

Aqueous Si-oxalate complexing, oxalate adsorption onto quartz, and the effect of oxalate upon quartz dissolution rates

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Received 3 September 1996; revised 22 October 1996; accepted 6 December 1996

Abstract

Previous experiments have indicated increased dissolution rates of quartz in the presence of oxalate, although the mechanism responsible is unclear. Possible explanations include a decrease in solution saturation state due to the presence of an aqueous Si-oxalate complex, or ligand promoted dissolution due to adsorption of oxalate onto the quartz surface.

Formation of an aqueous Si-oxalate complex has been investigated by titrating $\text{Si}(\text{OH})_4$ with $\text{K}_2\text{C}_2\text{O}_4$. Formation of proposed Si-oxalate complexes, such as a silicic acid-oxalate ester, should result in pH shifts of the titration curve compared to blank titrations. At an initial pH 5–6, titrations of $\text{Si}(\text{OH})_4$ solutions are identical to blank titrations (after correcting for the buffering effect of silicic acid), indicating that Si-oxalate complexing is negligible.

Oxalate adsorption onto quartz surfaces was studied for short-term (4–5 h, pH 4.3–7.1, oxalate = 5–20 μM) and long-term (1 week, autoclaved, pH 6.3–7.0, oxalate = 10–40 μM) experiments. Oxalate adsorption under these conditions is negligible, with a maximum adsorption of 3.0×10^{-9} mol/m².

The lack of aqueous Si-oxalate complexing and oxalate adsorption onto quartz indicate that these mechanisms will have no effect upon the dissolution rate of quartz in oxalate solutions. Re-evaluation of quartz dissolution rate data suggests that oxalate *per se* has little or no effect upon quartz dissolution rates, and the observed increase in dissolution rates with increasing oxalate concentration may be due to the corresponding increase of Na^+ concentration in solution. © 1997 Elsevier Science B.V.

Keywords: adsorption; complexing; dissolution rate; oxalate; quartz

1. Introduction

The interaction between organic acids and feldspar has been intensively investigated (see Blum and Stillings, 1995; Stillings et al., 1996). Much attention has been focused upon the behavior of oxalic acid, which is present in soil and rhizosphere environments (e.g., Syers and Iskandar, 1973; Drever and

Vance, 1994), forms strong complexes with Ca^{2+} and Al^{3+} (Martell and Smith, 1983; Smith and Martell, 1989), and may enhance silicate weathering rates (Drever, 1994; Drever and Vance, 1994).

Dissolved organic compounds are known to interact with quartz in a variety of field environments, although oxalic acid has not been specifically implicated. The formation of etch pits on quartz grains in ground waters with high concentrations of organic compounds has been observed in a peat bog (Bennett et al., 1991), and in an aquifer contaminated with

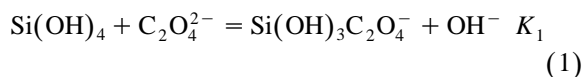
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crude oil (Bennett and Siegel, 1987; Hiebert and Bennett, 1992; Bennett et al., 1993). Hallbauer and Jahns (1977) observed the ability of the lichen *Parmelia conspersa* to corrode quartz, and while lichens can produce significant quantities of oxalic acid, they also produce numerous other chemical compounds which may be responsible for this corrosion (Syers and Iskandar, 1973). Biogeochemical quartz dissolution by the sponge *Chondrosia reniformis* has also been demonstrated (Bavestrello et al., 1995), with ascorbic acid being suggested as the responsible etching agent.

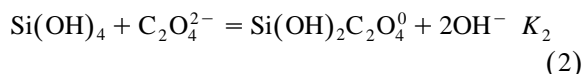
A number of experimental studies of the interaction between quartz and oxalate have been conducted. Dissolution rate studies (Bennett et al., 1988; Bennett, 1991; Bennett and Casey, 1994; Fein and Hestrin, 1994; Franklin et al., 1994; Welch and Ullman, 1996) indicate that quartz dissolution rates increase in the presence of oxalate, although total quartz solubility is only slightly increased. Bennett et al. (1988) have suggested a decrease in solution saturation state due to aqueous Si-oxalate complexing, or the adsorption of oxalate onto the silica surface, weakening framework Si–O–Si bonds, as possible explanations for the observed increased dissolution rates in the presence of oxalate.

A number of possible aqueous Si-oxalate complexes have been proposed. For example, unidentate and bidentate silicic acid-oxalate esters, and hydrogen-bonded species, might form as follows:

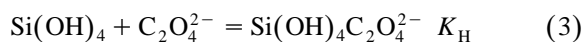
Unidentate ester:



Bidentate ester:



Hydrogen-bonding:



Spectroscopic studies of aqueous Si-oxalate complexing yield conflicting results, with the work of Marley et al. (1989) indicating the formation of a silicic acid-oxalate ester, but the work of Tait et al., 1997 (in prep.) found no evidence for covalent complexation between silicic acid and oxalate. Instead of a silicic acid-oxalate ester, Öhman et al. (1991)

found evidence for the formation of a weak silicic acid-oxalate hydrogen-bonded complex ($\log K_H = 0.04$). There are no studies available in the literature investigating the adsorption of oxalate onto quartz surfaces. Comparing Eqs. (1) and (2) with Eq. (3), it is apparent that silicic acid-oxalate esterification liberates hydroxide, whereas formation of a hydrogen-bonded complex does not. Hence, if significant esterification takes place, the pH of a solution should shift to a higher value.

Our study has investigated possible aqueous Si-oxalate complexing by a potentiometric titration method. We also investigated the adsorption of oxalate onto quartz, in order to try to identify the mechanism(s) responsible for increased quartz dissolution rates in the presence of oxalate.

2. Experimental methods

The formation of an aqueous Si-oxalate complex has been studied by titrating 2 mM Si(OH)_4 with 0.5 M $\text{K}_2\text{C}_2\text{O}_4$ at an initial pH of 5 and 6 at 22°C. Blank titrations (without Si(OH)_4) were also conducted, and all titrations were performed in the presence of 0.1 or 1 M NaNO_3 as a background electrolyte. Si(OH)_4 solutions were prepared using $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, and adjusting the pH with HNO_3 . Oxalate solutions were prepared using $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, and adjusting the pH to 5 or 6 with HNO_3 . Solutions were purged with N_2 to exclude CO_2 , and stirred with a teflon-covered magnetic stir bar inside a polyethylene container. pH was measured with an Orion Ross Sure-Flow combination electrode and a Beckman $\phi 21$ pH meter. pH measurements were taken two minutes after the addition of each titrant aliquot. Titrations of Si(OH)_4 and background electrolyte with HNO_3 were performed in a similar fashion.

Adsorption experiments were performed at 22°C using quartz powder (–325 mesh, 45 μm) with a BET surface area (three point N_2 method) of 1.33 m^2/g . All experiments used a suspension of 250 g quartz/kg solution, and were performed in polyethylene or polypropylene containers. Oxalate was added as a $\text{K}_2\text{C}_2\text{O}_4$ solution, and the pH was adjusted (if necessary) with HNO_3 . Short-term experiments (4–5 h) were conducted at pH 4.3–7.1, with oxalate concentrations of 5–20 μM . Typically, dis-

solution experiments have used oxalate concentrations in the range of 1–20 mM. Lower oxalate concentrations were used in our experiments, in order to lower the detection limits of oxalate adsorption. Long-term experiments (1 week) were autoclaved at 121°C for 30 min, to prevent microbial degradation of oxalate. Solutions were sampled at 1 h and 1 week after autoclaving. Long-term experiments were conducted at pH 6.3–7.0, with oxalate concentrations of 10–40 μM . All samples were filtered through an 0.45 μm syringe filter, and oxalate concentrations were measured with a Dionex DX-100 ion chromatograph, with an AS-4A column and an AG-4A guard column, using a carbonate-bicarbonate eluent. Quantity of oxalate adsorbed was calculated by difference, subtracting measured oxalate in solution at 4–5 h vs. initial oxalate (short-term experiments), or by subtracting measured oxalate at 1 week from measured oxalate at 1 h (long-term experiments).

Solution speciation calculations were performed using MINTEQA2 (Allison et al., 1991), after addition of formation constants for K-oxalate and Na-oxalate complexes (Smith and Martell, 1989) to the MINTEQA2 database.

3. Results

3.1. Aqueous Si-oxalate complexing

Titration curves of $\text{Si}(\text{OH})_4$ with oxalate are presented for initial pH values of 5 and 6 in Figs. 1 and

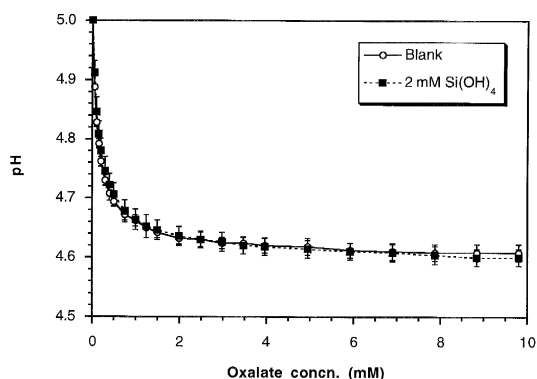


Fig. 1. Titration of $\text{K}_2\text{C}_2\text{O}_4$ vs. 2 mM $\text{Si}(\text{OH})_4$, initial pH 5. All titrations have 0.1 M NaNO_3 as a background electrolyte. Each point represents an average of five titrations, one σ error bars.

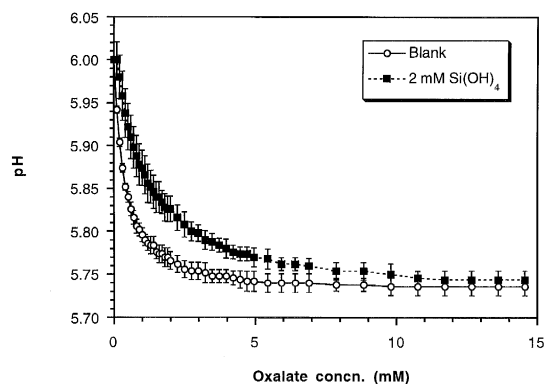


Fig. 2. Titration of $\text{K}_2\text{C}_2\text{O}_4$ vs. 2 mM $\text{Si}(\text{OH})_4$, initial pH 6. All titrations have 1 M NaNO_3 as a background electrolyte. Each point represents an average of five titrations, one σ error bars.

2, respectively. Fig. 1 demonstrates that, within analytical uncertainty, there is no difference between the titration curves obtained for $\text{Si}(\text{OH})_4$ and blank solutions at pH 5. Fig. 2 demonstrates an initial divergence in titration curves at pH 6, with convergence at higher oxalate concentrations. Titration of $\text{Si}(\text{OH})_4$ with HNO_3 indicates that dissolved silica acts as a pH buffer at pH 6, but not at pH 5 (Figs. 3 and 4).

Si-oxalate complexing has been modeled by performing a MINTEQA2 (Allison et al., 1991) calculation of titration of oxalate vs. $\text{Si}(\text{OH})_4$, at an initial pH 6, for various possible Si-oxalate complexes: the results are presented in Fig. 5. Calculations have been performed using $\text{K}_2\text{C}_2\text{O}_4$ as a titrant, and with 1 M NaNO_3 as a background electrolyte for: a blank titration; 2 mM $\text{Si}(\text{OH})_4$, with no Si-oxalate com-

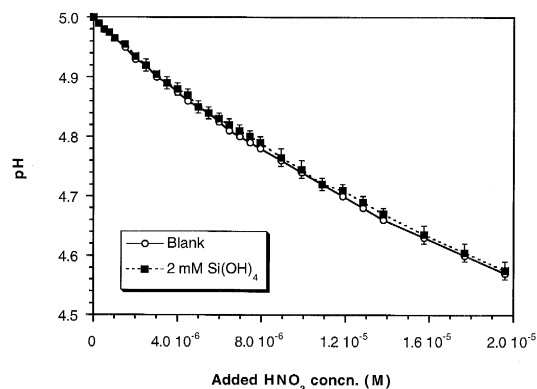


Fig. 3. Titration of HNO_3 vs. 2 mM $\text{Si}(\text{OH})_4$, initial pH 5. All titrations have 0.1 M NaNO_3 as a background electrolyte. Each point represents an average of two titrations, one σ error bars.

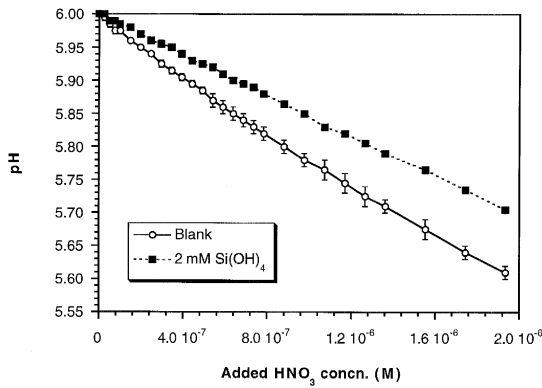


Fig. 4. Titration of HNO_3 vs. 2 mM Si(OH)_4 , initial pH 6. All titrations have 1 M NaNO_3 as a background electrolyte. Each point represents an average of two titrations, one σ error bars.

plexing; 2 mM Si(OH)_4 , with formation of a unidentate Si-oxalate ester (c.f. Eq. (1), $\log K_1 = -8.5$); 2 mM Si(OH)_4 , with formation of a bidentate Si-oxalate ester (c.f. Eq. (2), $\log K_2 = -16.5$); and 2 mM Si(OH)_4 , with formation of a Si-oxalate hydrogen-bonded complex (c.f. Eq. (3), $\log K_H = 1.5$). The values assigned for K_1 , K_2 , and K_H are for illustrative purposes only, and are intended to demonstrate the effect of Si-oxalate complex formation upon the observed titration curves. Smaller values of K_1 , K_2 , and K_H will result in titration curves

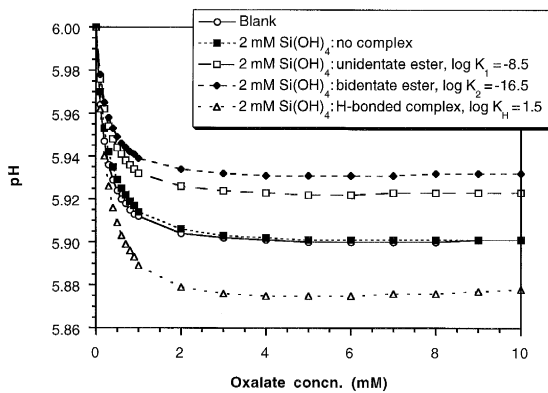


Fig. 5. MINTEQA2 calculations of titration of $\text{K}_2\text{C}_2\text{O}_4$ vs. 2 mM Si(OH)_4 , initial pH 6, for various possible Si-oxalate complexes, in the presence of 1 M NaNO_3 as a background electrolyte. See Eqs. (1)–(3) for the relevant formation equations for the unidentate ester, bidentate ester, and hydrogen-bonded complexes, respectively. Log K values used in the calculations are for illustrative purposes only, in order to demonstrate the expected shapes of the titration curves. See text for discussion.

being shifted closer towards the curve calculated for 2 mM Si(OH)_4 with no Si-oxalate complexing. While pH titration curves calculated using MINTEQA2 are significantly different from those measured experimentally (Fig. 2), the shapes of the titration curves are very similar. The difference between the calculated and measured values is attributed to the inability of MINTEQA2 to accurately model activity coefficients in these high ionic strength solutions (1 M NaNO_3).

As expected, calculations for the formation of unidentate and bidentate Si-oxalate esters indicate a shift in the titration curves to higher values of pH, due to the liberation of hydroxide during ester formation (Eqs. (1) and (2)). However, the curves show no sign of convergence with the blank solution at higher oxalate concentrations, as observed in the titration experiments (Fig. 2). The calculation for the formation of a Si-oxalate hydrogen-bonded complex indicates a shift in the titration curve to lower values of pH. The shift to lower values of pH was unexpected, as Eq. (3) does not directly involve the production of acidity. A possible explanation of this shift is that oxalate is tied up as the Si-oxalate complex, leaving a lower oxalate activity in solution (for a given total oxalate concentration) to buffer the initial drop in pH. In any case, this curve also shows little sign of convergence with the blank solution at higher oxalate concentrations.

Additional MINTEQA2 calculations of the titration of oxalate vs. 2, 4, or 10 mM Si(OH)_4 , at an

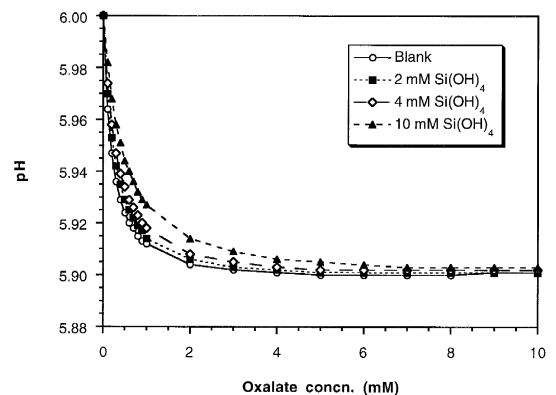


Fig. 6. MINTEQA2 calculations of titration of $\text{K}_2\text{C}_2\text{O}_4$ vs. 2, 4, or 10 mM Si(OH)_4 , initial pH 6, with no Si-oxalate complexing. All titrations have 1 M NaNO_3 as a background electrolyte.

initial pH 6, without Si-oxalate complex formation, have been performed to investigate the pH buffering effect of $\text{Si}(\text{OH})_4$, and the results are presented in Fig. 6. The titration curves in the presence of $\text{Si}(\text{OH})_4$ show an initial divergence from the blank solution, with convergence at higher oxalate concentrations. The shapes of these curves are very similar to the titration curves obtained experimentally (Fig. 2). The difference in the calculated vs. measured values is again attributed to the inability of MINTEQA2 to accurately model activity coefficients in these high ionic strength solutions.

3.2. Oxalate adsorption onto quartz

Adsorption reactions are typically considered to be relatively rapid, reaching completion in a couple of hours (Stumm, 1992; Stumm and Morgan, 1996). Hence, the majority of the adsorption experiments were performed with 4–5 h of contact time with quartz, over an experimental pH range of pH 4.3–7.1 (Fig. 7). Spectroscopic work by Bennett et al. (1988) suggested that aqueous $\text{Si}(\text{OH})_4$ –organic acid complexation may take place over longer time periods (> 5 days). Therefore, some adsorption experiments were performed with 1 week of contact time with quartz. As most dissolution experiments have been performed at pH 7 (Bennett et al., 1988; Bennett, 1991), the experiments were performed at pH 6.3–7.0 (Fig. 8).

Both Figs. 7 and 8 show negligible adsorption of oxalate. Considering analytical uncertainties, there

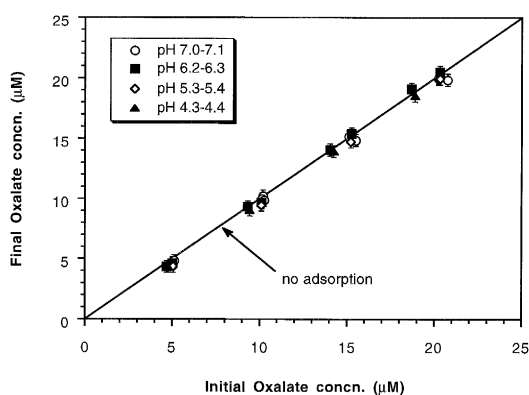


Fig. 7. Oxalate adsorption onto quartz, 4–5 h duration.

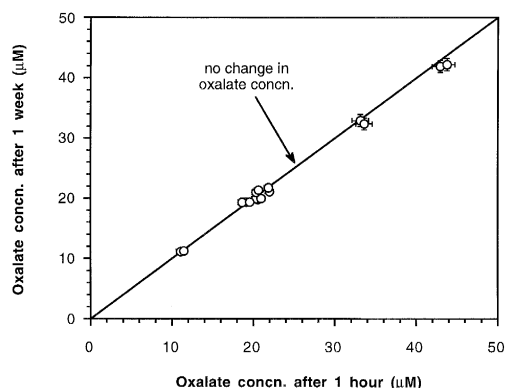


Fig. 8. Oxalate adsorption onto quartz, pH 6.3–7.0, one week duration. Some error bars are approximately the same size as the symbols.

could have been a maximum decrease of oxalate concentration of one μM due to adsorption, which equates to a maximum oxalate adsorption of 3.0×10^{-9} mol/m². Using a value of five surface “sites”/nm² (Schindler, 1981), this corresponds to a maximum of 3.6×10^{-4} oxalate ions adsorbed/“site”.

4. Discussion

Titration of $\text{Si}(\text{OH})_4$ with oxalate indicates that, within analytical uncertainty, there is no difference in the titration curves obtained for $\text{Si}(\text{OH})_4$ and blank solutions at pH 5 (Fig. 1). Similar titrations at pH 6 (Fig. 2) indicate an initial divergence of titration curves for $\text{Si}(\text{OH})_4$ and blank titrations, with a convergence of titration curves at higher oxalate concentrations. MINTEQA2 modeling (Fig. 5) indicates that significant Si-oxalate complex formation should result in little or no convergence of the titration curves at higher oxalate concentrations. The initial divergence of titration curves at pH 6 is produced by the small pH buffering effect of $\text{Si}(\text{OH})_4$ at this pH, as indicated by titrations with HNO_3 (Fig. 3) and additional MINTEQA2 modeling (Fig. 6). Hence, the data imply negligible Si-oxalate complex formation at pH 5 and 6. This would result in a minimal decrease in the solution saturation state during the dissolution of quartz, and therefore would

have a minimal effect upon the dissolution rate of quartz.

Adsorption experiments indicate negligible adsorption of oxalate onto quartz, with a maximum oxalate adsorption of 3.0×10^{-9} mol/m², corresponding to a maximum of 3.6×10^{-4} oxalate ions adsorbed/“site”. It seems unlikely that these very low concentrations of adsorbed oxalate will have any significant effect on framework Si–O–Si bonds, and hence they should have little effect upon dissolution rates of quartz.

A possible explanation for the apparent increase in quartz dissolution rates may be provided by a re-examination of some of the original dissolution rate data. Dove and co-workers (Dove and Crerar, 1990; Dove and Elston, 1992; Dove, 1994) have clearly demonstrated that quartz dissolution rates increase in the presence of NaCl (also recognized by Bennett, 1991). Quartz dissolution rate data in the presence of NaCl and Na₂oxalate is plotted vs. Na⁺ concentration in Fig. 9, and illustrates that the dissolution rate in the presence of Na₂oxalate is essentially the same as the dissolution rate in the presence of NaCl with the same Na⁺ concentration. Hence, it appears that the effect of oxalate *per se* upon quartz dissolution rates is small or zero, which would be consistent with the lack of significant aqueous silicic acid-oxalate complex formation, and the lack of significant adsorption of oxalate onto quartz surfaces observed in this study.

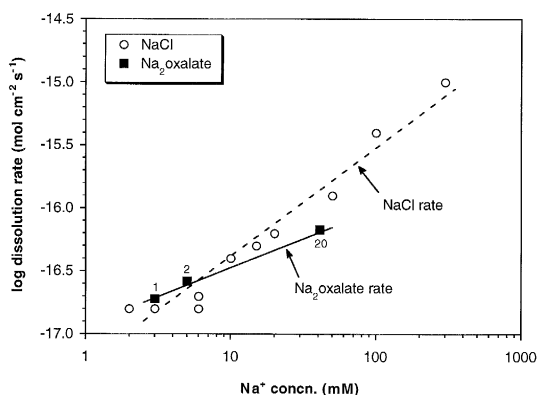


Fig. 9. Quartz dissolution rate vs. Na⁺ concentration, at 25°C, pH 7. Numbers next to oxalate data represent oxalate concentrations (mM). Data from Bennett et al. (1988) and Bennett (1991).

5. Conclusions

Potentiometric titrations of Si(OH)₄ with oxalate, and investigation of the adsorption of oxalate onto quartz have found:

1. no evidence for the significant formation of an aqueous silicic acid-oxalate complex; and
2. no evidence for any significant adsorption of oxalate onto quartz surfaces.

Re-evaluation of quartz dissolution rate data suggests that dissolution rates in the presence of Na₂oxalate are essentially the same as dissolution rates in the presence of NaCl of equivalent Na⁺ concentration. Hence, the effect of oxalate *per se* upon quartz dissolution rates appears to be small or zero, consistent with the lack of aqueous silicic acid-oxalate complex formation and the lack of oxalate adsorption onto quartz surfaces observed in this study.

Acknowledgements

The authors are grateful to C.D. Tait for providing a pre-print of the spectroscopic investigation of silica-organic acid complexing, and for reviews by A. Hajash Jr., and C.D. Tait. This research has been supported by the U.S. Air Force Office of Scientific Research (grant F49620-94-1-0194).

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