Colloid Mobilization During Soil Iron Redox Oscillations

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In redox-dynamic soils, iron reduction-oxidation events may initiate wide shifts in the concentration of colloidal and dissolved material because of either Fe mineral dissolution or pH shifts associated with Fe oxidation state changes. This can have profound effects on the mobilization of organic and metal constituents. We conducted laboratory studies of colloid dynamics in a Hawaiian soil subjected to four consecutive 14-day reduction-oxidation cycles across the "soil-Fe" (Fe(OH)₃)/(Fe²⁺(aq)) equilibrium. Size fractionated samples were isolated by differential centrifugation and characterized based on analysis of the framework and trace elements (Si, C, Fe, Ti, Al, Zr, Nb, La, and U). Intracycle oscillations in all colloidal (3 kDa to 160 nm) elements peaked during the reduction half-cycles, mobilizing 10% of total soil Ti and from 1-5% of total soil Zr, Nb, La, and U at peak dispersion. Colloid dynamics were dependent on pH shifts accompanying the redox oscillations rather than the fluctuating solubility of Fe oxides. TEM/EDS and massbalance calculations suggest a carbon-based colloid matrix with zones of metal enrichment. The cumulative effects of four redox cycles included an apparent increase in colloid stability. Proton production/consumption associated with Feredox cycling has important implications for mobilization colloid-borne trace elements and sorbed contaminants.

Introduction

As a result of high specific surface areas (>10 m^2g^{-1}) and reactive site densities, colloidal particles (ca. 1 nm -1μ m in size) often regulate the mobility of strongly sorbing constituents in soils, including heavy metals, sorbed contaminants, and refractory elements that are otherwise assumed to be "immobile" because of low aqueous solubility (1). The mobilization of colloids, also termed colloid dispersion, is strongly dependent on solution pH, ionic strength, and ionic composition because these parameters affect the magnitude and sign of particle surface charge and, as a result, interparticle electrostatic repulsion (2-4). In general, colloid dispersion is favored at pH values above the point of zero charge (pzc) of the particles, whereas rapid coagulation is promoted in the vicinity of the pzc (5). Natural organic matter (NOM) coatings on colloids often dominate particle surface charge characteristics, leading to the development of negative surface charge and interparticle repulsion upon dissociation

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of NOM functional groups (6-9). In many highly weathered, tropical forest soils this can yield a pzc below pH 4 (7).

The Fe redox cycle affects biogeochemical processes through the stoichiometry of oxidation/reduction reactions (10) as well as by producing/consuming high surface area ferric solids and catalytically reactive ferrous species (11). Reduction of ferric oxides under suboxic conditions can promote colloid dispersion by dissolving Fe-oxide cements that hold aggregates together (12). This mechanism was initially invoked to explain colloid release during the intrusion of anoxic water into an Fe-rich aquifer (13). Yet, later experiments suggested that concurrent shifts in aqueous phase parameters (pH and ionic strength) produced similar colloidal dispersion without the dissolution of Fe-oxides (4, 14). Indeed, the same solution chemical parameters that govern colloid stability in oxic systems-pH, ionic strength, and ionic composition (5)-are strongly influenced by dynamic shifts in Fe redox status. Thus, the interaction of Fe redox processes with colloid chemistry is complex. This complexity is further accentuated by the fact that soil microbes catalyze, at minimum, the reduction portion of the Fe redox cycle (15). Thus, concentrations of electron donors (e.g., organic C) and acceptors (e.g., O₂, NO₃⁻, etc.) and microbial population dynamics potentially influence colloidal stability in soils via biogeochemical pathways.

It is well-known that soil-Fe reduction results in hydroxide production and a corresponding increase in solution pH (10, 16-18), whereas Fe oxidation induces an equivalent production of protons. In fact, no other soil process results in shifts of 1-2 pH units over time scales as short as days to weeks (19). Despite the known impact of Fe redox chemistry on transient pH shifts, few studies have considered the interaction of redox fluctuations and colloid dispersion. In addition to pH-induced colloid dispersion/coagulation, alternating redox environments also provide the potential for direct, de novo colloid synthesis. Oxidation of Fe^{II}_(aq) can result in neoformation of colloidal Fe-oxides and/or FeIII-NOM complexes (20, 21). Thus, Fe redox shifts can influence colloidal mobilization directly via dissolution and precipitation or *indirectly* via changes in solution chemistry and particle surface charge. These processes have potentially significant implications for mobilization of sorbed contaminants and metal species in soils.

This work focuses on the effects of Fe reduction-oxidation cycles (a complete Fe redox cycle is defined here to comprise the reduction of Fe^{III} to Fe^{II} followed by its reoxidation back to Fe^{III}) on colloid-bound NOM and metals in a soil system. The research objective is to assess the influence of multiple Fe redox oscillations on the mass and chemical composition of suspended colloids, with a particular focus on implications for mobilization of colloid-bound "refractory" elements. We postulated that there would be oscillatory-as well as longterm or cumulative-effects of multiple redox oscillations on colloid chemistry. Specifically, we hypothesized that oscillation in Fe redox status would (A) trigger in situ colloid mobilization during the reducing cycles and (B) promote a long-term increase in colloid stability. Our approach was to force systematic redox oscillations on stirred soil suspensions while monitoring the elemental composition of various particle-size fractions. Our results indicate that colloid-bound refractory elements are mobilized during Fe reduction events-suggesting these elements cannot be considered as "immobile" in redox dynamic environments-and that colloids enriched in these elements exhibited increased stability after four full redox oscillations.

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Materials and Methods

Overall Approach. Experiments were designed to model the conditions of redox dynamic environments, specifically upland forest soils subjected to humid, tropical climate. This study also included a detailed mineralogical assessment (*22*), and additional experimental details are discussed therein. We targeted Fe valence state transitions by using a "soil-Fe":Fe^{II} equilibrium model to define progressive Eh-triggered mixtures of air or N₂ during the oxidizing half-cycles and real-time DOC measurements to define C additions during the reducing half-cycles.

Soil Selection. A soil was selected from within a wellcharacterized climate gradient on the island of Maui, HI that has documented Eh fluctuations (*23, 24*) and an abundance of short-range ordered (SRO) mineral–organic complexes characteristic of intermediate weathering stage basaltic soils (*25*). Details on the sample collection, handling, and mineralogical characterization can be found in ref *22*. A summary of the soil chemical composition is given in Table S-1 (Supporting Information).

Redox Reactor Design. A redox reactor system, consisting of sealed glass vessels with various ports for continuous and intermittent measurements, was designed and constructed to control Eh and pH status of triplicate soil suspensions (22). Redox conditions are controlled by automatic modulation of the constant gas flow between ultrapure air and N₂ to maintain selected Eh values. All gases were delivered to the reactors through a 4 M NaOH CO₂ trap/humidifier.

Redox Oscillation Experiment. *Reactor Operation.* Soil incubations were conducted at 25 °C, in the absence of light, using field moist soil suspended in 2.0 mM NaCl electrolyte solution at a solid (dry mass equivalent) to solution mass ratio of approximately 1:11 in triplicate reactors. The precise solid concentration was determined at each sampling point by oven-drying (110 °C) a premeasured mass of the slurry for 24 h prior to reweighing.

Several external constraints were applied to isolate the cumulative effects of multiple redox cycles. (A) A full oscillation consisted of 7 d of Fe reducing conditions followed by 7 d of Fe oxidizing conditions. (B) On the second day of each oxidizing half-cycle the pH was reset to 4.5 using 4 M NaOH or 0.5 M HCl. This measure was necessary to curtail the acidifying effects of organic acid accumulation that affected Fe transformation rates with increasing time in preliminary experiments. (C) The rate of O₂ addition during the oxidizing half-cycles was controlled by setting a target Eh that would produce an Fe^{II}_(aq) concentration of $1 \mu M$ in equilibrium with "soil-Fe" [Fe(OH)₃, assuming $K_{diss} = 15.74$ (26)]. This required adjusting the Eh set-point as the pH changed during the oxidizing half-cycle. (D) A supplemental C source (sucrose) was added to the reactors at the beginning of each Fe reducing half-cycle (excluding the first half-cycle) to reset initial aqueous C concentration to 100 mg L⁻¹, approximating that measured on unreacted soil. All reactors were operated for 8 weeks except reactor C, which malfunctioned in the middle of week 7.

Reactor Sampling Scheme. The reactors were sampled on days 1, 4, and 7 of each half-cycle. The sampling scheme included taking four 1-mL samples for targeted centrifugal separation of colloidal and dissolved suspension constituents in <160 nm, <30 nm, and <3 kDa particle size fractions and an additional 0.5-mL sample for dry mass analysis. All sample vials were flushed with N₂ gas immediately before and after adding the sample. Each sealed sample was transferred to a 95%:5% N₂:H₂ glovebox, then opened, and allowed to equilibrate for 5-min before resealing. After this point samples were opened only inside the glovebox.

Samples were particle size-fractionated using differential centrifugation in an Eppendorf 5417C centrifuge with an

F 45-30-11 rotor into <160 nm (3-min, 7200 RCF) and <30 nm (30-min, 18 000 RCF) size classes. Particle size fractions were estimated from Stokes' law assuming spherical geometry and a mean density of 2.72 g cm⁻³. Mean particle density was calculated from a preliminary elemental analysis of the colloids (Table S-1) assuming Al as gibbsite, Fe as goethite, Ti as anatase, Si as quartz, and C as organic matter containing 50% C by mass. After separation, the supernatant solutions were removed and acidified to pH 1 by addition of 6 M trace metal grade HCl (0.8% of solution volume). The <3 kDa fraction was centrifuged identically to the <30 nm fraction and then passed through a 3 kDa molecular weight cutoff (MWCO) Amicon-Microcon YM-3 regenerated cellulose filter using an Eppendorf Minispin-Plus centrifuge. The YM-3 filter apparatus does not seal tight enough to prevent the intrusion of O_2 , thus this portion of the particle separation was conducted inside the glovebox.

Batch pH Shift Experiment. To measure the effects of pH alone, a separate experiment was conducted under fixed oxic conditions. Batch soil suspensions were equilibrated at 20 and 40 mM ionic strength and pH 4 to 5.5, spanning the range observed from day 7 to 56 in the redox experiment. Preparation (sieving, etc.) and mass concentration of soil solids were the same as for the redox experiment. The sieved soil slurry was removed from the glovebox and bubbled with humidified air overnight to create an "oxic" sample. The suspension was divided into sixteen 30-mL polypropylene copolymer (PPCO) centrifuge tubes, and measured aliquots of 0.5 M KOH were added to give duplicate systems at pH 4.0, 4.5, 5.0, and 5.5 at each ionic strength. The samples were placed on a 7-rpm end-over-end rotator for 2 h and then sampled in a manner identical to that described for the redox reactor samples (e.g., differential centrifugation).

Chemical Analysis. Redox reactor pH and Eh voltages were logged continuously using a custom designed voltage amplifier/processor that fed a signal to a data logger (B&B Electronics). Gel-filled pH (VWR) and Eh (Omega) electrodes were used because of low electrolyte leak rates.

Total metal concentrations (Fe, Si, Al, Ti, K, Mg, Ca, Na, Zr, Nb, La, and U) were measured by inductively coupled plasma mass spectrometry (Perkin-Elmer DRC-II). Organic carbon (TOC) in the aqueous and solid phases was analyzed on a Shimadzu TOC V-CSH (5000A-SSM) analyzer. Glycerin contamination of the YM-3 filters prevented accurate measurement of C in the <3 kDa particle size fraction. The filters are saturated with glycerin by the manufacturer to prolong their shelf life, and, despite several attempts to remove it with successive acid and water leachings, the number of washes required invariably resulted in destruction of the filter membrane.

All concentration values are expressed in units of moles per kilogram of dry soil to compensate for any small variations in suspension solid concentration from sample to sample. Suspension dry mass was determined each time a sample was taken.

TEM Preparation and Analysis. Soil colloids were isolated for direct examination by transmission electron microscopy (TEM) by equilibrating a soil suspension at 0.025 M ionic strength (NaCl) and pH 6, size fractionating to obtain a suspension of particles less than 160 nm in size (see method above), and then preparing this suspension for TEM examination (200 mesh Cu grids, collodion and carbon coated; SPI Supplies) following the method of horizontal centrifugation and fixation in hydrophilic resin as described in ref *27*. Parallel blanks were prepared each time a sample was processed to test for particulate contamination.

TEM micrographs were obtained using a Hitachi H-8100 operating at 200 keV with a point-to-point resolution of 2.3 Å. The chemical composition of individual particles was deter-



FIGURE 1. Logarithmic colloidal metal concentrations ([M]_{colloid}) for the pH shift experiment normalized to the suspension solid concentration for (a) Fe, (b) Al, and (c) Ti.

mined with a Thermo_Noran EDS system with an accelerating voltage of 20 keV, a live time of 100 s, and a take of angle of 30°.

Notation. Element concentrations are denoted throughout the text as $[M]_{<160 \text{ nm}}$, $[M]_{<30 \text{ nm}}$, or $[M]_{<3kDa}$, where M is the element of interest, and the subscripted value denotes the particle size class defined above. The concentration of colloidal M, determined by subtracting $[M]_{<3kDa}$ from $[M]_{<160 \text{ nm}}$, is denoted $[M]_{colloid}$. Normalization of elements to their concentration in the whole soil is indicated by a superscript preceding the bracketed element symbol (e.g., soil[Ti]_{colloid}).

Results

Colloid Chemistry. Elements with low aqueous solubility that constitute a significant fraction of particle mass provide the most robust analytical choice for representing bulk colloid dynamics. We focus on Ti as a tracer of colloid behavior, noting that it represents ca. $3 \mod \%$ of the $30-160 \mod$ colloids (Table S-1), and it is highly correlated with major elements (Figure 1) and other low aqueous solubility trace metals in our experiments (Figure 2). Although, [Ti]_{colloid} tracks closely with [Fe]_{colloid}, [Al]_{colloid}, and [Si]_{colloid} (Figure 1), elevated levels of [Fe^{II}]_{<3kDa} during the redox experiments and increasing concentrations of [Si]_{<3kDa}—due to long-term dissolution—during the redox experiment preclude the use of Fe or Si.



FIGURE 2. Colloidal Zr, Nb, La, and U plotted against colloidal Ti for all redox experiment samples. Each element was normalized to its whole soil concentration. The dashed line signifies a 1:1 ratio of ^{soil}[Ti]_{colloid} to ^{soil}[M]_{colloid}. Note at full dispersion, colloidal Ti represents over 10% of the total soil Ti mass. Similarly, over 1% of Zr, Nb, La, and U are mobilized in a given event.

Isolation of pH Effects. A large increase in colloidal Fe, Al, and Ti was observed when pH of the soil suspension was increased at both ionic strengths (Figure 1). The data indicate a logarithmic increase in colloidal metals with increasing pH and a plateau at pH 4.8 at 20 mM ionic strength (*I*). At 40 mM *I*, colloidal dispersion is shifted to higher pH, and a plateau is not yet evident at pH 5.4. Dissolved (<3 kDa) metals also exhibited logarithmic increases in concentration with increasing pH (data not shown). Elemental analysis of particles dispersed above pH 4.8 (*I* = 20 mM) indicates that the larger colloids ([M] <160 nm - [M] <30 nm) are dominated by C (mole fraction = 0.16), Fe (0.05), Ti (0.03), Al (0.03), and Si (0.01) (Table S-1). Oxygen is estimated to constitute the bulk of the remainder (0.73 mole fraction).

TEM/EDS Observations. Transmission electron microscopy (TEM) reveals particles ranging in size from a few to over 100 nm with localized zones of high electron density (Figure 3a). Most colloids appear as aggregates of 1-5 nm particles held together by a matrix of low electron density material that, based on the high C content of this size fraction (ca. 100 g kg⁻¹), is likely NOM with adsorbed metal ions. Weak electron diffraction patterns indicate an overall lack of long-range crystal structure (Figure 3b), although highresolution images reveal lattice fringing in crystalline nanoparticles (Figure 3c). Electron dense clusters are of variable elemental composition; EDS reveals the clusters are composed of Fe, Al, and Si, with variable Ti abundance (Figure S-3).

Influence of Redox Oscillations. Data for Eh, pH, and $[Fe^{II}]_{<3kDa}$ are discussed in detail elsewhere (*22*) and are summarized in Figure 4 to facilitate subsequent interpretation of the colloid data. Briefly, reducing half-cycles were characterized by a decrease in Eh and increases in both pH and $[Fe^{II}]_{<3kDa}$, whereas the oxidizing half-cycles exhibited inverse trends. $[Fe^{II}]_{<3kDa}$ showed the same trends in all replicate reactors (Figure 4) as did $[C]_{<30 \text{ nm}}$ (Figure S-4).

Fe-redox cycling generates fluxes in proton production/ consumption that, when calculated from stoichiometric considerations, are found to be in large excess of the measured solution pH response or the weekly base/acid additions (Table S-2). This constitutes proton buffering by the soil solid-phase that averages ca. 40 mmol of H⁺ per kg of soil during any given half-cycle.

Analysis of supernatant solutions following differential centrifugation reveals that element concentrations in all particle size fractions fluctuate greatly between the reducing and oxidizing half-cycles with peaks occurring on the last



FIGURE 3. (a) TEM image of colloids in the \leq 160 nm size fraction. (b) Diffraction pattern showing faint rings indicating minor crystallinity. (c) Enlargement of area c showing lattice fringing. EDS spectra are shown in Figure S-3.

day of the reducing half-cycle (Figure 5a). Similar patterns in colloidal Ti ([Ti]colloid) are evident across all three reactors (Figure 5b). The large decrease in [Ti]_{colloid} observed during the first reducing cycle (0-7 d; Figure 5b) correlates with a substantial increase in ionic strength (1) from 7 mM to 20 mM due to the requisite leakage of KCl from the pH electrodes. After day 7, further increases were moderate with final I = 40 mM at the termination of the experiment. Thus all interpretation of colloid dynamics is restricted to days 7-56. Close examination of the [Ti]_{colloid} data on log scale (Figure 5c) reveals the strong influence of minor pH changes. For instance, the increase in [Ti]colloid during the second oxidizing cycle (21-28 d) in reactors A and B is correlated with small concurrent pH increases (Figure 4). Also, [Ti]_{colloid} did not increase in reactor C during the second oxidizing half-cycle where pH was constant. However, the increase in "baseline" [Ti]colloid (i.e., [Ti]colloid during the oxidizing halfcycles) cannot be explained by minor increases in pH over the course of the experiment (Figure 5c). The regression slope of (log [Ti])_{colloid} vs pH for all reactors decreases over time with values of $1.8(\pm 0.3)$, $1.5(\pm 0.2)$, $0.8(\pm 0.2)$, and $0.7(\pm 0.2)$ for cycles 1-4, respectively. This indicates a decreasing dependence of [Ti]_{colloid} on pH with reaction time.

Discussion

Colloid Composition. TEM (Figure 3) and atom abundances (Table S-1) suggest soil colloids <160 nm are composed of an organic matrix embedded with nanoscale mineral particles. Consistent with this interpretation, high-resolution inspection of electron-dense regions reveal ordered atomic structure (e.g., lattice fringing) and variable chemical composition (e.g., Ti content). Both results are suggestive of discrete nanoscale mineral particles (25), rather than a homogeneous mixture of metal ions and organic macromolecules. Consistent soil[M]colloid : soil[Ti]colloid ratios throughout the redox experiment (Figure 2) imply that colloid chemical composition is unimpacted by reductive or oxidative processing. Neither Fe reduction nor carbon oxidationboth of which were extensive in this experiment-significantly altered the relative proportions of elements in the colloids. However, the apparent increase in suspended colloids over time (Figure 5c) suggests that modification of colloid surface charge properties or de novo colloid synthesis (see Colloid Dynamics below) did occur.

Colloid Dynamics. Mineral–organic composites in Hawaiian rainforest soils exhibit variable surface charge. For these soils, the pH value where particle surface charge vanishes (i.e., the pzc) is typically quite low (pH < 4) (25). Thus, in the redox experiment, particle coagulation is predicted to coincide with oxidizing half-cycles (low pH), whereas dispersion is expected at higher pH. This was verified in the pH shift experiment under sustained oxic conditions (Figure 1). Concentrations of aqueous (<3 kDa) species also increased with pH, consistent with the dissolution of SOM–metal complexes at pH > 4.4 (not shown), but this contribution to the total element mass release was 10^1-10^4 times smaller than that observed for dispersed colloids.

In the redox experiments, reductive dissolution of Fe^{III}oxides covaries with increasing pH. The influence of reductive dissolution on colloidal dispersion can be evaluated by comparing the magnitude of colloidal element release during the reducing half-cycles with that measured at the same pH in the oxic, pH shift experiment. [Ti]_{colloid} in the pH shift and redox experiments have a similar dispersion magnitude at low ionic strength [I = 20 mM (Figure 1) or ~day 7–21 of the redox experiment (Figure 5b)]. This suggests that pH exerts principal control over colloid dispersion during any single redox cycle masking any direct influence reductive dissolution of Fe(III)-cementing agents may have on colloid dispersion (e.g., refs 12 and 13).

However, repeated cycling between Fe reduction and oxidation does appear to have a cumulative impact on colloidal stability. In our redox experiment, KCl leakage from the pH electrodes caused ionic strength to increase from ca. 20 mM to 40 mM over the course of the experiment. For like-charged particles, increased *I* diminishes interparticle electrostatic repulsion, thereby enhancing aggregation (and decreasing dispersion) at any pH (5). In the redox reactor experiments, the [Ti]_{colloid} dispersion magnitude is greater during the fourth reducing half-cycle than during the second reducing half-cycle (Figure 5b), despite a doubling in ionic strength (I increased from 20 to 40 mM). [Note: the large [Ti]_{colloid} dispersion at the onset of the experiment is excluded from analysis due to the very low ionic strength (ca. 7 mM); see Results]. For example, the measured pH values for reactor A at the end of the second and fourth reducing half-cycles are similar at 5.0 and 4.9, respectively (Figure 4b), yet they give corresponding [Ti]_{colloid} values of 5 and 13 nmol kg⁻¹,



FIGURE 4. (A) pE (Eh) and (B) pH data at the time of sampling for all reactors. (C) [Fe^{II}]_{<3kDa} for all reactors normalized to the sample solid concentration in the reactor. The dashed line corresponds to the equilibrium Fe²⁺ activity for "soil-Fe" - Fe(OH)₃ (*26*) at the pH and Eh values shown for reactor A. Reprinted with permission from Thompson, A.; Chadwick, O. A.; Rancourt, D. G.; Chorover, J. *Geochim. Cosmochim. Acta* 2006, *70*, 1710–1727. Copyright 1996 Elsevier.</sub>

respectively (Figure 5b). By comparison, at pH 5 in our oxic pH shift experiment, $[Ti]_{colloid}$ values were 9 and 2 nmol kg⁻¹ for 20 mM and 40 mM ionic strength, respectively (Figure 1c). Thus after four redox cycles, $[Ti]_{colloid}$ exceeds that predicted by pH effects alone. Furthermore, this cumulative increase in the $[Ti]_{colloid}$ dispersion magnitude coincides with a decrease in the pH-dependence of $[Ti]_{colloid}$ (see Results).

These observations indicate that redox fluctuations resulted in an overall increase in colloid stability. This could reflect a time-dependent change in colloid surface charge and/or size including either the de novo production of colloids with different surface charge properties or a modification of the surface properties of existing colloids. The data are consistent with—although not diagnostic for—a decrease in the average pzc of the particles, which would increase electrostatic repulsion across the pH range of the experiments. In the pH shift experiment, a plateau in [Ti]_{colloid} was observed above pH 4.8 (Figure 1, I = 20 mM). A decrease in mean colloid pzc would shift this plateau to a lower pH



FIGURE 5. (a) $[Ti]_{<160}$ nm, $[Ti]_{<30nm}$, and $[Ti]_{<3kDa}$ for reactor A only (normalized to the reactor solid concentration). (b) Concentration of colloidal Ti ($[Ti]_{<160nm} - [Ti]_{<3kDa}$) for all reactors normalized to the reactor solid concentration shown on linear (b) and logarithmic (c) scales.

and give a smaller slope to plots of [Ti]_{colloid} vs pH, as was observed (see Influence of Redox Oscillations).

Variable surface charge properties of soils result from the acidic functional groups associated with hydroxylated minerals and SOM. Soil organic matter contains carboxylic groups with pK_a values near 4 (moderately acidic), whereas hydroxyl groups of Fe- and Al-(hydr)oxides are more weakly acidic, giving rise to net negative surface charge only at pH > 7. Hawaiian soils of similar provenance exhibit surface charge behavior consistent with the saturation of SOM surface sites with noncrystalline and SRO Fe and Al species of weaker acidity (25). Therefore, a decrease in the pzc with redox cycling could be explained by an increase in the relative predomi-

nance of more strongly acidic SOM functionalities as might occur, for example, when the metals are dissociated from organic complexes and incorporated into crystalline minerals. A companion study (22) showed that repeated Fe redox cycling resulted in the transformation of SRO Fe-oxides (nanogoethite) into larger, crystalline Fe-oxides (goethite and hematite) in the bulk soil. We speculate that if this also occurred in the colloid pool, the release of poorly crystalline species from organic complexes and their incorporation into larger crystals might expose more of the underlying organic matrix and result in a decreased particle pzc. The experimental data presented here are consistent with this hypothesis, but they do not provide direct evidence. De novo production of colloids with a lower pzc could also explain the results.

Proton Flux. The Fe redox oscillations observed in this experiment generated a large proton flux that is not accounted for by changes in soil pH or periodic base additions. The ca. 80 mmol kg⁻¹ H⁺ production/consumption buffered by the soil during each full redox cycle can be attributed to surface charging, based on data collected for similar Hawaiian soils (*25*). Although mineral dissolution may also consume excess protons, aqueous phase metals (e.g., Al) decrease at low pH (the trend for [Al] _{<3kDa} is similar to [Ti] _{<3kDa} in Figure 5a), suggesting that dissolution of metal-oxides is less important than surface adsorption reactions.

Implications for Refractory Element Mobility and Contaminant Transport. These observations of colloid mobilization during Fe redox oscillations have implications for interpreting element mass balance data at the soil profile scale as well as for understanding the environmental fate of trace metals and colloid-sorbed contaminants. Many studies of soil formation rely on refractory elements to calculate accumulation and depletion of elements in a soil profile (28, 29). The general approach is to normalize the loss of all elements relative to their original composition in the parent material, assuming full conservation of an "immobile" element (30). Elements with low aqueous solubility and a tendency to reside in refractory minerals are the preferred choices for immobile elements (e.g., Ti, Zr, Nb, and Hf) (31). However, the central assumption of this paradigm-that these elements are not subjected to significant cumulative loss over the course of soil development-is only true if these elements are not bound to mobile colloids. At maximum dispersion during single reducing cycles, we observe over 10% of total soil Ti and between 1 and 4% of total soil Zr, Nb, La, and U are mobilized in colloidal form with dispersion increasing over time. Thus, potential significant loss of refractory elements via colloid mobilization seems likely during Fe reduction events. Variation in the dynamics of pH and Eh status with depth in a soil profile could separate the main loci of colloid dispersion/coagulation and lead to horizon specific depletion/enrichment of refractory elements. In particular, this seldom recognized mechanism may explain Ti mobility and enrichment that has been observed in many older Hawaiian soils (32-34).

Mobile colloids are widely recognized as potential carriers of sorbed contaminants (3), but the role of pH shifts resulting from Fe-redox cycling has not been previously recognized. The observed dispersion of colloidal U during Fe reduction events (Figure 2) illustrates the potential for mobilization of contaminants in redox dynamic environments. In environments that are subjected to variations in redox status, the frequency of redox shifts may regulate colloid mobility. Although it is widely appreciated that Fe oxidation–reduction results in changes in soil pH, the associated dispersion of soil colloids is often attributed to the mechanical dissolution of Fe-oxides. We observed that large scale oscillations in colloidal stability during redox cycles can be principally attributed to the indirect effects of Fe oxidation/reduction on soil pH. Thus, during Fe-redox oscillations, the dynamics of metal uptake and release by Fe-oxides is superimposed on a concomitant oscillation in particle coagulation and dispersion, which is primarily a result of particle surface charge fluctuations.

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Supporting Information Available

Tables of selected physical-chemical characteristics of the soil (S-1); proton balance for the redox experiment (S-2); TEM/EDS of the colloids (S-3); and aqueous carbon data for the redox experiment (S-4). This material is available free of charge via the Internet at http://pubs.acs.org.

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