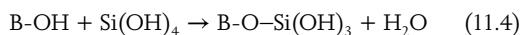
Figure 11.2. Transmission electron micrographs of silicified bacteria from a siliceous microstromatolite at Krisuvik, Iceland. (a) Filamentous cyanobacterium with epicellular, silica spheroids on outer sheath (arrow). Scale bar = 3 μm . (b) Lysed cyanobacterium with epicellular and intracellular silica precipitation. Note selective preservation of cell wall and sheath material (arrow). Scale bar = 1 μm .

precipitation (e.g., Ferris et al., 1986). These latter studies suggested that by reducing the activation energy barriers to nucleation, the microorganisms function as reactive interfaces, or templates, for heterogeneous nucleation. Because a sufficient supply of silica is generally available in hot spring effluent, often in excess of 400 ppm SiO₂ (e.g., Mountain et al., 2003), continued adsorption results in the surface sites becoming saturated, allowing particle nucleation to take place. After silica precipitation is initiated upon the bacterial surface, continued growth presumably occurs autocatalytically due to the increased surface area generated by the small silica phases. This was also used to explain the formation of substantial sinter deposits (silica growth rate \sim 20 kg year⁻¹ m⁻²) in a highly silica undersaturated geothermal outflow channel in Iceland (Tobler et al., 2008).

In the past few decades, a number of experimental studies have been designed to elucidate the actual mechanisms by which different microorganisms initiate the silicification process. Oehler (1976) was one of the first to experimentally subject various species of cyanobacteria to colloidal silica solutions over different lengths of time. At temperatures of \sim 100°C, several months were required for complete mineralization, while at higher temperatures (165°C), the cells mineralized quickly, but the filaments fragmented, the trichomes coalesced, intracellular components were destroyed, and there was a preferential preservation of the sheath and wall material. Francis et al. (1978) experimentally silicified 30

different species of algae, bacteria, and fungi for 2–24 weeks at temperatures of 55°C–60°C and found that some microorganisms silicified readily, whereas others were less susceptible to silicification. Westall et al. (1995) later showed that Gram-positive bacteria and eukaryotes silicified with ease, while Gram-negative bacteria did not readily silicify. Toporski et al. (2002) showed that at low silica concentrations, there were species-specific patterns of silicification, but under high silica concentrations, most bacteria suffered significant loss of shape and cellular detail.

Although these studies clearly indicate that silicification is an inevitable outcome of exposing microorganisms to silica supersaturated solutions, recent studies have demonstrated that the actual mechanisms of silicification rely, in part, on the microorganisms providing reactive surface ligands that adsorb silica from solution and, accordingly, reduce the activation energy barriers to heterogeneous nucleation. This means that cell surface charge may have a fundamental control on the initial silicification process. In an early attempt to describe the mechanisms of silicification, Leo and Barghoorn (1976) suggested that monomeric or low-molecular-weight polymeric silica was bound to the bacterial surface through hydrogen bonding as shown in the following reaction:



where B-OH represents a hydroxy group on the bacterial surface. This hypothesis appears best

corroborated by electron microscopic observations of microbial silicification, where the mineralization process appears to begin with the immobilization of preformed silica colloids onto the cell's surface (Schultze-Lam et al., 1995; Konhauser and Ferris, 1996; Phoenix et al., 2000). Similarly, recent experimental work with the cyanobacterium *Calothrix* sp. has demonstrated that silicification takes place on the cell's outer sheath (Yee et al., 2003). This structure is electrically neutral at pH 7, consisting predominantly of neutral sugars, along with smaller amounts of negatively charged carboxyl groups and positively charged amine groups, in approximately equal proportions. On the one hand, the low reactivity of *Calothrix*'s sheath gives its surface hydrophobic characteristics that facilitate their attachment to solid submerged substrates, i.e., siliceous sinters. On the other hand, the sheath's electroneutrality makes it less repulsive toward the polymeric silica fraction in solution, and hence, it may actually aid in the silicification process (Phoenix et al., 2002). Furthermore, Benning et al. (2004) used high-resolution synchrotron radiation Fourier transform infrared spectroscopy to show an increase in the integrated area of the absorbance spectra for the silica/polysaccharide region ($\text{Si}-\text{O}/\text{C}-\text{O}$; 1150 – 950 cm^{-1}), followed later by the occurrence and growth of a $\text{Si}-\text{O}$ band at 800 cm^{-1} . From this, a two-step process was determined, where in the first stage the polysaccharide sheath thickens (in response to incubation in a silica-supersaturated medium), followed by the abiotic accumulation of amorphous silica precipitates upon the cell surface through the condensation of silanol groups.

In contrast to *Calothrix*, the highly anionic nature of *Bacillus subtilis* may limit silicification from occurring on its cell wall as a result of electrostatic charge repulsion between the organic ligands and the negatively charged silica species. For such anionically charged cell wall surfaces, silicification necessitates some form of cation bridging (e.g., Fe(III) , Al(III)). In this regard, Fein et al. (2002) showed that *B. subtilis* precoated with Fe(III) and Al(III) hydroxides could act as templates for silica deposition (in undersaturated solutions) over a wide range of pH conditions. Compared to the negligible silica adsorption directly onto the cell surfaces in undersaturated solutions, virtually all of the monomeric silica was removed from solution by the presence of

either Fe or Al . Moreover, increasing the concentrations of Fe or Al increased the extent of silica adsorption over the entire concentration range studied. Following that study, Phoenix et al. (2003) measured the effects of iron bridging in mixed Fe-Si solutions. However, the solutions used were supersaturated with respect to amorphous silica and the cells were not precoated with iron. Their results demonstrate that *B. subtilis* cells immobilize more Fe than bacteria-free systems in solutions with iron concentrations $<50 \text{ ppm Fe}$, yet as iron concentrations increase, the difference between iron immobilization in bacterial and bacteria-free systems decreases as abiotic precipitation processes become increasingly dominant. Correspondingly, the bacterial and bacteria-free systems remove nearly identical amounts of silica from solution, whatever the iron concentration, again due to the dominance of abiotic precipitation processes. These results suggest that in natural hot spring systems, where the concentration of soluble silica far exceeds that of iron, not only will the amount of iron partitioned onto the microbial mats be insignificant compared to the abiotic reactions of silica with Fe(OH)_3 or various clay phases, but the vast majority of silica precipitated will occur without the aid of a cation bridge.

A third mechanism of silicification was recently discovered with the experimental silicification of the biofilm-forming thermophilic *Aquificales*. That work revealed that not only did the cells remain viable during silicification, but they also produced more rapidly and higher protein concentrations in batch cultures with increasing silica concentration, possibly as a stress response (Lalonde et al., 2005). Biofilm production was visually noted to be greater in cultures with increasing silica concentrations. Acid-base titrations indicated that amine functional groups are highly prominent on their biofilm surfaces and likely serve as positively charged ligands promoting silica colloid adsorption by electrostatic interaction within the protein-rich biofilm matrix. Because silicification was observed to be restricted to the extracellular polymeric substance (EPS), it was proposed that *Aquificales* may prevent cellular silicification to some degree by producing abundant reactive sites in the biofilm matrix and regulating EPS production appropriately in order to restrict sites of silicification away from the cell surfaces (Lalonde et al., 2005).

11.5 BIOMOBILIZATION OF SILICON AND OTHER CONSTITUENTS OF SILICATES (BIOWEATHERING)

Some bacteria and fungi play an important role in mobilization of silica and silicates in nature. The solubilizing action may involve the cleavage of Si–O–Si (siloxane) or Al–O framework bonds or the removal of cations from the crystal lattice of silicate, causing subsequent collapse of the silicate lattice structure. The mode of attack may be microbially produced by (1) ligands of cations; (2) organic or inorganic acids, which are a source of protons; (3) alkali (ammonia or amines); or (4) extracellular polysaccharides acting at acidic pH. The source of the polysaccharides may be the EPS of some bacteria.

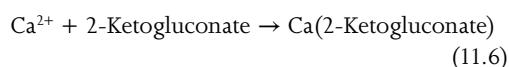
Bioweathering action of silica or silicates seems not only to be restricted to corrosive agents that have been excreted by appropriate microorganisms into the bulk phase but also to involve microbes attached to the surface of silica or silicates (Bennett et al., 1996, 2001). Because they are attached, their excreted metabolic products can attack the mineral surface in more concentrated form. Such attack may be manifested in etch marks. Some of the polysaccharides by which the microbes attach to the mineral surface may themselves be corrosive.

Bioweathering, like abiotic weathering, can lead to the formation of new minerals. This is the result of reprecipitation and crystallization of some of the mobilized constituents from the mineral that is weathered (Barker and Banfield, 1996; Adamo and Violante, 2000, Bonneville et al., 2009). New, secondary minerals may form on the surface of the weathered mineral. Microbes attached to the surface of minerals that are weathered may serve as nucleating agents in mineral neoformation (Macaskie et al., 1992; Schultze-Lam et al., 1996). In certain cases, attached microbes can exert substantial mechanical forces thereby inducing physical distortion of the mineral lattice structure that facilitates later chemical weathering (Bonneville et al., 2009).

11.5.1 Solubilization by Ligands

Microbially produced ligands of divalent cations have been shown to cause dissolution of calcium-containing silicates. For instance, a soil strain of *Pseudomonas* that produced 2-ketogluconic acid from

glucose dissolved synthetic silicates of calcium, zinc, and magnesium and the minerals wollastonite (CaSiO_3), apophyllite ($\text{KCa}_4\text{Si}_8\text{O}_{20}(\text{F},\text{OH}) \cdot 8\text{H}_2\text{O}$), and olivine ($(\text{Mg},\text{Fe})_2\text{SiO}_4$) (Webley et al., 1960). The demonstration consisted of culturing the organism for 4 days at 25°C on separate agar media, each containing 0.25% (w/v) of one of the synthetic or natural silicates, which rendered the medium turbid. A clear zone was observed around the bacterial colonies when silicate was dissolved (Figure 11.3). A similar silicate-dissolving action was also shown with a Gram-negative bacterium, strain D₁₁, which resembled *Erwinia* spp., and with *Erwinia herbicola* or some *Pseudomonas* strains, all of which were able to produce 2-ketogluconate from glucose (Duff et al., 1963). The action of these bacteria was tested in glucose-containing basal medium: KH_2PO_4 , 0.54 g; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.25 g; $(\text{NH}_4)_2\text{SO}_4$, 0.75 g; FeCl_3 , trace; Difco yeast extract, 2 g; glucose 40 g; distilled water, 1 L; and 5–500 mg pulverized mineral per 5–10 mL of medium. It was found that dissolution of silicates in these cases resulted from the complexation of the cationic components of the silicates by 2-ketogluconate. The complexes were apparently more stable than the silicate. For example,



The silicon that was liberated or released in these experiments and subsequently transformed took three forms: (1) low-molecular-weight or ammonium molybdate-reactive silicate (possibly monomeric); (2) a colloidal polymeric silicate of higher molecular weight, which did not react with dilute hydrofluoric acid; and (3) an amorphous form that could be removed from solution by centrifugation and dissolved in cold 5% aqueous carbonate (Duff et al., 1963). Polymerized silicate can be transformed by bacteria into monomeric silicate, as has been shown in studies with *Proteus mirabilis* and *Bacillus caldolyticus* (Lauwers and Heinen, 1974). The *Proteus* culture was able to assimilate some of the monomeric silicate. The mechanism of depolymerization has not been elucidated. It may involve an extracellular enzyme.

Gluconic acid produced from glucose by several different types of bacteria has been shown to

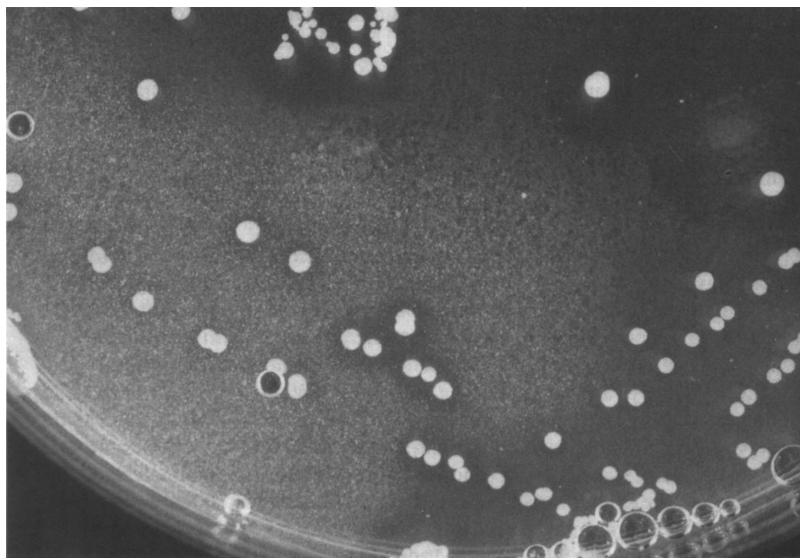


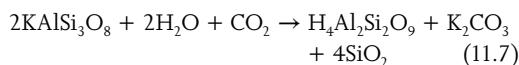
Figure 11.3. Colonies of bacterial isolate C-2 from a sample of weathered rock on synthetic calcium silicate selection medium showing evidence of calcium silicate dissolution around colonies. Basal medium was prepared by aseptically mixing 10 mL of sterile solution A (3 g dextrose or 3 g levulose in 100 mL distilled water), 10 mL of sterile solution B (0.5 g $(\text{NH}_4)_2\text{SO}_4$, 0.5 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.5 g Na_2HPO_4 , 0.5 g KH_2PO_4 , 2 g yeast extract, 0.05 g $\text{MnSO}_4 \cdot 2\text{H}_2\text{O}$ in 500 mL distilled water), and 20 mL of sterile 3% agar and distributing the mixture in Petri plates. Capping agar was prepared by mixing 10 mL of sterile synthetic CaSiO_3 suspension with 7.5 mL of sterile solution A, 7.5 mL of sterile solution B, and 15 mL of sterile 3% agar and distributing 3 mL of this mixture aseptically over the surface of the solidified basal agar in the plates.

solubilize bytownite, albite, kaolinite, and quartz at near-neutral pH (Vandevivere et al., 1994). The activity around neutral pH suggests that the mechanism of action of gluconate involves chelation.

Quartz (SiO_2) has been shown to be subject to slow dissolution by organic acids such as citric, oxalic, pyruvic, and humic acids (Bennett et al., 1988), all of which can be formed by fungi or bacteria. In a pH range of 3–7, the effect was greatest at pH 7, indicating that the mechanism of action was not protonation but chelation. Bennett et al. (1988) suggested that the chelation involved an electron donor–acceptor system. Acetate, fumarate, and tartrate were ineffective in dissolving silica as a complex.

11.5.2 Solubilization by Acids

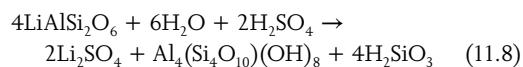
The effect of acids in solubilizing silicates has been noted in various studies. Waksman and Starkey (1931) cited the action of CO_2 on orthoclase



The CO_2 is, of course, very likely to be a product of respiration or fermentation.

Its weathering action is best viewed as based on the formation of the weak acid H_2CO_3 through hydration of CO_2 . Another example of a silicate attack by acid is that involving spodumene ($\text{LiAlSi}_2\text{O}_6$) (Karavaiko et al., 1979). In this instance, an in situ correlation was observed between the extent of alteration of a spodumene sample and the acidity it produced when in aqueous suspension. Unweathered spodumene generated a pH in the range of 5.1–7.5, whereas altered spodumene generated a pH in the range of 4.2–6.4. Non-spore-forming heterotrophs were found to predominate in weathered spodumene. They included bacteria such as *Arthrobacter pascens*, *A. globiformis*, and *A. simplex* as well as *Nocardia globurula*, *Pseudomonas fluorescens*, *P. putida*, and *P. testeronii* and fungi such as *Trichoderma lignorum*, *Cephalosporium atrium*, and *Penicillium decumbens*.

Acid decomposition of spodumene may be formulated as follows (Karavaiko et al., 1979):



The aluminosilicate product in this reaction is kaolinite.

Further investigation into microbial spodumene degradation revealed that among the most active organisms are the fungi *Penicillium notatum* and *Aspergillus niger*, thionic bacteria like *Thiobacillus thiooxidans*, and the slime-producing bacterium *Bacillus mucilaginosus* var. *siliceous* (Karavaiko et al., 1980; Avakyan et al., 1986). The fungi and *T. thiooxidans*, which produce acid, were most effective in solubilizing Li and Al. *B. mucilaginosus* was effective in solubilizing Si in addition to Li and Al by reaction of its extracellular polysaccharide with the silicate in spodumene.

Solubilization of silica along with other constituents in the primary minerals amphibolite, biotite, and orthoclase by acids (presumably citric and oxalic acids) formed by several fungi and yeasts at the expense of glucose has also been demonstrated (Eckhardt, 1980; see also Barker et al., 1997). These findings of silica mobilization are similar to those in earlier studies on the action of the fungi *Botrytis*, *Mucor*, *Penicillium*, and *Trichoderma* isolated from rock surfaces and weathered stone. In these experiments, citric and oxalic acids produced by the fungi solubilized Ca, Mg, and Zn silicates (Webley et al., 1963). In studies by Henderson and Duff (1963), *A. niger* has been shown to release Si from apophyllite, olivine, saponite, vermiculite, and wollastonite, but not augite, garnet, heulandite, hornblende, hypersthene, illite, kaolinite, labradorite, orthoclase, or talc. However, Berner et al. (1980) found in laboratory experiments that augite, hypersthene, hornblende, and diopside in soil samples were subject to weathering by soil acids, presumably of biological origin. Organisms different from those used by Henderson and Duff (1963) and, as a result, different metabolic products were probably involved. *Penicillium simplicissimus* released Si from basalt, granite, granodiorite, rhyolite, andesite, peridotite, dunite, and quartzite with metabolically produced citric acid (Silverman and Munoz, 1970). Acid formed by *P. notatum* and *Pseudomonas* sp. releases Si from plagioclase and nepheline (Aristovskaya and Kutuzova, 1968; Kutuzova, 1969).

In a study of weathering by organic and inorganic acids of three different plagioclase specimens (Ca–Na feldspars), it was found that steady-state dissolution rates were highest at approximately pH 3 and decreased as the pH was increased toward neutrality (Welch and Ullman, 1993). The organic and inorganic acids whose

weathering action was studied are representative of some end products of microbial metabolism. Polyfunctional acids, including oxalate, citrate, succinate, pyruvate, and 2-ketoglutarate, were the most effective, whereas acetate and propionate were less effective. However, all organic acids were more effective than the inorganic acids HCl and HNO₃. The polyfunctional acids acted mostly as acidulants at very acidic pH and mainly as chelators at near-neutral pH. Ullman et al. (1996) found that in some instances, the combined effect of protonation and chelation enhanced the solubilizing action of some polyfunctional acids on feldspars by a factor of 10 above the expected proton-promoted rate. Ca and Na were rapidly released in these experiments. The chelate attack appeared to be at the Al sites. Those organic acids that preferentially chelated Al were the most effective in enhancing plagioclase dissolution. Although the products of dissolution of feldspars are usually considered to include separate aluminum and silicate species, soluble aluminosilicate complexes may be intermediates (Browne and Driscoll, 1992).

The practical effect of acid attack of aluminosilicates can be seen in the corrosion of concrete sewer pipes. Concrete is formed from a mixture of cement (heated limestone, clay, and gypsum) and sand. On setting, the cement includes the compounds Ca₂SiO₄, Ca₃SiO₅, and Ca(AlO₃)₂, which hold the sand in their matrix. H₂S produced by microbial mineralization of organic sulfur compounds and by bacterial sulfate reduction of sulfate in sewage can itself corrode concrete. But corrosion is enhanced if the H₂S is first oxidized to sulfuric acid by thiobacilli *Thiobacillus neapolitanus* (now renamed *Halothiobacillus neapolitanus*), *T. intermedius*, *T. novellus*, and *T. thiooxidans* (now renamed *Acidithiobacillus thiooxidans*) (Parker, 1947; Milde et al., 1983; Sand and Bock, 1984; Okabe et al., 2007).

Groundwater pollution with biodegradable substances has been found to result in silicate weathering of aquifer rock. Products of microbial degradation of the substances cause the weathering. This was observed in an oil-polluted aquifer near Bemidji, Minnesota (Hiebert and Bennett, 1992). Microcosm experiments of 14 months' duration in the aquifer with a mixture of crystals such as albite, anorthite, anorthoclase, and microcline (all feldspar minerals) and quartz revealed microbial colonization of the mineral surfaces by

individual cells and small clusters. Intense etching of the feldspar minerals and light etching of the quartz occurred at or near where the bacteria were seen. Such aquifer rock weathering can affect water quality.

11.5.3 Solubilization by Alkali

Alkaline conditions are very conducive for mobilizing silica, whether from silicates, aluminosilicates, or even quartz (Karavaiko et al., 1984). This is attributable to the significant lability of the Al–O and Si–O bonds under these conditions, because both types of bonds are susceptible to nucleophilic attack (see discussion by Karavaiko et al., 1984). *Sarcina ureae* growing in peptone–urea broth released silica readily from nepheline, plagioclase, and quartz (Aristovskaya and Kutuzova, 1968; Kutuzova, 1969). In this instance, ammonia resulting from the hydrolysis of urea was the source of the alkali. In microbial spodumene degradation, alkaline pH also favors silica release (Karavaiko et al., 1980).

Pseudomonas mendocina was able to enhance mobilization of Al, Si, and Fe impurities from kaolinite in a succinate-mineral salts medium in which the pH rose from 7.7 to 9.2 in 4 days of growth under aerobic conditions (Maurice et al., 2001).

11.5.4 Solubilization by Extracellular Polysaccharide

Extracellular polysaccharide has been claimed to play an important role in silica release, especially in the case of quartz. Such polysaccharide is able to react with siloxanes to form organic siloxanes. It can be of bacterial origin (e.g., from *B. mucilaginosus* var. siliceous; Avakyan et al., 1986) or fungal origin (e.g., from *A. niger*; Holzapfel and Engel, 1954a). The reaction appears not to be enzyme-catalyzed because polysaccharide from which the cells have been removed is reactive. Indeed, such organic silica-containing compounds can be formed with reagent-grade organics (Holzapfel, 1951; Weiss et al., 1961) and have been isolated from various biological sources other than microbes (Schwarz, 1973). With polysaccharide from *B. mucilaginosus*, the reaction appears to be favored by acid metabolites (Malinovskaya et al., 1990). It should be noted that Welch and Vandevivere (1995) found that polysaccharides from different sources had either no effect or interfered with solubilization

of plagioclase by gluconate at a pH between 6.5 and 7.

Barker and Banfield (1996) described the weathering by bacteria and lichens of amphibole syenite associated with the Stettin complex near Wausau, Wisconsin. The process involved penetration of grain boundaries, cleavages, and cracks. Mineral surfaces were coated with EPS. During the weathering process, dissolution by metabolically produced corrosive agents and selective transport of mobilized constituents, probably mediated by acid mucopolysaccharides, occurred. Some mobilized constituents reprecipitated, leading to the formation of clay minerals.

A more detailed study revealed that the site of bioweathering by lichens (in this instance a symbiotic consortium of a fungus and an alga) could be divided into four zones (Barker and Banfield, 1998). The authors concluded that in the uppermost zone (zone 1), represented by the upper lichen thallus, no weathering occurs. This is the photosynthetic zone. In zone 2, involving the lower lichen thallus, active weathering due to interaction with lichen products occurs. Mineral fragments coated with organic polymers of incipient secondary minerals that resulted from the weathering may appear in the thallus. In zone 3, reactions occur, which are an indirect consequence of lichen action. In zone 4, any weathering, if it occurs, is due to abiotic processes.

11.6 ROLE OF MICROBES IN THE SILICA CYCLE

As the foregoing discussion shows, some microbes, and even some plants, have a significant influence on the distribution and form of silicon in the biosphere. Those organisms that assimilate silicon clearly act as concentrators of it. Those that degrade silica and silicate minerals act as agents of silicon dispersion. They are an important source of dissolved silica on which the concentrators depend, and they are also important agents of rock weathering. Comparative electron microscopic studies provide clues to the extent of microbial weathering action (see Berner et al., 1980; Callot et al., 1987; Barker and Banfield, 1998).

It has been argued that silicate-mobilizing reactions by microbially produced acids and complexing agents under laboratory conditions occurred at glucose concentrations that may not be encountered in nature and may therefore, be laboratory artifacts. A counterargument can be

made, however, that microenvironments exist in soil and sediment that have appropriately high concentrations of utilizable carbohydrates, nitrogenous compounds, and other needed nutrients. They originate from the excretory products and dead remains of organisms from which appropriate bacteria and fungi can form the compounds that can promote breakdown of silica and silicate minerals. Indeed, fungal hyphae in the litter zone and A horizon of several different soils have been shown by SEM to carry calcium oxalate crystals attached to them. This is evidence for extensive *in situ* production of oxalate by the fungus (Graustein et al., 1977). The basidiomycete *Hysterangium crassum* was shown to weather clay *in situ* with the oxalic acid it produced (Cromack et al., 1979). Lichens show evidence, observable *in situ*, of extensive rock weathering activity (Jones et al., 1981). Although Ahmadjian (1967) and Hale (1967) cast doubt on this ability of lichens, current evidence strongly supports the rock weathering activity of these organisms. Biodegradation of silica and silicate minerals is usually a slower process in nature than in the laboratory because the conditions in natural environments are usually less favorable. If this were not so, rock in the biosphere would be very unstable.

At the opposite end of the Si cycle, several planktonic organisms precipitate skeletons comprised of amorphous silica. Today, the oceans are undersaturated with regard to amorphous silica (seawater <10 ppm) predominantly because of the activity of diatoms, but to a lesser extent radiolarians and silicoflagellates as well (Tréguer et al., 1995; Yool and Tyrrell, 2003). Some estimates suggest that diatoms produce annually 240 Tmol silica, which is approximately 40 times greater than estimated silica inputs to the oceans (Tréguer et al., 1995). This discrepancy is balanced by an extremely efficient silica recycling mechanisms by which 97% of the biogenic silica is dissolved in the surface waters and seafloor upon cell lysis. The dissolved silica is then reused by other silica-secreting organisms. Estimates suggest that the Si delivered to the oceans passes through a biological uptake and dissolution cycle on average about 39 times before ultimately being removed to marine sediments (Tréguer et al., 1995).

Thus, silicon in nature may follow a series of cyclic biogeochemical transformations (Harriss, 1972; Lauwers and Heinen, 1974; Kuznetsov, 1975).

Silica and silicate minerals in rocks are subject to the weathering action of biological, chemical, and physical agents. The extent of the contribution of each of these agents must depend on the particular environmental circumstances. Silica liberated in these processes may be leached away by surface water or groundwater, and it may be removed from these waters by abiotic and biologically induced precipitation at new sites, or it may be swept into bodies of freshwater or the sea. There, silicon will tend to be removed by biological agents. Upon their death, other biological agents will release this silicon back into the solution or the siliceous remains will be incorporated into the sediment (Weaver and Wise, 1974; Allison, 1981; Patrick and Holding, 1985), where some or all of the silicon may later be returned to solution by weathering. The sediments of the ocean appear to be a sink for excess silica swept into the oceans because the silica concentrations of seawater tend to remain relatively constant. But over geologic time, this silicon in the sediments is not permanently immobilized. Plate tectonics will ultimately cause it to be recycled.

11.7 SUMMARY

The environmental distribution of silicon is significantly influenced by microbial activity. Certain microorganisms assimilate it and build it into cell-support structures. They include diatoms, some chrysophytes, silicoflagellates, some xanthophytes, radiolarians, and actinopods. Silicon uptake rates by diatoms have been measured, but the mechanism by which silicon is assimilated is still only partially understood. These silicon-assimilating microorganisms are important in the formation of siliceous oozes in the oceans and in lakes. By contrast, some bacteria, fungi, and lichens are able to solubilize silicates and silica. They accomplish this by forming chelators, acids, bases, and exopolysaccharides that react with silica and silicates. These reactions are important in weathering of rock and cycling silicon in nature.

REFERENCES

- Adamo P and Violante P. 2000. Weathering of rocks and neogenesis of minerals associated with lichen activity. *Applied Clay Science* 16:229–256.

- Afanasieva MS, Amon EO, Agarkov YV, Boltovskoy DS. 2005. Radiolarians in the geological annals. *Paleontol J* 39:135–392.
- Ahmadjian V. 1967. *The Lichen Symbiosis*. Waltham, MA: Blaidsell.
- Allison CW. 1981. Siliceous microfossils from the Lower Cambrian of northwest Canada: Possible source for biogenic chert. *Science* 211:53–55.
- Anderson GM. 1972. Silica solubility. In: Fairbridge RW (ed.) *The Encyclopedia of Geochemistry and Environmental Sciences*. Encyclopedia of Earth Science Series, Vol. IVA. New York: Van Nostrand Reinhold, pp. 1085–1088.
- Aristovskaya TV, Kutuzova RS. 1968. Microbiological factors in the mobilization of silicon from poorly soluble natural compounds. *Pochvovedenie* 12:59–66.
- Avakyan ZA, Belkanova NP, Karavaiko GI, Piskunov VP. 1985. Silicon compounds in solution during bacterial quartz degradation. *Mikrobiologiya* 54:301–307 (English translation pp. 250–256).
- Avakyan ZA, Pivovarova TA, Karavaiko GI. 1986. Properties of a new species, *Bacillus mucilaginosus*. *Mikrobiologiya* 55:477–482 (English translation pp. 477–482).
- Azam F. 1974. Silicic-acid uptake in diatoms studied with [^{68}Ge]germanic acid as tracer. *Planta* 121:205–212.
- Azam F, Hemmingsen B, Volcani BE. 1973. Germanium incorporation into the silica of diatom cell walls. *Arch Microbiol* 92:11–20.
- Azam F, Hemmingsen B, Volcani BE. 1974. Role of silicon in diatom metabolism. V. Silicic acid transport and metabolism in the heterotrophic diatom *Nitzschia alba*. *Arch Mikrobiol* 97:103–114.
- Azam F, Volcani B. 1974. Role of silicon in diatom metabolism. VI. Active transport of germanic acid in the heterotrophic diatom *Nitzschia alba*. *Arch Microbiol* 101:1–8.
- Barker WW, Banfield JF. 1996. Biologically versus inorganically mediated weathering reactions: Relationships between minerals and extracellular microbial polymers in lithiobiotic communities. *Chem Geol* 132:55–69.
- Barker WW, Banfield JF. 1998. Zones of chemical and physical interactions at interfaces between microbial communities and minerals. A model. *Geomicrobiol J* 15:223–244.
- Barker WW, Welch SA, Banfield JF. 1997. Biogeochemical weathering of silicate minerals. In: Banfield JF, Nealson KH (eds.) *Geomicrobiology: Interactions Between Microbes and Minerals*. Reviews in Mineralogy, Vol. 35. Washington, DC: Mineralogical Society of America, pp. 391–428.
- Barnes RD. 1982. *Invertebrate Zoology*. Philadelphia, PA: Holt-Saunders International.
- Bartley JK. 1996. Actualistic taphonomy of cyanobacteria: Implications for the Precambrian fossil record. *Palaios* 11:571–586.
- Bennett PC, Hiebert FK, Choi WJ. 1996. Microbial colonization and weathering of silicates in a petroleum-contaminated aquifer. *Chem Geol* 132:45–53.
- Bennett PC, Melcer ME, Siegel DI, Hassett JP. 1988. The dissolution of quartz in dilute aqueous solutions of organic acids at 25°C. *Geochim Cosmochim Acta* 52:1521–1530.
- Bennett PC, Rogers JR, Choi WJ, Hiebert FK. 2001. Silicates, silicate weathering, and microbial ecology. *Geomicrobiol J* 18:3–19.
- Benning LG, Phoenix V, Yee N, Konhauser KO. 2004. The dynamics of cyanobacterial silicification: An infrared micro-spectroscopic investigation. *Geochim Cosmochim Acta* 68:743–757.
- Bergquist PR. 1978. *Sponges*. London, U.K.: Hutchinson.
- Berner RA, Sjoeborg EL, Velbel MA, Krom MD. 1980. Dissolution of pyroxenes and amphiboles during weathering. *Science* 207:1205–1206.
- Bidle KD, Azam F. 2001. Bacterial control of silicon regeneration from diatom detritus: Significance of bacterial ectohydrolases and species identity. *Limnol Oceanogr* 46:1606–1623.
- Blair Hedges S, Chen H, Kumar S, Wang DYC, Thompson AS, Watanabe H. 2001. A genomic timescale for the origin of eukaryotes. *BMC Evol Biol* 1:4.
- Blank GS, Sullivan CW. 1979. Diatom mineralization of silicic acid. III. $\text{Si}(\text{OH})_4$ binding and light dependent transport in *Nitzschia angularis*. *Arch Microbiol* 123:17–164.
- Bonneville S, Smits MM, Brown A, Harrington J, Leake JR, Brydson R, Benning LG. 2009. Plant-driven fungal weathering: Early stages of mineral alteration at the nanometer scale. *Geology* 37:615–618.
- Bowen HJM. 1966. *Trace Elements in Biochemistry*. London, U.K.: Academic Press.
- Bowen HJM. 1979. *Environmental Chemistry of the Elements*. London, U.K.: Academic Press.
- Browne BA, Driscoll CT. 1992. Soluble aluminum silicates: Stoichiometry, stability, and implications for environmental geochemistry. *Science* 256:1667–1670.
- Braun A, Chen J, Waloszek D, Maas A. 2013. First early Cambrian radiolaria. *Geol Soc Lond* 286:143–149.
- Callot B, Maurette M, Pottier L, Dubois A. 1987. Biogenic etching of microfractures in amorphous and crystalline silicates. *Nature (London)* 328:147–149.

- Chisholm SW, Azam F, Eppley RW. 1978. Silicic acid incorporation in marine diatoms on light-dark cycles: Use as an assay for phased cell division. *Limnol Oceanogr* 23:518–529.
- Coombs J, Volcani BE. 1968. The biochemistry and fine structure of silica shell formation in diatoms. Silicon induced metabolic transients in *Navicula pelliculosa*. *Planta* 80:264–279.
- Crerar DA, Axtmann EV, Axtmann RC. 1981. Growth and ripening of silica polymers in aqueous solutions. *Geochim Cosmochim Acta* 45:1259–1266.
- Cromack K, Jr., Sollins P, Graustein WC, Speidel K, Todd AW, Spycher G, Li CY, Todd RL. 1979. Calcium oxalate accumulation and soil weathering in mats of the hypogenous fungus *Hysterangium crassum*. *Soil Biol Biochem* 11:463–468.
- Darley WM, Volcani BE. 1969. Role of silicon in diatom metabolism. A silicon requirement for deoxyribonucleic acid synthesis in the diatom *Cylindrotheca fusiformis*, Reiman and Lewin. *Exp Cell Res* 58:334–343.
- Dashman T, Stotzky G. 1986. Microbial utilization of amino acids and a peptide bond on homoionic montmorillonite and kaolinite. *Soil Biol Biochem* 18:5–14.
- De La Rocha CL, Brzezinski MA, DeNiro MJ. 1997. Fractionation of silicon isotopes by marine diatoms during biogenic silica formation. *Geochim Cosmochim Acta* 61:5051–5056.
- De La Rocha CL, Brzezinski MA, DeNiro MJ. 2000. A first look at the distribution of the stable isotopes of silicon in natural waters. *Geochim Cosmochim Acta* 64:2467–2477.
- de Vrind-de Jong EW, de Vrind JPM. 1997. Algal deposition of carbonates and silicates. In: Banfield JF, Nealson KH (eds.) *Geomicrobiology: Interactions Between Microbes and Minerals*. Reviews in Mineralogy, Vol. 35. Washington, DC: Mineralogical Society of America, pp. 267–307.
- De Wever P, Dumitrica P, Caulet J-P, Nigrini C, Caridroit M. 2001. *Radiolarians in the Sedimentary Record*. London, U.K.: Gordon and Breach.
- Dommergues Y, Mangenot F. 1970. *Écologie Microbienne du Sol*. Paris, France: Masson.
- Duff RB, Webley DM, Scott RO. 1963. Solubilization of minerals and related minerals by 2-ketogluconic acid-producing bacteria. *Soil Sci* 95:105–114.
- Eckhardt FEW. 1980. Microbial degradation of silicates. Release of cations from aluminosilicate minerals by yeast and filamentous fungi. In: Oxley TA, Becker G, Allsopp D (eds.) *Biodeterioration. Proceedings of the 4th International Biodeterioration Symposium*. London, U.K.: Pitman, pp. 107–116.
- Ehrlich HL. 1982. Enhanced removal of Mn²⁺ from seawater by marine sediment and clay minerals in the presence of bacteria. *Can J Microbiol* 28:1389–1395.
- Fein JB, Scott S, Rivera N. 2002. The effect of Fe on Si adsorption by *Bacillus subtilis* cell walls: Insights into non-metabolic bacterial precipitation of silicate minerals. *Chem Geol* 182:265–273.
- Ferris FG, Beveridge TJ, Fyfe WS. 1986. Iron-silica crystallite nucleation by bacteria in a geothermal sediment. *Nature* 320:609–611.
- Fournier RO. 1985. The behaviour of silica in hydrothermal solutions. In: Berger BR, Bethke PM (eds.) *Geology and Geochemistry of Epithermal Systems. Reviews in Economic Geology*, Vol. 2. El Paso, TX: The Economic Geology Publishing Co., pp. 45–61.
- Francis S, Margulis L, Barghoorn ES. 1978. On the experimental silicification of microorganisms. II. On the time of appearance of eukaryotic organisms in the fossil record. *Precamb Res* 6:65–100.
- Garrels RM. 1965. Silica: Role in the buffering of natural waters. *Science* 148:69.
- Graustein WC, Cromack K, Jr., Sollins P. 1977. Calcium oxalate: Occurrence in soils and effect on nutrient and geochemical cycles. *Science* 198:1252–1254.
- Gunnarsson I, Arnórsson S. 2000. Amorphous silica solubility and the thermodynamic properties of H₄SiO₄ in the range of 0° to 350°C at P_{sat}. *Geochim Cosmochim Acta* 64:2295–2307.
- Hale ME, Jr. 1967. *The Biology of Lichens*. London, U.K.: Edward Arnold.
- Hall FR. 1972. Silica cycle. In: Fairbridge RW (ed.) *The Encyclopedia of Geochemistry and Environmental Sciences. Encyclopedia of Earth Science Series*, Vol. IVA. New York: Van Nostrand Reinhold, pp. 1082–1085.
- Harriss RC. 1972. Silica–biogeochemical cycle. In: Fairbridge RW (ed.) *The Encyclopedia of Geochemistry and Environmental Sciences. Encyclopedia of Earth Science Series*, Vol. IVA. New York: Van Nostrand Reinhold, pp. 1080–1082.
- Healy FP, Combs J, Volcani BE. 1967. Changes in pigment content of the diatom *Navicula pelliculosa* in silicon starvation synchrony. *Arch Mikrobiol* 59:131–142.
- Heinen W. 1960. Silicium-Stoffwechsel bei Mikroorganismen. I. Mitteilung. Aufnahme von Silicium durch Bakterien. *Arch Mikrobiol* 37:199–210.
- Helmcke J-G. 1954. Die Feinstruktur der Kieselsäure und ihre physiologische Bedeutung in Diatomschalen. *Naturwissenschaften* 11:254–255.
- Henderson MEK, Duff RB. 1963. The release of metallic and silicate ions from minerals, rocks and soils by fungal activity. *J Soil Sci* 14:236–246.

- Hiebert FK, Bennett PC. 1992. Microbial control of silicate weathering in organic-rich ground water. *Science* 258:278–281.
- Holzapfel L. 1951. Siliziumverbindung in biologischen Systemen. Organ. Kieselsäureverbindungen. XX. Mitteilung. *Z Elektrochem* 55:577–580.
- Holzapfel L, Engel W. 1954a. Der Einfluss organischer Kieselsäureverbindungen auf das Wachstum von *Aspergillus niger* und *Triticum*. *Z Naturforsch* 9b:602–606.
- Holzapfel L, Engel W. 1954b. Über die Abhängigkeit der Wachstumsgeschwindigkeit von *Aspergillus niger* in Kieselsäurelösungen bei O₂-Belüftung. *Naturwissenschaften* 41:191–192.
- Iler R. 1979. *Chemistry of Silica*. New York: Wiley.
- Imsiecke G, Steffen R, Custodio M, Borojevic R, Muller WEG. 1995. Formation of spicules by sclerocytes from the freshwater sponge *Ephydatia muelleri* in short-term cultures in vitro. *In Vitro Cell Dev Biol Anim* 31:528–535.
- Jones B, Renaut RW, Rosen MR. 1997. Biogenicity of silica precipitation around geysers and hot-spring vents, North Island, New Zealand. *J Sed Res* 67:88–104.
- Jones D, Wilson MJ, McHardy WJ. 1981. Lichen weathering of rock-forming minerals: Application of scanning electron microscopy and microprobe analysis. *J Microsc* 124(1):95–104.
- Jorgensen EG. 1955. Solubility of silica in diatoms. *Physiol Plant* 8:864–851.
- Karavaiko GI, Avakyan ZA, Krutsko VS, Mel'nikova EO, Zhdanov V, Piskunov VP. 1979. Microbiological investigations on a spodumene deposit. *Mikrobiologiya* 48:502–508 (English translation pp. 383–398).
- Karavaiko GI, Belkanova NP, Eroshchev-Shak VA, Avakyan ZA. 1984. Role of microorganisms and some physicochemical factors of the medium in quartz destruction. *Mikrobiologiya* 53:976–981 (English translation pp. 795–800).
- Karavaiko GI, Krutsko VS, Mel'nikova EO, Avakyan ZA, Ostroushko YI. 1980. Role of microorganisms in spodumene degradation. *Mikrobiologiya* 49:547–551 (English translation pp. 402–406).
- Katami A. 1982. Dissolution rates of silica from diatoms decomposing at various temperatures. *Marine Biol (Berlin)* 68:91–96.
- Konhauser KO, Ferris FG. 1996. Diversity of iron and silica precipitation by microbial mats in hydrothermal waters, Iceland: Implications for Precambrian iron formations. *Geology* 24:323–326.
- Konhauser KO, Jones B, Phoenix VR, Ferris G, Renaut RW. 2004. The microbial role in hot spring silicification. *Ambio* 33:552–558.
- Konhauser KO, Phoenix VR, Bottrell SH, Adams DG, Head IM. 2001. Microbial-silica interactions in modern hot spring sinter: Possible analogues for Precambrian siliceous stromatolites. *Sedimentology* 48:415–435.
- Kooistra WHCF, Medlin LK. 1996. Evolution of the diatoms (Bacillariophyta): IV. A reconstruction of their age from small subunit rRNA coding regions and the fossil record. *Mol Phylogenet Evol* 6:391–407.
- Kretz R. 1972. Silicon: Element and geochemistry. In: Fairbridge RW (ed) *The Encyclopedia of Geochemistry and Environmental Sciences*. Encyclopedia of Earth Science Series, Vol. IVA. New York: Van Nostrand Reinhold, pp. 1091–1092.
- Kutuzova RS. 1969. Release of silica from minerals as result of microbial activity. *Mikrobiologiya* 38:714–721 (English translation pp. 596–602).
- Kuznetsov SI. 1975. The role of microorganisms in the formation of lake bottom deposits and their diagenesis. *Soil Sci* 119:81–88.
- Lalonde SV, Konhauser KO, Reysenbach A-L, Ferris FG. 2005. The experimental silicification of Aquificales and their role in hot spring sinter formation. *Geobiology* 3:41–52.
- Latimer WM, Hildebrand JH. 1940. *Reference Book of Inorganic Chemistry*. Revised edition. New York: Macmillan.
- Lauwers AM, Heinen W. 1974. Bio-degradation and utilization of silica and quartz. *Arch Microbiol* 95:67–78.
- Leo RF, Barghoorn ES. 1976. Silicification of wood. *Bot Mus Leafl, Harvard Univ* 25:1–29.
- Lewin JC. 1957. Silicon metabolism in diatoms. IV. Growth and frustule formation in *Navicula pelliculosa*. *J Gen Physiol* 39:1–10.
- Lewin JC. 1965. Silicification. In: Lewin RA (ed) *Physiology and Biochemistry of Algae*. New York: Academic Press, pp. 445–455.
- Liebau F. 1985. *Structural Chemistry of Silicates. Structure, Bonding and Classification*. Berlin, Germany: Springer.
- Macaskie LE, Empson RM, Cheetham AK, Gey CP, Skarnulis AJ. 1992. Uranium bioaccumulation by a *Citrobacter* sp. as a result of enzymatically mediated growth of polycrystalline HUO_2PO_4 . *Science* 257:782–784.
- Malinovskaya IM, Kosenko LV, Votselko SK, Podgorskii VS. 1990. Role of *Bacillus mucilaginosus* polysaccharide in degradation of silicate minerals. *Mikrobiologiya* 59:70–78 (English translation pp. 49–55).
- Mann DG. 1999. The species concept of diatoms. *Phycologia* 38:437–494.
- Marine Chemistry. 1971. *A Report on the Marine Chemistry Panel of the Committee of Oceanography*. Washington, DC: National Academy of Sciences.

- Marshall KC. 1971. Sorption interactions between soil particles and microorganisms. In: McLaren AD, Skujins J (eds.) *Soil Biochemistry*, Vol. 2. New York: Marcel Dekker, pp. 409–445.
- Marshman NA, Marshall KC. 1981a. Bacterial growth on proteins in the presence of clay minerals. *Soil Biol Biochem* 13:127–134.
- Marshman NA, Marshall KC. 1981b. Some effect of montmorillonite on the growth of mixed microbial cultures. *Soil Biol Biochem* 13:135–141.
- Martin-Jézéquel V, Hildebrand M, Brezinski MA. 2000. Silicon metabolism in diatoms: Implications for growth. *J Phycol* 36:821–824.
- Maurice PA, Vierkoen MA, Hersman LE, Fulghum JE, Ferryman A. 2001. Enhancement of kaolinite dissolution by an aerobic *Pseudomonas mendocina* bacterium. *Geomicrobiol J* 18:21–35.
- McCartney K. 1993. Silicoflagellates. In: Lipps, JH (ed.) *Fossil Prokaryotes and Protists*. Boston, MA: Blackwell Science, pp. 143–154.
- McCartney K, Loper DE. 1989. Optimized skeletal morphologies of silicoflagellate genera *Dictyocha* and *Distephanus*. *Palaeobiology* 15(3):283–298.
- Milde K, Sand W, Wolff W, Bock E. 1983. Thiobacilli of the corroded concrete walls of the Hamburg sewer system. *J Gen Microbiol* 129:1327–1333.
- Mitchell RL. 1955. Trace elements. In: Bear FE (ed.) *Chemistry of the Soil*. New York: Van Nostrand Reinhold, pp. 235–285.
- Mountain BW, Benning LG, Boerema JA. 2003. Experimental studies on New Zealand hot spring sinters: Rates of growth and textural development. *Can J Earth Sci* 40:1643–1667.
- Oehler JH. 1976. Experimental studies in Precambrian paleontology: Structural and chemical changes in blue-green algae during simulated fossilization in synthetic chert. *Geol Soc Am Bull* 87:117–129.
- Okabe S, Odagiri M, Ito T, Satoh H. 2007. Succession of sulfur-oxidizing bacteria in the microbial community on corroding concrete in sewer systems. *App Environ Microbiol* 73:971–978.
- Parker CD. 1947. Species of sulfur bacteria associated with corrosion of concrete. *Nature (London)* 159:439.
- Patrick S, Holding AJ. 1985. The effect of bacteria on the solubilization of silica in diatom frustules. *J Appl Microbiol* 59:7–16.
- Phoenix VR, Adams DG, Konhauser KO. 2000. Cyanobacterial viability during hydrothermal biomineralization. *Chem Geol* 169:329–338.
- Phoenix VR, Konhauser KO. 2008. Benefits of bacterial biomineralization. *Geobiology* 6:303–308.
- Phoenix VR, Konhauser KO, Ferris FG. 2003. Experimental study of iron and silica immobilization by bacteria in mixed Fe-Si systems: Implications for microbial silicification in hot springs. *Can J Earth Sci* 40(11):1669–1678.
- Phoenix VR, Martinez RE, Konhauser KO, Ferris FG. 2002. Characterization and implications of the cell surface reactivity of the cyanobacteria *Calothrix* sp. *App Environ Microbiol* 68:4827–4834.
- Reeves CD, Volcani BE. 1984. Role of silicon in diatom metabolism. Patterns of protein phosphorylation in *Cylindrotheca fusiformis* during recovery from silicon starvation. *Arch Microbiol* 137:291–294.
- Rogall E. 1939. Über den Feinbau der Kieselmembran der Diatomeen. *Planta* 29:279–291.
- Round FE, Crawford RM. 1990. *The Diatoms. Biology and Morphology of the Genera*. Cambridge, U.K.: Cambridge University Press.
- Sand W, Bock E. 1984. Concrete corrosion in the Hamburg sewer system. *Environ Technol Lett* 5:517–528.
- Schultze-Lam S, Fortin D, Davis BS, Beveridge TJ. 1996. Mineralization of bacterial surfaces. *Chem Geol* 132:171–181.
- Schwarz K. 1973. A bound form of silicon in glycosaminoglycans and polyuronides. *Proc Natl Acad Sci USA* 70:1608–1612.
- Schultze-Lam S, Ferris FG, Konhauser KO, Wiese RG. 1995. In situ silicification of an Icelandic hot spring microbial mat: Implications for microfossil formation. *Can J Earth Sci* 32:2021–2026.
- Sillén LG. 1967. The ocean as chemical system. *Science* 156:1189–1197.
- Silverman MP, Munoz EF. 1970. Fungal attack on rock: Solubilization and altered infrared spectra. *Science* 169:985–987.
- Sperling EA, Robinson JM, Pisani D, Peterson KJ. 2010. Where's the glass? Biomarkers, molecular clocks, and microRNAs suggest a 200-Myr missing Precambrian record of siliceous sponge spicules. *Geobiology* 8:24–36.
- Stotzky G. 1986. Influences of soil mineral colloids on metabolic processes, growth, adhesion, and ecology of microbes and viruses. In: Huang PM, Schnitzer M (eds.) *Interaction of Soil Minerals with Organics and Microbes*. SSSA Special Publication No 17. Madison, WI: Soil Science Society of America, pp. 305–428.
- Sullivan CW. 1971. A silicic acid requirement for DNA polymerase, thymidylate kinase, and DNA synthesis in the marine diatom *Cylindrica fusiformis*. PhD Thesis, University of California, San Diego, CA.

- Sullivan CW, Volcani EB. 1973. Role of silicon in diatom metabolism. The effects of silicic acid on DNA polymerase, TMP kinase and DNA synthesis in *Cyclothecea fusiformis*. *Biochim Biophys Acta* 308:212–229.
- Tan KH. 1986. Degradation of soil minerals by organic acids. In: Huang PM, Schnitzer M (eds.) *Interaction of Soil Minerals with Organics and Microbes*. SSSA Special Publication No 17. Madison, WI: Soil Science Society of America, pp. 1–27.
- Tobler DJ, Benning LG. 2013. In situ and time resolved nucleation and growth of silica nanoparticles forming under simulated geothermal conditions. *Geochim Cosmochim Acta* 114:156–168.
- Tobler DJ, Stefánsson A, Benning LG. 2008. In-situ grown silica sinters in Icelandic geothermal areas. *Geobiology* 6:481–502.
- Tobler DJ, Shaw S, Benning LG. 2009. Quantification of initial steps of nucleation and growth of silica nanoparticles: An in-situ SAXS and DLS study. *Geochim Cosmochim Acta* 73:5377–5393.
- Toporski JKW, Steele A, Westall F, Thomas-Keprrta KL, McKay DS. 2002. The simulated silicification of bacteria—New clues to the modes and timing of bacterial preservation and implications for the search for extraterrestrial microfossils. *Astrobiology* 2:1–26.
- Toth SJ. 1955. Colloidal chemistry of soils. In: Bear FE (ed.) *Chemistry of the Soil*. New York: Van Nostrand Reinhold, pp. 85–106.
- Tréguer P, Nelson DM, Van Bennekom AJ, DeMaster DJ, Leynaert A, Quéguiner B. 1995. The silica balance in the world ocean: A reestimate. *Science* 268:375–379.
- Ullman WJ, Kirchman DL, Welch SA, Vandevivere P. 1996. Laboratory evidence for microbially mediated silicate mineral dissolution in nature. *Chem Geol* 132:11–17.
- Vandevivere P, Welch SA, Ullman WJ, Kirchman DL. 1994. Enhanced dissolution of silicate minerals by bacteria at near-neutral pH. *Microb Ecol* 27:241–251.
- Waksman SA, Starkey RL. 1931. *The Soil and the Microbe*. New York: Wiley.
- Walter MR. 1976. *Geyserites of Yellowstone National Park: An example of abiogenic “stromatolites”*. In: Walter MR (ed.) *Stromatolites. Developments in Sedimentology*, Vol. 20. Amsterdam, the Netherlands: Elsevier, pp. 88–112.
- Walter MR, Bauld J, Brock TD. 1972. Siliceous algal and bacterial stromatolites in hot spring and geyser effluents of Yellowstone National Park. *Science* 178:402–405.
- Weaver FM, Wise SW, Jr. 1974. Opaline sediments of the southeastern coastal plain and horizon A: Biogenic origin. *Science* 184:899–901.
- Weaver TL, Dugan PR. 1972. Enhancement of bacteria methane oxidation by clay minerals. *Nature (London)* 237:518.
- Webley DM, Duff RB, Mitchell WA. 1960. A plate method for studying the breakdown of synthetic and natural silicates by soil bacteria. *Nature (London)* 188:766–767.
- Webley DM, Henderson MEF, Taylor IF. 1963. The microbiology of rocks and weathered stones. *J Soil Sci* 14:102–112.
- Weiss A, Reiff G, Weiss A. 1961. Zur Kenntnis wasserbeständiger Kieselsäureesster. *Z Anorg Chem* 311:151–179.
- Welch SA, Ullman WJ. 1993. The effect of organic acids on plagioclase dissolution rates and stoichiometry. *Geochim Cosmochim Acta* 57:2725–2736.
- Welch SA, Vandevivere P. 1995. Effect of microbial and other naturally occurring polymers on mineral dissolution. *Geomicrobiol J* 12:227–238.
- Werner D. 1966. Die Kieselsäure im Stoffwechsel von *Cyclotella cryptica* Reimann, Lewin und Guillard. *Arch Mikrobiol* 55:278–308.
- Werner D. 1967. Hemmung der Chlorophyllsynthese und des NADP-abhängigen Glyzeraldehyd-3-phosphat-dehydrogenase durch Germaniumsäure bei *Cyclotella cryptica*. *Arch Mikrobiol* 57:51–60.
- Westall F, Boni L, Guerzoni E. 1995. The experimental silicification of microorganisms. *Palaeontology* 38:495–528.
- Yee N, Phoenix VR, Konhauser KO, Benning LG, Ferris FG. 2003. The effect of cyanobacteria on silica precipitation at neutral pH: Implications for bacterial silicification in geothermal hot springs. *Chem Geol* 199:83–90.
- Yool A, Tyrrell T. 2003. Role of diatoms in regulating the ocean's silicon cycle. *Global Biogeochem Cycles* 17:14.1–14.21.