Particle morphological and roughness controls on mineral surface charge development

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Abstract

Effects of mineral particle morphology and roughness on potential determining ion ($p.d.i.$; H^+, OH^-) loadings achieved at synthetic lepidocrocite (γ-FeOOH) surfaces were predominantly investigated by potentiometry and thermodynamic modeling. Nanosized rod- (RL) and lath-shaped (LL) particles exhibiting different proportions of the same predominant crystallographic faces acquired largely comparable pH, ionic strength and counterion (NaCl, NaClO₄) dependencies on $p.d.i.$ loadings. These results supported previous claims that faces ideally containing proton silent sites only, are likely populated by additional proton active sites. This concept was supported further by results of roughened LL-like particles (LLR) also showing highly congruent pH-, ionic strength- and composition-dependent $p.d.i.$ loadings with those of LL and RL. These loadings thereby correspond to maximal levels allowed by net attractive and repulsive forces at each solution composition, irrespective of particle morphology. Contrasting equilibration times required to achieve these loadings revealed considerably slower exchange of $p.d.i.$ and electrolyte ions near the point of zero charge in the rough LLR than in the more idealized LL and RL particles.

Thermodynamic modeling was used to test various concepts accounting for these results. The model made use of a novel framework capable of isolating electrostatic contributions from different faces, and of accounting for ion-specific double-layer properties within a single crystallographic face. These efforts made use of capacitance values for each electrolyte ions within the framework of a recently developed Variable Capacitance Model. Attempts at modeling all three particle types were used to suggest that the (0 1 0) face contains ∼0.9 site nm^{-2} of proton active sites, a value notably constrained by recently published Na^+, Cl^-, and ClO_4^- loadings derived by cryogenic X-ray photoelectron spectroscopy. The model presented in this work thus provides a means to predict $p.d.i.$ loadings on multifaceted mineral particle surfaces, and can therefore be used to constrain further our understanding of mineral/water interface reactivity.

1. INTRODUCTION

Mineral/water interfacial reactions are of widespread importance in terrestrial, aquatic and technological settings (Ertl, 1997; Ertl et al., 1999; Schwertmann and Cornell, 2003). Iron (oxy)(hydr)oxides are of particular importance given their high specific surface area and strong reactivity.

Their surfaces participate in processes that are central to important biogeochemical cycles (Schwertmann and Cornell, 2003), as well as to various (photo)(electro)chemical pathways (Ertl et al., 1999). Interactions taking place with liquid water are of particular relevance and involve reactions including (ad)sorption, charge development, dissolution, crystal growth, particle aggregation/flocculation, electron transfer, amongst others. Understanding the molecular controls to these reactions is thus essential for predicting the impact of iron (oxy)(hydr)oxide surfaces in settings of geochemical importance. This level of knowledge

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requires a thorough understanding of both interfacial water and electric double layer structures for predicting the nature and magnitude of the physicochemical forces exerted on ions and molecules approaching mineral surfaces.

A central aspect for understanding mineral surface reactivity lies in the identities, distributions and densities of (hydr)oxo groups responsible for adsorption reactions. At iron (oxy)hydroxide surfaces these groups are bound to one ($\equiv$FeOH; –OH), two ($\equiv$Fe$_2$OH; μ-OH) or three ($\equiv$Fe$_3$OH; μ$_3$-OH) underlying Fe atoms, and can possess distinct proton binding and ligand exchange energies (Venema et al., 1998). As the distributions and densities of these groups in crystalline materials are strongly controlled by the orientation of the terminating surface, particles of identical compositions but of different morphologies can have highly contrasting interfacial properties. Goethite (α-FeO-OH), for example, exhibits more homogeneous distributions of reactive and exchangeable –OH groups than lepidocrocite (γ-FeOOH), where these groups tend to be concentrated at particle edges (Fig. 1). The remaining (010) face is ideally terminated by proton silent μ–OH groups. Connected to this issue lies the question of whether electrostatic potentials on such ideally-shaped particles should be treated as separate terms in thermodynamic models, or that sufficiently high levels of proton active sites at defects and/or steps of the (010) plane of lepidocrocite would override the need for face-specific electrostatic potentials.

In a previous study from our group (Kozin et al., 2013) differences in potential-determining ions (p.d.i.; H$^+$, OH$^-$) and electrolyte ion loadings on lepidocrocite particles with different morphologies set such possibilities aside in an effort to compare results with goethite particles exhibiting considerably greater variations in surface porosity. As other studies have more specifically invoked surface defects and/or microporosity on the (010) face of lepidocrocite (Madrid and Diazbarrientos, 1988; Zhang et al., 1992; Hiemstra and van Riemsdijk, 2007) as well as in other minerals terminated with faces also exhibiting proton-silent μ-OH groups (Bargar et al., 2004; Trainor et al., 2004; Waychunas et al., 2005; Shchukarev et al., 2007; Catalano, 2011) these effects warranted further investigation.

In this study three different forms of synthetic lepidocrocite particles exhibiting contrasting proportions of the (010) face are studied to resolve the impact of particle morphology

and/or roughness on p.d.i. loadings (Fig. 1). Lepidocrocite forms from the oxidation of circumneutral ferrous iron solutions, passing through platy green rust particles as an intermediate oxidation product. Although not as widespread in occurrence as its goethite polymorph in nature, lepidocrocite tends to occur more in hydromorphic and poorly drained soils where oxygen supply is limited (Schwertmann and Cornell, 2003). Its surface reactivity has thereby been the object of numerous studies (Schwertmann and Taylor, 1972; Lewis and Farmer, 1986; Cornell and Giovanoli, 1988; Madrid and Diazbarrientos, 1988; Zhang et al., 1992; Biber and Stumm, 1994; Gehring and Hofmeister, 1994; Rustad et al., 1996; Venema et al., 1998; Randall et al., 1999; Manceau et al., 2000; Sudakar et al., 2003; Peacock and Sherman, 2004; Cudennec and Lecerf, 2005; Ona-Nguema et al., 2005; Hug and Bahnemann, 2006; Hiemstra and van Riemsdijk, 2007; Borer et al., 2009; Kim et al., 2011). In the laboratory, particles can be synthesized by oxidizing circumneutral ferrous chloride solution to rod- (RL) or lath-shaped (LL) morphologies (Fig. 1). While fast crystallization rates under low pH conditions tend to promote hedgehog-like particles, pin-cushion aggregates or even undefined morphology, slower rates under circumneutral conditions tend to result in RL-type particles. Furthermore, addition of NaCl under these latter conditions tends to hinder growth along the (010) face, thus producing LL particles. This salt effect, which was also observed in the formation of tabular hematite particles (Shchukarev et al., 2007), is thought to arise from interactions between μ-OH groups with Na$^+$ and Cl$^-$ ions, and thus provides initial clues to differences in reactivity between the (001) and (010) faces of lepidocrocite. This aspect of lepidocrocite surface reactivity, just as any other tabular-shaped metal (oxy)(hydr)oxide (e.g., gibbsite, hematite, green rust) or clay (e.g., kaolinite, illite, montmorillonite) particles commonly present in a variety of terrestrial and oceanic geochemical settings, also raises the question as to whether charges on one plane should impact adsorption free energies on other planes. It is highly relevant for understanding mineral particle growth mechanisms (e.g., solute precipitation, oriented particle aggregation). It is also a key aspect for understanding how bulk electron conduction can be driven by differences in electrostatic surface potentials in adjacent planes of semiconducting minerals, and therefore of strongly contrasting interfacial processes such as in the documented case of hematite (Yanina and Rosso, 2008).

Synthetic RL and LL particles were used for this work to evaluate the impact of differences in particle morphology on the adsorption of p.d.i. on different crystallographic faces. A third preparation consisting of rough LL (LLR) particles (Fig. 1) was also used to assess effects of surface roughness in facilitating p.d.i. uptake. High precision potentiometric titrations of aqueous suspensions of these particles in solutions of 3–100 mM NaCl and NaClO$_4$ were used to evaluate the possibility in predicting RL and LL surface reactivity based on a priori knowledge of differences in proportions of crystallographic planes. This was notably tested using a multisite complexation (MUSIC) (Venema et al., 1998) model describing charge development on co-existing (001) and (010) faces, but that also accounts
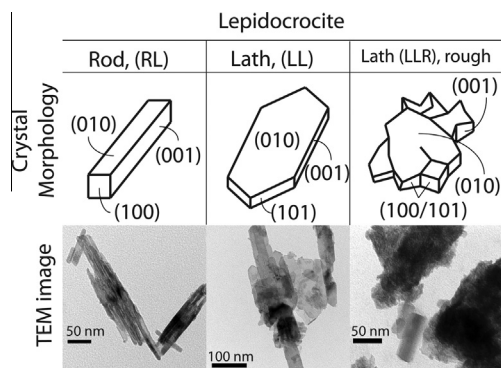

Fig. 1. Schematic representations (top) and TEM images (bottom) of RL, LL and LLR particles.