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Iron and Phosphate Dissolution during Abiotic Reduction of Ferrihydrite-Boehmite Mixtures

G. Christopher Murray and Dean Hesterberg*

ABSTRACT

Excessive phosphorus loss from soils poses a threat to surface-water quality. Soils comprise assemblages of multiple minerals, with Fe- and Al-oxides being important for phosphate sorption. Our objective was to measure reductive dissolution of an Fe-oxide and sorbed orthophosphate as affected by the presence of an Al-(hydr)-oxide mineral. Aqueous suspensions containing 0.5 g ferrihydrite kg^{-1} and up to 0.7 g boehmite kg^{-1} and KH_2PO_4 added at 750 mmol kg^{-1} of ferrihydrite were abiotically reduced at pH 6.0 for 72 h using 0.5% $H_{2(g)}$ in the presence of a Pt catalyst. A sharp decrease in zero-order Fe(II) dissolution rate coefficients was observed between 0 and 0.008 g kg^{-1} of added boehmite, whereas net Fe(II) dissolution was essentially null for boehmite additions ≥ 0.02 g kg^{-1}. Although net dissolution of PO_4 occurred over time in the absence of boehmite, a net uptake occurred in the presence of boehmite. Auxiliary experiments suggested that Al(III) dissolved from boehmite decreased Fe(II) dissolution during reduction by sorbing to the ferrihydrite surface and blocking electron transfer. Because PO_4 was taken up in excess of the maximum boehmite sorption capacity in systems with ≤ 0.008 g boehmite kg^{-1}, results suggested the formation of Al-phosphate or an Al(III)–PO_4 complex on ferrihydrite surfaces. Phosphorus K-XANES spectroscopy of samples collected during reduction of a 1:1 ferrihydrite/boehmite mixture showed no consistent change in sorbed PO_4 associated with Fe(III) versus Al(III).

PARTICULATE and dissolved phosphorus losses from soils can result in P discharge into surface waters (Sharpley et al., 1993). Application of commercial fertilizers or animal wastes has caused buildup of P in some agricultural soils (Eghball and Power, 1999). In 1999, USDA changed its nutrient management policy such that the Natural Resources Conservation Service in each state must revise its technical standard for nutrient management plans (Sharpley et al., 2003) to consider the risk of P transport, particularly from sites receiving animal waste. Although environmental impacts and transport mechanisms of soil P have been documented (reviewed by Hegemann et al., 1983; Sims et al., 1998; Daniel et al., 1998; Correll, 1998; Hansen et al., 2002; Sharpley et al., 2002), there are still gaps in our knowledge about chemical reactions affecting P solubility and mobility in the environment. A more detailed understanding of these reactions is important for optimizing best management practices for P in a variety of land-use scenarios.

It is well known that P dissolution in soils tends to increase under reduced conditions (Patrick et al., 1973, Holford and Patrick, 1979, DeLaune et al., 1981, Husin et al., 1987, Sallade and Sims, 1997, Young and Ross, 2001). This phenomenon has usually been attributed to reductive dissolution of Fe(III)-phosphate minerals or Fe-oxides with adsorbed PO_4.

Sallade and Sims (1997) conducted a laboratory incubation study in which sediments with varying degrees of P saturation were maintained under oxygen-free conditions for 21 d. A significant correlation was found between dissolved P and Fe in solution for certain sediments in the study. Similar results were observed by DeLaune et al. (1981), Moore and Reddy (1994), and Vadas and Sims (1998).

Although a large body of literature supports the hypothesis of reductive P dissolution being related to Fe-oxide reduction, other research has shown little correlation between redox potential and dissolved P. For example, Khalid et al. (1977) found no increase in dissolved PO_4 in soils that were microbially reduced for 15 d. Vadas and Sims (1998) reported increases in dissolved P with reduction for some soils used in their study, but other soils showed decreases in dissolved P during reduction. Hutchison and Hesterberg (2004) indicated that soil Fe-oxide dissolution was less important for P dissolution than mechanisms involving dissolved organic matter. Further research is needed to understand how processes and interactions involving multiple soil components (Fe-oxides, Al-oxides, organic matter) affect reductive P dissolution.

Many studies have shown that measures of poorly crystalline Fe- and Al-(hydr)oxide mineral contents of soils are a reliable indicator of soil P sorption capacity (reviewed by Beauchemin and Simard, 1999). Thus, such high P-sorbing minerals are considered most important for P retention in many soils.

Aluminum(III) is stable under redox conditions found in soils (Darke and Walbridge, 2000); therefore, Al-oxides may be more important P sorbents than Fe(III)-oxides in reduced (anaerobic) soils. The P sorption capacity of Al-oxide minerals also increases with increasing specific surface area (Richardson et al., 1988, Parfitt, 1989). For example, Darke and Walbridge (2000) found phosphate sorption to be highly correlated with oxalate-extractable aluminum in soils from a floodplain. Richardson (1985) found poorly crystalline Al-oxides to be the predominant sorbents of P in wetland environments, most likely due to the integrity of these constituents under reducing conditions. Additional research has also highlighted the importance of Al-oxides as P sorbents under reducing conditions (Lockaby and Walbridge, 1998, Axt and Walbridge, 1999, Darke and Walbridge, 2000). Consequently, soils containing substantial amounts

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of poorly crystalline Al-oxide minerals could retard soil P dissolution during soil reduction.

Biotic reduction by native microbes using soil organic matter (SOM) and external electron acceptors is typically used in reductive P dissolution experiments. Organic materials have been shown to enhance PO_4 sorption on mineral surfaces (Borggaard et al., 1990), suppress PO_4 sorption by competing for mineral surfaces (Sibanda and Young, 1986, Violante et al., 1991), or form ternary aqueous complexes with Fe, Al and phosphate (Bloom, 1981, Gerke and Hermann, 1992). Consequently, SOM may affect reductive dissolution of P, making the effects of the mineral reduction itself difficult to discern. Studies aimed at understanding the interactive effects of Fe- and Al-oxides on reductive P dissolution without complicating effects of organic matter and microbial reduction are lacking. Abiotic reduction of soils and minerals using $H_{2(g)}$ as a reducing agent has been used to study soil and mineral redox reactions without relying on microbial reduction (Collins and Buol, 1970, Amacher, 1991, Brennan and Lindsay, 1998). As a reductant, $H_{2(g)}$ is oxidized to $H_2O(l)$. Therefore, complications from formation of strong surface complexes, which could occur with a reducing agent such as sulfide, are avoided. However, a catalyst such as Pt is needed to enhance abiotic reduction when using $H_{2(g)}$, as has been documented (Willet and Cunningham, 1983, Brennan and Lindsay, 1998). Although catalyst addition complicates the system, abiotic reduction provides a more controlled means than microbial reduction for studying mechanisms of reductive dissolution of Fe(II) and PO_4 in phosphate-sorbed mineral systems.

The goal of this research was to determine how mixtures of redox-active and non–redox-active minerals (as occur in soils) affect dissolution and the potential mobility of P. The specific objectives were (i) to determine rates of abiotic reductive dissolution of ferrihydrite (synthetic ferric hydroxide [$Fe(OH)_3$]) and PO_4 as affected by the presence of microcrystalline boehmite (α-AlOOH) and (ii) to determine possible mechanisms underlying any changes in net reductive dissolution of P as affected by boehmite. This research serves as a basis for more complex experiments that include SOM and microbial (biotic) reduction.

MATERIALS AND METHODS

Stock Suspension Synthesis and Characterization

Ferrihydrite was synthesized by adding 310 mL of 1 mol L^{-1} KOH to 500 mL of a stirred $Fe(NO_3)_3 \cdot 9H_2O$ solution and adjusting to pH 7.5 (Schwertmann and Cornell, 1991). To prepare a K-saturated stock ferrihydrite suspension, the material was divided among six 250-mL centrifuge bottles and centrifuged. The centrifuged pellets were washed twice with 1 mol L^{-1} KCl and deionized water. Fifteen batches of ferrihydrite were prepared and the solids from each batch were combined into six 250-mL centrifuge bottles. The ferrihydrite was washed twice with 0.01 mol L^{-1} KCl, combined into a high-density polyethylene (HDPE) storage bottle, adjusted to pH 6.2, and stored in the dark at 4°C. The solids concentration in this stock suspension (42.9 g kg^{-1}) was determined by drying subsamples at 110°C and correcting for KCl salt (Khare et al., 2004).

Boehmite was purchased in a pharmaceutical grade gel form under the trade name Rehydragel HPA (Reheis Co., Berkeley Heights, NJ). An amount of KCl sufficient to give a 1 mol L^{-1} background (104 g) was added to 1000 g of the aqueous boehmite gel. The material was adjusted to pH 6.2, equally divided among six 250-mL centrifuge bottles, and centrifuged. The boehmite in each bottle was washed three times with 0.01 mol L^{-1} KCl and combined into a 2-L HDPE bottle, adjusted to pH 6.2, and stored in the dark at 4°C. The solids concentration of our poorly crystalline boehmite stock was 14 g kg^{-1}. This material has been shown to posses a surface area (by H_2O adsorption) of 514 ± 45 m^2 g^{-1} (Wang et al., 2003).

After 1 mo of aging at 4°C, PO_4 adsorption isotherms were conducted on subsamples of the ferrihydrite and boehmite stock suspensions (pH 6.0, 22°C) following the procedure of Khare et al. (2004).

Near-maximum PO_4 sorption capacities of ferrihydrite and boehmite were periodically determined on subsamples from the stock suspensions for a single input concentration of 2000 (ferrihydrite) or 1200 (boehmite) mmol PO_4 kg^{-1}. To monitor crystallization of ferrihydrite over time (Schwertmann et al., 2000), subsamples of the stock suspension were periodically analyzed for HCl-extractable Fe (Cornell and Schneider, 1989). Ferrihydrite solids (0.1 g) were reacted for 30 min at 25°C with 100 mL of standardized 0.4 mol L^{-1} HCl solution (Cornell et al., 1990, Tichang et al., 1996). Samples were filtered to <0.2-μm using Millipore Isopore polycarbonate filter membranes (Millipore Corp., Bedford, MA). Dissolved Fe in the filtrate was analyzed by flame atomic absorption spectrometry.

Redox Reactor Experiments

Abiotic reduction experiments were conducted on aqueous suspensions in a 2-L water-jacketed glass reactor vessel (Wilmad-Labglass Corp., Buena, NJ). The reactor suspensions were maintained at a constant pH of 6.0 using a Radiometer Analytical Model TM 850 Autotitrator (Radiometer Analytical Corp., Lyon, France) with reservoirs of 0.01 *M* HCl or KOH. A constant suspension temperature of 25°C was achieved using a circulating water bath system.

Suspensions prepared for the redox reactor contained 0.5 g ferrihydrite kg^{-1} and between 0 and 0.7 g boehmite kg^{-1} (Table 1) in 0.01 mol L^{-1} KCl solution (1 kg initial suspension mass). The concentration of ferrihydrite was kept constant to maintain equivalent amounts of reducible mineral for each system. To avoid systematic changes in results due to possible

Table 1. Experimental-design parameters for suspensions in redox reactors. All systems contained 0.5 g ferrihydrite kg^{-1} and 750 mmol PO_4 added per kg of ferrihydrite.

Mass of boehmite	Total P sorption capacity†	Sorption capacity from boehmite
g kg^{-1}	μmol	%
0	800	0
0.002	801.3	0.2
0.004	802.6	0.3
0.008	805.2	0.6
0.02	813	1.6
0.08	852	7
0.2	930	16
0.3	995	20
0.7	1255	36

† Total initial sorption capacity from both minerals in reactors, based on P sorption capacities of 1600 mmol P kg^{-1} ferrihydrite and 650 mmol P kg^{-1} boehmite determined before the first reduction experiment.

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aging effects on stock minerals, experiments were conducted in a predominantly random chronological order. Stock mineral suspensions were shaken for at least 30 min before weighing into a tared, 2-L HDPE bottle. The reactor suspension was brought to approximately 70% of the final mass with 0.01 mol L^{-1} KCl and stirred rapidly on a magnetic stirrer. A solution of 0.01 mol L^{-1} KH_2PO_4 was added to yield 750 mmol P per kg of ferrihydrite. The pH was brought to 6.0 by adding 0.01 mol L^{-1} HCl or KOH solution while stirring. The suspension was brought to 1 kg mass with 0.01 mol L^{-1} KCl and transferred from the HDPE bottle to the 2-L reactor vessel.

The phosphate was reacted in the mixed suspensions for 24 h by purging with $N_{2(g)}$ (through a gas dispersion tube) before starting the flow of H_2 to induce reducing conditions. This period was considered long enough for adsorption of most phosphate while avoiding longer-term surface precipitation or substantial diffusion into micropores as has been indicated by van Riemsdijk and Lyklema (1980) and Torrent et al. (1992) for phosphate sorption on gibbsite or goethite.

After equilibration, mineral suspensions were abiotically reduced for 72 h by purging with 0.005 mol $H_{2(g)}$ mol^{-1} $N_{2(g)}$ (Collins and Buol, 1970, Brennan and Lindsay, 1998). The reduction of Fe(III)-oxide with H_2 gas can be described by the following thermodynamically favorable (log K = 16.4) reaction (Sposito, 1989):

$$1/2\,H_{2(g)} + Fe(OH)_{3(s)} + 2\,H^{+}_{(aq)} \overset{\text{catalyst}}{\longleftrightarrow} Fe^{2+}_{(aq)} + 3\,H_2O_{(l)} \qquad [1]$$

Initial evaluation of the redox reactor system confirmed the need for a catalyst to expedite ferrihydrite reduction. A Pt catalyst generally enhances the reactivity of hydrogen by atomizing molecular H_2 through chemisorption (Campbell, 1988). In our systems, the catalyst promotes electron transfer from H_2 to the Fe(III)-oxide surface. The activity of the Pt catalyst is further enhanced by a high surface area–activated carbon carrier. Therefore, we added a catalyst of 10% Pt on activated carbon (Pt/C) (Sigma Aldrich Co., Milwaukee, WI) to each reactor system at a rate of 0.25 g g^{-1} ferrihydrite, consistent with previous studies (Williams and Patrick, 1971, Willet and Cunningham, 1983, Brennan and Lindsay, 1998).

During reduction experiments, E_H and pH electrodes used to monitor the reactor suspensions were cleaned daily by soaking for 20 min in ammonium oxalate (pH 3.0) and recalibrated. Suspension samples of 25 mL were collected periodically between 0 and 72 h with a glass syringe connected to a sampling tube inserted into the suspension through a port in the reactor lid. This suspension was immediately vacuum filtered through a 0.2-μm Millipore Isopore polycarbonate filter membrane. Filter holders were contained in an N_2 purged glovebox, and the headspace above the suspensions was continuously purged with high-purity $N_{2(g)}$ during filtration. Filtration was conducted under a safelight to prevent photo-oxidation of ferrous iron. The filtrate was transferred into a 50-mL, evacuated, amber-colored serum bottle.

A portion of the filtrate was immediately analyzed colorimetrically for Fe(II) using the o-phenanthroline complexation method (Olson and Ellis, 1982). Dissolved phosphate was analyzed colorimetrically using the Murphy-Riley method (Murphy and Riley, 1962, Olsen and Sommers, 1982). Colorimetric analyses were done on a Shimadzu Model UV 2101-PC spectrophotometer (Shimadzu Corp., Colombia, MD) using wavelengths of 510 and 840 nm for Fe(II) and PO_4, respectively. Cuvettes of 1-cm path length were used for Fe(II), whereas cells of 1- or 5-cm paths were used for PO_4, depending on dissolved concentration.

Phosphorus K-XANES Analysis

To evaluate whether PO_4 transferred between ferrihydrite and boehmite during abiotic reduction, an aqueous suspension containing a mixture of 0.9 g kg^{-1} of each mineral was reduced for 168 h as described previously. In this case, PO_4 was added to the system at a rate of 750 mmol P kg^{-1} total solids and pre-equilibrated for 24 h. These mineral concentrations and P input were more suitable for XANES detection of PO_4 transfer between the minerals than suspension conditions used in the redox experiments described previously. After 0, 24, 72, 96, 144, and 168 h of reduction, 25-mL subsamples of suspension were collected and analyzed for ferrous iron and phosphate as described previously. A 100-mL sample was withdrawn, centrifuged, and the solids were mounted for XANES analysis as described by Khare et al. (2004). In addition to the reactor samples, single-mineral standards of PO_4 adsorbed on ferrihydrite (1000 mmol kg^{-1}) or boehmite (500 mmol kg^{-1}) were prepared for XANES analysis. Included in the XANES analysis were standards of noncrystalline Al- and Fe(III)-phosphate, verified by X-ray diffraction analysis and diluted in boron nitride to 400 mmol P kg^{-1}.

Phosphorus K-XANES data were collected at Beamline X19A at the National Synchrotron Light Source, Brookhaven National Laboratory in Upton, NY. An electron beam energy of 2.5 GeV and a maximum beam current of 300 mA were used. The dual-crystal, Si(111) monochromator was detuned by 50% to reject higher-order harmonics. The monochromator was calibrated to 2149 eV at the phosphorus K edge for a standard of variscite (400 mmol P kg^{-1} in boron nitride), and the calibration was re-checked with this standard after analyzing every fourth sample (Khare et al., 2004). Data were collected in fluorescence mode between 2119 and 2249 eV (−30 to 100 eV relative to the 2149 eV calibration energy) using a Passivated Implanted Planar Silicon detector mounted into a $He_{(g)}$-purged sample chamber (Khare et al., 2004). Two to three scans with consistent baselines were averaged, with the exception of the 24 and 144 h samples where a single, high-quality scan was used.

Normalization of averaged XANES spectra to obtain concentration-independent data was done using the Athena data analysis software (Ravel and Newville, 2005). We used a linear baseline correction between −30 and −15 eV (relative energy), and normalization was done on the flat region at the high-energy end of the spectrum (between 70 and 100 eV) (Sayers and Bunker, 1988).

Least-squares linear combination fitting of XANES spectra (Beauchemin et al., 2003; Khare et al., 2004) from samples taken between 0 and 168 h of reduction was completed using the Athena software. Samples were fit using all possible combinations of the four standards described previously. Linear combination fitting calculates the fraction (weighting factor) of each standard spectrum that, when summed, yields the least-squares fit to a sample spectrum. To quantify the proportion of PO_4 associated with Fe(III) versus Al(III), fitting was done across the pre-edge feature (−6 to −1 eV relative energy), which shows features that are characteristic of Fe(III)-bound PO_4 (Khare et al., 2004). The weighting factors for standard spectra in a fit were not constrained in Athena such that they must sum to 1 but were within 10%. The resulting weighting factors were subsequently normalized to a sum of 1 and expressed as percentages (Beauchemin et al., 2003). Because calibration checks of the beamline monochromator energy during XANES data collection showed no detectable shift in the energy scale, the energy scale was not allowed to shift in the XANES fitting analysis.

Fits for each sample (11 combinations of two, three, or four standards) were ranked according to goodness of fit (based on

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R factors calculated in Athena), and the two best fits were averaged for reporting here. Because the pre-edge region is not sensitve to the form of Al(III)-bound PO_4, we summed the weighting factors for standards of PO_4 on boehmite and noncrystalline Al-phosphate. The two best fits included one or both of these Al(III)-bound phosphate standards. We also fit an expanded energy range across the white-line peak (−10 to 30 eV) to try to differentiate between PO_4 adsorbed on boehmite versus noncrystalline Al-phosphate.

Fe(II) Sorption on Boehmite

An adsorption isotherm experiment was conducted to evaluate the sorption capacity of boehmite for ferrous iron. Various amounts of 0.01 mol L^{-1} $FeCl_2{\cdot}4H_2O$ solution were added to 0.5 g boehmite kg^{-1} suspensions at pH 6.0 (brought to 70% of the final mass with 0.01 mol L^{-1} KCl) in 50-mL polycarbonate centrifuge bottles. The samples were brought to a final mass of 30 g, adjusted back to pH 6.0, and periodically re-adjusted to pH 6.0 with trivial additions of 0.01 mol L^{-1} KOH or HCl throughout a 24-h equilibration period. Samples were shaken at 0.5 s^{-1} on a reciprocating water bath shaker at 25°C under $N_{2(g)}$. Additions of $FeCl_2{\cdot}4H_2O$, and any subsequent pH adjustments were conducted in an N_2-purged glovebox. The samples were filtered, and Fe(II) in the filtrate was quantified as described previously.

Al(III) Effects on Ferrihydrite Reduction

We hypothesized that Al dissolved from boehmite may affect reductive dissolution of ferrihydrite and PO_4. To evaluate the ability of Al(III) to inhibit ferrihydrite reduction, aqueous Al(III) was reacted with ferrihydrite before abiotic reduction as described previously. Additions of aqueous $AlCl_3$ solutions containing equivalent molar amounts of Al as in 0, 0.002, 0.008, or 0.08 g boehmite were slowly added to a stirred ferrihydrite suspension (at 50% of the final mass of 1 kg in 0.01 mol L^{-1} KCl) in a 2-L HDPE bottle. These additions were made after the suspension pH had been lowered to 3.0. Although a pH this low typically does not occur in soils, the idea was to promote adsorption of Al(III) to ferrihydrite under conditions that were undersaturated with respect to Al-hydroxide precipitation. The ferrihydrite suspension was brought to 70% of the final mass with 0.01 mol L^{-1} KCl, and a 25-mL subsample was withdrawn with a glass syringe to quantify the amount of Al(III) sorbed to the ferrihydrite at pH 3.0 (by loss from solution) (Sposito, 1989). The suspension was manually brought to pH 6.0, adjusted to a final mass of 1 kg, and transferred from the HDPE bottle to a 2-L glass reactor vessel. Each suspension was sampled and analyzed during 48 h of abiotic reduction as described previously.

RESULTS

Adsorption Isotherms

Adsorption isotherms for PO_4 on ferrihydrite and boehmite, and Fe(II) on boehmite, all at pH 6.0, are shown in Fig. 1. The isotherms were L-curves fitted with Freundlich equations. The maximum observed sorption capacity of ferrihydrite (1900 mmol kg^{-1}) was more than threefold greater than that of boehmite (650 mmol kg^{-1}). The Fe(II) sorption capacity of boehmite (approximately 200 mmol kg^{-1}) was threefold less than the PO_4 sorption capacity at pH 6.0, and the Fe(II) sorption capacity measured on our ferrihydrite was ~300 mmol kg^{-1} (limited data not shown). The Fe(II) sorption capacity of the 10% Pt/C catalyst was approximately 160 mmol kg^{-1} (data not shown).

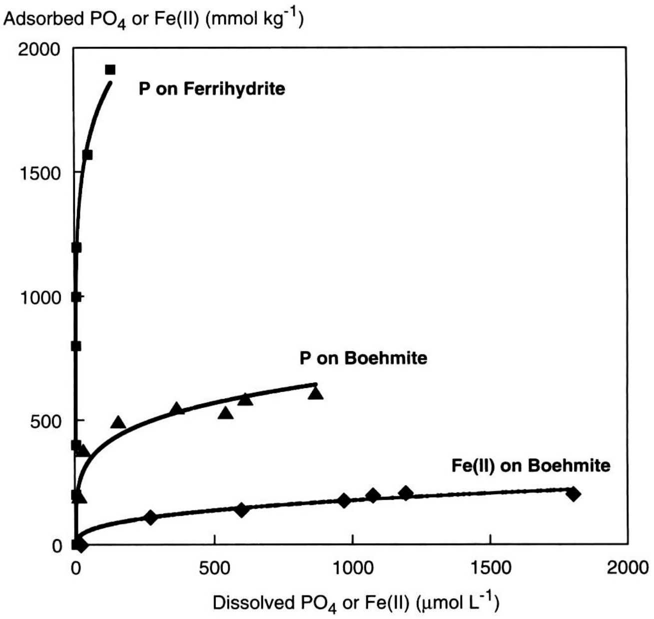

Fig. 1. Adsorption isotherms for PO_4 on ferrihydrite or boehmite (22°C) and Fe(II) on boehmite (25°C) at pH 6.0 in 0.01 mol L^{-1} KCl background. Smooth curves are Freundlich model fits to the data.

Between 10 and 560 d of storage, the PO_4 adsorption capacity of the stock ferrihydrite (for an input of 2000 mmol PO_4 kg^{-1}) decreased significantly ($p < 0.05$) from 1900 mmol kg^{-1} to 1200 mmol kg^{-1} (Murray, 2004). Over the same period, HCl-extractable Fe (Cornell and Schneider, 1989) decreased significantly ($p < 0.05$) from 4.1 to 3.3 mol kg^{-1} (Murray, 2004). These amounts represent between 44 and 31% of Fe in the stock mineral, assuming a chemical formula of $Fe(OH)_3$. Furthermore, X-ray diffraction patterns of ferrihydrite (not shown) collected after all experiments were completed showed the presence of goethite, indicating that ferrihydrite progressively transformed to goethite during > 560 d of storage. The PO_4 adsorption capacity of stock boehmite (for an input of 1200 mmol kg^{-1}) did not change significantly ($p > 0.05$; $n = 8$) between 10 and 280 d of storage (610 ± 30 mmol PO_4 kg^{-1}) (Murray, 2004).

Kinetics of Fe(II) Dissolution

The Eh of all mixed mineral suspensions decreased and stabilized at approximately –200 mV within 24 h after initiating $H_{2(g)}$ flow (Murray, 2004). Ferrous iron was released into solution during abiotic reduction of ferrihydrite–boehmite mixtures at pH 6.0 (Fig. 2), indicating reductive dissolution of ferrihydrite. Dissolution of Fe(II) followed linear trends (zero-order kinetics) over the 70-h period of our observations, and the dissolution rate decreased with increasing inputs of boehmite. Data for boehmite inputs ≥ 0.02 g kg^{-1} suspension were similar to those for an input of 0.008 g kg^{-1} (Murray, 2004). A significant ($p < 0.01$) decrease in the rate coefficient for net Fe(II) dissolution between 0 and 0.002 g boehmite kg^{-1} indicated that a boehmite in-

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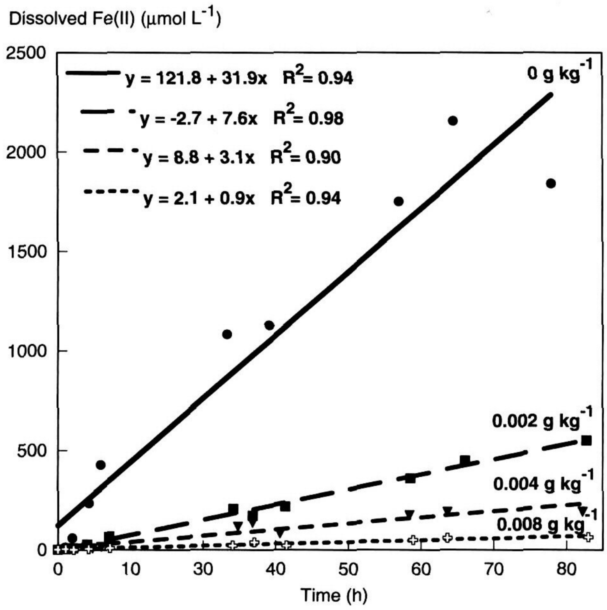

Fig. 2. Selected data for temporal changes in dissolved Fe(II) during abiotic reduction of ferrihydrite–boehmite mixtures containing 0.5 g ferrihydrite kg^{-1} suspension, 0–0.008 g boehmite kg^{-1} suspension, and 750 mmol P kg^{-1} ferrihydrite.

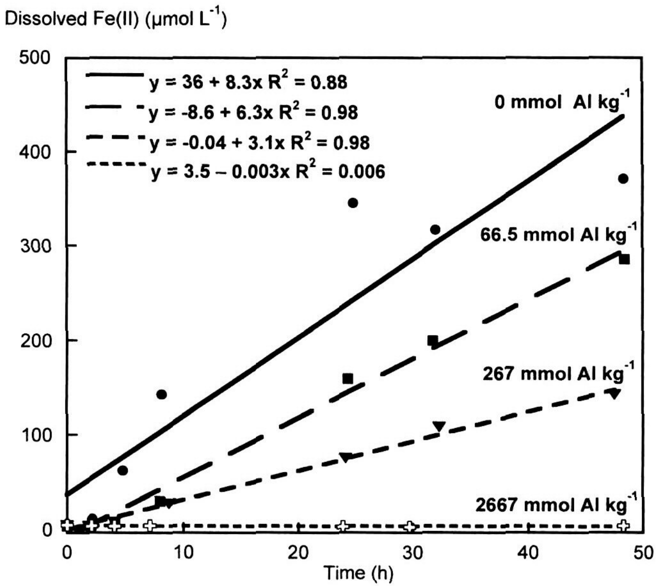

Fig. 3. Trends in dissolved Fe(II) during abiotic reduction (pH 6.0) of ferrihydrite after adding aqueous Al(III) at rates equivalent to Al(III) additions with 0, 0.002, 0.008, or 0.08 g boehmite kg^{-1} suspension. Aqueous Al(III) rates were 0–2667 mmol kg^{-1} ferrihydrite (0–1.33 mmol kg^{-1} suspension).

put 250-fold less than that of ferrihydrite decreased reductive dissolution of ferrihydrite. Although dissolved Fe(II) can enhance transformation of ferrihydrite to more redox-stable goethite (Hansel et al., 2003), the changes in ferrihydrite reduction rates shown in Fig. 2 are more indicative of boehmite/Al(III) effects than Fe(II) effects.

Because of the decreases in reductive Fe(II) dissolution from Fe-oxide when Al-oxide was added to our reactor systems, we hypothesized that dissolved Al(III) from boehmite inhibited reduction. Although 320 µmol Al(III) L^{-1} was detected in an aliquot of our boehmite stock suspension stored at pH 6.2, dissolved Al(III) was not detected in solutions collected from our mixed-mineral suspensions during reduction experiments. Presumably, any Al(III) dissolved from boehmite was sorbed by ferrihydrite. Reduction experiments using dissolved Al(III) rather than boehmite additions evaluated these hypotheses.

Results of reduction experiments on 0.5 g ferrihydrite kg^{-1} with dissolved Al(III) added at rates analogous to the total amounts of Al(III) in 0, 0.002, 0.008, and 0.08 g boehmite are shown in Fig. 3. Because the Al(III) was added at pH $\leq$ 3.0, we assumed that the Al(III) was adsorbed or surface precipitated on ferrihydrite rather than precipitated as a separate Al-oxide phase. However, for the greatest Al(III) input (2667 mmol kg^{-1} ferrihydrite), only 430 mmol Al(III) kg^{-1} were sorbed at pH 3 (quantified as loss from solution). Thus, for this sample, much of the added Al(III) probably precipitated when the suspension pH was slowly increased to pH 6 before starting reduction.

Similar to the ferrihydrite/boehmite mixtures, the reductive dissolution rate of ferrihydrite decreased with increasing amounts of pre-sorbed Al(III) (Fig. 3). Differences in dissolved Fe(II) between ferrihydrite/boehmite mixtures (Fig. 2) and ferrihydrite with pre-sorbed Al(III) (Fig. 3) at reduction times up to 48 h were attributed to a decrease in Fe-oxide solubility because of crystallization (e.g., transformation to goethite) during aging of the stock suspension (Murray, 2004). The experiments with presorbed Al(III) were conducted approximately 90 d after the experiments on ferrihydrite/boehmite mixtures were completed.

Zero-order rate coefficients for net Fe(II) dissolution followed similar trends with respect to Al(III) inputs (Fig. 4), regardless of whether the Al(III) was added as boehmite or dissolved Al(III). Iron(II) dissolution rates were inversely proportional to Al(III) input concentrations, as shown by the model fit (Fig. 4, inset). The rate coefficient from our 72-h experiments decreased sharply between 0 and 0.13 mmol Al(III) kg^{-1} suspension, with essentially no net Fe(II) dissolution occurring for Al(III) inputs >0.33 mmol kg^{-1} suspension (1/Al <3 kg mmol^{-1}) (Fig. 4, inset). We do not know the extent of boehmite dissolution and subsequent sorption of Al(III) by ferrihydrite in our systems. However, if all added Al(III) was dissolved and sorbed from aqueous form by ferrihydrite, an input of 0.22 mmol Al(III) kg^{-1} suspension would be equivalent to the maximum sorbed Al(III) found at pH 3 (430 mmol kg^{-1} ferrihydrite). The kinetic data in Fig. 4 suggest that the dissolution rate of ferrihydrite decreased with increasing surface coverage of Al(III).

Kinetics of Phosphate Dissolution

Trends in dissolved PO_4 concentrations for selected mixed-mineral redox experiments are shown in Fig. 5. In the absence of boehmite (0 g kg^{-1}), dissolved PO_4 increased by up to 15-fold over time, reaching a maximum concentration of 15 µmol L^{-1} (0.47 mg P L^{-1}) after 70 h.

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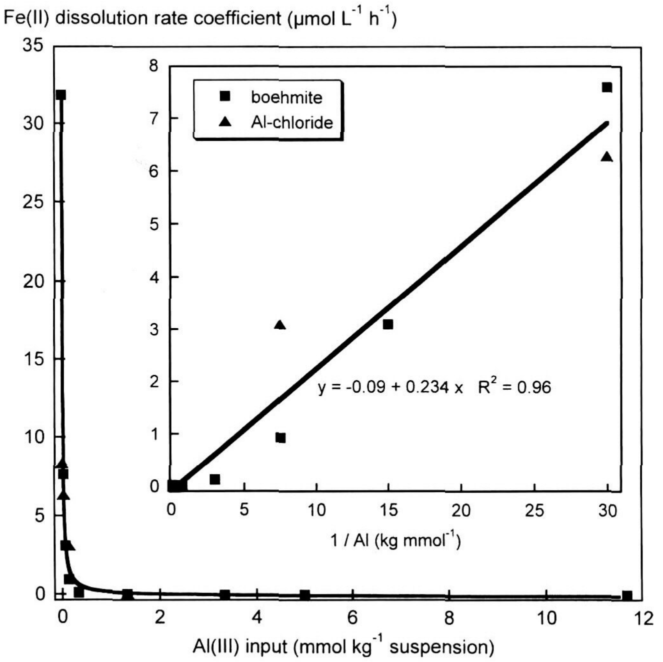

Fig. 4. Trends in zero-order rate coefficients for Fe(II) dissolution during abiotic reduction of mixed-mineral suspensions as a function of added Al(III) (mmol kg^{-1} suspension) as boehmite or aqueous Al(III) ($AlCl_3$). The inset figure shows the model fit to the data excluding inputs of 0 mmol Al kg^{-1}, for which the inverse of the Al(III) input (1/Al) is undefined.

In contrast, all mixed-mineral suspensions showed a decrease in dissolved PO_4 (by up to twofold) during reduction, as illustrated for representative samples in Fig. 5. That is, abiotic reduction caused a net uptake of PO_4 in the presence of boehmite. Rate coefficients for PO_4 uptake showed no significant difference with respect to boehmite inputs (Murray, 2004), indicating that uptake rates were independent of added boehmite for the input levels used.

Phosphorus K-XANES spectroscopy from an independent abiotic–reduction experiment were aimed at determining whether net PO_4 uptake during reduction of mixed-mineral suspensions (Fig. 5) resulted from transfer of PO_4 from redox-active ferrihydrite to redox-inactive boehmite. XANES spectra for samples collected at different times after reduction were similar (Fig. 6). Minor differences were found in the intensity of the white-line peak for two samples (24- and 96-h samples; Fig. 6a, inset), and the intensity of the pre-edge peak for one sample (144-h sample; Fig. 6b). We found no systematic trends in XANES spectra with time of reduction.

In the white line region, the spectra were most similar to standards of PO_4 adsorbed on ferrihydrite or boehmite, with the latter standard exhibiting a shift in the white-line peak to lower energy. If substantial amounts of PO_4 had precipitated as noncrystalline Al- or Fe-phosphate in our experimental systems, then XANES spectra should show a strong reduction in the white-line peak intensity (Fig. 6a) (Khare et al., 2005). The pre-edge peak between −5 and −2 eV (Fig. 6b) is indicative of PO_4 bonding with Fe(III) (Khare et al., 2004; 2005). This peak is stronger for Fe-phosphate solids than for PO_4 adsorbed on Fe-oxides (Fig. 6b) (see Hesterberg et al., 1999; Beauchemin et al., 2003). The pre-edge peaks for the mixed-mineral samples taken at different times after reduction exhibited intensities between those of PO_4 adsorbed on ferrihydrite and boehmite (or noncrystalline Al-phosphate), indicating a mixture of Fe(III)- and Al(III)-bonded PO_4.

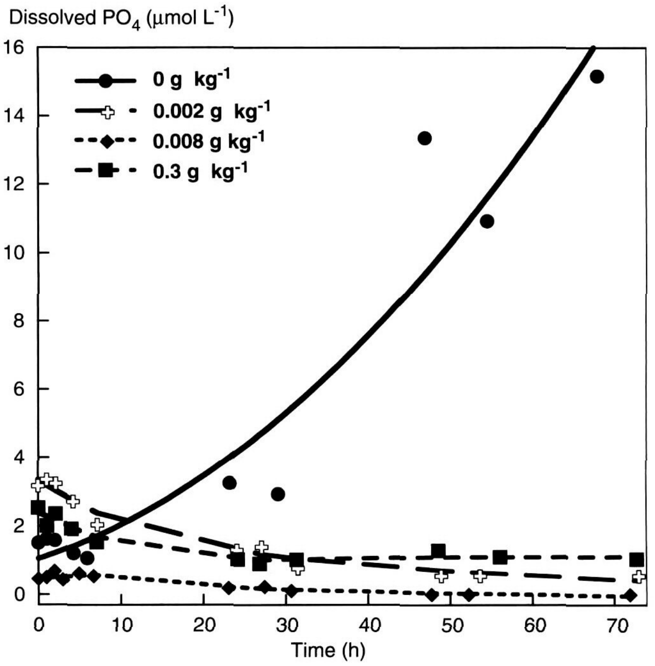

Fig. 5. Temporal changes in dissolved PO_4 for selected abiotic reduction experiments on suspensions containing 0.5 g ferrihydrite kg^{-1}; 0, 0.002, 0.008, or 0.3 g boehmite kg^{-1}; and 750 mmol P kg^{-1} ferrihydrite. Each suspension containing boehmite exhibited trends analogous to those shown.

Results of linear combination fitting of XANES spectra for mixed-mineral samples using standards shown in Fig. 6 confirmed a mixture of Fe(III)- and Al(III)-bonded PO_4 in all cases, with 60 to 80 mol% of phosphate being associated with ferrihydrite (Table 2). Results showed no consistent trend that would indicate a progressive transfer of PO_4 from ferrihydrite to boehmite (or to Al-phosphate) as reduction progressed. Such a trend could partially explain a progressive decrease in dissolved PO_4 during reduction (Fig. 5). Compared with the pre-edge region of P K-XANES spectra (Fig. 6b), the white-line region is more sensitive to the formation of Al-phosphate (Fig. 6a). The two best XANES fits across the spectral region dominated by the white line (−10 to 30 eV) for samples reduced for 96, 144, or 168 h indicated the presence of noncrystalline Al-phosphate rather than PO_4 adsorbed on boehmite (see Table 2). However, these fits indicated a dominance of PO_4 on ferrihydrite (60 to 97 mol%). P K-XANES spectral features are sensitive to the local molecular coordination of the PO_4 to Fe(III) versus Al(III). As such, XANES analysis would not easily distinguish, for example, between PO_4 associated with boehmite versus with Al(III) dissolved from boehmite and sorbed on ferrihydrite. Regardless of the mechanism, boehmite additions resulted in a net uptake of PO_4 (Fig. 4),

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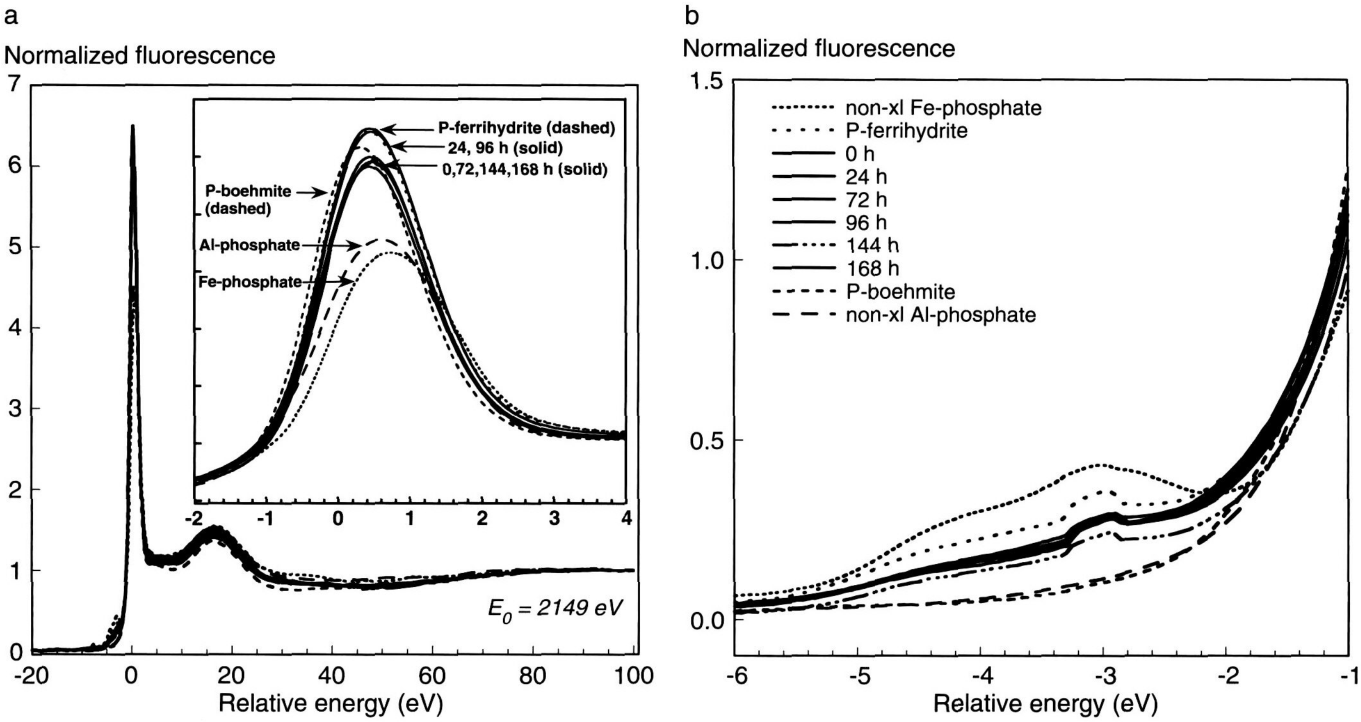

Fig. 6. Phosphorus K-XANES spectra with an inset of the white-line region (a) and the pre-edge region of XANES spectra (b) for moist samples collected at various times from an abiotic reduction experiment on a suspension containing 1:1 by mass ferrihydrite/boehmite and 750 mmol P kg^{-1} total solids. Spectra for standards of PO_4 adsorbed on boehmite (500 mmol kg^{-1}) or ferrihydrite (1000 mmol kg^{-1}) and noncrystalline (non-xl) Al(III)- and Fe(III)-phosphate are included.

in part by inhibiting the reductive dissolution of ferrihydrite in our experimental systems.

Acid Additions during Abiotic Reduction

According to reaction 1, reductive dissolution of ferrihydrite by $H_{2(g)}$ would consume 2 moles of H^+ per mole of Fe(II) produced. Figure 7 shows linear relationships between dissolved Fe(II) and added acid (to maintain pH 6.0) in our redox reactor systems. In the absence of boehmite, reductive dissolution of ferrihydrite (with 750 mmol adsorbed PO_4 kg^{-1}) produced 0.5 mol dissolved Fe(II) per mol of H^+ consumed, consistent with the theoretical ratio [1 Fe(II)/2H+] shown by Reaction 1. Slopes of the linear regression models decreased with

Table 2. Linear combination fitting results for the pre-edge region (−6 to −1 eV relative energy) of XANES spectra for samples collected over a 168 h reduction experiment. Data show best fits using weighted combinations of standards of phosphate adsorbed on ferrihydrite (1000 mmol kg^{-1}) or boehmite (500 mmol kg^{-1}), noncrystalline (non-xl) Al-phosphate, and noncrystalline Fe-phosphate.†

Sample	P-ferrihydrite	P-boehmite + non-xl Al-phosphate	Standard deviation	R-factor‡ × 1000
	mol%			
0 h	72	28	2	1.1 (0.2)
24 h	64	36	2	1.9 (0.2)
72 h	75.3	24.7	0.4	0.7 (0.0)
96 h	74.3	25.7§	0.6	0.9 (0.0)
144 h	65.4	34.6§	<0.1	1.1 (0.0)
168 h	81.5	18.5§	0.4	0.8 (0.0)

† Percentages represent means of the two best fits (lowest R-factors) for each sample, where percentages on P-boehmite and non-xl Al-phosphate were summed. Standard deviations apply to both means.

‡ R-factor = Σ (data − fit)^2/Σ (data)^2; mean and standard deviation (in parentheses) for both fits. Standard deviations given as 0.0 were ≤ 0.01.

§ Two best fits over the −10 to 30 eV range included only noncrystalline Al-phosphate with no P-boehmite.

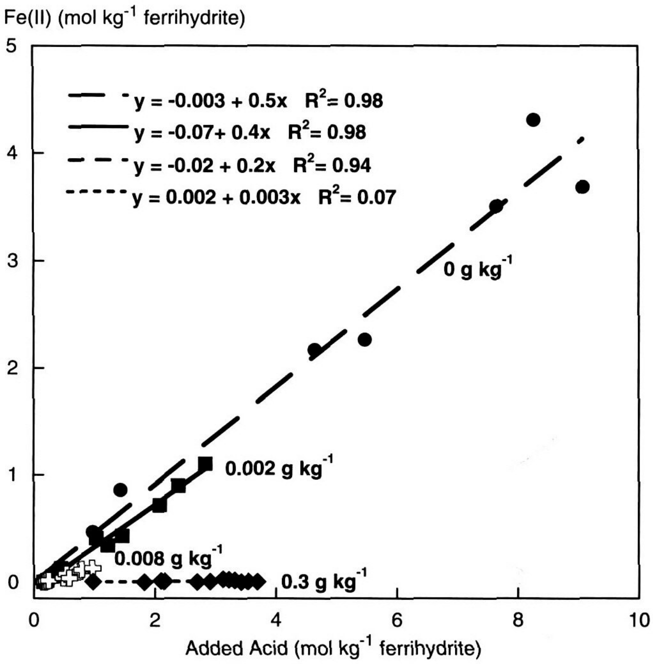

Fig. 7. Dissolved Fe(II) as a function of acid added to maintain pH 6.0 in selected reduction reactor experiments. Suspensions contained 0.5 g ferrihydrite kg^{-1}, 750 mmol P kg^{-1} ferrihydrite, and boehmite additions of 0, 0.002, 0.008, or 0.3 g kg^{-1} suspension.

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increasing additions of boehmite (representative data shown in Fig. 7), indicating increasing proton consumption by reactions other than reductive dissolution of ferrihydrite. Murray (2004) discussed a number of pH-dependent chemical reactions that may occur during abiotic reduction of ferrihydrite-boehmite mixtures with pre-sorbed PO_4. Of these reactions, reductive dissolution of ferrihydrite (Reaction 1) and dissolution of boehmite to aqueous Al^{3+}, $AlOH^{2+}$, or $Al(OH)_2{}^+$ are proton-consuming reactions. Any subsequent precipitation of Al-phosphate or adsorption of Al^{3+} as an inner-sphere complex on ferrihydrite would release protons to solution. In general, greater consumption of protons relative to Fe(II) dissolution in the presence of boehmite can be explained at least qualitatively by dissolution of boehmite in these systems, as we hypothesized.

DISCUSSION

With increasing concentrations of added boehmite in ferrihydrite/boehmite mixtures undergoing abiotic reduction, the net rate of reductive Fe(II) dissolution decreased to the point of being negligible for boehmite additions > 0.02 g kg^{-1} suspension (>0.33 mmol Al kg^{-1}) (Fig. 2 and 4). The presence of boehmite also inhibited dissolution of adsorbed PO_4 during reduction and caused a net uptake of dissolved PO_4 (Fig. 5). The decrease in net Fe(II) dissolution with increasing concentrations of added boehmite cannot be explained by sorption of Fe(II) by boehmite. For example, the measured Fe(II) adsorption capacity of boehmite (225 mmol kg^{-1} boehmite; see Fig. 1) was an order of magnitude less than that needed (2850 mmol kg^{-1} boehmite) to account for the maximum difference in dissolved Fe(II) [~ 2300 μmol Fe(II) L^{-1}] found during reduction of ferrihydrite systems containing 0 g boehmite kg^{-1} (Fig. 2) versus 0.7 g boehmite kg^{-1}. Because a net dissolution of Fe(II) occurred in the absence of added boehmite, we discounted Fe(II) sorption to ferrihydrite as an explanation for diminished Fe(II) dissolution in the presence of boehmite.

We propose that reductive dissolution of Fe-oxide in our ferrihydrite/boehmite mixtures was inhibited by Al(III) dissolution from boehmite and subsequent sorption on ferrihydrite surfaces. This explanation was supported by redox results from ferrihydrite suspensions containing Al(III) pre-sorbed from aqueous solution before reduction (Fig. 4). Inhibition of iron oxide dissolution from the precipitation of Al surface coatings has been hypothesized previously (Segal and Sellers, 1984, Bousserrhine et al., 1998). The proposed mechanism is redox-inactive Al(III) blocking electron transfer (from H_2 via the catalyst) to surface Fe(III). This mechanism is consistent with net Fe(II) dissolution rates sharply approaching zero with increasing Al(III) inputs between 0 and 0.33 mmol kg^{-1} suspension. An Al(III) input of 0.33 mmol kg^{-1} suspension corresponds to 660 mmol Al(III) kg^{-1} ferrihydrite (at pH 6), which exceeds the maximum sorption capacity of 430 mmol Al(III) kg^{-1} ferrihydrite based on measurements at pH 3. It is conceivable that boehmite dissolves, aqueous Al(III) is sorbed on ferrihydrite, and the rate of Fe(II) dissolution becomes negligible as the sorbed Al(III) approaches the maximum capacity of ferrihydrite (perhaps monolayer surface coverage).

We cannot discount from our results the possibility that Al(III) from boehmite inhibited ferrihydrite dissolution by deactivating the Pt/C catalyst. The catalyst sorbed 190 mmol Al(III) kg^{-1} at pH 3.6 (for an input of 266 mmol Al kg^{-1}) (Murray, 2004). However, Murray (2004) found no conclusive evidence that Al(III) pre-sorbed on the catalyst inhibited its ability to promote ferrihydrite reduction. Furthermore, for experiments in which aqueous Al(III) was pre-sorbed on ferrihydrite, the Al(III) must first desorb from the ferrihydrite, then bind to the catalyst to deactivate it.

The effects of added boehmite on acid consumption and dissolved phosphate concentration during reduction of mineral mixtures are also consistent with a mechanism involving boehmite dissolution. For example, consider the incongruent dissolution of boehmite to form $AlPO_4(s)$ in the presence of aqueous PO_4:

$$\mathrm{AlOOH\,(boehmite)} + \mathrm{H^+(aq)} + \mathrm{H_2PO_4^-(aq)} \longleftrightarrow \mathrm{AlPO_4(s)} + 2\,\mathrm{H_2O(l)} \quad [2]$$

This reaction shows consumption of protons, which is consistent with acid additions during pH-controlled reduction experiments, even as Fe(II) dissolution decreased (Fig. 7). Also, unlike precipitation of Al-phosphate, PO_4 adsorption alone by added boehmite cannot fully account for our observed uptake of dissolved PO_4. Consider, for example, the reduction experiment on a ferrihydrite mixture containing 0.002 g boehmite kg^{-1} suspension (=0.033 mmol Al kg^{-1} suspension or 67 mmol Al kg^{-1} ferrihydrite). Given a maximum PO_4 adsorption capacity of 650 mmol kg^{-1} boehmite (Fig. 1), the added boehmite in this system could remove a maximum of 1.3 μmol PO_4 kg^{-1} suspension (~ 1.3 μmol PO_4 L^{-1}) by adsorption. Our data showed that in the presence of 0.002 g boehmite kg^{-1} dissolved PO_4 decreased by up to 13 μmol PO_4 L^{-1} relative to the system with no added boehmite (Fig. 5). If the Al added with boehmite completely dissolved and reacted with aqueous PO_4 to form $AlPO_4(s)$ according to Reaction 2, then the amount of dissolved PO_4 that could potentially be precipitated as an $AlPO_4$ solid could be as high as 32 μmol PO_4 L^{-1}. This amount exceeds by more than twofold the observed difference in dissolved PO_4 between suspensions with 0 versus 0.002 g boehmite kg^{-1} (Fig. 5), indicating that the Al(III) added in the latter case (if dissolved) should be more than adequate to precipitate any PO_4 released during reduction of ferrihydrite. The net uptake of dissolved PO_4 in the presence of boehmite was not solely attributed to inhibition of ferrihydrite dissolution. For example, the dissolution of ferrihydrite (and the potential for concomitant release of associated phosphate) was significant for an input of 0.002 g boehmite kg^{-1} (Fig. 2).

Phosphorus K-XANES analyses on 1:1 (by mass) boehmite/ferrihydrite mixtures gave stronger evidence for the presence of noncrystalline Al-phosphate relative

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to PO_4 adsorbed on boehmite, particularly after longer reduction times (Table 2). However, we could not definitively distinguish from our XANES data whether Al-bonded phosphate occurred as an independent Al-phosphate phase, an Al-phosphate surface precipitate, or as a ternary surface complex of PO_4 bound to ferrihydrite-adsorbed Al. Such ternary surface complexes have been reported in the literature (Clark and McBride, 1985; Ler and Stanforth, 2003). Also, Khare et al. (2005) found PO_4 associated with Al(III) in excess of the PO_4 sorption capacity of goethite/boehmite mixtures, suggesting the formation of ternary Al(III)–PO_4 surface complexes on goethite. In general, uptake of PO_4 as an Al-bound solid during reduction of ferrihydrite/boehmite mixtures may be inconsequential if Al dissolved from boehmite completely inhibits reductive dissolution of PO_4–sorbed ferrihydrite (Fig. 4).

CONCLUSIONS

The rate of abiotic, reductive dissolution of ferrihydrite in aqueous suspensions containing adsorbed PO_4 was inversely proportional to the amount of Al(III) added as boehmite or aqueous Al(III). The proposed mechanism for this inhibition of ferrihydrite reduction is that dissolution of Al(III) from boehmite was sorbed on ferrihydrite, thereby blocking electron transfer from the reductant (H_2) to surface Fe(III). Net uptake of aqueous PO_4 occurred during reduction of ferrhydrite-boehmite mixtures, in contrast to a net release of PO_4 to solution during reductive dissolution of ferrihydrite alone. We propose that changes in dissolved Fe(II) and PO_4 during abiotic reduction of ferrihydrite-boehmite mixtures were governed by two different processes: (i) with increasing surface coverage of boehmite-derived Al(III) on ferrihydrite, reductive dissolution of Fe(II) and concomitant release of adsorbed PO_4 was increasingly inhibited; and (ii) at lower concentrations of added boehmite, any PO_4 released during reductive dissolution of ferrihydrite was precipitated as Al-phosphate or formed a ternary ferrihydrite-Al-phosphate surface complex. Phosphate uptake rates in mineral mixtures were independent of added boehmite, consistent with the amounts of Al(III) added with boehmite being in excess of released PO_4. Our results suggest that in soils, electron transfer to Fe-oxide surfaces may be inhibited by sorbed Al(III) dissolved from Al-bearing soil minerals. Hence, interactions between redox-inactive minerals such as Al-oxides and redox-active Fe-oxide minerals may affect reductive dissolution rates of PO_4 and Fe(II). These interactions may be further modified by other soil components, such as organic matter.

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