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Interaction of Fe(II) with phosphate and sulfate on iron oxide surfaces

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Abstract

Sulfate and phosphate, oxoanions common in natural systems, affect iron oxide growth and dissolution processes, the adsorption behavior of divalent cations, and iron oxide phase transformations. These oxoanions may thus influence Fe(II) adsorption behavior and subsequently alter the mechanisms and products of Fe(II)-catalyzed Fe(III) oxide recrystallization processes, such as trace metal repartitioning. In this study, the macroscopic and molecular-scale effects of the coadsorption of Fe(II) and sulfate or phosphate onto Fe(III) oxide surfaces were investigated. Macroscopic adsorption edges show that both sulfate and phosphate increase Fe(II) adsorption and that Fe(II) increases sulfate and phosphate adsorption. Attenuated total reflectance Fourier transform infrared spectroscopy shows that the cooperative adsorption behavior of oxoanions and aqueous Fe(II) likely results from a combination of ternary complexation and electrostatic interactions. Surface complexation modeling requires the inclusion of ternary complexes to simulate all conditions of the macroscopic data, further suggesting that these oxoanions and Fe(II) form ternary complexes on Fe(III) oxide surfaces. Despite clear evidence in previous research for Fe(II) oxidation upon adsorption on iron oxide surfaces, this work shows that Fe(II) also displays macroscopic and molecular-scale behaviors associated with divalent (i.e., non-oxidative) cation adsorption. Prior work has shown that metal release from iron oxides caused by ET-AE reactions is directly proportional to the macroscopically-determined Fe(II) surface coverage. Predicting the effects of sulfate and phosphate on processes controlled by ET-AE reactions at redox interfaces, such as mineral phase transformations and trace element repartitioning, may thus not require the explicit consideration of electron transfer processes.

1. INTRODUCTION

Biogeochemical iron cycling occurs in many environments, including sediments, estuaries, wetlands, acid mine and rock drainage sites, carbonate springs and caves, and soils (Tugel et al., 1986; Canfield et al., 1993; Johnson et al., 1993; Sobolev and Roden, 2002; Northup et al., 2003; Kappler and Straub, 2005; Thompson et al., 2006; Weber et al., 2006; Baskar et al., 2008), leading to the coexistence of aqueous Fe(II) and solid Fe(III) oxide minerals. Reactions between these iron species result in mineral phase transitions from metastable iron oxides to more thermodynamically stable forms, iron isotope fractionation, and simultaneous growth and dissolution of crystalline iron oxide surfaces (Williams and Scherer, 2004; Crosby et al.,

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2005; Hansel et al., 2005; Catalano et al., 2010). Recent studies have shown that aqueous Fe(II) and solid Fe(III) oxides react via interfacial electron transfer and atom exchange (ET-AE) processes, involving the coupled oxidative adsorption of aqueous Fe(II) and the reductive dissolution of a spatially separated Fe(III) surface site, resulting in mineral recrystallization (Williams and Scherer, 2004; Larese-Casanova and Scherer, 2007; Yanina and Rosso, 2008; Handler et al., 2009; Rosso et al., 2010).

Oxoanions such as phosphate and sulfate can influence mineral surface reactions, affecting mineral nucleation, precipitation, and dissolution. Oxoanion surface complexes may block reactive surface sites (e.g., steps, defects, kinks) involved in iron oxide dissolution and growth (Bondietti et al., 1993; Stumm, 1997; Eggleston et al., 1998; Majzlan and Myneni, 2005; Borch et al., 2007). Phosphate adsorption decreases the reductive dissolution of ferrihydrite by dissimilatory iron reducing bacterium (Borch et al., 2007), suppresses the reductive dissolution of goethite (Stumm, 1993) and hematite (Stumm, 1997) by H_2S, and inhibits the ligand promoted dissolution of lepidocrocite by ethylenediaminetetraacetic acid (Stumm, 1997). Sulfate can alter Fe(III) oxide nucleation and precipitation processes, affecting Fe(III) oxide formation under acid drainage conditions (Majzlan and Myneni, 2005).

The presence of oxoanions can also affect the adsorption mechanism of cations on iron oxide surfaces through the formation of ternary complexes, enhanced electrostatic effects, or competitive adsorption. Previous studies indicate that sulfate increases Cd(II) adsorption onto goethite (Balistrieri and Murray, 1982; Hoins, 1993; Zhang and Peak, 2007; Swedlund et al., 2009) and ferrihydrite (Swedlund et al., 2003), Cu(II) adsorption onto goethite (Balistrieri and Murray, 1982; Ali and Dzombak, 1996; Juang and Wu, 2002; Swedlund et al., 2009) and ferrihydrite (Swedlund and Webster, 2001), Pb(II) adsorption onto goethite (Ostergren et al., 2000) and ferrihydrite (Swedlund et al., 2003), and Zn(II) adsorption onto goethite (Balistrieri and Murray, 1982; Swedlund et al., 2009) and ferrihydrite (Swedlund and Webster, 2001). Phosphate has also been found to enhance cation adsorption onto iron oxide surfaces, such as Cd(II) (Venema et al., 1997; Collins et al., 1999) and Zn(II) (Diaz-Barrientos et al., 1990; Madrid et al., 1991). Although there are disparities between some X-ray absorption fine structure (XAFS) and Fourier transform infrared (FTIR) spectroscopic studies (e.g., Collins et al., 1999; Zhang and Peak, 2007), many spectroscopic, macroscopic, and modeling studies have indicated that cations and oxoanions commonly form ternary complexes on Fe(III) oxide surfaces (Benjamin and Leckie, 1982; Hoins, 1993; Ali and Dzombak, 1996; Ostergren et al., 2000; Elzinga et al., 2001; Swedlund and Webster, 2001; Zhang and Peak, 2007; Swedlund et al., 2009; Elzinga and Kretzschmar, 2013).

Studies specifically focused on Fe(II)-oxoanion coadsorption are limited. Jeon et al. (2001) found that sulfate substantially enhanced Fe(II) adsorption onto hematite, with 1.0 mM sulfate shifting the Fe(II) adsorption edge by more than two pH units. The effect of Fe(II) on sulfate adsorption, however, has not been studied macroscopically or spectroscopically and the Fe(II)-sulfate coadsorption mechanism(s) remains uncertain. A study of Fe(II) and arsenate coadsorption onto goethite and hematite indicates that while the adsorption of both species is somewhat increased there is no change in arsenate adsorption mechanisms, suggesting that Fe(II) and arsenate do not directly interact (Catalano et al., 2011). A recent study probing the effect of silicate, bicarbonate, and phosphate on Fe(II)-Fe(III) ET-AE reactions demonstrated that phosphate has a small enhancing effect on the rate and extent of Fe atom exchange with goethite and does not prevent electron transfer; the mechanism through which phosphate enhances Fe atom exchange, however, is unknown (Latta et al., 2012). These studies suggest that oxoanions may affect Fe(II) adsorption, which could impact a wide array of subsequent processes, such as mineral recrystallization and trace element repartitioning. However, the nature and extent of Fe(II)-oxoanion coadsorption reactions are currently unclear.

This paper describes an investigation of the coadsorption behavior of Fe(II) and two oxoanions common in natural systems, phosphate and sulfate, on hematite and goethite. The macroscopic effects of coadsorption were investigated in batch experiments that examined a wide pH range and varying adsorbate concentrations. The effect of Fe(II) on sulfate and phosphate adsorption mechanisms was further probed by attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy to determine if specific molecular interactions occur between these species on iron oxide surfaces. A surface complexation model (SCM) was also developed to determine if the molecular-scale processes inferred from spectroscopic measurements could explain the observed macroscopic behavior.

2. MATERIALS AND METHODS

2.1. Iron oxide syntheses

Iron oxide minerals were prepared following modified procedures outlined by Schwertmann and Cornell (2000). Goethite was synthesized by hydrolysis of 100 mL of a 1 M $Fe(NO_3)_3 \cdot 9H_2O$ solution with 180 mL of a 5 M NaOH solution in a 1 L polypropylene bottle, resulting in the rapid precipitation of ferrihydrite. The resulting suspension was diluted to 1 L with deionized water (>18.2 MΩ cm), and aged for 60 h at 70 °C, forming a yellow precipitate. Hematite was synthesized by the addition of 40 g of $Fe(NO_3)_3 \cdot 9H_2O$ to 500 mL deionized water, 300 mL of a 1 M KOH solution, and 50 mL of a 1 M $NaHCO_3$ solution in a 1 L polypropylene bottle. The pH of the solution was checked to ensure it was above 8 but below 8.5. The suspension was then aged for 5 days at 98 °C, forming a red precipitate. Excess electrolytes were removed from both final solids by vacuum filtration and rinsing with deionized water. The resulting wet pastes were resuspended in deionized water and stored in clear polypropylene bottles wrapped with aluminum foil.

After synthesis, the mineral suspensions were transferred to an anaerobic chamber (Coy Laboratory Products, Inc.)