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## Dissolution and precipitation of silica at low temperatures

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**Abstract**—The dissolution of amorphous silica as monosilicic acid and the establishment of solubility equilibrium with silica gel and with colloidal silica have been demonstrated in recent chemical papers. The rates of dissolution and precipitation are slow at ordinary temperatures; at temperatures near the boiling-point both solubilities and rates of dissolution are much higher. The solubility is little affected by pH between values of 1 and 9, but rises rapidly at pH's over 9.

On the basis of this work and supplementary experiments, the geologic literature on the low-temperature solubility of silica is reviewed and various geologic applications are suggested. Much of the confusion in the literature can be traced to failure to recognize the slowness with which silica dissolves and precipitates or polymerizes. Opal dissolves in hot water to about the same extent as other forms of amorphous silica; probably it has a comparable solubility also at lower temperatures, but the rate of dissolution is so extremely slow that massive opal and diatomite can exist almost indefinitely in the presence of natural waters.

In sea water amorphous silica has about the same solubility as in fresh water. Silica in true solution is not precipitated by electrolytes; colloidal silica may be precipitated by electrolytes, the rate and completeness of precipitation depending on pH and on the kind and concentration of the ions.

Most of the silica in natural waters is in true solution rather than in colloidal dispersion. This means that silica brought to the sea by streams cannot be coagulated by the electrolytes of sea water. The factors that keep the concentration of silica below its equilibrium solubility (with respect to amorphous silica) in most natural waters are not completely understood; the slowness of dissolution, the use of silica by organisms, and slowly-established equilibria with crystalline silica or with authigenic silicates doubtless all play a part. The origin of sedimentary chert may be plausibly ascribed to dissolution of remains of siliceous organisms and reprecipitation of the silica (initially as amorphous silica), but not in general to direct inorganic precipitation.

### INTRODUCTION

THE behaviour of silica in water solutions at low temperatures remains one of the most stubborn problems of geochemistry. The solubility at high temperatures is well known, through the work of MOREY and HESSELGESSER (1951), KENNEDY (1950), HITCHEN (1945), and others, but study of the low-temperature solubility has been difficult because of the sluggishness of the reactions and the great stability of silica sols.

One recurrent question is the state of silica in dilute solutions. Is it in "true solution" (synonyms often used are "crystalloid" or "in molecular dispersion"), or in the form of a colloid, or both? Another familiar query concerns the mechanism of precipitation: can silica be flocculated from dilute natural solutions by simple admixture with electrolytes, or does precipitation require evaporation or the activity of organisms? Many other questions are derivatives of these two; for example, what limits the amount of silica natural waters can hold? How is the silica content of natural waters affected by changes of pH and temperature? What is the origin of the various kinds of chert and opal? All of these are questions to which contradictory answers can be found in geologic literature.

Much of the difficulty in such questions has been cleared up by recent chemical studies, especially the work of ALEXANDER, HESTON, and ILER (1954). These investigators, having shown that monosilicic acid in true solution is unequivocally determined by the colorimetric test with ammonium molybdate, use the test to measure silica solubility under a variety of conditions. The purpose of the present paper is to follow up the geologic consequences of these measurements, both by an attempt to reconcile them with geologic literature and by an extension of the experimental work.

To avoid ambiguity, the following terms will be used in reference to the various forms of silica:

*Silica.*  $\text{SiO}_2$  in any of its crystalline or amorphous forms.

*Crystalline silica.* Quartz, tridymite, or cristobalite.

*Amorphous silica.* A general term for any form of silica lacking crystal structure. It includes the following:

- (a) *Silica gel.* Hard amorphous silica containing 20-30% water, prepared commercially either as a chemical reagent or as a desiccant.
- (b) *Gelatinous silica.* Amorphous silica which appears in solution as gelatinous flocs or as a continuous gel, formed either by evaporation of a silica solution, by allowing a supersaturated solution to stand, or by acidifying a fairly concentrated solution of an alkali silicate.
- (c) *Silica sol or colloidal silica.* Silica dispersed in water in particles of colloidal dimensions.
- (d) *Opal* (including the silica of diatomite and radiolarite). Naturally-occurring amorphous silica, generally with less than 12% water. Some varieties of opal appear to be transitional to crystalline material (cristobalite), as shown by X-ray diffraction patterns.
- (e) *Silica glass.* Amorphous silica prepared by the rapid cooling of a silica melt.

*Dissolved silica.* Silica in the form of monosilicic acid; the silica that reacts with ammonium molybdate within two minutes after the solutions are mixed. Strictly speaking, "dissolved silica" should include also polysilicic acids with molecules smaller than the colloidal range, but for present purposes it is convenient to restrict the term to the monomer.

*Monosilicic acid or monomeric silicic acid.*  $\text{H}_4\text{SiO}_4$ ; this is the principal form of silica in dilute solutions (less than 100 p.p.m.) and in freshly prepared solutions of higher concentrations.

*Polysilicic acids.* Silicic acids containing two (disilicic), three (trisilicic) or more atoms of silicon per molecule. The simpler polysilicic acids react slowly with ammonium molybdate (or dissociate slowly to the monomer), but were not found in appreciable quantity in the experiments described in this report.

#### HISTORY OF THE INVESTIGATION

In 1947 K. J. MURATA, working with water samples collected by D. E. WHITE at Steamboat Springs, Nevada, noted that the concentration of colorimetrically determinable silica in many samples decreased markedly on standing, whereas the total silica decreased only slightly. Following up this observation, during the next year WHITE and W. W. BRANNOCK made detailed measurements of temperature, silica content, salinity, and pH, both at the springs themselves and in water samples allowed to stand in bottles for periods of several weeks. These measurements led WHITE, BRANNOCK, and MURATA to several tentative generalizations, of which the following are pertinent to the present work:

1. Amorphous silica establishes a solubility equilibrium in water with 105–120 p.p.m. of silica in true solution (determinable colorimetrically) at ordinary temperatures.

2. The rates of reaction are slow, permitting supersaturation and undersaturation to exist for considerable times.

3. The solubility is not much influenced by pH in the range 2–9; if anything, the solubility is greater in acid than in weakly alkaline solutions.

In 1954 the author, in collaboration with WHITE, began a series of experiments designed to test these conclusions in the laboratory. The experimental work fully confirmed the deductions from hot-spring data. In the meantime ALEXANDER and his co-workers published their 1954 paper, arriving at similar conclusions independently on the basis of experimental work alone.

The present report is based chiefly on the laboratory work, and as such is essentially a geologic supplement to the chemical data of ALEXANDER *et al.* The hot-spring measurements are discussed in a separate paper by WHITE, MURATA, and BRANNOCK (1956).

To WHITE the author is greatly indebted for suggesting the investigation, for continual helpful discussion as the work progressed, and for criticism of the manuscript. To BRANNOCK he would express appreciation for permission to take up and complete a study for which BRANNOCK had already laid the groundwork. The author also wishes to thank the Shell Oil Company for a grant for fundamental research which supplied much of the equipment used in the experiments.

#### REVIEW OF PREVIOUS WORK

The literature on the geologic role of silica at low temperatures is exceedingly voluminous, but four excellent critical summaries of recent years (HITCHEN, 1945; ROY, 1945; KENNEDY, 1950; and EITEL, 1954) make it unnecessary to cite any but the most important of the older papers. HITCHEN's review marshals fairly convincing evidence for a definite solubility of amorphous silica and for the colloidal nature of the "dissolved" silica. This seemingly anomalous combination of properties HITCHEN attempts to explain by postulating a "peptization equilibrium" involving solid gel, silica in true solution, and silica in the form of a sol. HITCHEN's case for colloidal silica rests on experiments showing that mono- and disilicic acids polymerize rapidly on standing, and on MOORE and MAYNARD's (1929) well-known demonstration that silica is partly coagulated by electrolytes from "solutions" containing as little as 30 p.p.m. of silica. In the second review article, ROY calls attention to evidence amassed by chemists showing that dissolved silica is stable in dilute solutions, emphasizing the detailed study of HARMAN (1925, 1926, 1927) and an observation of DIÉNER and WANDENBULCKE (1924) that colloidal silica in dilute (salinity 2%) sea water breaks down spontaneously into dissolved silica. Less cogent evidence leads ROY to guess further that silicate ions rather than neutral molecules make up the bulk of silica in solution. KENNEDY, in the third summary, agrees with HITCHEN that available data indicate a "rather definite equilibrium solubility in water" for amorphous silica, but follows ROY in finding the evidence favourable to molecular rather than colloidal silica in the equilibrium solution. EITEL's more noncommittal review adds modern data confirming the continuous change on standing of low-molecular-weight sols to high-molecular-weight sols, and notes also that silica sols are relatively stable in acid solution but are readily flocculated by electrolytes in alkali.

To the argument as to whether silica in dilute solutions has a colloidal or a molecular character, FREDERICKSON and COX (1954) added a statement favouring the colloidal side, based on electron micrographs of solutions resulting from high-temperature bomb experiments on the mechanism of dissolution of quartz. BRUEVICH (1953), on the other hand, argues for true solution in sea water because of the rapid reaction with ammonium molybdate, and un-ionized rather than

ionized silicic acid because of the small dissociation constant. IWASAKI, TARUTANI, KATSURA, and TACHIBANA (1954) report an observation similar to that of MURATA, WHITE, and BRANNOCK at Steamboat Springs: hot-spring water on standing contains progressively less colorimetrically determinable silica, presumably because part of the silica in true solution changes gradually into colloidal silica.

The related controversy over the manner of formation of bedded and nodular chert from silica solution has been ably summarized by PETTIJOHN (1949, pp. 328-332). Experimental data on the inorganic precipitation of silica by electrolytes are reviewed, as well as the familiar geologic evidence for the origin of some cherts by reworking of siliceous organic remains and by later replacement. PETTIJOHN feels that geologic evidence favours replacement during diagenesis as the mode of origin of most cherts. BRAMLETTE (1946, p. 43) also has reviewed ideas about the origin of chert, especially in relation to the opaline cherts of the Monterey formation; as an argument against direct inorganic precipitation from sea water, he notes the variability in concentration of silica at different depths in the sea. BRUEVICH (1953) notes that sea water is undersaturated with silica (because silica is more concentrated, hence closer to its solubility, in the interstitial water of bottom sediments), and concludes that deposition of silica from sea water must be due to organisms rather than to inorganic precipitation.

The recent work of ALEXANDER (1953), ALEXANDER, HESTON, and ILER (1954), and ILER (1955) is concerned with strictly chemical problems of solubility equilibrium and the form of silica in solution. Having developed methods for preparing and identifying silicic acids of low molecular weight, ALEXANDER *et al.* then verified the statement of WEITZ, FRANCK, and SCHUCHARD (1950) that the molybdate colour reaction is a valid test for the monomeric acid. This test, although widely used since it was first publicized by DIÉNERT and WANDENBULCKE (1923), has had a somewhat dubious status because the precise form or forms of silica which responded to it were uncertain (see ROY (1945) for a summary of opinions; CORRENS (1941), and TOURKY and BANGHAM (1936) in particular have doubted its validity). The difficulty is resolved by the demonstration of ALEXANDER *et al.* that the molybdate reaction is *rapid* with the monomer but *slow* for the dimer and all higher polymers, and that the difference in rate makes the test a reliable method for determining the monomer if the colour is measured within 2 min after formation. Using the test, ALEXANDER *et al.* measure the amount of monosilicic acid present in solutions of different forms of amorphous silica, including colloidal silica, and find that with time such solutions (at pH's below 9 and at 25°C) approach a constant concentration in the range 100-140 p.p.m. To see if this represents a true solubility equilibrium, they prepare a more concentrated solution of monosilicic acid and test the amount of monomer present at intervals, finding that the concentration falls slowly to the same range as before. These experiments, corroborating the exploratory work of DIÉNERT and WANDENBULCKE (1924), show conclusively that solubility equilibrium with respect to amorphous silica is reached; the equilibrium concentration is not determined more precisely because of the extreme slowness of both the dissolution and polymerization reactions. Regarding the effect of pH, ALEXANDER *et al.* find that the solubility is practically unaffected by pH changes below 9, but climbs rapidly as this figure is exceeded. Such behaviour is consistent with the postulate that silicic acid is practically un-ionized in acid and neutral solutions, but dissociates in alkali. In these respects silicic acid is exactly analogous to carbonic acid, except that the latter (because of a larger dissociation constant) dissociates appreciably at pH's as low as 6.

ALEXANDER *et al.* thus show clearly that the colloidal-versus-molecular argument over silica in dilute solution must be decided in favour of true solution, at least for solutions more than a few weeks or months old. The slowness of reaction, however, makes it possible on the one hand for solutions far more concentrated than the equilibrium value to exist temporarily, and on the other hand for sols to have a brief existence at concentrations far below the equilibrium value. These apparently anomalous solutions, which approach equilibrium only slowly, probably account for much of the confusion and contradiction in the older papers on silica solubility.

#### EXPERIMENTAL METHODS

Experiments were set up to extend the work of ALEXANDER *et al.* in two principal directions: the effect of temperature on the solubility equilibrium, and the conditions under which silica

is precipitated by sea water. Because the slowness of reaction makes accurate solubility measurements difficult at best, and because the work was intended to apply to complex natural systems where a number of factors may influence solubility, great precision was not attempted in the analyses or in the control of external conditions. Effort was directed toward obtaining many semi-quantitative results of geologic significance rather than a few strictly quantitative data.

The colorimetric method depending on the yellow colour developed on addition of ammonium molybdate was used exclusively for the analyses, except for a few gravimetric determinations run as a check. Details of procedure were based on methods used by the U.S. Geological Survey and the U.S. Public Health Service. Concentrations of dissolved silica to be determined were brought into the range 5-25 p.p.m. by dilution; HCl and  $(\text{NH}_4)_2\text{MoO}_4$  solutions were added to give final concentrations of about 0.02 M acid and 0.5% molybdate; colour standards were made up by mixing and diluting solutions of potassium chromate and borax. Concentrations of acid and molybdate may vary over a considerable range without markedly affecting the colour; the molybdate solution must be prepared fresh every few days to insure reproducibility. Total silica (colloidal plus dissolved) may be found by heating a sample with pellets of sodium hydroxide before making the colorimetric test. The colour intensity at 420 mu was measured with a Kruger spectrophotometer. Values for dissolved silica should be accurate to within 1 or 2%, and for total silica to within 3 or 4%.

Experiments were conducted in Pyrex flasks and bottles, previously cleaned with hot dichromate solution. Dissolution of silica from the glass was troublesome in only a few runs, and could be satisfactorily allowed for by using blanks. Temperature control was crude: for low-temperature work the solutions had the prevailing laboratory temperature, 22-27°C, and for high temperatures an oven was used which kept temperatures in the range 85-95°C. Acidities were adjusted by adding NaOH or HCl, and were measured with a Beckman pH meter. The water-glass used in making up solutions was a commercial product, and the silica gel was a commercial dehydrating agent containing about 24% water.

The silico-molybdate colour was obtained under conditions similar to those employed by ALEXANDER, HESTON, and ILER (1954), conditions which (according to these authors) insure reaction of at least 98% of the monomeric silicic acid within two minutes from the time when the solutions are mixed. In most of the experiments the colour intensity increased steadily for the first two minutes and thereafter remained approximately constant, indicating that the dissolved silica was almost exclusively in the monomeric form. In a few runs the intensity continued to increase slightly but perceptibly after the first two minutes, betraying the presence of small concentrations of the lower polymeric acids. In such runs only the readings taken at the end of the first two minutes were used.

#### THE SOLUBILITY OF AMORPHOUS SILICA

*General.* In accord with general physico-chemical principles, the least stable form of silica (amorphous silica) shows the greatest solubility and the most stable form (quartz) the least. This is analogous to the greater solubility of aragonite as compared to its more stable dimorph calcite, but silica is unique in the enormous difference in solubility among its polymorphs. For quartz at ordinary temperatures the solubility in near-neutral solutions is no higher than 6 p.p.m. (GARDNER, 1938) and may be much less (G. C. KENNEDY, personal communication), while amorphous silica has a solubility over 100 p.p.m. Theoretically quartz should crystallize from a solution saturated with respect to amorphous silica, but fails to do so in any humanly reasonable time, apparently because of the extreme slowness of the reaction. Hence, silica may be carried indefinitely in solution in surface waters at concentrations far in excess of the solubility of quartz (or of cristobalite or tridymite).

Previous measurements of the solubility of amorphous silica are well summarized by ILER (1955, pp. 6, 7). He shows that the measurements are fairly consistent,

regardless of the kind of amorphous silica used by different experimenters— anhydrous silica, silica gel with various degrees of hydration, and colloidal silica. The uniformity of solubility measurements seems surprising, inasmuch as these different forms of amorphous silica might be expected to have vastly different surface areas and hence different solubilities (KENNEDY, 1950, p. 652). ILER (p. 10) attempts to explain the apparent lack of relationship between surface area and solubility on the basis of the probable (but as yet not measured) low interfacial surface energy between amorphous silica and water. Some differences in solubility among the various forms of amorphous silica are not excluded by the experimental data, and differences of some sort would certainly be expected, but experiments to date suggest strongly that the differences are not large. Thus one can speak without ambiguity of a possible "solubility equilibrium" between amorphous silica in general and silica dissolved in water.

ILER also comments (pp. 14 and 16) on the pronounced decrease in the solubility of amorphous silica effected by traces of aluminium or magnesium ions. Presumably the decrease is due to formation of a protective surface layer of aluminium or magnesium silicate, and hence can be ascribed to an effect on the rate of dissolution rather than on ultimate solubility. Nevertheless, the rate effect is large enough to change laboratory measurements of apparent solubility markedly.

Because the solubility of amorphous silica is influenced by certain cations, because it probably is somewhat affected by particle size, and because the molybdate colour reaction is responsive both to monomeric and low-polymeric forms of silicic acid, measurements of the solubility cannot be made precise without elaborate attention to the nature and purity of reagents. For present purposes it will be sufficient to record the solubility as a range of values rather than a single figure—a procedure also adopted in much of the previous work.

*Amorphous silica at room temperature.* Two solubility measurements older than the work of ALEXANDER *et al.* need brief discussion because of the frequent references to them in geologic literature.

LENHER and MERRILL (1917), using silica gel in triply distilled water in platinum bottles, obtained a reproducible value of 160 p.p.m. at 25°C. This is somewhat higher than the range found by ALEXANDER *et al.* (100–140 p.p.m.), and the reason for the discrepancy is not clear. LENHER and MERRILL measured gravimetrically all the silica that passed through a fine filter paper, and hence would have included any of the lower polysilicic acids that might have been present either in the solution or as colloidal particles; but no colloidal material should have existed unless the original gel contributed fine suspended particles or unless the temperature varied during a run. (A rise in temperature would tend to dissolve more silica which would then become colloidal as the temperature falls.) The discrepancy, whatever its origin, is not large enough to be serious.

More troublesome are the solubility data reported by CORRENS (1941). For gravimetrically determined silica in solutions that had stood for eight months at various pH's in contact with silica gel (prepared by hydrolysis of  $\text{SiCl}_4$ ) in glass, CORRENS obtained:

|                |    |    |     |     |            |
|----------------|----|----|-----|-----|------------|
| pH             | 0  | 3  | 5   | 6   | 11         |
| $\text{SiO}_2$ | 99 | 39 | 109 | 219 | 378 p.p.m. |

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The figures for pH 0, 5, and 11 are consistent with the data of ALEXANDER *et al.*, but 39 p.p.m. at pH 3 is far too small, and 219 p.p.m. at pH 6 is much too high. Like LENHER and MERRILL, CORRENS by his method would have determined fine colloidal silica as well as dissolved silica, but there is no obvious reason for colloidal material to be present unless the temperature varied considerably during the experiment. In any event, the more detailed study by ALEXANDER *et al.* casts serious doubt on CORRENS'S conclusion that the solubility of amorphous silica fluctuates greatly with the pH, passing through a minimum near pH 3.

The work of ALEXANDER *et al.* is an advance over previous studies in that the solubility is determined not only by dissolving amorphous silica (prepared by burning  $\text{SiH}_4$ ) but also by allowing supersaturated solutions to polymerize, so that the existence of a definite solubility equilibrium is established. This conclusion is fully corroborated by experiments in the present study. The concentration of silica in water standing over silica gel gradually increased to a maximum of about 100 p.p.m., and supersaturated solutions prepared by neutralizing water-glass showed a gradual decrease in dissolved silica as colloidal particles formed, the rate of change becoming imperceptible after concentrations of 100-140 p.p.m. were reached (Fig. 1 and Table 1). Times required for the range 100-140 p.p.m. to be reached (in neutral and alkaline solutions) ranged from several days to a few weeks.

In acid solutions the rate of polymerization of supersaturated solutions is especially slow (the last three solutions in Table 1 and the first solution in Table 3

Table 1. Polymerization of dissolved silica.

|                                   | I       | II      | III     | IV      | V       |
|-----------------------------------|---------|---------|---------|---------|---------|
| pH during run                     | 7.7-8.3 | 7.3-7.9 | 4.8-5.3 | 6.9-7.3 | 8.0-9.1 |
| Original total $\text{SiO}_2$     | 320     | 975     | 171     | 171     | 171     |
| Original dissolved $\text{SiO}_2$ | 284     | 544     | 162     | 162     | 164     |
| Dissolved $\text{SiO}_2$ after    |         |         |         |         |         |
| 1 day                             |         | 172     | 163     | 163     | 164     |
| 2 days                            |         | 167     |         |         |         |
| 3 days                            | 173     |         |         |         |         |
| 8 days                            |         |         | 164     | 163     | 165     |
| 10 days                           | 148     |         |         |         |         |
| 12 days                           |         | 135     |         |         |         |
| 19 days                           |         |         | 165     | 163     | 161     |
| 24 days                           | 131     |         |         |         |         |
| 26 days                           |         | 130     |         |         |         |
| 38 days                           | 122     |         |         |         |         |
| 39 days                           |         | 130     |         |         |         |
| 52 days                           | 115     |         |         |         |         |
| 68 days                           | 113     |         |         |         |         |
| 128 days                          |         |         | 160     | 156     | 149     |

Temperature 22-27°C. Pyrex bottles with glass stoppers. Sample I: hot-spring water boiled to dissolve most of the silica (Curve I, Fig. 1). Sample II:  $\text{Na}_2\text{SiO}_3$  solution neutralized with HCl (Curve II, Fig. 1). Samples III, IV, V:  $\text{Na}_2\text{SiO}_3$  solution boiled, diluted, and neutralized with HCl.

illustrate the contrasting rates in acid and base), or possibly the equilibrium solubility is higher, since at pH's less than 6.5 the change in silica concentration showed a levelling off at values of 160-180 p.p.m. rather than 100-140. ALEXANDER *et al.* unfortunately do not report polymerization experiments at pH's below 7, but solubilities obtained by dissolution experiments were in the normal range. ILER (1955, p. 46) emphasizes the slowness of polymerization in acid, and this seems the most probable explanation of the apparent anomaly. Geologically, the important

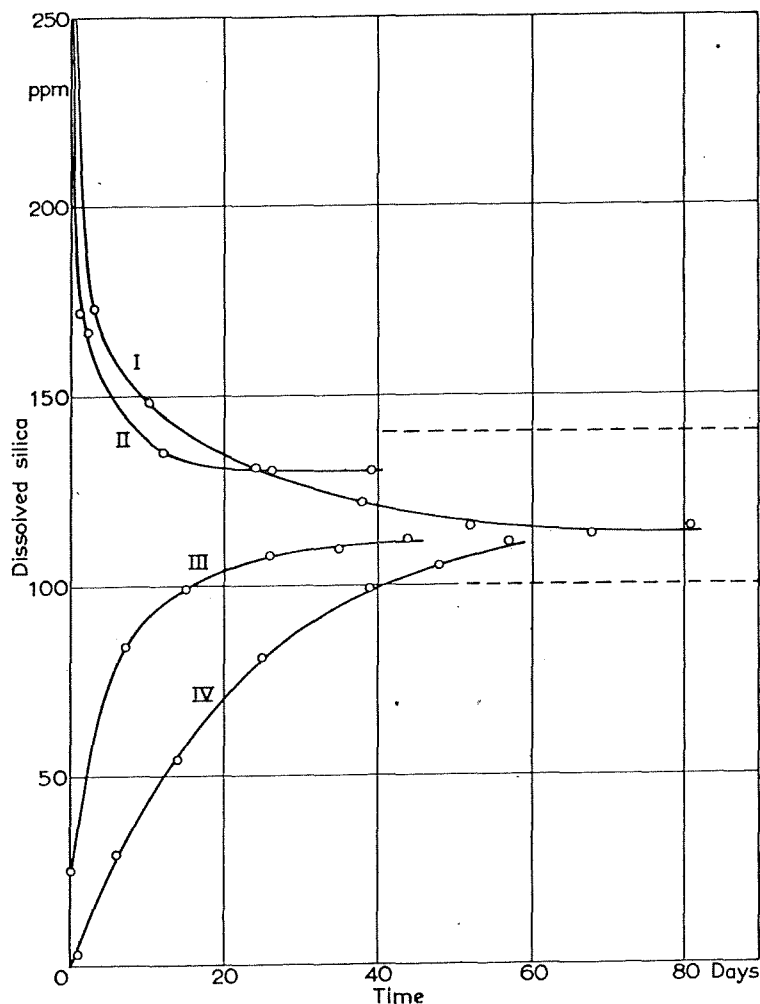


Fig. 1. Representative runs showing approach to the solubility equilibrium from both sides. Dashed lines show the solubility range for 25°C, 100-140 p.p.m.  $\text{SiO}_2$ , as given by ALEXANDER, HESTON, and ILER (1954).

Curve I: Hot-spring water boiled to dissolve most of the silica. Initial total  $\text{SiO}_2$  320 p.p.m.; initial dissolved  $\text{SiO}_2$  284 p.p.m.; pH during run 7.7-8.3.

Curve II:  $\text{Na}_2\text{SiO}_3$  solution neutralized with HCl. Initial total  $\text{SiO}_2$  975 p.p.m.; initial soluble  $\text{SiO}_2$  544 p.p.m.; pH during run 7.3-7.9.

Curve III:  $\text{Na}_2\text{SiO}_3$  solution neutralized with HCl, aged and diluted. Initial total  $\text{SiO}_2$  187 p.p.m.; initial dissolved  $\text{SiO}_2$  25 p.p.m.; pH 8.3-7.4. Same as Curve I in Fig. 2.

Curve IV: Silica gel in distilled water. pH 5.2-5.6.



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conclusion is that the solubility of amorphous silica is *at least as great* in acid as in dilute alkali, so that leaching of silica need not be ascribed only to alkaline solutions.

Another observation of ALEXANDER *et al.*, that silica sols (with most of the dissolved silica removed) slowly disaggregate on standing—in other words, that amorphous silica in the form of colloidal particles dissolves just as it does in other forms—was likewise confirmed in the present experiments. The dissolved silica after a few weeks reaches a constant value in the range 100–140 p.p.m. (provided, of course, that at least this much silica was present originally). Representative data are shown in Table 2 and Fig. 2. Why the rate of dissolution should be greater for one set of sols than for the other is not clear; the slower rate is for hot-spring water, in which other dissolved material is present and in which the sol particles

Table 2. Disaggregation of silica sols

| pH  | Initial concentrations of silica |        | Dissolved silica after |         |         |         |         |         |         |
|-----|----------------------------------|--------|------------------------|---------|---------|---------|---------|---------|---------|
|     | Total                            | Dslvd. | 3 days                 | 10 days | 24 days | 38 days | 52 days | 68 days | 81 days |
| 8.2 | 150                              | 53     | 59                     | 66      | 78      | 90      | 93      | 95      | 98      |
| 7.9 | 75                               | 27     | 31                     | 36      | 51      | 62      | 64      | 68      | 70      |

*First run:* Temperature 22–27°C. Erlenmeyer flasks with cork stoppers. Solutions are diluted hot-spring water. All concentrations in parts per million of SiO<sub>2</sub>.

| pH  | Initial concentrations of silica |        | Dissolved silica after |         |         |         |         |          | Total after 35 days |
|-----|----------------------------------|--------|------------------------|---------|---------|---------|---------|----------|---------------------|
|     | Total                            | Dslvd. | 7 days                 | 15 days | 26 days | 35 days | 44 days | 151 days |                     |
| 7.4 | 187                              | 25     | 84                     | 99      | 108     | 109     | 112     | 113      | 180                 |
| 7.1 | 94                               | 13     | 47                     | 60      | 67      | 67      | 70      | 71       | 90                  |
| 6.9 | 47                               | 6      | 23                     | 30      | 34      | 36      | 37      | 39       | 46                  |

*Second run:* Temperature 22–27°C. Pyrex bottles with glass stoppers. Solutions made by ageing and diluting a Na<sub>2</sub>SiO<sub>3</sub> solution neutralized with HCl.

have had a much longer time to age (9½ years versus a few weeks). The similarity in solubility between silica gel and silica sols indicates a similarity in structure between these two forms of amorphous silica, as ALEXANDER *et al.* have pointed out.

A solubility equilibrium is clearly set up between dissolved silica and colloidal silica, and between dissolved silica and hydrous gelatinous silica. It is not altogether certain, however, that a true equilibrium is established with partly dehydrated silica gel, in the sense that silica coming out of solution deposits in partly dehydrated form on the gel surface. Quite possibly the reverse reaction in the equilibrium consists of silica coming out of solution in the form of colloidal particles which coalesce to form hydrous gelatinous masses. Such a postulate would explain the

appearance of gelatinous flakes in solutions that have stood in contact with the dehydrated gel for several weeks. It is even less certain that a true solubility equilibrium would be set up under laboratory conditions between opal and dissolved silica. ILER (1955, p. 15) expresses the opinion that under conditions of slow evaporation, silica may deposit on a solid surface in "a continuous dense layer of

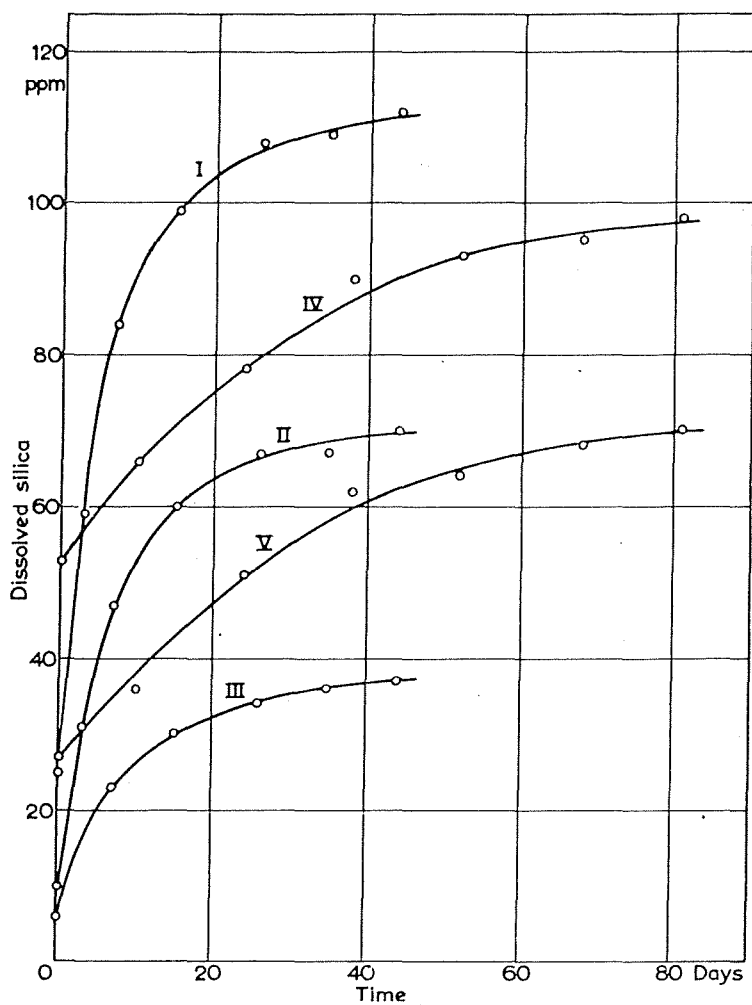


Fig. 2. Disaggregation of silica sols on standing. Data in Table I. Curves I, II, and III represent solutions made by ageing and diluting a  $\text{Na}_2\text{SiO}_3$  solution neutralized with HCl. Curves IV and V represent solutions made by diluting hot-spring water which had stood in a glass bottle for nearly ten years.

Curve I: Total silica 187 p.p.m. initially, 180 near end of run; pH 7.4-8.3. Final dissolved silica is in the solubility range of ALEXANDER, HESTON, and ILER (1954).

Curve II: Total silica 94 p.p.m. initially, 90 near end of run, pH 7.1-7.8. Final dissolved silica only 80% of total.

Curve III: Total silica 47 p.p.m. initially, 46 near end of run; pH 6.9-7.8. Final dissolved silica only 85% of total.

Curve IV: Total silica 150 p.p.m., pH 8.2. Final dissolved silica is close to solubility range of ALEXANDER, HESTON, and ILER.

Curve V: Total silica 75 p.p.m., pH 7.9. Final dissolved silica is 93% of total.

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anhydrous  $\text{SiO}_2$ ," but that if evaporation is rapid the silica will probably polymerize in the solution and deposit as a hydrated gel. Whether evaporation occurs or not, it seems probable that the deposition or nondeposition of anhydrous silica will depend on the rate of reaction and on the constancy of temperature, pressure, and concentration of electrolytes.

Table 3. Effect of gel on precipitation of silica, and influence of pH on rates of polymerization and precipitation.

|          | Filtered solution |        |     | Solution with gel |        |     |
|----------|-------------------|--------|-----|-------------------|--------|-----|
|          | Total             | Dslvd. | pH  | Total             | Dslvd. | pH  |
| Original | 332               | 332    |     | 332               | 332    |     |
| 1 day    |                   | 330    | 6.6 |                   | 304    | 6.8 |
| 4 days   |                   | 326    |     |                   | 262    |     |
| 8 days   |                   | 296    |     |                   | 214    |     |
| 14 days  |                   | 296    |     | 198               | 189    |     |
| 24 days  | 320               | 300    | 6.2 | 177               | 172    | 6.9 |
| 24 days  | 320               | 300    | 8.6 | 177               | 172    | 8.3 |
| 25 days  |                   | 268    | 8.0 |                   | 169    | 7.5 |
| 28 days  |                   | 210    | 8.0 |                   | 148    | 7.5 |
| 35 days  | 312               | 150    | 7.8 | 138               | 133    | 7.9 |

Temperature 22-27°C. Erlenmeyer flasks with cork stoppers. Solution obtained from dissolution of silica gel at 90°. First sample filtered, second left in contact with gel. pH changed on the twenty-fourth day by addition of NaOH solution. All concentrations in parts per million of  $\text{SiO}_2$ .

An experiment bearing on this problem is summarized in Table 3. The two solutions are identical except for the presence of grains of partly dehydrated gel in the second; the gel obviously speeded up the coagulation of the supersaturated dissolved silica. On the other hand, a few hydrous gelatinous flocs collected as the solution stood, so deposition of silica directly on the gel is not conclusively demonstrated.

*Rates of dissolution and polymerization.* No attempt was made to study rates in detail, but the apparent effects of various factors described in the preceding paragraphs are worth noting:

1. Dissolution of colloidal silica is faster than dissolution of silica gel (Curves III and IV, Fig. 1).
2. Disaggregation of aged sols is slower than disaggregation of freshly prepared sols (Fig. 2).
3. Polymerization of dissolved silica is speeded up by the presence of silica gel (Table 3, first two solutions).
4. Polymerization of dissolved silica is slower in acid than in base (Table 3, first solution, and Table 1, solutions III, IV, V).

Another effect on rate of polymerization is illustrated by Samples I, II, and V in Table 1. These solutions are all alkaline, and differ principally in the amounts of

silica present initially; evidently, the greater the original degree of supersaturation, the faster is polymerization. In a solution only slightly supersaturated (Sample V) the equilibrium concentration of dissolved silica had not been reached in over four months, whereas in a strongly supersaturated solution (Sample II) the equilibrium concentration was attained in less than two weeks. A similar relation between rate and degree of supersaturation has been noted by WHITE and BRANNOCK (1956) in hot-spring waters.

It will be shown presently that rates of both dissolution and polymerization are increased at high temperatures, and are faster in sea water than in fresh water.

*Silica gel at other temperatures.* By plotting the data of previous workers, ALEXANDER *et al.* show that the solubility of amorphous silica has a roughly linear relation to temperature. The graph is drawn through the points 400 p.p.m. at 94°C and 135 p.p.m. at 25°C, and is extrapolated to 40 p.p.m. at 0°C. The present experiments give 300-380 p.p.m. for the range 85-95° and 60-80 p.p.m. for the

Table 4. Solubility of amorphous silica at 90 ± 5°C and at 0-5°C.

|       | Dissolved silica after |        |        |         |         |         | Total   | pH     |
|-------|------------------------|--------|--------|---------|---------|---------|---------|--------|
|       | 1 day                  | 4 days | 8 days | 12 days | 18 days | 26 days | 18 days | 8 days |
| Blank | 2                      | 4      | 9      | 39      | 43      | 60      | 43      | 8.7    |
| Gel   | 193                    | 264    | 355    | 375     | 330     | —       | 330     | 7.9    |
| Opal  | 79                     | 136    | 161    | 165     | 194     | 334*    | 194     | 8.3    |

\* The bottle containing opal leaked excessively after 18 days, so that the last high reading may be an effect of concentration by evaporation more than of dissolution.

*At 90 ± 5°C:* Finely crushed opal and commercial silica gel placed in ordinary distilled water in glass-stoppered Pyrex bottles. Bottles shaken once daily. All concentrations in parts per million of SiO<sub>2</sub>.

| Dissolved silica after                    | 0 days | 8 days | 15 days | 23 days | 32 days |
|---|--------|--------|---------|---------|---------|
| Gel + distilled water                     | 0      | 22     | 36      | 46      | 56      |
| Na <sub>2</sub> SiO <sub>3</sub> solution | 312    | 96     | 88      | 85      | 84      |

*At 0-5°C:* First solution commercial silica gel in distilled water. Second solution prepared by neutralizing with HCl a Na<sub>2</sub>SiO<sub>3</sub> solution containing initially 1440 p.p.m. SiO<sub>2</sub>. Second solution clear for 15 days; then a heavy gelatinous mass collected on the sides and bottom of the bottle. Both solutions in glass-stoppered Pyrex bottles.

range 0-5°C (Table 4), and indicate 115 or 120 as a better average than 135 for 25°C. These figures would give a temperature-solubility curve lying a little below that of ALEXANDER *et al.*, and flattening markedly at its lower end.

LENHER and MERRILL's (1917) early determination of solubility at 90°C, 428 p.p.m., is somewhat higher than any of these figures, and the discrepancy is just as

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Dissolution and precipitation of silica at low temperatures

mysterious as for the figures at 25°C. HITCHEN's (1953) acceptance of LENHER and MERRILL's figures on the grounds that they lie on an extrapolation of his curve for higher temperatures is not adequate substantiation, because the smaller values fit the extrapolated curve equally well or better.

*Silica gel in sea water.* Applicability of the ammonium molybdate reaction to the determination of silica in sea water has been studied by CHOW and ROBINSON (1953). They find that the test is valid, but that for experimental conditions similar to those used in the present work apparent concentrations of silica must be multiplied by a "salt factor" of 1.23. The factor is the same in artificial and natural sea water, and is constant over a wide range of pH and silica concentrations. All values in Tables 5-9 for silica concentrations in sea water have been corrected by this factor.

Table 5. Solubility of amorphous silica in sea water.

|   | Dissolved silica after |        |        |         |         |         | Total   | pH     |
|---|------------------------|--------|--------|---------|---------|---------|---------|--------|
|   | 1 day                  | 3 days | 7 days | 13 days | 20 days | 28 days | 20 days | 7 days |
| At 22-27°C:                               |                        |        |        |         |         |         |         |        |
| Gel + artificial s.w.                     |                        | 37     | 65     | 101     | 102     | 105     | 105     | 5.9    |
| Gel + artificial s.w. + CaCO <sub>3</sub> |                        | 59     | 92     | 106     | 103     | 105     |         | 8.0    |
| Gel + natural s.w.                        |                        | 85     | 101    | 107     | 104     | 102     | 106     | 7.4    |
| At 85-95°C:                               |                        |        |        |         |         |         |         |        |
| Blank (artificial s.w.)                   |                        | 12     | 49     | 49      | 69      | 82      |         | 7.9    |
| Gel + artificial s.w.                     |                        | 305    | 286    | 308     | 283     | 304     |         | 6.9    |
| Diatomite + artificial s.w.               | 59                     | 89     | 181    |         | 244     | —       |         |        |

Artificial "sea water" prepared by dissolving 24 g NaCl, 11.5 g Na<sub>2</sub>SO<sub>4</sub> · 10H<sub>2</sub>O, and 10.5 g MgCl<sub>2</sub> · 6H<sub>2</sub>O to make one litre of solution. Natural sea water contains 35 p.p.m. SiO<sub>2</sub> dissolved from the soft-glass bottle in which it had stood several months. Experiments were carried out in glass-stoppered Pyrex bottles. Stirred once daily. Bottle with diatomite leaked after 20 days.

The solubility of silica gel in sea water (Table 5) is not significantly different from that in fresh water: 100-110 p.p.m. at 22-27° and 280-310 at 85-95°. The speed of dissolution is markedly greater, as was also observed by CHOW and ROBINSON (1953). No significant differences in rate of dissolution or in equilibrium concentration were noted between artificial sea water, natural sea water, and sea water with CaCO<sub>3</sub> added to keep the pH near 8.

DIÉNERT and WANDENBULCKE (1924) note that a silica sol containing 120 p.p.m. of SiO<sub>2</sub> becomes dissolved silica when placed in a 2% solution of marine salt

(roughly half the concentration of sea water), rapidly at 90° and over a period of more than seven days at 37°. TOURKY and BANGHAM (1936), although arguing for the existence of colloidal silica in very dilute solutions, record that sea water "appears to exert a peptizing action," for the silica in a dilute sol added to sea water gradually became colorimetrically determinable on standing. BRUEVIC (1953) also emphasizes that sea water, far from acting as a coagulant for silica, causes dilute sols to disaggregate.

*Opal.* Opal dissolves much more slowly than silica gel or colloidal silica, as might be expected from its smaller surface area. At room temperature, crushed opal in contact with distilled water dissolved only to the extent of 3 p.p.m. in two months, whereas silica gel reached its equilibrium solubility (110 p.p.m.) in a month and a half. At 90°C, crushed opal in distilled water yielded 194 p.p.m. after eighteen days, and diatomite in sea water yielded 244 p.p.m. after twenty days (compare with equilibrium solubility of silica gel, 300–380 p.p.m.; see Tables 4 and 5). At the ends of these periods bottles containing the opal and diatomite developed leaks, so that the runs were not carried to the establishment of equilibrium. The observed quantities in solution are large enough, however, to suggest that ultimate solubilities would be at least comparable with those for silica gel. This extrapolation also seems reasonable for lower temperatures. ILLER's (1955) compilation of solubility data, as mentioned above, gives further justification for assuming that all forms of amorphous silica, regardless of degree of hydration or surface area, have equilibrium solubilities within the same order of magnitude.

Opal occurs naturally in many different forms, and some of these forms give sufficiently definite X-ray patterns to suggest that the material has a crude regularity of structure approaching that of cristobalite. Very possibly, therefore, opal might show a greater range of solubility than other forms of amorphous silica, perhaps ranging all the way from that of silica gel to that of cristobalite (unknown). For the present, since no other data are known to the writer, the experiments described above will be taken to indicate that much opal at least has a solubility differing from that of silica gel by no more than a factor of 2.

The fact that diatomite is soluble in hot sea water implies that tests of dead diatoms and radiolaria are preserved in contact with sea water only by the extreme slowness of reaction at low temperatures (possibly even slower than normal because of adsorption of magnesium and/or aluminium on the surfaces). MURRAY and IRVINE (1891), in fact, have shown that siliceous remains are appreciably soluble in cold sea water containing  $\text{CaCO}_3$  and decaying organic matter. The solubility of opal lends support to the hypothesis suggested by BRAMLETTE (1946, p. 54) for converting diatomite to opaline chert by dissolution and redeposition of the silica; dissolution and deposition in approximately the same place can be explained by assuming a slight difference in solubility, due to difference in surface energy, between the delicate diatom structures and massive opal. The mystery is not how opaline chert forms, but why it does not occur more commonly in diatomite beds.

*Silica glass.* The low-temperature solubility of silica glass has not been recorded. Extrapolation of KENNEDY's (1950) results at high temperatures would indicate a much lower solubility than for other forms of amorphous silica; but KENNEDY himself (p. 653) questions whether equilibrium was attained toward the low end of

his temperature range. Silica glass, having the least surface area of the different forms of amorphous silica, would be expected to dissolve most slowly and to have the smallest solubility (ILER, 1955, p. 14); the difference in solubility probably would not be large, but prediction is hazardous from present data.

*Silicate ion or silicic acid?* The demonstration that silica in dilute solution is present largely as particles of molecular size leaves open a question as to which silicic acid makes up the particles and a further question as to how extensively the acid is ionized. The most reasonable formula for the acid is  $H_4SiO_4$ , rather than the often-suggested  $H_2SiO_3$ , simply because silicon in most of its compounds shows a co-ordination number of 4 (for a complete discussion, see e.g. ILER, 1955, p. 11-13, 18-19). Additional evidence is derived by MOSEBACH (1955) from KENNEDY's data, on the grounds that at higher temperatures the ratio (concentration of  $SiO_2$  vapour)/(concentration of water vapour)<sup>2</sup> is constant, suggesting an equilibrium reaction of the form  $SiO_2 + 2H_2O = H_4SiO_4$ . BRADY (1953), also on the basis of published data regarding the volatility of  $SiO_2$  in steam, concludes that in the vapour state  $H_4SiO_4$  predominates at high pressures and  $Si_2O(OH)_6$  at low pressures. The fact that the equilibrium solubility is little affected by pH up to values as high as 9 indicates that the acid is largely undissociated, an assumption consistent with the small first ionization constant of silicic acid (ca.  $10^{-10}$ , according to several investigators; see ALEXANDER *et al.*, 1954). In solutions more alkaline than pH 9 the ion  $H_3SiO_4^-$  becomes important, exceeding  $H_4SiO_4$  at a pH somewhat over 10 (ILER, 1955, p. 25). Other ions of the acid play a role only in solutions too alkaline to be of geologic interest.

*Summary.* Amorphous silica dissolves in water to the extent of roughly 70 p.p.m. at 0°C, 120 p.p.m. at 25°C, and 350 p.p.m. at 90°C. The solubility in sea water is not substantially different. A true solubility equilibrium is set up between  $H_4SiO_4$  molecules in the solution and either gelatinous silica or the colloidal particles of a sol. The reactions leading to equilibrium from either side are slow, so that nonequilibrium solutions can persist for days or weeks, or even for years at low pH's. Opal probably has about the same equilibrium solubility as other forms of amorphous silica, but its dissolution is extremely slow, especially at ordinary temperatures. The dissolved silicic acid is un-ionized except in fairly alkaline solutions.

In natural waters silica *may* be either colloidal or in true solution, but the colloidal particles are unstable and will disappear spontaneously in the course of a few days or weeks (provided total silica is less than about 100 p.p.m.). Hence the great majority of natural waters should have silica in true solution only, a conclusion corroborated by reports of commercial analysts that silica determined colorimetrically nearly always coincides with total silica (WEITZ, FRANCK, and SCHUCHARD, 1950; see also references cited by ROY, 1945).

The problems of dissolution of silica are by no means entirely solved, as witness (1) the necessity for stating solubility at a given temperature as a range rather than a specific value, (2) the inadequately explained differences in rate of dissolution from one solution to another, as illustrated by Figs. 1 and 2, and (3) the uncertainty about establishment of true reversible equilibrium with nonhydrous forms of amorphous silica. Despite these gaps in present knowledge, the geologically

important conclusion that silica at low concentrations forms a true solution rather than a colloid seems established beyond reasonable doubt.

#### THE PRECIPITATION OF SILICA

*General.* When an alkaline solution of silica is neutralized, or when a saturated solution at a high temperature is cooled, the silica normally does not precipitate, but remains in supersaturated solution. Over a period of weeks or months the supersaturated solution changes to a sol, until the amount of silica left in molecular form is equal to the equilibrium solubility of amorphous silica at the prevailing temperature. If the original solution is very concentrated or if the solution later becomes concentrated by evaporation, gelatinous silica will separate out or the entire solution may set to a gel. Fluid sols at concentrations of a few hundred parts per million, however, are remarkably stable.

In nature, the precipitation of silica by cooling and evaporation is observed on the aprons of many hot springs. Gelatinous silica is sometimes found in pools fed by such springs, and also has been reported from cavities and fissures underground (see references in HITCHEN, 1935). Of more general interest is the possibility of precipitation from cool, fairly dilute sols or from solutions containing only molecular silica; it is this kind of precipitation, presumably, which must account for the formation of most cherts and other siliceous sediments.

Since sea water contains much less silica than river water and since silica is known to form sols very readily, an attractive hypothesis can be set up according to which silica brought to the sea by streams is coagulated on contact with the electrolytes of sea water. From the preceding discussion one would hardly expect such a mechanism to play a significant role, except possibly locally where silica is brought to the sea in unusual amounts. Many geologists, however, assuming that most of the silica carried by rivers is colloidal, have tried to test experimentally the effect of sea water on various kinds of silica solutions. The results have been ambiguous and often contradictory, as might be expected if the slow changes that occur in laboratory solutions are not recognized. In an effort to clarify the situation, some of the older work will be discussed before the present experiments are described.

*Previous work.* TARR (1917) was the first to investigate in detail and to advocate strongly the hypothesis of origin of chert through coagulation of silica by electrolytes. He based the hypothesis on experiments in which gelatinous silica precipitated immediately when a silica solution was poured into sea water. Unfortunately, the experiments are only sketchily described. Silica was added "at the rate of 27 p.p.m.," but whether this figure refers to the original silica solution or to the final sea-water mixture is not clear. No later investigator has been able to duplicate TARR's results; MOORE and MAYNARD (1929), after thorough discussion, conclude that his silica solutions must have been more concentrated than he thought.

LOVERING (1923) found that sea water had no effect on  $\text{Na}_2\text{SiO}_3$  solutions containing 33 p.p.m.  $\text{SiO}_2$ , but that silica was precipitated from more concentrated solutions until 250 p.p.m. was left in solution (or suspension), provided that the amount of sea water added was in excess of 1 ml per 0.15 g of silica. The pH and time of standing are not recorded, but LOVERING's results may well mean that his more-concentrated solutions had 250-280 p.p.m. of silica in true solution, either because the pH was above 9 or because equilibrium had not been reached, and that the colloidal remainder of the silica was coagulated.



CORRENS (1926) used silica both in the form of "reine verdünnte Kieselsäuresole" (presumably purified by dialysis; concentration, pH, and time of standing not specified) and  $\text{Na}_2\text{SiO}_3$  solutions. The pure silica sols could not be flocculated by sea water (either natural or artificial) at pH's less than 10. When  $\text{Na}_2\text{SiO}_3$  solution was added drop by drop to sea water, immediate flocculation occurred after each drop for solutions more concentrated than 3000 p.p.m.; slight flocculation was visible after five days when solutions containing 2300 p.p.m. were added until the final concentration was 46 p.p.m.; and no flocculation occurred on adding solutions with 570 p.p.m. Details of preparation of the  $\text{Na}_2\text{SiO}_3$  solutions are not given, so the proportion of silica present as colloid cannot be guessed; nor is the time of standing specified for the more dilute solutions. CORRENS has apparently proved that solutions with many times more silica than ordinary streams show no flocculation in sea water, but has not perhaps made adequate allowance for a possible slow precipitation over a long period of time.

The most difficult of the previous work to reconcile with the present study is the often-cited paper of MOORE and MAYNARD (1939). Using solutions containing 30 p.p.m.  $\text{SiO}_2$ , both as  $\text{Na}_2\text{SiO}_3$  and as dialysed sols, and various electrolytes including sea salt (added as solids), these investigators report agreement with LOVERING and CORRENS that no precipitate forms immediately, but note the slow formation over periods of twenty-five and seventy-five days of a flocculent precipitate containing silica. The coagulation was never complete, mostly only a few percent, but in two experiments amounted to two-thirds of the original silica. The reactions were carried out in test tubes, and some reaction with the glass is indicated by the slowly increasing total silica (dissolved + precipitated). Other important experimental details are lacking—pH, temperature, amount of stirring, manner of preparing the silica solutions. But the details are hardly needed to make it evident that the silica was not behaving like a simple solution of monomeric silicic acid. MOORE and MAYNARD's conclusion seems amply justified, that the silica in these very dilute solutions was mostly or entirely colloidal.

To anticipate a little, experiments in the present study have confirmed MOORE and MAYNARD's observation that a small amount of precipitate appears in mixtures of dilute silica solutions ( $\text{SiO}_2$  less than 100 p.p.m.) and sea water, but have failed to confirm a progressive removal of silica from the solutions on standing. Up to the equilibrium solubility for amorphous silica at a given temperature, silica appears to be perfectly stable in sea water for periods of at least several months. The tiny flocs of gelatinous precipitate that form in such experiments remain a mystery. According to MOORE and MAYNARD, they increase in amount over a period of time; in the present experiments they appeared within a day or two, probably representing the coagulation of a precipitate that formed immediately on mixing, and thereafter did not change. Now, one may assume that the original solutions in both sets of experiments contained some colloidal silica, and that this was precipitated before its normal slow disaggregation could take place; but after several weeks the precipitate should redissolve, since the total silica in solution is well below the equilibrium concentration. Qualitative experiments described below suggest that the precipitate is in part a magnesium silicate rather than pure silica, hence less easily dissolved. But for present purposes the precipitate is a minor complication, and its nature was not studied in detail. The discrepancy with MOORE and MAYNARD's results remains unexplained, but certainly the present experiments give no indication that silica in true solution is affected by the electrolytes of sea water.

One other earlier paper needs discussion here. FRONDEL (1938), although not directly concerned with coagulation by sea water, argues for the colloidal nature of very dilute silica on the basis of experiments in which a dialysed sol containing 2000 p.p.m. of silica is diluted to 100 p.p.m. and remains colloidal. Proof of the colloidal nature rests on observation of particles with an ultra-microscope, and on coagulation of the silica when the solution is saturated with NaCl. The original dialysed sol was of course almost exclusively colloidal, and dilution would not immediately alter the colloid, so that FRONDEL's observations are entirely consistent with the preceding discussion. If he had allowed the 100-p.p.m. solution to stand for a few weeks before testing its colloidal nature, however, his conclusions would doubtless have been very different.

Thus the discordant observations in previous papers can be partly reconciled on the basis of failure to take account of the slow reactions involved in the silica solubility equilibrium. MOORE

and MAYNARD's report of slow removal of silica from dilute solution by electrolytes cannot be so explained, but this observation could not be confirmed by the present experiments.

*Experiments.* The general behaviour of silica solutions when added to sea water is illustrated by Tables 6 and 7. In each experiment a part of the silica was dissolved and a part colloidal; the salt concentration was adjusted to make the final quantity equivalent to that in sea water.

Table 6. Silica solutions added to sea water.

|                                 |     |      |      |     |      |     |
|---------------------------------|-----|------|------|-----|------|-----|
| Initial total SiO <sub>2</sub>  | 264 | 264  | 264  | 132 | 132  | 66  |
| Initial dslvd. SiO <sub>2</sub> | 234 | 234  | 234  | 117 | 117  | 59  |
| Initial pH                      | 4.9 | 7.1  | 9.2  | 5.6 | 7.8  | 8.2 |
| pH after 74 days                | 5.3 | 6.9  | 7.6  | 6.1 | 7.1  | 7.3 |
| Dslvd. SiO <sub>2</sub> after   |     |      |      |     |      |     |
| 1 hour                          | 234 | 206* | 148* | 104 | 108  | 53  |
| 6 hours                         | 224 | 203  | 123  | 114 | 114  | 53  |
| 48 hours                        | 224 | 194  | 111  | 114 | 114  | 58  |
| 14 days                         | 224 | 153  | 111  | 117 | 112* | 60* |
| 40 days                         | 209 | 142  | 120  | 113 | 111  | 60  |
| 74 days                         | 199 | 132  | 129  | 111 | 108  | 60  |
| 95 days                         | 201 | 132  | 123  | 113 | 111  | 59  |
| Total SiO <sub>2</sub> after    |     |      |      |     |      |     |
| 74 days                         | 275 | 141  | 129  | 138 | 116  | 63  |

\* Asterisks indicate that formation of a gelatinous precipitate was noted, copious in first two and very slight in last two.

Temperature 22-27°C. Erlenmeyer flasks with cork stoppers. Silica solutions prepared by adding HCl to Na<sub>2</sub>SiO<sub>3</sub> solution. Salt concentration (NaCl + MgCl<sub>2</sub> + Na<sub>2</sub>SO<sub>4</sub>) equivalent to sea water. All concentrations in parts per million of SiO<sub>2</sub>.

Table 7. Silica solutions added to sea water.

|   |     |     |     |    |    |    |
|---|-----|-----|-----|----|----|----|
| Theoretical total SiO <sub>2</sub> , including precipitate  | 464 | 232 | 116 | 58 | 29 | 15 |
| Initial dissolved SiO <sub>2</sub>                          | 230 | 115 | 58  | 29 | 14 | 7  |
| Measured total SiO <sub>2</sub> , not including precipitate | 172 | 165 | 96  | 46 | 25 | 14 |
| Measured dissolved SiO <sub>2</sub>                         | 157 | 142 | 74  | 38 | 20 | 10 |

Changes in most concentrated solution on standing

|                            | Initial | 1 day | 10 days | 25 days |
|----------------------------|---------|-------|---------|---------|
| Total SiO <sub>2</sub>     | 172     | 165   | 134     | 127     |
| Dissolved SiO <sub>2</sub> | 157     | 146   | 128     | 127     |

Temperature 22-27°C. Large Pyrex test tubes. Na<sub>2</sub>SiO<sub>3</sub> solutions made up by diluting solution containing 928 p.p.m. total SiO<sub>2</sub> and 460 p.p.m. dissolved SiO<sub>2</sub>. Artificial sea water prepared as in Table 5, but twice as concentrated. At each dilution, 10 ml. Na<sub>2</sub>SiO<sub>3</sub> solution added to 10 ml. concentrated sea water, so final salt concentration equals that of sea water. pH's all adjusted to 8.0-8.4. First three solutions analysed within one hour after precipitation, last three after five hours. Visible precipitate in all except last sample.

Dissolution and precipitation of silica at low temperatures

The experiments show clearly that the dissolved part of the silica is not affected unless its concentration is greater than the equilibrium value (100-140 p.p.m.). All or part of the colloidal silica is coagulated, the fraction being greater if the initial concentration is large and if the pH is high. In solutions at pH's over 7, high concentrations of dissolved silica are reduced to the equilibrium solubility in a day or so, but at pH's less than 7 the solution may remain supersaturated for months (see, for example, the first column of Table 6). In acid solutions the coagulation of colloidal silica is also very slow. These results are consistent with observations cited by ILER (1955, p. 46) that both the polymerization of monosilicic acid and the gelling of colloidal silica are slow at low pH's. Once the amount of dissolved silica has reached the equilibrium solubility, it shows no further change (except for minor fluctuations probably in response to temperature changes), in disagreement with MOORE and MAYNARD's statement that the silica in solution steadily decreases.

To try experiments more closely similar to those of MOORE and MAYNARD, samples were prepared containing 35-45 p.p.m. of SiO<sub>2</sub> in solutions with a salt content and pH equal to those of sea water, and differing in the initial ratio of dissolved to colloidal silica (Table 8). Over a

Table 8. Dilute silica solutions added to sea water.

|                          | High dissolved silica |    | Low dissolved silica |     | NaCl solution |
|--------------------------|-----------------------|----|----------------------|-----|---------------|
| Initial total            | 39                    | 19 | 39                   | 19  | 19            |
| Initial dissolved        | 39                    | 19 | 6.4                  | 3.2 | 3.2           |
| Dissolved after 6 hours  | 39                    | 19 | 15                   | 6.8 | 6.8           |
| Dissolved after 24 hours | 39                    | 20 | 23                   | 12  | 13            |
| Total after 24 hours     | 40                    | 21 | 25                   | 11  | 12            |
| Dissolved after 5 days   | 38                    | 20 | 39                   | 20  | 20            |

Three similar solutions allowed to stand 40 days

|               | Total | Dslvd. | Total | Dslvd. | Total | Dslvd. |
|---------------|-------|--------|-------|--------|-------|--------|
| Initial       | 49    | 5      | 50    | 33     | 55    | 48     |
| After 40 days | 59    | 54     | 53    | 44     | 56    | 49     |

Temperature 22-27°C. Glass-stoppered Pyrex bottles. Final salt concentration equivalent to sea water. Solution with low dissolved silica prepared by ageing and diluting a neutralized Na<sub>2</sub>SiO<sub>3</sub> solution. Solution with high dissolved silica prepared by boiling and diluting an alkaline Na<sub>2</sub>SiO<sub>3</sub> solution. Slight precipitation visible in all bottles; more abundant in solutions with low initial dissolved silica. All pH's in range 8.0-8.4.

period of two days a very small amount of gelatinous precipitate formed in each bottle, more slowly in the ones with least colloidal silica initially. On standing for several weeks, there was no change in the amount of precipitate; the total silica appeared to increase slightly, presumably because of reaction with the glass; the colorimetric silica increased to 85-100% of the total silica, and thereafter remained constant.

The nature of the precipitate was investigated only by a few qualitative tests. The amount of the precipitate appears to be larger if a considerable fraction of the original silica is colloidal, if the solutions are mixed rapidly, and if the pH of the mixture is permitted to rise above 10 before adjustment; by boiling the silica to insure complete depolymerization of the colloid and by adding it slowly while the pH is maintained in the range 7.8-8.8, the precipitate can be reduced in amount, but not eliminated completely. If the precipitate (from a fairly concentrated silica

solution) is filtered, washed, and placed in distilled water, it yields silica to the water much more slowly than does silica gel. If some of the washed precipitate is heated with HF and H<sub>2</sub>SO<sub>4</sub>, and if the residue is dissolved and tested with NH<sub>3</sub> and NaH<sub>2</sub>PO<sub>4</sub>, a white precipitate shows the presence of magnesium. These observations indicate that the precipitate is not silica alone, but possibly a mixture of silica and a hydrous magnesium silicate, as suggested for similar precipitates by MURRAY and IRVINE (1891) and by MOORE and MAYNARD themselves for the precipitate obtained on adding magnesium salts to dilute silica solutions. This suggestion does not completely explain the behaviour of the precipitate, but further investigation did not seem pertinent to the present study.

Table 9. Effect of calcite, clay, and ferric oxide on the coagulation of silica.

| Substance added                    | Artificial sea water |                                |        | Distilled water |                   |                                |
|------------------------------------|----------------------|--------------------------------|--------|-----------------|-------------------|--------------------------------|
|                                    | CaCO <sub>3</sub>    | Fe <sub>2</sub> O <sub>3</sub> | Kaolin | Montmor         | CaCO <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> |
| Initial total SiO <sub>2</sub>     | 132                  | 132                            | 1060   | 1060            | 1270              | 1270                           |
| Initial dissolved SiO <sub>2</sub> | 111                  | 111                            | 133    | 133             | 124               | 124                            |
| Initial pH                         | 8.1                  | 7.8                            | 7.4    | 8.3             | 8.1               | 8.2                            |
| pH after 40 days                   | 8.1                  |                                | 6.2    | 8.0             | 8.1*              | 7.2*                           |
| Dissolved SiO <sub>2</sub> after   |                      |                                |        |                 |                   |                                |
| 2 days                             | 113                  | 105                            | 130    | 144             | 1088†             | 488†                           |
| 14 days                            | 114                  | 102                            | 128    | 139             | 121               | 115                            |
| 40 days                            | 117                  | 102                            | 125    | 132             |                   |                                |
| 71 days                            | 114                  | 104                            | 124    | 129             |                   |                                |
| 95 days                            | 116                  | 105                            |        | 128             |                   |                                |
| Total after 40 days                | 123                  | 104                            | 1270   | 1030            | 1032*             | 540*                           |

\* After 14 days.  
 † Total SiO<sub>2</sub>.

Temperature 22-27°C. Erlenmeyer flasks with cork stoppers. Ferric oxide precipitated in the solution by adding FeCl<sub>3</sub> and adjusting pH. Calcite, kaolinite, and montmorillonite added as finely divided solids. All concentrations in parts per million of SiO<sub>2</sub>.

To see whether the precipitation of silica might be affected by other suspended materials, experiments were tried with added montmorillonite, kaolin, calcite, and hydrous ferric oxide (Table 9). None of these substances reduced the concentration of dissolved silica below the equilibrium value in two months' time, but ferric oxide co-precipitated much of the colloidal silica (in agreement with MOORE and MAYNARD, 1929). Calcite had little effect on the coagulation of silica.

*Discussion and summary.* Dissolved silica in basic solution, according to these experiments, is not coagulated by sea water, nor is stable indefinitely in concentrations up to the equilibrium values determined by dissolving amorphous silica directly. Colloidal silica precipitates on addition to sea water, and dissolved silica in supersaturated solution is polymerized and precipitated. Both the polymerization and precipitation are much faster in basic than in acid solutions. Even in basic solution the precipitation is not immediately complete, but requires several days or weeks to attain a steady state.

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As an explanation for the behaviour of colloidal silica, EITEL (1954, p. 317) described the alkaline sols, which are more easily precipitable by electrolytes, as "hydrophobic," and the acid sols, which are little affected by electrolytes but form gels more readily when concentrated, as "hydrophilic"; but these terms are hardly more than names for the phenomena observed. ILER, (1955, pp. 41, 42), on the basis of more recent work, suggests that the colloidal particles in alkaline solution are negatively charged, hence susceptible to neutralization by cations, while in acid solution the particles are largely uncharged but kept from precipitating by the scarcity of  $\text{OH}^-$  to act as a catalyst.

A question which the experiments leave unanswered is whether colloidal silica in a solution with only traces of electrolyte is indefinitely stable. Solutions containing 1000 p.p.m. or more of  $\text{SiO}_2$  showed a very gradual decrease in total silica on standing, at a rate of the order of a few tens of parts per million in several months, and most of the hot-spring samples described by WHITE, MURATA, and BRANNOCK (1956) also showed a slight falling off in total silica. On the other hand, laboratory solutions with pH's below 7 containing a few hundred p.p.m. of colloidal  $\text{SiO}_2$  did not change detectably, and a few of the hot-spring samples retained nearly their original amount of colloidal silica after several years' standing. While the theoretical question about the stability of colloidal silica remains unanswered, these observations suggest that its coagulation in the absence of fairly concentrated electrolytes is so very slow that transportation of silica in this form may locally be of geologic importance.

The experimental results agree with most previous work, the outstanding exceptions being CORRENS's (1926) statement that colloidal silica is not precipitated by sea water at pH's below 10, and MOORE and MAYNARD's (1929) conclusion that silica even in very dilute solution is progressively coagulated over a period of several weeks. On these points the experiments simply disagree, and the discrepancy remains unexplained. Also unexplained are certain details in the present experiments, such as the small amount of apparently insoluble precipitate that appears in dilute solutions and the common failure of colorimetrically determined silica to be quite equal to total unprecipitated silica. But the important conclusion for present purposes—and about this the experiments leave no room for doubt except by appeal to unknown processes acting over periods longer than several weeks—is that silica in concentrations up to several tens of parts per million is completely stable in contact with the electrolytes of sea water.

#### CONTROL OF SILICA IN NATURAL SOLUTIONS

If amorphous silica is soluble to the extent of 100 p.p.m. at ordinary temperatures and 70 p.p.m. at  $0^\circ$ , and if colloidal silica is stable enough so that it can readily be transported in excess of its solubility, then how does it happen that silica concentrations in most surface waters are so small? River water and ordinary groundwater have silica contents in the range 5–30 p.p.m., occasionally higher (CLARKE, 1924, pp. 68–109 and 184–201); connate water commonly has 20–60 p.p.m. (D. E. WHITE, personal communication). These waters are in contact with silica and with weathering silicates much of the time, so one might expect that they would normally be saturated or more than saturated.

The explanation must depend on many factors, some of them difficult to evaluate. The only kind of silica that dissolves with appreciable speed at ordinary temperatures is silica gel, which is probably not common in nature. Any crystalline form of silica would give much less than 100 p.p.m., even if contact were prolonged until equilibrium was established. Opal would (probably) provide on the order of 100 p.p.m. eventually, but the reaction is exceedingly slow, and opal is not of common occurrence. The weathering of silicates presumably results in soluble silicic acid (CORRENS, 1949) but this again is a very slow process: also significant is the formation of monomeric silica by the action of salt solution on several silicate minerals (GARDNER, 1938) and by the action of HCl on olivine (WEITZ, FRANCK, and SCHUCHARD, 1950). Silica is extracted from solution at least locally by fresh-water diatoms; the role of fresh-water sponges in removing silica from Lake Baikal is emphasized by BOTINTSEV (1948). The combination of slow reactions, dilution by rainwater, possible approach to equilibrium with crystalline silica, and removal by organisms is probably sufficient to explain the scarcity of saturated silica solutions in nature.

A more difficult problem is the extremely low concentration in sea water. Experiments show that the electrolytes of sea water have no effect on soluble silica; why then does not silica brought to the sea simply accumulate to a concentration of 70-100 p.p.m.? Diatoms and radiolaria are an obvious answer for near-surface waters, where the silica content is known to fluctuate seasonally (0.5-2 p.p.m.) as the plankton population waxes and wanes. The capacity of diatoms for removing silica is impressively demonstrated by the experiments of JØRGENSEN (1953), in which two species reduced silica concentrations from initial values of 0.65-1.25 p.p.m. to the range 0.065-0.085 p.p.m. The silica-secreting plankton build their shells out of opal, and evidently have a capacity for maintaining this material in contact with a medium which should dissolve it: HERR (1955, p. 16) guesses that this is accomplished either by the adsorption of  $Mg^{++}$  or by the formation of organo-silicon complexes on the surface. The ability to keep opal from dissolving is presumably lost when the organisms die, and the shells should start to dissolve as they sink into the sea. But the dissolution of opal is exceedingly slow at ordinary temperatures and still slower at the near-freezing temperatures of the deep ocean, so that diatom and radiolarian remains can accumulate on the ocean floor; that some dissolution does occur is indicated by the absence of the more delicate shells of diatoms from deposits below a depth of 5700 metres (SVERDRUP *et al.*, 1946, p. 978). Deep-ocean water has a higher silica content (5-10 p.p.m.) than surface water, which is another indication that siliceous shells dissolve. But seemingly the concentration should be higher: the ocean remains in contact with diatom and radiolarian deposits for geologic periods, and surely this should be long enough for even the slow dissolution of opal to approach equilibrium.

Three factors, none of which can be quantitatively evaluated, may play a role in keeping the silica content low. (1) If the circulation of the ocean is rapid enough compared with the rate of dissolution of opal, the silica may be steadily depleted as the deep water is brought up into the plankton-rich surface layers. (2) Siliceous sponges, which are not limited to the zone of light penetration, may remove large

amounts of silica; an indication of the importance of sponges is given by the abundance of sponge spicules in some European cherts (CORRENS, 1949) and in cherts of the Phosphoria formation (CRESSMAN, 1955, p. 25). (3) Some silica is removed in the formation of authigenic silicates, such as glauconite, phillipsite, and illite. Whether silica in the clay fraction of marine sediments is largely derived from sea water or from detrital clay particles is not known, but there is no clear evidence against the assumption that large amounts of silica could be removed in this manner. A similar suggestion regarding the possible removal of dissolved silica by reaction with  $\text{Al}(\text{OH})_3$  has been made by MURRAY and GRAVENOR (1953).

These considerations have an obvious application to the old problem of the origin of chert. TARR's (1917) hypothesis of inorganic origin by the flocculation of silica colloids must be abandoned, except locally where concentrated silica solutions were poured into the sea during volcanic episodes (e.g., the cherts commonly associated with pillow lavas). The hypothesis of diagenetic alteration of deposits initially composed of siliceous organic remains, elaborated by BRAMLETTE (1946) for the specific example of the opaline cherts in the Monterey formation and suggested in more general terms by CORRENS (1926, 1949), is in good agreement with the behaviour of silica as here outlined. Some chert is clearly of later replacement origin, as is emphasized by VAN TUYL (1918) and by PETTIJOHN (1949, p. 328-332). The relative importance of diagenesis and later replacement is still a matter of argument.

#### SUMMARY

Experiments on natural and artificial silica solutions, together with experimental results reported in recent chemical literature, lead to the following conclusions about the behaviour of silica in geologic environments:

(1) Amorphous silica is soluble to the extent of 60-80 p.p.m. at  $0^\circ$ , 100-140 p.p.m. at  $25^\circ$ , and 300-380 p.p.m. at  $90^\circ$ . This is true solution (molecular dispersion), not colloidal dispersion. Most or all of the dissolved silica is in the form of monosilicic acid,  $\text{H}_4\text{SiO}_4$ . The crystalline forms of silica have lower solubilities, quartz least of all.

(2) The solubility of amorphous silica is little affected by changes of pH in the range 0-9, but increases rapidly as the pH rises above 9. In other words, silica is no more soluble in very dilute alkali than in acid, contrary to a common geologic assumption. Silicate ion is present in appreciable amounts only at pH's over 9; in more acid solutions the silicic acid is essentially un-ionized.

(3) When a supersaturated solution of silica is prepared, either by cooling a saturated solution or by neutralizing an alkaline silicate solution, the silica ordinarily does not precipitate, but in time becomes a colloid. In concentrated solutions the colloid may eventually precipitate out as flocculent masses (in weakly basic solutions) or may set to a gel (in weakly acid solutions). In dilute solutions the colloid is a colourless, transparent sol, remarkably stable with respect to long standing, to temperature changes, and to mechanical disturbances.

(4) A silica sol with a total  $\text{SiO}_2$  content less than the solubilities given in (1) above gradually disaggregates until all the silica is in true solution as  $\text{H}_4\text{SiO}_4$ .

A sol with total  $\text{SiO}_2$  greater than these solubilities disaggregates until the equilibrium amount of  $\text{H}_4\text{SiO}_4$  is in solution together with the remainder of the sol. In other words, equilibrium is established between sol particles and silica in true solution, the equilibrium amount in solution being the same as that for other forms of amorphous silica.

(5) The processes of dissolution and polymerization of silica in dilute solution are slow. At ordinary temperatures silica gel requires several weeks to reach solubility equilibrium; opal dissolves so slowly that equilibrium probably is not reached for years. Supersaturated solutions require days or weeks to form sols and to establish equilibrium between the dissolved and colloidal fractions; in acid solutions the period may be months or years. The sluggishness of reaction means that non-equilibrium solutions—both supersaturated solutions and solutions containing colloidal silica well below the equilibrium solubility—may exist long enough to be of geologic interest. All the rates are enormously faster, of course, at temperatures near the boiling-point.

(6) Colloidal silica may be precipitated by evaporation, by co-precipitation with other colloids, and by fairly concentrated solutions of electrolytes. Precipitation by electrolytes is fastest in basic solution and extremely slow in solutions with a pH less than 6. Silica in true solution is not affected by either electrolytes (except for possible precipitation of metal silicates) or other colloids, unless the solution is supersaturated; in this case only the amount of silica in excess of the equilibrium solubility is precipitated.

(7) By comparison with the other rates, the coagulation of a silica sol by electrolytes is fast. This means that a silica precipitate may appear in a mixture of solutions containing far less than the saturation concentration, provided that a part of the silica originally was colloidal. Herein lies the explanation for some alleged "proofs" that silica in very dilute solution is always colloidal.

(8) Amorphous silica has about the same solubility in sea water as in fresh water. Silica below the equilibrium solubility is in true solution, and is not precipitable by the electrolytes of sea water, or by suspended solids like calcite, iron oxide, kaolinite or montmorillonite. The dissolved silica may, however, be used by organisms, and under favourable conditions may be reduced by this means to a figure only a thousandth of the equilibrium concentration.

(9) Silica is added to natural waters by (1) volcanoes and springs associated with volcanic activity, and by (2) dissolution of silica and silicates during weathering. Probably most of the silica from weathering is in true solution. Volcanic and hot-spring silica may be initially in true solution, but, if the concentration is high, will partly change to the colloidal form as the solutions cool. Colloidal silica may also form in natural waters by partial evaporation. Thus both dissolved and colloidal silica may be expected in natural waters, but the former is by far the more common.

(10) The silica in most stream water, being in true solution, is *not* coagulated on contact with sea water. Where hot springs supply silica to the sea in large amounts, precipitation of the colloidal part of the silica will take place, but this should be a rare and local phenomenon.

(11) The undersaturation of most terrestrial waters with silica can be attributed

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to the slowness with which silica and the silicates dissolve and to the activity of organisms which use silica. The very great undersaturation of sea water may also be plausibly ascribed to organisms, particularly diatoms, radiolaria, and siliceous sponges. Extremely slow attainment of solubility equilibrium with crystalline forms of silica and with authigenic silicates may also play a role.

(12) The origin of chert in marine sediments cannot be accounted for by inorganic precipitation, except locally near volcanic centres. The accumulation of siliceous organic remains, followed by partial dissolution and redeposition of the silica, is consistent with the properties of silica just outlined. Later introduction of silica from widely circulating solutions is also a possible mechanism for some cherts.

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