

Dissolution Kinetics of Hornblende in Organic Acid Solutions

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ABSTRACT

The dissolution rates of most primary and secondary minerals are promoted by the presence of proton- and complex-forming ligands. Effects on the rates of dissolution of hornblende by naturally occurring organic acids at concentrations commonly encountered in soil solutions and surface waters was studied in a pH 4.0, 0.01 M HOAc–LiOAc buffer. Crushed hornblende samples were purified by magnetic and density separation, followed by an initial period of weathering in a buffered aqueous solution for 39 d. After the initial weathering the rate of dissolution was measured at different concentrations of citric, oxalic, polygalacturonic, tannic, and fulvic acids at pH 4.0 for another 32 d in a batch-type reactor. Although nearly linear kinetics were observed for the release of Si, the release of Al, Fe, and Mg decreased with time. The dissolution was nonstoichiometric during the study period with preferential release of Al, Fe, and Mg relative to Si. All ligands studied were found to accelerate the dissolution process and the rates increased with solution concentrations of organic acids. The reaction orders with respect to dissolved organic C were generally low, ranging from near zero to 0.37 for different organic acids. At a concentration of 2.5 mM of dissolved C the relative effectiveness of these ligands on promoting dissolution was oxalic > citric > tannic > polygalacturonic > fulvic acid. The strengths of organic acids to promote dissolution is related to the quantity of phenolic and carboxylic functional groups present on the organic compounds, and it is related to the strength of the metal–ligand complex formed in solution or on the mineral surface.

ALUMINOSILICATE DISSOLUTION is generally considered a process controlled by reactions at mineral surfaces (Blum and Lasaga, 1991). The dissolution rate of a mineral depends on the chemistry of weathering fluid, such as the concentration of proton and organic acids. Adsorption of organic acids by minerals has been shown to increase the dissolution rates of most aluminosilicates (Huang and Kiang, 1972; Grandstaff, 1986; Manley and Evans, 1986; Chin and Mills, 1991), goethite (Holmen and Casey, 1996), and silicates (Bennett et al., 1988; Wogelius and Walther, 1992), but the effect of organic acids on hornblende dissolution has not been investigated. Hornblende is an important mineral in proton neutralization and base-release processes in many soils. Water soluble, low molecular weight organic acids that are produced as microbial metabolites or plant exudates

from living and dead cells and high molecular weight humic substances synthesized in soils are commonly present in soil solutions and groundwater. These organic compounds will react with soil minerals by forming water soluble or insoluble organic complexes with metal ions at the surface and weakening the metal–oxygen bonds of the solid by bond polarization, thus increasing mineral weathering rates.

Most studies on the effects of organic acids on dissolution have used concentrations of organic compounds much higher than are commonly found in soil solutions and natural waters. In some studies the pH was not controlled, which made it difficult to separate the effect of pH from that of organic ligand–surface complexation. Also, the use of freshly ground minerals in most studies introduced artifacts created by grinding, thus affecting an accurate rate determination. The freshly ground minerals usually show a rapid initial dissolution rate that decreases with time to a steady state (e.g., Huang and Kiang, 1972; Luce et al., 1972; Talman and Nesbitt, 1988). For hornblende, it took ≈ 30 d reaction in pH 4.0, 0.01 M HOAc–LiOAc buffer to reduce the grinding effect and reach such a steady state (Zhang et al., 1996). Surface complexation models have been applied to model the promoted dissolution of anorthite (Amrhein and Suarez, 1988) as well as oxides and silicates (Wieland et al., 1988) in the presence of complex-forming ligands. These researchers observed that the rate of dissolution was linearly related to the surface concentration of absorbed ligands. Similar results were observed for the ligand-promoted dissolution of microcline (Nater and Huang, 1988), where the rate of release of Al and K was highly correlated with the Al–ligand complexation constants for several low molecular weight aliphatic acids at pH 4.5. The rate of quartz dissolution was also enhanced in the presence of 20 mM kg^{-1} concentrations of citrate, oxalate, and salicylate (Bennett et al., 1988), although those carboxylic acids were not previously known to form complexes with silica. Holmen and Casey (1996) reported that the rate of goethite dissolution was dominated by the ligand-induced reaction at pH >4.0. Chin and Mills (1991) found that low molecular weight organic ligands markedly increased the dissolution rates of both Al and Si from kaolinite in the following order:

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Published in Soil Sci. Soc. Am. J. 63:815–822 (1999).

Abbreviations: DCP, direct current plasma emission spectroscopy; EDTA, ethylenediamine tetra-acetic acid; FA, fulvic acid; ICP, inductively coupled plasma emission spectroscopy.

oxalate > malonate ≈ salicylate > o-phthalate. They also found the rate of Al dissolution was greater than the rate for Si in the presence of organic ligands; and soil humic acids and organic matter dissolved in stream water did not promote the dissolution of kaolinite at 50 and 40 mg L⁻¹, respectively. Mast and Drever (1987), however, found no significant effects of oxalate (0.5 and 1 mM) on the dissolution rate of tremolite nor on the steady state release of Si from oligoclase.

In the present study five complex-forming organic acids, including a fulvic acid extracted from soil at concentrations similar to those occurring in natural systems, were used in batch weathering of hornblende that used an initially reacted sample to study (i) the effect of ligand concentrations on dissolution rate, (ii) the relative strength of different organic species on promoting dissolution, and (iii) the mechanisms causing ligand-promoted dissolution.

MATERIALS AND METHODS

Mineral Sample

The hornblende sample was obtained from Dr. Richard April, Colgate University, Hamilton, NY. The same sample was used in our previous studies of the morphology and chemistry of hornblende dissolution products (Zhang et al., 1990) and the relationship of dissolution rates to surface area (Zhang et al., 1993). The bulk rock sample was crushed mechanically using a disk grinder until all samples passed a 2.0-mm sieve. The crushed material was fractionated by dry-sieving to obtain a 0.25- to 0.50-mm fraction. Magnetic impurities were removed with a Frantz isodynamic magnetic separator (S.G. Frantz Co., Trenton, NJ), and light impurities were removed by heavy liquid separation (CHBr₃, sp gr 2.89). A majority of the ultrafine particles produced by grinding were removed by ultrasonic cleaning in acetone until a clear supernatant was obtained prior to magnetic and density separation. The identity of the mineral was verified by powder X-ray diffraction, which did not show the presence of any minerals other than hornblende. Samples treated as described above are referred to as an *ultrasonically cleaned* sample. Scanning electron microscopy of ultrasonically cleaned grains showed few fine particles adhering to the surface.

A preliminary study of hornblende dissolution performed on the ultrasonically cleaned sample showed rapid initial dissolution, which is an artifact of pretreatment resulting from the production of surface strain, ultrafine particles, and other high energy defects (Holdren and Berner, 1979). To minimize the effects of high energy surface sites produced by grinding and to simulate dissolution rates that resemble those of naturally weathered samples, the ultrasonically cleaned samples were first weathered in the laboratory for 39 d in a pH 4.0, 0.01 M HOAc–LiOAc solution at 298 K. The initial weathering was conducted in 250-mL plastic bottles with solid/solution ratio of 1/20. Bottles were placed in a thermostated water bath and agitated at 80 (±2) cycles min⁻¹. The initially weathered particles were rinsed with deionized and distilled water and air-dried at room temperature. The surface area of the initially weathered starting materials was determined by using the 3-point BET-N₂ adsorption method with a Quantasorb surface area analyzer (Quantachrome Corp., Syosset, NY); it was 0.266 m² g⁻¹.

The average chemical composition of the initially weathered sample [determined by direct current plasma emission spectroscopy (DCP) after fusion with Li-metaborate (Bank-

ston et al., 1979)] was: K_{0.11}Na_{0.66}Ca_{1.66}(Mg_{3.11}Fe_{1.02}²⁺Al_{0.79}Fe_{0.32}³⁺)(Al_{1.64}Si_{6.36})O₂₂(OH,F)₂.

Solutions

The 0.01 M LiOAc–HOAc buffer solution was prepared using reagent grade LiOH and analytical reagent grade glacial acetic acid, and it was adjusted to pH 4.00 with additional acetic acid or LiOH.

Five different organic acids, with three concentrations of each, were used to study the dependency of hornblende dissolution rate on organic acid concentrations. Reagent grade polygalacturonic acid, tannic acid, Na–citrate, and Na–oxalate were used to prepare solutions of organic acids. A fulvic acid extracted using methods employed for the preparation of reference samples of the International Humic Substance Society, based on the separation scheme described by Thurman and Malcolm (1981) from a Histosol (Terric Borosaprist, collected in Beltrami County, MN) was also used. All organic acid solutions were made in a pH 4.0, 0.01 M HOAc–LiOAc buffer. The buffer was sufficient to maintain the solution pH during the dissolution experiment. The concentrations of organic acids ranged from 0.1 to 1.0 mM. A small quantity (≈3 drops L⁻¹) of chloroform was added to all solutions to prevent microbial breakdown of the organic acids.

Dissolution Experiment

The dissolution of hornblende was conducted in acid-washed, 250-mL polyethylene bottles at 298 K. Two grams of initially weathered sample were placed into 200 mL of 0.01 M LiOAc–HOAc buffer solution with the treatments listed in Table 1. The bottles were placed horizontally in a thermostated water bath and agitated at 80 (±2) cycles min⁻¹. Periodically, the bottles were removed from the bath and centrifuged at 6000 rpm for 15 min. Twenty five-milliliter aliquots were removed and acidified to pH ≈1.0 using concentrated HNO₃ to prevent loss of Al from solution and to prevent oxidation and precipitation of Fe during storage. Twenty five milliliters of fresh buffering solution was added after each sampling to maintain the mineral/solution ratio. Solutions were analyzed for Al, Ca, Fe, Mg, and Si by inductively coupled plasma (ICP) emission spectroscopy. The total quantity of elements released at each sampling time was calculated after correcting for dissolved material removed in the previous sampling. The pH of

Table 1. Summary of experimental conditions and dissolution rates.

Organic acids	Concentration	Rate			
		Al	Fe	Mg	Si
	mM C L ⁻¹	M m ⁻² s ⁻¹ × 10 ⁻¹²			
Control	Acetate buffer	3.57	5.18	8.08	7.28
Oxalic acid	0.20	4.77	5.96	10.5	15.6
	0.80	8.94	9.91	18.0	24.8
	2.00	10.9	11.8	23.1	30.4
Citric acid	0.60	5.98	8.02	13.1	17.2
	2.40	10.7	12.9	22.7	25.7
	6.00	12.3	13.7	25.9	29.8
Tannic acid	7.60	6.66	8.61	16.0	18.8
	38.0	10.1	11.6	21.1	22.1
	76.0	11.8	12.8	23.8	24.8
Polygalacturonic acid	0.62	4.35	5.76	8.53	9.74
	2.84	4.83	6.16	10.1	12.0
	6.18	5.27	6.41	10.8	12.8
Fulvic acid	0.50	3.75	5.92	9.03	9.89
	2.00	3.80	5.50	8.67	10.1
	4.20	4.52	5.86	9.26	13.8

the supernatant and initial buffering solution was determined using a combination pH electrode.

Elemental release data were fitted to a power equation using a Marquardt algorithm, least squares nonlinear fit (Bevington, 1969):

$$E = aT^n \quad [1]$$

where T is time in seconds, E is the amount of element released at time T in mol g^{-1} , and a and n are empirical constants. The variance s^2 was used as the measure of goodness of fit. The instantaneous dissolution rates were calculated from the slope of the best fit curve, that is, the derivative of Eq. [1]:

$$R = dE/dt = anT^{n-1} \quad [2]$$

The slope was divided by the initial specific surface area (m^2) to yield a surface area-based rate (in $\text{mol m}^{-2} \text{s}^{-1}$). Because the rates changed with time, particularly for Al, Fe, and Mg, the integrated mean rates from 15 to 30 d were computed from Eq. [2] and used to represent the rate of that treatment for correlation of the dissolution rates with organic C concentrations.

RESULTS AND DISCUSSION

Effects of Organic Acid Concentration on Dissolution Rates

The rates of mass transfer of Al, Fe, Mg, and Si from hornblende grains into solution increased with the addition of organic acids (Fig. 1 shows the data for citric acid

as an example). The release of Si was almost constant throughout the experimental period, but data for Al, Fe, and Mg release (Fig. 1) decreased with time, which suggests nonlinear release for those elements. For each acid studied, the rates of all elements increased with increasing organic acid concentrations. The concentration of Ca in solution (data not shown) was too low to be reported (detection limit by ICP for Ca is 0.07 mg L^{-1}). The stoichiometry of Ca release is not discussed here as a consequence of very rapid dissolution of CaCO_3 impurities during the initial stage (Zhang et al., 1996). Element release patterns in other organic acid solutions were similar to those in citric acid, as shown in Fig. 1 with slight differences in slope and linearity. Our patterns are similar to those Chin and Mills (1991) found for kaolinite dissolution in organic acid solutions.

The elemental release curves in Fig. 1 were fitted with the power function (Eq. [1]), and dissolution rates were calculated from the slope of the best fit curve (Eq. [2]). The fit was generally good with $s^2 < 0.2$. The rates in citric acid are plotted vs. time in Fig. 2. The decrease in rates with time for Al, Fe, and Mg was greater with increasing concentrations of organic acids. This suggests that the initial release rates of these elements were greatly enhanced by the addition of complex-forming ligands. The rates became stabilized after ≈ 15 d. The dissolution rates for Si were more stable than other elements but increased slightly with time. Similar release

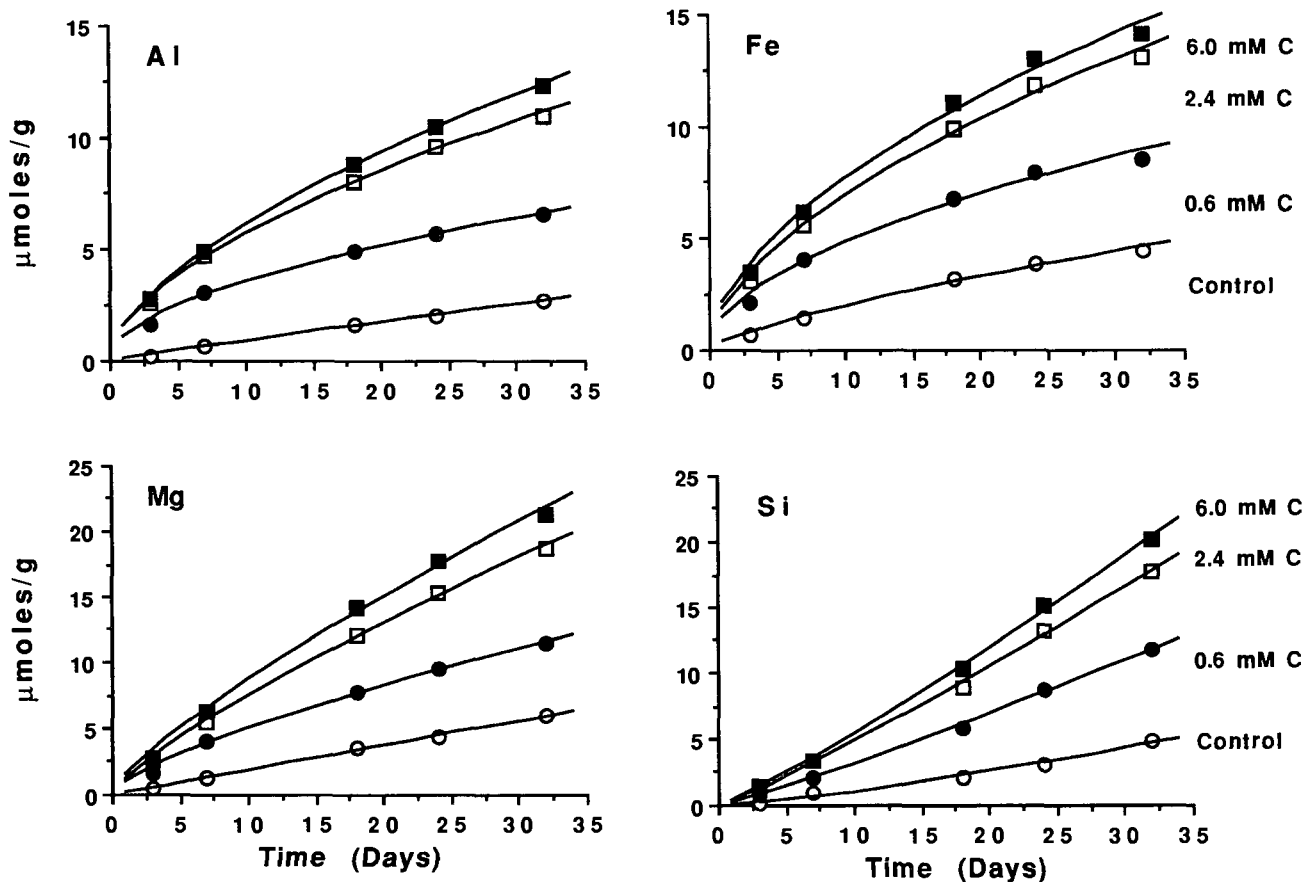


Fig. 1. Quantity of Al, Fe, Mg, and Si vs. time from initially weathered hornblende into citric acid solution in a 0.01 M HOAc-LiOAc buffer at pH 4.0 and 298 K.

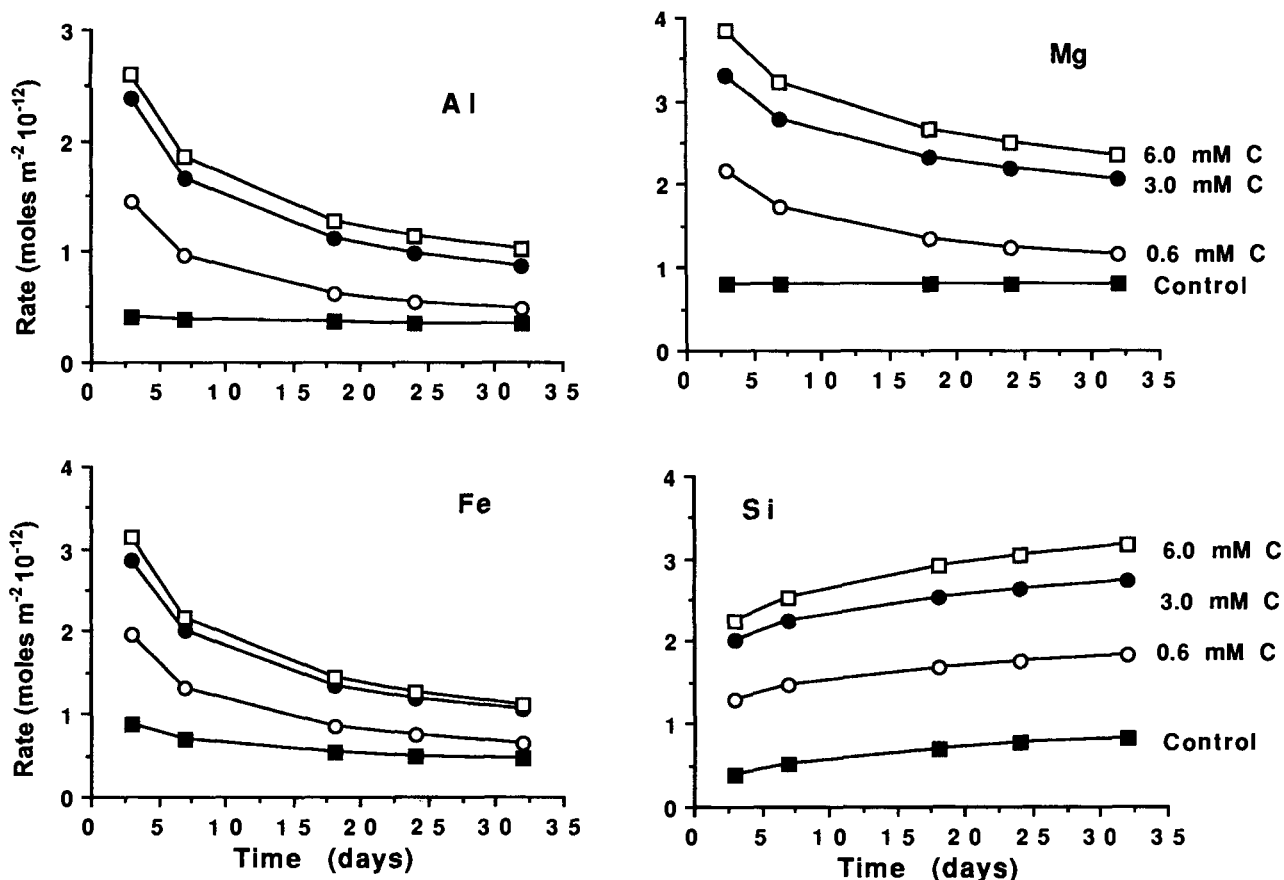


Fig. 2. Dissolution rates for Al, Fe, Mg, and Si calculated using the slope of the empirical equation $E = aT^n$ and the mass transfer data shown in Fig. 1 vs. time.

patterns were also found for fulvic, oxalic, tannic, and polygalacturonic acids, but these organic acids differed in their degree of promotion of dissolution.

Integrated mean release rates in citric acid solutions from 15 to 30 d were calculated from the data plotted in Fig. 2, since dissolution reached a steady rate after 15 d. Rates of all the organic acids used are shown in Table 1. The initial rates were still higher for Al, Fe, and Mg (although the starting material was preweathered to remove any artifacts from grinding) while Si release rate increased slightly over time. Rates increased as the organic acid concentrations did for all the compounds used. However, some compounds enhanced dissolution more than others. The effects of concentration of citric, oxalic, and tannic acids on dissolution rates were greater than those of fulvic and polygalacturonic acids.

The dependence of dissolution rates of oxides and silicate minerals on organic ligand concentration has been related to the quantity of ligand adsorbed (Stumm and Furrer, 1987; Wieland et al., 1988). If the adsorption of ligand can be expressed using a power function (Freundlich equation), the rate dependence of dissolution on ligand concentration in solution can be expressed as

$$R_T = R_{HOAc} + R_L + R_{H^+} = k_{Ac} [Ac^-]^n + k_H [H^+]^j + k_L A_L^m \quad [3]$$

where R_T is the overall rate, R_{HOAc} is the dissolution

rate in 0.01 M LiOAc-HOAc buffer solution, R_L is the reaction rate attributed to added organic ligand, R_{H^+} is the rate of proton-promoted reaction, k is the rate constant of organic ligands and proton, $[Ac^-]$ is the activity of acetic acid, A_L is the activity of free organic ligand, and n , m , and j are the order of reaction with respect to acetic acid, other organic ligand, and proton activity, respectively.

In acetate the equation reduces to

$$R_{HOAc} = k_{Ac} [Ac^-]^n + k_H [H^+]^j \quad [4]$$

In unbuffered LiCl solution the equation further reduces to

$$R_{H^+} = k_H [H^+]^j \quad [5]$$

Our data showed that at pH 4.0 in 0.01 M LiOAc-HOAc buffer solution $R_{HOAc} = 3(k_H [H^+]^j)$ (Zhang et al., 1996). This indicates that $k_{Ac} [Ac^-]^n$ is twice $k_H [H^+]^j$. We expect OAc⁻ adsorption to be weak and nonspecific, but it does increase the dissolution rate.

The order of dependence on ligand concentration at constant pH, m , can be obtained from the plot of log R_T (total rates) vs. the log of organic ligand concentration (Fig. 3 shows log-log plots in citric and oxalic acids). The reaction orders calculated from the slope of those figures by linear regression are given in Table 2. The log-log plots (Fig. 3), however, are not quite linear; they show a decrease in slope at higher organic acid

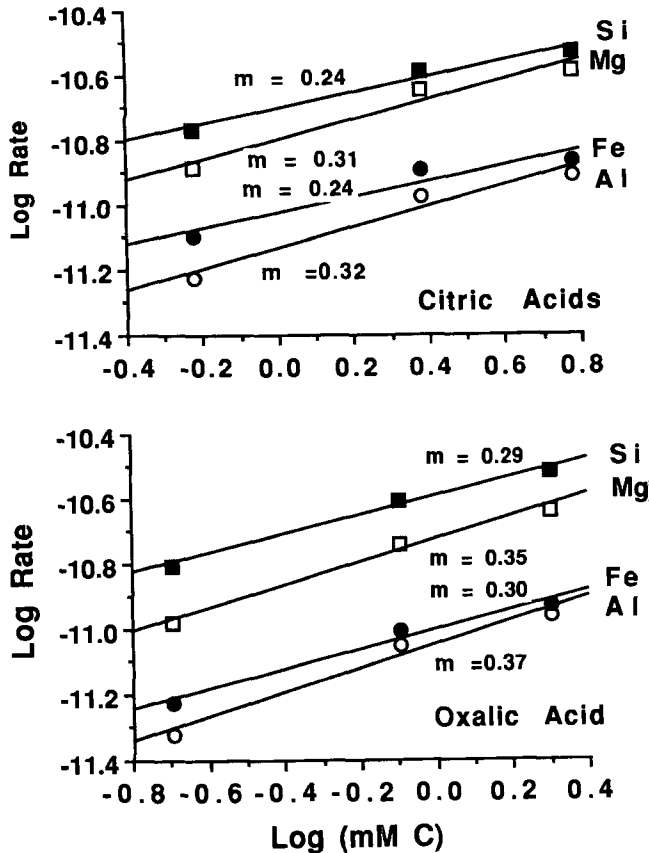


Fig. 3. Dependence of the reaction rates for Al, Fe, Mg, and Si with respect to the dissolved organic C concentrations of citric and oxalic acids. The rates were calculated as integrated means from 15 to 30 d.

concentrations, although the overall r^2 values ranged from 0.91 to 0.97. The shape of the plots suggests a Langmuir-type equation would fit better than a power-type (Freundlich) equation, but more data are needed to evaluate the fit of a Langmuir-type model.

The ligand-promoted dissolution reaction orders were generally low in this study (Table 2), ranging from 0.12 to 0.37 for tannic, citric, and oxalic acids, and close to zero for fulvic and polygalacturonic acids. The acetate we used as a buffer may to some extent inhibit ligand adsorption. As a result, the effects of additional organic ligands on dissolution observed may be lower than the effects when acetate is absent. Mast and Drever (1987) found that addition of 0.5 to 1.0 mM oxalic acid produced no effect on the dissolution of tremolite. Tremolite is an amphibole that is structurally similar to horn-

Table 2. Reaction order dependence (m) on organic acid concentrations in 0.01 M LiOAc-HOAc at pH 4.0.

Organic acids	Reaction order				OFG† mM
	Al	Fe	Mg	Si	
Oxalic	0.37	0.30	0.35	0.29	2.50
Citric	0.32	0.24	0.31	0.24	1.67
Tannic	0.25	0.17	0.17	0.12	0.36
Polygalacturonic	0.08	0.05	0.10	0.12	1.76
Fulvic	0.08	0	0.01	0.16	0.12

† OFG, oxygen containing functional groups (summation of -OH and -COOH) in mM at 2.5 mM C.

blende but contains only Mg as a major cation. They concluded that dissolved organic compounds in the concentrations commonly observed in soil solutions and surface waters would have a minimal effect on the dissolution rates of feldspars and amphiboles in dilute solutions. Addition of oxalic acid, however, was found to enhance the dissolution rate of hornblende in this study. Silicon released five times faster in 2.0 mM C L⁻¹ oxalic acid than in the control. Grandstaff (1986) found that the dissolution rate of olivine from a Hawaiian beach sand was proportional to the square root of fulvic acid, phthalate, and ethylenediamine tetra-acetic acid (EDTA) concentrations at pH 4.5; however, the concentration ranges used in that study were higher than those used in this study. Chin and Mills (1991) found soil humic acids and stream water-dissolved organic matter did not promote the dissolution of kaolinite at 50 and 40 mg L⁻¹, respectively. The different reaction orders with respect to organic acid concentration found in different studies may be attributed to experimental conditions, varieties of minerals, manners of sample preparation, and the concentration range used.

Incongruity of Dissolution

Reaction stoichiometry was examined by comparing reaction rate ratios of metal ions to Si with the molar ratios of metal ions to Si in the unreacted mineral (Table 3). The Al to Si ratio indicated that Al release was close to stoichiometric, but Fe and Mg were still released preferentially to Si, even after 39 d initial weathering. As discussed in Zhang et al., 1996, cations were depleted to a significant degree during the prereaction period, particularly Ca. Drying of the prereacted sample can also produce high incongruence (Zhang et al., 1996). The increase in rates following drying may be due to disruption caused by oxidation of surface Fe(II) to Fe(III). Dehydration of silica-rich surface material during drying causes additional strain, which can also contribute to the increase in dissolution rates.

Incongruent dissolution is typical for hornblende

Table 3. Metal ions to Si rate ratios during hornblende weathering in organic acid solutions.

Treatment	Concentration mM C	Rate ratio		
		Al/Si	Fe/Si	Mg/Si
Bulk mineral		0.38	0.21	0.49
Control	Buffer	0.49	0.71	1.11
Oxalic acid	0.20	0.31	0.38	0.67
	0.80	0.36	0.40	0.73
	2.00	0.36	0.39	0.76
Citric acid	0.60	0.35	0.47	0.76
	2.40	0.41	0.50	0.88
	6.00	0.41	0.46	0.87
Tannic acid	7.60	0.36	0.46	0.85
	38.0	0.46	0.53	0.95
	76.0	0.47	0.52	0.96
Polygalacturonic acid	0.62	0.45	0.59	0.88
	2.84	0.40	0.51	0.84
	6.18	0.41	0.50	0.84
Fulvic acid	0.50	0.38	0.60	0.91
	2.00	0.38	0.54	0.86
	4.20	0.33	0.42	0.67

weathering in the laboratory. Several hypotheses have been proposed to explain dissolution incongruence in aluminosilicates (Bloom and Nater, 1990). Two of these hypotheses are the leached layer hypothesis and the precipitation layer hypothesis. In the first case the preferential leaching of mobile elements occurs at the mineral surface and leads to the formation of a residual hydrated layer enriched in Si or in Al and Si (Luce et al., 1972; Mogk and Locke, 1988). In addition to the surface hydration, hydration along crystallographic planes of weakness and the consequent exchange or release of components along those planes are also responsible for the dissolution incongruence. For the second mechanism a layer of secondary solid phase forms on the surface (Holdren and Berner, 1979), and the incongruence is attributed to the loss of components (mostly Si and Al) that are precipitated from the solution phase. Precipitation of a secondary phase could not have occurred in our experiments, since solutions were maintained below saturation of aluminosilicate minerals. Leaching of the surface to create a surface excess of Al and Si did occur. The rate ratio of Al/Si was never 30% greater than the stoichiometric ratio, while the Mg/Si ratio was two or more times and the Fe/Si ratio was generally 50% greater than the stoichiometric ratios. Thus, the dissolution of Al–Si chains in the structure appears to be approximately stoichiometric, while the Mg and Fe between the chains are selectively depleted during the observed extents of the reaction. The decreasing Mg/Si and Fe/Si ratios with addition of organic acids suggests that the organic acids promote the decomposition of the Al–Si chains that increases the rate of Si and Al release. Chin and Mills (1991) found the rate of Al dissolution was promoted in the presence of organic ligands during kaolinite dissolution. The decrease in Fe/Si and Mg/Si ratios was greatest for oxalic and citric acids, the ligands that had the greatest effect on hornblende dissolution rates.

Relative Strength of Organic Acids in Promoting Dissolution

The relative effectiveness of different organic acids on hornblende dissolution was compared on the basis of dissolved organic C added to the acetic acid used as buffering agent. The rate of dissolution in each organic acid was normalized to the same concentration, 2.5 mM C L^{-1} (a concentration commonly found in soil solutions). The relative rates of Fe, Mg, and Si dissolution (Fig. 4) followed the sequence: oxalic > citric > tannic > polygalacturonic > fulvic acids. Aluminum release rates were greater in citric acid than in oxalic acid, but the above sequence was followed for the remainder of the organic acids. At 2.5 mM dissolved organic C and pH 4.0, the dissolution rates of Si were a factor of 1.4, 1.6, 2.3, 3.5, and 4.9 greater in fulvic, polygalacturonic, tannic, citric, and oxalic acids, respectively, than in the acetate buffer control. The order is generally consistent with similar studies, but Grandstaff (1986) reported that the effect of fulvic acid (FA) at 0.83 to 8.3 mM C on dissolution of olivine was greater than the effects of

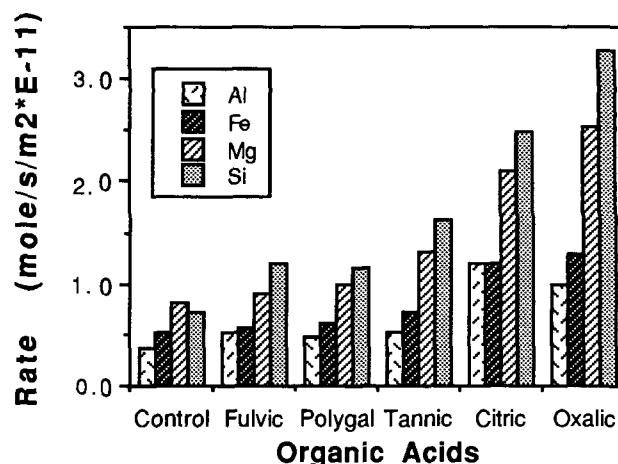


Fig. 4. The relative strength of five organic acids on promoting hornblende dissolution at 2.5 mM C in a pH 4.0, $0.01 \text{ M LiOAc-HOAc}$ buffer at 298 K .

citric and oxalic acids. Vicente-Hernandez and Robert (1979) (as cited in Robert and Berthelin, 1986) found that the weathering effect of FA would depend on its concentration in solution. At higher concentration (1.0 g L^{-1} FA, equivalent to 41.6 mM C), the effect is similar to that of strong complexing acids, but at lower concentration (0.1 g L^{-1} FA) the effect is greatly diminished. Stillings et al., (1996) found oxalic acid at 1 mM increased anorthite dissolution rates by a factor of 2 to 5 at pH 3. Chin and Mills (1991) also found oxalate to be the strongest organic compound in promoting kaolinite dissolution, but no effects were seen from soil humic acid and dissolved organic matter from stream waters.

Huang and Kiang (1972) and Manley and Evans (1986) have also studied the effect of organic acids on dissolution rates, but unfortunately, they failed to control solution pH. It is important to separate the pH effects of the addition of organic acids from those due to surface complexation. The above investigators also used organic acids with higher concentrations than commonly found in soil solutions and surface water under natural conditions.

Mechanisms of Ligand Promoted Dissolution

It is commonly accepted that the rate-controlling steps in the dissolution of most oxides and aluminosilicates are surface reaction processes rather than solution or surface transport processes (e.g., Stumm and Furrer, 1987). Thus, the reaction rates should depend on the concentration of surface species. During dissolution, aqueous ligands become adsorbed and form surface complexes with surface ions. The quantity of organic acids adsorbed on the surface is a function of solution concentration; thus, the rate of dissolution will be a function of the solution concentration in a similar fashion. Furrer and Stumm (1986) experimentally determined the surface concentrations of ligands for Al_2O_3 and determined the surface coordination equilibrium constants. They concluded that the rate law can be expressed in terms of the concentration of solutes, and

Table 4. Activation energy of element release in organic acid solutions.

Organic acids	Activation energy (kJ M ⁻¹ K ⁻¹)			
	Al	Fe	Mg	Si
Oxalic	15.8	9.70	18.0	50.1
Citric	29.6	24.6	36.7	63.0
Tannic	41.6	31.7	43.4	67.7
Polygalacturonic	7.90	29.5	19.9	43.0
Fulvic	13.5	17.3	29.6	42.6
Acetic	31.5	34.4	54.4	78.4

the surface concentrations of ligands are proportional to the ligand concentration in a fractional power function.

Chelating organic ligands accelerated the dissolution of Al, Fe, Mg, and Si from hornblende, suggesting that complex formation of organic ligands with surface metals may facilitate the release of ions from the surface to solution. Stumm et al. (1985) found that oxalate enhanced the dissolution rate of aluminum oxides, because the formation of surface complexes weakens Al-O bonds, thereby enhancing the detachment of Al and accelerating dissolution. Removal of Al removes the charge sites that bind Mg and Fe, which makes them unstable. As a consequence, Si will also be unstable. Magnesium and iron divalent cations also can form complexes with organic ligands, which can contribute to the enhanced dissolution. The formation of surface complexes could lower the activation energy of the rate-limiting step of dissolution, thereby increasing the apparent solubility of hornblende in aqueous solution as well as increasing the rate of dissolution. The apparent activation energy of Si release from hornblende in control was decreased in solutions with complex-forming ligand addition. Activation energy was also lowered for cation release in the presence of complex-forming ligands (Table 4).

If the separation of Al complex from the surface is the rate determining step, the order of dissolution rates in different organic acids should be in accord with the strengths of the cation-ligand complexes. In general, the sequence of acceleration found here is in accord with the strengths of the metal-ligand complexes. Grandstaff (1986) also found the relative order of organic ligands on olivine dissolution was in accord with the strengths of the Mg-ligand complexes. A strong positive correlation ($r^2 > 0.96$) between the release rates of K and Al from microcline and Al-ligand stability constants was reported by Nater and Huang (1988). The chemistry of organo-silicon interaction in aqueous solution is not well documented, but laboratory and field evidence have demonstrated that solutions of citric, oxalic, humic, and salicylic acids accelerate the dissolution of quartz in aqueous solution at pH 7.0 (Bennett et al., 1988). Results obtained by Bennett et al. (1988) suggested that dissolved silica was complexed by citrate, oxalate, and pyruvate at neutral pH. The formation of silica-organic complexes in solution and on surfaces may also be important in increasing dissolution rates. The enhanced removal of Al during hornblende dissolution disrupts the chain structure and enhances the removal of Si.

The ability of organic ligands to form surface com-

plexes is probably related to the quantity of O-containing functional groups that were added, rather than to the total dissolved C content (Inskeep, 1989). Casey and Ludwig (1995) showed that dissolution rate coefficients increased with the number of functional groups coordinated to the surface metal. This indicates that organic ligand-promoted dissolution of mineral surfaces is similar to ligand exchange around dissolved metal-ligand complexes. The important functional groups of the organic ligands used in this study include R-OH and R-COOH. The quantity of those groups added at 2.5 mM C are listed in Table 2. With the exception of polygalacturonic acid, the order of functional group abundance is in general accord with the ligands' relative effectiveness at promoting dissolution, as discussed earlier. On the other hand, much of the O content of polygalacturonic acid is from alcohol groups, which are not important in complex formation, unlike phenolic-OH and carboxyl groups in the other ligands.

CONCLUSIONS

Water soluble organic acids in soil solutions and groundwater can accelerate dissolution rates of amphiboles and other aluminosilicate minerals. The dependence of dissolution rate on organic acid concentrations found in the natural environment may be lower than that of many laboratory studies that have been done with higher concentrations of organic acids. Our data suggest that organic acids in natural environments increase mineral weathering rates, but this effect is small, especially for the high molecular weight organics, such as fulvic and humic acids.

The relative strengths of ligands at promoting dissolution rates is related to the quantity of O-containing functional groups present and to the strength of the metal-ligand complex formation. The dissolution of hornblende was incongruent, even with the initially weathered minerals, but the mechanism of incongruence is not yet well characterized. The enhanced dissolution in organic acid solution is due to the complexation of surface ions with ligands at constant pH and temperature. Effects of organic acids may be greatest for the chain-forming elements, Al and Si.

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