Metal oxyhydroxide dissolution as promoted by structurally diverse siderophores and oxalate

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Abstract

Siderophores, a class of biogenic ligands with high affinities for Fe(III), promote the dissolution of metal ions from sparingly soluble mineral phases. However, most geochemical studies have focused on quantifying the reactivity of DFOB, a model trishydroxamate siderophore. This study utilized three different siderophores, desferrioxamine B, rhizoferrin, and protochelin, with structures that contain the most commonly observed binding moieties of microbial siderophores to examine the siderophore-promoted dissolution rates of FeOOH, CoOOH, and MnOOH in the absence and presence of the ubiquitous low molecular mass organic acid oxalate by utilizing batch dissolution experiments at pH = 5–9. Metal-siderophore complex and total dissolved metal concentrations were monitored for durations of one hour to fourteen days, depending on the metal oxyhydroxide identity and solution pH. The results demonstrate that MnOOH and CoOOH generally dissolve more quickly in the presence of siderophores than FeOOH. Whereas FeOOH dissolved exclusively by a ligand-promoted dissolution mechanism, MnOOH and CoOOH dissolved predominantly by a reductive dissolution mechanism under most experimental conditions. For FeOOH, siderophore-promoted dissolution rates trended with the stability constant of the corresponding aqueous Fe(III) complex. In the presence of oxalate, measured siderophore-promoted dissolution rates were found to increase, decrease, or remain unchanged as compared to the observed rates in single-ligand systems, depending on the pH of the system, the siderophore present, and the identity of the metal oxyhydroxide. Increases in observed dissolution rates in the presence of oxalate were generally greater for FeOOH than for MnOOH or CoOOH. These results elucidate potential dissolution mechanisms of both ferric and non-ferric oxyhydroxide minerals by siderophores in the environment, and may provide further insights into the biological strategies of metal acquisition facilitated by coordinated exudation of low molecular weight organic acids and siderophores.

1. INTRODUCTION

All organisms require transition metals, such as Co, Mn, and Fe, for use in the metalloproteins and enzymes that are necessary for proper metabolic function (Frausto da Silva and Williams, 1991). Under oxic conditions at circumneutral pH, these metals tend to be entrained in insoluble oxide and hydroxide minerals that are not readily available for

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biological uptake (Adriano, 2001). To overcome the potential limits on organism nutrition caused by the low bioavailability of iron and possibly other metals, graminaceous plants, bacteria, and fungi exude organic molecules, such as low molecular mass organic acids and siderophores, that promote the dissolution, solubilization, and uptake of nutrient metals (Marschner et al., 1986; Kraemer, 2004; Winkelmann, 2007).

Siderophores (derived from Greek meaning "iron carrier") are specialized chelating agents exuded by microorganisms during periods of iron stress to enhance iron bioavailability. Currently, about 500 different types of siderophores have been discovered (Hider and Kong, 2010). Despite this structural diversity, microbial siderophores are typically characterized as tetra- or hexa-dentate ligands with oxygen-bearing moieties (commonly hydroxamate, catecholate, salicylate, α-hydroxycarboxylate, or carboxylate) that directly bind a central metal ion [viz. Fe(III)] (Crumbliss and Harrington, 2009). These configurations result in thermodynamically stable, soluble complexes that can be taken up via specific cellular receptors (Stintzi et al., 2000; Harrington and Crumbliss, 2009). Although most geochemical studies to date have utilized the trishydroxamate siderophore desferrioxamine B (DFOB), it is reasonable to assume that siderophores may display a range of reactivity that will be largely dictated by the nature of the ligand moieties that interact directly with the metal center.

An important proposed role of siderophores in soils is promoting the dissolution of iron from low solubility minerals. Desferrioxamine B promotes iron dissolution from a number of different phases, including oxides, hydroxides, phosphates, sulfides, and clay minerals (Watteau and Berthelin, 1994; Liermann et al., 2000, 2005; Cervini-Silva and Sposito, 2002; Rosenberg and Maurice, 2003; Wolff-Boenisch and Traina, 2007a; Cornejo-Garrido et al., 2008; Haack et al., 2008; Cervini-Silva et al., 2012). The DFOB-promoted dissolution of FeOOH has been shown to proceed by a surface-controlled mechanism, resulting in the formation of a Fe(III)HDFOB$^+$ complex (Cocozza et al., 2002). Interestingly, in the presence of DFOB and low molecular mass organic acids (such as oxalate), the dissolution rate of goethite is enhanced beyond a simple combination of the single-component dissolution rates (Cervini-Silva and Sposito, 2002; Cheah et al., 2003; Wolff-Boenisch and Traina, 2007b). This "synergistic" effect results from oxalate acting as an iron shuttle that delivers Fe(III) to dissolved siderophores, with rate of detachment of a labile pool of Fe(III)-oxalate surface complexes enhanced by the presence of the siderophore (Reichard et al., 2007a,b; Loring et al., 2008).

Recent studies have suggested that siderophores may play diverse roles in the environment beyond promoting Fe(III) solubilization and uptake (Kraepiel et al., 2009; Duckworth et al., 2009a,b; Schalk et al., 2011). Despite the assumed high specificity of siderophores for Fe(III), strong interactions between DFOB and other metals have been recognized for over 50 years (Anderegg et al., 1963). In fact, metal ions such as Mn(III) and Co(III) may have stability constants with siderophores that rival or exceed those of Fe (Parker et al., 2004; Duckworth and Sposito,

2005a; Duckworth et al., 2009b; Harrington et al., 2012a,b). Interestingly, in the small number of studies that have probed the siderophore-promoted dissolution rates of Mn- and Co-bearing minerals, both reductive and ligand-promoted dissolution mechanisms have been observed (Duckworth and Sposito, 2005b, 2007; Peña et al., 2007; Bi et al., 2010). Whether a reductive or ligand-promoted dissolution mechanism predominates may be controlled by the electrode potential of the mineral (Bi et al., 2010).

The interactions between DFOB and Fe(III)-bearing minerals have been well studied, but only a limited number of studies exist that have explored mineral dissolution rates and mechanisms as promoted by other siderophores (Hersman et al., 1995; Reichard et al., 2005; Wolff-Boenisch and Traina, 2007b; Cervini-Silva, 2008; Haack et al., 2008; Dehner et al., 2010), a fact that limits our understanding of the function of siderophores in soils and natural waters (Kraemer, 2004). In addition, to our knowledge there have been no published studies that examine the interactions of siderophores other than DFOB with Mn(III) and Co(III)-bearing minerals. The goals of this study were to quantify and compare the dissolution rates of FeOOH, MnOOH, and CoOOH as promoted by several
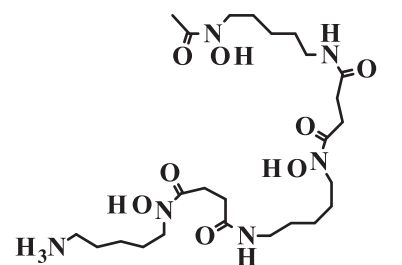
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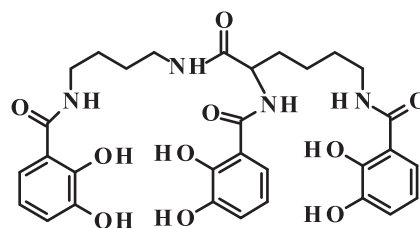
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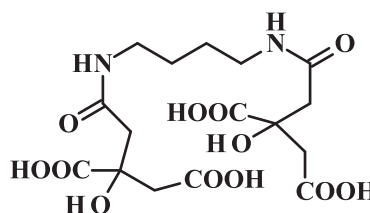
Rhizoferrin

Fig. 1. Structures of the siderophores selected for use in this study, which were chosen to span the structural diversity of common binding moieties found in microbial siderophores.