Solubility and Dissolution Rate of Amorphous Silica in Distilled and Sea Water at 20°C*

Kikuo Kato and Yasushi Kitano**

Abstract: The solubility of amorphous silica in sea water is about 85 mg-SiO₂/l at 20°C, which is less than that in distilled water (about 113 mg-SiO₂/l). The dissolution rate seems to be controlled by the amount of silica gel present and its solubility. Silica gel in sea water is transformed to dissolved silica at a much faster rate than in distilled water. A maximum value of dissolved silica is observed during the process of dissolution under no abrasion condition, when the dissolution rate is very large. The differences in the solubility and in the dissolution rate of amorphous silica in distilled and in sea water cannot be explained by the difference in pH values of the waters but seem to be due to the salts present in sea water.

1. Introduction

On the solubility of amorphous silica and quartz, a large number of data have been reported by many workers. And attempts have been made to account for the dissolved silica content of natural water by the aid of these fundamental data.

However, the dissolved silica content of natural water is often controlled by the dissolution rate rather than by the solubility of silica and depends on the properties of the mineral or the rock in contact with the water. Only a few papers have been presented on the dissolution rate of silica in natural water.

For the understanding of the dissolved silica content of natural water, we must consider the salt contained in natural water. Most workers have used a colorimetric method of molybdo-silicate for the determination of dissolved silica. In order to determine the dissolved silica in salt solutions, we must make clear the salt effect in this method.

The colorimetric molybdo-silicate determination of dissolved silica in sea water, which was used in this work, was examined and reported by Kato and Kitano (1966). We found that 2 ml of acid from 4 to 6 N (normal) should be added to 50 ml of sample solution, prior to addition of 2 ml of 10% ammonium molybdate solution to 50 ml of a sample solution.

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Fig. 1. Relationship between relative absorbance and the amount of sulfuric acid added. The change in absorbance was measured at 400 mμ one hour after the addition of 2 ml of sulfuric acid from 0.5 to 9.0 N and 2 ml of 10% ammonium molybdate solution to 50 ml of a sample solution.

--- Distilled water
--- Artificial sea water
--- 1 M NaCl solution
--- 0.5 M Na₂SO₄ solution

(1)
If 2 ml of less than 4 N acid are added to 50 ml of sample solution, the value of salt factor not only becomes larger but also varies widely with decreasing normality of acid added. Therefore, previous data about the silica content of sea water which were obtained by adding less than the proper amount of acid should be re-examined.

So, in the present work we examined the solubility and the dissolution rate of amorphous silica (silica gel) in distilled and in sea water at 20±1°C, according to the proposed procedure. The main purpose was to study the differences in solubility and dissolution rate of amorphous silica in distilled and in sea water, and the relation between the dissolution rate and the amount of silica gel present.

2. Experimental method

The change in the dissolved silica content with time was measured in distilled water and in natural and artificial sea water, containing between 10 mg and 10 g of powdered silica gel (SiO₂) per litre. The silica gel used was of analytical reagent grade and less than 325 mesh in grain size. The distilled water used was completely free of silica.

The runs were made in polyethylene bottles at 20±1°C. Each sample solution was stirred immediately after addition of silica gel.

Dissolved silica was determined colorimetrically using the procedure of KATO and KITANO (1966); 2 ml of 4 N sulfuric acid and 2 ml of 10% ammonium molybdate solution were added to 50 ml of sample solution.

The absorbance of the solution containing the molybdisilicic acid was determined 10~20 minutes after the addition of the reagent solutions, at 400 mp on a Hitachi Perkin-Elmer 139 type spectrophotometer with a recorder. A calibration curve was drawn for each determination. Some of sample solutions were diluted by proper amounts of distilled water to keep the absorbance low enough to insure a good sensitivity. The determinations were accurate to 2% of the amount of dissolved silica present. The colorimetric results were corrected for the salt effect using the salt factor 1.02.

The standard silica solution was prepared as follows. About 500 mg of powdered silica gel or quartz were dried at about 700°C, fused with 4.0 g of sodium carbonate, and dissolved in dilute hydrochloric acid to adjust the pH value to about 7.0. The silica solution was standardized gravimetrically.

Artificial sea water, free of silica and flourine, with a chlorinity of 19% was prepared by the procedure of SUBOW (1931)*.

3. Results and discussion

Table 1 and Fig. 2 show the change in the dissolved silica content with time. All solutions given in Table 1 are considered to be in a homodispersed system.

The following conclusions can be drawn from Fig. 2 and Table 1.

1) Initially the dissolved silica content increases faster with an increase in the amount of silica gel present. And then, however, the dissolved silica content ceases to be proportional to the amount of silica gel present and the dissolution rate of silica decreases. Therefore, the dissolution rate is considered to be controlled not only by the amount of silica gel present but also by the difference between its solubility and the amount of dissolved silica present. GREENBERG (1957) reported that the dissolution rate was directly proportional to the amount of silica present in sodium hydroxide solutions. SUITO et al. (1951) reported that the time required for a complete dissolution in a homodispersed system of spherical particles was independent of the quantities of added particles, the size of which was very fine. Greenberg's result (1957) is in good agreement with the result of SUITO et al. (1951). Our result, however, does not agree with that of SUITO et al. (1951) and suggests that the rate is more complicated.

<table>
<thead>
<tr>
<th>Salt</th>
<th>g to 1,000.000 g water</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>26.518</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>2.447</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>3.305</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>1.141</td>
</tr>
<tr>
<td>KCl</td>
<td>0.725</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>0.202</td>
</tr>
<tr>
<td>NaBr</td>
<td>0.083</td>
</tr>
</tbody>
</table>

* Salt g to 1,000.000 g water
Solubility and Dissolution Rate of Amorphous Silica in Distilled and Sea Water at 20°C

Table 1. Change in dissolved silica content with time at 20±1°C (mg-SiO₂/l).

<table>
<thead>
<tr>
<th>Solution</th>
<th>Amount of silica gel added to original solution (mg-SiO₂/l)</th>
<th>Dissolved SiO₂ after (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>Artificial sea water (pH 7.5)</td>
<td>10</td>
<td>5.7</td>
</tr>
<tr>
<td>Artificial sea water (pH 5.6)</td>
<td>50</td>
<td>7.0</td>
</tr>
<tr>
<td>Distilled water (pH 5.6)</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Distilled water (pH 7.5)</td>
<td>50</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2. Change in dissolved silica content with time at 20±1°C. Amount of silica gel added to the original solution: 1. 10 mg-SiO₂/l 2. 50 mg-SiO₂/l 3. 100 mg-SiO₂/l 4. 1.0 g-SiO₂/l 5. 10 g-SiO₂/l.

- Distilled water
- Artificial sea water
- Natural sea water

2) Silica gel in natural and in artificial sea water is transformed to dissolved silica at almost the same rate. Silica gel in natural and artificial sea water changes to dissolved silica much faster than in distilled water. CHOW and ROBINSON (1953) and KRAUSKOFF (1956) also observed the same trend. The amount of silica gel added in their distilled water runs was different from that in their sea water runs.

In this study, we found that silica gel in sea water changes to dissolved silica very fast. For example, it takes only 10 days for all the silica gel in 10 mg to change entirely to dissolved silica in sea water. On the other hand, in distilled water containing the same amount of silica gel, only 1 mg of silica gel dissolves even after over half a year. Thus, the dissolution rate is several thousand times faster in sea water than in distilled water.

3) The change in the dissolved silica content of sea water with time, shown in Fig. 2, is very interesting because the amount of dissolved silica reaches a maximum value and then falls gradually to the solubility value. The similar phenomena to this were already found under abrasion condition resulting in greater rounding of the particles. Fournier's experiments (1960) indicated that abrasion may produce the supersaturated solution of quartz. MOREY et al. (1962, 1964) reported the dissolution of quartz, cristobalite, silica glass and silica gel during an abrasion process. However, this is the first report found in no rotation process. With increasing amount of silica gel present, the appearance of the maximum value is accelerated and the maximum value increases. The maximum value appears approximately on the 16th, 33rd and 400th day in sea water containing 10 g, 1.0 g and 100 mg of powdered silica gel per litre, respectively.

4) The solubility of amorphous silica in distilled water is about 113 mg-SiO₂/l at 20±
The value is approximately the same as that reported previously (ALEXANDER et al., 1954; ILER, 1955; KRAUSKOPF, 1956, 1959; SIEVER, 1962 and MOREY et al., 1964).

The solubility of amorphous silica in sea water is about 85 mg-SiO$_2$/l at 20±1°C and smaller than that in distilled water. GREENBERG and PRICE (1957) found that the solubility in neutral 1 N sodium chloride solution was less than 10 per cent of the solubility in distilled water, finding no appreciable effect of the concentration up to 0.10 N sodium chloride and 0.20 N sodium sulfate solutions. On the other hand, KRAUSKOPF (1956) and SIEVER (1962) observed that the solubility in sea water was approximately the same as that in distilled water and that the ionic strength had little effect on the solubility up to that of sea water. GREENBERG and PRICE (1957), KRAUSKOPF (1956) and SIEVER (1962) determined the dissolved silica colorimetrically using the analytical procedure of ALEXANDER et al. (1954). KRAUSKOPF (1956) and SIEVER (1962) corrected colorimetric results for the salt effect using the salt factor 1.23 (CHOW and ROBINSON, 1953), but GREENBERG and PRICE (1957) made no mention of salt effect. The salt effect of 1 N sodium chloride is greater than that of sea water (IWASAKI and TARUTANI, 1959; KATO and KITANO, 1966, see Fig. 1). They could not make the exact correction for the silica determination. So it has been believed that the solubility in sea water is approximately the same as that in distilled water (for example, HOLLAND, 1967).

The discrepancy between our results and those of KRAUSKOPF (1956) and SIEVER (1982) may be due to the following facts. The value of the salt factor varies widely with the normality of acid added in the molybdosilicate determination of dissolved silica in sea water, as shown in Fig. 1. They underestimated the value of salt factor. Also, the dissolved silica content reaches a maximum value and then falls gradually to the solubility value, as shown in Fig. 2. They might not notice the appearance of the maximum value in the dissolution process. It is considered that previous workers did not determine the true solubility in sea water.

Next we examined whether the differences in the solubility and dissolution rate of amorphous silica in distilled and in sea water are due to the difference in pH value or to the amount of coexisting salts. Fig. 3 shows the change in the dissolved silica content at different pH values with time. The difference in the dissolved silica content between different curves for different pH values indicates the difference in the dissolution rate at the different pH values. The result shows the same trend as that previously reported by IWASAKI et al. (1954) and GOTO (1955). Fig. 3 also shows the change in the solubility with pH. The result shows the same trend as that previously reported by ALEXANDER et al. (1954), KRAUSKOPF (1956, 1959) and MOREY et al. (1964).

The pH value is 5.6 in distilled water, 7.5 in artificial sea water and 8.0 in natural sea water. According to the data shown in Fig. 3, the solubility is independent of pH values between 5.6 and 8.0 and the pH in the range 5.6 to 8.0 has only a slight effect on the dissolution rate. Furthermore, we determined the change with time in the dissolved silica content in distilled and in sea water at the same pH values. The results are shown in Fig. 4. Both in distilled and in sea water, it was seen that the pH has only the slight effect as shown in Fig. 3. Even at the same pH value, silica gel in sea water changes to dissolved silica much faster than in distilled water as shown above.
We found that the solubility in sea water is smaller than in distilled water and that the dissolution rate of silica gel is several thousand times faster in sea water than in distilled water. The differences in the solubility and in the dissolution rate of amorphous silica in distilled and in sea water cannot be explained by the difference in pH value. Therefore, it is likely that the differences are due to the amounts of coexisting salts in distilled and in sea water.

Further studies are underway to clarify the relation between the amount of coexisting salts and the effect on the solubility and dissolution rate, and the mechanisms for dissolution and polymerization of silica in solutions with and without coexisting salts.

Acknowledgements

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References


無定形ケイ酸の 20°C の蒸留水および海水における溶解度と溶解速度

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要旨 20°C における海水中の無定形ケイ酸の溶解度は 85 mg-SiO₂/l で、蒸留水の 113 mg-SiO₂/l よりは小さい。溶解速度は溶液に存在するケイ酸の量と溶解度に制約される。海水における溶解速度は蒸留水におけるより遙かに大きい。溶解速度が大きいときは、溶解過程において無定形ケイ酸の溶解量は極大値を示すことを知った。海水と蒸留水中における溶解度と溶解速度の違いは溶液の pH にはよらず、溶存塩の量および種類によるものと思われる。