

## THE SILICA BUDGET IN THE SEDIMENTARY CYCLE\*

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## ABSTRACT

The source, transportation, and precipitation of silica in solution on and near the earth's surface are evaluated to arrive at the silica budget in sediments. The forms of silica stable at low temperatures and their solubilities are summarized. The primary source of silica in solution is the chemical weathering of silicate minerals formed at high temperatures and/or pressures. Formation and alteration of clay minerals in soils and hot springs are other sources. Marine diagenesis of clays probably does not contribute much silica to solution. The major source of soluble silica in the early diagenesis of sediments is the dissolution of the remains of siliceous organisms. Solution of silica in deeply buried rocks is related to the pressure and temperature coefficients of solubility. Most natural waters are undersaturated with respect to amorphous silica and much of the ocean is undersaturated with respect to quartz. Hot spring and some soil waters may be supersaturated and inorganically precipitate silica, but the major mechanism for the precipitation of silica on the surface of the earth is biochemical. It is the diatoms, radiolaria, and other silica secreting organisms that are responsible for extracting silica from the sea. Crystalline quartz is precipitated from deep formation waters, given enough time. The silica cycle starts with the weathering of silicate minerals, goes through the stages of transportation and precipitation and, via metamorphism, comes back to reconstituted silicate minerals. The silica cycle in the past is discussed with reference to the development of the silica-secreting organisms and the conclusion is reached that since the beginning of the Paleozoic, and perhaps earlier, the silica cycle operated much as today.

## INTRODUCTION

It is the purpose of this paper to discuss the sources, transportation, and precipitation of silica at or near the surface of the earth's crust in relation to the polymorphic forms of silica found in ancient and modern sediments. The discussion will not treat questions of silica movement, concentration, and precipitation involved in metamorphic or igneous processes other than to note that these processes are involved in the total cycle of silica in the crust.

Much of the material discussed here is built on modern chemical and crystal chemical ideas on the forms of solid and colloidal silica, the types of dissolved species in aqueous solutions, and the equilibria between solid and dissolved species at low temperatures and pressures, summarized most recently by Iler (1955). The application of these concepts to geologic situations has been covered in part by two recent papers (Krauskopf, 1956; White, Brannock, and Murata, 1956).

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## FORMS OF SOLID SILICA

*Crystalline*

It is necessary to briefly summarize our present knowledge of the various forms of solid silica that are germane to this discussion and are of geological significance. The crystalline modification of  $\text{SiO}_2$  that is stable at low temperatures and pressures,  $\alpha$ -quartz, is the most abundant single mineral in sediments. As a detrital mineral it is present as the product of the mechanical weathering of quartzose igneous, metamorphic, and sedimentary rocks; its dominance as a detrital mineral is largely the result of its physical properties: hardness and lack of cleavage, and its chemical properties: extremely low solubility in water and non-reactivity. Quartz is also ubiquitous as a chemically precipitated constituent of sedimentary rocks; it has been observed as secondary overgrowths on detrital quartz grains, as pore fillings, as authigenic euhedra in carbonate rocks, as replacements of carbonate structures such as oolites, and as the essential constituent, as microcrystals, of many cherts and other siliceous sediments.

The crystalline silica polymorphs that are stable at higher temperatures and pressures ( $\beta$ -quartz, tridymite, cristobalite, coesite) are not of much interest in the consideration of normal sediments except insofar as some of these minerals do occur geologically and may be a minor source of silica in solid or dissolved form.

*Chert*

Some controversy has existed over the nature of the silica in chert, one of the most common siliceous rocks. There seems to be little doubt that microcrystalline quartz is present in most cherts. This conclusion is based on petrographic evidence (Pettijohn, 1956, p. 437-8) and  $x$ -ray diffraction patterns (Midgley, 1951; Folk and Weaver, 1952). The question at issue is whether chalcedony consists only of fibers of quartz, or as others have concluded (Sosman, 1927; Correns and Nagelschmidt, 1933; Donnay, 1936), of a mixture of fibrous quartz and amorphous silica. It is probable that the  $x$ -ray diffraction evidence on this point is inconclusive, for crystalline quartz has a high  $x$ -ray scattering efficiency and amorphous silica scatters  $x$ -rays very poorly; in a mixture of the two, where the quartz may be of extremely fine size, it is probably impossible to distinguish the broad, low intensity scattering maximum of amorphous silica unless it is present in amounts over 10-15%. Perhaps more refined techniques, such as the analysis of low-angle scattering, will help to distinguish the two forms of silica.

In a recent paper, Peltó (1956) sought to elucidate the structure of chalcedony and tried to explain its reactivity with alkalis (known from

studies of concrete) in terms of composition and structure. Peltó drew an analogy between the chalcedony structure and the behavior of grain boundaries in metals and came to the conclusion that the properties could be explained by islands of poor fit, or dislocations, between sub-parallel bundles of quartz fibers. The reactivity with alkalis during the setting of concretes and solubility larger than that of quartz was explained as the result of the distortion at and around the dislocations.

Because of the finely crystalline state of the quartz in chert, and the highly variable amount of porosity (internal surface) between adjacent microcrystals or fibers, chert may have not only appreciably different mechanical abrasion characteristics from quartz but, insofar as solubility is affected by grain size, may have variable solubilities in water that are higher than quartz. Obviously, if there is interstitial amorphous silica in chalcedony, the solubility will be higher. The writer is not aware of accurate solubility measurements of cherts other than that by Peltó (1956), who immersed chalcedony in water at 95° C. for seventeen hours and observed solution of 51 p.p.m. It is likely, in the light of the known difficulty of attaining equilibrium between silica and water at low temperatures in a short time (Alexander, Heston, and Iler, 1954; Kennedy, 1950) that this time was inadequate for equilibrium to be attained.

### *Opal*

Opal, or opaline silica, is a disordered hydrated form of silica whose properties are markedly different from the ordered crystalline quartz polymorphs. It appears to be a form of amorphous silica, more or less hydrated, that has formed from the partial dehydration and solidification of a silica gel. Opal is of some geologic significance in sediments both as a possible product of weathering in some soils, as an alteration product of volcanic ash (Frye and Swineford, 1946) and as a precipitate (opaline sinters) deposited from thermal spring waters (White, Brannock, and Murata, 1956). However, in terms of its abundance in surface and near surface rocks exposed to weathering, and as a constituent of sediments, it is relatively unimportant.

### *Amorphous Silica*

Amorphous silica is a term used to describe materials whose composition is relatively pure  $\text{SiO}_2$  that are in the mesomorphous state, that is, have only a transitory crystallographic order, such as that found in some liquids, and do not show the definite periodicity of atomic or ionic arrangement characteristic of crystalline solids. It is probably most nearly accurate, in the structural sense, to refer to amorphous silica as a dis-

ordered association of cristobalite crystallites of a size very little larger than one unit cell and therefore not properly designated as crystalline cristobalite (Warren and Biscoe, 1938). As a result of the extremely small size of the particles and the disordered arrangement, some of its physical and chemical properties are different from either quartz or cristobalite.

Under the classification of amorphous silica are included all of the various kinds of hydrated and dehydrated silica gels, silica glass, siliceous sinters, powders from the condensation of vapor phases, and, of greater geological importance, the skeletal materials of many silica-secreting organisms, such as diatoms, radiolaria, and siliceous sponges.

### SOLUBILITIES IN AQUEOUS SOLUTIONS

#### *Amorphous Silica*

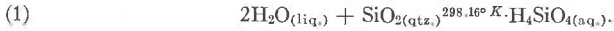
The metastable equilibrium solubilities of various kinds of amorphous silicas have been extensively investigated, most recently by Alexander, Heston, and Iler (1954) and Krauskopf (1956). The essential facts seem to be that all forms of amorphous silica have an equilibrium solubility in the range 120–140 p.p.m., and that opal may be slightly lower, about 100 p.p.m. The solubility is essentially independent of pH at pH values below about 9, and the dominant species in near-neutral and acid solutions, as measured by lowering of freezing point determinations (Weitz, Franck, and Schuchard, 1950) and diffusion rates (Jander and Jahr, 1934), is monomeric silicic acid,  $\text{H}_4\text{SiO}_4$ . In dilute solutions  $\text{H}_4\text{SiO}_4$  is probably hydrated, with one layer of water molecules surrounding the  $\text{Si}(\text{OH})_4$  tetrahedra (Iler and Dalton, 1956). At pH of 9.8 and higher,  $\text{H}_4\text{SiO}_4$  becomes dissociated to a significant extent (Roller and Ervin, 1940), the solubility increases greatly, and various other species in solution appear, such as silicate ions, and dimeric and higher polymeric forms of silicic acid (Iler, 1955, pp. 20–25). In the following discussions 140 p.p.m. will be used as the figure for the equilibrium solubility of all forms of amorphous silica at 25° C. in pure water, recognizing that it is not a precise figure. Krauskopf (1956) found that there were no significant differences in silica solubility between pure water and sea water.

#### *Quartz*

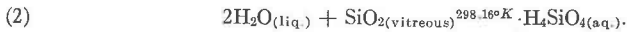
The solubility of quartz is much lower than that of amorphous silica. The precise determination of the equilibrium solubility of quartz at room temperatures has not yet been made, although figures varying from 6 p.p.m. (Gardner, 1938) to 30 p.p.m. (Lenher, 1921) have been reported. The laboratory determination of quartz solubility at low temperatures is difficult because of the long times necessary to achieve equilibrium and the necessity for eliminating traces of certain metals, notably aluminum,

and fluoride ion from the system. However, there is a way to estimate quartz solubility from known thermodynamic quantities.

We will assume, following the discussion of amorphous silica solubility above, that the only dissolved species in pure water in equilibrium with quartz at 25° C. and at pH below 9, is monomeric, undissociated silicic acid. Then the reaction of interest is



If we know the standard free energy of formation of all of the reactants and products in this equation we can calculate the change in standard free energy of the reaction, and so the solubility. We know the  $\Delta F_f^\circ$  of water and of quartz, but not of silicic acid. The latter, however, can be estimated from the reaction



For reaction (2) we do not know the  $\Delta F_f^\circ$  of  $\text{H}_4\text{SiO}_4$  either, but the free energy of the reaction can be calculated from the known equilibrium solubility of amorphous silica, 140 p.p.m., and thus the  $\Delta F_f^\circ$  of  $\text{H}_4\text{SiO}_4$ . For reaction (2) we write

$$(3) \quad \frac{(\text{H}_4\text{SiO}_4)}{(\text{H}_2\text{O})^2(\text{SiO}_2)} = K_{\text{eq.}} \text{ where } ( ) \text{ indicates activity ("Thermodynamic concentration").}$$

In such dilute solutions at atmospheric pressure the activity of solid silica and water can be taken as unity, and thus:

$$(4) \quad K_{\text{eq.}} = (\text{H}_4\text{SiO}_4)$$

In very dilute solutions and considering the  $\text{H}_4\text{SiO}_4$  is essentially undissociated at pH values lower than 9, we are justified in writing:

$$(5) \quad K_{\text{eq.}} = (\text{H}_4\text{SiO}_4) = [\text{H}_4\text{SiO}_4], \text{ where } [ ] \text{ indicates concentration in moles/li.}$$

Then, knowing  $[\text{H}_4\text{SiO}_4]$  from the solubility of silica, 140 p.p.m.  $\text{SiO}_2$ , we use the relation:

$$(6) \quad \Delta F^\circ_{(\text{reaction})} = -RT \ln K.$$

We thus calculate  $\Delta F^\circ_{(\text{reaction})}$  for (2) to be 3.6 kcal./mole. Substituting in the relation:

$$(7) \quad \Delta F^\circ_{(\text{reaction})} = \sum F_f^\circ_{(\text{products})} - \sum F_f^\circ_{(\text{reactants})}$$

we get

$$3.6 = \Delta F_f^\circ_{(\text{H}_4\text{SiO}_4)} - (-2 \times 56.7 - 190.9)$$

$$\Delta F_f^\circ_{(\text{H}_4\text{SiO}_4)} = -300.7 \text{ kcal./mole.}$$

(Free energy data from Latimer, 1952.)

With this estimate for the standard free energy of formation of  $\text{H}_4\text{SiO}_4$ , we now return to reaction (1), and, using relation (7), get  $\Delta F^\circ_{(\text{reaction})} = 5.1$  kcal. Using equation (6) we calculate  $K_{\text{eq.}}$  to be  $10^{-3.64}$

= $[\text{H}_4\text{SiO}_4]$ . Multiplying by the molecular weight of  $\text{SiO}_2$  we get the equilibrium solubility, approximately 14 p.p.m.  $\text{SiO}_2$ .

An alternative method for the estimation of  $\Delta F_f^\circ_{\text{H}_4\text{SiO}_4}$  is to use the  $\Delta F_f^\circ$  value of  $\text{H}_2\text{SiO}_3$  ("crystalline") given by Latimer (1952),  $-244.5$  kcal., and assume that the free energy of hydration to make  $\text{H}_4\text{SiO}_4$  by adding one molecule of water is negligible. Thus

$$(8) \quad \Delta F_f^\circ_{(\text{H}_4\text{SiO}_4)} = \Delta F_f^\circ_{(\text{H}_2\text{SiO}_3)} + \Delta F_f^\circ_{(\text{H}_2\text{O})} = -244.5 + (-55.7) = 300.19 \text{ kcal./mole.}$$

From this value we may calculate the solubility of quartz in the same way as above to get 7.25 p.p.m., a figure which checks more closely with the figure of 6 p.p.m. given by Gardner (1938) and Kennedy (as quoted by Krauskopf, 1956).

It will be seen that the difference between 7.25 p.p.m. and 14 p.p.m. is dependent only on the difference between the two values for  $\Delta F_f^\circ_{(\text{H}_4\text{SiO}_4)}$ ,  $-300.7$  and  $-300.19$  kcal. As Garrels (1957) has emphasized, precise solubility calculations can be made only from extremely accurate values for the appropriate thermodynamic quantities. In spite of this, however, both values, 7.25 and 14 p.p.m., are of the same order of magnitude and give us some notion as to the low solubility of quartz relative to amorphous silica.

#### *Rates of Reaction*

The attainment of equilibrium with water is a slow process for amorphous silica but can demonstrably be achieved in the laboratory (Alexander, Heston, and Iler, 1954; Krauskopf, 1956). The rate of attainment is strongly influenced by particle size, type of material (gel, powder, or other), pH, and in supersaturated solutions, by the extent of supersaturation. The rate of attainment of equilibrium in the quartz-water system at room temperature has not been measured but must be very much slower than for amorphous silica.

At room temperatures and atmospheric pressure, amorphous silica is metastable with respect to quartz, the thermodynamically stable modification of  $\text{SiO}_2$ . However, in all cases, the precipitate formed from supersaturated solutions at low temperatures is amorphous silica rather than quartz (Iler, 1955, p. 15). Solutions undersaturated with respect to amorphous silica ( $<140$  p.p.m.) but supersaturated with respect to quartz are stable over a period of years. The studies of the synthesis of quartz crystals have shown that clear crystalline quartz, by methods so far known, cannot be formed directly from solution at anywhere near room temperatures and atmospheric pressure (Buehler and Walker, 1949; Corwin, et al, 1953). The difficulty experienced in precipitating crystalline quartz at low temperatures and pressures in the laboratory as con-

trasted with the obvious ease with which nature accomplishes the synthesis may be related to several different factors. Perhaps the most important need that is absent in the laboratory is sufficient time; the rate of attainment of equilibrium in the quartz-water system at low temperatures may be so slow that several thousand years may be needed to either precipitate or convert amorphous silica to quartz.

Another factor is the relative structural complexities of the various forms of solid  $\text{SiO}_2$ . Applying Ostwald's rule, or the amplification and extension of it as a "simplicity" principle by Goldsmith (1953), one may characterize amorphous silica as a close relative to the cristobalite structure, the high temperature phase that is formed more easily than the low temperature, more complex structure, quartz. On the other hand, Buerger (1935, 1954) has pointed out that the high temperature silica polymorphs may be stable by virtue of the stuffing of their more open structures by impurity cations that balance valence deficiencies produced by substitution of small amounts of Al for Si. The more close-packed quartz structure cannot accommodate these impurities and presumably any inversion from high to low temperature forms must be accompanied by expulsion of impurities.

#### *Ionic Strength*

There is little effect of ionic strength of aqueous solutions on the solubility of amorphous silica (Krauskopf, 1936), at least insofar as salt concentrations of the order of magnitude of sea water are concerned. This might be expected on the basis that monomeric silicic acid is essentially undissociated at pH lower than 9, thus electrically neutral and unaffected by the distribution of ionic charges in the solution. Solutions of high ionic strength, however, may have an effect on the solubility at high pH, where silicate ions are present, and where the activity of water is lowered significantly.

It is of interest that the amorphous silica of diatom tests is less soluble (or dissolves more slowly) than inorganic silicas. This may be because the organisms complex the silica with aluminum or other cations, such complexes being extremely insoluble (Iler, 1955, p. 16).

#### SOURCES OF SILICA IN SOLUTION

##### *Weathering of Silicates*

The primary source of silica in solution on the surface of the earth is the chemical weathering of silicate minerals. In the chemical degradation of these minerals by water solutions, varying amounts of  $\text{SiO}_2$  are contributed at varying rates, depending on climate, relief, and the nature of the original material. We are probably justified in assuming from labo-

ratory experiments that in most geological conditions, where the pH is less than 9.5, the silica in solution is dominantly undissociated  $\text{H}_4\text{SiO}_4$ . This may be an oversimplification, however, for it has been established that wollastonite treated with acid gives soluble polysilicic acids rather than monomeric (Weitz, Franck, and Schuchard, 1950) and Murata (1946) has pointed out that in aluminosilicates with a high Si:Al ratio there may remain a silica network after Al has been removed by acid. But it is probable that such open silica networks are appreciably soluble (to give monomeric silicic acid) and that eventually the polysilicic acids formed from solutions of metasilicates such as wollastonite, and other silicates in very alkaline waters will depolymerize in near-neutral or slightly acid stream waters to give monomeric  $\text{H}_4\text{SiO}_4$ .

The silicate minerals of igneous and metamorphic origin, feldspars, amphiboles, pyroxenes, etc., that break down rather rapidly under many soil forming conditions may be expected to supply the greatest proportion of  $\text{H}_4\text{SiO}_4$ . Quartz from igneous and metamorphic rocks and from quartzose sediments, considering its low solubility and slow rate of solution, probably supplies a less significant amount.

#### *Weathering of Clays*

The weathering of clay minerals may or may not yield free silica to solutions. For example, the alteration of an illitic (micaceous) clay that has the approximate composition and structure of muscovite, to kaolinite, does not yield silica, for, despite the different arrangement of Al and Si in the two structures, the stoichiometric proportions of Al:Si in the two minerals are the same. But if, under extreme weathering conditions, kaolinite alters to gibbsite (bauxite), we may expect large quantities of silica to be contributed to solution. On the other hand it may be possible for an illitic clay to weather to montmorillonite. If the montmorillonite that is formed by this alteration is one in which there is very little substitution of Al for Si in the tetrahedral layer, there will be an addition of silica to the clay, the silica being withdrawn from available solutions. Thus this transformation would be a net reducer of the quantity of silica in solution. But if the "montmorillonite" formed from weathering of mica has the tetrahedral composition of the original mica, a more probable situation,\* there would be no net change in silica.

#### *Thermal Springs*

Another source of silica in solution at the surface is from thermal spring waters (see White, Brannock, and Murata, 1956). Although the absolute amount of silica in these waters is small compared with the total contri-

\* W. F. Bradley, personal communication.



bution from all surface waters, the concentration of  $H_4SiO_4$  in thermal waters may be quite high. White and co-workers have shown that as these waters suddenly cool at the surface they become supersaturated and precipitate siliceous and opaline sinters; the remaining saturated silica solutions then merge with the general run-off of the region.

#### *Marine Alteration of Clays*

The marine alteration of some clay minerals that has been postulated to explain the distribution and occurrence of clay minerals in modern sediments (Grim, Dietz, and Bradley, 1949; Millot, 1949; Grim, 1953; Grim and Bradley, 1955) may be a source of silica in solution. The same considerations discussed above with reference to the weathering of clay minerals apply here. Alteration of kaolinite to illite, if such a reaction does actually occur, would involve no net change in silica. But if there is appreciable alteration of montmorillonite to illite and/or chloritic clay minerals there should be a net loss of silica in the solids, the excess presumably going into solution, at least temporarily. However, it has not yet been generally accepted that such changes in clay composition as a result of marine diagenesis (or penecontemporaneous alteration) involve any part of the structures other than cation-exchange positions (Grim and Bradley, 1955) and it is change in composition of the tetrahedral layers that affects the silica contribution. It may be that these layers are inherited intact from the source areas and it is only in the milieu of subaerial weathering that clay minerals can be a source of silica.

#### *Water of Compaction*

Johnson (1920) has suggested a source for the silica secondarily precipitated in sediments in the squeezing out of water from shales during the compaction process. This squeezing out process will give silica in solution only if the original interstitial water contained much silica in solution. Silica in solution in interstitial waters, neglecting for the moment biochemical factors, can originate from one of several sources. One possibility is from the alteration of clay minerals; as we have seen in the discussion above, this seems unlikely. Another source is the dissolution of extremely fine-grained quartz that is often found in shales. Iler (1955, p. 9) has calculated quartz solubility as a function of particle size and found that the solubility starts increasing only when sizes as fine as 10 millimicrons are approached. The question is, then, do muds and shales contain quartz particles of this size? It is known that the  $<0.1$  micron size fraction prepared by settling of suspensions of many modern and ancient sediments normally contain practically all clay minerals and no quartz, as estimated by  $x$ -ray diffraction methods. Now, one might argue that such fine quartz particles are not there because they have al-

ready dissolved. But is it not much more probable that these extremely fine sizes of quartz were dissolved in the transporting waters before the detritus ever reached the depositional site? One final possibility is that temperatures attendant on burial and compaction are high enough to dissolve large amounts of silica. But Kennedy (1950) showed that below 140° C. quartz solubility remains very low and it is unlikely that temperatures above 100° C. would be reached before the shale was almost completely compacted and most of the water squeezed out. Therefore it seems that waters of compaction would not ordinarily contain more dissolved silica than the original entrapped sedimentation water.\*

### *Biochemical*

One of the major sources of silica in solution in the early diagenesis of sediments is the dissolution of siliceous organisms such as diatoms, radiolaria, and siliceous sponges. These materials are essentially amorphous or opaline silica and have a solubility of about 140 p.p.m. Bruevich (1953), Bezrukhov (1955), and Lisitsyn (1955) measured relatively high concentrations of dissolved silica in the interstitial waters of the bottom sediments of the Bering Sea and observed corroded and partially dissolved diatom shells in the sediments. Emery and Rittenberg (1952) noted concentrations of silica in interstitial waters in California basin sediments that are much higher than in the overlying sea water. The silica-secreting population can extract huge quantities of silica from sea water and, during life, can protect their siliceous parts from dissolving in sea water, which is undersaturated with respect to amorphous silica. Some time after death and the cessation of metabolic processes that protect the silica tests from dissolution, the tests slowly dissolve in the undersaturated solutions around them. This mechanism undoubtedly accounts for a large part of the silica in solution in the interstitial waters of modern sediments.

### *Diagenesis*

The solution of quartz at depth during diagenesis of sediments may be a source of much of the silica in solution in deep underground waters, as proposed some years ago by Waldschmidt (1941).† More recently Heald (1956) has offered excellent petrographic evidence that there has been interpenetration and solution of quartz grains in a quartz-cemented sandstone, and suggested that it is the pressure of overburden borne on grain-to-grain contacts that is responsible and called such effects the

\* A recent article that has just come to my attention (Fothergill, 1955) suggests that there may be a mechanism involving the compacting muds behaving as a dialytic membrane and concentrating, among other dissolved species, silica.

† See Pettijohn, 1957, pp. 656-659 for an excellent summary of silica cementation.

result of "pressure solution." The work of Taylor (1950), relating increasing interpenetration of quartz grains to depth of burial, would seem to corroborate this explanation. Kennedy (1950) has shown quantitatively how quartz solubility increases with temperature. To the extent that very deep burial is tied to increase in temperature due to the geothermal gradient, solution effects due to temperature should become appreciable at depths of over 10,000 feet. At shallower depths one would not expect the temperature effect to be great. The pressure effect at relatively low temperatures on the solubility of quartz that Heald (1956) inferred from petrographic evidence has not yet been adequately investigated in the laboratory, although Maxwell and Verrall (1954) suggested that temperature is more important than pressure for silica solution and precipitation. It may be that quartz solution effects observed in rocks that have never been deeply buried is to be correlated with the chemical nature of the formation waters. Walker (1957), for example, believes that quartz replaced by carbonate minerals may supply a great deal of the silica precipitated as cement.

#### CONCENTRATIONS OF DISSOLVED SILICA IN SURFACE AND FORMATION WATERS

It now remains to discuss the concentrations of silica in solution in natural waters to evaluate the possibilities of inorganic precipitation of quartz or amorphous silica from saturated or supersaturated solutions. Most of the data in this section are taken from Clarke (1924). The following discussion is predicated on the assumption that in most natural waters, the pH is below 9.8 and that, as a result, the dominant species in solution is undissociated  $H_4SiO_4$  and the equilibrium solubility is approximately that measured in the laboratory. As the solubility of amorphous silica is about 140 p.p.m. at 25° C., no inorganic precipitation of any variety of amorphous silica can occur at concentrations below this value. Conceivably, crystalline quartz could inorganically precipitate from any solution with more than 6–8 p.p.m.  $SiO_2$ , given enough time and the optimum conditions (whatever they may be at low temperatures). But there is no clearcut observational evidence to show that crystalline quartz is in fact being inorganically precipitated anywhere from surface waters and this taken together with the practical impossibility of precipitating quartz in the laboratory at room temperatures makes this possibility unlikely.

#### *Soil Waters*

It is rather difficult to get a clear picture of the amount of dissolved silica in soil waters; this is mainly due to the lack of good chemical analyses of soil waters but also due to the difficulty of sampling of soil

waters and interpreting the validity of the samples. Obviously, however, the concentration of silica will depend on the extent of chemical weathering, with all that that term implies in relation to climate, topography, bedrock character, and maturity of soil development, and also the amount of water passing through the soil. All one can say at the present is that a few analyses show solutions which are undersaturated with respect to amorphous silica (Mohr and Van Baren, 1954). The great amount of silica released in the extensive weathering and breakdown of silicate minerals in lateritic and bauxitic tropical soils probably leads to much higher silica concentrations than might be found in more temperate podzol, rendzina, and tchernozem soils. Indeed, the presence of amorphous silica veinlets and nodules in laterites must be taken as evidence of silica-supersaturated soil waters.

Whether soil waters are or are not supersaturated with silica, they remain so only while they are still in the soil. After they percolate through the soil profile and merge with bedrock groundwaters or drain into streams, they become diluted and so undersaturated. If the soil waters become super-saturated, gels may form and become part of the soil. But how does the soil water become supersaturated in the first place? It would seem that the most likely opportunity for supersaturation would be a change from very alkaline (pH above 9.8) conditions where minerals such as feldspar are actively hydrolizing and decomposing (Garrels and Howard, 1957) and silica is more soluble, to more neutral or slightly acid conditions lower in the soil profile, where silica is less soluble. In this case, the formation of gel from the supersaturated solution would depend on the gelling rate, which is dependent on pH, degree of supersaturation,  $\text{OH}^-$  and  $\text{F}^-$  ions, and other factors (Iler, 1955, pp. 45-55).

### *Rivers*

Almost all streams and rivers, regardless of size, are undersaturated in silica as shown by the analyses in Clarke (1924, pp. 74-109) and emphasized by Krauskopf (1956). Of all the analyses quoted only two rivers in South America are supersaturated. Most of the others fall into a range from a few parts per million to 35 p.p.m. A very small number range from 35-75 p.p.m. Clarke, speaking with reference to the abundance of  $\text{SiO}_2$  with respect to the other dissolved solids, made the point that, in general, silica will be highest in the upper parts of streams that drain a metamorphic and/or igneous terrain where chemical weathering is at a maximum. In these streams, silica only ranges up to 25-35 p.p.m., even though it may be the dominant constituent of the dissolved matter.

As the streams travel on to their middle and lower courses they become more and more diluted by run-off waters that are low in silica and tend to

range from 8–15 p.p.m.  $\text{SiO}_2$ , very little more than the amount in equilibrium with crystalline quartz.

One may ask the pertinent question as to whether these analyses reflect  $\text{SiO}_2$  carried in colloidal suspension, which, if it were included, would raise the total amount. As pointed out by Roy (1945) and Krauskopf (1956) this is most unlikely; in the normal range of pH values of river waters any colloidal silica should equilibrate fairly rapidly and dissolve. In addition, gravimetric and colorimetric determinations usually agree closely; as the colorimetric analysis is not sensitive to colloidal particles one infers that there is little or no colloid present.

Although lakes are not volumetrically important, they may have relatively high concentrations of dissolved silica. This is particularly true of alkaline lakes in which, due to the high pH and the consequent formation of silicate ions, the solubility of silica may be much higher than 140 p.p.m. Owens Lake, California, for example (Clarke, 1924, p. 162) has 300 p.p.m. dissolved silica. One might expect that lowering of the pH of these lakes, the consequent disappearance of silicate ions and the resultant lowering of silica solubility, would result in the inorganic precipitation of amorphous silica.

#### *Groundwaters*

Some groundwater analyses (Meents *et al.*, 1952) show that in the upper zones of fresh water there is little silica in solution and the solutions are vastly undersaturated. But the situation in the deeper groundwaters, in which there may be mixing of meteoric and connate (or more properly, formation) waters and the total amount of dissolved solids may rise to 30,000 p.p.m. or higher, may be quite different. Some of the deep formation waters have as much as 50–60 p.p.m. silica. Some of the highest values for dissolved silica in deep formation waters, exclusive of areas near hot springs, indicate that the solutions are still undersaturated with respect to amorphous silica, particularly when the temperature increase in solubility is taken into account. It may be that some very deep formation waters, very concentrated with respect to all dissolved solids, and at higher temperatures due to the geothermal gradient, have much more silica dissolved and may even reach saturation. In these cases one may expect that some change in condition, such as temperature decrease, would result in precipitation of amorphous silica.

#### *The Oceans*

According to the data in Sverdrup, Johnson, and Fleming (1942, p. 180) the oceans are undersaturated with respect to amorphous silica at all depths. The dissolved silica in most ocean waters is only a few parts or

even tenths of a part per million. The maximum quoted by Sverdrup *et al* is about 8 p.p.m. A later figure that is somewhat higher was given by Bruevitch (1953), who reported concentrations up to 12 p.p.m. in bottom waters of the Bering Sea. Thus from the present ocean there is no possibility of inorganically precipitating amorphous silica from such undersaturated solutions. It is even doubtful whether most ocean waters are saturated with respect to quartz, although some bottom waters may be.

It is also possible to speculate that in some areas on the ocean floor there may be a thin unmixed layer of water just above the sediment-water interface, in which silica concentrations may be much higher due to diffusion of silica saturated waters expelled from the compacting sediment. Some bottom sediments have been reported as having concentrations up to 68 p.p.m. (Emery and Rittenberg, 1952). Unfortunately we have too little information on the chemical composition of interstitial waters of modern sediments to generalize.

#### PRECIPITATION OF SILICA

It is obvious that a silica solution must be supersaturated with respect to amorphous silica before inorganic precipitation of a gel or colloidal particles can take place. In the previous section we have seen that the only natural waters at or near the earth's surface that are supersaturated are thermal spring waters.

The one mechanism that seems to be responsible for precipitating amorphous silica is biochemical. It is known that diatoms, radiolaria, and other silica-secreting organisms are efficient in extracting silica from solutions under-saturated with respect to amorphous silica. The diatoms deplete such solutions to concentrations of 65–85 micrograms per liter (Iler, 1955, p. 281). In the absence of an inorganic mechanism for silica precipitation, and in view of the biochemical efficiency of silica extraction, it appears that the siliceous organisms are probably responsible for keeping the oceans so undersaturated in silica. Partial evidence for this is the increase in abundance of diatoms following volcanic ash falls, which release abundant silica in the process of glass alteration.

Another biochemical source of precipitated silica may be silica-secreting floral species. A number of land plants (horsetail, bamboo, are two examples) secrete small quantities of silica and it may be that some marine species do so also. Although the amount of silica per organism may be quite small, the absolute amount contributed by large populations may be significant.

Although many surface waters are supersaturated with respect to crystalline quartz there is no clearcut observational evidence that crystalline quartz is being precipitated from these waters. The very fact

that these waters maintain silica in solution far in excess of that amount in equilibrium with quartz for long times suggests that quartz crystallizes from natural solutions extremely slowly in the range of room temperatures. As mentioned earlier, laboratory experiments have not been successful in precipitating quartz at room temperatures. Of course, one can always invoke some unknown catalyst that can make the reaction proceed at a measurable rate at room temperature but the nature of such a catalyst (if indeed, one exists) eludes us at present. We can only invoke time for this extremely slow reaction.

The time is available in the diagenetic stage of the history of a sedimentary rock. After burial the formation waters containing silica in solution may gradually equilibrate with quartz, the excess silica crystallizing as clear authigenic overgrowths on detrital quartz grains, as small quartz euhedra in limestones, or possibly as microcrystalline, chalcedonic quartz aggregates. But even in Paleozoic sandstones buried 3000–4000' (Meents, *et al.*, 1952) there may still be more silica dissolved in the formation waters than is in equilibrium with quartz. The increased solubility of quartz due to temperature increase along the geothermal gradient is probably insufficient at this depth to account for the amount of silica found in solution. The explanation for this is either the extraordinary length of time necessary for equilibration, or more probably, to the fact that the formation waters may be much younger than the sediments that contain them. The evaluation of whether formation waters are in equilibrium with quartz at depths below about 10,000' must wait on more precise determinations of the solubility of quartz in the temperature range 25°–150° C.

In few formation waters is there more silica in solution than is in equilibrium with amorphous silica and so it is unlikely that this kind of silica is precipitated during diagenesis.

A graphic representation, using an architectural metaphor, of the abundance of silica in various waters is shown in Fig. 1. The volumes of the buildings are crudely proportional to the total amount of water; their heights are proportional to the concentration of soluble silica. The base represents the kind of silica precipitated and at the bottoms of the buildings are representations of the amount of silica precipitated. Superimposed are two planes representing the solubilities of quartz and amorphous silica. Thus no building below its appropriate solubility plane can precipitate silica inorganically.

The sea water building has a great volume but a very low concentration of silica. At the opposite extreme is the hot springs "skyscraper," small in volume but high in silica concentration. River and formation waters lie in between. The soil waters building is of unknown height and

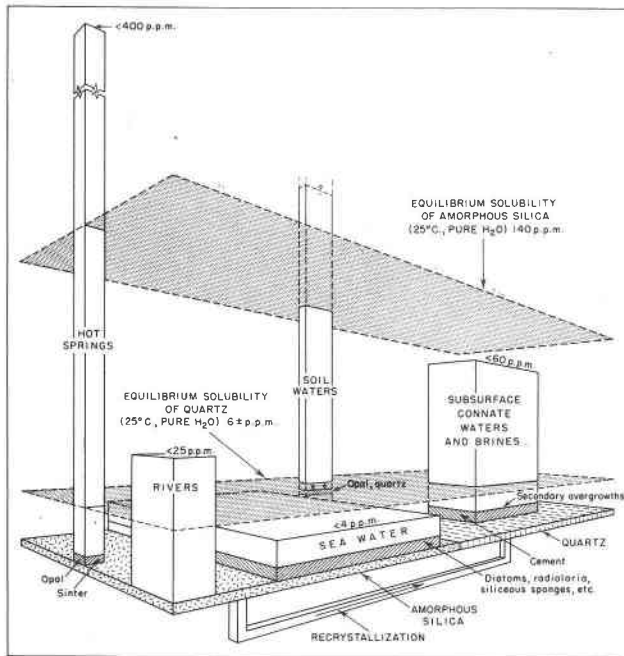


FIG. 1. Silica abundance in natural waters. Volume of "buildings" roughly proportional to absolute amounts of silica in solution. Height of "buildings" roughly proportional to concentrations of silica in solution.

relatively small volume. All of the buildings except that of formation waters and part of soil waters rest on an amorphous silica base, i.e., this is the material primarily precipitated. The formation waters building and part of the soil waters building rest on a quartz base signifying that crystalline quartz is precipitated directly from these waters. The amorphous silica is converted to quartz in the "sub-basement" by recrystallization or by solution and reprecipitation in formation waters.

### *The Silica Cycle*

We can now proceed to outline the silica cycle, as shown diagrammatically in Fig. 2. We start with the silicate minerals that are the ultimate source of silica in solution. Through the weathering process the silicate minerals contribute silica in solution to surface waters and may be concomitantly altered to colloidal aluminosilicates (the clay minerals). The silica in surface waters, being far under the concentrations necessary to precipitate amorphous silica and not having sufficient time available to precipitate crystalline quartz, is carried to either the oceans or to formation waters. In the ocean, via biochemical precipitation by siliceous



organisms, the silica is precipitated as amorphous silica or opaline silica. The concentration of silica in the sea is controlled by silica-secreting organisms. During diagenesis the amorphous silica deposited in the oceans recrystallizes to quartz and the silica in solution in formation waters gradually comes to equilibrium with quartz by precipitation of secondary overgrowths, authigenic crystals, etc. During diagenesis,

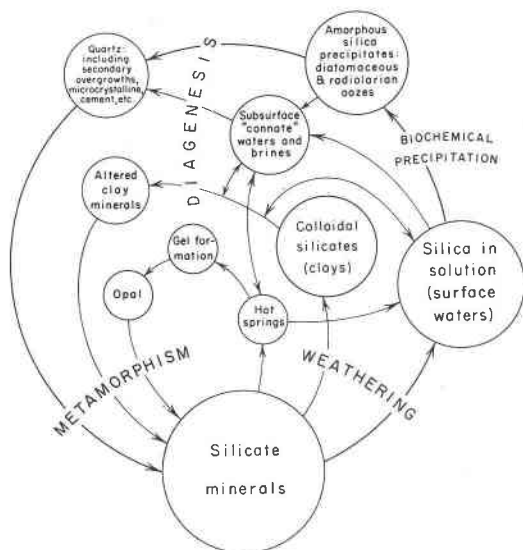


FIG. 2. The silica cycle.

either early (penecontemporaneous) or late, the clay minerals originally formed as weathering products may alter to different species and, depending on the specific transformation involved, as described previously, will either contribute to or take away silica in solutions.

Hot spring waters (White, Brannock, and Murata, 1956) derive their silica content by solution and alteration of silicate minerals plus a background amount of silica that may have been present in the original unheated ground-waters. Some juvenile water may be included. The hot spring waters then contribute back to formation waters, or to surface waters. Hot spring waters precipitate silica, as they cool at the surface and become supersaturated, forming opaline or siliceous sinters through intermediate stages of gel formation. Thermal waters may also circulate without emerging as hot springs and so precipitate silica in pore spaces as the waters cool in near surface rocks. The full cycle is then completed by metamorphism of the sedimentary silicate minerals and reorganization into minerals stable at high temperatures and/or pressures.

*The Silica Cycle in the Past*

We may ask whether the silica cycle, at least that part of it involved in the sedimentary cycle, operated in the same way throughout the known history of the earth. Certainly the general flow pattern outlined must have started after the beginning of the weathering process and the accumulation of the primitive oceans sometime early in the pre-Cambrian. The concentration of silica in surface waters may have been quite different from today, however. We can suppose that the extensive weathering of silicate rocks by rain waters with an amount of  $\text{CO}_2$  dissolved somewhat higher than at present (Rubey, 1951, p. 1124) would contribute much more silica to solution (or at a faster rate) than at present. At the same time there may have been no large population of silica-secreting organisms that would biochemically precipitate silica and maintain low concentrations of silica in the oceans. The presence of algal structures in some pre-Cambrian siliceous rocks might be taken as tenuous evidence of the early evolution of silica-secreting organisms, at least in the later pre-Cambrian, but all of the definitely documented algae from the pre-Cambrian seem to have been lime-depositors (Whittard, 1953). It is also possible that the algae in these siliceous rocks have been diagenetically silicified. The diatoms and radiolaria had not yet evolved, and it is uncertain how early the siliceous sponges developed. Hence, depending on the uncertainties of silica-secreting organism development, and further depending on the difficulty of estimating the absolute amount of silica contributed to the oceans per unit time, we may postulate a primitive ocean that was saturated with  $\text{Si}(\text{OH})_4$  (in acid or near-neutral ocean water). As additional silica was added amorphous silica must have started to precipitate inorganically. The inorganic precipitation must have continued to keep pace with addition of silica derived from weathering until the population of siliceous organisms increased to the point where they could reduce concentrations to below saturation levels. The evidence from the rock column seems to indicate that this development took place at least as early as the later pre-Cambrian. Primary silica deposits, such as some bedded cherts of inorganic origin, may be slightly more abundant in the pre-Cambrian than in the younger rock columns but the difficulty of arriving at some kind of valid statistical estimate is so great that no firm arguments can be based on present knowledge. Paleozoic columns do not seem to have a greater proportion of inorganic primary siliceous rocks than younger rocks. We do know that radiolaria and siliceous sponges had evolved by the early Paleozoic; these organisms were probably responsible for holding down silica concentrations in sea water and thus preventing inorganic silica precipitation, at least from the

Paleozoic on. Much later, in the Mesozoic, the diatoms appeared and from this time on the cycle must have operated much as today.

According to this argument, most bedded cherts formed since the early Paleozoic (or possibly even later pre-Cambrian) must have originated in much the same way as Bramlette (1946) suggested for the Monterey chert, a diagenetic reorganization of a biochemical silica precipitate (diatomite). The abundance of diatoms in this case, as perhaps in most cases, was related to silica produced by alteration of pyroclastic material. This is not to say that there cannot have been inorganic silica deposits at some times and places. The extensive marine alteration of waterlaid volcanic materials during periods of intense volcanism would have liberated large amounts of silica to solution, and if the waters did not rapidly mix with the open ocean reservoir and if siliceous organisms were not present in large numbers, an inorganic silica precipitate would form. This is similar in general outline to the origin proposed by Rubey (1929, p. 168) for the siliceous Mowry shale, which involved the subaqueous decomposition of volcanic glass into amorphous silica.

#### SUMMARY

We have seen that the silica-water system is properly considered in terms of two subsystems, a metastable amorphous silica-water system and a stable crystalline quartz-water system. Most natural surface and near-surface waters do not have enough silica dissolved to precipitate amorphous silica inorganically; the only significant exceptions to this are the thermal spring waters, which precipitate siliceous and opaline sinters. Many surface waters are supersaturated with respect to quartz, and though, theoretically, quartz should precipitate, no deposits of crystalline quartz have been observed in rivers, lakes, or the oceans, probably the result of the very long times needed to reach equilibrium at low temperatures. A large amount of amorphous silica is precipitated from the oceans by diatoms, radiolaria, sponges, etc., and as these materials are buried in the sediment, the amorphous silica dissolves and eventually becomes reprecipitated as quartz. All lines of evidence point to interstitial formation waters, originally trapped in the sediment and later modified by chemical processes and groundwater movement, as the solution that precipitates crystalline quartz in the diagenetic stage of the history of a sedimentary rock. This implies that almost all primary silica deposits were originally in the form of amorphous silica.

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