1 **Effect of Phosphate and Sulfate on Ni Repartitioning During Fe(II)-Catalyzed**
2 **Fe(III) Oxide Mineral Recrystallization**

3 Margaret A. G. Hinkle* and Jeffrey G. Catalano

4
5
6 Department of Earth and Planetary Sciences, Washington University, 1 Brookings Drive, Saint
7 Louis, MO 63130 USA
8

9
10 *Corresponding author: Tel.: +1 314-935-4922; Fax: +1 314-935-7361; E-mail:
11 mhinkle@eps.wustl.edu

12 Submitted to *Geochimica et Cosmochimica Acta*
13 January 2015
14 Revised April 2015

ABSTRACT

Dissolved Fe(II) activates coupled oxidative growth and reductive dissolution of Fe(III) oxide minerals, causing recrystallization and the repartitioning of structurally-compatible trace metals. Phosphate and sulfate, two ligands common to natural aquatic systems, alter Fe(II) adsorption onto Fe(III) oxides and affect Fe(III) oxide dissolution and precipitation. However, the effect of these oxoanions on trace metal repartitioning during Fe(II)-catalyzed Fe(III) oxide recrystallization is unclear. The effects of phosphate and sulfate on Ni adsorption and Ni repartitioning during Fe(II)-catalyzed Fe(III) oxide recrystallization were investigated as such repartitioning may be affected by both Fe(II)-oxoanion and metal-oxoanion interactions. In most systems examined, phosphate alters Ni repartitioning during Fe(II)-catalyzed recrystallization to a larger extent than sulfate. Phosphate substantially enhances Ni adsorption onto hematite but decreases (nearly inhibiting) Fe(II)-catalyzed Ni incorporation into and release from this mineral. In the goethite system, however, phosphate suppresses Ni release but enhances Ni incorporation in the presence of aqueous Fe(II). In contrast, sulfate has little effect on macroscopic Ni adsorption and release of Ni from Fe(III) oxides, but substantially enhances Ni incorporation into goethite. This demonstrates that phosphate and sulfate have unique, mineral-specific interactions with Ni during Fe(II)-catalyzed Fe(III) oxide recrystallization. This research suggests that micronutrient bioavailability at redox interfaces in hematite-dominated systems may be especially suppressed by phosphate, while both oxoanions likely have limited effects in goethite-rich soils or sediments. Phosphate may also exert a large control on contaminant fate at redox interfaces, increasing Ni retention on iron oxide surfaces. These results further indicate that trace metal retention by iron oxides during lithification and later repartitioning during diagenesis may be substantially altered in the presence of oxoanions.

1. INTRODUCTION

Fe(III) oxide minerals are prevalent in modern and ancient soils and sediments (Cornell and Schwertmann, 2003) and often control the concentrations of trace elements through adsorption processes (Brown et al., 1999; Brown and Parks, 2001). The biogeochemical cycling of Fe results in the coexistence of aqueous Fe(II) and solid Fe(III) oxides at redox interfaces in natural aquatic systems. Such Fe cycling activates secondary abiotic reactions between aqueous Fe(II) and solid Fe(III) oxides, involving the oxidative adsorption of Fe(II) and the subsequent reduction of a structural Fe(III) cation elsewhere on the surface via interfacial electron transfer and atom exchange (ET-AE) processes (Williams and Scherer, 2004; Larese-Casanova and Scherer, 2007; Yanina and Rosso, 2008; Handler et al., 2009; Gorski and Scherer, 2011; Handler et al., 2014). Fe(II)-Fe(III) ET-AE reactions result in spatially separated growth and dissolution, leading to self-recrystallization of crystalline Fe(III) oxides (Handler et al., 2009; Catalano et al., 2010; Handler et al., 2014), Fe isotope fractionation and equilibration (Pedersen et al., 2005; Crosby et al., 2005; Wu et al., 2010; Beard et al., 2010), and metastable Fe oxide phase transitions (Hansel et al., 2003; Hansel et al., 2004; Pedersen et al., 2005; Hansel et al., 2005; Yang et al., 2010).

Previous work has shown that the presence of aqueous Fe(II) leads to the incorporation of structurally compatible trace elements, such as Ni (Friedrich et al., 2011), into goethite and hematite. Conversely, Fe(II) also causes the release to solution of trace metals preincorporated into Fe(III) oxides (Latta et al., 2012b; Friedrich and Catalano, 2012). This dynamic Fe(II)-catalyzed trace element cycling scales with Fe(II) surface coverage (Friedrich and Catalano, 2012), and is fundamentally the result of Fe(III) oxide mineral recrystallization (Pedersen et al., 2005; Handler et al., 2009; Latta et al., 2012b; Gorski et al., 2012; Friedrich et

al., 2014).

Fe(III) oxide recrystallization, dissolution, and precipitation processes are affected by phosphate and sulfate (Bondietti et al., 1993; Stumm, 1997; Eggleston et al., 1998; Majzlan and Myneni, 2005; Borch et al., 2007), two oxoanions common in natural aquatic systems. Isotope tracer experiments show that phosphate enhances the extent of Fe(II)-Fe(III) atom exchange with goethite (Latta et al., 2012a). Recent research shows that both sulfate and phosphate enhance Fe(II) adsorption onto hematite and goethite through a combination of ternary complexation and electrostatic interactions, with the specific interaction dependent on both mineral and oxoanion identity (Hinkle et al., 2015). Processes associated with ET-AE reactions may thus be affected differently by phosphate and sulfate and vary with iron mineralogy.

In this study, we examine how phosphate and sulfate alter Ni repartitioning during Fe(II)-catalyzed Fe(III) oxide recrystallization. To identify how phosphate and sulfate alter Ni redistribution during Fe(III) oxide recrystallization, the effect of these oxoanions on Fe(II)-catalyzed Ni release from and incorporation into hematite and goethite was studied. The effect of phosphate and sulfate on macroscopic Ni adsorption was also investigated, as Ni adsorption is an important intermediate during Ni incorporation into and release from Fe oxides and oxoanions often enhance the adsorption of divalent metal cations, e.g., Cd, Co, Cu, Fe, Pb, and Zn (Benjamin and Bloom, 1981; Balistrieri and Murray, 1982; Diaz-Barrientos et al., 1990; Madrid et al., 1991; Hoins, 1993; Venema et al., 1997; Collins et al., 1999; Jeon et al., 2001; Juang and Wu, 2002; Swedlund et al., 2003; Hinkle et al., 2015). Ni partitioning between adsorbed, incorporated, and aqueous Ni phases was determined through combined X-ray absorption fine structure (XAFS) spectroscopy and mass balance calculations.

2. MATERIALS AND METHODS

2.1 Fe Oxide Preparation

Pure and Ni-substituted hematite and goethite (Hem, NiHem, Goe, and NiGoe, respectively) were prepared following previously published syntheses (Frierdich et al., 2011; Hinkle et al., 2015), modified from the procedures described in Schwertmann and Cornell (2000). After synthesis, Hem and Goe were rinsed and filtered with deionized (DI) water ($>18.2 \text{ M}\Omega\cdot\text{cm}$) to remove excess electrolytes. The NiHem and NiGoe were filtered and washed with 0.25 M HCl for two hours to remove adsorbed Ni, and were then rinsed and filtered with DI water to remove excess electrolytes. The iron oxides were resuspended in DI water and stored in polypropylene bottles wrapped in aluminum foil.

The mineral suspensions were subsequently moved to an anaerobic chamber (Coy Laboratory Products, Inc., 3% H_2 /97% N_2 atmosphere with Pd catalysts) and sparged with the anaerobic chamber atmosphere, as described elsewhere (Hinkle et al., 2015). The mineral suspensions were sparged until a colorimetric indicator test (CHEMets® Kit K-7540) indicated that dissolved O_2 was below the detection limit ($2.5 \mu\text{g L}^{-1}$). A portion of each mineral suspension was then dried at 70°C for mineral characterization by BET analysis (N_2 adsorption, Quantachrome Instruments Autosorb-1) for surface area determination, powder X-ray diffraction (XRD; Bruker D8 Advance X-ray diffractometer, $\text{Cu K}\alpha$ radiation) for phase identification, and fractional and total acid dissolution [described in past research (Frierdich et al., 2011)] for the distribution and extent of Ni substitution. Fluorescence-yield Ni K-edge XAFS spectra were obtained for NiHem and NiGoe wet pastes to ensure consistency with previously published works (Frierdich et al., 2011); the preparation of these samples and collection of these measurements are described below.

2.2 Stock Solution Preparation

An Fe(II) stock solution was prepared from $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ in the anaerobic chamber using deoxygenated DI water, acidified to pH 2 with HCl, and stored in amber polypropylene bottles to prevent photo-oxidation. Na_2HPO_4 , Na_2SO_4 , NiCl_2 , NaCl, and 3-(N-morpholino)propanesulfonic acid hemisodium salt (MOPS) buffer stock solutions were also prepared in the anaerobic chamber using deoxygenated DI water. HCl and NaOH solutions for pH adjustments were transferred to and sparged in the anaerobic chamber more than 90 days before use.

2.3 Macroscopic Ni Adsorption Experiments

The effect of phosphate and sulfate on Ni adsorption onto Fe(III) oxides was investigated through a series of adsorption experiments. The experiments consisted of 1 g L⁻¹ Hem (or Goe) reacted 0 or 0.1 mM phosphate (or sulfate), 10 mM NaCl (for ionic strength buffering), 1.0 mM MOPS buffer, and varying initial Ni concentrations at pH 7.00 ± 0.05 . The experiments were also conducted with mineral-free blanks to assess systematic errors in the initial Ni concentrations and in triplicate for samples reacted with an initial 100 μM Ni. The samples were prepared by adding phosphate (or sulfate), NaCl, MOPS buffer, and Ni to the appropriate amount of deoxygenated DI water in 15 mL conical centrifuge tubes. An aliquot of Hem (or Goe) suspension was then added to the sample, marking the start of the reaction, and the pH of the sample was adjusted to pH 7.00 ± 0.05 using HCl or NaOH. The centrifuge tubes were rotated on end-over-end rotators for five days while wrapped in aluminum foil. The sample pH was checked and adjusted if necessary after 24 hours reaction time. After 5 days of reaction, the pH of each sample was recorded and the samples were filtered (0.22 μm MCE filters; Fisher

Scientific), discarding the first 1 mL of filtrate. The samples were removed from the anaerobic chamber and immediately acidified to 2% HNO₃ (trace metal grade; Fisher Scientific) for inductively coupled plasma-optical emission spectroscopic (ICP-OES; Perkin Elmer Optima 7300 DV) analysis for dissolved P and Ni concentrations. Sulfate concentrations were measured by ion chromatography (IC; Metrohm 881 Compact IC Pro), with samples acidified to 0.5% HCl (trace metal grade; Fisher Scientific). The sample uncertainty (95% confidence level) was calculated for ICP-OES analyses using the triplicate samples and the instrument triplicate measurements.

2.4 Ni Release Experiments

The rate and extent of Fe(II)-catalyzed Ni release from NiHem and NiGoe in the absence and presence of phosphate and sulfate were probed by macroscopic Ni release and X-ray absorption near edge structure (XANES) spectroscopy, heretofore collectively referred to as “Ni release experiments.” The macroscopic Ni release experiments were conducted following the protocol outlined in Frierdich and Catalano (2012): each sample consisted of 1 g L⁻¹ NiHem (or NiGoe), 10 mM NaCl, 1.0 mM MOPS buffer, and 0 or 1.0 mM Fe(II), with samples reacted for 1 hour, 3 hours, 1 day, 2 days, 3 days, 5 days, 8 days, and 14 days. Experiments employed 0 or 0.1 mM phosphate (or sulfate) concentrations; the 14 days samples were prepared in triplicate. The samples were prepared by adding deoxygenated DI water with the appropriate aliquots of NaCl, MOPS buffer, Fe(II), and phosphate (or sulfate). The solutions were adjusted to pH 7.00 ± 0.05. The appropriate amount of NiHem or NiGoe was then added to the solution, marking the beginning of the experiment. Sample pH was checked and adjusted for drift if necessary. The samples were then wrapped in aluminum foil and placed on an end-over-end rotator. At the end

of the prescribed reaction time, the sample pH was recorded and the sample was filtered using 0.22 μm MCE filters (Fisher Scientific). The filtrate samples were acidified and analyzed for dissolved Fe, Ni, and P concentration with ICP-OES and sulfate concentrations with IC following the procedures outlined in the previous section. The macroscopic Ni release data were fit using a second order kinetic model (Electronic Annex), using the approach described by Frierdich and Catalano (2012). To determine how solid-associated Ni partitioning is altered during Ni release in the presence of oxoanions, large batches of the 14 day samples equilibrated at pH 7.5 (to increase the possibility of detecting adsorbed Ni, if present) were filtered and prepared following procedures described below for XAFS spectroscopic measurements. Previous research indicates that increasing pH from 7 to 8 does not alter overall macroscopic Ni release from NiGoe (Frierdich and Catalano, 2012), thus overall macroscopic Ni release likely exhibits the same behavior at pH 7 and 7.5.

2.5 Ni Incorporation Experiments

The effect of sulfate and phosphate on Ni incorporation into Hem and Goe in the presence of aqueous Fe(II) was investigated following a previously published procedure (Frierdich et al., 2011). In these experiments, 4 g L⁻¹ Hem or Goe was reacted with a solution consisting of 0.2 mM Ni, 10 mM NaCl, 1.0 mM MOPS buffer, and varying concentrations of Fe(II), sulfate or phosphate at pH 7.50 ± 0.05 for 30 days. The sulfate experiment samples were reacted with 1.0 mM Fe(II) and 0, 0.1, or 1.0 mM sulfate to maintain consistency with previous research on aqueous Fe(II)-oxoanion-Fe(III) oxide systems conducted under similar conditions (Hinkle et al., 2015). To prevent the precipitation of secondary mineral phases (e.g., vivianite), the phosphate samples were reacted with lower Fe(II) and oxoanion concentrations: 0.5 mM

Fe(II) and 0, 0.1, or 0.5 mM phosphate. At the end of the experiment, the suspensions were filtered and prepared for XAFS spectroscopic measurements following the procedures described below, while the filtrate was collected for ICP-OES analysis. These experiments will be referred to as “Ni incorporation experiments” throughout the paper.

2.6 XAFS Spectroscopic Measurements

Fluorescence-yield Ni K-edge XAFS spectra were collected for samples from the Ni release and Ni incorporation experiments, as well as end-member standards: NiHem, NiGoe, and Ni adsorbed onto Hem and Goe in the presence of sulfate and phosphate. For comparison to the two different sets of experiments, Ni adsorbed samples were prepared by reacting the maximum concentration of phosphate (or sulfate) and the appropriate concentration of Hem (or Goe) for the applicable experiment with 0.2 mM Ni, 10 mM NaCl, and 1.0 mM MOPS buffer for 5 days. The samples were filtered (reusable syringe filter; 0.22 μ m MCE membrane; Fisher Scientific) to collect both filtered solids and filtrate. The filtered solids were packed as wet pastes in polycarbonate sample holders, sealed with 25 μ m Kapton tape, and heat sealed in polyethylene bags to maintain anoxic conditions. Samples were prepared within 48 hours of transport to the Advanced Photon Source (APS) at Argonne National Laboratory. XAFS spectra of samples the standard for the Ni release experiments were collected at beamline 12-BM-B, while XAFS measurements for the Ni incorporation experiment XAFS were made at beamline 9-BM-C. Both beamlines employ Si (111) fixed-offset double-crystal monochromators, which were detuned 30% to reduce the harmonic content of the incident X-ray beam, as well as torroidal focusing and flat harmonic rejection mirrors. The monochromators were calibrated at the Ni K-edge (8333 eV) using a Ni metal foil. Fluorescence-yield spectra were collected using a 12-element energy

dispersive Ge detector.

2.7 Analysis of XAFS Spectra

XAFS spectra were averaged and normalized using IFEFFIT (Newville, 2001) via the Athena interface (Ravel and Newville, 2005). Linear combination fitting (LCF) of normalized XANES spectra was performed using Athena, with Ni-substituted hematite and goethite (NiHem and NiGoe) and Ni adsorbed onto pure hematite (Hem) and goethite (Goe) as end-member standards. The k^3 -weighted extended X-ray absorption fine structure (EXAFS) spectra of Ni adsorbed Hem and Goe standards were quantitatively fit using SixPack (Webb, 2005) using backscattering phase and amplitude functions generated in FEFF 9.6. (Rehr et al., 2010) from the crystal structure of trevorite (NiFe_2O_4) (Hill et al., 1979) and sarcopside $[(\text{Ni}_{0.89}\text{Fe}_{2.11})\text{P}_2\text{O}_8]$ (Ericsson and Nord, 1984). Nonlinear least-squares fits were obtained by refining coordination number (N), interatomic distance (R), and σ^2 (a Debye-Waller type factor) (Table EA1). The EXAFS spectra were fit in R-space from 1-4.2 Å for Ni adsorbed onto goethite and 1-5 Å for Ni adsorbed onto hematite. S_0^2 , the amplitude reduction factor, was fixed to 0.9 (Friedrich et al., 2011). The σ^2 values were determined using a preliminary fit, and were kept constant for each mineral set (e.g., σ^2 of Ni-Fe1 for Hem and Goe is 0.01 and 0.004, respectively; σ^2 of Ni-Fe2 for Hem and Goe is 0.009 and 0.008, respectively) to better compare fits between different conditions and oxoanions.

3. RESULTS

3.1 Properties of Minerals and Materials

The minerals prepared and used in these experiments have similar properties as those

reported in previous studies (Friedrich et al., 2011; Hinkle et al., 2015). BET surface areas for Hem, Goe, NiHem and NiGoe are 30.1, 42.0, 12.0, and 21.7 m² g⁻¹, respectively. The Ni content of NiHem and NiGoe are 1.9 and 1.4 mol %, respectively. The fractional dissolution of Ni and Fe from NiHem and NiGoe is near congruent (Fig. EA1), in agreement with prior studies of Ni substitution in Fe oxides (Sidhu et al., 1978; Lim-Nunez and Gilkes, 1985; Wells et al., 2001; Friedrich and Catalano, 2012). Ni EXAFS spectral fits of the NiHem and NiGoe materials (not shown) are consistent with EXAFS spectra from previous studies, and are described in detail therein (Singh et al., 2002; Friedrich et al., 2011).

3.2 Sulfate and Phosphate Coadsorption with Ni

The macroscopic adsorption of Ni onto both Hem and Goe in the presence and absence of phosphate or sulfate are well described by Langmuir isotherms (Fig. 1, Table 1). Consistent with previous research (Arai, 2008), Hem shows a greater affinity for Ni than Goe. The presence of 0.1 mM sulfate has little effect on Ni adsorption onto Goe, but slightly enhances Ni adsorption onto Hem. The addition of 0.1 mM phosphate, however, increases Ni adsorption by ~165% for both the Goe and Hem systems. Ni enhances both phosphate and sulfate adsorption onto Hem to a greater degree than onto Goe (Figs. EA2-3). Phosphate adsorption increases linearly with increasing Ni adsorption ($R^2 > 0.8$) (Fig. EA2B), but there is no clear trend for sulfate adsorption (Fig. EA3B).

The EXAFS spectra of Ni adsorbed onto Hem and Goe in the presence of sulfate or phosphate show little variation with oxoanion or mineral concentration and are well reproduced by structural model fits (Fig. 2). The local coordination environment of Ni adsorbed to Goe and Hem, with the exception of 1 g L⁻¹ Hem reacted with phosphate, are in agreement with the

observations of Frierdich et al. (2011) and Arai (2008) for oxoanion-free systems. This indicates that sulfate has little effect on Ni adsorption mechanisms onto Fe(III) oxides. Phosphate also has no observed effect on Ni adsorption mechanisms on goethite or, at high mineral concentrations (4 g L^{-1} , used for the Ni incorporation experiments), on hematite. However, at low Hem concentration (1 g L^{-1} , used for the Ni release experiments), Ni coordination changes, suggesting the presence of a Ni- PO_4 ternary complexes. This is supported by the need to include a P neighbor at $\sim 3.8 \text{ \AA}$ to reproduce the EXAFS spectrum of this sample (Table EA1). In addition, the corner-sharing Ni complex (interatomic Ni-Fe distance of $\sim 4.10 \text{ \AA}$) does not appear due to a low availability of surface sites. These large effects on Ni adsorption in the presence of phosphate indicate that Ni-phosphate ternary complexes form, while the effect of sulfate is less substantial, suggesting that Ni-sulfate interactions may be dominated by electrostatic interactions.

3.3 Effect of Sulfate and Phosphate on Ni Release

NiHem and NiGoe were reacted in the presence and absence of sulfate, phosphate, and Fe(II) to investigate how oxoanions alter Ni release to solution. In the absence of aqueous Fe(II) and oxoanions, 0.8 and $0.7 \text{ }\mu\text{M}$ Ni is released from NiHem and NiGoe, respectively, to solution over 14 days, corresponding to 0.32 and 0.44% of the total incorporated Ni being released (Fig. 3). Sulfate does not affect Ni release from either mineral in the Fe(II)-free system. The presence of phosphate, however, suppresses Ni release from NiGoe to $0.31 \text{ }\mu\text{M}$ Ni and inhibits Ni release from NiHem, with the amount of Ni released below the detection limit ($0.1 \text{ }\mu\text{M}$).

The presence of aqueous Fe(II) greatly increases Ni release from Ni-substituted Fe(III) oxides (Frierdich et al., 2011; Frierdich and Catalano, 2012) due to Fe(II)-Fe(III) ET-AE

reactions increasing the rate of iron oxide recrystallization (Pedersen et al., 2005; Handler et al., 2009; Latta et al., 2012b; Gorski et al., 2012; Frierdich et al., 2014). The addition of oxoanions does not appear to alter the rate of Ni release from Fe(III) oxides, but the overall amount of Ni released is substantially suppressed by phosphate. Fe(II)-catalyzed Ni release from NiHem and NiGoe in the presence and absence of oxoanions is consistent with a second-order rate reaction, in agreement with past research of oxoanion-free systems (Frierdich and Catalano, 2012). The second-order rate reaction describing the Ni release data in the current paper was confirmed following the integral method (Brantley and Conrad, 2008). The kinetic fit parameters (Table 2) show that the overall amount of Ni released is less for NiHem than for NiGoe in the absence of oxoanions (with 1.3% and 9% of substituted Ni released, respectively), consistent with past research (Frierdich et al., 2011; Frierdich and Catalano, 2012). The addition of 0.1 mM sulfate has no effect on Ni release from NiHem and NiGoe, with the fit results within error of those for the oxoanion-free system. Phosphate suppresses the total Ni released from NiHem and NiGoe to just 0.64% and 1.6%, respectively, meaning that an additional 0.66% and 7.4% of the preincorporated Ni remains associated with the solid phase relative to the oxoanion-free experiments.

To investigate the origin of the increase in solid-associated Ni upon phosphate addition during these Ni release experiment, the relative amounts of incorporated and adsorbed Ni were determined with XANES spectroscopy. The fraction of Ni associated with the solid that remains incorporated at the end of the Ni release experiments was calculated by least-squares linear combination fitting (LCF) of the XANES data, using the Ni substituted Fe(III) oxides and Ni adsorbed onto Fe (III) oxides as end-member standards. The LCF results (Fig. 4, Table 2) show that there is no change in the fraction of Ni incorporated, when in the absence or presence of

oxoanions, for either the NiHem or NiGoe systems, with 1.00 and 0.98, respectively, of solid-associated Ni remaining incorporated at the end of the release experiments. These results show that Ni is not accumulating as an adsorbed layer during Ni release; any Ni that readsorbs to the surface is reincorporated during Fe(II)-catalyzed Fe(III) oxide recrystallization. Thus, these results show that the decrease in macroscopic Ni release from Goe with phosphate cannot solely be due to enhanced readsorption, because that scenario requires 7.4% of the solid-associated Ni to be adsorbed, well in excess of the LCF uncertainty ($\pm 2\%$). In the hematite system, the LCF uncertainty is greater than the increase in Ni adsorption needed to explain the decrease in macroscopic Ni release from NiHem with phosphate. However, Ni adsorption onto both Hem and Goe increases substantially upon phosphate addition and it is thus unlikely that buildup of adsorbed Ni during Ni release is an important process for Hem but is irrelevant in the Goe system.

3.4 Effect of Sulfate and Phosphate on Ni Incorporation

XAFS spectroscopy was also used to assess the effect of sulfate and phosphate on the reverse process, Fe(II)-catalyzed Ni incorporation into pure Hem and Goe (Fig. 5). The presence of three isosbestic points when comparing the XANES spectra of the experimental samples and the adsorbed Ni and Ni substituted Fe(III) oxide standards (Fig. EA4) suggest that the samples contain mixtures of adsorbed and incorporated Ni. This is consistent with previous findings of Fe(II)-catalyzed Ni incorporation into Hem and Goe (Friedrich et al., 2011). Fitting of the experimental XANES spectra (Table 3) quantified the fraction of solid-associated Ni that is incorporated versus adsorbed. These fitting results were combined with the total concentration of Ni associated with the solid, obtained from the filtrate ICP-OES data, to calculate by mass

balance the concentration of incorporated and adsorbed Ni (Table 3). The uncertainties in the calculated incorporated and adsorbed Ni concentrations were obtained using both the uncertainty in the triplicate ICP-OES measurements and the uncertainty in the LCF calculations. In the absence of Fe(II), ~85% of the initial Ni reacted with Hem and Goe is associated with the solid phase at the end of the 30 day reaction. Of that solid-associated Ni, $1 \pm 4 \mu\text{M}$ and $27 \pm 3 \mu\text{M}$ Ni is incorporated into Hem and Goe, respectively, consistent with past studies of Ni incorporation into goethite in natural and aged synthetic samples (Manceau et al., 2000; Singh et al., 2002; Carvalho-e-Silva et al., 2003). The addition of sulfate increases overall Ni incorporation into Hem and Goe. In contrast, addition of phosphate suppresses Ni incorporation into Goe; Ni incorporation into Hem is within error of zero regardless of the amount of phosphate present. These results indicate that Ni incorporation into Fe(III) oxide minerals in the absence of Fe(II) is affected by oxoanions.

The addition of Fe(II) substantially increases Ni incorporation into Goe, but suppresses the overall amount of sorbed Ni in the Goe system, indicative of competitive adsorption between aqueous Fe(II) and Ni (Table 3). Aqueous Fe(II) does not alter the total amount of sorbed Ni in the Hem system, but does increase Ni incorporation. The lack of competitive adsorption effects between Ni and Fe(II) on Hem suggests that the Ni binding affinity for Hem is greater than for Goe, consistent with the adsorption isotherm measurements (Fig. 1) and past observations (Arai, 2008). In the presence of 1.0 mM Fe(II), equivalent Ni concentrations incorporate into the solid phases and adsorb to the mineral surfaces, with $92 \pm 6 \mu\text{M}$ and $52 \pm 3 \mu\text{M}$ Ni both incorporated and adsorbed in the Hem and Goe systems, respectively. Addition of 0.5 mM Fe(II) (used in the phosphate experiments to prevent vivianite precipitation) results in less Ni incorporation, with $0.67 \pm 4 \mu\text{M}$ and $0.49 \pm 3 \mu\text{M}$ Ni incorporated into Hem and Goe, respectively.

Sulfate modifies the partitioning of Ni during Fe(II)-catalyzed Hem and Goe recrystallization. The co-addition of 0.1 mM sulfate and 1.0 mM Fe(II) to a Goe suspension increases the overall concentration of Ni associated with the solid as a result of increased Ni incorporation (Table 3). The addition of 1.0 mM sulfate to this system slightly reduces Ni incorporation relative to the 0.1 mM sulfate experiment. In both Goe experiments, Ni adsorption remains statistically invariant. In contrast, 0.1 mM sulfate has no effect on Ni incorporation into or adsorption onto Hem in the presence of 1.0 mM Fe(II), while 1.0 mM sulfate causes a reduction in Ni incorporation but an increase in Ni adsorption.

Phosphate also affects Ni partitioning during Fe(II)-catalyzed recrystallization of Hem and Goe, but these effects are distinct from the changes caused by sulfate. The addition of 0.5 mM phosphate and Fe(II) substantially increases Ni adsorption onto the Goe surface (Table 3). In addition, phosphate enhances the amount of Ni incorporated into Goe (Table 3). In the Hem system, however, the addition of phosphate substantially decreases Ni incorporation, with 0.5 mM phosphate causing complete inhibition. The effects of phosphate are not the result of precipitation of phosphate-bearing solids. The Ni K-edge XANES spectra (Fig. 5) lack a shoulder at ~8334 eV that is present in the spectrum of Ni-phosphate minerals (e.g., arupite, $\text{Ni}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) (Singh, 2006). Prior work shows that vivianite will not form under the conditions studied (Hinkle et al., 2015), and the spectrum of Ni substituting in vivianite is also expected to display a shoulder given the similarity of the Ni XANES spectrum of arupite (Singh, 2006) and the Fe XANES spectrum of vivianite (Cosmidis et al., 2014).

4. DISCUSSION

4.1 Oxoanion- and Mineral-Specific Effects on Ni Repartitioning

4.1.1 Mechanisms of Oxoanion Effects on Ni Repartitioning

Phosphate in general has a substantially greater effect on Ni repartitioning during Fe(II)-catalyzed recrystallization than sulfate. In the hematite system, phosphate strongly suppresses Ni incorporation into and release from the mineral while sulfate only slightly alters the behavior seen in oxoanion-free systems. Fe(II)-catalyzed Ni repartitioning in Fe(III) oxides is fundamentally controlled by adsorption reactions and the effects of oxoanions on this process are likely the result of molecular interactions of adsorbates on mineral surfaces. Both phosphate and sulfate form surface complexes with bidentate symmetry on hematite (Paul et al., 2005; Elzinga and Kretzschmar, 2013; Jubb et al., 2013; Hinkle et al., 2015). While phosphate clearly forms bidentate binuclear surface complexes, the nature of sulfate surface complexes is unclear regarding whether these are inner- or outer-sphere (or a mixture). The formation of bidentate binuclear surface complexes likely suppresses hematite dissolution and growth (Bondietti et al., 1993; Stumm, 1997). Therefore phosphate surface complexes may effectively prevent hematite recrystallization, inhibiting Fe(II)-catalyzed Ni repartitioning. Adsorbate inhibition of recrystallization, however, cannot be a dominant process in the sulfate-hematite system because Ni incorporation into hematite in the absence of Fe(II) actually increases upon addition of sulfate. The subsequent decrease in Ni incorporation into hematite when 1.0 mM sulfate and 1.0 mM Fe(II) are added thus suggests that Fe(II)-sulfate-hematite interactions, which include the formation of Fe(II)-sulfate ternary surface complexes (Hinkle et al., 2015), are likely responsible for the observed effect.

Oxoanion-Fe(II) interactions are also important in controlling Ni repartitioning behavior in the phosphate-goethite system, as phosphate suppresses Ni incorporation in the absence of Fe(II) but enhances Ni incorporation in the presence of Fe(II) (Table 3). The Fe(II)-free

experiments are in agreement with previous research finding that phosphate suppresses goethite dissolution in the absence of Fe(II) (Stumm, 1993; Biber et al., 1994). The effect of phosphate in the Fe(II) system is consistent with a recent isotope exchange study demonstrating that phosphate enhances the rate and extent of Fe atom exchange between goethite and aqueous Fe(II) (Latta et al., 2012a). It should be noted that the present study was conducted under different Fe(II) and phosphate surface loadings, therefore a direct comparison with the results from Latta et al. (2012a) is not possible. If phosphate does enhance Fe(II)-catalyzed goethite recrystallization under the conditions used in the current study, then macroscopic Ni release should also increase. In phosphate-free Fe(II)-catalyzed Ni release experiments, most (>85%) of the Ni released is actually reincorporated into goethite rather than remaining in the aqueous phase (Friedrich et al., 2012). Because phosphate substantially increases Ni adsorption (Fig. 1; Table 1), a necessary intermediate step during incorporation, phosphate likely increases Ni reincorporation during Fe(II)-catalyzed goethite recrystallization, thereby decreasing macroscopic Ni release. Phosphate may thus enhance Ni incorporation into goethite in both the Fe(II)-catalyzed Ni release and Ni incorporation experiments by increasing Fe(II)-catalyzed goethite recrystallization (Latta et al., 2012a) through increased Fe(II) surface coverage (Hinkle et al., 2015), and by substantially increasing Ni (re)adsorption to (and therefore Ni (re)incorporation into) the surface.

Although sulfate also enhances Fe(II)-catalyzed Ni incorporation into goethite, its effect on Ni release differs substantially from the phosphate-goethite system. Interestingly, sulfate exhibits different effects on total macroscopic Ni sorption onto goethite in the absence (Fig. 1; Table 1) and presence of Fe(II) (Table 3). These results suggest that sulfate moderates Ni-Fe(II) competitive adsorption on goethite, preferentially increasing overall Ni sorption without

affecting Fe(II) surface coverage. By lessening Ni-Fe(II) competitive adsorption effects on goethite, sulfate allows more Ni to adsorb to the surface and thus become incorporated into goethite. Competitive adsorption of Ni and Fe(II) is likely less substantial in the Ni release experiments because of the lower Ni concentrations. As a result, sulfate does not appreciably affect Ni release.

4.1.2 Mineral-Specific Effects

Although the mechanisms through which each oxoanion alters Ni cycling in Fe(III) oxides differ depending on the specific oxoanion-mineral system, goethite- and hematite-specific effects are observed, suggesting these minerals exhibit distinct behaviors during biogeochemical Fe cycling in the presence of oxoanions. Both oxoanions decrease Fe(II)-catalyzed incorporation of Ni into hematite and phosphate suppresses Ni release from this mineral. These observations suggest that Fe(II)-catalyzed Ni cycling through hematite is inhibited by oxoanions because such species alter Fe(II) adsorption mechanisms and hematite recrystallization. Conversely, this research indicates that phosphate and sulfate do not prevent Ni repartitioning during Fe(II)-catalyzed goethite recrystallization, suggesting that these oxoanions do not interfere with Fe(II)-Fe(III) ET-AE processes. Instead, phosphate and sulfate largely affect Ni cycling through goethite by increasing the extent of Ni adsorption. These results suggest that the mineral identity is an important controlling factor in predicting how oxoanions may alter processes associated with Fe(II)-Fe(III) ET-AE reactions.

4.2 Environmental and Geological Implications of Trace Element Fate

This study demonstrates that oxoanions common to aquatic systems affect trace element

fate at redox interfaces in environmental and geological systems. Because trace metals are often associated with (Singh and Gilkes, 1992; Manceau et al., 2002; Cornell and Schwertmann, 2003) and incorporated into (Singh and Gilkes, 1992; Manceau et al., 2000; Carvalho-e-Silva et al., 2003) naturally-occurring iron oxides, micronutrient bioavailability is often limited by the extractability of these trace metals from iron oxides. Phosphate suppresses net Fe(II)-catalyzed Ni release from hematite. Therefore Ni bioavailability in hematite-dominated environments with Fe redox gradients may be lower in systems with substantial phosphate uptake by iron oxides [e.g., hydrothermal vents (Froelich et al., 1982; Berner et al., 1993) and waterlogged subtropical or tropical soils (Parfitt, 1989; Chacon, 2006)]. However, Ni bioavailability in systems with large reactive goethite fractions and coexisting aqueous Fe(II) [e.g., soils, lacustrine and marine sediments (Drodt et al., 1997; Cornell and Schwertmann, 2003; van der Zee et al., 2003)] will likely not be affected by oxoanion concentration, as phosphate and sulfate do not impede Ni cycling through goethite.

Heavy metal contamination of soils and aquatic systems is often mediated by iron or manganese oxide adsorption processes (Mench et al., 1994; Fuller and Harvey, 2000; Sowder et al., 2003; Isaure et al., 2005; Waychunas et al., 2005; Tankere-Muller et al., 2007). Phosphate exerts a large effect on macroscopic Ni adsorption onto both hematite and goethite, resulting in decreased Ni concentrations in the aqueous phase. Thus, phosphate may exert a substantial control on Ni retention in riparian soils by increasing Ni adsorption to iron oxide minerals, an important control on the contamination of nearby soils (Sowder et al., 2003). Further entrapment of Ni by incorporation into hematite may, however, be prevented by phosphate and sulfate in these systems. Conversely, enhanced Ni incorporation into goethite by sulfate and phosphate does not translate into increased Ni entrapment, as Ni cycling is not obstructed by either

452 oxoanion.

453 This research shows that Ni cycling in iron oxides is altered by phosphate and sulfate
454 differently depending on both the mineral identity and the concentration and identity of the
455 oxoanions, which may have important ramifications for the preservation of Ni in the rock record.
456 For example, these results indicate that the amount of Ni incorporated into banded iron
457 formations (BIFs), which formed in oceans containing dissolved Fe(II) (Holland, 1973; Holland,
458 1984; Derry and Jacobsen, 1990; Holland, 2006), was likely dependent on a number of factors,
459 including the oceanic sulfate and phosphate concentrations. The results of this research also
460 indicate that the retention of Ni may have been affected by the identity of minerals formed
461 through phase transformations of initial iron (oxyhydr)oxide precipitates during BIF deposition,
462 burial, and lithification. Phosphate could further affect the amount of Ni incorporated into BIFs
463 during lithification by preferentially enhancing Ni adsorption onto iron oxides. Phosphate and
464 sulfate may also alter trace element partitioning during diagenesis and fluid flow through
465 sediments. Thus, the relationship between Ni concentrations in BIFs and ancient seawater is
466 almost certainly not straightforward, as has been assumed in prior studies, e.g., (Konhauser et al.,
467 2009). Instead, recorded Ni concentrations will have a highly non-linear dependence on fluid
468 composition, mineral properties, and depositional and post-depositional processes. The present
469 work clearly shows that species incompatible with Fe(III) oxide structures, such as phosphate
470 and sulfate, still have substantial impacts on the partitioning of structurally compatible metals in
471 a variety of environments, potentially altering micronutrient bioavailability, contaminant
472 sequestration, and geochemical proxies.

474 **5. ACKNOWLEDGMENTS**

This research was supported by the National Science Foundation (NSF), Division of Earth Sciences, Geobiology and Low-Temperature Geochemistry Program through Grant No. EAR-1056480. ICP-OES analyses were conducted at the Nano Research Facility at Washington University, supported by the NSF through award no. ECS-0335765. Use of the Bruker D8 Advance XRD at Washington University in St. Louis is supported by the National Science Foundation through award no. EAR-1161543. XAFS spectra were collected at beamlines 9-BM-C and 12-BM-B at the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, which is supported by the U.S. DOE under Contract No. DE-AC02-06CH11357. The authors thank Jennifer Houghton and Sanmathi Chavalmane for their help with collecting IC and ICP-OES analyses, respectively.

ASSOCIATED CONTENT

Electronic Annex. Additional information regarding second order kinetic fits of the macroscopic Ni release data, figures of fractional dissolution of Ni substituted Fe(III) oxides and macroscopic oxoanion adsorption, and a table of XAFS fitting results for Ni adsorbed onto Fe(III) oxides.

6. REFERENCES

- Arai Y. (2008) Spectroscopic evidence for Ni(II) surface speciation at the iron oxyhydroxides–water interface. *Environ. Sci. Technol.* **42**, 1151-1156.
- Balistrieri L. S. and Murray J. W. (1982) The adsorption of Cu, Pb, Zn, and Cd on goethite from major ion seawater. *Geochim. Cosmochim. Acta* **40**, 1253-1265.
- Beard B. L., Handler R. M., Scherer M. M., Wu L., Czaja A. D., Heimann A. and Johnson C. M. (2010) Iron isotope fractionation between aqueous ferrous iron and goethite. *Earth Planet. Sci. Lett.* **295**, 241-250.

- 501 Benjamin M. M. and Bloom N. S. (1981) Effects of strong binding of anionic adsorbates on
502 adsorption of trace metals on amorphous iron oxyhydroxide. In *Adsorption From*
503 *Aqueous Solutions* (ed. P.H. Tewari), Plenum Press, New York. pp. 41-60.
- 504 Berner R. A., Ruttenberg K. C., Ingall E. D. and Rao, J. L. (1993) The nature of phosphorus
505 burial in modern marine sediments. In *Interactions of C, N, P, and S Biogeochemical*
506 *Cycles and Global Change* (eds. R. Wollast, F.T. Mackenzie and L. Chou), Springer-
507 Verlag, Berlin. pp. 365-378.
- 508 Biber M. V., dos Santos Afonso M. and Stumm W. (1994) The coordination chemistry of
509 weathering: IV. Inhibition of the dissolution of oxide minerals. *Geochim. Cosmochim.*
510 *Acta* **58**, 1999-2010.
- 511 Bondietti G., Sinniger J. and Stumm W. (1993) The reactivity of Fe(III) (hydr)oxides: effects of
512 ligands in inhibiting the dissolution. *Colloids Surf., A* **79**, 157-167.
- 513 Borch T., Masue, Y., Kukkadapu R. K. and Fendorf S. (2007) Phosphate imposed limitations on
514 biological reduction and alteration of ferrihydrite. *Environ. Sci. Technol.* **41**, 166-172.
- 515 Brantley S. L. and Conrad C. F. (2008) Analysis of Rates of Geochemical Reactions, In *Kinetics*
516 *of Water-Rock Interaction* (eds. J.D. Kubicki and A.F. White). Springer, New York. pp.
517 1-37.
- 518 Brown G. E., Henrich V., Casey W., Clark D. and Eggleston C. M. (1999) Metal oxide surfaces
519 and their interactions with aqueous solutions and microbial organisms. *Chem. Rev.* **99**,
520 77-174.
- 521 Brown G. E. and Parks G. A. (2001) Sorption of trace elements on mineral surfaces: Modern
522 perspectives from spectroscopic studies, and comments on sorption in the marine
523 environment. *Int. Geol. Rev.* **43**, 963-1073.
- 524 Carvalho-e-Silva M. L., Ramos A. Y., Tolentino H. C. N., Enzweiler J., Netto S. M. and Alves
525 M. D. C. M. (2003) Incorporation of Ni into natural goethite: An investigation by X-ray
526 absorption spectroscopy. *Am. Mineral.* **88**, 876-882.
- 527 Catalano J. G., Fenter P., Park C., Zhang Z. and Rosso K. M. (2010) Structure and oxidation
528 state of hematite surfaces reacted with aqueous Fe(II) at acidic and neutral pH. *Geochim.*
529 *Cosmochim. Acta* **74**, 1498-1512.
- 530 Chacon N., Silver W. L., Dubinsky E. A. and Cusak D. F. (2006) Iron reduction and soil
531 phosphorus solubilization in humid tropical forests soils: The roles of labile carbon pools
532 and an electron shuttle compound. *Biogeochemistry* **78**, 67-84.
- 533 Collins C. R., Ragnarsdottir K. V. and Sherman D. M. (1999) Effect of inorganic and organic
534 ligands on the mechanism of cadmium sorption to goethite. *Geochim. Cosmochim. Acta*
535 **63**, 2989-3002.
- 536 Cosmidis J., Benzerara K., Morin G., Busigny V., Lebeau O., Jézéquel D., Noël V., Dublet G.

- 537 and Othmane G. (2014) Biomineralization of iron-phosphates in the water column of
538 Lake Pavin (Massif Central, France). *Geochim. Cosmochim. Acta* **126**, 78-96.
- 539 Cornell R. M. and Schwertmann U. (2003) *The iron oxides: Structure, properties, reactions,*
540 *occurrences and uses*. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
- 541 Crosby H. A., Johnson C. M., Roden E. E. and Beard B. L. (2005) Coupled Fe(II)-Fe(III)
542 electron and atom exchange as a mechanism for Fe isotope fractionation during
543 dissimilatory iron oxide reduction. *Environ. Sci. Technol.* **39**, 6698-6704.
- 544 Derry L. A. and Jacobsen S. B. (1990) The chemical evolution of Precambrian seawater:
545 Evidence from REEs in banded iron formations. *Geochim. Cosmochim. Acta* **54**, 2965-
546 2977.
- 547 Diaz-Barrientos E., Madrid L., Contreras M. C. and Morillo E. (1990) Simultaneous adsorption
548 of zinc and phosphate on synthetic lepidocrocite. *Aust. J. Soil Res.* **28**, 549-557.
- 549 Drodt M., Trautwein A. X., König I., Suess E. and Koch C. B. (1997) Mössbauer spectroscopic
550 studies on the iron forms of deep-sea sediments. *Phys. Chem. Miner.* **24**, 281-293.
- 551 Eggleston C. M., Hug S., Stumm W., Sulzberger B. and Dos Santos Afonso M. (1998) Surface
552 complexation of sulfate by hematite surfaces: FTIR and STM observations. *Geochim.*
553 *Cosmochim. Acta* **62**, 585-593.
- 554 Elzinga E. J. and Kretzschmar R. (2013) *In situ* ATR-FTIR spectroscopic analysis of the co-
555 adsorption of orthophosphate and Cd(II) onto hematite. *Geochim. Cosmochim. Acta* **117**,
556 53-64.
- 557 Ericsson T. and Nord A. G. (1984) Strong cation ordering in olivine-related (Ni, Fe)-sarcopsides:
558 A combined Mössbauer, X-ray and neutron diffraction study. *Am. Mineral.* **69**, 889-895.
- 559 Frierdich A. J., Beard B. L., Reddy T. R., Scherer M. M. and Johnson C. M. (2014) Iron isotope
560 fractionation between aqueous Fe(II) and goethite revisited: New insights based on a
561 multi-direction approach to equilibrium and isotopic exchange rate modification.
562 *Geochim. Cosmochim. Acta* **139**, 383-398.
- 563 Frierdich A. J. and Catalano J. G. (2012) Controls on Fe(II)-activated trace element release from
564 goethite and hematite. *Environ. Sci. Technol.* **46**, 1519-1526.
- 565 Frierdich A. J., Luo Y. and Catalano J. G. (2011) Trace element cycling through iron oxide
566 minerals during redox-driven dynamic recrystallization. *Geol.* **39**, 1083-1086.
- 567 Frierdich A. J., Scherer M. M., Bachman J. E., Engelhard M. H., Rapponotti B. W. and Catalano
568 J. G. (2012) Inhibition of trace element release during Fe(II)-activated recrystallization of
569 Al-, Cr-, and Sn-substituted goethite and hematite. *Environ. Sci. Technol.* **46**, 10031-
570 10039.
- 571 Froelich P. N., Bender M. L. and Luedtke N. A. (1982) The marine phosphorus cycle. *Am. J. Sci.*

572 **282**, 474-511.

573 Fuller C. C. and Harvey J. W. (2000) Reactive uptake of trace metals in the hyporheic zone of a
574 mining-contaminated stream, Pinal Creek, Arizona. *Environ. Sci. Technol.* **34**, 1150-
575 1155.

576 Gorski C. A., Handler R. M., Beard B. L., Pasakarnis T., Johnson C. M. and Scherer M. M.
577 (2012) Fe atom exchange between aqueous Fe²⁺ and magnetite. *Environ. Sci. Technol.*
578 **46**, 12399-12407.

579 Gorski C. A. and Scherer M. M. (2011) Fe²⁺ sorption at the Fe oxide-water interface: A revised
580 conceptual framework. *Aquatic Redox Chemistry* **1071**, 477-517.

581 Handler R. M., Beard B. L., Johnson C. M. and Scherer M. M. (2009) Atom exchange between
582 aqueous Fe(II) and goethite: an Fe isotope tracer study. *Environ. Sci. Technol.* **43**, 1102-
583 1107.

584 Handler R. M., Friedrich A. J., Johnson C. M., Rosso K. M., Beard B. L., Wang C., Latta D. E.,
585 Neumann A., Pasakarnis T. and Premaratne W. (2014) Fe (II)-catalyzed recrystallization
586 of goethite revisited. *Environ. Sci. Technol.* **48**, 11302-11311.

587 Hansel C. M., Benner S. G. and Fendorf S. (2005) Competing Fe(II)-induced mineralization
588 pathways of ferrihydrite. *Environ. Sci. Technol.* **39**, 7147-7153.

589 Hansel C. M., Benner S. G., Neiss J., Dohnalkova A., Kukkadapu R. K. and Fendorf S. (2003)
590 Secondary mineralization pathways induced by dissimilatory iron reduction of
591 ferrihydrite under advective flow. *Geochim. Cosmochim. Acta* **67**, 2977-2992.

592 Hansel C. M., Benner S. G., Nico P. and Fendorf S. (2004) Structural constraints of ferric
593 (hydr)oxides on dissimilatory iron reduction and the fate of Fe(II). *Geochim. Cosmochim.*
594 *Acta* **68**, 3217-3229.

595 Hill R. J., Craig, J. R. and Gibbs, G. V. (1979) Systematics of the spinel structure type. *Phys.*
596 *Chem. Miner.* **4**, 317-339.

597 Hinkle M. A. G., Wang Z., Giammar D. E. and Catalano J. G. (2015) Interaction of Fe(II) with
598 phosphate and sulfate on iron oxide surfaces. *Geochim. Cosmochim. Acta* **158**, 130-146..

599 Hoins U. (1993) Ligand effect on the adsorption of heavy metals: The sulfate-cadmium-goethite
600 case. *Water, Air, Soil Pollut.* **68**, 241-255.

601 Holland H. D. (1973) The Oceans; A Possible Source of Iron in Iron-Formations. *Econ. Geol.*
602 **68**, 1169-1172.

603 Holland H. D. (1984) *The chemical evolution of the atmosphere and oceans*. Princeton
604 University Press, New Jersey.

605 Holland H. D. (2006) The oxygenation of the atmosphere and oceans. *Philos. T. Roy. Soc. B*.

- 606 **361**, 903-915.
- 607 Isaure M. -P., Manceau A., Geoffroy N., Laboudigue A., Tamura N. and Marcus M. A. (2005)
608 Zinc mobility and speciation in soil covered by contaminated dredged sediment using
609 micrometer-scale and bulk-averaging X-ray fluorescence, absorption and diffraction
610 techniques. *Geochim. Cosmochim. Acta* **69**, 1173-1198.
- 611 Jeon B. H., Dempsey B. A., Burgos W. D. and Royer R. A. (2001) Reactions of ferrous iron with
612 hematite. *Colloids Surf., A* **191**, 41-55.
- 613 Juang R. and Wu W. (2002) Adsorption of sulfate and copper(II) on goethite in relation to the
614 changes of zeta potentials. *J. Colloid Interface Sci.* **249**, 22-29.
- 615 Jubb A. M., Verreault D., Posner R., Criscenti L. J., Katz L. E. and Allen H. C. (2013) Sulfate
616 adsorption at the buried hematite/solution interface investigated using total internal
617 reflection (TIR)-Raman spectroscopy. *J. Colloid Interface Sci.* **400**, 140-146.
- 618 Konhauser K., Pecoits E., Lalonde S. V., Papineau D., Nisbet E. G., Barley M. E., Arndt N. T.,
619 Zahnle K. and Kamber B. S. (2009) Oceanic nickel depletion and a methanogen famine
620 before the Great Oxidation Event. *Nature* **458**, 750-753.
- 621 Larese-Casanova P. and Scherer M. M. (2007) Fe(II) sorption on hematite: New insights based
622 on spectroscopic measurements. *Environ. Sci. Technol.* **41**, 471-477.
- 623 Latta D. E., Bachman J. E. and Scherer M. M. (2012a) Fe electron transfer and atom exchange in
624 goethite: Influence of Al-substitution and anion sorption. *Environ. Sci. Technol.* **46**,
625 10614-10623.
- 626 Latta D. E., Gorski C. A. and Scherer M. M. (2012b) Influence of Fe²⁺-catalyzed iron oxide
627 recrystallization on metal cycling. *Biochem. Soc. T.* **40**, 1191-7.
- 628 Lim-Nunez R. and Gilkes R. J. (1985) Acid dissolution of synthetic metal-containing goethites
629 and hematites. In *Proceedings of the International Clay Conference*, pp. 197-204.
- 630 Madrid L., Diaz-Barrientos E. and Contreras M. C. (1991) Relationships between zinc and
631 phosphate adsorption on montmorillonite and an iron oxyhydroxide. *Aust. J. Soil Res.* **29**,
632 239-247.
- 633 Majzlan J. and Myneni S. C. B. (2005) Speciation of iron and sulfate in acid waters: Aqueous
634 clusters to mineral precipitates. *Environ. Sci. Technol.* **39**, 188-194.
- 635 Manceau A., Schlegel M. L., Musso M., Sole V. A., Gauthier C., Petit P. E. and Trolard F.
636 (2000) Crystal chemistry of trace elements in natural and synthetic goethite. *Geochim.*
637 *Cosmochim. Acta* **64**, 3643-3661.
- 638 Manceau A., Tamura N., Celestre R. S., MacDowell A. A., Geoffroy N., Sposito G. and Padmore
639 H. A. (2002) Molecular-scale speciation of Zn and Ni in soil ferromanganese nodules
640 from loess soils of the Mississippi Basin. *Environ. Sci. Technol.* **37**, 75-80.

- 641 Mench M. J., Didier V. L., Loffler M., Gomez A. and Masson P. (1994) A mimicked in situ
642 remediation study of metal-contaminated soils with emphasis on cadmium lead. *J.*
643 *Environ. Qual.* **23**, 58-63.
- 644 Newville M. (2001) IFEFFIT: interactive EXAFS analysis and FEFF fitting. *J. Synchrotron*
645 *Radiat.* **8**, 322-324.
- 646 Parfitt R. L., Hume L. J. and Sparling G.P. (1989) Loss of availability of phosphate in New
647 Zealand soils. *J. Soil Sci.* **40**, 371-382.
- 648 Paul K. W., Borda M. J., Kubicki J. D. and Sparks D. L. (2005) Effect of dehydration on sulfate
649 coordination and speciation at the Fe-(hydr)oxide-water interface: A Molecular
650 Orbital/Density Functional Theory and Fourier transform infrared spectroscopic
651 investigation. *Langmuir* **21**, 11071-11078.
- 652 Pedersen H. D., Postma D., Jakobsen R. and Larsen O. (2005) Fast transformation of iron
653 oxyhydroxides by the catalytic action of aqueous Fe(II). *Geochim. Cosmochim. Acta* **69**,
654 3967-3977.
- 655 Ravel B. and Newville M. (2005) ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-
656 ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Radiat.* **12**, 537-541.
- 657 Rehr J. J., Kas J. J., Vila F. D., Prange M. P. and Jorissen K. (2010) Parameter-free calculations
658 of x-ray spectra with FEFF9. *Phys. Chem. Chem. Phys.* **12**, 5503-5513.
- 659 Schwertmann U. and Cornell R. M. (2000) *Iron oxides in the laboratory: preparation and*
660 *characterization*. Wiley-VCH, Weinheim.
- 661 Sidhu P. S., Gilkes R. J. and Posner A. M. (1978) The synthesis and some properties of Co, Ni,
662 Zn, Cu, Mn and Cd substituted magnetites. *J. Inorg. Nucl. Chem.* **40**, 429-435.
- 663 Singh B. and Gilkes R. J. (1992) Properties and distribution of iron oxides and their association
664 with minor elements in the soils of south-western Australia. *J. Soil Sci.* **43**, 77-98.
- 665 Singh B., Sherman D. M., Gilkes R. J., Wells M. A. and Mosselmans J. F. W. (2002)
666 Incorporation of Cr, Mn and Ni into goethite (α -FeOOH): mechanism from extended X-
667 ray absorption fine structure spectroscopy. *Clay Miner.* **37**, 639-649.
- 668 Singh V. K. (2006) Bonding parameter, phase parameter and Ni K-edge position studies of some
669 Ni systems. *Indian J. Pure Appl. Phys.* **44**, 20-24.
- 670 Sowder A. G., Bertsch P. M. and Morris P. J. (2003) Partitioning and availability of uranium and
671 nickel in contaminated riparian sediments. *J. Environ. Qual.* **32**, 885-898.
- 672 Stumm W. (1993) From surface acidity to surface reactivity; inhibition of oxide dissolution.
673 *Aquat. Sci.* **55**, 273-280.
- 674 Stumm W. (1997) Reactivity at the mineral-water interface: dissolution and inhibition. *Colloids*

675 *Surf., A* **120**, 143-166.

676 Swedlund P. J., Webster J. G. and Miskelly G. M. (2003) The effect of SO₄ on the ferrihydrite
677 adsorption of Co, Pb and Cd: ternary complexes and site heterogeneity. *Appl. Geochem.*
678 **18**, 1671-1689.

679 Tankere-Muller S., Zhang H., Davison W., Finke N., Larsen O., Stahl H. and Glud R. N. (2007)
680 Fine scale remobilisation of Fe, Mn, Co, Ni, Cu and Cd in contaminated marine
681 sediment. *Mar. Chem.* **106**, 192-207.

682 van der Zee C., Roberts D. R., Rancourt D. G. and Slomp C. P. (2003) Nanogoethite is the
683 dominant reactive oxyhydroxide phase in lake and marine sediments. *Geol.* **31**, 993-996.

684 Venema P., Hiemstra T. and van Riemsdijk W. H. (1997) Interaction of Cadmium with
685 Phosphate on Goethite. *J. Colloid Interface Sci.* **192**, 94-103.

686 Waychunas G. A., Kim C. S. and Banfield J. F. (2005) Nanoparticulate iron oxide minerals in
687 soils and sediments: unique properties and contaminant scavenging mechanisms. *J.*
688 *Nanopart. Res.* **7**, 409-433.

689 Webb S. M. (2005) SIXPack: A Graphical User Interface for XAS Analysis using IFEFFIT.
690 *Physica Scripta* **T115**, 1011-1014.

691 Wells M. A., Gilkes R. J. and Fitzpatrick R. W. (2001) Properties and acid dissolution of metal-
692 substituted hematites. *Clays Clay Miner.* **49**, 60-72.

693 Williams A. G. B. and Scherer M. M. (2004) Spectroscopic evidence for Fe(II)-Fe(III) electron
694 transfer at the iron oxide-water interface. *Environ. Sci. Technol.* **38**, 4782-90.

695 Wu L., Beard B. L., Roden E. E., Kennedy C. B. and Johnson C. M. (2010) Stable Fe isotope
696 fractionations produced by aqueous Fe(II)-hematite surface interactions. *Geochim.*
697 *Cosmochim. Acta* **74**, 4249-4265.

698 Yang L., Steefel C. I., Marcus M. A. and Bargar J. R. (2010) Kinetics of Fe (II)-catalyzed
699 transformation of 6-line ferrihydrite under anaerobic flow conditions. *Environ. Sci.*
700 *Technol.* **44**, 5469-5475.

701 Yanina S. V. and Rosso K. M. (2008) Linked reactivity at mineral-water interfaces through bulk
702 crystal conduction. *Science* **320**, 218-22.

703

TABLES

Table 1. Langmuir isotherm parameters determined for Ni adsorption to goethite and hematite.

Sample	$\Gamma_{\max}$ ($\mu\text{mol g}^{-1}$)	K (mL μmol^{-1})
Hematite		
Oxoanion-free	44 ± 6	12 ± 4
0.1 mM SO ₄	58 ± 7	11 ± 3
0.1 mM PO ₄	117 ± 2	82 ± 6
Goethite		
Oxoanion-free	15 ± 2	80 ± 40
0.1 mM SO ₄	16 ± 2	110 ± 60
0.1 mM PO ₄	40 ± 2	250 ± 70

Table 2. Kinetic fit parameters, extent of Ni release, and final solid phase Ni speciation following reaction of 1.0 mM Fe(II) with Ni-substituted Fe(III) oxides.

Sample	k_{obs} ($\mu\text{M d}^{-1}$) ^a	[Ni] _{eq} (μM) ^a	Total Release (%) ^b	f(Ni incorporated) ^c
NiHem				
Oxoanion-free	1.3 ± 0.9	3.2 ± 0.3	1.3 ± 0.1	1.000 ± 0.001
0.1 mM SO ₄	0.8 ± 0.6	3.4 ± 0.4	1.4 ± 0.1	1.000 ± 0.001
0.1 mM PO ₄	21 ± 13	1.6 ± 0.2	0.64 ± 0.04	1.00 ± 0.03
NiGoe				
Oxoanion-free	0.03 ± 0.02	14 ± 2	9 ± 1	0.98 ± 0.02
0.1 mM SO ₄	0.04 ± 0.02	13 ± 1	8 ± 1	0.98 ± 0.02
0.1 mM PO ₄	90 ± 75	2.6 ± 0.2	1.61 ± 0.06	0.99 ± 0.02

^a Second order kinetics fitting parameters for Fe(II)-catalyzed Ni release from Fe(III) oxides (see Electronic Annex).

^b Fraction of initial incorporated Ni released from the mineral during reaction.

^c Speciation of solid-associated Ni at the end of reaction as determined by LCF of Ni XANES spectra.

Table 3. Final fraction of solid-associated Ni, corresponding Ni distributions, and Fe concentrations in the Ni incorporation experiments.

Sample	f(Ni incorporated) ^a	[Ni] _{inc} (μM) ^b	[Ni] _{ads} (μM) ^b	[Fe] _{aq} (μM) ^c
<i>Hematite Fe(II)-free</i>				
Oxoanion-free	0.004 ± 0.002	1 ± 4	174 ± 4	5 ± 1
0.1 mM PO ₄	0 ± 0.03	0 ± 6	190 ± 6	BDL ^d
0.5 mM PO ₄	0.02 ± 0.03	3 ± 5	196 ± 5	BDL
0.1 mM SO ₄	0.02 ± 0.02	3 ± 3	170 ± 3	BDL
1.0 mM SO ₄	0.09 ± 0.02	18 ± 4	170 ± 4	BDL
<i>Hematite + 0.5 mM Fe(II)</i>				
Oxoanion-free	0.36 ± 0.02	67 ± 4	118 ± 4	195 ± 7
0.1 mM PO ₄	0.17 ± 0.04	32 ± 7	158 ± 7	115 ± 3
0.5 mM PO ₄	0.05 ± 0.02	10 ± 4	189 ± 4	6.4 ± 0.1
<i>Hematite + 1.0 mM Fe(II)</i>				
Oxoanion-free	0.50 ± 0.03	92 ± 6	93 ± 6	403 ± 3
0.1 mM SO ₄	0.48 ± 0.03	89 ± 6	96 ± 6	545 ± 5
1.0 mM SO ₄	0.40 ± 0.03	75 ± 5	112 ± 5	430 ± 6
<i>Goethite Fe(II)-free</i>				
Oxoanion-free	0.17 ± 0.02	27 ± 3	138 ± 3	BDL
0.1 mM PO ₄	0.14 ± 0.03	22 ± 6	138 ± 7	BDL
0.5 mM PO ₄	0.04 ± 0.03	7 ± 5	180 ± 6	BDL
0.1 mM SO ₄	0.25 ± 0.02	40 ± 3	120 ± 3	8 ± 1
1.0 mM SO ₄	0.19 ± 0.03	29 ± 4	125 ± 4	23.9 ± 0.5
<i>Goethite + 0.5 mM Fe(II)</i>				
Oxoanion-free	0.44 ± 0.02	49 ± 3	63 ± 3	234 ± 5
0.1 mM PO ₄	0.44 ± 0.03	52 ± 4	66 ± 4	214 ± 5
0.5 mM PO ₄	0.32 ± 0.02	58 ± 4	126 ± 6	32.5 ± 0.4
<i>Goethite + 1.0 mM Fe(II)</i>				
Oxoanion-free	0.50 ± 0.03	52 ± 3	52 ± 3	638 ± 16
0.1 mM SO ₄	0.62 ± 0.03	83 ± 4	50 ± 4	674 ± 15
1.0 mM SO ₄	0.58 ± 0.02	74 ± 4	54 ± 4	657 ± 9

^a Fraction of solid-associated Ni incorporated into the Fe(III) oxide, calculated by LCF of XANES spectra. Component sums of f(Ni incorporated) and f(Ni adsorbed) are included in the Electronic Annex (Table EA2).

^b Concentration of Ni that is incorporated or adsorbed, calculated using final aqueous Ni concentrations determined by ICP-OES and the LCF XANES spectral fits.

^c Concentration of Fe remaining in solution at the end of the 30-day Ni incorporation experiments, determined by ICP-OES of the filtrate.

^d Measured analyte below detection limit (BDL).

FIGURE CAPTIONS

Figure 1. Ni adsorption isotherms at pH 7 on Hem (A) and Goe (B). Lines represent Langmuir isotherm fits to the data.

Figure 2. Ni fluorescence EXAFS spectra (points) and structural model fits (red lines) for Ni adsorbed onto hematite (A, B) and goethite (C, D) with (i) 0.1 mM phosphate and 1 g L⁻¹ Fe(III) oxide, (ii) 0.5 mM phosphate and 4 g L⁻¹ Fe(III) oxide, (iii) 0.1 mM sulfate and 1 g L⁻¹ Fe(III) oxide, and (iv) 1.0 mM sulfate and 4 g L⁻¹ Fe(III) oxide.

Figure 3. Ni release at pH 7 from NiHem (A) and NiGoe (B). Filled symbols represent samples reacted with 1 mM Fe(II); open symbols represent samples reacted in the absence of Fe(II). Lines represent second-order kinetic fits to the data.

Figure 4. Ni fluorescence XANES of standards used for LCF fitting of Ni release experiments with goethite (A) or hematite (B): Adsorbed Ni with 0.1 mM phosphate (i) or 0.1 mM sulfate (ii), and incorporated Ni (iii); and XANES (points) and LCF fits (red lines) for solids collected at the end of Ni release experiments at pH 7.5 with NiGoe (C) and NiHem (D) for samples reacted with 0.1 mM phosphate (i), with 0.1 mM sulfate (ii), and without oxoanions (iii).

Figure 5. Ni XANES spectra of standards used for LCF fitting of Ni incorporation experiments with goethite (A) or hematite (B): Adsorbed Ni with 0.5 mM phosphate (i) or 1.0 mM sulfate (ii), and incorporated Ni (iii); XANES spectra (points) and LCF fits (red lines) for Ni incorporation experiments at pH 7.5 without Fe(II) [Goe (C) and Hem (D)] and with Fe(II) [Goe (E) and Hem (F)] reacted for 30 days with 0.1 mM phosphate (i), 0.5 mM phosphate (ii), 0.1 mM sulfate (iii), 1.0 mM sulfate (iv), without oxoanions (v) [and 0.5 mM Fe(II) in E and F], or (vi) without oxoanions and 1.0 mM Fe(II).

760 **FIGURE**
761

762
763 **Figure 1.** Ni adsorption isotherms at pH 7 on Hem (A) and Goe (B). Lines represent Langmuir
764 isotherm fits to the data.

765

766 **Figure 2.** Ni fluorescence EXAFS spectra (points) and structural model fits (red lines) for Ni
 767 adsorbed onto hematite (A, B) and goethite (C, D) with (i) 0.1 mM phosphate and 1 g L⁻¹ Fe(III)
 768 oxide, (ii) 0.5 mM phosphate and 4 g L⁻¹ Fe(III) oxide, (iii) 0.1 mM sulfate and 1 g L⁻¹ Fe(III)
 769 oxide, and (iv) 1.0 mM sulfate and 4 g L⁻¹ Fe(III) oxide.

770

771 **Figure 3.** Ni release at pH 7 from NiHem (A) and NiGoe (B). Filled symbols represent samples
 772 reacted with 1 mM Fe(II); open symbols represent samples reacted in the absence of Fe(II).
 773 Lines represent second-order kinetic fits to the data.

Figure 4. Ni fluorescence XANES of standards used for LCF fitting of Ni release experiments with goethite (A) or hematite (B): Adsorbed Ni with 0.1 mM phosphate (i) or 0.1 mM sulfate (ii), and incorporated Ni (iii); and XANES (points) and LCF fits (red lines) for solids collected at the end of Ni release experiments at pH 7.5 with NiGoe (C) and NiHem (D) for samples reacted with 0.1 mM phosphate (i), with 0.1 mM sulfate (ii), and without oxoanions (iii).

Figure 5. Ni XANES spectra of standards used for LCF fitting of Ni incorporation experiments with goethite (A) or hematite (B): Adsorbed Ni with 0.5 mM phosphate (i) or 1.0 mM sulfate (ii), and incorporated Ni (iii); XANES spectra (points) and LCF fits (red lines) for Ni incorporation experiments at pH 7.5 without Fe(II) [Goe (C) and Hem (D)] and with Fe(II) [Goe (E) and Hem (F)] reacted for 30 days with 0.1 mM phosphate (i), 0.5 mM phosphate (ii), 0.1 mM sulfate (iii), 1.0 mM sulfate (iv), without oxoanions (v) [and 0.5 mM Fe(II) in E and F], or (vi) without oxoanions and 1.0 mM Fe(II).