# Effects of organic acids and dissolved oxygen on apatite and chalcopyrite dissolution: Implications for using elements as organomarkers and oxymarkers

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## Abstract

We have previously suggested that mobility patterns of P and Y in paleosols could serve as "organomarkers" to denote the presence of organic ligands secreted by terrestrial organisms on early Earth. In addition, our data indicate that Cu depletion may provide a viable oxymarker for determining the presence of atmospheric oxygen during soil weathering processes. In this research, we continue pursuing the potential for utilizing these elements as markers by investigating dissolution of Durango apatite ($Ca_5$ $(PO_4)_{2.82}(F,Cl,OH)_{1.54}$) and Messina chalcopyrite ($CuFeS_2$) reacted under batch conditions in the presence and absence of two aliphatic and aromatic organic acids under oxic and anoxic conditions. In general, results show that organic acids enhance element release from apatite (Ca, P and Y) and chalcopyrite (Cu, Fe, and Y), and increasing organic acid concentrations from 1 to 10 mM results in greater dissolution. The aliphatic organic acid citrate enhances mineral dissolution to the greatest extent and dissolution in the presence of aromatic salicylate or absence of ligand is lowest. Release of Ca, P, and Y from apatite was not impacted by dissolved $O_2(g)$ while release of Cu from chalcopyrite was impacted. Aqueous Cu concentrations at the end of batch experiments with chalcopyrite are four orders of magnitude greater under oxic conditions, whereas Fe concentrations are substantially higher under anoxic conditions. These data support the hypothesis that release of P and Y from apatite is enhanced by organic acids and that Cu release is impacted significantly by dissolved $O_2(g)$ and, to a lesser extent, organic acids. Thus, it seems plausible that geochemical and mineralogical signatures of P, Y, and Cu may have utility for distinguishing the presence of terrestrial organisms and atmospheric conditions during soil weathering processes on early Earth.
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Keywords: Apatite; Chalcopyrite; Organic acids; Dissolution; Organomarker; Oxymarker

## 1. Introduction

Low-molecular-weight organic acids (LMWOAs) are typical constituents of mineral soils believed to be important for rock and mineral weathering, metal mobilization and transport, and solubilization of plant nutrients (Stevenson, 1994). These aliphatic and

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aromatic compounds are detected commonly in soil solutions (Fox and Comford, 1990; Baziramakenga et al., 1995; Krzyszowska et al., 1996) at concentrations ranging from micro- to millimolar (Stevenson, 1991). Origins of LMWOAs in soil are attributed to secretion products of prokaryotes, fungi, lichens, and plant roots (Jones, 1998; Neaman et al., 2005b), biomolecule and humic substance decomposition (Tan, 1986; Stevenson, 1994), and leaf litter leaching (Fox, 1995) and concentrations of these compounds in soil porewaters may have changed over geologic time (Neaman et al., 2005b). Organic acids may increase rock and soil mineral dissolution by increasing proton concentration (proton-promoted dissolution; Tan, 1986; Furrer and Stumm, 1986), forming surface complexes that weaken and then break metal–oxygen lattice bonds (ligand-promoted dissolution; Furrer and Stumm, 1986; Stumm, 1997), and through the formation of aqueous metal–ligand complexes that reduce the extent of relative saturation of solution with respect to the dissolving phases (Drever and Stillings, 1997).

Recent studies by Neaman et al. (2005a,b, in press) investigated the effects of LMWOAs and dissolved $O_2$ (g) on dissolution of Columbia River basalt (BCR-1; Bridal Veil Flow Quarry, Washington) and Tuolumne River granite (Yosemite National Park, CA). The major findings of these studies were (1) the release of many elements from whole rocks was enhanced by LMWOAs relative to ligand-free experiments; (2) differences in elemental release from the rocks were correlated with metal–ligand stability constants, (3) aliphatic ligands enhance dissolution to a greater extent than aromatic ligands at pH 6 due to the protonation of aromatic ligand functional groups; (4) P and Y mobility patterns in paleosols may serve as a proxy to indicate the presence of organic ligands during soil weathering (i.e., "orga-nomarkers") due to enhanced release from rocks reacted with ligands; and (5) Cu release is enhanced substantially by oxic conditions (basalt only), thus Cu could possibly serve to indicate the presence of molecular oxygen (i.e., oxymarker) during paleosol formation from basalts on early Earth. Additional studies are required to document whether similar signatures of element mobility are observed in other systems. Furthermore, investigations on monomineralic systems are needed in order to extrapolate results for systems with complex chemistry.

Numerous previous studies and reviews of the literature have documented enhanced mineral and rock dissolution in the presence of organic acids (e.g., Furrer and Stumm, 1986; Song and Huang, 1988; Chin and Mills, 1991; Bennett and Casey, 1994; Zhang and Bloom, 1999; Welch and Ullman, 2000; Welch et al., 2002; Brantley, 2004; Neaman et al., 2005a,b, in press). The vast majority of this research has focused on metal oxide and silicate dissolution, and significantly less research has focused on trace minerals such as apatite and chalcopyrite, despite the fact that such phases likely control the rate of P and Cu release to solution. Illmer and Schinner (1995) found no significant effect of gluconate (0–5000 μM) on hydroxyapatite or brushite dissolution from pH 4–7. Hydroxyapatite dissolution was found to be inhibited by polyaspartate and polyglutamate, relative to ligand-free experiments, because the polymeric ligands were adsorbed to particle surfaces (Poumier et al., 1999). Inhibition was elimi-nated, however, when free ligands were added to solution resulting in formation of aqueous phase Ca–ligand complexes. Tang et al. (2003) studied impacts of citrate on dissolution of calcium phosphates (i.e., brushite, beta-tricalcium phosphate, octacalcium phos-phate, carbonated apatite, and hydroxyapatite). They found that citrate enhanced beta-tricalcium phosphate dissolution inhibited hydroxyapatite dissolution and had no impact on dissolution of other minerals studied.

However, Arbel et al. (1991) determined that citrate and EDTA-accelerated hydroxyapatite dissolution when present in high concentrations, and Welch et al. (2002) documented increased apatite dissolution from acidic to near-neutral pH when oxalate and acetate were present in solution. These findings are in agreement with other studies that have documented the importance of organic acids produced by microorganisms, fungi, and plant roots for phosphate mineral dissolution (Lipton et al., 1987; Sayer et al., 1997; Rogers et al., 1998; Wallander, 2000; Nakamaru et al., 2000; Reyes et al., 2001; Welch et al., 2002; Adeyemi and Gadd, 2005).

In contrast to apatite dissolution, we have been unable to document any studies that have investigated organic acid effects on chalcopyrite dissolution. Davis et al. (1995) reported that aromatic organic acids enhanced CdS(s) dissolution and aliphatic organic acids had little to no effect.

It should be noted that not all agree on the importance of organic acid weathering in natural systems (e.g., Drever, 1994; Drever and Vance, 1994; Drever and Stillings, 1997). Drever (1994) states that organic acids play a small role in the weathering of primary minerals, except in microenvironments close to plant roots and fungal hyphae where the effect may be larger. However, evidence suggests that LMWOAs play an important pedogenic role, particularly in the podzolization process through chelation and transport of Fe and Al from eluvial to underlying illuvial horizons where Fe and Al

accumulate (DeConinck, 1980; McKeague et al., 1983, 1986; Fox and Comford, 1990; Lundström, 1994; Lundström et al., 1995; Tani and Higashi, 1999). As discussed in Neaman et al. (2005b), organic acids on early Earth were presumably low in concentration and primarily aliphatic in nature. However, organic acid concentrations, aromaticity, and molecular weight likely increased with time and evolution of prokaryotes, fungi, lichens, and vascular plants (Neaman et al., 2005b). Thus, it seems plausible that organic compounds may have left signatures in paleosols indicative of their presence on early Earth, and if such signatures exist, the aromaticity of the organic molecules may also be documented.

In this study, we continue pursuing the possibility of utilizing the elements P, Cu and Y as organomarkers and oxymarkers, by investigating effects of aliphatic and aromatic organic acids on dissolution of apatite and chalcopyrite under oxic and anoxic conditions. Apatite and chalcopyrite were chosen for model system studies because mineralogical analyses of the granite and basalt studied by Neaman et al. (2005a,b, in press) indicated that P was primarily present as fluoroapatite, and Cu was present as Cu/Fe sulfides (presumed to be chalcopyrite). Y in basalt was found to be present, almost solely, within fluoroapatite crystals, and Y in the granite occurred within fluoroapatite and sphene (CaTiSiO$_5$). These interpretations are consistent with other references indicating that fluoroapatite is a common P mineral found in igneous rocks (Kohn et al., 2002) that concentrates rare earth elements and Y (Hall, 1987; Grauch, 1989), and that Cu occurs as sulfides in most igneous rocks (Albarède, 2004). We recognize that the reactivities of apatite and chalcopyrite toward organic acids and dissolved oxygen are likely to be very different. However, we include results on both of these phases in this work because doing so provides data complementary to that of our prior whole rock dissolution studies. Specifically, our objective is to test directly whether apatite and chalcopyrite are responsible for the P, Cu and Y dissolution patterns reported by Neaman et al. (2005a,b, in press).

## 2. Materials and methods

### 2.1. Minerals

Research grade apatite (Durango, Mexico) and chalcopyrite (Messina, Transvaal, R.S.A.) were purchased from Ward's Natural Science (Rochester, NY), Stock Numbers 49 V 5855 and 49 V 5864, respectively.

Minerals were fractured using a zirconia ceramic vial/ball set and ball mill (SPEX Certiprep, Metuchen, NJ) and sieved to obtain 75–150 μm (100–200 mesh) particle size fraction. Fine particles were removed through repeated ultrasonication in Barnstead Nanopure water followed by repeated ultrasonication in HPLC-grade acetone until supernatant solutions were clear, and samples were dried for 12 h at 60 °C. Powder X-ray diffraction (XRD) analyses were conducted on randomly oriented, back-filled 15 mm × 5 mm circular samples mounted in spinning holders to confirm mineral composition. All patterns were collected using a Philips X'pert MPD diffractometer equipped with spinning stage and X'Celerator multiple strip detector using Ni-filtered CuK$_\alpha$ radiation at 50 kV and 40 mA. A continuous scan mode was used to collect $2\theta$ data from 3° to 80° with a step size of approximately 0.017°. The divergent slit was 0.1250°.

Mineral element composition was determined by Activation Laboratories Ltd. (ActLabs, Tucson, AZ) using lithium metaborate/tetraborate fusion followed by aqueous phase analyses using inductively coupled plasma (ICP)–optical emission spectrometry (OES) and ICP–mass spectrometry (MS) for major and trace elements, respectively. Analyses were performed in triplicate (chalcopyrite) or quadruplicate (apatite). Total S content of chalcopyrite was measured in duplicate by ActLabs using gravimetric analysis. A summary of the data, normalized to 100% volatile free mass, is provided in Table 1, and these data were used to calculate chemical formulae of Ca$_5$(PO$_4$)$_{2.82}$(F,Cl,OH)$_{1.54}$ and CuFeS$_2$ for apatite and chalcopyrite, respectively.

Table 1
Mean elemental composition of apatite and chalcopyrite

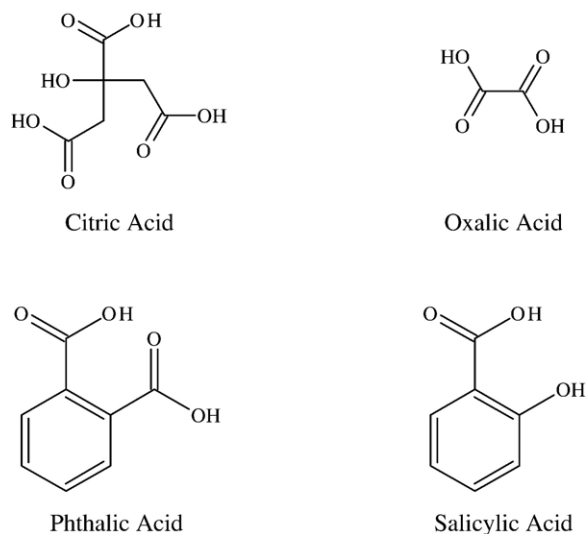| Element | Apatite | | Chalcopyrite | |
|---|---|---|---|---|
| | Mean (%) | 95% CI[a] | Mean (%) | 95% CI |
| Si | 0.32 | 0.03 | 1.67 | 0.08 |
| Al | 0.03 | 0.01 | 0.39 | 0.02 |
| Fe | 0.05 | 0.02 | 28.29 | 0.37 |
| Mn | 0.01 | 0.00 | 0.04 | 0.03 |
| Mg | 0.01 | 0.01 | 0.05 | 0.01 |
| Ca | 39.52 | 0.09 | 0.16 | 0.01 |
| Na | 0.17 | 0.03 | 0.04 | 0.00 |
| K | 0.01 | 0.01 | 0.04 | 0.01 |
| Ti | <0.01 | – | 0.03 | 0.00 |
| P | 17.20 | 0.30 | <0.01 | – |
| Cu | <0.01 | – | 32.65 | 0.29 |
| S | – | – | 32.04 | 0.67 |
| | Mean (mg kg$^{-1}$) | 95% CI | Mean (mg kg$^{-1}$) | 95% CI |
| Y | 1027.50 | 4.90 | 1.80 | 0.88 |

[a] 95% confidence interval.

Fig. 1. Kekulé structures of aliphatic and aromatic organic acids used in dissolution experiments.

## 2.2. Organic acids

Mineral dissolution was investigated in the absence and presence of aliphatic (citrate and oxalate) and aromatic (phthalate and salicylate) organic acids. Neaman et al. (2005b, in press) noted that these organic acids significantly enhance basalt and granite dissolution during batch reactions. Although Neaman et al. observed that the aromatic organic acid gallate enhanced

dissolution to a greater extent than the aromatic compounds used in this study, gallate was found to be incompatible with the alkali metal ($Li^+$) chosen to serve as a background electrolyte in the present work. Kekulé structures of the organic acids studied are represented in Fig. 1, and acid dissociation constants ($I=0$ M and 298 K) for the compounds are shown in Fig. 2.

### 2.3. Oxic and anoxic dissolution experiments

Dissolution experiments were conducted under oxic and anoxic conditions using acid-washed, 50-mL Teflon centrifuge tubes as batch reactors. A mineral mass of 0.3 g was added to each tube and the precise mass added was measured to 0.0001 mg. Reaction vessels with and without mineral (mineral-free controls) were autoclaved to prevent microbial growth. Organic acid stock solutions were prepared 24 h prior to each experiment by dissolving individual organic acids (Fluka and Sigma, ≥99% purity) in amber glass jars containing 0.01 M LiCl (Sigma, 99.99+% purity), and adding 0.01 M HCl (EM Science, Omni*Trace* Ultrapure) or 0.1 M LiOH (Sigma, ≥99% purity) as needed to achieve pH 5. An ionic strength of 0.01 M and pH 5 were chosen because they are representative of natural soil solution conditions (Harter and Naidu, 2001). Amber glass jars and LiCl solutions were autoclaved prior to use, and Al foil was wrapped around amber jars containing organic acid solutions to prevent photodegradation. Organic
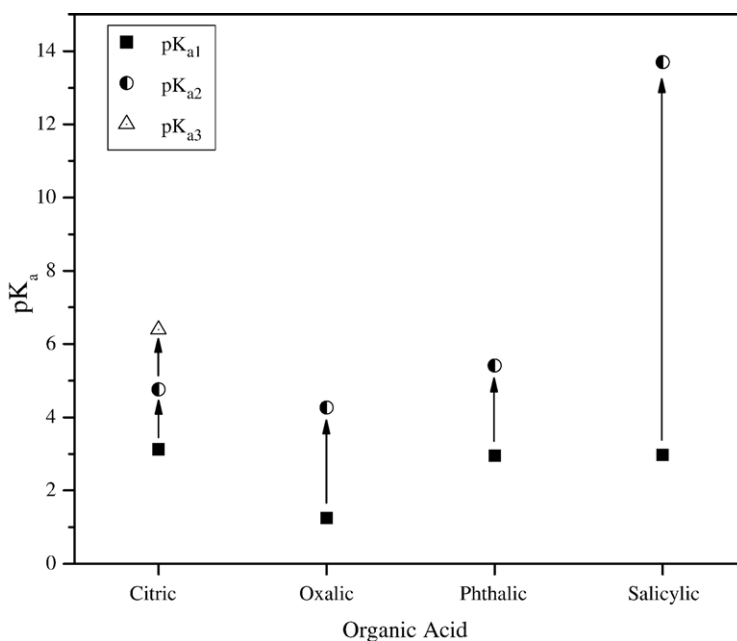


Fig. 2. Acid dissociation constants ($pK_a$) of the organic acids used in dissolution experiments (Martell and Smith, 2003).

acid stock solutions were filter-sterilized (Corning, sterilized 0.2 μm polyethersulfone filtration units) within a sterile laminar flow-hood immediately prior to the start of an experiment. Dissolution experiments were initiated by adding to reaction vessels appropriate quantities of organic acid stock solutions and/or 0.01 M LiCl to achieve initial organic acid concentrations of 0, 1, 5, and 10 mM at pH 5 and a solid-to-solution ratio of 1:100 (0.3 g per 30 mL). Solutions were added via pipette using sterilized pipette tips. Mineral-free blanks were prepared concurrently, and all experiments were conducted in triplicate. Reaction vessels were wrapped in Al foil and reacted on end-over-end shakers (8 rpm) at $23 \pm 2$ °C for 28 days. At the end of the reaction period, samples were centrifuged at 26,000 rcf for 15 min and supernatant solutions were removed by pipette. Mineral pellets were washed twice in ethanol and once in water prior to freeze-drying. A Barnstead NANOpure ultrafiltration/ultraviolet water unit served as the water source throughout the experiments.

As noted previously, experiments were conducted in the presence and absence of $O_2$. Although experiments followed the general protocol outlined above, there were some differences between the two types of experiments. In the case of oxic experiments, reaction vessels were exposed to ambient atmosphere (within a sterile laminar flow-hood) three times a week to maintain equilibrium with atmospheric $O_2$ (g). For anoxic experiments, autoclaved reaction vessels and 0.01 M LiCl solution (purged 30 min with filter sterilized $N_2$ (g)) were placed in a Coy oxygen-free ($<1$ ppm) anaerobic chamber 1 week prior to starting an experiment. Preliminary trials indicated that 1 week was sufficient time for oxygen to diffuse from vessels and solutions into the chamber's atmosphere where it is removed by reaction with a palladium catalyst. Organic acid stock solutions were prepared outside the anaerobic chamber using deoxygenated 0.01 M LiCl, followed by a 30-min purge with $N_2$ (g). Stock solutions (loosely capped) were placed on a stir plate within the anaerobic chamber and allowed to mix for 24 h prior to filter sterilization. All solution additions to reaction vessels were conducted within the anaerobic chamber, and centrifuged samples were opened only after reintroduction to the oxygen-free atmosphere.

### 2.4. Aqueous phase analyses

After centrifugation, supernatant solutions were partitioned into four separate vials for aqueous phase analyses. Aliquots used for elemental analysis by induc-

tively coupled plasma–mass spectrometry (ICP-MS) were added to acid-washed polypropylene tubes, acidified to pH $<2$ with 6N HCl (Omni*Trace* Ultrapure), and stored at 4 °C. Aqueous phase concentrations of different elements were determined by a Perkin-Elmer Elan DRC II ICP-MS with attached dynamic reaction cell (DRC). Precautions were taken to investigate multiple isotopes to ensure that polyatomic interferences did not compromise measured concentrations. Concentration measurements for Ca, Co, Cr, and K were performed using DRC mode to eliminate interferences for these elements. Non-acidified samples analyzed by ion chromatography (IC; Dionex DX-600) for organic acids, sulfate, fluoride, and phosphate were stored in 4-mL glass amber vials and wrapped in aluminum foil, and samples were analyzed within 48 h. Measurement of pH (Orion, Ross semi-micro combination electrode), Eh (Orion, Redox/ORP combination electrode), and dissolved oxygen (DO; VWR Model 4000) was conducted immediately following the end of the experiment using samples stored in 40-mL glass amber vials. Sulfide was measured using an Orion, Ag/S combination electrode by adding an aliquot of solution samples to vials containing an equivalent volume of sulfide anti-oxidant buffer. Anoxic samples used for ICP-MS analyses were acidified in the anaerobic chamber prior to removal and storage at 4 °C, and all other anoxic samples were stored and analyzed (except IC analysis) within the chamber.

### 2.5. Speciation and dissolution modeling

Calculations were performed using MINTEQA2 for Windows, Version 1.50 (Allison Geoscience Consultants and HydroGeoLogic, 2003) to speciate aqueous phase ions and predict mineral saturation indices ($\Omega$). Systems were modeled using final measured element and organic acid concentrations, pH, and Eh. Speciation calculations were executed by disallowing secondary phase mineral precipitation, and $CO_2(g) = 3.8 \times 10^{-4}$ atm (Keeling et al., 2005) was added as an additional parameter to all model runs. Due to the time required for $CO_2(g)$ concentration in the anaerobic chamber to achieve equilibrium with the ambient atmosphere and periodic purging of the chamber with $N_2(g)$ and $H_2(g)$, the $CO_2(g)$ concentration in the anaerobic system may have been slightly lower than $3.8 \times 10^{-4}$ atm. However, differences in speciation calculations for models including or excluding $CO_2(g)$ were negligible. The MINTEQA2 stability constant database was supplemented, as necessary, by adding stability constants ($I = 0$ M and 25 °C) obtained from the NIST Standard Reference Database 46 Version 7.0 (Martell and Smith,
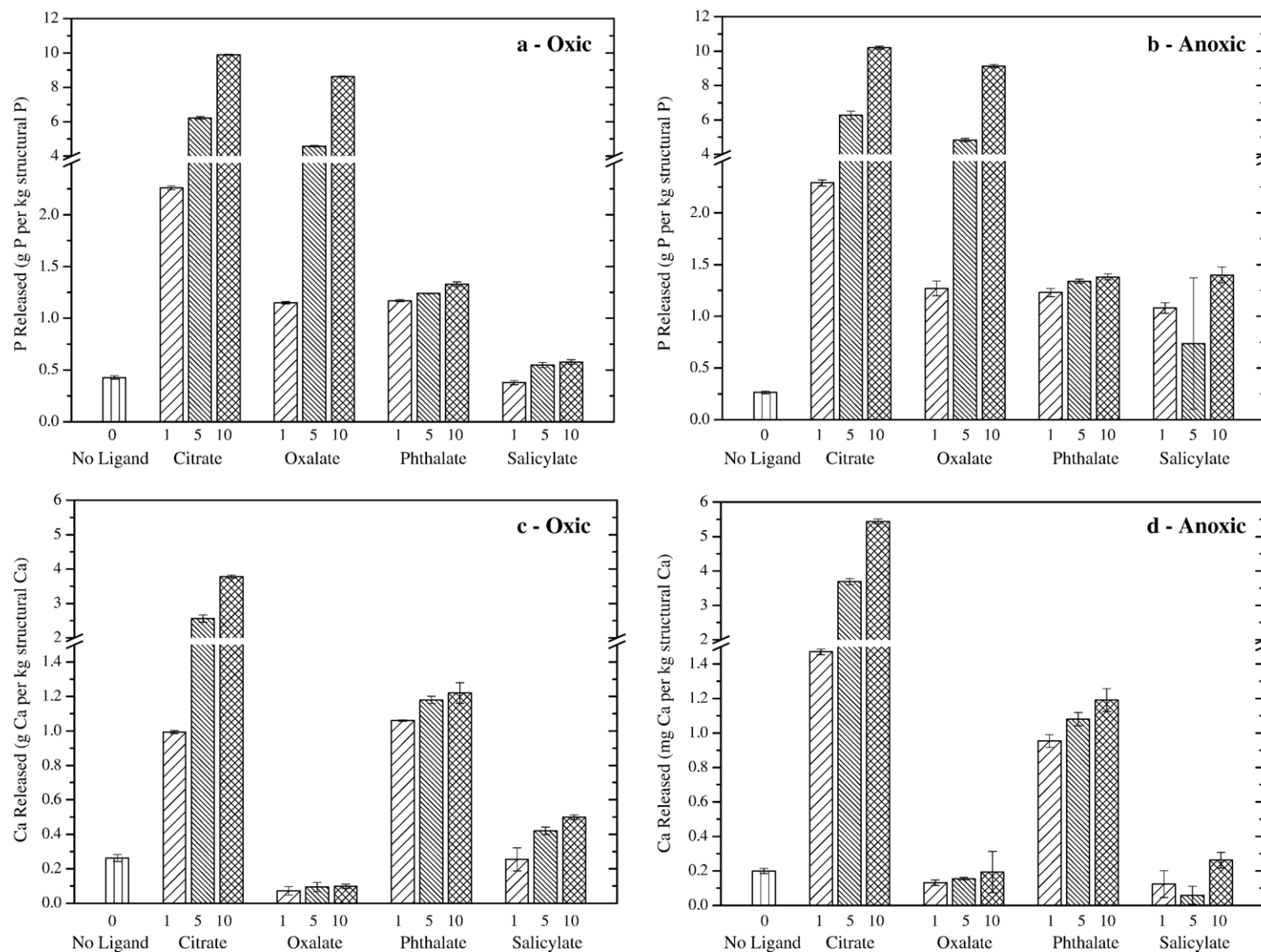
Fig. 3. Effect of organic acids and organic acid concentration (0, 1, 5, 10 mM) on apatite dissolution. Phosphorus released under (a) oxic conditions and (b) anoxic conditions. Calcium released under (c) oxic conditions and (d) anoxic conditions. The release of each element from apatite is expressed as milligrams of element released per kilogram of total elemental content in unweathered mineral. Error bars, where observed, represent the 95% confidence interval from triplicate aqueous phase sample analyses.

Table 2
Mean blank corrected concentrations of Ca, P, and Y released from apatite reacted with organic acids under oxic and anoxic conditions

| Oxygen status | Organic acid | Ca ($\mu$M) | | | | P ($\mu$M) | | | | Y (nM) | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | | Organic acid concentration (mM) | | | | | | | | | | | |
| | | 0 | 1 | 5 | 10 | 0 | 1 | 5 | 10 | 0 | 1 | 5 | 10 |
| Oxic | No ligand | 27.2 | | | | 23.9 | | | | 1.44 | | | |
| | Citrate | | 99.9 | 254 | 377 | | 126 | 347 | 552 | | 260 | 746 | 1150 |
| | Oxalate | | 8.67 | 11.4 | 14.0 | | 63.9 | 255 | 480 | | 5.94 | 21.7 | 31.1 |
| | Phthalate | | 107 | 119 | 125 | | 65.2 | 69.0 | 73.7 | | 3.18 | 21.9 | 46.8 |
| | Salicylate | | 32.7 | 43.3 | 54.8 | | 21.0 | 30.4 | 32.0 | | 0.68 | 0.42 | 0.53 |
| Anoxic | No ligand | 19.6 | | | | 14.5 | | | | 0.61 | | | |
| | Citrate | | 144 | 364 | 531 | | 125 | 348 | 561 | | 275 | 744 | 1150 |
| | Oxalate | | 13.3 | 15.9 | 20.3 | | 70.5 | 268 | 507 | | 10.1 | 30.3 | 57.8 |
| | Phthalate | | 94.9 | 108 | 119 | | 68.6 | 74.6 | 76.7 | | 3.55 | 17.3 | 38.0 |
| | Salicylate | | 12.3 | 8.02 | 26.1 | | 19.6 | 18.4 | 25.4 | | 0.36 | 1.16 | 1.88 |

2003) and the literature (Santana-Casiano et al., 2004). Based on recent study by Matocha et al. (2005) demonstrating the potential for $Fe^{2+}$ to reduce $Cu^{2+}$ anoxic solutions, speciation modeling of anoxic chalcopyrite solutions was performed by allowing and disallowing Cu reduction. Results from both simulations are presented.

## 2.6. Infrared spectroscopy

After centrifugation and removal of supernatant solution, mineral pellets were washed twice with ethanol and once with Barnstead NANOpure water. Pellets were stored in a $-20$ °C freezer and freeze-dried prior to infrared analysis. Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy was employed to investigate formation of secondary mineral phases. Spectra of minerals were obtained using a neat technique (no KBr) by averaging 400 scans at 4 $cm^{-1}$ resolution collected with a Nicolet Magna 560 spectrometer.

## 3. Results and discussion

### 3.1. Apatite dissolution

Effects on apatite dissolution of LMWOA type and concentrations, and a general lack of dissolved $O_2(g)$ effect are evident in Fig. 3a–d and Table 2. Due to the fact that Ca and P do not undergo oxidation–reduction reactions, it was anticipated that differences in dissolved $O_2(g)$ would have negligible impact on apatite dissolution. These data do, however, indicate that the experiments conducted are highly reproducible because oxic and anoxic experiments were conducted at different times using freshly prepared organic acid stock solutions.

Phosphorus release is highest when apatite is reacted with aliphatic citrate and oxalate and the release is observed to be lower with aromatic LMWOAs (Fig. 3a and b). It is also observed that P release in the presence of salicylate was approximately equivalent to the ligand-free case under oxic conditions. Increasing concentrations of citrate and oxalate enhance P and increasing concentrations of citrate enhance Ca release to a greater extent than increasing concentrations of phthalate and salicylate. Solution phase concentrations of Ca are low in the case of oxalate, despite high P release (Fig. 3c and d), suggesting formation of Ca-oxalate precipitates during the experiments. Geochemical modeling shows oversaturation or near-saturation for two Ca-oxalate precipitates (Table 3). These results are in agreement with final solution phase oxalate concentrations that showed a 10–14% decrease relative to control samples. Others have also observed Ca-oxalate precipitate formation during mineral dissolution experiments (Welch et al., 2002; Adeyemi and Gadd, 2005; Neaman et al., 2005b), resulting in decreased aqueous phase Ca concentrations. Solutions from all apatite

Table 3
Saturation indices ($\Omega$) for Ca-oxalate precipitates at the end of oxalic acid experiments

| Oxygen status | Precipitate | Saturation index ($\Omega$) | | |
| --- | --- | --- | --- | --- |
| | | Ligand concentration (mM) | | |
| | | 1 | 5 | 10 |
| Oxic | Ca(oxalate)·(3H$_2$O) | $-0.45$ | 0.00 | 0.15 |
| | Ca(oxalate)·(H$_2$O) | $-0.02$ | 0.43 | 0.58 |
| Anoxic | Ca(oxalate)·(3H$_2$O) | $-0.20$ | 0.15 | $-0.69$ |
| | Ca(oxalate)·(H$_2$O) | 0.23 | 0.58 | $-0.26$ |

Table 4
Ratio of Ca/P in solution at the end of apatite dissolution experiments normalized to Ca/P ratio in parent mineral

| Oxygen status | Ligand | Ca/P [a] | | | |
|---|---|---|---|---|---|
| | | Ligand concentration (mM) | | | |
| | | 0 | 1 | 5 | 10 |
| Oxic | No ligand | 0.61 | | | |
| | Citrate | | 0.44 | 0.41 | 0.38 |
| | Oxalate | | 0.05 | 0.02 | 0.01 |
| | Phthalate | | 0.90 | 0.95 | 0.92 |
| | Salicylate | | 0.67 | 0.76 | 0.72 |
| Anoxic | No ligand | 0.76 | | | |
| | Citrate | | 0.64 | 0.59 | 0.53 |
| | Oxalate | | 0.10 | 0.03 | 0.021 |
| | Phthalate | | 0.77 | 0.80 | 0.86 |
| | Salicylate | | 0.35 | 0.15 | 0.40 |

[a] Mineral normalized Ca/P ratio=1 represents stoichiometric dissolution.

experiments remained undersaturated ($\Omega=-3.5$ to $-18.5$) with respect to hydroxylapatite (log $K_{sp}=-44.33$; Allison Geoscience Consultants and Hydro-GeoLogic, 2003).

Ca and P release from apatite was nonstoichiometric for all experiments (Table 4), as evidenced by mineral-normalized molar Ca/P release ratios, $(Ca/P)_n$, less than 1. Ratios for oxalate are much lower than for other ligands investigated, presumably due to formation of Ca-oxalate precipitates. Welch et al. (2002) observed similar results for oxalate in apatite dissolution experiments. However, in contrast to our data, Welch et al. (2002) observed $(Ca/P)_n>1$ when acetate or no ligand was present in solution. The mechanism of non-stoichiometric dissolution is not readily determined from the data collected. However, it may be due to

precipitation of Ca-containing solids (Welch et al., 2002), slower kinetics of Ca–ligand release from the mineral surface (relative to ligand exchange with phosphate; Stumm, 1997), or re-adsorption of Ca to the mineral surface (Wu et al., 1991; Nagy, 1995). The first two explanations, although plausible, do not seem to agree well with our results. Speciation results indicated that only oxalate systems achieved saturation with respect to secondary precipitates (Ca-oxalate), and we also observe $(Ca/P)_n<1$ for apatite in absence of LMWOAs. Therefore, the most likely mechanism causing non-stoichiometric apatite dissolution, in experiments other than those containing oxalate, is Ca re-adsorption to the mineral surface. Wu et al. (1991) characterized apatite surface charge properties and reported a point of zero net proton charge (pznpc) of 8.15. Based on surface charge distribution diagrams presented by Wu et al. (1991), we estimate that 15% of the $\equiv P-OH$ surface functional groups will be dissociated ($\equiv P-O^-$) at pH 6. We hypothesize that Ca is adsorbing to $\equiv P-O^-$ or displacing protons from $\equiv P-OH$ apatite surface functional groups resulting in decreased aqueous phase Ca concentrations.

As noted by Drever (1994), distinguishing between ligand and pH effects is complicated in studies where pH is not held constant by buffering agents. We intentionally did not use pH buffers in our experiments to minimize sorption artifacts and element contamination. Such additions could result in high element background levels resulting in large errors or masking differences after blank correction. Although all experiments were initiated at pH 5, pH values over the 28-day reaction period did change (Table 5). The data show that pH values for ligand-free, oxalate, and salicylate are relatively comparable (pH 6.5–7.5), and

Table 5
Mean pH, Eh, and dissolved oxygen (DO) measured at end of apatite dissolution experiments

| Oxygen status | Ligand | pH | | | | Eh (mV) | | | | DO (mg L$^{-1}$) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Ligand concentration (mM) | | | | | | | | | | | |
| | | 0 | 1 | 5 | 10 | 0 | 1 | 5 | 10 | 0 | 1 | 5 | 10 |
| Oxic | No ligand | 6.84 | | | | 537 | | | | 3.29 | | | |
| | Citrate | | 5.46 | 5.25 | 5.18 | | 552 | 538 | 528 | | 3.84 | 3.76 | 3.74 |
| | Oxalate | | 6.72 | 6.67 | 6.61 | | 471 | 459 | 455 | | 3.76 | 3.88 | 4.03 |
| | Phthalate | | 5.31 | 5.07 | 4.98 | | 589 | 577 | 567 | | 3.83 | 3.67 | 3.73 |
| | Salicylate | | 6.80 | 6.69 | 6.42 | | 578 | 554 | 544 | | 4.11 | 4.19 | 4.12 |
| Anoxic | No ligand | 7.34 | | | | −355 | | | | 0.00 | | | |
| | Citrate | | 5.45 | 5.25 | 5.18 | | −269 | −258 | −254 | | 0.00 | 0.00 | 0.00 |
| | Oxalate | | 6.89 | 6.78 | 6.64 | | −359 | −351 | −343 | | 0.00 | 0.00 | 0.00 |
| | Phthalate | | 5.28 | 5.06 | 5.01 | | −264 | −250 | −247 | | 0.00 | 0.00 | 0.00 |
| | Salicylate | | 7.24 | 6.91 | 6.67 | | −359 | −352 | −341 | | 0.00 | 0.00 | 0.00 |
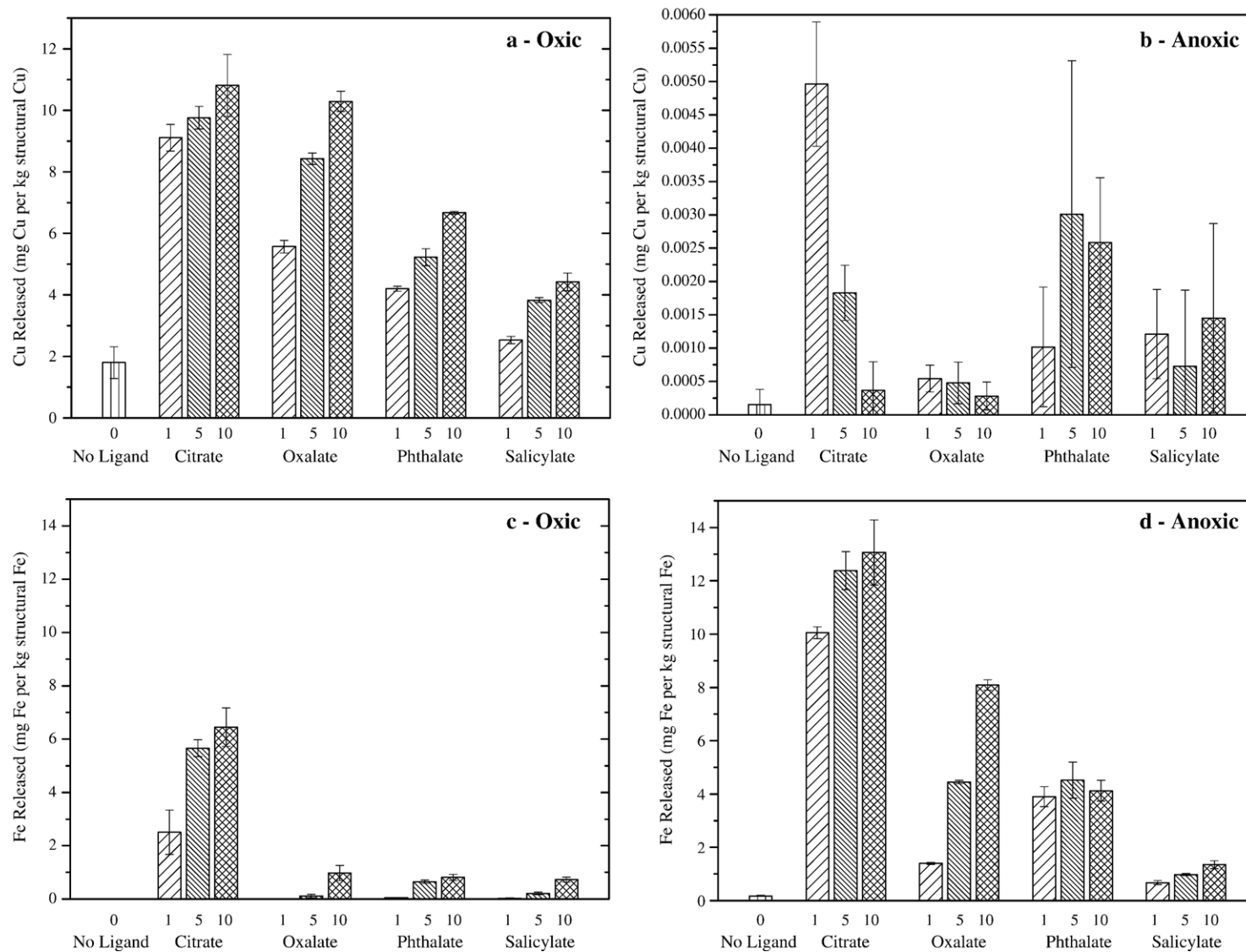
Fig. 4. Effect of organic acids and organic acid concentration (0, 1, 5, 10 mM) on chalcopyrite dissolution. Copper released under (a) oxic conditions and (b) anoxic conditions. Iron released under (c) oxic conditions and (d) anoxic conditions. The release of each element from chalcopyrite is expressed as milligrams of element released per kilogram of total elemental content in unweathered mineral. Please note the difference in ordinate scale for copper graphs (c and d). Error bars, where observed, represent the 95% confidence interval from triplicate aqueous phase sample analyses.

Welch et al. (2002) and Guidry and Mackenzie (2003) demonstrated that the rate of apatite dissolution is invariant above pH 5.5. Thus, these data demonstrate that oxalate accelerates apatite dissolution. Citrate and phthalate system pH values were also similar signifying the enhanced ability of citrate to promote dissolution relative to phthalate. We attribute greater dissolution in the presence of aliphatic relative to aromatic acids to the higher $pK_{a2}$ values for the aromatic acids (Fig. 2; Neaman et al., 2005b, in press). The weaker acidity of the phthalate and salicylate likely diminishes the extent of surface cation complexation at the experimental pH (Furrer and Stumm, 1986).

### 3.2. Chalcopyrite dissolution

Data for the release of Cu and Fe from chalcopyrite (Fig. 4a–d; Table 6) demonstrate that dissolution of this mineral is impacted by both the presence of dissolved $O_2(g)$ and LMWOAs. Copper release (Fig. 4a and b) is four to five orders of magnitude greater under oxic conditions relative to anoxic conditions. This is attributable to sulfide oxidation that diminishes the relative saturation of solution with respect to CuS phases (Lindsay, 1979; Yin et al., 1995; Todd et al., 2003; Abraitis et al., 2004; Neaman et al., 2005a,b). The effects of LMWOAs and their concentrations on Cu release under oxic conditions are evident in Fig. 4a. It is apparent that (1) Cu release is greater in the presence of LMWOAs compared to ligand-free samples; (2) aliphatic organic acids are more effective agents than aromatic organic acids for chalcopyrite dissolution; and (3) $CuFeS_2(s)$ dissolution is positively correlated with LMWOA concentration. The same

trends are not apparent for anoxic conditions (Fig. 4b), where very low aqueous phase concentrations of Cu were measured.

Our results are in contrast to Davis et al. (1995) and Neaman et al. (2005b) who reported that aromatic ligands release metals from sulfide minerals to a greater extent than aliphatic ligands under oxic conditions. In their study of Cd release from CdS(s), Davis et al. (1995) observed little effect of citrate and oxalate on Cd release but phthalate and salicylate released significantly more metal than ligand-free solutions at pH values similar to those of this study. Neaman et al. (2005b) reported that aromatic gallate enhanced Cu release to a greater extent than aliphatic citrate and malonate, and they postulated that salicylate would have a similar effect as gallate. However, experimental data were not available to support this hypothesis.

Saturation indices ($\Omega$) were calculated for oxic and anoxic chalcopyrite experiments using MINTEQA2. Sulfate minerals are not predicted to precipitate from oxic solutions. The data indicate that all oxic solutions are oversaturated with respect to cupric ferrite ($Cu^{2+}$ ($Fe^{3+}$)$_2O_4$) and in specific cases, the model predicts potential formation of tenorite ($Cu^{2+}O$) and atacamite (($Cu^{2+}$)$_2Cl(OH)_3$). In the case of anoxic experiments, the model disallowing $Cu^{2+}$ reduction predicts that solutions achieve oversaturation for covellite ($Cu^{2+}S$) and chalcopyrite. The model permitting copper reduction also indicates that solutions are oversaturated with respect to several $Cu^+$, $Cu^{2+}$, and mixed Fe–Cu minerals. The exact cause of chalcopyrite oversaturation is not clear. It may be attributed to erroneously low thermodynamic constants for chalcopyrite dissolution ($K_{sp}=-35.27$) and metal–ligand complexes in the

Table 6
Mean blank corrected concentrations of Fe, Cu, and Y released from chalcopyrite reacted with organic acids under oxic and anoxic conditions

| Oxygen status | Organic acid | Fe (µM) | | | | Cu (µM) | | | | Y (nM) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Organic acid concentration (mM) | | | | | | | | | | | |
| | | 0 | 1 | 5 | 10 | 0 | 1 | 5 | 10 | 0 | 1 | 5 | 10 |
| Oxic | No ligand | 2.62 | | | | 93.1 | | | | 2.23 | | | |
| | Citrate | | 131 | 289 | 331 | | 477 | 504 | 560 | | 10.0 | 21.6 | 22.2 |
| | Oxalate | | 0.92 | 6.49 | 50.4 | | 286 | 433 | 529 | | 0.58 | 3.71 | 7.95 |
| | Phthalate | | 2.76 | 32.8 | 41.2 | | 216 | 269 | 343 | | 2.66 | 4.61 | 5.86 |
| | Salicylate | | 2.39 | 11.8 | 37.7 | | 130 | 197 | 227 | | 1.47 | 1.28 | 2.75 |
| Anoxic | No ligand | 10.5 | | | | 0.0172 | | | | 0.12 | | | |
| | Citrate | | 504 | 617 | 651 | | 0.26 | 0.09 | 0.02 | | 31.7 | 40.8 | 44.7 |
| | Oxalate | | 71.8 | 226 | 411 | | 0.05 | 0.16 | 0.21 | | 10.4 | 16.7 | 31.3 |
| | Phthalate | | 197 | 229 | 209 | | 0.06 | 0.16 | 0.14 | | 5.85 | 11.0 | 11.0 |
| | Salicylate | | 35.7 | 51.7 | 70.6 | | 0.07 | 0.07 | 0.14 | | 0.51 | 0.31 | 0.78 |
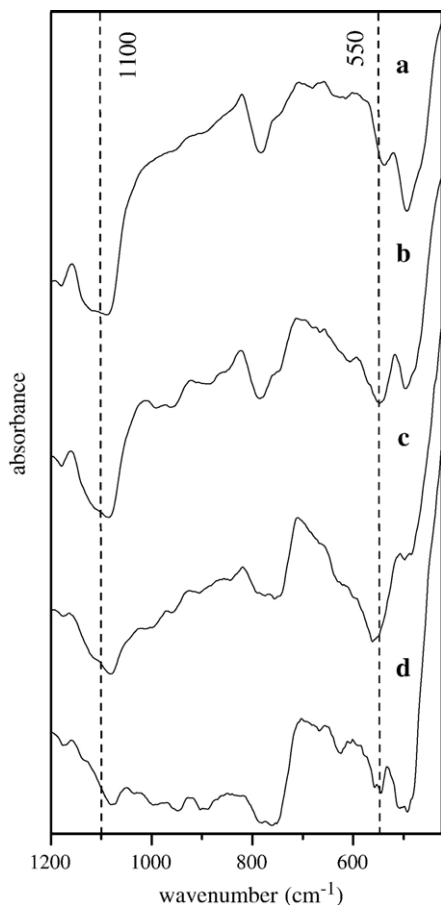
Fig. 5. Diffuse reflectance infrared Fourier transform (DRIFT) spectra of chalcopyrite reacted with (a) 10 mM citric acid, (b) 1 mM citric acid, and (c) 0.01 M LiCl (ligand-free) under anoxic conditions. Spectrum (d) is unreacted chalcopyrite.

model database, mineral impurities that are more soluble than chalcopyrite, or a combination of these factors.

Precipitation of covellite during anoxic experiments may explain non-stoichiometric chalcopyrite dissolution and the very low Cu concentrations observed (Habashi, 1978). Matocha et al. (2005) observed formation of atacamite under anoxic conditions upon reaction of $Cu^{2+}$ and $Fe^{2+}$ in solutions containing $Cl^-$ and $H^+$ concentrations similar to our experiments. However, S was not present in their experimental system and our model results do not indicate that anoxic solutions in this study are oversaturated with respect to atacamite. DRIFT spectra (Fig. 5) show the formation of secondary phase minerals when chalcopyrite is reacted in solution under anoxic conditions. Although we cannot conclusively determine the mineral phases formed,

significant changes in spectra of reacted minerals occurring between 1100–550 $cm^{-1}$ are attributed to formation of Cu and Fe precipitates (Liese, 1975; Schwertmann and Cornell, 2000; Martens et al., 2003; Matocha et al., 2005).

Based on Fig. 4c and d, Fe release from chalcopyrite is apparently higher in absence of molecular oxygen. This is attributed to the formation of Fe(III) (hydr) oxides in oxic solutions that effectively reduce aqueous Fe concentrations (Stumm and Morgann, 1996). We noted the presence of Fe oxides (visual observation of reddish-brown coatings on minerals and walls of reaction vessels) in batch reactors at the end of chalcopyrite experiments. This is in agreement with model predictions indicating that solutions were over-saturated with respect to several Fe(III) minerals and DRIFT spectra of reacted minerals showing formation of new peaks that may be attributed to Fe (hydr)oxides (data not shown).

Todd et al. (2003) investigated surface oxidation of chalcopyrite at ambient atmospheric conditions in aqueous solutions (pH 2–10) using X-ray adsorption (XAS) and emission (XES) spectroscopy, and determined that, at slightly acidic to near neutral pH, oxidation reactions result in formation of a Cu-depleted, Fe-rich surface coating. They attribute this to Cu leaching from the surface and formation of $Fe_2O_3$ at the surface. Fe released during anoxic experiments (Fig. 4d) demonstrates that organic acids enhance mineral dissolution. When chalcopyrite was reacted with organic acids, citrate induced the greatest Fe release, while salicylate was least effective. The removal of Fe by phthalate does not appear to be influenced by concentration of ligand in solution. At lower organic acid concentrations (i.e., 1 and 5 mM), phthalate is equally or more effective than oxalate for inducing Fe release.

Overall, Cu release under oxic conditions and Fe release in absence of oxygen correlate well with cation–ligand stability constants (Figs. 6 and 7, respectively), although salicylate is an exception. We hypothesize that the poor correlation between metal release and the $M^{z+}$–salicylate stability constant is attributed to the very high $pK_{a2}$ (13.7) of salicylic acid (Fig. 2), reducing the ability of this ligand to complex with metals at the study pH. We tested this hypothesis by performing simulations investigating total aqueous $Fe^{2+}$–ligand complex concentrations in solutions containing equal concentrations of $Fe^{2+}$ and ligand at experimental pH values. The model results suggest that total $Fe^{2+}$–ligand complex concentrations should follow the order: $Fe^{2+}H_x(citrate)_y > Fe^{2+}H_x$
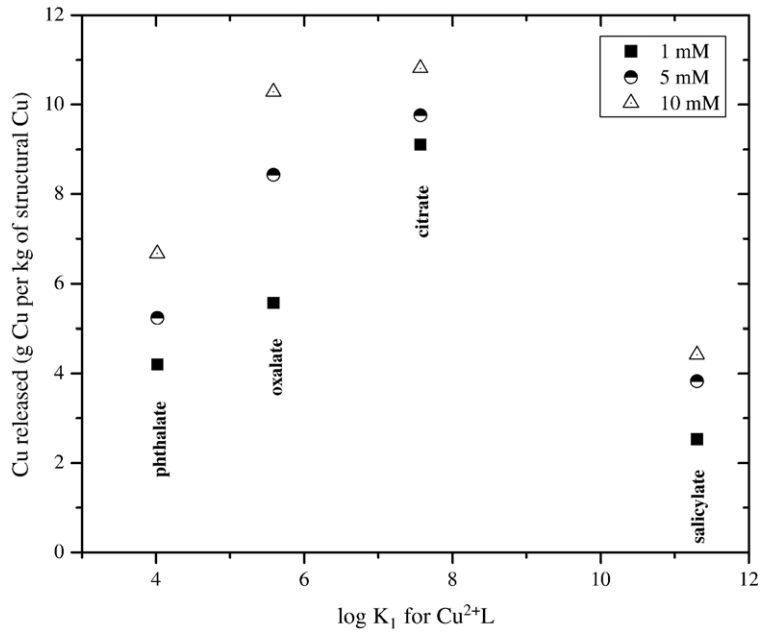
Fig. 6. Release of Cu from chalcopyrite during oxic experiments (1, 5, and 10 mM ligand concentrations) in relation to $Cu^{2+}$–ligand stability complex ($K_1 = [ML]/[M][L]$, where $[ML]$, $[M]$, and $[L]$ are concentrations of metal–ligand complex, free metal ion, and free ligand, respectively).

$(oxalate)_y > Fe^{2+}H_x(phthalate)_y > Fe^{2+}H_x(salicylate)_y$. The same trend is observed in our experimental results for Fe release from chalcopyrite (Figs. 4d and 7). Thus, the simulations support our hypothesis.

As with apatite experiments, protons were consumed during the course of oxic and anoxic chalcopyrite dissolution resulting in an increase in solution pH relative to the initial condition of pH 5 (Table 7).
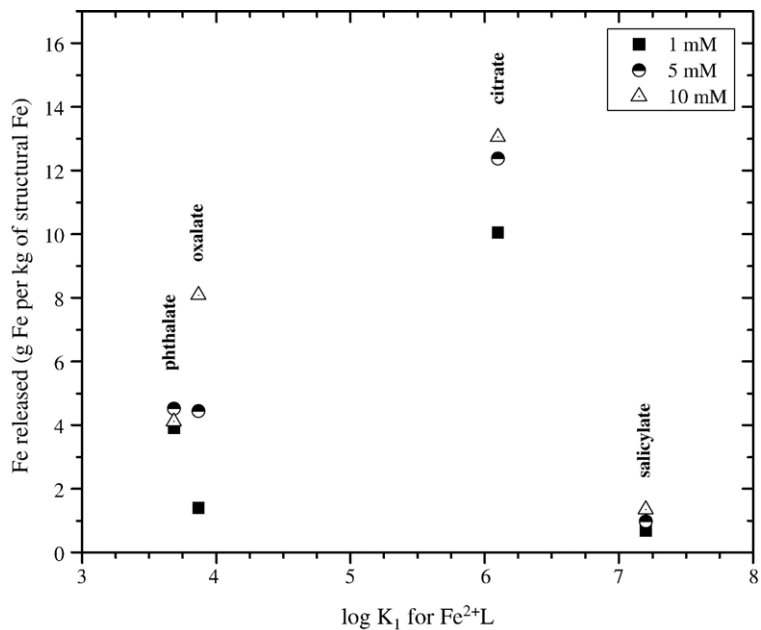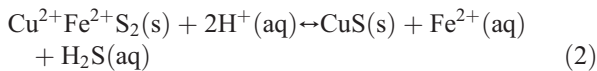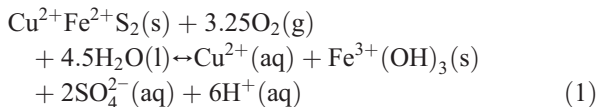


Fig. 7. Release of Fe from chalcopyrite during anoxic experiments (1, 5, and 10 mM ligand concentrations) in relation to $Fe^{2+}$–ligand stability complex ($K_1 = [ML]/[M][L]$, where $[ML]$, $[M]$, and $[L]$ are concentrations of metal–ligand complex, free metal ion, and free ligand, respectively).

Table 7
Mean pH, Eh, and dissolved oxygen (DO) measured at end of chalcopyrite dissolution experiments

| Oxygen status | Organic acid | pH | | | | Eh (mV) | | | | DO (mg L$^{-1}$) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Organic acid concentration (mM) | | | | | | | | | | | |
| | | 0 | 1 | 5 | 10 | 0 | 1 | 5 | 10 | 0 | 1 | 5 | 10 |
| Oxic | No ligand | 6.13 | | | | 581 | | | | 2.64 | | | |
| | Citrate | | 5.58 | 5.34 | 5.20 | | 540 | 532 | 532 | | 3.84 | 3.74 | 3.87 |
| | Oxalate | | 7.01 | 7.21 | 7.17 | | 488 | 444 | 431 | | 3.88 | 3.85 | 3.94 |
| | Phthalate | | 5.63 | 5.15 | 5.05 | | 540 | 485 | 474 | | 3.47 | 4.15 | 3.35 |
| | Salicylate | | 6.45 | 6.69 | 6.69 | | 560 | 539 | 528 | | 3.75 | 3.61 | 3.75 |
| Anoxic | No ligand | 7.22 | | | | −350 | | | | 0.00 | | | |
| | Citrate | | 6.58 | 5.38 | 5.24 | | −330 | −193 | −165 | | 0.00 | 0.00 | 0.00 |
| | Oxalate | | 6.92 | 6.87 | 6.87 | | −353 | −339 | −320 | | 0.00 | 0.00 | 0.00 |
| | Phthalate | | 5.77 | 5.15 | 5.05 | | −291 | −255 | −249 | | 0.00 | 0.00 | 0.00 |
| | Salicylate | | 6.64 | 6.47 | 6.22 | | −339 | −334 | −331 | | 0.00 | 0.00 | 0.00 |

Considering the expected composite dissolution reactions occurring under anoxic conditions,

$$Cu^{2+}Fe^{2+}S_2(s) + 3.25O_2(g)$$
$$+ 4.5H_2O(l) \leftrightarrow Cu^{2+}(aq) + Fe^{3+}(OH)_3(s)$$
$$+ 2SO_4^{2-}(aq) + 6H^+(aq) \qquad (1)$$

$$Cu^{2+}Fe^{2+}S_2(s) + 2H^+(aq) \leftrightarrow CuS(s) + Fe^{2+}(aq)$$
$$+ H_2S(aq) \qquad (2)$$

for chalcopyrite dissolution under oxic Eq. (1) and anoxic Eq. (2) conditions, respectively, we expect that dissolution will increase with pH under oxic conditions, but decrease with pH under anoxic conditions. Cu oxic dissolution data (Fig. 4a) demonstrate that citrate and phthalate released more Cu than ligand-free samples, despite having lower pH values (Table 7). In other words, although citrate and phthalate samples experience pH conditions less conducive for chalcopyrite dissolution (Eq. (1)), the presence of ligands enhanced mineral dissolution to a greater extent than ligand-free samples having higher pH values. It is difficult to differentiate pH and ligand effects for anoxic Fe data (Fig. 4d). However, we observe that Fe release is higher for oxalate relative to ligand-free samples and the pH difference between the two experiments is small (0.35 pH units; Table 7).

## 3.3. Yttrium release

Yttrium release from apatite and chalcopyrite reacted under oxic and anoxic conditions is shown in Fig. 8a–d. It should be noted that although the mass fraction of Y released from chalcopyrite is 1–2 orders of magnitude greater than that for apatite, Y concentrations in apatite are substantially higher than those in chalcopyrite (1028 and 1.80 mg kg$^{-1}$, respectively; Table 1). Release of Y is

very low in the absence of ligand or in the presence of salicylate in all four graphs. However, reactions conducted in the presence of oxalate, phthalate, and especially citrate result in substantial Y release from both minerals. Examination of 1 mM data in Fig. 8a and b demonstrates the effectiveness of citrate for enhanced Y release from apatite, because experimental solution pH values (Table 5) fall in the pH range (5.5–8) where proton concentration has a negligible effect on apatite dissolution (Welch et al., 2002; Guidry and Mackenzie, 2003).

Yttrium release from apatite was not affected by dissolved O$_2$(g), although the same is not true for chalcopyrite (Fig. 8c and d) where Y release under anoxic conditions exceeded that of oxic conditions by 3–4 times. Given the high Cu and low Fe concentrations in solution under oxic conditions, we attribute this difference to the formation of Fe oxides during oxic chalcopyrite weathering that may have adsorbed or incorporated Y into the mineral structure (i.e., scavenging). Bau (1999) demonstrated the ability of precipitating Fe oxyhydroxides to scavenge Y from solutions with pH values similar to our experiments.

## 3.4. Implications for using P, Y and Cu as organo- or oxymarkers

Our results support the idea proposed by Neaman et al. (2005a,b, in press) that P and Y may have utility as organomarkers indicating the existence of organic acids in early Earth weathering environments. The presence of aliphatic and, to a lesser extent, aromatic ligands enhances P and Y release from apatite, which is a very common Y-containing mineral found in soil and igneous, metamorphic, and sedimentary rocks (Lindsay et al., 1989; Taunton et al., 2000). Further support for using P
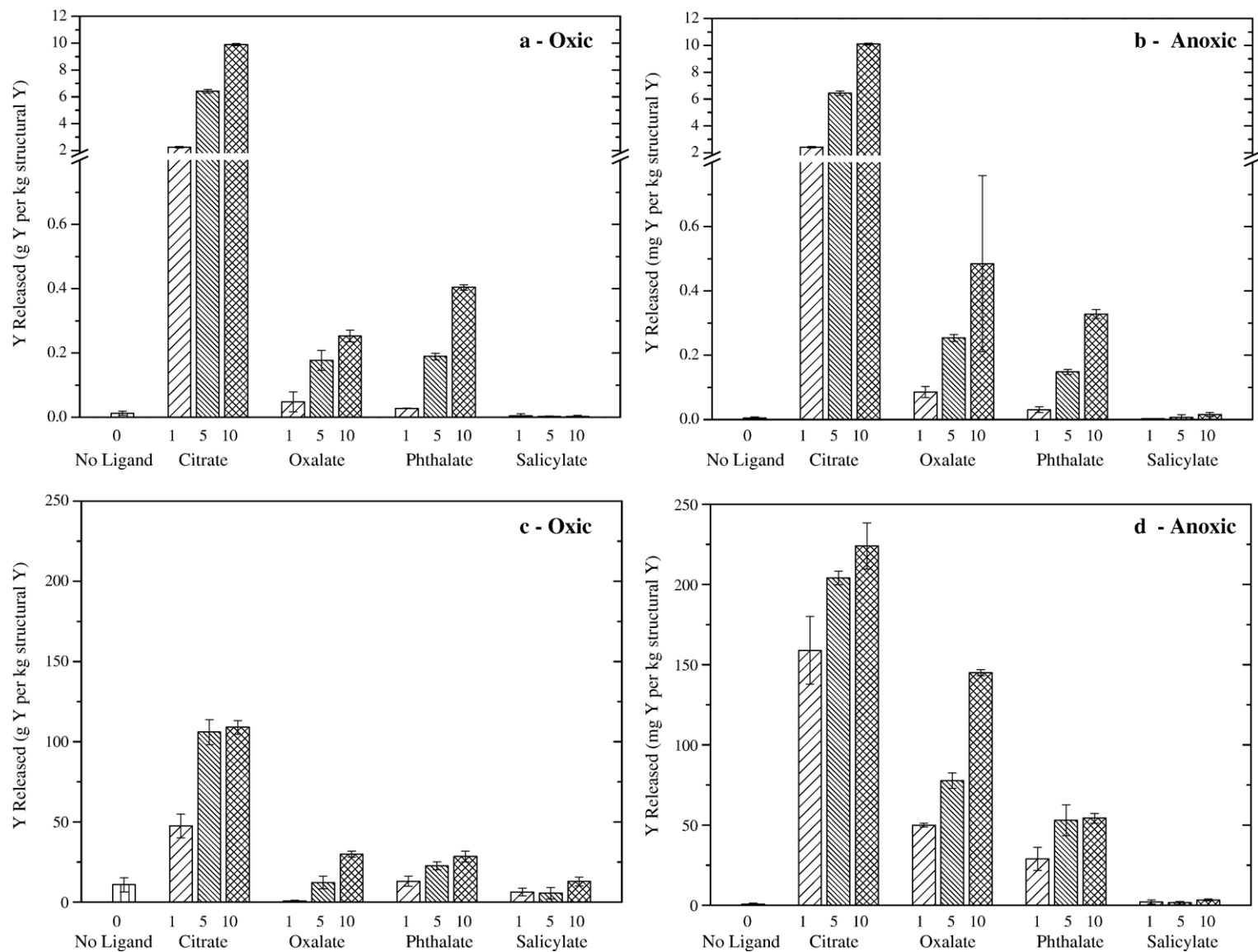
Fig. 8. Effect of organic acid and organic acid concentrations (0, 1, 5, 10 mM) on Y release from apatite under (a) oxic and (b) anoxic conditions, and from chalcopyrite under (c) oxic and (d) anoxic conditions. The release of each element from apatite and chalcopyrite is expressed as milligrams of element released per kilogram of total elemental content in unweathered mineral. Error bars, where observed, represent the 95% confidence interval from triplicate aqueous phase sample analyses.

and Y as organomarkers can be found in the work of Rogers et al. (1998), Taunton et al. (2000), and Neaman et al. (2005a). Rogers et al. (1998) demonstrated that microcline and plagioclase specimens containing apatite (0.25–0.28 % $P_2O_5$) were heavily colonized by micro-organisms and deeply weathered after 12 m submersion in C-rich, N- and P-deficient, anoxic aquifers. In contrast, microcline and plagioclase specimens containing no detectable P ($<0.01\%$ $P_2O_5$) were barren of attached organisms and remained unweathered. Rogers et al. (1998) hypothesize that apatite P in specific feldspars is released by microbially produced acidity and chelating organic ligands, thus promoting microbial growth and enhanced silicate weathering. Taunton et al. (2000) documented decreased apatite and Y concentrations as a function of increased weathering in granitic soils and saprolite. Relict apatite etch pits in samples collected from 0.25 to 1 m depths were observed to contain dehydrated objects presumed to be bacteria and fungal hyphae. Concurrent with decreased incidence of apatite in the profile and increased weathering, Y depletion was observed. In addition, Neaman et al. (2005a) noted P depletion in Mount Roe paleosol 2 (core 1) which is in agreement with evidence collected by Rye and Holland (2000) suggesting the existence of life during formation of this paleosol sample.

Our data also support the possibility that Cu mobility patterns may serve to distinguish if oxygen was present in the atmosphere during weathering reactions. We observe a 10,000–200,000-fold increase in Cu release under oxic conditions as compared to anoxic conditions. Using Mount Roe and Hekpoort paleosols as examples, Neaman et al. (2005a) were able to demonstrate that Cu was depleted in Hekpoort paleosol (i.e., oxic conditions were present at time of formation) while it was retained in the Mount Roe paleosol (i.e., anoxic conditions were present at time of formation). This interpretation is consistent with prior studies investigating Fe mobility in these paleosols (Holland and Rye, 1997; Rye and Holland, 1998, 2000; Yang and Holland, 2003) and supports the prospect of using Cu as an oxymarker. Ligands also increase Cu release, resulting in a maximum 20-fold enhancement over ligand-free experiments. Although this effect is small compared to impacts of oxidation, Cu may have use as an organomarker as well. Utilization of Cu as an organomarker is supported by the work of Viers et al. (1997) and their observation that Cu export from tropical watersheds is positively correlated with increasing dissolved organic carbon concentration.

There are, however, limitations to using these elements as organo- or oxymarkers. Soils are dynamic,

open systems and their formation is influenced by parent material, climate, topography, organisms, and time (Jenny, 1941), and these five factors result in extreme soil diversity in terrestrial ecosystems. Thus, we do not expect that P, Y, and Cu mobility patterns can be applied universally to elucidate the presence of ligands or oxygen during rock weathering and soil formation. Neaman et al. (2005b) discuss potential pitfalls for utilizing these proposed organo- and oxymarkers, and they conclude the greatest potential for using these elements as markers is within environments having low rainfall and pH > 5.5. However, even in these environments, other factors must also be considered when interpreting element mobility patterns (e.g., secondary mineral formation, element adsorption/desorption, erosion and depositional events, solute flux through the profile, etc.). Although the current work highlights the potential for using trace element signatures as organo-markers, the presence of organic matter on early Earth cannot be attributed unambiguously to the presence of life. In particular, the potential effects of organic matter introduced from extraterrestrial sources (i.e., exogenous organic matter from meteoritic and cometary debris; Anders, 1989; Becker et al., 1999; Jenniskens et al., 2000) must also be considered.

To interpret paleosols, element mobility patterns should be investigated in concert with mineralogical characterization to analyze whether elements act as organo- or oxymarkers. Documenting mineralogy (e.g., apatite and metal sulfides) and element concentrations in the soil profile and parent material should enhance our ability to determine if organic ligands or oxygen were present at the time of soil formation. For example, if Cu mobility patterns do not show Cu depletion within a profile due to adsorption or secondary mineral formation, mineralogical data documenting the absence of Cu-sulfides in the weathered profile but the presence in parent material would still suggest oxygenated conditions during soil formation (Neaman et al., 2005b). Similarly, iron oxides adsorb P very strongly through inner-sphere complexes (Sposito, 1989) which may limit loss from soils. However, documented loss of apatite in weathered soil surface horizons and a continuum of increased apatite with depth (i.e., less weathering and lower organic acid concentrations) would be indicative of ligand presence at time of weathering.

## 4. Conclusions

Results show that organic acids enhance Ca, P, and Y release from apatite and Cu, Fe and Y release from

chalcopyrite to a greater extent than when ligands are not present. Increased concentration of aliphatic ligands in solution results in greater mineral dissolution, although the same is not always true for aromatic organic acids. Within the group of organic ligands investigated, citrate enhances mineral dissolution to the greatest extent and salicylate enhances mineral dissolution to the least extent. Apatite dissolution was not impacted by the presence or absence of molecular oxygen. However, the presence of dissolved oxygen enhances dramatically chalcopyrite dissolution, resulting in a 10,000–200,000-fold increase in Cu release relative to anoxic conditions. Scavenging of Y by Fe oxides is thought to result in lower Y concentrations at the end of oxic chalcopyrite experiments. These data support our previous work indicating that P and Y mobility is enhanced by organic acids and Cu release is impacted significantly by dissolved $O_2(g)$. Thus, we conclude that P and Y may have utility as organomarkers and Cu as an oxymarker for distinguishing the presence of terrestrial organisms and atmospheric conditions during soil weathering processes on early Earth. Importantly, if a researcher seeks to determine whether mobilization of elements in a soil can be attributed to oxygen or organic concentrations, P may be the organomarker of choice since its mobilization is not affected by the presence of oxygen.

## Acknowledgements

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