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Solubility experiments were performed at 5 °C by reacting 1 g of powdered gibbsite with 45 g of aqueous H_2SO_4–NaCl and HCl–NaCl (0.01 m H⁺) solutions at 0.1 m ionic strength. The kinetics of dissolution were monitored under extremely undersaturated conditions and appeared to favor a zero-order rate-determining process. The dissolution rate of gibbsite in the sulfate solution was approximately 10 times faster than in the HCl solution, which is consistent with trends reported in the literature for studies performed at higher temperatures. The enhanced dissolution kinetics of gibbsite (and by analogy, other aluminum-containing minerals) in the presence of sulfate may contribute to the elevated Al concentrations observed in natural low-temperature waters associated with acid rain and acid mine drainage.

Introduction

High Al concentrations have been reported in natural surface waters receiving large inputs of acid–sulfate solution, such as acid rain and acid mine drainage. Frequently, these surface waters occur at high altitudes or high latitudes (*1–3*), have average temperatures of only 5–10 °C, and are "acid-sensitive". Acid-sensitive waters have insufficient neutralizing capacity to compensate for increases in acid input (*3*), leading to dissolution of Al-bearing minerals, Al remobilization, and transport.

Experimental studies have suggested that sulfate enhances the dissolution rate of gibbsite [Al(OH)₃], a common soil mineral, relative to other acid anions (*4, 5*). Observed high Al concentrations in acid–sulfate surface waters may therefore result from an increase in the dissolution rates of Al-bearing minerals (e.g., gibbsite). The earlier studies (*4, 5*), however, were performed at 20–65 °C, significantly higher temperatures than those found in many natural groundwaters and surface waters, and were sufficiently unconstrained that the significance of the acid anion remains equivocal. The solubility experiments presented here were performed to examine gibbsite dissolution at low temperatures and acid pH values, such as may be found in natural surface waters affected by high Al and sulfate levels. Unlike the previous studies, these experiments were also performed at near-constant ionic

strength and hydrogen ion molality in order to isolate the effect of sulfate relative to chloride on the dissolution rate.

Experimental Section

Materials. The preparation and standardization of HCl, NaOH, and NaCl stock solutions were described in earlier papers by Wesolowski (*6*) and Wesolowski and Palmer (*7*). The sulfuric acid stock solution (1 N Baker analyzed reagent, Lot No. H13528) was standardized by pH titration with the NaOH stock solution. Two experimental solutions containing (1) 0.005002 m H_2SO_4 and (2) 0.01001 m HCl with sufficient NaCl to fix the stoichiometric molal ionic strength at 0.1 were prepared from the stock solutions. Although the aluminum concentration was not measured in the original starting solutions, the concentration of Al measured in a second batch of solutions prepared from the same stock solutions were $10^{-7.13}$ and less than $10^{-7.7}$ m for the H_2SO_4 and HCl solutions, respectively. The gibbsite was from the same batch as that used in the earlier studies (*6, 7*). Wesolowski (*6*) described the pretreatment and characterization of the gibbsite following the procedure of Bloom and Weaver (*8*).

Procedure. In duplicate experiments, approximately 1 g of gibbsite and 45 g of experimental solution, prechilled to 5 °C, were loaded into 50-mL, disposable, sterile, polypropylene/polyethylene syringes. The capped syringes were then placed on a rotating rack in a thermostated water bath, at 5 ± 0.05 °C, and allowed to react for 2.5 h; at which point the solution was discarded and replaced with fresh, prechilled starting solution. The syringes were recapped, gently agitated, and then sampled immediately before being placed on the rotating rack. This initial sampling was considered as the starting point (i.e., the zero time value) of the solubility experiments. The temperature of the water bath was monitored throughout the experiment.

Analytical Methods. The syringes were sampled at intervals as shown in Table 1. At each sampling, the syringes were fitted with 0.2-μm poly(vinylidene fluoride) (PVDF) membrane filters through which a small volume of solution was initially dispensed and discarded. A 1-mL sample was then collected directly into a 5-mL disposable, sterile, polypropylene/polyethylene syringe attached to the filter and refrigerated immediately. The filtered samples showed no visible evidence of entrained particulates or precipitates.

The total dissolved Al concentration in each sample was determined by ion chromatography within 3 days of sampling (*7*). Sample storage was minimized in order to prevent losses due to adsorption. Samples were diluted in purified water, prior to analysis, to approximately 10^{-5} m total aluminum, which corresponded to dilution factors of approximately 3 and 20 for the HCl and H_2SO_4 samples, respectively. The water used to dilute the samples was purified by passing distilled water through a Barnstead four-stage deionizing system that yielded water with a resistivity of 0.18 MΩ·m. Aliquots of two samples were diluted with 0.01 N HCl rather than pure water (Table 1). The similarity within experimental error of total Al concentrations of these aliquots indicates that Al precipitates did not form in the samples diluted in purified water: no precipitates would have formed in the acid diluent. To further test whether particulates were sampled through the 0.2-μm membrane filters, two samples were filtered a second time through 0.025-μm membrane filters. No significant differences were detected in the total Al concentration (Table 1). The gibbsite to solution ratio increased during the course of the experiment; however, this change would not have influenced the results of this study as the ratio of gibbsite to solution remained uniform between the H_2SO_4 and HCl samples.

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**TABLE 1. Solution Compositions for Dissolution of Gibbsite in Aqueous H₂SO₄—NaCl and HCl—NaCl Media**

| | H₂SO₄—NaCl media | | | | HCl—NaCl media | | | |
| | solution 1 | | solution 2 | | solution 1 | | solution 2 | |
time (h)	log[Al$_{tot}$]	pH^a	log[Al$_{tot}$]	pH^a	log[Al$_{tot}$]	pH^a	log[Al$_{tot}$]	pH^a
0.0	−5.331	2.03	−5.254	2.03	−5.773	2.00	−5.862	2.00
22.0	−4.985	2.03	−4.908	2.03	−5.481	2.00	−5.483	2.00
22.0	−5.011^b	2.03						
47.0	−4.822	2.03	−4.504	2.03	−5.320	2.00	−5.248	2.00
70.0	−4.530	2.03						
94.5			−4.354	2.03			−5.136	2.00
118.0	−4.376	2.03			−5.149	2.00		
144.5			−4.224	2.03			−5.120^c	2.00
144.5							−5.142^c	2.00
165.5	−4.264	2.03			−5.033	2.00		
238.0			−4.038	2.03			−4.982	2.00
288.0	−4.056	2.03			−4.866	2.00		
288.0	−4.078^b	2.03						
333.5			−3.903	2.03			−4.867	2.00
497.0	−3.518^c	2.05^d	−3.521	2.06^d	−4.556	2.00^d		2.00^d
497.0	−3.595^c							
1054.0	−3.379	2.03	−3.342	2.03	−4.294	2.01	−4.319	2.01
1054.0	−3.396^e	2.03			−4.295^e	2.01		

^{a} Defined as −log[H⁺] for this study. Value calculated from solution composition unless otherwise noted. ^{b} Solution filtered through 0.025-μm membrane filters prior to analysis. ^{c} Duplicate analyses of a single sample. ^{d} Value measured using procedure outlined in text. ^{e} Sample diluted with 0.01 N HCl prior to analysis.

The pH values (defined as −log[H⁺], in molal concentration units) of the experimental solutions were calculated from the known initial solution stoichiometries. However, pH was also measured once during the experiment at 5 °C using the procedure described by Wesolowski and Palmer (7). After collecting samples for Al analysis, a further 1 mL filtered sample was collected and placed in the 5 °C water bath. A Ross glass pH electrode was standardized at 5 °C with four solutions containing 0.001−0.01 m HCl in NaCl with an ionic strength of 0.1 m. The potential reading (in millivolts) corresponding to each of the standards was recorded, and a calibration curve was constructed. The potential of each sample was then recorded, and the H⁺ concentration was calculated from the calibration curve (Table 1). No drift in the potential readings of the standards was observed during the period required to measure the four samples. The measured pH values were found to be in excellent agreement with the calculated pH values (Table 1).

Results and Discussion

The difference in gibbsite dissolution rates in the two media is significant and evident from the first sampling (Figure 1, Table 1). In the absence of complexing species, the total Al concentration in a solution in equilibrium with gibbsite is controlled by the dissolution of gibbsite

$$Al(OH)_3 + 3H^+ \rightleftharpoons Al^{3+} + 3H_2O \tag{1}$$
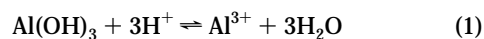
and the hydrolysis of Al³⁺

$$Al^{3+} + nH_2O \rightleftharpoons Al(OH)_n^{3-n} + nH^+ \tag{2}$$
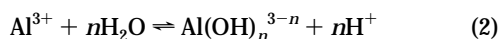
Al hydrolysis species are negligible in these experiments, because the first hydrolysis constant is $10^{-5.99}$ at 5 °C and 0.1 m (9), the ratio of [Al(OH)²⁺] to [Al³⁺] will exceed 1:1000 only when the solution pH exceeds 3. The addition of sulfate requires consideration of sodium sulfate and aluminum sulfate species. Sodium sulfate ion pairs are weak (10) and comprise less than 1% of the total sulfate species. Aluminum sulfate complexes are significant (11−17), and form by the following reaction:
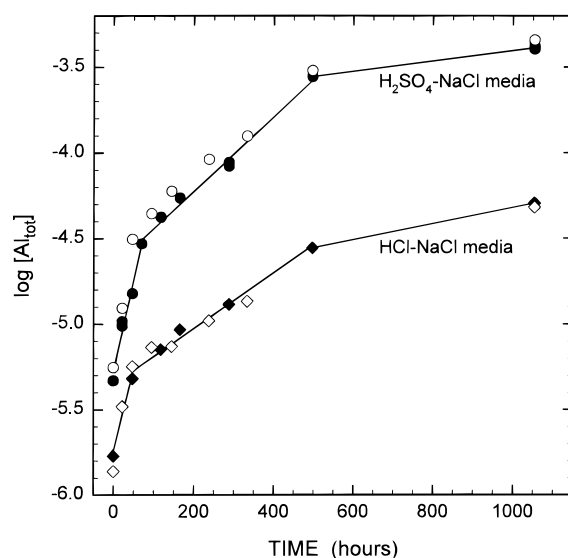
$$Al^{3+} + nSO_4^{2-} \rightleftharpoons Al(SO_4)_n^{3-2n} \tag{3}$$

FIGURE 1. Plot of the logarithm of total dissolved aluminum, representing the dissolution of gibbsite as a function of time, in 0.005 m H₂SO₄ and 0.01 m HCl, at 5 °C and 0.1 m ionic strength. (The open and filled symbols distinguish between duplicate samples).

The total dissolved Al³⁺ in acidic sulfate solutions can therefore be calculated from the mass balance equation:

$$\sum Al^{3+} = [Al^{3+}] + [Al(OH)^{2+}] + [Al(OH)_2^+] +$$
$$[Al(OH)_3^0] + [Al(OH)_4^-] + [Al(SO_4)^+] + [Al(SO_4)_2^-] ... \tag{4}$$

The thermodynamics of gibbsite dissolution in aqueous solutions have been studied extensively (6, 7, 18, 19), and the resulting solubility constants have been modeled over a wide range of temperatures and ionic strengths. The solubility quotient for reaction 1 is $10^{9.64}$ at 5 °C and 0.1 m ionic strength (19). Tentative values for the molal formation quotients for Al(SO₄)⁺ and Al(SO₄)₂⁻ (reaction 3) at 5 °C and 0.1 m are $10^{3.13}$ and $10^{6.28}$, respectively (16), based on recent potentiometric studies in this laboratory. Additional independent experiments are in progress to verify these values.

Total Al concentrations at equilibrium with gibbsite, calculated using the above equilibrium quotients, are 7−8
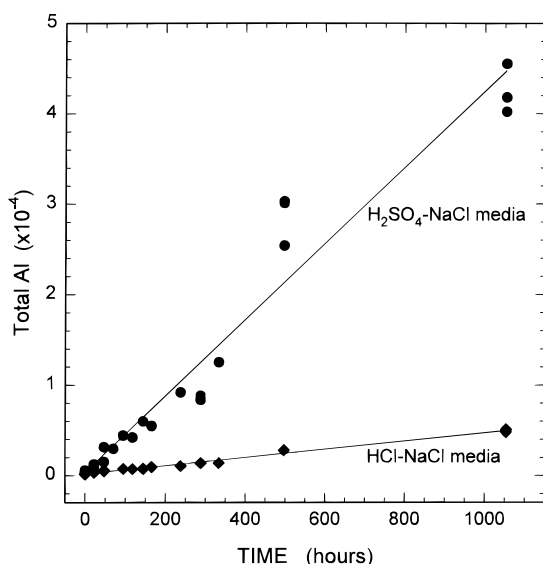
FIGURE 2. Plot of total dissolved aluminum, representing the dissolution of gibbsite as a function of time, in 0.005 m H_2SO_4 and 0.01 m HCl, at 5 °C and 0.1 m ionic strength.

orders of magnitude greater than the final values measured during this study (Table 1). Clearly these solutions are still very undersaturated. Previous studies have suggested a slow equilibration rate for gibbsite dissolution in acidic, low-temperature solutions (*19, 20*), and few natural low-temperature environments reach equilibrium (*2, 21, 22*).

An initial difference in the concentration of dissolved Al^{3+} (at time zero) is apparent from Figure 1, this difference may result partially from the incomplete removal of all starting solution during the initial rinsing. The concentration of total dissolved Al^{3+} during the first 70 h of this experiment may be described by first-order rate constants of 0.027 and 0.026 h^{-1} for the sulfate and HCl solutions, respectively, equivalent to half-lives of 26 and 27 h (for doubling the concentration of total dissolved Al^{3+}) (*23*). The second step (70−500 h) in Figure 1 for each solution also follows first-order kinetics. Rate constants for the increase in total dissolved Al^{3+} of 0.0049 h^{-1} for the sulfate solution and 0.0034 h^{-1} for HCl (equivalent to half-lives of 142 and 204 h, respectively) were derived. From Figure 1, it appears that a third stage of first-order rate behavior is evident in the final 500 h of the experiment. Perhaps these stepwise, first-order rate constants indicate that the more active surfaces are still being preferentially removed during these initial phases of dissolution, despite the pretreatment process employed to eliminate active surface sites. The initial (time zero) difference between the concentrations of aluminum in solution for the two media is then likely to be the result of more rapid dissolution of the highest energy surfaces in the sulfate solution. If first-order kinetics indeed prevail, then it is apparent from Figure 1 that the rate constants become more similar with time. The gibbsite used in these experiments, however, has been extensively preconditioned in an attempt to remove fine particles and defects.

On the other hand, the entire data sets are described in a consistent and continuous manner by zero-order rate constants (Figure 2) of 4.21×10^{-7} and 4.56×10^{-8} $m \cdot h^{-1}$ for the sulfate and HCl solutions, respectively. Based on these rate constants, the half-lives of the two reactions (i.e., the appearance of half the Al^{3+} concentration expected at equilibrium) are 5.2×10^9 and 4.8×10^{10} h for the sulfate and HCl solutions, respectively. Although zero-order rate constants appear to describe the kinetics of dissolution implying a constant rate of production of Al^{3+}, the order of any reaction cannot generally be determined unambiguously from the initial (far from equilibrium) rate data. Given the large mass of solid to solution volume ratio, which actually increases

during the experiments but does not inherently affect the zero-order rate plots, it is not surprising that zero-order kinetics are observed, and in fact this condition would be expected in the natural environment involving leaching of aluminum from subsurface minerals. Moreover, these experiments were conducted at constant pH and ionic strength so that their effects on the dissolution rate were also constant during the experiment.

Two earlier studies describe the rate of gibbsite dissolution as a function of acid anion type (*4, 5*) and report increases in gibbsite dissolution in aqueous sulfate solutions. Bloom and Erich (*4*) found that gibbsite dissolution occurred 50 times faster in sulfate solutions than in nitrate solutions at 25 or 40 °C. A comparison with the present results is not possible, because they maintained neither constant ionic strength nor constant pH during the course of their experiments. Packter and Dhillon (*5*) found that sulfuric acid solutions dissolve gibbsite 15−30 times faster than perchloric acid of equal molar anion concentrations. The pH of the sulfuric acid solutions in their study was lower than the perchloric acid solutions because sulfuric acid is diprotic. Therefore, faster dissolution in the sulfuric acid solutions is likely to be a pH as well as a sulfate effect. Packter and Dhillon's (*5*) study was performed at temperatures from 20 to 65 °C with the dissolution rate of gibbsite increasing with increasing temperature, but no ionic strength information was reported.

Solution pH and the distribution of Al species can be calculated from the known solution stoichiometry, measured total Al concentrations, the equilibrium quotients listed above, and the dissociation quotient for bisulfate, which is $10^{-1.26}$ at 5 °C and 0.1 m (*24*). Solution pH remained constant throughout the experiment (Table 1) due to the very low total Al concentrations relative to the H^+ concentrations. Initial pH values calculated from known solution stoichiometry were 2.03 and 2.00 for the sulfate and HCl experimental solutions, respectively. These calculated values agree with initial measured pH values of 2.03 and 2.01 for the sulfate and HCl solutions. Measured pH values of the reacted solutions of 2.05 and 2.06 for the sulfate samples and of 2.00 for the HCl samples were obtained (Table 1) and are in good agreement with the corresponding calculated values.

Total Al in the H_2SO_4−NaCl solution (eq 4) is approximately 10 times greater than total Al (which will be equal to free Al^{3+}) in the HCl−NaCl solution (eq 1). The distribution of Al species, based on our recent potentiometric data, indicates that aluminum sulfate species dominate the H_2SO_4−NaCl solution (Figure 3a). Because the preliminary results of our potentiometric study (*16*) suggest that aluminum sulfate complexes may be stronger at low temperature than previously reported and may increase in stability with decreasing temperature, literature data were also used to distribute the Al species (Figure 3b). Literature data below 25 °C are unavailable; therefore, the 25 °C formation constants of Izatt et al. (*12*) were used as a conservative estimate of the 5 °C formation constants. Although no temperature corrections were applied to the data of Izatt et al. (*12*), the extended Debye−Hückel equation employed by Pitzer (*25*) was used to adjust the ionic strength to 0.1 m at 5 °C, providing association quotients of $10^{1.50}$ and $10^{2.88}$ for $Al(SO_4)^+$ and $Al(SO_4)_2^-$, respectively. The dominant Al species is Al^{3+} when the weaker aluminum sulfate formation quotients are used to calculate the distribution of Al species (Figure 3b). Calculated sulfate and bisulfate concentrations show little change during this study (Figure 3a,b). The formation of aluminum hydroxysulfate phases in natural waters have been observed when the acid sulfate waters are neutralized or pH is increased (*26−29*), neither of which occur during the course of this study.

The present study is the first to demonstrate unequivocally that the dissolution of gibbsite in acidic low-temperature solutions is significantly enhanced by the presence of sulfate,
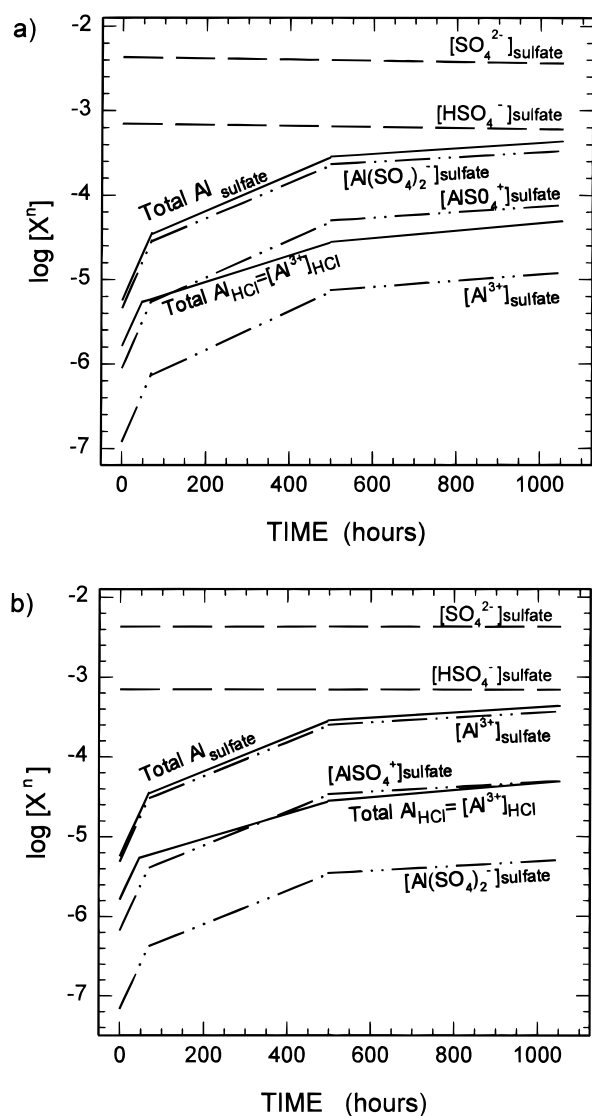
FIGURE 3. Aluminum and sulfate speciation in the H_2SO_4–NaCl and HCl–NaCl solutions, calculated from the measured total Al concentrations and known solution stoichiometry. The $\log[X^n]$ on the ordinate represents the concentration of total Al, $AlSO_4^+$, $Al(SO_4)_2^-$, HSO_4^-, and SO_4^{2-} in the H_2SO_4–NaCl solution, and total Al in the HCl–NaCl solution. Concentrations of aluminum hydroxide species are less than 10^{-7} m. The association quotients used for $Al(SO_4)^+$ and $Al(SO_4)_2^-$ were (a) $Q_1 = 10^{3.13}$ and $Q_2 = 10^{6.28}$; (b) $Q_1 = 10^{1.50}$ and $Q_2 = 10^{2.88}$.

relative to chloride, when all other solution parameters are fixed (Figure 1). This enhanced dissolution of gibbsite (and by analogy, other aluminum-containing minerals) may contribute to the high Al concentrations observed in natural waters (*2, 21, 22*) that receive input of acid sulfate waters, such as acid rain and acid mine effluents. Although the residence time of these waters is insufficient for them to attain equilibrium with the solid phase, this study suggests that high concentrations of dissolved Al are possibly due to the enhanced dissolution kinetics. Furthermore, fine grained material present in natural systems would dissolve more rapidly, further increasing the dissolution rate (note that the grain size of the gibbsite in this study was $10-35~\mu$m). The eventual neutralization of acid sulfate solutions—resulting from processes such as mixing and dilution with other waters and through water–rock interactions—will cause the sulfate solutions to become supersaturated with respect to Al-bearing minerals, with the consequent precipitation of Al phases (*25–*

28). Understanding the dissolution kinetics of Al-bearing minerals (such as the gibbsite used in this study, and albite and kaolinite) and the role of sulfate complexation in the dissolution process is therefore essential to understanding (1) the controls on Al concentration in surface waters and groundwater; (2) the speciation of Al in natural waters; (3) the effects of sulfur input into the atmosphere and climate changes on weathering rates; and (4) the biogeochemical cycling of Al in the environment.

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