Influence of CO₂ on silica in solution*

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Abstract—Laboratory experiments show that H₄SiO₄ (monomeric silica) up to 80ppm in seawater is stable under all CO₂ pressures from 0 to 17.2×10^3 kg/m². CaCO₃, AlCl₃·6H₂O, MgCl₂, and standard clays, when added individually, did not remove silica from solutions containing silica from 50 to 80ppm under these CO₂ pressures. Addition of CaCO₃ and AlCl₃·6H₂O together, however, removed silica from solution in inverse proportion to the CO₂ pressure. CO₂ serves to inhibit the removal of silica from solution containing CaCO₃ and aluminum chloride. The CaCO₃ functions as a buffer to maintain the acid to neutral pH. The final reaction appears to follow:

In an open system, where CO₂ can escape to the atmosphere, the removal of silica from solution is controlled by the available AlCl₃·6H₂O and CaCO₃. Electron microscopy and infrared analyses confirm that the principal precipitates were clayey sediments and trace amounts of sepiolite. This suggests an intimate interrelationship between the geochemical cycles of carbon dioxide, calcium carbonate, aluminum, and silica in nature.

INTRODUCTION

The transformation of crustal rocks into sediments and various dissolved constituents is the core of the continental geochemical cycle. By-products of this process are the formation of seawater and the atmosphere. The gross aspects of continental weathering are well understood; however, the processes of accumulation of the dissolved constituents in seawater and cycling of gases in the atmosphere are not clear. Particularly puzzling is the chemical history of the ocean waters and the vast amounts of authigenic silicon sediments formed in the oceans (BONATTI, 1963). The genesis of these sediments is not clearly understood.

SILLÉN (1961) proposed that the oceans represent the salt of a huge acid-base titration, the bases originating as metals from crystalline rocks and the acids as volcanic emanations. He suggested the following equations for the reaction:

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In the steady state ocean system the dissolved ionic products must be removed as rapidly as they are produced, so it follows that silica, too, must be rapidly removed from the ocean water. MACKENZIE and GARRELS (1966) calculated that the large quantity of HCO_3^- carried by freshwater into the ocean, if not removed, would turn the ocean into an alkaline lake. They proposed that silica and HCO_3^- in the ocean react with amorphous silicates to form new clay minerals and CO_2 . SILLÉN (1961) and GARRELS (1965) suggested that silicates play an important role in buffering the ocean, and PYTKOWICZ (1967) pointed out that this perhaps is true in terms of geological ages; however, for spans not exceeding 1,000y calcium carbonate is the dominant buffer.

In summary, it seems that an intricate and delicate balance between the species, carbon dioxide, calcium carbonate, silica and silicates, occurs in nature. Although the cycling of carbon dioxide, calcium carbonate, and silica is also influenced by biogenic activity, the importance of chemical control cannot be overemphasized. During the Precambrian, prior to the appearance of life, formation of the oceans and atmosphere must have been controlled by physicochemical reactions. To elucidate the behavior of silica in a prebiotic solution containing CO_2 , calcium carbonate, silicates, and aluminum, a series of experiments was conducted; the results with respect to the CO_2 -silica system are described in this paper.

Removal of silica from solution by other than biological mechanisms has been studied by many investigators. Possible precipitation of silica from solution by reaction with Al^{3+} has been postulated by KRAUSKOPF (1959). The effect of 1 atm CO_2 over a neutral solution supersaturated with silica at room temperature, as contrasted to 1 atm air, was determined over a period of five months by LOVERING and PATTEN (1962). They reported that 1 atm of CO_2 caused precipitation of about two-thirds of the total silica from supersaturated solutions, but did not appreciably affect the concentration of monomeric silica. They observed no differences in the precipitation of silica gel in the presence of calcite and dolomite with and without increase in CO_2 pressure. Removal of silica by hydroxide from solution containing 150mg/l SiO_2 has been demonstrated by experiments conducted by SIFFERT (1962). HÉNIN and CAILLÉRE (1963), and GASTUCHE (1964) concluded that one of the prerequisites for the formation of aluminosilicate minerals from solutions containing silica is the presence of a gibbsite or pre-gibbsite type structure. Formation of hydroxide-silicates from solutions containing 3mg/l silica and 0.3mg/l aluminum oxide has been reported by HARDER (1964). He noted that removal of silica by adsorption depends on temperature, Al/Si ratio in solution, and the physical condition of crystallization. POLZER *et al.* (1967) reported that crystalline aluminosilicate resembling a kaoline-type mineral can be produced from dilute solutions of aluminum and silica at low temperature and pressure. The mineral formed had a molar ratio of aluminum to silica near unity and remained so even when silica concentration in solution exceeded that of aluminum by a factor of between 10 and 100.

EXPERIMENTAL

Organic free synthetic seawater used in this study was prepared from "Rila" marine mix (Rila Products, Teaneck, N. J.). Solutions containing 80ppm silica as sodium metasilicate dissolved in synthetic seawater and distilled water were prepared, adjusted to pH 7.8, transferred to one-liter Pyrex bottles, and stored for six months. At the end of six months, the silica concentrations were identical with the original solutions.

Solutions containing 50 and 80ppm silica in synthetic seawater and distilled water were prepared. The pH of these solutions was adjusted to 7.8 and allowed to stabilize. At the end of the two months the pH and the silica concentrations were measured. Four sets of 12 Pyrex bottles, each containing 500ml of solution, were arranged so that each set included three bottles containing 0, 50 and 80ppm silica in distilled water, three bottles containing the same concentration as above with sand added, and six bottles with similar combinations in seawater. The Ottawa quartz sand, prior to addition, was washed with dilute HCl and distilled water. Three of these four sets were connected in series and CO₂ introduced to one end so that the carbon dioxide pressure of 17.2×10^3 kg/m² in the first set, 13.7×10^3 kg/m² in the second set, and 10.2×10^3 kg/m² in the third set was maintained. The carbon dioxide pressure and flow in each set were controlled by mercury columns and a gas valve attached at the end of the set. The bottles to be subjected to CO₂ pressure were flushed with CO₂ gas to displace air at the beginning of each experiment. Air was circulated continuously during the experiments through the fourth set. The samples in the bottles were shaken periodically and samples for silica analyses were withdrawn at intervals over a period of seven weeks. The samples withdrawn were immediately diluted and silica in solution was measured.

At the end of seven weeks one gram of calcium carbonate was added to each bottle in all four sets, and then silica was monitored for another five weeks. At the end of this period, 0.5g AlCl₃ · 6H₂O was added to each bottle and silica in solution was measured over a period of six months.

The second experiment was run under similar conditions using only seawater with 50 and 80ppm silica in solution and in the absence of quartz sand. Removal of silica from solutions of various concentrations by the addition of calcium carbonate, aluminum chloride, magnesium chloride, kaolinite, montmorillonite, and illite (standard API clays) under various carbon dioxide pressures was monitored.

Under atmospheric conditions the removal of silica from solutions containing up to 80ppm silica was monitored following the addition of successive increments of AlCl₃ · 6H₂O in the presence of 2ppt CaCO₃, and also following successive increments of CaCO₃ in the presence of 2ppt AlCl₃ · 6H₂O. The pH of the solutions during the experiments was also monitored. Precipitates formed by addition of CaCO₃ and AlCl₃ ·

$6\text{H}_2\text{O}$ to the seawater and distilled water containing silica were removed by filtration and examined with petrographic and electron microscopes, X-ray diffraction, and infrared analyses. For each experiment, seawater and distilled water containing silica and without minerals were monitored as control, to determine the effects that suspended material and leaching of silica from bottles might have on this system.

RESULTS AND DISCUSSION

Seawater and distilled water containing up to 80ppm silica in solution were found to be stable under normal atmospheric conditions; the precipitation of silica from these solutions did not occur over a period of six months. Silica in distilled water and seawater in the same concentration was also stable under carbon dioxide pressure up to $17.2 \times 10^3 \text{ kg/m}^2$. The presence of quartz sand which may offer nucleation for the precipitation of silica did not remove silica from the above solutions either under atmospheric conditions or under carbon dioxide pressure. The addition of a large quantity of powdered calcium carbonate (2,000ppm) in the above solution also did not precipitate silica. The simultaneous additions of calcium carbonate and aluminum chloride, however, removed silica as a precipitate from both solutions and the percentage removal of silica was inversely related to the carbon dioxide pressure (Fig.1). Approximately 80% of the silica was removed after one week.

The individual addition of magnesium chloride, aluminum chloride, standard API

Fig.1. Removal of silica from seawater and distilled water containing silica (50 and 80ppm) with sand and without sand, 2ppt calcium carbonate, and 1ppt aluminum chloride under carbon dioxide pressure.

montmorillonite, kaolinite, and illite did not remove silica from seawater under atmospheric conditions or under elevated carbon dioxide pressure. The addition of calcium carbonate to these solutions with illite and aluminum chloride resulted in the precipitation of silica. In the case of illite, silica precipitated only under atmospheric conditions and the amount precipitated was less than 10% of the initial concentration. In the case of aluminum chloride and calcium carbonate the removal of silica was similar to that observed earlier.

The effects of relative concentrations of calcium carbonate and aluminum chloride on silica precipitation in seawater were studied under atmospheric conditions. Successive amounts of aluminum chloride when added to solutions containing silica and calcium carbonate resulted in the precipitation of silica in proportion to the amounts of aluminum chloride added, till complete precipitation occurred. Similarly, the addition of calcium chloride in solutions containing silica and aluminum chloride removed silica in proportion to the amounts of calcium carbonate added. The changes in the pH of the solutions are shown in Figs. 2, 3 and 4.

The precipitate obtained by addition of calcium carbonate and aluminum chloride was washed with dilute hydrochloric acid to remove calcium carbonate and was filter dried at 50°C. The petrographic examination of the precipitate indicated clayey sediments. Electron photomicrographs of the precipitate showed the presence of crystalline and amorphous minerals (Pl. 1 and 2). Sepiolite was detected by infrared analyses (Fig.5).

Fig.2. Removal of silica from seawater containing 45 ppm silica and 2ppt calcium carbonate by the addition of aluminum chloride.

Fig. 3. Removal of silica from seawater containing 80ppm silica and 2ppt calcium carbonate by the addition of aluminum chloride.

Fig. 4. Removal of silica from seawater containing 80ppm silica and 2ppt aluminum chloride by the addition of calcium carbonate.

Pl. 1. Electron micrograph of the product precipitated from seawater containing sodium metasilicate, aluminum chloride, and calcium carbonate.
Magnification $\approx 2,000 \times$.

Pl. 2. Electron diffractogram showing the crystal lattice of the precipitate obtained from seawater by adding sodium metasilicate, aluminum chloride, and calcium carbonate.

The presence of the minerals, illite, chlorite, montmorillonite and halloysite in the ocean suggests that these silicates may be in equilibrium with ocean water. The question remains whether these minerals can be synthesized from similar solutions and how far the ionic composition of the solution is controlled by formation or dissolution of these minerals. Recent investigations tend to indicate the formation of authigenic

Fig.5. Infrared absorption spectrum of the seawater precipitate produced by addition of sodium metasilicate, aluminum chloride and calcium carbonate compared with the spectra of minerals, magnesium silicates and brucite.

minerals in the oceans (GARRELS, 1965; MACKENZIE and GARRELS, 1966; HOLLAND, 1965). SILLÉN (1961) proposed on the basis of theoretical calculations that silica and cation fixation in aluminum-silicates is an important step in the control of the pH of the oceans by mineral-seawater equilibrium. The evidence of the presence of authigenic phyllosilicates on the sea floor has been presented by MOBERLY *et al.* (1968). The formation of kaolinite in soil has been observed at low pH and it has been pointed out that kaolinite is stable in seawater.

The experiments described here bring two observations in focus: 1) The removal of silica (formation of silicate) does not occur by simply adding $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ to the solution containing silica, and 2) the removal of silica and aluminum in the presence of CaCO_3 is inversely proportional to the CO_2 pressure. Furthermore, the initial pH, which is dependent upon the amount of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ added to neutral seawater, does not affect the removal of silica from solution. The first step, the addition of AlCl_3 , results in hydration and formation of Al ion with six coordinates.

Although it is recognized that various aluminum ions are hydrated in solution, for the sake of convenience in the following discussion all hydrated forms are not included in the ionic formulae.

For example, relative concentrations of different ions in solution calculated at pH 4 indicated $\text{Al}(\text{OH})_2^+ = 10^{-4}\text{M}$, $\text{Al}(\text{OH})^{2+} = 10^{-3.3}\text{M}$, $\text{Al}^{3+} = 10^{-2.3}\text{M}$, and $\text{Al}(\text{OH})_4^- = 10^{-8.8}\text{M}$ for the total Al = $10^{-2.25}\text{M}$. It is suggested that all these cationic species are involved in the reaction.

The second stage is proposed by SIFFERT (1962) in the following reactions:

The end product of the first reaction has tetrahedral-octahedral-tetrahedral layers, while the product from the second reaction contains only tetrahedral-octahedral layers.

The complete reaction therefore can be written as follows:

By combining the above equations we get:

It is postulated that calcium carbonate added to the solution containing aluminum chloride and silica reacts with acid ions, thus raising the pH, and therefore free OH ions combine with aluminum to form $[\text{Al}(\text{H}_2\text{O})_4(\text{OH})_2]^+$. The reaction between $[\text{Al}(\text{H}_2\text{O})_4(\text{OH})_2]^+$ and H_4SiO_4 proceeds as long as calcium carbonate is present to neutralize the acid ions, and aluminum is available to form hydrated aluminum ions.

However, as soon as the aluminum ions are depleted, the magnesium ions are hydrolysed which react with H_4SiO_4 to form sepiolite (WOLLAST *et al.*, 1968). The first occurrence of recent sepiolite in a deep-sea environment on the mid-Atlantic ridge has been reported by HATHAWAY and SACHS (1965). Sepiolite may have been formed by the reaction of Mg in solution with silica dissolved from silicic volcanic ash. The mechanism of formation of precipitate described here therefore may shed light on the genesis of the authigenic aluminosilicates in nature. BRICKER and GARRELS (1967) concluded that silica in low temperature natural waters is primarily derived from silicate minerals and suggested that because of silicate control, silica concentrations and ratios of cations to H^+ have certain genetic pattern. It is therefore probable that prior to the evolution of living organisms the concentration of silica in oceans and the cycling of carbon dioxide were directly related. Presently, however, they are perhaps completely or partially controlled by production of organic carbon in ocean surface water. Biogenic carbon produced by marine organisms seems to have a certain silicon to carbon ratio. In the absence of biogenic control such as in deep ocean waters silica and carbon dioxide equilibrium is probably maintained by chemical reaction.

CONCLUSIONS

- 1) Silica up to 80ppm in sea and distilled water is stable.
- 2) CO_2 pressure of $17.2 \times 10^3 \text{ kg/m}^2$ does not alter the concentration of silica in solutions containing 80ppm.
- 3) Behavior of silica in seawater is similar to that in distilled water.
- 4) The presence of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, MgCl_2 , CaCO_3 , kaolinite, and montmorillonite does not affect the concentration of silica (up to 80ppm) with or without carbon dioxide pressure.
- 5) The simultaneous addition of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and CaCO_3 caused removal of silica from solutions.
- 6) The percentage precipitation of removal of silica from a solution containing silica, calcium carbonate, and aluminum chloride is inversely proportional to CO_2 pressure.

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