

Element mobility patterns record organic ligands in soils on early Earth

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ABSTRACT

Considerable mobilization of Fe without mobilization of Al in Precambrian paleosols has been documented and attributed to either anoxic- or ligand-promoted dissolution. To elucidate these mechanisms, basalt was dissolved under oxic and anoxic conditions with and without citrate, and the mobility of several elements was analyzed. The extent of release of Fe and P was minor (in citrate-free conditions) or considerable (with citrate) regardless of oxygen pressure. Release of Al was minor in all cases, whereas release of Cu was minor (in anoxic conditions) or considerable (in oxic conditions). Release of Cu was enhanced by citrate. In comparison, in the weathered surface of two of the oldest-known basalt-derived paleosols—the Mount Roe (2.76 Ga) and the Hekpoort (2.25 Ga)—Fe and P were considerably depleted and Al retained, consistent with the presence of organic ligands. Cu, retained in the Mount Roe paleosol but considerably mobilized in the Hekpoort paleosol, documents formation under an anoxic atmosphere and an oxic atmosphere, respectively, as inferred by others on the basis of Fe mobility. The immobility of Al in both paleosols is consistent with formation under conditions in which the annual volume of rainwater was lower than the topsoil pore volume. Mobilization of P in such paleosols developed under low-rainfall conditions provides a new proxy for identification of ligands secreted by terrestrial organisms on early Earth.

Keywords: Precambrian paleosols, organic ligands, basalt, element mobility, dissolution, early Earth.

INTRODUCTION

The presence of microorganisms in soils in the Precambrian has been inferred from isotopic and microfossil data (Horodyski and Knauth, 1994; Rye and Holland, 2000; Watanabe et al., 2000). In modern soils, these prokaryotes are known to secrete organic ligands to solubilize nutrients (Jones, 1998). Such ligands, if considerable in paleosol solutions, could have mobilized elements from minerals, leaving signatures in weathered rocks. For example, considerable mobilization of Fe without mobilization of Al in Precambrian paleosols has been documented and attributed to either anoxic- or ligand-promoted dissolution (e.g., Beukes et al., 2002; Holland and Rye, 1997; Ohmoto, 1997; Yang and Holland, 2003).

Interpretations of elemental cycling in paleosols are based upon assumptions of early Earth surface conditions. On the basis of geologic observations and calculations (Sleep et al., 2001), we assume element surface conditions at 2.8 Ga and a minimum methane concentration of ~100 ppmv, consistent with models of atmospheric evolution (Kasting et al., 2001). Given these conditions, CO₂ pressure (P_{CO_2}) was not higher than today's value (~0.0003 atm). This P_{CO_2} implies a rainwater pH of 5.6, a circumstance in which biotic uptake of Fe is difficult owing to insoluble oxides and sulfides under oxic and anoxic conditions, respectively. Organic ligands such as citrate are secreted by soil

prokaryotes to chelate Fe in response to Fe deficiency in modern soils (Laboure and Briat, 1993). Concentrations of aliphatic organic ligands in modern soil solutions range from ~0.001M to ~0.004M (Stevenson, 1991).

We investigated mobilization of Fe in the presence of ligands by dissolving Columbia River Basalt with and without 0.01M citrate in batch experiments at pH 6 ± 0.5 . Experiments were conducted under oxic ($P_{\text{O}_2} = 0.2$ atm) and anoxic (95% N₂, 5% H₂, O₂ < 1 ppmv [$<0.0005\%$ of the present atmospheric level]) atmospheres. The latter O₂ level is less than levels suggested for pre-2.3 Ga paleosols ($<0.5\%$ of the present atmospheric level) (Yang and Holland, 2003).

EXPERIMENTAL RESULTS

Values of Eh at 28 days in batch solutions measured by a platinum electrode were 400–500 mV (in oxic conditions) and <100 mV (in anoxic conditions). Consistent with these findings, at 28 days, ~30%–50% (in oxic conditions) or ~90%–100% (in anoxic conditions) of total Fe_(aq) after 0.2 μm filtration was Fe^{II}.

Ti released into solution represented <0.01 wt% (ligand free), 0.13% (oxic with citrate), and 0.20% (anoxic with citrate) of total basalt Ti. The Ti-normalized elemental content of 28-day-weathered basalt $R_i^w (= C_i^w/C_{\text{Ti}}^w)$, where C_i^w represents the weight percent of element i in the weathered basalt) was calculated by mass balance from the starting basalt composition and aqueous concentrations at 28 days. The difference between R_i^w and the same ratio for parent basalt $R_i^p (= C_i^p/C_{\text{Ti}}^p)$, where C_i^p represents weight percent of element i in the parent basalt) can be expressed as

$$\Delta_i = [(R_i^w - R_i^p) \times 100]/R_i^p. \quad (1)$$

Negative or positive values of Δ_i (in percent) represent loss or gain of element i , respectively, relative to Ti (Fig. 1).

In citrate-free controls (Figs. 1A, 1B), relative loss of Fe, Al, and P was <0.1% regardless of P_{O_2} . Relative loss of Cu was minor (in anoxic conditions) or considerable (in oxic conditions). Relative loss of Fe and P was considerable in the presence of citrate regardless of P_{O_2} (Figs. 1C, 1D). With citrate, Δ_{Cu} indicates minor relative Cu gain (in anoxic conditions) or considerable loss (in oxic conditions) (Fig. 1D). Relative loss of Al, although considerably smaller than relative loss of Fe, was enhanced slightly by citrate regardless of P_{O_2} (Figs. 1A–1D).

Relative loss of elements—Fe, P, Cu \gg Al (oxic with citrate); Fe, P \gg Al > Cu (anoxic with citrate); Cu > Fe, Al, P (oxic without citrate); and Fe > P, Cu > Al (anoxic without citrate)—is related to mineralogy of weathering. Like most basalts, the Columbia River Basalt is composed of Fe^{II}-rich minerals (see materials description in the appendix). Relative loss of Fe was ~22 (in oxic conditions) or ~25 (in anoxic conditions) times greater than relative loss of Al, consistent with decreasing cation-oxygen bond strength from trivalent to divalent cations (Birkeland, 1999). Precipitation of iron (oxyhydr)oxide(s) is expected (Bethke, 2002) in these oxic experiments even with citrate, explaining the smaller loss of Fe as compared to P under oxic conditions. Under anoxic conditions with citrate in our experiments, MnHPO₄ and manganese (oxyhydr)oxides are calculated to be over-

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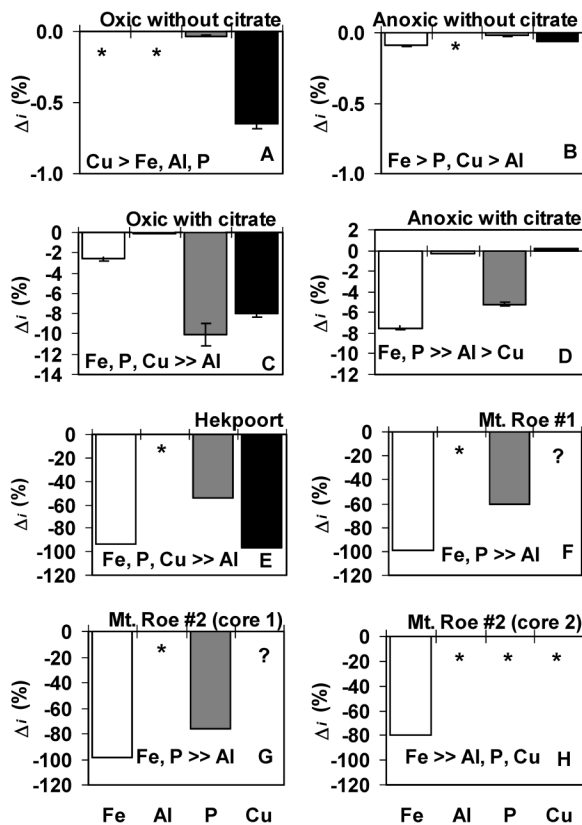


Figure 1. Geochemical signatures (as defined in equation 1; negative or positive values of Δ_i represent loss or gain of element i , respectively, relative to Ti) of basalt dissolved in batch experiments and of sericite zones of some selected basalt-derived paleosols: A: Oxidic without citrate. B: Anoxic without citrate. C: Oxidic with citrate. D: Anoxic with citrate. E: Hekpoort paleosol (Yang and Holland, 2003). F: Mount Roe #1 paleosol (Macfarlane et al., 1994). G: Mount Roe #2 paleosol (core 1) (Macfarlane et al., 1994). H: Mount Roe #2 paleosol (core 2) (Yang et al., 2002). Asterisks correspond to values below detection limits of 0.01% (batch experiments) or to neither loss nor gain of element in paleosols. Question marks are used where data are unavailable for Cu.

saturated or undersaturated, respectively; the reverse was calculated to be true for oxidic conditions (Bethke, 2002). Smaller relative loss of P as compared to Fe under anoxic conditions is thus attributed to precipitation of manganese phosphates under anoxic conditions.

PROPOSED SCHEMES FOR PALEOSOL INTERPRETATIONS

Cu is present in the basalt as copper sulfide, as observed for many igneous rocks (Best and Christiansen, 2001). The solubility products of chalcocite (Cu_2S) and covellite (CuS) are low ($\log K_{sp} = -48.6$ and -36.1 , respectively), but these sulfides dissolve under oxidic conditions via oxidation (Lindsay, 1979). Organic ligands enhance oxidic dissolution of copper sulfide (Fig. 1C) by forming complexes with Cu as observed for other sulfides (Davis et al., 1995). However, when released from primary sulfides, Cu can be retained in soils by incorporation into or adsorption onto secondary minerals (e.g., retention of Cu in a basalt-derived soil from Israel; Navrot and Singer, 1976), in contrast to our short-term batch experiments. Therefore, even if Cu is retained by secondary minerals in topsoil, depletion of copper sulfides in the topsoil relative to parent rock implies oxidic conditions (Fig. 2A).

P is present in the basalt as the common accessory mineral fluorapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$ (Best and Christiansen, 2001), whose solubility

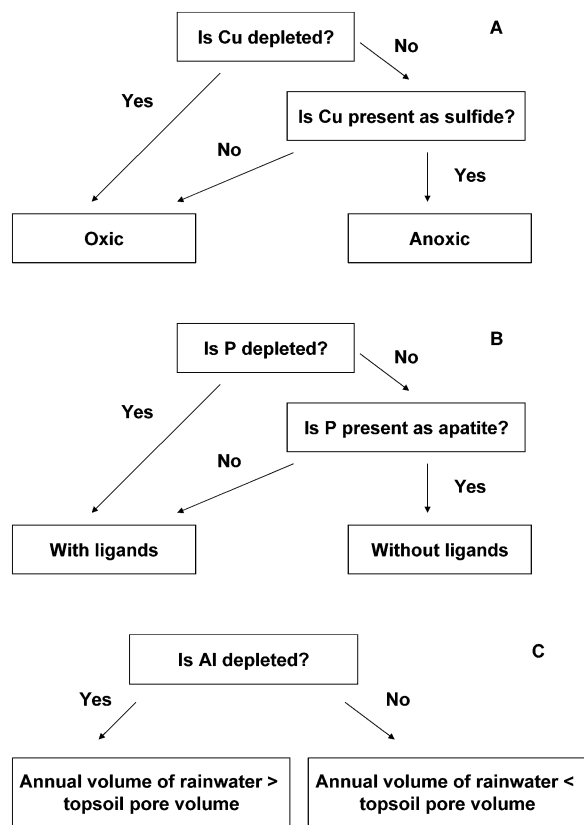


Figure 2. Proposed schemes to distinguish between topsoils weathered in environments characterized as (A) oxidic vs. anoxic, (B) ligand rich vs. ligand poor, and (C) humid vs. dry. Schemes are valid for rocks in which P is originally present as apatite and Cu is originally present as copper sulfide, as in most igneous rocks (Best and Christiansen, 2001). Scheme B is valid above pH 5.5 and under conditions in which annual volume of rainwater is smaller than pore volume of topsoil.

product is very low ($\log K_{sp} = -60$) (Wedepohl, 1970). Apatite is classed as a stable mineral during weathering (Banfield et al., 1991; Pettijohn, 1941). Organic ligands enhance dissolution of apatite (Figs. 1A–1D) by forming complexes with calcium (Welch et al., 2002). Apatite is the most common P-bearing mineral in soils (Lindsay et al., 1989), but surprisingly few data are available on apatite distribution in soil profiles. In one study (Shipp and Matelski, 1960), the content of apatite in a soil profile developed on loess decreased to depths of ~ 1 m, then remained constant deeper than 1 m. The depletion of apatite in this soil is consistent with higher concentrations of organic ligands in the topsoil than in the subsoil as observed in other soils (Jardine et al., 1989). Similar to Cu, however, P may not be depleted in the presence of organic ligands if adsorption of P onto iron and aluminum oxyhydroxides occurs, as observed in Hawaiian forest soils (Miller et al., 2001). Therefore, depletion of apatite is more diagnostic of the presence of organic ligands because P may be retained by secondary phases (Fig. 2B).

Minor release of P in ligand-free controls (Figs. 1A, 1B) suggests that apatite can be weathered under high rainfall conditions, and such weathering has been observed in soils in Cameroon (Braun et al., 1990); apatite was replaced by secondary phosphates even at 10 m depth, where organic ligands are not expected to be present in considerable concentrations. Furthermore, the dissolution rate of fluorapatite is invariant above pH 5.5 but increases significantly below pH 5 (Guidry and Mackenzie, 2003); therefore, apatite can be dissolved under acidic conditions even in the absence of organic ligands. Thus, the

TABLE 1. GEOCHEMICAL SIGNATURES OF THE HEKPOORT (2.25 Ga) AND MOUNT ROE (2.76 Ga) PALEOSOL PROFILES

Profile	Soil horizon	No.*	R_{Fe}^{\dagger}		R_{Al}^{\dagger}		R_P^{\dagger}		R_{Cu}^{\dagger}	
			Average	STD	Average	STD	Average	STD	Average	STD
Hekpoort [§]	Ferricrete	4	154	35	25.7	9.1	0.22	0.04	0.35	0.34
	Mottled	8	11	15	21.2	2.8	0.06	0.02	0.006	0.003
	Sericite (pallid)	9	1.28	0.72	22.4	2.5	0.05	0.02	0.005	0.000
	Chlorite (saprolite)	23	25	11	20.1	2.3	0.08	0.04	0.27	0.88
	Parent basalt	11	19.8	3.5	20.4	2.3	0.11	0.02	0.12	0.10
#1 Mt. Roe [#]	Sericite (pallid)	8	0.06	0.05	9.32**	0.13	0.11	0.08	nr	
	Chlorite (saprolite)	1	7.78		9.15		0.29		nr	
	Parent basalt	1	6.04		8.89		0.28		nr	
#2 Mt. Roe [#] (core 1)	Sericite (pallid)	11	0.18	0.29	10.18**	0.35	0.06	0.05	nr	
	Chlorite (saprolite)	1	25.9		10.43		0.23		nr	
	Parent basalt	1	11.6		9.72		0.22		nr	
#2 Mt. Roe ^{††} (core 2)	Sericite (pallid)	4	2.02	0.62	9.52	0.17	0.22	0.02	0.003	0.001
	Chlorite (saprolite) ^{§§}	11	9.97	4.34	9.68	0.75	0.22	0.05	0.003	0.002

Note: nr indicates not reported.

*The number of samples reported by the authors cited and used for calculation of average and standard deviation (STD).

[†] $R_i = C_i/C_{Ti}$, where C_i represents weight percentage of element i in the weathered or parent basalt for $i = Fe, Al, P,$ and Cu .

[§]Yang and Holland (2003).

[#]Macfarlane et al. (1994).

** Δ_{Al} of ~5% is not considered because only one data point is reported for parent basalt.

^{††}Yang et al. (2002).

^{§§}The data for parent basalt are not reported. Δ_i calculated by using the data for saprolite.

validity of the suggested model in Figure 2B should be limited to soil solution pH >5.5 and to low rainfall conditions.

The rainfall on early Earth can be estimated from Al mobility in paleosol profiles. In basalt-derived soils in Hawaii, Al is mobile under humid conditions (>1400 mm/yr rainfall) and immobile under dry conditions (Chadwick et al., 2003). The threshold (~1400 mm) was attributed to the annual volume of water required to fill pores in the top meter of soil (i.e., topsoil). Thus, depletion of Al from the topsoil due to flushing serves as a marker for rainfall: considerable depletion of Al is consistent with the annual volume of rainwater larger than the pore volume of topsoil (Fig. 2C).

PALEOSOL INTERPRETATIONS

We calculated R_i (Table 1) and Δ_i (Figs. 1E–1H) for $i = Fe, Al, P,$ and (when available) Cu for two of the oldest-known basalt-derived paleosols, the Hekpoort (ca. 2.25 Ga) (Yang and Holland, 2003) and the Mount Roe (ca. 2.76 Ga) (Macfarlane et al., 1994; Yang et al., 2002). The immobility of Al in Mount Roe and Hekpoort paleosols (Figs. 1E–1H) is attributed to its incorporation in secondary sesquioxides and clays (Macfarlane et al., 1994; Yang and Holland, 2003; Yang et al., 2002), suggesting soil formation in a relatively dry climate with the annual volume of rainwater lower than the pore volume of topsoil (Fig. 2C), as observed for modern basalt-derived soils in Hawaii (Chadwick et al., 2003).

Relatively dry climate and rainwater pH of ~6 on early Earth allow us to suggest that the scheme in Figure 2B is useful for interpretation of the Mount Roe and Hekpoort paleosols. The geochemical signatures of the top (sericite or pallid) zone of the Hekpoort paleosol (Fig. 1E) are most similar to signatures obtained in batch experiments with citrate under oxic conditions (Fig. 1C). Depletion of P from this top part of the paleosol profile can therefore be attributed to the presence of organic ligands, and depletion of Cu can be attributed to the presence of oxygen. The P- and Cu-enriched ferric duricrust (ferricrete) above the sericite (pallid) zone in this paleosol is consistent with adsorption of P and Cu onto hematite, which is abundant in this zone (Yang and Holland, 2003). Mineralogical data for P- and Cu-bearing minerals in the paleosol (currently unavailable) are needed to confirm this interpretation.

The sequence of horizons in the Hekpoort paleosol is similar to that in some modern laterites (Beukes et al., 2002): Fe is depleted in

the sericite (pallid) zone and enriched in ferric duricrust (ferricrete) above this zone (Aleva, 1994). There is no general consensus on the mechanisms of Fe depletion in pallid zones of modern laterites. Some researchers (Nahon, 1986) attribute the mobilization of Fe to purely geochemical processes of Fe reduction due to waterlogging during wet seasons. However, other researchers think that an abundance of microorganisms is essential to laterite formation (Aleva, 1994). These researchers think that chelation of Fe^{III} by organic compounds secreted by microorganisms plays an important role in the mobilization of Fe (McFarlane, 1987). Laterite profiles extend to tens of meters in depth. Isolation of microorganisms from laterite profiles at horizons below the top meter of the profile (McFarlane, 1987) is in agreement with the possible role of microorganisms in Fe mobilization. Similarities in element mobility (Figs. 1C, 1E) are most consistent with Fe mobilization in the Hekpoort paleosols as Fe-bearing organic species.

The geochemical signatures of Mount Roe paleosols #1 and #2 (core 1) (Macfarlane et al., 1994) (Figs. 1F, 1G) are similar to the signatures obtained in the batch experiments with citrate regardless of P_{O_2} (Figs. 1C, 1D). Retention of Cu in core 2 of Mount Roe paleosol #2 (Fig. 1H) is most consistent with anoxic conditions, as suggested previously on the basis of Fe mobility (Yang et al., 2002). This interpretation would be strengthened if copper sulfides were documented in this paleosol (data are unavailable). However, core 2 of Mount Roe paleosol #2 (Fig. 1H) is geochemically different from core 1 of this paleosol (Fig. 1G) with respect to P mobility and is, therefore, more similar to the anoxic batch experiment without citrate (Fig. 1B).

In the Mount Roe paleosols #1 and #2 (core 1), depletion of P from the topsoil can be attributed to organic ligands, in agreement with previous evidence for the existence of life in paleosol #2 (Rye and Holland, 2000). Fe was therefore most probably mobilized in these paleosols as both Fe^{II} and Fe-bearing organic species. If both cores 1 and 2 of Mount Roe paleosol #2 developed under similar hydrologic conditions, then retention of P in core 2 (Fig. 1H) may be attributed to the absence of organic ligands. Lack of consistency between cores 1 and 2 of Mount Roe paleosol #2 would therefore document that terrestrial organisms had not colonized all soils on Earth at that time.

SUMMARY

Careful consideration of mineralogical mobility (Fig. 2) recorded in soils and paleosols compared to controlled laboratory experiments

such as those reported here clarifies interpretations of climate and biological activity on early Earth. Phosphorus mobility can be a new proxy for identification of ligands secreted by terrestrial organisms on early Earth.

APPENDIX 1. MATERIALS AND METHODS

Basalt sampled from the same quarry as the U.S. Geological Survey BCR-1 (Flanagan, 1967) was hammer-broken, cleaned with distilled water, crushed and powdered with a tungsten carbide jaw crusher and disk mill, sieved to 100–200 mesh (75–150 μm), and cleaned of fine particles by ultrasonication, acetone washing, and drying at 60 °C.

Minerals in the basalt (X-ray diffraction and electron-probe microanalysis) include plagioclase ($\text{Ca}_{0.52}\text{Na}_{0.50}\text{K}_{0.03}\text{Si}_{2.53}\text{Al}_{1.43}\text{O}_8$), alkali feldspar ($\text{Na}_{0.37}\text{K}_{0.34}\text{Ca}_{0.02}\text{Si}_{3.27}\text{Al}_{0.72}\text{O}_8$), augite ($\text{Mg}_{0.91}\text{Fe}_{0.68}^{2+}\text{Ca}_{0.42}\text{Mn}_{0.02}\text{Ti}_{0.02}\text{Na}_{0.01}\text{Si}_{1.92}\text{Al}_{0.05}\text{O}_6$), and quartz. Minor phases include ilmenite ($\text{Fe}_{1.00}^{2+}\text{Ti}_{0.98}\text{Mg}_{0.02}\text{Mn}_{0.01}\text{O}_3$) and magnetite-ulvöspinel [$\text{Mg}_{0.02}\text{Fe}_{0.47}^{2+}\text{Fe}_{0.50}^{3+}(\text{Ti}_{0.72}\text{Fe}_{1.20}^{2+}\text{Al}_{0.06}\text{Mn}_{0.02})\text{O}_4$]. Trace phases include fluorapatite, copper sulfide, and iron sulfide. The basalt also contained glass.

Acid-washed 50 mL Pyrex tubes with Teflon-lined plastic caps were filled with basalt and autoclaved: 30 mL of 10^{-2}M citrate and ligand-free solutions adjusted to pH 6.0 with NH_4OH , filter sterilized, and sodium azide (NaN_3) was added at concentrations of 0.05%. Solid to solution ratios were set at 1:100 g/mL. Tubes were continuously agitated end over end in the dark at room temperature. Experiments were opened to room atmosphere three times per week (in oxic conditions) or performed in a Coy oxygen-free glove box (in anoxic conditions). We did not observe any turbidity during the experiments.

Aliquots of the suspension were sampled at 28 days, measured for pH and Eh, filtered (0.2 μm), measured for Fe^{II} with Ferrozine, and acidified with nitric acid for analyses. Element concentrations were determined by inductively coupled plasma–atomic emission spectrometry (ICP-AES) and ICP–mass spectrometry (ICP-MS). Concentrations are derived from both ICP-AES and ICP-MS analyses (Fe, Al, P, and Ti) or from ICP-MS analysis for more than one isotope (Cu). Average values are reported for triplicate experiments.

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