Redox-induced nucleation and growth of goethite on synthetic hematite nanoparticles

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ABSTRACT

The iron (oxyhydr)oxides hematite (α-Fe₂O₃) and goethite (α-FeOOH) are natural and reactive minerals common in soils and sediments, and their adsorption of Fe(II) produces reactive surface sites that facilitate reduction of oxidized environmental pollutants. Single-exposure experiments with 4-chloronitrobenzene showed that hematite is more reactive than goethite, when normalized by surface area loading. Interestingly, the product of Fe(II) oxidation is a mixture of goethite and hematite, and the goethite to hematite ratio depends on the distribution of Fe(II) activated surface sites, which is a function of aqueous Fe(II) concentration, surface area loading, and pH. More goethite is produced under conditions of higher Fe(II), lower surface area loading, and higher pH. Recurrent-exposure experiments showed a substantial decrease in reaction rate after one to three exposures, a trend suggestive of reaction contributions from the increasing goethite surface area over time. Using known atomic surface geometry for goethite and hematite, the hematite {012} facet is proposed as the site of primary mineral growth with goethite {021} at the interface between the two minerals. These results have implications in contaminant fate modeling, where the mineral phases present in the environment, the minerals likely to form, and the surrounding aqueous conditions all have an impact on contaminant reaction rate.

Keywords: Goethite, hematite, oxidative growth, evolving reactivity, Fe(II); Nanominerals and Mineral Nanoparticles

INTRODUCTION

Iron is one of the most abundant elements on Earth, and its oxides, oxyhydroxides, and hydroxides (collectively termed “iron oxides”) are currently tabulated at 17 recognized crystal structures (Fairvre 2016). Iron oxide minerals form in a range of mild to extreme environmental conditions, with phases produced dependent on temperature, pressure, pH, aqueous ion concentrations, hydration state, and oxygen fugacity (Schwertmann and Murad 1983; Cornell and Schwertmann 1996; Lagoix et al. 2016).

Anthropogenic influences, however, rapidly alter minerals, and the geological impacts of industrial activities like mining (Chopard et al. 2017; Valencia-Avellan et al. 2017) and agriculture (Maqueda et al. 2017) are still under investigation. The release of highly oxidized chemicals into reduced groundwaters facilitates redox reactions that not only transform the contaminants (Elsner et al. 2004a; Howard and Muir 2013), but alter mineral surfaces as well (Chun et al. 2006; Strehlau et al. 2016). Minerals are recognized as important tools for environmental remediation via natural attenuation (Pecher et al. 2002; Elsner et al. 2004b), permeable reactive barriers (Scherer et al. 2000), or in situ redox manipulation (Boparai et al. 2008), but alterations from inadvertent anthropogenic influences must also be considered so that they are recognized, rather than mistaken for natural processes.

The specific adsorption of Fe(II) to iron oxide surfaces is known to occur through bidentate complexes with contiguous singly coordinated hydroxyl group pairs (Wehrli et al. 1989; Barron and Torrent 1996). The subsequent electron transfer to the bulk oxide results in the formation of new Fe(III) surface structures (Tanwar et al. 2008; Catalano et al. 2010) and activates these minerals for participation in redox reactions. This electron transfer process has been demonstrated for goethite and hematite using Mössbauer spectroscopy (Williams and Scherer 2004; Larese-Casanova and Scherer 2007; Rosso et al. 2010) and calculated in detail for hematite using molecular orbital calculations (Rosso et al. 2003). Many highly oxidized environmental contaminants, such as nitroaromatic compounds, are readily reduced when they encounter these Fe(II)-activated surfaces (Hofstetter et al. 1999; Dunnivant et al. 1992; Klausen et al. 1995; Ju and Parales 2010). Measuring the concurrent oxidative mineral growth provides important information about which surfaces were readily accessible to and most reactive with aqueous Fe(II) (Chun et al. 2006; Vindedahl et al. 2015; Strehlau et al. 2016).

It has been proposed that Fe(II) adsorption on hematite leads to magnetite precipitation (Jeon et al. 2001, 2003), but this proposal has not been supported in other works (Pedersen et al. 2005; Tanwar et al. 2008). Rather, observations of Fe(II) adsorption on hematite {012} by crystal truncation rod diffraction indicate that the oxidized surficial Fe(III) have Fe-O bond lengths of 1.93–2.18 Å, which is in agreement with Fe-O bond lengths in the bulk lattice of both goethite and hematite but not magnetite (Yang et al. 2006; Tanwar et al. 2008). These reports of Fe(III) surface structures

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