

## THE DISSOLUTION OF AMORPHOUS SILICA IN THE PRESENCE OF TROPOLONE UNDER ACIDIC CONDITIONS

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**Abstract**—Dissolution of amorphous silica or silicate is an important reaction to release silicic acid in natural water and this reaction is affected by several factors. The existence of a natural organic compound, tropolone, because of its abundance, is of particular importance. In the present study, the dissolution of amorphous silica in the presence of tropolone (HL) was investigated in an aqueous solution under acidic conditions. The dissolution is controlled by the reaction between silicic acid and tropolone ( $\text{Si}(\text{OH})_4 + 3\text{HL} + \text{H}^+ \rightleftharpoons \text{SiL}_3^+ + 4\text{H}_2\text{O}$ ), where the conditional formation constant  $K = [\text{SiL}_3^+]/[\text{Si}(\text{OH})_4][\text{HL}]^3[\text{H}^+]$ . The solubility of amorphous silica in the presence of tropolone was significantly greater than that in pure water due to the formation of the Si-tropolonate complex in the solution. The acceleration of silica dissolution by tropolone depends on the reaction pH and tropolone concentration. The solubility of the amorphous silica in the tropolone solution at pH 1 was approximately ten times greater than in the 0.1 mol/dm<sup>3</sup> HCl used as a reference. This increase in the solubility correlates to a K value of the Si-tropolone complex at each pH. From the solubility experiments, the conditional formation constants (log K) of the Si-tropolonate complex at each reaction pH 1, 2, and 3 were 6.39, 5.88, and 5.77, respectively. The significant acceleration of the dissolution of amorphous silica by tropolone at pH 1 can be attributed to the large formation constant of the Si-tropolonate complex.

**Key Words**—Amorphous Silica Dissolution, Dissolution Rate Constant, Solubility, Tropolone.

### INTRODUCTION

Silicon (Si) is the second most abundant element in the Earth's crust and exists as silicate, crystalline silica such as quartz, and amorphous silica. Although the form of Si in natural water depends on the pH, temperature, and coexisting compounds, Si typically dissolves as monosilicic acid ( $\text{Si}(\text{OH})_4$ ) in natural water due to the dissolution of silicate and silica. The dissolution reaction is expressed in equation 1 (Iler, 1979):



Previous studies of the dissolution of silica have been conducted on (1) the solubility of silica and (2) the dissolution rate of silica. The solubility of amorphous silica in water is only slightly dependent on pH within the range 2–8.5, and is  $\approx 1.8$  mM (50 ppm Si) at 25°C (Iler, 1979). Kinetic analysis of the dissolution of amorphous silica (Plettinck *et al.*, 1994) revealed a well defined effect of pH on the dissolution rate, on both sides of a minimum rate at pH 2–3, in accord with the point of zero charge (pzc) of amorphous silica. From pH 2 to 8.5, silicic acid is present as neutral monosilicic acid ( $\text{Si}(\text{OH})_4$ ); on the other hand,  $\text{Si}(\text{OH})_4$  begins to

dissociate  $\text{H}^+$  with increasing pH above pH 8.5 to form a silicate ion (*e.g.*  $\text{SiO}(\text{OH})_3^-$ ). The solubility of amorphous silica between pH 2 and pH 8.5 is equal to the concentration of  $\text{Si}(\text{OH})_4$ , while, above pH 8.5, it increases. The solubility above pH 8.5 corresponds to the sum of the concentrations of  $\text{Si}(\text{OH})_4 + \text{SiO}(\text{OH})_3^-$  (silicate ions). Below pH 2, only a few studies on the solubility of amorphous silica have been conducted.

Based on the two independent research directions regarding the dissolution of silica, the effect of coexisting components on the dissolution of amorphous silica has also been investigated. Because silica and silicate are abundant, the effects of coexisting compounds such as metal ions and organic compounds on their dissolution have been investigated. The effect of organic compounds, in particular, has been investigated widely. Since the formation of etch pits in quartz grains in peat-bog groundwaters with high organic-compound concentrations was reported by Bennett and Siegel (1987), the influence of oxalic, acetic, lactic, and formic acids, which are produced by bacteria or fungi in the lithosphere, on the dissolution of amorphous silica has been investigated (Dandurand and Schott, 1987; Bennett *et al.*, 1988; Öhman *et al.*, 1991; Poulson *et al.*, 1997). Although the dissolution of amorphous silica or quartz is thought to be accelerated by such organic acids, Poulson *et al.* (1997) concluded that the oxalic acid has no effect on the dissolution of quartz. Recently, the effect of amino acid on the dissolution rate of amorphous silica

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has also been investigated. Basic amino acids such as histidine, lysine, and arginine interact more with the negatively charged surface of amorphous silica than other amino acids and accelerate the dissolution of amorphous silica (Kawano and Obotake, 2007). In addition, those authors also reported the enhancement of dissolution of amorphous silica in the presence of bovine serum albumin and the functional molecules of basic amino acids (Kawano and Hwang, 2010a, 2010b). Although these basic amino acids can increase the dissolution rate of amorphous silica, the solubility of amorphous silica in the presence of amino acids has not been investigated. On the other hand, Tiron (disodium catechol-3, 5-disulfonate), a catechol derivative, can form a stable 1:3 Si-Tiron complex in solution and the solubility of amorphous silica in the Tiron solution can reach ~100 ppm (as Si), according to Bai *et al.* (2008). These results suggest strongly that the contribution of organic compounds that can interact with silicic acid (or a silica surface) can notably increase the Si concentration in natural water. To reveal the effects of organic compounds on the dissolution of amorphous silica, an investigation that combines both the equilibrium discussion and kinetic analysis is essential. In the present study, the focus was on tropolone (2-hydroxy-2,4,6-cycloheptatrien-1-one, HL) as the organic compound because some derivatives of tropolone are abundant in more evolved plants (*e.g.* conifers such as cedar and pine). For example, *thujaplicine* (4-isopropyl tropolone, *thpl*) has been found in many conifers and can be isolated from those trees as a cationic Si-*thpl* complex (Weiss and Herzog, 1978). Based on potentiometric titration and  $^{29}\text{Si}$  nuclear magnetic resonance (NMR) measurements, tropolone has been reported to form a stable 1:3 Si-tropolonate complex under acidic conditions (Sjöberg *et al.*, 1985), though any investigation of the effect of tropolone on the dissolution of silica or silicate has been insufficient.

In addition to the solubility of amorphous silica in the presence of tropolone, the dissolution-rate constant of the amorphous silica in acidic conditions was also evaluated because the investigation is not viable other than in the presence of hydrogen fluoride.

## EXPERIMENTAL METHODS

### Materials

All reagents used were of analytical grade. All solutions were prepared with ultra pure water (Milli-Q Reference, Millipore). A Wako gel<sup>®</sup> C-200 for column chromatography (BET surface area: 450 m<sup>2</sup>/g, 75–150  $\mu\text{m}$  in size) was purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) as the source of amorphous silica. Prior to the dissolution experiment, the Wako gel was immersed in pure water (pH 5.5–5.6) and shaken for 5 h and then washed with ultra-pure water at least three times to remove any ultrafine particles. The

tropolone was purchased from Tokyo Chemical Industry Co., Ltd (Tokyo, Japan). For the  $^{29}\text{Si}$  NMR measurements, a sodium silicate solution prepared by dissolving  $^{29}\text{Si}$ -enriched  $\text{SiO}_2$  (98.7%  $^{29}\text{Si}$ , Cambridge Isotope Laboratories, Inc. (Massachusetts, USA)) in the sodium hydroxide solution was used. Hydrochloric acid (HCl) (Wako Pure Chemical Industries, Ltd.) was used to adjust the pH.

### Dissolution experiments

The dissolution experiment in the presence of tropolone was conducted not only for the determination of the solubility but also for the estimation of the dissolution rate constant. The 0.1 mol/dm<sup>3</sup> (M) tropolone solution (200 or 500 cm<sup>3</sup>) was prepared by the dissolution of solid tropolone in water. The pH in the tropolone solution was adjusted to pH between 1 and 3 by adding HCl. Silica gel powder (2 or 5 g) was added to the tropolone solution and the suspended solution was shaken by a shaker (100 min<sup>-1</sup>) at 30±0.2°C. Aliquots of the suspended solution were taken at adequate intervals and filtered with a 0.45  $\mu\text{m}$  membrane filter. The silicic-acid concentration in the filtrates was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Optima 5300 DV, Perkin Elmer: Shelton, Connecticut, USA). The solubility of amorphous silica in HCl was used as a control. The effect of tropolone concentration on the dissolution of amorphous silica was examined by the same procedure – the amount of tropolone adsorbed on the surface of amorphous silica was measured by elemental analysis (Total Organic Carbon Analyzer TOC-V<sub>E</sub>, Shimadzu, Japan).

### NMR measurements

After the dissolution experiment, the  $^{13}\text{C}$  NMR spectra for the filtrates were measured. The  $^{13}\text{C}$  NMR spectra were recorded using a JEOL JNM-AL 400 FT NMR spectrometer (JEOL, Japan) with a 5 mm multi-nuclear probe head. All measurements were conducted at a resonance frequency of 100.40 MHz. The pulse delay and transients were 17.6 s and 17,000, respectively. Chemical shifts were recorded with respect to  $\text{Si}(\text{CH}_3)_4$  (tetramethylsilane, TMS) using  $\text{C}_6\text{H}_{15}\text{NaO}_3\text{SSi}$  (sodium 3-(trimethyl-silyl)-1-propanesulfonate, DSS) as a secondary liquid reference. The NMR measurements were carried out at room temperature.

To elucidate the effect of pH on the complexation between silicic acid and tropolone, the mixed solutions of silicic acid (1.8 mM) and tropolone (18 mM) were prepared at various pH values.  $^{29}\text{Si}$  NMR spectra of the mixed solutions were also recorded using the same instrument as previously. This time, all measurements were conducted at a resonance frequency of 79.30 MHz. The pulse delay and transients were 30.0 s and 9000, respectively. Chemical shifts were recorded with respect to external TMS.

### Electron-spray ionization mass spectroscopy (ESI-MS) measurements

Electron-spray ionization mass spectroscopy measurements were carried out to examine the stoichiometry of the Si-tropolonate complex. The sample solution contained 1.8 mM silicic acid and 18 mM tropolone at pH 1. The ESI-MS measurements were performed using a Waters Quattromicro API mass spectrometer in the positive ionization mode. The solutions were introduced into the spectrometer at a flow-rate of 2  $\mu\text{L}/\text{min}$ . The operating conditions were as follows: capillary voltage 3.0 kV, sample cone voltage 50 V, RF lens 0 V, source temperature 120°C, desolvation temperature 150°C, cone gas flow rate 50 L/h, and desolvation gas flow rate 600 L/h.

## RESULTS AND DISCUSSION

### Formation of the Si-tropolonate complex under acidic conditions

The  $^{29}\text{Si}$  NMR spectra of mixed solutions containing silicic acid (1.8 mM) and tropolone (18 mM) of pH 1–3 were measured (Figure 1) to reveal the complexation between silicic acid and tropolone under acidic conditions. The peak at  $-72$  ppm is due to the free monosilicic acid ( $\text{Si}(\text{OH})_4$ ) and that at  $-141$  ppm, to a 6-coordinated Si in the Si-tropolonate complex. This chemical shift is similar to that found by Sjöberg *et al.* (1985). The formation of the Si-tropolonate complex depends heavily

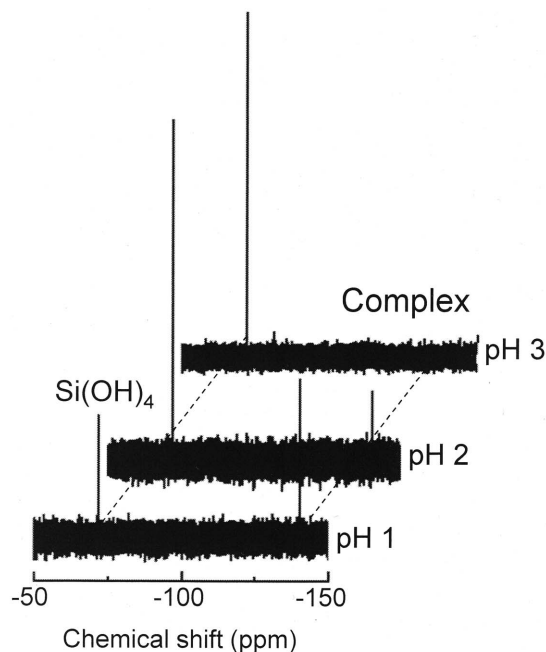


Figure 1.  $^{29}\text{Si}$  NMR spectra of mixed solutions containing silicic acid (1.8 mM) and tropolone (18 mM) under acidic conditions. Notice that the horizontal scale is offset for each pattern for clarity.

on the reaction pH. To confirm the stoichiometry of the Si-tropolonate complex, a positive-mode ESI mass spectrum for the mixed solution was obtained (Figure 2). The concentration of silicic acid and tropolone in the sample solution was identical to that used for the  $^{29}\text{Si}$  NMR measurement. The peak at  $m/z$  121.1 was assigned to free protonated tropolone ( $\text{H}_2\text{L}^+$ ). A dominant peak at  $m/z$  393.1 corresponded to a Si-tropolonate complex. From the  $m/z$  value, the composition of this complex is a 1:3 Si-tropolonate complex.

The formation constant ( $\log K$ ) of the Si-tropolonate complex, which forms according to the following reaction (equation 2), was reported by Sjöberg *et al.* (1985):

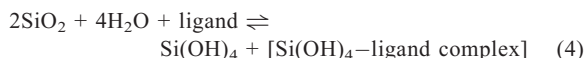


$$K = [\text{SiL}_3^+]/[\text{Si}(\text{OH})_4][\text{HL}]^3[\text{H}^+] \quad (3)$$

The formation constants of the Si-tropolonate complex ( $\text{SiL}_3^+$ ) ( $\log K$  ( $M^{-4}$ )) were reported from potentiometric titration to be  $\log K = 7.08 \pm 0.03$  (Sjöberg *et al.*, 1985). In the present study, each conditional formation constant ( $\log \beta$  ( $M^{-4}$ )) was determined from the integrated  $^{29}\text{Si}$  NMR spectra (Figure 1) at pH 1 and 2 and estimated to be 7.40 and 6.16, respectively.

### Solubility of amorphous silica in the presence of tropolone

When the formation of a silicic acid–organic compound complex in aqueous solution is considered, the solubility of amorphous silica can be represented as the sum of the free  $\text{Si}(\text{OH})_4$  and the complex concentrations (equation 4).



Using this reaction, Tiron was found (Bai *et al.*, 2008) to form a Si-Tiron complex and can increase the solubility of amorphous silica at pH 6.

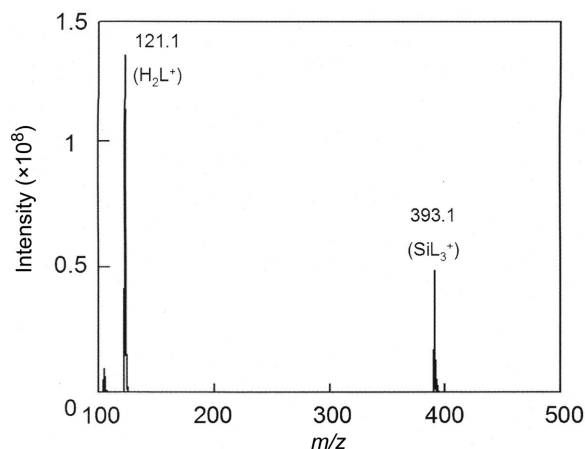


Figure 2. ESI-MS spectrum of a mixed solution containing silicic acid (1.8 mM) and tropolone (18 mM) at pH 1.

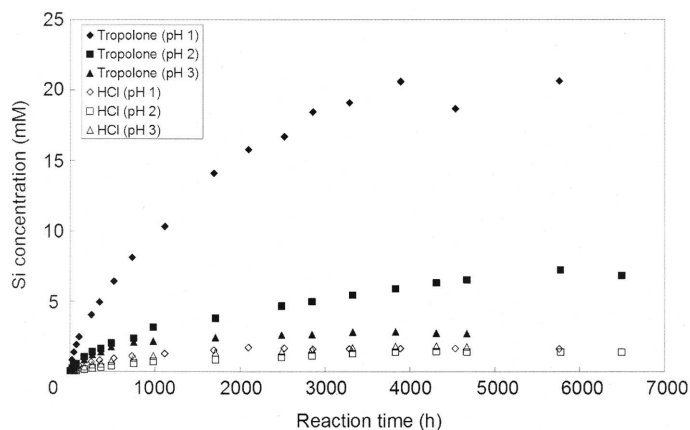


Figure 3. Time course of dissolution of amorphous silica in the presence of tropolone under acidic conditions. Initial tropolone concentration: 0.1 M; volume: 500 cm<sup>3</sup>; silica gel powder: 5 g.

The time course of Si concentration during the solubility experiment in the presence of tropolone (Figure 3) revealed that tropolone increased the dissolution rate at all pH values and that the rate at pH 1 was much greater than at pH 2 or 3. The solubility was defined as the point at which the Si concentration in solution reached a constant value (Figure 3, Table 1). These findings also agree with the results from <sup>29</sup>Si NMR spectra of silicic acid and tropolone mixed solutions (Figure 1).

The possible formation of the Si-tropolonate complex (SiL<sub>3</sub><sup>+</sup>) during the solubility experiments was probed using <sup>13</sup>C NMR spectroscopy of the filtrate. Results from the pH 1 treatment at equilibrium confirmed the formation of SiL<sub>3</sub><sup>+</sup> in solution. The <sup>13</sup>C NMR spectrum of the filtrate is shown in Figure 4. The peak prime symbol indicates a peak assigned to SiL<sub>3</sub><sup>+</sup> and the peak without the prime symbol indicates the free ligand. Integration of <sup>13</sup>C NMR peaks (total ligand concentration: 0.1 M) revealed that the molar ratio of [ligand]<sub>free</sub> to [ligand]<sub>complex</sub> was 1–1.3 at equilibrium and the calculated concentration of [SiL<sub>3</sub><sup>+</sup>] was 18.1 mM. Considering this molar ratio of ligand to the total silicic acid concentration (19.8 mM) at equilibrium, the

calculated concentration of [Si(OH)<sub>4</sub>] in the solubility experiment at equilibrium was 1.7 mM. Therefore, at the end of this experiment, the concentration of monosilicic acid almost reached the solubility of amorphous silica. Because the sample solutions at pH 2 and pH 3 have a relatively low Si-tropolonate complex content compared with those at pH 1, the peak due to the Si-tropolonate complex was not observed on the <sup>13</sup>C NMR spectra (not shown here). However, the formation of the Si-tropolonate complex should occur even at pH 2 and 3 because the dissolution of amorphous silica was accelerated. The <sup>13</sup>C NMR peak due to the complex was apparently not detected because of low sensitivity. In particular, the solubility in tropolone solution at pH 1 was approximately ten times greater than that of the 0.1 M HCl as control. The values of log β for the Si-tropolonate complex at each reaction pH were calculated using the solubility of amorphous silica in the presence of tropolone and are summarized in Table 1.

Basic amino acid increases the dissolution rate (according to Kawano and Obotake, 2007) by the formation of monodentate outer-sphere complexes on the surface of amorphous silica. The greater reactivity of

Table 1. The solubility and dissolution-rate constants of amorphous silica in the presence of tropolone under acidic conditions.

| Reaction pH | Solubility of amorphous silica (mM) |                  | Log β* of Si-tropolonate complex | Rate constants (k) (mM/min)                         |   |
|-------------|-------------------------------------|------------------|----------------------------------|---|---|
|             | HCl system                          | Tropolone system |                                  | HCl system  | Tropolone system                                    |
| 1           | 1.67                                | 19.8             | 6.39                             | 4 × 10 <sup>-4</sup><br>(**r <sup>2</sup> = 0.9989) | 3.7 × 10 <sup>-3</sup><br>(r <sup>2</sup> = 0.9733) |
| 2           | 1.39                                | 6.86             | 5.88                             | 1 × 10 <sup>-4</sup><br>(r <sup>2</sup> = 0.9980)   | 1 × 10 <sup>-3</sup><br>(r <sup>2</sup> = 0.9995)   |
| 3           | 1.78                                | 2.78             | 5.77                             | 8 × 10 <sup>-5</sup><br>(r <sup>2</sup> = 0.9960)   | 5 × 10 <sup>-4</sup><br>(r <sup>2</sup> = 0.9985)   |

\* Log β: conditional formation constant of Si-tropolonate complex calculated from the solubility of amorphous silica in tropolone solution.

\*\* r<sup>2</sup>: The correlation coefficient of each result in the kinetic analysis.

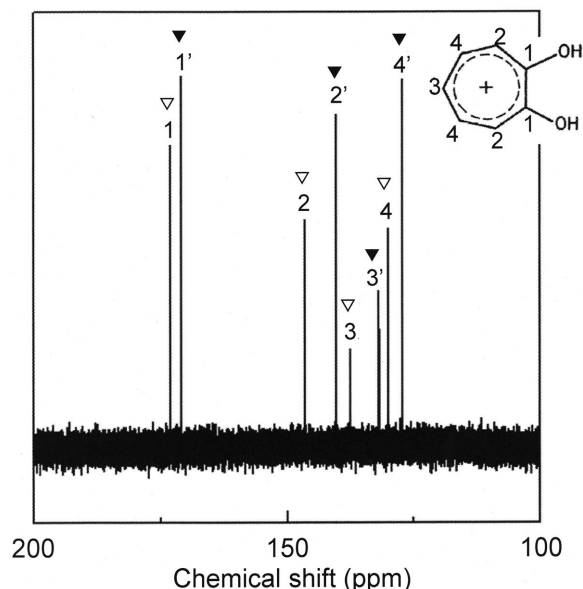


Figure 4.  $^{13}\text{C}$  NMR spectrum of the filtrate after the solubility experiment at pH 1 (Figure 3). The number on each carbon atom in the molecular structure of tropolone in the figure indicates the chemical state of carbon atoms. The numbers with prime symbols indicate that the peaks are due to Si-tropolonate complex. The numbers without prime symbols indicate that the peaks are due to free tropolone.

such amino acids is due to the formation of cationic amino acid species (Kawano and Obotake, 2007). On the other hand, the adsorption of tropolone on the surface of amorphous silica was not observed. Therefore, the acceleration mechanism of tropolone is considered to be different from such amino acids. Because the  $\text{p}K_{\text{a}1}$  and  $\text{p}K_{\text{a}2}$  values of tropolone are  $-0.52$  and  $6.7$ , almost all of tropolone exists as HL under the present experimental condition and the adsorption of tropolone on the surface of amorphous silica did not occur as described above.

In addition, due to the relatively large formation constant of the Si-tropolonate complex in aqueous solution, the dissolved monosilicic acid can easily form a 1:3 Si-tropolonate complex and the concentration of monosilicic acid decreases to the lower concentration than the solubility of amorphous silica by the complexation. As a consequence, the dissolution reaction (equation 1) was accelerated. From the complexation reaction represented in equation 2, the  $\text{H}^+$  concentration in the system is also important for the complexation between silicic acid and tropolone. Thus, strong pH dependence was observed.

The solubility of amorphous silica in Tiron solution can reach 100 ppm (as Si) due to the formation of stable 1:3 Si-Tiron complex, according to Bai *et al.* (2008). In addition, the conditional formation constant ( $\log \beta$ ) of the Si-Tiron complex was estimated to be  $\sim 0.3\text{--}0.6$  ( $\text{M}^{-1}$ ) (Bai *et al.*, 2011). The solubility of amorphous silica in tropolone solution was approximately six times

greater than the result for Tiron due to the difference in the  $\log \beta$  values between the Si-Tiron complex ( $\log \beta$ :  $0.3\text{--}0.6$ ) and the Si-tropolonate complex ( $\log \beta$ :  $5.8\text{--}6.9$ ) (see Table 1).

From a model calculation using the  $K$  value of  $\text{SiL}_3^+$ , Sjöberg *et al.* (1985) concluded that the acceleration of the dissolution of quartz and amorphous silica scarcely occurs at pH 2 and 3. However, in the present study, tropolone was revealed to accelerate dissolution of amorphous silica even at pH 2 and 3.

The dissolution of amorphous silica at pH 1 also depended on the tropolone concentration (Figure 5). When the concentration of tropolone was 0.001 M, the dissolution rate was similar to that of the HCl system used as a control, whereas the rate at 0.1 M was much greater.

#### *Dissolution rate of amorphous silica in the presence of tropolone*

A kinetic analysis was applied to the dissolution of amorphous silica in the presence of tropolone for the initial 5 h period (Figure 6). The analysis was performed using the method described by Bird *et al.* (1986). The calculation scheme is summarized briefly below. The equation for the dissolution kinetics of amorphous silica can be defined using equations 5 and 6 when the dissolution and deposition reactions are considered simultaneously as shown in equation 1.

$$(dC/dt)_{\text{forward}} = k_+(A/M) \quad (5)$$

$$(dC/dt)_{\text{backward}} = k_-(A/M) \quad (6)$$

where  $C$  indicates the monosilicic acid concentration,  $t$  is reaction time, and  $k_+$  and  $k_-$  are rate constants for the dissolution and deposition reactions of amorphous silica, respectively. The term  $A$  represents the surface area of the silica and  $M$  is the mass of the water. From equation 1,

$$K_{\text{eq}} = [\text{Si}(\text{OH})_4] / \{[\text{SiO}_{2\text{solid}}][\text{H}_2\text{O}]^2\} \quad (7)$$

The activity coefficients for  $\text{SiO}_2$  (solid) and  $\text{H}_2\text{O}$  were assumed to be unity and  $(dC/dt) = 0$  was also assumed at equilibrium.

$$k_+/k_- = K_{\text{eq}} = C_{\text{eq}} \quad (8)$$

$K_{\text{eq}}$  and  $C_{\text{eq}}$  represent the equilibrium constant and the equilibrium concentration (solubility), respectively. If  $(A/M)$  can be constant during the dissolution experiments, from equations 5 to 8, then equation 9 is obtained ( $k_+(A/M)$  was replaced by  $N$ )

$$-C_{\text{eq}} \ln[1 - C/C_{\text{eq}}] = Nt \quad (9)$$

By analyzing the results of the initial 300 min (Figure 6), a linear relationship was obtained (Figure 7). The dissolution-rate constant in each solution,  $k_+$ , can be estimated from the slope of each straight line. The dissolution-rate constants for each experimental condition and the correlation coefficient of each result ( $r^2$ ) are summarized in Table 1.

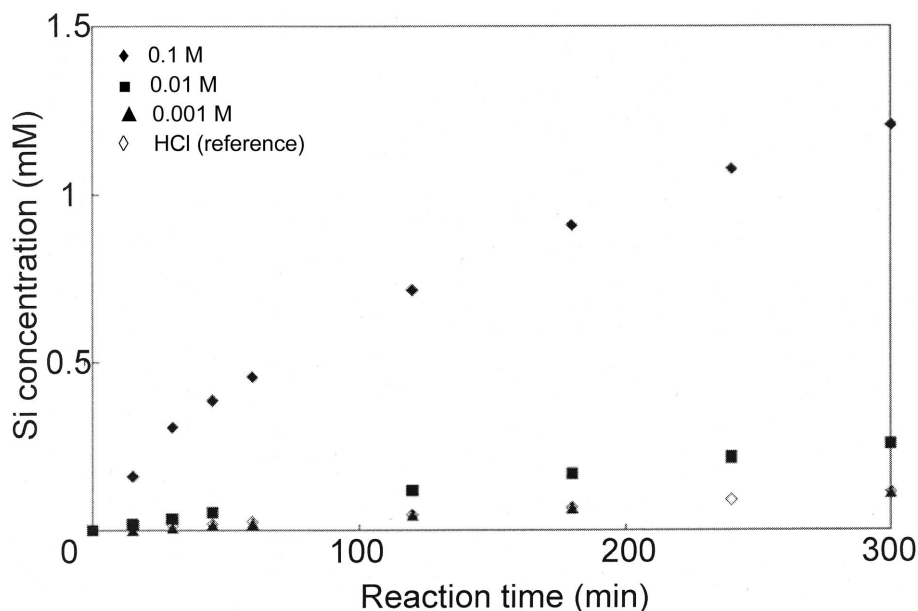


Figure 5. Effect of tropolone concentration on the dissolution of amorphous silica at pH 1. Initial tropolone concentrations: (◆) 0.1 M, (■) 0.01 M, and (▲) 0.001 M. (◇) HCl was used as a control. Volume: 200 cm<sup>3</sup>; silica gel powder: 2 g; reaction time: 300 min.

Characteristically, in HCl systems, the dissolution-rate constant at pH 1 was greater than those at pH 2 and 3. The dissolution rate of amorphous silica at pH 1 was reported by Plettinck *et al.* (1994) to be larger than those at pH 2 and pH 3, which is in agreement with the present results. The dissolution rate of quartz increases with activity of the proton at  $0 < \text{pH} < 3$  (Pokrovsky *et al.*, 2006), which suggests the adsorption of H<sup>+</sup> on the

mineral surface, leading to polarization of Si–O bonds and detachment of the silicon atom from the structure. In the present study, a protonated silanol group (SiOH<sub>2</sub><sup>+</sup>) may be formed by the adsorption of H<sup>+</sup> at pH 1 and the electron density of the silica framework may decrease and the detachment of a silicon atom from the structure may occur more easily. As well as the solubility of amorphous silica, the dissolution rate constant in the

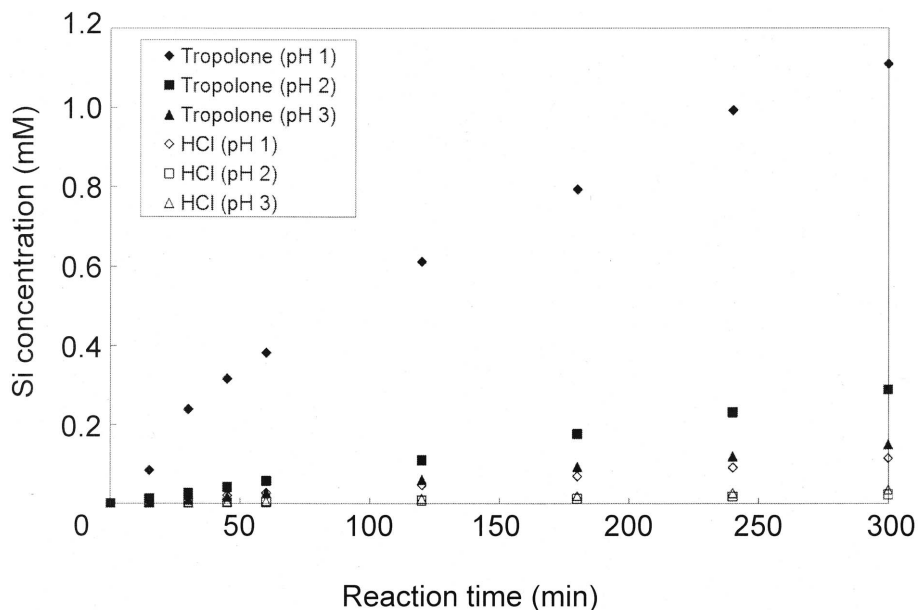


Figure 6. Time course of dissolution of amorphous silica during an initial 300 min in the presence of tropolone under acidic conditions. Initial tropolone concentration: 0.1 M; volume: 200 cm<sup>3</sup>; silica gel powder: 2 g; reaction time: 300 min.

tropolone solution was greater than those in the HCl system and have a clear pH dependence. The dissolution rate constant in tropolone solution was  $\sim 10$  times greater than that of the reference. In addition, the plots ( $\blacklozenge$  in Figure 7) deviate slightly from the straight line. Approximately 3–5% of protonated tropolone ( $\text{H}_2\text{L}^+$ ) species exist at pH 1 and  $\text{H}_2\text{L}^+$  can interact more easily with silicic acid because of positive charge. At the early stage of dissolution of amorphous silica at pH 1, therefore, the reaction between silicic acid and  $\text{H}_2\text{L}^+$  may have an effect on the dissolution of amorphous silica. Considering the percentage of  $\text{H}_2\text{L}^+$  species involved, this effect is less than that of the reaction between silicic acid and HL.

Tropolone and its derivatives are naturally abundant in leaves of conifers. The present results suggest strongly that the Si concentration in natural water can increase due to the organic compound which can interact with silicic acid through the formation of Si-organic compound complexes. From the present results, natural organic compounds such as humic substances which exist abundantly in nature may release Si in nature.

## CONCLUSIONS

The dissolution of amorphous silica in the presence of tropolone under acidic conditions was investigated. The dissolution was strongly accelerated over that in HCl due to the formation of the Si-tropolonate complex in the solution. The solubility of amorphous silica in the tropolone solution was approximately ten times greater than that in HCl (the control) at pH 1. According to NMR measurements, the increase in the Si concentration at equilibrium is due to the formation of a Si-tropolonate complex. The effect of tropolone on the dissolution of amorphous silica depends heavily on the reaction pH and tropolone concentration. The solubility in the tropolone solution was significantly greater than that in solutions of other organic compounds such as Tiron which can form Si complexes in solution. The significant acceleration of the dissolution by tropolone is due to the large formation constant of the Si-tropolonate complex. These results suggest strongly that the acceleration of the dissolution of silica through the interaction between the organic compounds and silicic acid is an important

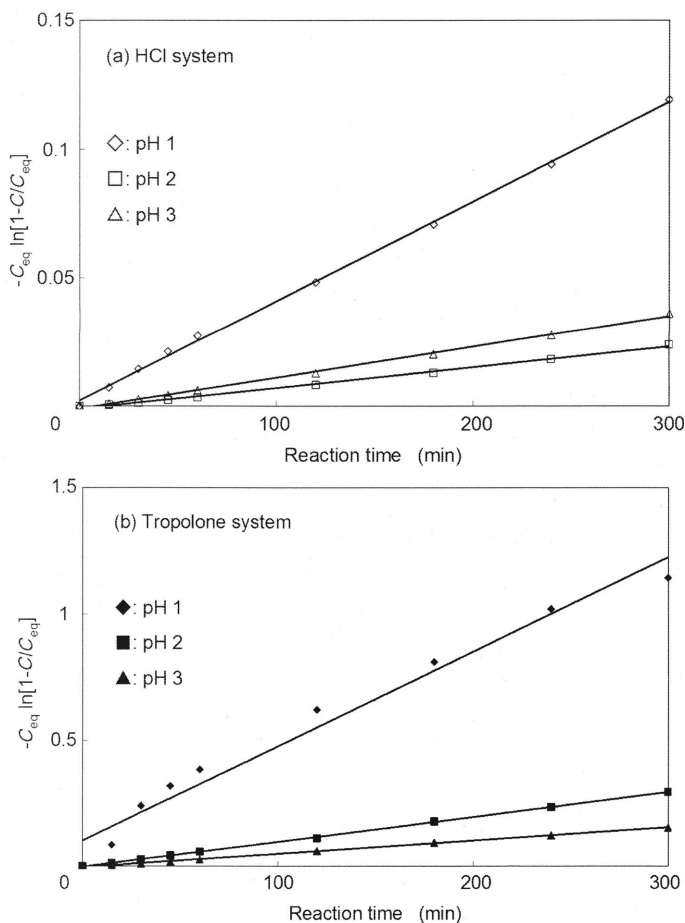


Figure 7. Relationship between  $-C_{eq} \ln(1-C/C_{eq})$  and reaction time obtained from Figure 6.  $C$ : monosilicic acid concentration at time  $t$ ;  $C_{eq}$ : solubility of amorphous silica in each system (see Table 1).

reaction for release of silica as silicic acid into solution in the lithosphere.

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