

EFFECTS OF ORGANIC LIGANDS ON GRANITE DISSOLUTION IN BATCH EXPERIMENTS AT pH 6

ALEXANDER NEAMAN^{*,**,*†}, JON CHOROVER^{***}, and SUSAN L. BRANTLEY^{*}

ABSTRACT. Yosemite granite from the Tuolumne River series was dissolved under oxic and anoxic conditions in the presence (0.001 or 0.01 M) and absence of organic ligands in batch experiments at pH 6. Release of all elements was enhanced considerably in the presence of organic ligands. Citrate (tridentate) and gallate (tetradentate) increased element release to the greatest extent among the aliphatic and aromatic ligands, respectively. The extent of element mobilization observed for the aliphatic ligands decreased in the order citrate > oxalate \approx malonate and for the aromatic ligands gallate > salicylate \approx phthalate. The effects of the ligands generally followed trends in cation-ligand stability constants, but aromatic ligands were less effective in element mobilization than aliphatic ligands. This was attributed to protonation of the functional groups of aromatic ligands at pH 6. Rock dissolution was non-stoichiometric regardless of the presence or absence of organic ligands. Release of P and Cu (% of total element content in the unweathered rock) in the presence of organic ligands was considerably greater than that of other elements.

Findings of the present study were compared to the findings of our previous study on dissolution of basalt. Differences in the mobility patterns of Y, Fe, Cu, Ti, and Zr during dissolution of granite and basalt were observed. In basalt, release of Y was enhanced considerably in the presence of citrate. In contrast, in the present study, release of Y from granite with and without citrate was at the detection limit. This difference was attributed to the difference in Y-hosting parent minerals: apatite (basalt) and sphene (granite). With and without organic ligands, no significant differences were observed in the extent of Fe released from granite under oxic versus anoxic conditions, while the extent of Fe release from basalt was considerably greater under anoxic versus oxic conditions with and without organic ligands. These differences can be attributed to the difference in major Fe-hosting phases in the rocks: biotite (granite) versus glass and augite (basalt). In the granite, concentrations of Cu released increased considerably in the presence of organic ligands under both oxic and anoxic conditions. In contrast, concentrations of Cu released from basalt were increased considerably only under oxic conditions, especially in the presence of organic ligands. This difference was attributed to the different extent of Fe release from basalt and granite that affected dissolution of Cu/Fe-sulfides. Although both Ti and Zr can be mobilized in the presence of organic ligands, in the rock where zircons hosted Zr (granite), this element was the most immobile, while in the rock where Fe/Ti oxides hosted Zr (basalt), Ti was the most immobile.

INTRODUCTION

The importance of low-molecular-weight organic acids (LMWOA) in weathering of primary minerals has been debated. For example, Drever (1994) reported that oxalate at millimolar concentration had a negligible effect on the dissolution rate of alkali feldspars, but some effect on calcic feldspars and olivine. The author thus argued that the overall effect of LMWOA on the weathering rate of silicate minerals in nature is likely to be small since concentrations of LMWOA is thought to be small in most soil bulk solutions, in the range from $\sim 1 \times 10^{-3}$ to $\sim 4 \times 10^{-3}$ M and from $\sim 8 \times 10^{-5}$ to $\sim 3 \times 10^{-4}$ M for aliphatic and aromatic organic ligands, respectively (Stevenson, 1991). Drever (1994) pointed out that the effect of plants on weathering rate through

*Department of Geosciences, Pennsylvania State University, University Park, Pennsylvania 16802, USA

**Facultad de Agronomía, Pontificia Universidad Católica de Valparaíso, Casilla 4-D, Quillota, Chile

***Department of Soil, Water and Environmental Science, University of Arizona, Tucson, Arizona 85721, USA

†Corresponding author: alexander.neaman@ucv.cl

changes in soil-solution chemistry is small for granitic rocks, but it may be greater for mafic rocks.

Despite these arguments, several lines of evidence suggest that LMWOA are essential in the formation of many soils (for example, McKeague and others, 1986), including Podzols (World Reference Base for Soil Resources, FAO, 1998) or Spodosols (US Soil Taxonomy, Soil Survey Staff, 1999), which are characterized by the presence of a highly-leached horizon and by an underlying horizon of Fe and Al accumulation. It is believed that LMWOA are responsible for transport of Fe and Al by chelation, and that precipitation of Fe and Al in the subsoil is caused by microbial breakdown of LMWOA (for example, Lundström, 1994; Lundström and others, 1995).

Although numerous data are available on the effects of organic acids on dissolution of monomineralic specimens (for example, Song and Huang, 1988; Chin and Mills, 1991; Barman and others, 1992; Davis and others, 1995; Drever and Stillings, 1997; Zhang and Bloom, 1999; Welch and others, 2002; Brantley, 2004), very few analogous data are available for bulk rocks. Moreover, these studies on monomineralic specimens emphasized mobility of major, rather than minor and trace elements.

In previous work (Neaman and others, 2005a, 2005b), we investigated the effect of LMWOA on minor and trace element release from basalt in batch experiments at pH 6 under oxic and anoxic conditions. We have observed that the extent of release of elements from basalt was affected considerably by the presence or absence of organic ligands and the oxygen concentration. In this paper, we summarize similar experiments on granite and discuss our observations with respect to release especially of minor and trace elements as a function of rock lithology.

MATERIALS AND METHODS

Organic Ligands

We have selected aliphatic ligands (acetate, citrate, formate, fumarate, glutarate, lactate, malonate, oxalate, and succinate) and aromatic ligands (benzoate, gallate, phthalate, and salicylate) for the study. The criteria for selecting these particular ligands were that (i) they are common secretion products of prokaryotes, fungi, lichens, and plant roots, and (ii) are common products of degradation of biomolecules (Neaman and others, 2005b), (iii) they are common low-molecular-weight constituents of dissolved organic matter in soil solutions (Baziramakenga and others, 1995; Krzyszowska and others, 1996; Jones, 1998), (iv) they exhibit a wide range of molecular structure (fig. 1) that could influence their coordination chemistry with surface-bound and aqueous-phase metals (Furrer and Stumm, 1986), and (v) carboxyl acidity constants span a wide range (table 1).

In the first series of experiments, the above-mentioned thirteen ligands were reacted at concentrations of 0.001 M with granite. For the second series of experiments, the four ligands (citrate, gallate, oxalate, and malonate), that were observed to have the greatest effect on the enhancement of dissolution, were reacted at concentrations of 0.01 M with granite. However, data for the 0.01 M oxalate experiments are not considered here due to the precipitation of Ca-oxalate in those experiments.

The above-mentioned concentrations of organic ligands used in the experiments are similar to those found in most soil bulk solutions for aliphatic ligands (from $\sim 1 \times 10^{-3}$ to $\sim 4 \times 10^{-3}$), while greater than those found for aromatic ligands (from $\sim 8 \times 10^{-5}$ to $\sim 3 \times 10^{-4}$ M) (Stevenson, 1991).

Starting Material

Granite from the Tuolumne River series was sampled in Yosemite National Park at Olmsted Point along Highway 120. The sample was broken with a hammer, cleaned with distilled water, crushed with a tungsten carbide jaw crusher, and

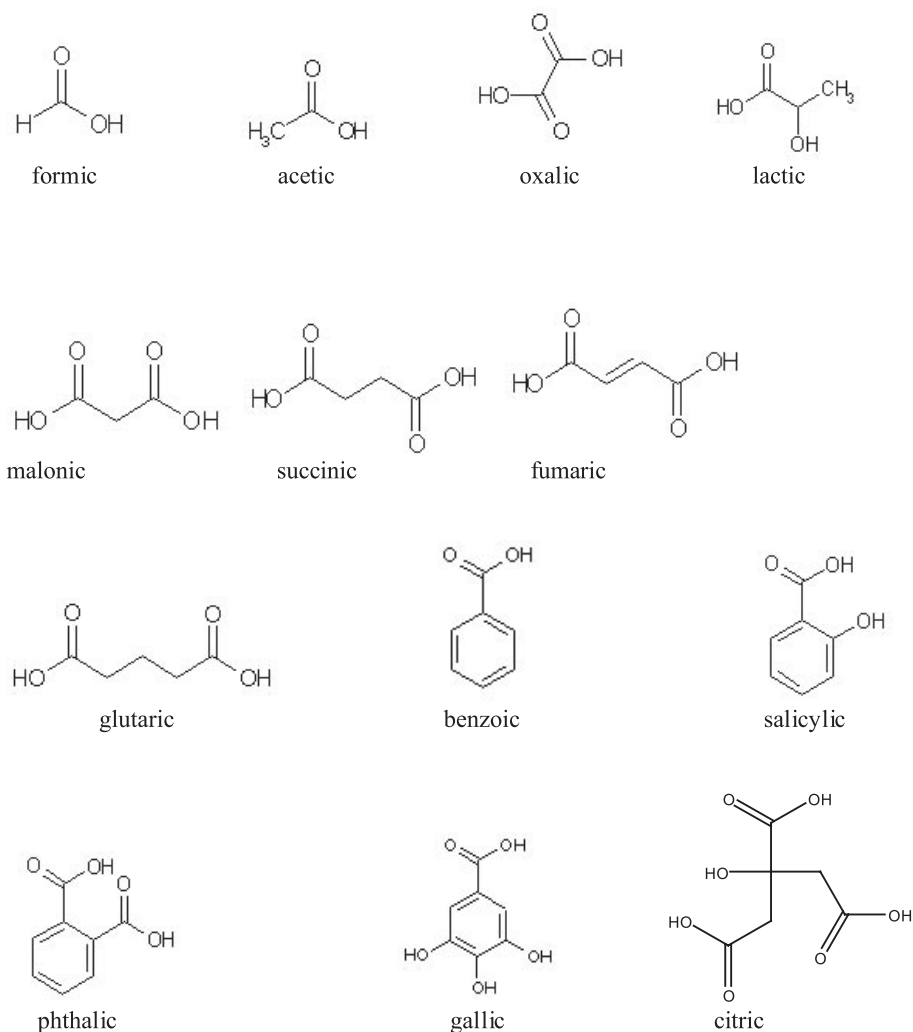


Fig. 1. Structural formulae of aliphatic and aromatic carboxylic acids used in the present study.

powdered with a tungsten carbide disk mill. Powder was sieved to obtain the 100 to 200 mesh (75 – 150 μm) fraction. Fine particles were then removed by ultrasonication for about 5 minutes, washed in spectroscopic-grade acetone, and dried at 60°C. Specific surface area of the ground granite was calculated as 0.14 m^2/g using multi-point adsorption data from the linear segment of the krypton adsorption isotherms (Micromeritics®, model ASAP 2000) by the Brunauer-Emmett-Teller (BET) method.

The contents of major and trace elements in the granite were determined by X-ray fluorescence (XRF) at the GeoAnalytical Laboratory, Washington State University (Johnson and others, 1999). A single low-dilution (2:1 Li-tetraborate/sample) fused bead was used for both major and trace elements. The major element concentrations were normalized to 100 percent (on the basis of volatile-free mass), with all the iron expressed as FeO. Analyses, carried out in duplicate, are reported as average values

TABLE 1
Acidity constants of the organic acids used in the present study

Acid	pK _{a1}	pK _{a2}	pK _{a3}	pK _{a4}
Oxalic	1.25	4.26	n/a *	n/a
Malonic	2.85	5.70	n/a	n/a
Phthalic	2.95	5.41	n/a	n/a
Salicylic	2.97	13.7	n/a	n/a
Fumaric	3.02	4.48	n/a	n/a
Citric	3.13	4.76	6.40	n/a
Lactic	3.86	n/a	n/a	n/a
Formic	3.74	n/a	n/a	n/a
Benzoic	4.20	n/a	n/a	n/a
Succinic	4.21	5.64	n/a	n/a
Glutaric	4.35	5.42	n/a	n/a
Gallic	4.44	9.11	12.0	13.7
Acetic	4.76	n/a	n/a	n/a

*n/a = not applicable.

Ordering of the acids is intended to show the trend in pK_{a1}. For monodentate ligands: K_{a1} = [HL]/[H][L]. For bidentate ligands: K_{a1} = [H₂L]/[H][HL] and K_{a2} = [HL]/[H][L]. For citrate, a tridentate ligand: K_{a1} = [H₃L]/[H][H₂L], K_{a2} = [H₂L]/[H][HL], and K_{a3} = [HL]/[H][L]. For gallate, a tetridentate ligand: K_{a1} = [H₄L]/[H][H₃L], K_{a2} = [H₃L]/[H][H₂L], K_{a3} = [H₂L]/[H][HL], and K_{a4} = [HL]/[H][L], where [HL] and [H₂L] and [H₃L] and [H₄L] are concentrations of protonated ligands while [H] and [L] are concentrations of the proton ion and the deprotonated ligand ion, respectively. Complex stability constants are reported for I = 0 M and 25°C (IUPAC, 2000).

(table 2). An attempt has been made to analyze sulfur content in the granite using an elemental analyzer, but it was below detection limit (<50 mg/kg).

Mineralogical composition of the rocks was determined by X-ray diffraction (XRD) and inferred from electron probe microanalysis (EPMA). The granite contains the major phases biotite (Ca_{0.01}Na_{0.01}K_{0.91}Fe^{II}_{1.14}Mg_{1.41}Mn_{0.04}Al_{1.29}Si_{2.86}Ti_{0.15}O₁₀(OH)₂), quartz, plagioclase feldspar (Ca_{0.28}Na_{0.73}K_{0.01}Si_{2.71}Al_{1.28}O₈), and alkali feldspar (Na_{0.08}K_{0.91}Si_{3.00}Al_{1.01}O₈). The minor phases determined by EPMA include sphene, Fe oxide, hornblende (K_{0.03}Na_{0.16}Ca_{1.88}[Mg_{3.25}Fe^{II}_{1.48}Mn_{0.09}Ti_{0.02}]Si_{7.60}Al_{0.59}O₂₂(OH)₂), and chlorite (Fe^{II}_{1.96}Mg_{2.57}Al_{1.25}Mn_{0.07}Si_{2.89}Al_{1.11}O₁₀(OH)₈). The oxidation state of Fe in chlorite, hornblende, and biotite was assumed to be Fe^{II}. Trace phases analyzed qualitatively by EPMA include zircon, fluorapatite, and Cu/Fe-sulfide inclusions in Fe oxide phases.

Elemental compositions of the Fe-oxide phases hosting Cu/Fe-sulfide inclusions were analyzed by EPMA in a mode that determines oxygen directly (and not by stoichiometry). Oxygen K-alpha X-ray intensity was measured on a PC2 synthetic multilayer crystal with a nominal d-spacing of 95 angstroms in a low pressure spectrometer. Synthetic fayalite was used as a calibration standard for both iron and oxygen. The Fe-oxide phases contained Fe in the range of 71.3 to 71.7 weight percent and O in the range of 26.5 to 26.6 weight percent, consistent with the stoichiometry of magnetite Fe^{III}₂O₃ · Fe^{II}O.

EPMA was also used to investigate the presence of Y in minerals within the basalt in one polished section (discussed below).

Batch Dissolution Experiments

We used 50-ml Pyrex® tubes with Teflon®-lined plastic caps (Corning® Co.) as batch reactors. The tubes and caps were acid-washed prior to use. Organic ligand

TABLE 2
Elemental composition of the Yosemite granite used in the present study

Weight %	
SiO ₂	69.58
Al ₂ O ₃	15.12
TiO ₂	0.42
FeO	3.68
MnO	0.05
CaO	3.65
MgO	1.04
K ₂ O	2.70
Na ₂ O	3.69
P ₂ O ₅	0.07
Total	100.00
ppm	
Ni	7
Cr	5
Sc	12
V	63
Ba	766
Rb	87
Sr	524
Zr	71
Y	13
Nb	11
Ga	16
Cu	11
Zn	43
Pb	18
La	22
Ce	50
Th	18

solutions were prepared from Sigma® and Aldrich® chemicals. We used 0.001 or 0.01 M ligand solutions, as well as ligand-free solution adjusted to pH 6.0 by adding NaOH. We also performed granite-free control experiments for all ligand and ligand-free solutions. The solid/solution ratio was 1:1000 g/ml (0.03 g / 30 ml) for 0.001 M ligand and 1:100 g/ml (0.3 g / 30 ml) for 0.01 M ligand experiments. All experiments were run at ambient temperature (~25°C). Tubes, agitated continuously using end-over-end rotators, were covered with aluminum foil to prevent photoreductive dissolution of Fe-containing minerals (for example, Cornell and Schwertmann, 1996).

We took particular care to prevent microbial growth in the reactors: tubes with granite powder were autoclaved before solution was added. Solutions of organic acids, to which sodium azide (NaN₃) was added to achieve a concentration of 0.05 w/v percent, were sterilized through 0.2-µm filters. Azide binds tightly to the ferric form of cytochrome a₃, preventing electron transport, and its inhibitory action is very potent

(Garrett and Grisham, 1999). We did not observe any turbidity at the end of the experiments, as expected in the absence of microbial contamination.

We performed the experiments under both oxic and anoxic conditions. Oxic experiments were exposed to the ambient atmosphere three times per week (by loosening the caps in a sterile hood) in order to assure exchange with atmospheric $O_2(g)$. Anoxic experiments were carried out in a Coy® oxygen-free glove box (with oxygen concentration < 1 ppm as measured by Coy® gas analyzer).

Duration of the experiments was four weeks. Aliquots of the suspension were taken for pH (combined glass electrode) and Eh (Pt electrode) measurements at the end of the experiments. For anoxic experiments, pH and Eh were measured in the glove box. Then, suspensions were filtered at $0.2 \mu m$ and acidified with nitric acid. Concentrations of aqueous Fe^{II} in the solutions were determined using the Ferrozine® method within 1 hour of sampling (Lovley and Phillips, 1986). Solutions from the anaerobic experiments were mixed with Ferrozine® in the glove box. Element concentrations were determined by inductively coupled plasma -atomic emission spectrometry (ICP-AES) and -mass spectrometry (ICP-MS). Concentrations of Fe, Al, P, and Ti measured using both ICP-AES and ICP-MS showed no significant differences between the techniques. Concentrations for Cu are derived from ICP-MS analysis for more than one isotope, and were observed to be consistent among the isotopes.

Batch experiments were carried out in duplicate (0.001 M ligands) or triplicate (0.01 M ligands). We analyzed major and minor elements (Si, Ca, K, Mn, Al, Fe, Mg, P, and Ti) and several trace elements (V, Cr, Cu, Rb, Y, Zr, and Ba). Analysis for Na release was not possible due to the presence of sodium azide. Data for Si, Ca, and Mn were not considered due to release of these elements from the tubes used (as observed in the granite-free control experiments). In these granite-free control experiments, the following concentrations were detected: 2.9 or 0.4 ppm of Si, 55 or 30 ppm of Ca, and 100 or 50 ppb of Mn, in the presence or absence of ligands, respectively. For all other elements, concentrations in solution from the granite-free control experiments were beneath detection (< 0.1 ppm for Al, Fe, and Mg and < 1 ppb for all other elements). Data for K are not considered due to contamination from NaOH used for pH adjustment or from the electrode salt bridge. In 0.001 M ligand experiments, small concentrations of all trace elements released into solution did not allow their accurate analysis.

The deviations in the values obtained from the duplicate or triplicate runs were < 10 percent. The average values are shown here (figs. 2 and 3, tables 3–6). The release of each element from granite is expressed as a percentage of total element content in the unweathered rock. Concentrations of elements in the solution for experiments with 0.001 M or 0.01 M ligands are presented in Appendices 1–4.

RESULTS AND DISCUSSION

Solution Chemistry and Rates of Dissolution

As mentioned above, data for Si, Ca, and Mn were not considered due to release of these elements from the tubes (as observed in the granite-free control experiments). Calculation of the chemical speciation of the solutions [Geochemist's Workbench®, Bethke (2002), database thermo_minteq_gwb4] suggests that solutions were oversaturated with respect to hematite, magnetite, goethite, and lepidocrocite while solutions were undersaturated with respect to other minerals in the granite dissolution experiments. Thus, the low concentrations of Si, Ca, and Mn released from the tubes were too small to inhibit the dissolution of minerals in the granite.

Values of pH at the end of the experiments were in the range from 6.0 to 6.5. Values of Eh at the end of the experiments were in the range of 300 to 450 mV in the case of oxic experiments and < 100 mV in the case of anoxic experiments as measured

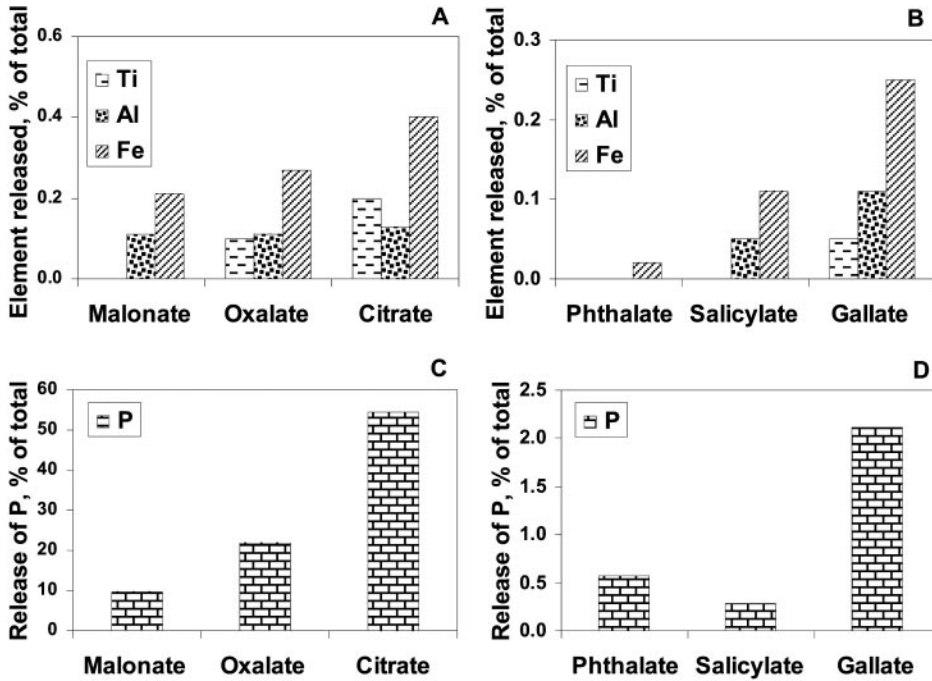


Fig. 2. The effect of 0.001 M ligands on granite dissolution at pH 6 under oxic conditions: release of Ti, Al, and Fe with (A) aliphatic and (B) aromatic ligands, and release of P with (C) aliphatic and (D) aromatic ligands. Note the differences in scale of the ordinate. The release of each element from granite is expressed as a percentage of total elements contained in the unweathered rock. In some cases, release of Ti was below detection of the instrument ($<0.01\%$).

by a platinum electrode and corrected to the standard hydrogen electrode. Variation in Eh in the solution was not observed to correlate with dissolved ligand concentrations.

Comparison of absolute values of the percentage of element release between 0.001 M (tables 3 and 4) and 0.01 M (tables 5 and 6) experiments is ambiguous because of different solid/solution ratios in these two experiments. However, it is still possible to compare the surface area-normalized rates of dissolution. Although these rates were calculated based on just one data point at 28 days, we could consider them as estimated average rates for the study period of time. We note that the surface area-normalized rates of dissolution were similar between 0.001 and 0.01 M ligand experiments (table 7). Calculations demonstrate that ligand/rock ratio was equal for both ligand concentrations (1 mmol ligand per 1 g of rock). Equal ligand/rock ratio explains the similar surface area-normalized dissolution rates between 0.001 and 0.01 M ligand experiments.

Comparison between the surface area-normalized rates of dissolution for basalt (data from Neaman and others, 2005b) and granite (present study) with and without 0.01 M organic ligands shows that these rates of dissolution were consistently greater in the case of granite, for all elements and all ligands (table 8). However, the values of the percentage of element release (and, in turn, mass-normalized dissolution rates) were considerably greater in the case of basalt (see data in Neaman and others, 2005b) in comparison to granite (for example, 0.19 and 0.21 % of total Fe was released from granite in comparison to 2.62 and 7.51 % of total Fe released from basalt, under oxic and anoxic conditions, respectively).

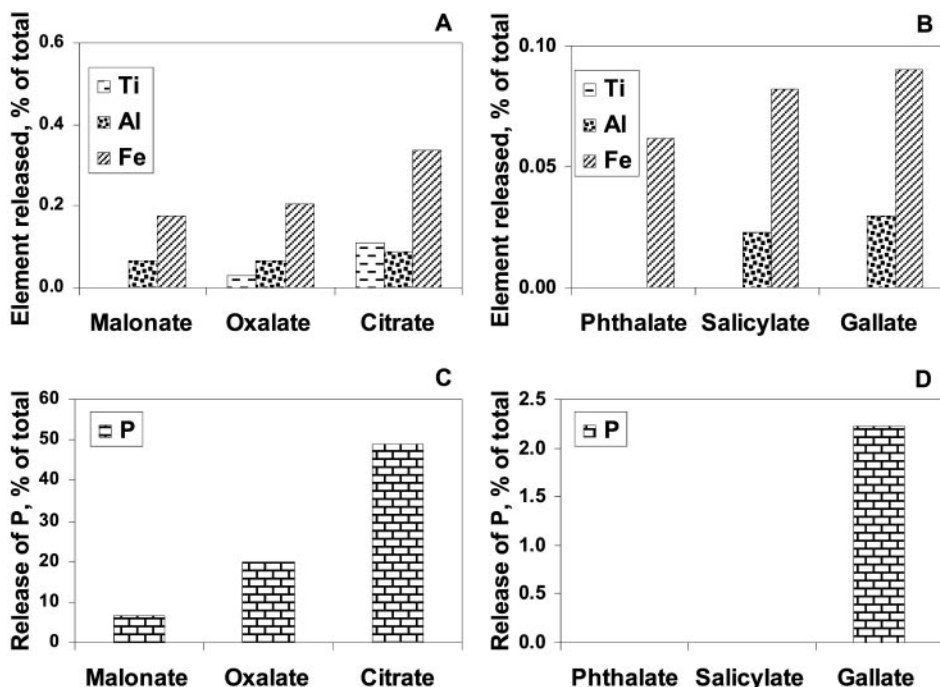


Fig. 3. The effect of 0.001 M ligands on granite dissolution at pH 6 under anoxic conditions: release of Ti, Al, and Fe with (A) aliphatic and (B) aromatic ligands, and release of P with (C) aliphatic and (D) aromatic ligands. Note the differences in scale of ordinate. The release of each element from granite is expressed as a percentage of total elements contained in the unweathered rock. In some cases, release of Ti was below detection ($<0.01\%$).

This apparent contradiction could be explained by the difference in surface areas of the rocks: $8.69\text{ m}^2/\text{g}$ in the case of basalt and $0.14\text{ m}^2/\text{g}$ in the case of granite. The latter value is in agreement with the values reported for silicate minerals of the same grain size as used in the present study (Brantley and Mellott, 2000). The relatively elevated surface area of basalt is due to the presence of micro- and mesopores in the rock, as detected by the gas adsorption analysis (unpublished data).

Ligand Trends

Extent of release of all elements was enhanced considerably in the presence of organic ligands in comparison to ligand-free experiments (figs. 2 and 3, tables 3–6). The extent of element release differs considerably among the ligands used (tables 3 and 4, figs. 2 and 3). Citrate, a tridentate ligand, and gallate, a tetradentate ligand, increased granite dissolution to the greatest extent among all ligands and among aromatic ligands, respectively. Generalizing for all elements, the extent of dissolution observed for the aliphatic ligands decreased in the order: citrate $>$ oxalate \approx malonate, and for the aromatic ligands: gallate $>$ salicylate \approx phthalate. All other ligands affected release only slightly, if at all (tables 3 and 4). These ligand trends were observed for both oxic and anoxic conditions. Release of all elements was similar under oxic and anoxic conditions (tables 3–6).

We have observed the same ligand trends (citrate $>$ oxalate \approx malonate for the aliphatic ligands and gallate $>$ salicylate \approx phthalate for the aromatic ligands) during dissolution of basalt using the same experimental conditions as in the present study

TABLE 3

Dissolution of granite at pH 6 in 0.001 M organic ligands under oxic conditions

Ligand	Element released, % from total *			
	Al	Fe	P	Ti
Acetate	0.01	0.02	0.16	bd **
Benzoate	0.01	0.01	0.47	bd
Citrate	0.13	0.40	54.5	0.20
Formate	0.01	0.02	0.93	bd
Fumarate	0.01	0.02	0.90	bd
Gallate	0.11	0.25	2.11	0.05
Glutarate	0.01	0.04	0.01	bd
Lactate	0.01	0.03	0.68	bd
Malonate	0.11	0.21	9.69	bd
Oxalate	0.11	0.27	21.8	0.10
Phthalate	bd	0.02	0.57	bd
Salicylate	0.05	0.11	bd	bd
Succinate	0.01	0.04	0.97	bd
Ligand-free	0.01	0.03	bd	bd

*percent of total element in the unweathered rock. Concentrations of elements in the solutions are presented in Appendix 1.

**bd = below detection (<0.01%)

(Neaman and others, 2005b). As in the case of basalt dissolution (Neaman and others, 2005b), the differences among the ligands in affecting the extent of element release from granite can be explained by the difference in cation-ligand stability constants (reported for I = 0.1 M and 25°C, IUPAC, 2000). For example, release of Fe and Al from granite increased with an increase in complex stability constants of Fe^{3+} and Al^{3+} with ligands, respectively (figs. 4A-D). Although Fe in the granite is most likely present as Fe^{II} , stability constants for Fe^{3+} have been used because constants for Fe^{2+} were not available for all ligands.

However, aromatic ligands used in the present study had a considerably smaller effect on the enhancement of release of Fe and Al in comparison to aliphatic ligands (figs. 4A-D), in spite of greater complex stability constants of aromatic ligands with Fe^{3+} and Al^{3+} in comparison to aliphatic ligands. A similar observation has been made with respect to the effect of aliphatic versus aromatic ligand on dissolution of basalt (Neaman and others, 2005a, 2005b). Also, the effect of aromatic ligands on the dissolution of Al oxides (Furrer and Stumm, 1986) and kaolinite (Chin and Mills, 1991) in acidic media has been observed to be considerably smaller than that of aliphatic ligands. This leads to the generalization that aromatic ligands (such as salicylate and gallate) enhance the release of Fe and Al from minerals and rocks to a lesser extent than aliphatic ligands at $\text{pH} \leq 6$. To explain this, we note that the $\text{pK}_{\text{a}2}$ values of the salicylate (13.7) and gallate (9.11) are considerably greater than those of aliphatic ligands ($\text{pK}_{\text{a}2}$ in the range 4.26 to 5.7, table 1). The $\text{pK}_{\text{a}2}$ values of these aromatic ligands imply that, in neutral and acidic media, the proportion of protonated species is greater for salicylate and gallate in comparison to the aliphatic ligands (Furrer and Stumm, 1986). Hence aromatic ligands are predicted to have a considerably smaller effect on the enhancement of release of Fe and Al from minerals and rocks in neutral and acidic media in comparison to aliphatic ligands. These effects can be extrapolated to other metals: for example, gallate, an aromatic ligand, exhibited a

TABLE 4
Dissolution of granite at pH 6 in 0.001 M organic ligands under anoxic conditions

Ligand	Element released, % from total *			
	Al	Fe	P	Ti
Acetate	bd **	0.06	bd	bd
Benzoate	bd	0.06	bd	bd
Citrate	0.09	0.34	48.8	0.11
Formate	bd	0.07	0.43	bd
Fumarate	0.03	0.07	2.22	bd
Gallate	bd	0.03	bd	bd
Glutarate	bd	0.06	bd	bd
Lactate	bd	0.07	bd	bd
Malonate	0.07	0.17	6.67	bd
Oxalate	0.07	0.21	20.0	bd
Phthalate	bd	0.06	bd	bd
Salicylate	0.02	0.08	bd	bd
Succinate	bd	0.07	0.35	bd
Ligand-free	0.01	0.03	bd	bd

*percent of total element in the unweathered rock. Concentrations of elements in the solutions are presented in Appendix 2.

**bd = below detection (<0.01%).

considerably smaller effect on the enhancement of release of Cu from granite in comparison to the aliphatic ligands (malonate and citrate), under both oxic and anoxic conditions (fig. 5).

Release of P from granite can also be predicted by stability constants. Phosphorus in the granite is present predominantly as fluorapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$. Extent of release of

TABLE 5
Release of major and minor elements from granite at pH 6 under oxic and anoxic conditions in 0.01 M organic ligands

Ligand	Element released, % of total *				
	Oxic				
	Al	Fe	Mg	P	Ti
Citrate	0.07	0.19	0.86	34.1	0.13
Malonate	0.06	0.16	0.79	3.05	0.10
Gallate	0.09	0.13	0.78	0.85	bd
Ligand-free	bd **	bd	0.85	0.11	bd
	Anoxic				
Citrate	0.09	0.21	0.58	45.0	0.15
Malonate	0.07	0.13	0.48	2.06	0.12
Gallate	0.09	0.22	0.50	0.41	bd
Ligand-free	bd	bd	0.42	0.11	bd

*percent of total element in the unweathered rock. Concentrations of elements in the solutions are presented in Appendix 1 (Al, Fe, and Mg) or Appendix 2 (P and Ti).

**bd = below detection (<0.01%).

TABLE 6
*Release of trace elements from granite at pH 6 under oxic and anoxic conditions
 in 0.01 M organic ligands*

Ligand	Element released, % of total *						
	Oxic						
	V	Cr	Cu	Rb	Y	Zr	Ba
Citrate	0.32	bd	7.67	0.23	0.50	bd	0.18
Malonate	0.28	bd	10.8	0.26	bd	bd	0.16
Gallate	0.30	bd	5.80	0.26	bd	bd	0.16
Ligand-free	bd **	bd	bd	0.18	bd	bd	0.16
	Anoxic						
Citrate	0.33	bd	8.84	0.21	0.71	bd	0.13
Malonate	0.28	bd	6.61	0.21	bd	bd	0.18
Gallate	0.29	bd	4.50	0.19	bd	bd	0.12
Ligand-free	0.16	bd	bd	0.28	bd	bd	0.14

*percent of total element content in the unweathered rock. Concentrations of elements in the solutions are presented in Appendix 2.

**bd = below detection (<0.01%)

P from the rock increased with an increase in complex stability constants of Ca^{2+} with aliphatic and aromatic ligands (figs. 4E and 4F). We infer that organic ligands enhance dissolution of fluorapatite by forming complexes with calcium. However, in spite of similar complex stability constants of Ca^{2+} with aromatic ligands in comparison to aliphatic ligands, the former ligands showed a considerably smaller effect on the enhancement of release of P in comparison to the aliphatic ligands (figs. 4E and F). This observation is presumably related to the above-discussed pH effect.

Furrer and Stumm (1986) suggested that the effect of bidentate ligands on the extent of dissolution of Al oxides decreases with the increase in the length of chain required to form a bidentate chelate ring: oxalate > malonate > succinate (five-, six-, and seven-member rings, respectively) for aliphatic ligands, and salicylate > phthalate (six-, and seven-member chelate rings, respectively) for aromatic ligands. Chin and Mills (1991) reported the same sequences of bidentate ligands with respect to the enhancement of release of Al from kaolinite: oxalate > malonate for aliphatic ligands, and salicylate > phthalate for aromatic ligands.

Our experimental results are in partial agreement with the findings of Furrer and Stumm (1986) and Chin and Mills (1991). In agreement with their findings, oxalate and malonate, which form five- and six-member chelate rings, respectively, increased element release to the greatest extent among the aliphatic bidentate ligands used in our experiments. Other aliphatic bidentate ligands with seven- or eight-member chelate rings (fumarate, glutarate, and succinate) enhanced element release very slightly, if at all (tables 3 and 4). However, the sequences oxalate > malonate for Al release and salicylate > phthalate for P release were not observed in the present study (fig. 4) nor in our previous study on dissolution of basalt (Neaman and others, 2005a, 2005b).

The experiments of Furrer and Stumm (1986) and Chin and Mills (1991) were carried out between pH 3 and 5 as compared to pH 6 of the present study. The pK_{a2} for oxalate is smaller than that for malonate (table 1). The pK_{a2} values of the above-mentioned ligands imply that, at pH values between 3 and 5, the proportion of protonated species is greater for malonate in comparison to oxalate. Bidentate ligands

TABLE 7

The log rate of release ($\text{mol element m}^{-2} \text{sec}^{-1}$) from granite in batch experiments at pH 6 with and without 0.001 and 0.01 M organic ligands. Rate was calculated based on a single point at 28 days

Ligand	0.001 M ligand				0.01 M ligand			
	Al	Fe	P	Ti	Al	Fe	P	Ti
Oxic conditions								
Acetate	-12.3	-12.6	bd*	bd	nd**	nd	nd	nd
Benzoate	-12.1	-13.0	-12.9	bd	nd	nd	nd	nd
Citrate	-10.9	-11.2	-10.8	-12.5	-11.2	-11.6	-11.0	-12.7
Formate	-11.9	-12.4	-12.6	bd	nd	nd	nd	nd
Fumarate	-11.9	-12.6	-12.6	bd	nd	nd	nd	nd
Gallate	-11.0	-11.4	-12.2	-13.1	-11.1	-11.7	-12.6	bd
Glutarate	-12.0	-12.2	bd	bd	nd	nd	nd	nd
Lactate	-12.0	-12.4	-12.7	bd	nd	nd	nd	nd
Malonate	-11.0	-11.5	-11.6	bd	-11.3	-11.6	-12.1	-12.8
Oxalate	-11.0	-11.4	-11.2	-12.8	nc***	nc	nc	nc
Phthalate		-12.5	-12.8	bd	nd	nd	nd	nd
Salicylate	-11.4	-11.8	-13.1	bd	nd	nd	nd	nd
Succinate	-11.9	-12.2	-12.6	bd	nd	nd	nd	nd
Ligand-free	-12.2	-12.4	-13.1	bd	bd	bd	-13.5	bd
Anoxic conditions								
Acetate	bd	-12.0	bd	bd	nd	nd	nd	nd
Benzoate	bd	-12.1	-13.1	bd	nd	nd	nd	nd
Citrate	-11.1	-11.3	-10.9	-12.8	-11.1	-11.5	-10.9	-12.7
Formate	bd	-12.0	-12.9	bd	nd	nd	nd	nd
Fumarate	-11.6	-12.0	-12.2	bd	-11.1	-11.5	-13.0	bd
Gallate	bd	-12.4	-13.3	bd	nd	nd	nd	nd
Glutarate	bd	-12.0	bd	bd	nd	nd	nd	nd
Lactate	bd	-12.0	bd	bd	nd	nd	nd	nd
Malonate	-11.2	-11.6	-11.7	bd	-11.2	-11.7	-12.3	-12.7
Oxalate	-11.2	-11.5	-11.3	-13.3	nc	nc	nc	nc
Phthalate	bd	-12.0	bd	bd	nd	nd	nd	nd
Salicylate	-11.7	-11.9	bd	bd	nd	nd	nd	nd
Succinate	bd	-12.0	-13.0	bd	nd	nd	nd	nd
Ligand-free	-12.3	-12.3	-13.2	bd	bd	bd	-13.5	bd

*bd = concentration of the element was below detection limit (<1 ppb for Al and Fe for 0.001 M ligands or <0.1 ppm for Al and Fe for 0.01 M ligands, and <1 ppb for P and Ti for both 0.001 and 0.01 M ligands)

**nd = not determined

***nc = not considered due to the precipitation of Ca-oxalate

are thought to lose their ability to complex cations and, in turn, to enhance mineral dissolution, when protonated (Furrer and Stumm, 1986). At pH < 6, malonate is therefore expected to be less effective in complexing Al than oxalate. Thus, the difference in the sequences of malonate and oxalate observed by the above-mentioned authors and in the present study is attributed to the difference in pH.

Similarly, the pK_{a2} for phthalate is smaller than that for salicylate (table 1). The pK_{a2} values of the above-mentioned ligands imply that, at pH \leq 6, the proportion of

TABLE 8

The log rate of release ($\text{mol element m}^{-2} \text{s}^{-1}$) from basalt (Neaman et al., 2005b) and granite (present study) in batch experiments at pH 6 with and without 0.01 M organic ligands. Rate was calculated based on a single point at 28 days

Ligand	log rate ($\text{mol m}^{-2} \text{sec}^{-1}$)				
	Al	Fe	Mg	P	Ti
Basalt, oxic conditions					
Citrate	-12.5	-11.7	-12.1	-12.6	-13.8
Malonate	-12.6	-11.9	-12.3	-13.8	bd
Gallate	-12.7	-12.1	-12.3	-14.2	bd
Ligand-free	bd	bd	-12.5	-15.1	bd
Basalt, anoxic conditions					
Citrate	-12.2	-11.2	-11.8	-12.9	-13.6
Malonate	-12.4	-11.8	-12.2	-14.0	bd
Gallate	-12.3	-11.3	-11.9	-14.0	-13.8
Ligand-free	bd	-13.1	-12.6	-15.3	bd
Granite, oxic conditions					
Citrate	-11.2	-11.6	-11.2	-11.0	-12.7
Malonate	-11.3	-11.6	-11.2	-12.1	-12.8
Gallate	-11.1	-11.7	-11.2	-12.6	bd
Ligand-free	bd	bd	-11.2	-13.5	bd
Granite, anoxic conditions					
Citrate	-11.1	-11.5	-11.4	-10.9	-12.7
Malonate	-11.2	-11.7	-11.4	-12.3	-12.7
Gallate	-11.1	-11.5	-11.4	-13.0	bd
Ligand-free	bd	bd	-12.0	-13.5	bd

*bd = concentration of the element was below detection limit (<0.1 ppm for Al, Fe, and Mg or <1 ppb for P and Ti)

protonated species is greater for salicylate in comparison to phthalate. At $\text{pH} \leq 6$, salicylate is therefore expected to be less effective in complexing metals than phthalate. In agreement with that, speciation calculations using the Visual MINTEQ program (Gustafsson, 2005) demonstrates that phthalate is more effective in complexing Ca than salicylate at $\text{pH} \leq 6$. This is in agreement with the observed sequence salicylate < phthalate for the extent of release of P from granite (fig. 4F) and basalt (Neaman and others, 2005b).

However, salicylate was more effective than phthalate in enhancement of Al release from granite (fig. 4D), kaolinite (Chin and Mills, 1991), and Al-oxide (Furrer and Stumm, 1986). The pK_{a2} value of salicylate is 13.7, suggesting that salicylate is protonated at $\text{pH} \leq 6$. One could expect salicylate to be ineffective in complexing Al at $\text{pH} \leq 6$ due to its protonation. We note, however, that the log of the complex stability constant of Al^{3+} with salicylate is 13.8 (fig. 4D) and that the stability constant of Al^{3+} with salicylate is greater than the pK_{a2} of salicylate. Thus ligand complexation with Al^{3+} is expected to be more favorable than complexation with H^+ ,

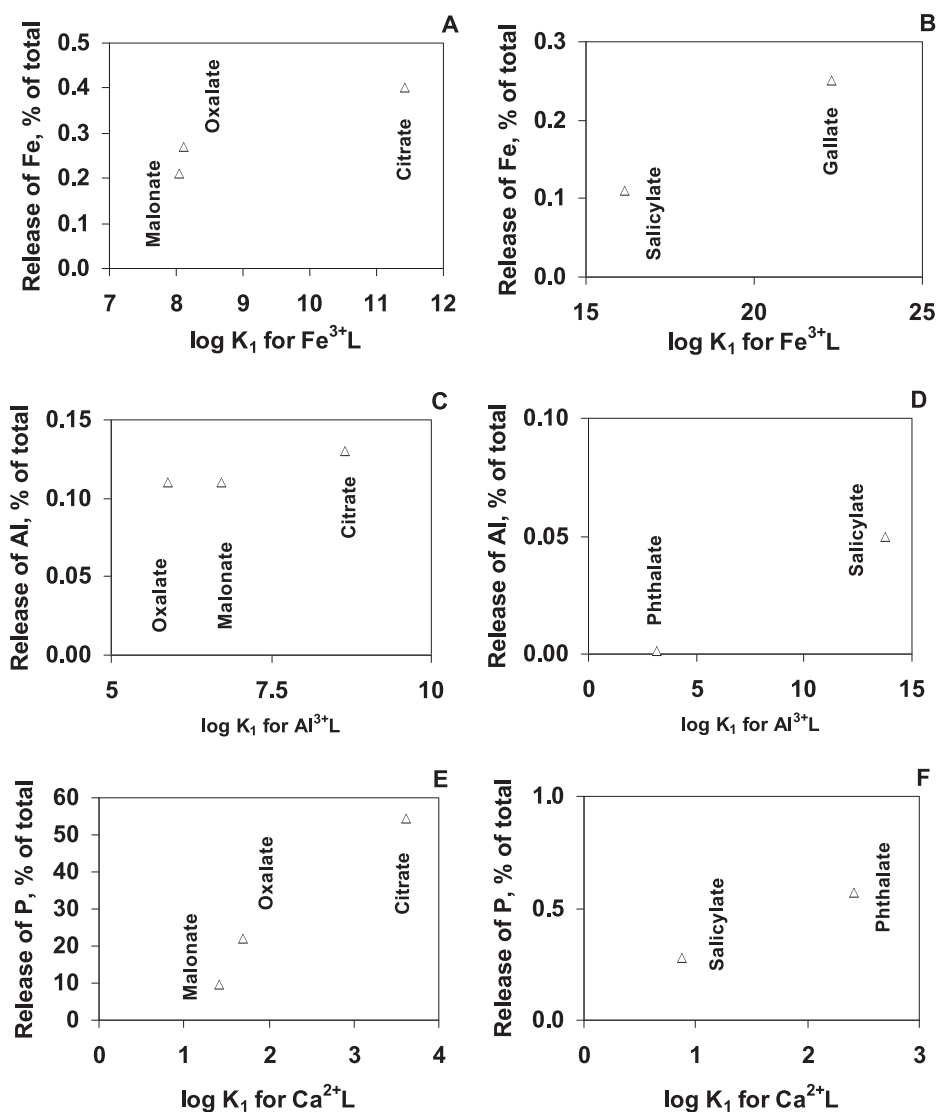


Fig. 4. The effects of 0.001 M ligands on dissolution of granite at pH 6 under oxic conditions: release of Fe vs. complex stability constant of Fe^{3+} with (A) aliphatic and (B) aromatic ligands, release of Al vs. complex stability constant of Al^{3+} with (C) aliphatic and (D) aromatic ligands, and release of P vs. complex stability constant of Ca^{2+} with (E) aliphatic and (F) aromatic ligands. $K_1 = [\text{ML}]/[\text{M}][\text{L}]$, where $[\text{ML}]$, $[\text{M}]$, and $[\text{L}]$ are concentrations of metal-ligand complex, free metal ion, and free ligand ion, respectively. Similar trends were observed for dissolution under anoxic conditions. Complex stability constants for Ca^{2+} -gallate, Al^{3+} -gallate, and Fe^{3+} -phthalate were not available. Complex stability constants are reported for $I = 0.1$ M and 25°C (IUPAC, 2000). Note the difference in scale of ordinate for aliphatic (A, C, and E) and aromatic (B, D, and F) ligands.

in agreement with the above-mentioned experimental observations. Consistent with that, speciation calculations using the Visual MINTEQ program (Gustafsson, 2005) demonstrates that salicylate is more effective in complexing Al than phthalate at $\text{pH} \leq 6$.

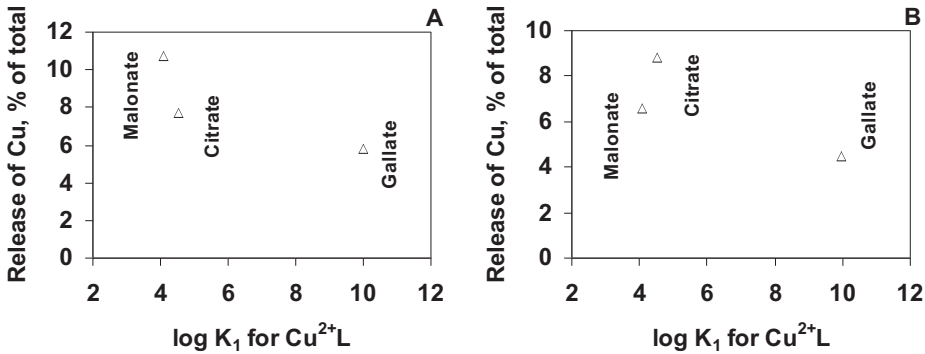


Fig. 5. The effects of 0.01 M ligands on dissolution of granite at pH 6: release of Cu vs. complex stability constant of Cu^{2+} with gallate (Abu-Bakr and others, 1994), citrate, and malonate (IUPAC, 2000) under (A) oxic and (B) anoxic conditions. $K_1 = [\text{ML}]/[\text{M}][\text{L}]$, where $[\text{ML}]$, $[\text{M}]$, and $[\text{L}]$ are concentrations of metal-ligand complex, free metal ion, and free ligand ion, respectively. Complex stability constants are reported for $I = 0.1 \text{ M}$ and 25°C .

Order of Element Release

Rock dissolution was non-stoichiometric regardless of the presence or absence of organic ligands (tables 3–6). As mentioned above, no significant differences were observed in the extent of elements released under oxic versus anoxic conditions. Generalizing for both oxic and anoxic conditions, extent of release of elements (expressed as a percentage of the total element content in the unweathered granite) decreased in the following order:

With ligands: $\text{P, Cu} > \text{Mg} > \text{V, Rb, Fe, Ba} > \text{Ti, Al, Y} > \text{Cr, Zr}$

Ligand-free: $\text{Mg} > \text{P, V, Rb, Ba} > \text{Al, Fe, Ti, Cr, Cu, Y, Zr}$

The above-mentioned orders of extent of element release may vary, of course, for other granites of different chemical and mineralogical composition. Nonetheless, the following important observations can be made with respect to element mobility as function of rock lithology:

1) Release of P was enhanced considerably in the presence of organic ligands, especially in the presence of citrate (figs. 2 and 3, tables 3–5), similar to basalt. However, we note that, in the presence of organic ligands, release of Y from granite was minor in the present study, in contrast to considerable Y release from basalt observed in our previous study (Neaman and others, 2005b).

2) No significant differences were observed in the extent of Fe released from granite under oxic versus anoxic conditions. In contrast, release of Fe from basalt was considerably greater under anoxic versus oxic conditions.

3) Concentrations of Cu released were at the detection limit in ligand-free experiments but were enhanced considerably in the presence of ligands under both oxic and anoxic conditions (table 6). In contrast, concentrations of Cu released from basalt were below the detection limit under anoxic conditions but increased considerably under oxic conditions, especially in the presence of organic ligands.

4) Release of Ti from granite was enhanced in the presence of citrate, oxalate, and malonate, while Zr was immobile in the presence of organic ligands (table 6). In contrast, in the basalt, Ti was less mobile than Zr in the presence of organic acids.

These observations will be discussed in the following sections.

P and Y Mobility

Based on EPMA analysis, P in the granite studied is present as fluorapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$, a very common accessory mineral in igneous rocks (McConnell, 1973; Best and Christiansen, 2001). The solubility product of fluorapatite is very low ($\log K_{\text{sp}} = -60$) (Wedepohl, 1970), and apatite is generally classed as a stable mineral, placed in decreasing order of stability during mineral weathering between biotite and ilmenite (Pettijohn, 1941) or between rutile and magnetite (Banfield and others, 1991). As discussed previously, organic ligands, especially citrate, enhance release of P from granite (figs. 2 and 3, tables 3–5) by forming complexes with Ca. Similarly, organic ligands considerably enhanced dissolution of apatite (Welch and others, 2002; Goyne and others, 2006).

Phosphorus is an essential plant nutrient. Plant roots typically exude aliphatic carboxylic acids with different chain lengths ($\text{C}_1\text{--}\text{C}_6$) including acetic, lactic, fumaric, malic, malonic, citric, isocitric, succinic, oxalic, glycolic, tartaric, propionic, butyric, valeric, and aconitic acids (Curl and Truelove, 1986; Stone, 1997; Jones, 1998 and references therein; Dakora and Phillips, 2002). The release of these organic acids by the roots has been observed to be increased under a variety of nutrient stresses (Lipton and others, 1987; Shen and others, 2002) and is thus considered important in solubilizing inorganic nutrient substances (Jones, 1998 and references therein; Dakora and Phillips, 2002). Our observations showing considerable enhancement in P release from the granite in the presence of organic ligands are consistent with these observations.

Apatite in igneous rocks is known to concentrate rare earth elements and yttrium [REY] (for example, Hall, 1987; Winter, 2001). Enhanced dissolution rate of apatite during weathering in the presence of organic acids may affect mobilization of these elements. In our previous study on dissolution of basalt (Neaman and others, 2005b), we observed that, similar to P, release of Y was at the detection limit in the ligand-free experiment but was enhanced considerably in the presence of citrate: extent of release of Y was directly correlated with that of P. In contrast, in the present study, release of Y from granite with and without citrate was at the detection limit (Appendix 4).

EPMA analysis indicated Y content of ~ 400 ppm in fluorapatite crystals. None of the REY-phosphate phases [such as monazite, $(\text{Ce}, \text{La}, \text{Th}, \text{Nd}, \text{Y})\text{PO}_4$, or xenotime, YPO_4] were detected under EPMA. Calculations demonstrate that this concentration of Y in apatite is equal to ~ 15 percent of the total Y content in the granite studied, assuming that all P in the rock is present as fluorapatite. EPMA was also used to investigate the presence of Y in other minerals within the granite in one polished section. Yttrium content of several thousand ppm was observed in some sphene (CaTiSiO_5) grains, which appeared to be less reactive than apatite in the presence of organic ligands. In contrast, EPMA analysis indicated that Y was mainly present in apatite in the basalt in our previous study (Neaman and others, 2005b). Thus, the difference in the extent of release of Y in the presence of organic ligands observed in basalt (Neaman and others, 2005b) and in granite (the present study) is attributed to the difference in Y-hosting parent minerals.

In igneous rocks, several minerals, including apatite and sphene, are known to concentrate REY (Best and Christiansen, 2001). For this reason, no generalization of whether Y would be mobile in basalt and granite in the presence of organic ligands can be drawn because Y mobility would depend on the nature of Y-hosting parent minerals.

Fe and Cu Mobility

No significant differences were observed in the extent of Fe released from granite under oxic versus anoxic conditions with and without organic ligands (tables 3–5, 7 and 8; Appendix 3). In contrast, release of Fe from basalt was considerably greater under anoxic

versus oxic conditions with and without organic ligands (Neaman and others, 2005b). These differences can be attributed to the difference in concentrations of total Fe in the solution in the case of basalt and granite dissolution under oxic conditions: up to 70 ppm (basalt) versus up to 0.5 ppm (granite) (Neaman and others, 2005b, Appendix 3).

The difference in concentrations of total Fe in the solution can be attributed in turn to the difference in major Fe-hosting phases in the rocks: biotite (granite) versus glass and augite (basalt). Biotite is generally classed as a stable mineral (for example, Pettijohn, 1941), while augite is generally considered as unstable in mineral stability series (for example, Goldich, 1938; Wasklewicz, 1994). Recent studies also indicate that augite was one of the first minerals to weather in basalts in Costa Rica (Sak and others, 2004), while biotite was one of the last minerals to weather out of granite in Puerto Rico (Murphy and others, 1998). Also, rates of dissolution of basaltic glass are generally greater than those of crystalline minerals (such as biotite and augite) (for example, Gislason and Eugster, 1987).

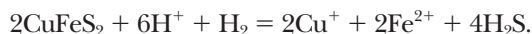
Chemical speciation of the oxic solutions [calculated with Geochemist's Workbench®, Bethke (2002), database thermo_minteq_gwb4] suggests that, in the case of basalt dissolution, solutions were oversaturated with respect to ferrihydrite, even with organic ligands present. In contrast, in the case of granite dissolution with organic ligands, solutions were oversaturated with respect to hematite, magnetite, goethite, and lepidocrocite and undersaturated for ferrihydrite. Extensive precipitation of Fe^{III} phases could explain the smaller release of Fe under oxic as compared to anoxic conditions in basalt experiments. In contrast, in the case of granite, similarity in the concentrations of Fe under oxic and anoxic conditions with organic ligands suggest that Fe^{III} phases did not precipitate extensively during the study period (28 days), consistent with solution phase undersaturation for ferrihydrite, the phase expected to precipitate first.

Concentrations of Cu released were below the detection limit (Appendix 4) in ligand-free experiments, but increased considerably in the presence of organic ligands under both oxic and anoxic conditions (table 6). Copper is a predominantly chalcophile element (Hall, 1987) and is present as sulfides in most igneous rocks (Best and Christiansen, 2001). In contrast, occurrences of sulfate minerals are not known in igneous rocks (Marshall and Fairbridge, 1999).

As mentioned above, some small (micron-size) sulfide inclusions have been observed under EPMA in magnetite phases. These inclusions were too small for accurate quantitative analysis, but qualitative analysis indicated that they are Cu/Fe-sulfides, most probably chalcopyrite, a very common accessory mineral in igneous rocks (for example, Wedepohl, 1974; Best and Christiansen, 2001).

The solubility of chalcopyrite is low: $\text{CuFeS}_2 + 2\text{H}^+ = \text{Cu}^{2+} + \text{Fe}^{2+} + 2\text{HS}^-$, $\log K = -35.27$ (Bethke, 2002, database thermo_minteq_gwb4). Sulfides dissolve under oxic conditions via oxidation (Lindsay, 1979). Consistent with this, in our previous study on dissolution of basalt (Neaman and others, 2005b), we observed that concentrations of Cu released from basalt were below the detection limit under anoxic conditions but increased considerably under oxic conditions, especially in the presence of organic ligands. Neaman and others (2005a, 2005b) have argued that organic ligands enhance oxic dissolution of Cu-sulfides by forming complexes with Cu as observed for other sulfides (Davis and others, 1995). Likewise, Goynes and others (2006) found that Cu release to solution from chalcopyrite dissolution was increased by four orders of magnitude under oxic versus anoxic conditions.

Despite these arguments, in the present study, Cu/Fe-sulfides in granite were soluble in the presence of organic ligands regardless of oxygen levels as reflected by similar concentrations of Cu released under oxic and anoxic conditions. Under anoxic conditions in our experiments (pH = 6-6.5 and Eh < 100 mV), aqueous Cu is expected to be present as Cu^I (for example, Pourbaix, 1966). Thus, solubilization of chalcopyrite can be expressed for anoxic conditions as:



The equilibrium of this reaction is expected to be shifted towards reactants (to the left) in the solution with larger concentration of aqueous Fe^{2+} and towards products (to the right) in solution with smaller concentrations of Fe^{2+} . Concentrations of total Fe in the solution were up to 70 ppm and up to 0.6 ppm in the case of basalt and granite dissolution, respectively, in the presence of organic ligands under anoxic conditions (Neaman and others, 2005b; Appendix 3). This could explain why chalcopyrite was soluble under anoxic conditions in granite, but not in basalt.

Ti and Zr Mobility

Enhanced release of Ti in the presence of citrate, oxalate and malonate (figs. 2 and 3, tables 3 – 5) is of particular interest. Ti is often considered as an immobile element to calculate mass balance in weathering soil systems and is thought to be more suitable than Zr for mass-balance calculations for some lithologies because of its greater concentrations in soils and rocks (as discussed for example by Teutsch and others, 1999). Similarly, Dawson and others (1991) studied the depletion of first-row transition metals (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn) in a chronosequence of soils in New Zealand and reported, after applying corrections to relate elemental concentrations to a soil volume at time zero, that all the elements (except Ti) became depleted with time. Similarly, White (1995) investigated weathering of granite in the Rio Icacos basin, Luquillo Experimental Forest, Puerto Rico. He reported that both Ti and Zr were essentially immobile in the soil during weathering.

In contrast, our results suggest that the mobility of Ti from Yosemite granite is increased in the presence of organic ligands at concentrations of 0.001 and 0.01 M. Such Ti mobilization was observed previously by Viers and others (1997) in six of the nine organic-rich waters as compared to organic-poor waters of a tropical watershed draining a granitic rock. Thus, in organic-rich soil environments, Ti may be problematic when considered as an immobile element in mass-balance calculations for granite reactivity.

In the present study, Zr was less mobile than Ti in the presence of organic ligands. Similarly, Hodson (2002) reported that Zr was the least mobile element in a Soxhlet-extraction experiment on A and B horizons of a granitic Podzol that naturally contained organic acids. However, Viers and others (1997) and Oliva and others (1999) reported, for a tropical watershed draining a granitic rock, mobilization of Zr in organic-rich water samples analyzed. Similarly, Neaman and others (2005b) reported that the mobility of Zr during dissolution of basalt was increased in the presence of 0.01 M citrate and that Ti was the least mobile among the analyzed elements. Also, Kurtz and others (2000) reported mobility of Zr in basalt-derived soils on Hawaii.

In the granite used in the present study, Zr was found in zircons, while, in the basalt studied by Neaman and others (2005b), Zr was only found in Fe/Ti oxides, which were more reactive than zircons. Although both Ti and Zr can be mobilized in the presence of organic ligands, mobility of Ti and Zr may be affected by the nature of the Ti- and Zr-hosting parent minerals.

The most important and abundant mineral containing Zr is zircon (Wedepohl, 1974; Best and Christiansen, 2001). This suggests that, in general, use of Zr as an immobile element would be useful even in an organic rich-environment for both basalt and granite. However, if Zr in the rock is not present in zircon but in Fe/Ti oxides or other phases, its use as immobile element would be misleading. Thus, no generalization of whether Zr or Ti is preferable to use as immobile element can be drawn. Further work should test the relative importance of lithology and mineralogy on immobility of these two elements.

CONCLUSIONS

1) Release of all elements from granite was enhanced considerably in the presence of 0.001 M and 0.01 M organic ligands in comparison to ligand-free dissolution experiments. These findings emphasize the importance of low-molecular-weight organic acids in weathering of primary minerals.

2) The extent of element mobilization was greater for tetradentate and tridentate as compared to bidentate ligands. Monodentate ligands enhanced element mobilization very slightly, if at all.

3) Differences among the ligands used with respect to the extent of element release are best explained by the difference in cation-ligand stability constants. However, aromatic ligands used in the present study had a considerably smaller effect on the enhancement of release of all elements in comparison to aliphatic ligands. This was attributed to protonation of the functional groups of aromatic ligands at the experimental pH of 6.

4) Rock dissolution was non-stoichiometric regardless of the presence or absence of organic ligands. Release of P and Cu (expressed as a percentage of total element content in the unweathered rock) in the presence of organic ligands was considerably greater than that of other elements.

5) Findings of the present study on dissolution of granite were compared to the findings of our previous study on dissolution of basalt. Considerable differences in the mobility patterns of Y, Fe, Cu, Ti, and Zr during dissolution of granite and basalt were observed.

6) With and without organic ligands, no significant differences were observed in the extent of Fe released from granite under oxic versus anoxic conditions, while the extent of Fe release from basalt was considerably greater under anoxic versus oxic conditions with and without organic ligands. These differences can be attributed to the difference in major Fe-hosting phases in the rocks: biotite (granite) versus glass and augite (basalt).

7) In basalt, release of Y was at the detection limit in the ligand-free experiment but was enhanced considerably in the presence of citrate. In contrast, in the present study, release of Y from granite in the presence of citrate was at the detection limit. This difference was attributed to the difference in Y-hosting parent minerals in the rocks: apatite in the basalt and sphene in the granite.

8) In the granite, concentrations of Cu released were below the detection limit in ligand-free experiments, but increased considerably in the presence of organic ligands under both oxic and anoxic conditions. In contrast, concentrations of Cu released from basalt were below the detection limit under anoxic conditions but increased considerably under oxic conditions, especially in the presence of organic ligands. This difference was attributed to the different extent of Fe release from basalt and granite that affected dissolution of Cu/Fe-sulfides and, in turn, the mobility patterns of Cu during dissolution of these two rocks.

9) In the granite, Zr was less mobile than Ti in the presence of organic acids, while the reverse was true in the case of basalt. In the granite, Zr was found in zircons, while, in the basalt, Zr was only found in Fe/Ti oxides, which were more reactive than zircons. Although both Ti and Zr can be mobilized in the presence of organic ligands, mobility of Ti and Zr may be affected by the nature of the Ti- and Zr-hosting parent minerals.

ACKNOWLEDGMENTS

The authors wish to thank D. Egler, A. Rose, H. Barnes, and H. Ohmoto for helpful comments, J. Chesley (University of Arizona) for sampling the granite, D. Johnson (Washington State University) for XRF analyses, T. Furman, C. House, and Z. Zhang for assistance and laboratory equipment, N. Wonderling for XRD analysis, T. Rusnak for surface area analysis, H. Gong for ICP-AES analysis, K. Cowan for total organic carbon analysis, M. Angelone for EPMA analysis, B. Alexander and J. Kittleson

for ICP-MS analysis. The study was funded by NASA grant NAG5-12330, the Penn State Astrobiology Research Center, and the Penn State Biogeochemical Research Initiative for Education (BRIE) (NSF grant DGE-9972759). We acknowledge helpful reviews by Harvey Doner and an anonymous reviewer.

APPENDIX 1

Concentrations of elements released from granite at pH 6 under oxic conditions in 0.001 M organic ligands

Ligand	Concentrations in solution, ppb			
	Al	Fe	P	Ti
Acetate	4.7	5.0	bd *	bd
Benzoate	7.9	1.8	1.3	bd
Citrate	106	112	155	4.8
Formate	11	7.0	2.6	bd
Fumarate	11	4.7	2.6	bd
Gallate	88	70	6.0	1.3
Glutarate	10	11	bd	bd
Lactate	8.2	7.6	1.9	bd
Malonate	84	58	28	bd
Oxalate	84	77	62	2.4
Phthalate	bd	6.5	1.6	bd
Salicylate	37	32	bd	bd
Succinate	12	12	2.8	bd
Ligand-free	6.0	7.1	bd	bd

*bd = below detection (<1 ppb). Concentrations of elements presented in the table were below detection (<1 ppb) in granite-free controls.

APPENDIX 2

Concentrations of elements released from granite at pH 6 under anoxic conditions in 0.001 M organic ligands

Ligand	Concentrations in solution, ppb			
	Al	Fe	P	Ti
Acetate	bd *	17	bd	bd
Benzoate	bd	16	bd	bd
Citrate	70	95	139	2.7
Formate	bd	19	1.2	bd
Fumarate	24	19	6.3	bd
Gallate	bd	7.1	bd	bd
Glutarate	bd	18	bd	bd
Lactate	bd	20	bd	bd
Malonate	51	49	19	bd
Oxalate	52	58	57	bd
Phthalate	bd	17	bd	bd
Salicylate	18	23	bd	bd
Succinate	bd	21	1.0	bd
Ligand-free	4.2	8.5	bd	bd

*bd = below detection (<1 ppb). Concentrations of elements presented in the table were below detection (<1 ppb) in granite-free controls.

APPENDIX 3

Concentrations of Al, Fe, and Mg released from granite at pH 6 under oxic and anoxic conditions in 0.01 M organic ligands

Ligand	Concentrations in solution, ppm		
	Al	Fe	Mg
	Oxic		
Citrate	0.55	0.53	0.53
Malonate	0.51	0.45	0.49
Gallate	0.70	0.36	0.48
Ligand-free	bd	bd	0.53
	Anoxic		
Citrate	0.72	0.59	0.36
Malonate	0.58	0.37	0.30
Gallate	0.69	0.62	0.31
Ligand-free	bd	bd	0.26

*bd = below detection (<0.1 ppm). Concentrations of elements presented in the table were below detection (<0.1 ppm) in granite-free controls.

APPENDIX 4

Concentrations of minor and trace elements released from granite at pH 6 under oxic and anoxic conditions in 0.01 M organic ligands

Ligand	Concentrations in solution, ppb								
	P	Ti	V	Cr	Cu	Rb	Y	Zr	Ba
	Oxic								
Citrate	970	33	2.0	bd	8.4	2.0	0.7	bd	14
Malonate	87	25	1.8	bd	12	2.3	bd	bd	12
Gallate	24	bd	1.9	bd	6.4	2.3	bd	bd	13
Ligand-free	3.1	bd	bd	bd	bd	1.6	bd	bd	12
	Anoxic								
Citrate	1278	36	2.1	bd	10	1.8	1.0	bd	10
Malonate	58	30	1.8	bd	7.3	1.8	bd	bd	6.1
Gallate	12	bd	1.8	bd	5.0	1.7	bd	bd	8.9
Ligand-free	3.1	bd	1.0	bd	bd	2.4	bd	bd	3.2

*bd = below detection (<1 ppb). Concentrations of elements presented in the table were below detection (<1 ppb) in granite-free controls.

REFERENCES

- Abu-Bakr, M. S., Rageh, H. M., Hashem, E. Y., and Moustafa, M. H., 1994, Studies on the mixed-ligand complexes of copper(II) with gallic acid and pyridine carboxylic acids and their benzologues: *Monatshefte für Chemie - Chemical Monthly*, v. 125, p. 1197–1205.
- Banfield, J. F., Jones, B. F., and Veblen, D. R., 1991, An AEM-TEM study of weathering and diagenesis, Abert Lake, Oregon: I. Weathering reactions in the volcanics: *Geochimica et Cosmochimica Acta*, v. 55, p. 2781–2793.
- Barman, A. K., Varadachari, C., and Ghosh, K., 1992, Weathering of silicate minerals by organic acids: I. Nature of cation solubilization: *Geoderma*, v. 53, p. 45–63.
- Baziramakenga, R., Simard, R. R., and Leroux, G. D., 1995, Determination of organic-acids in soil extracts by ion chromatography: *Soil Biology and Biochemistry*, v. 27, p. 349–356.
- Best, M. G., and Christiansen, E. H., 2001, *Igneous petrology: Malden, Massachusetts, Blackwell Science*, 455 p.
- Bethke, C. M., 2002, *The Geochemist's Workbench®. Release 4.0. A User's Guide to Rxn, Act2, Tact, React, and Gtplot.*, University of Illinois.
- Brantley, S. L., 2004, Reaction kinetics of primary rock-forming minerals under ambient conditions, *in* Drever, J. I., editor, *Surface and ground water, weathering, and soils: Treatise on Geochemistry*, v. 5: Oxford, United Kingdom, Elsevier-Pergamon, p. 73–117.
- Brantley, S. L., and Mellott, N. P., 2000, Surface area and porosity of primary silicate minerals: *American Mineralogist*, v. 85, p. 1767–1783.
- Chin, P. K. F., and Mills, G. L., 1991, Kinetics and mechanisms of kaolinite dissolution: effects of organic ligands: *Chemical Geology*, v. 90, p. 307–317.
- Cornell, R. M., and Schwertmann, U., 1996, *The iron oxides: Structure, properties, reactions, occurrences and uses: Weinheim, Germany, Wiley-VCH*, 600 p.
- Curl, E. A., and Truelove, B., 1986, *The rhizosphere: Berlin, Germany, Springer-Verlag*, 288 p.
- Dakora, F. D., and Phillips, D. A., 2002, Root exudates as mediators of mineral acquisition in low-nutrient environments: *Plant and Soil*, v. 245, p. 35–47.
- Davis, A. P., Hsieh, Y. H., and Huang, C. P., 1995, Photo-oxidative dissolution of CdS(s): The effect of complexing agents: *Chemosphere*, v. 31, p. 3093–3104.
- Dawson, B. S. W., Fergusson, J. E., Campbell, A. S., and Cutler, E. J. B., 1991, Depletion of first-row transition metals in a chronosequence of soils in the reefton area of New Zealand: *Geoderma*, v. 48, p. 271–296.
- Drever, J. I., 1994, The effect of land plants on weathering rates of silicate minerals: *Geochimica et Cosmochimica Acta*, v. 58, p. 2325–2332.
- Drever, J. I., and Stillings, L. L., 1997, The role of organic acids in mineral weathering: *Colloids and Surfaces*, v. A 120, p. 167–181.
- FAO, 1998, *World Reference Base for Soil Resources: Rome, Italy, Food and Agriculture Organization of the United Nations, International Society of Soil Science, International Soil Reference and Information Center.*
- Furrer, G., and Stumm, W., 1986, The coordination chemistry of weathering: I. Dissolution kinetics of α - Al_2O_3 and BeO: *Geochimica et Cosmochimica Acta*, v. 50, p. 1847–1860.
- Garrett, R. H., and Grisham, C. M., 1999, *Biochemistry: Fort Worth, Texas, Saunders College Publishing*, 1200 p.
- Gislason, S. R., and Eugster, H. P., 1987, Meteoric water-basalt interactions. I: A laboratory study: *Geochimica et Cosmochimica Acta*, v. 51, p. 2827–2840.
- Goldich, S. S., 1938, A study of rock weathering: *Journal of Geology*, v. 46, p. 17–58.
- Goynes, K. W., Brantley, S. L., and Chorover, J., 2006, Effects of organic acids and dissolved oxygen on apatite and chalcopyrite dissolution: Implications for using elements as organomakers and oxymarkers: *Chemical Geology*, doi: 10.1016/j.chemgeo.2006.04.003.
- Gustafsson, J. P., 2005, Visual MINTEQ, version 2.31, <http://www.lwr.kth.se/english/OurSoftWare/Vminteq/>.
- Hall, A., 1987, *Igneous Petrology: New York, New York, John Wiley and Sons*, 573 p.
- Hodson, M., 2002, Experimental evidence for mobility of Zr and other trace elements in soils: *Geochimica et Cosmochimica Acta*, v. 66, p. 819–828.
- IUPAC, 2000, *IUPAC Stability Constants Database. Release 5, International Union of Pure and Applied Chemistry and Academic Software* <http://www.acadsoft.co.uk>.
- Johnson, D. M., Hooper, P. R., and Conrey, R. M., 1999, XRF analysis of rocks and minerals for major and trace elements on a single low dilution Li-tetraborate fused bead: *Advances in X-ray Analysis*, v. 41, p. 843–867.
- Jones, D. L., 1998, Organic acids in the rhizosphere: A critical review: *Plant and Soil*, v. 205, p. 25–44.
- Krzyszowska, A. J., Blaylock, M. J., Vance, G. F., and David, M. B., 1996, Ion-chromatographic analysis of low molecular weight organic acids in Spodosol forest floor solutions: *Soil Science Society of America Journal*, v. 60, p. 1565–1571.
- Kurtz, A., Derry, L., Chadwick, O., and Alfano, M., 2000, Refractory element mobility in volcanic soils: *Geology*, v. 28, p. 683–686.
- Lindsay, W. L., 1979, *Chemical equilibria in soils: New York, New York, John Wiley and Sons*, 412 p.
- Lipton, D. S., Blanchard, R. W., and Blevins, D. G., 1987, Citrate, malate, and succinate concentration in exudates from P-sufficient and P-stressed *Medicago sativa* L. seedlings: *Plant Physiology*, v. 85, p. 315–317.
- Lovley, D. R., and Phillips, E. J. P., 1986, Availability of ferric iron for microbial reduction in bottom sediments of the fresh-water tidal Potomac River: *Applied and Environmental Microbiology*, v. 52, p. 751–757.

- Lundström, U. S., 1994, Significance of organic acids for weathering and the podzolization process: *Environment International*, v. 20, p. 21–30.
- Lundström, U. S., VanBreemen, N., and Jongmans, A. G., 1995, Evidence for microbial decomposition of organic acids during podzolization: *European Journal of Soil Science*, v. 46, p. 489–496.
- Marshall, C. P., and Fairbridge, R. W., 1999, *Encyclopedia of geochemistry*: Dordrecht, Kluwer Academic Publishers, 712 p.
- McConnell, D., 1973, Apatite: Its crystal chemistry, mineralogy, utilization, and geologic and biologic occurrences: *Applied Mineralogy*, 5: New York, New York, Springer-Verlag, 111 p.
- McKeague, J. A., Cheshire, M. V., Andreux, F., and Berthelin, J., 1986, Organo-mineral complexes in relation to pedogenesis, in Huang, P. M., and Schnitzer, M., editors, *Interactions of Soil Minerals with Natural Organics and Microbes*: Madison, Wisconsin, Soil Science Society of America, p. 549–592.
- Murphy, S. F., Brantley, S. L., Blum, A. E., White, A. F., and Dong, H., 1998, Chemical weathering in a tropical watershed, Luquillo Mountains, Puerto Rico: II. Rate and mechanism of biotite weathering: *Geochimica et Cosmochimica Acta*, v. 62, p. 227–244.
- Neaman, A., Chorover, J., and Brantley, S. L., 2005a, Element mobility patterns records organic ligands in soils on early Earth: *Geology*, v. 33, p. 117–120.
- 2005b, Implications of the evolution of organic acid moieties for basalt weathering over geological time: *American Journal of Science*, v. 305, p. 147–185.
- Oliva, P., Viers, J., Dupré, B., Fortuné, J., Martín, F., Braun, J., Nahon, D., and Robain, H., 1999, The effect of organic matter on chemical weathering: Study of a small tropical watershed: Nsimi-Zoétéle site, Cameroon: *Geochimica et Cosmochimica Acta*, v. 63, p. 4013–4035.
- Pettijohn, F. J., 1941, Persistence of heavy minerals and geologic age: *Journal of Geology*, v. 46, p. 610–625.
- Pourbaix, M., 1966, *Atlas of Electrochemical Equilibria in Aqueous Solutions*: Oxford, United Kingdom, Pergamon Press, 644 p.
- Sak, P. B., Fisher, D., Gardner, T., Murphy, K. M., and Brantley, S. L., 2004, Rates of weathering and rind formation on Costa Rican basalt: *Geochimica et Cosmochimica Acta*, v. 68, p. 1453–1472.
- Shen, H., Yan, X. L., Zhao, M., Zheng, S. L., and Wang, X. R., 2002, Exudation of organic acids in common bean as related to mobilization of aluminum- and iron-bound phosphates: *Environmental and Experimental Botany*, v. 48, p. 1–9.
- Soil Survey Staff, 1999, *Soil Taxonomy: A Basic System of Soil Classification for Making and Interpreting Soil Surveys*: Washington, D. C., U.S. Dept. of Agriculture, Natural Resources Conservation Service.
- Song, S. K., and Huang, P. M., 1988, Dynamics of potassium release from potassium-bearing minerals as influenced by oxalic and citric acids: *Soil Science Society of America Journal*, v. 52, p. 383–390.
- Stevenson, F. J., 1991, Organic matter-micronutrient reactions in soil, in Mortvedt, J. J., editor, *Micronutrients in Agriculture*: Madison, Wisconsin, Soil Science Society of America, p. 145–186.
- Stone, A. T., 1997, Reactions of extracellular organic ligands with dissolved metal ions and mineral surfaces, in Banfield, J. F., and Nealson, K. H., editors, *Geomicrobiology: Interactions between microbes and minerals*: Reviews in Mineralogy, 35: Washington, DC, Mineralogical Society of America, p. 309–344.
- Teutsch, N., Erel, Y., Halicz, L., and Chadwick, O. A., 1999, The influence of rainfall on metal concentration and behavior in the soil: *Geochimica et Cosmochimica Acta*, v. 63, p. 3499–3511.
- Viers, J., Dupre, B., Polve, M., Schott, J., Dandurand, J. L., and Braun, J. J., 1997, Chemical weathering in the drainage basin of a tropical watershed (Nsimi-Zoetele site, Cameroon): Comparison between organic-poor and organic-rich waters: *Chemical Geology*, v. 140, p. 181–206.
- Wasklewicz, T. A., 1994, Importance of environment on the order of mineral weathering in olivine basalts, Hawaii: *Earth Surface Processes and Landforms*, v. 19, p. 715–734.
- Wedepohl, K. H., 1970, *Handbook of Geochemistry*, Vol. II/2: Berlin, Germany, Springer-Verlag, 667 p.
- 1974, *Handbook of Geochemistry*, Vol. II/4: Berlin, Germany, Springer-Verlag.
- Welch, S. A., Taunton, A. E., and Banfield, J. F., 2002, Effect of microorganisms and microbial metabolites on apatite dissolution: *Geomicrobiology Journal*, v. 19, p. 343–367.
- White, A. F., 1995, Chemical weathering rates of silicate minerals in soils, in White, A. F., and Brantley, S. L., editors, *Chemical weathering rates of silicate minerals: Reviews in Mineralogy*, v. 31: Washington, D.C., Mineralogical Society of America, p. 407–461.
- Winter, J. D., 2001, *An introduction to igneous and metamorphic petrology*: Upper Saddle River, New Jersey, Prentice Hall, 697 p.
- Zhang, H., and Bloom, P. R., 1999, Dissolution kinetics of hornblende in organic acid solutions: *Soil Science Society of America Journal*, v. 63, p. 815–822.