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Surface and mineral structure of ferrihydrite

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Abstract

Ferrihydrite (Fh) is an yet enigmatic nano Fe(III)-oxide material, omnipresent in nature that can bind ions in large quantities, regulating bioavailability and ion mobility. Although extensively studied, to date no proper view exists on the surface structure and composition, while it is of vital importance to our understanding of ion complexation in terrestrial and aquatic systems. Here, the surface structure of Fh is elucidated in relation to that of the mineral core, showing a unique surface composition differing from the mineral core. The mineral core is basically defect-free for all Fh particles. Key for understanding Fh is the very large contribution of the surface as an "inter-phase". The surface of Fh is depleted by two specific types of polyhedra (Fe2,Fe3). Surface depletion (SD) explains the observed particle size dependency of the (a) Pair Distribution Function (PDF) derived from High Energy X-ray total Scattering (HEXS), (b) thermogravimetric water content, and (c) mass density. It also explains the isotopic ^{57}Fe exchange ratio. Due to surface groups, two-line Fh particles are water rich but its mineral core is hydrogen poor.

The SD model elucidates the surface structure of crystal faces of idealized Fh such as the 1 −1 0 and 1 −1 1 type of faces that may strongly contribute (e.g. ~75 ± 10%) to the total surface area. These faces are terminated by protruding Fe1 octahedra, creating the singly-coordinated ≡FeOH(H) groups at the Fh surface. Alternating rows of Fe1 octahedra with singly-coordinated surface groups enable the formation of either double corner (^{2}C) or edge (^{1}E) surface complexes. For Fh, the site densities derived are much higher than for goethite. In combination with the high surface area, it makes Fh to an extremely reactive natural phase.

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1. INTRODUCTION

Primary nano-oxide particles (1–10 nm) are very important in nature (Hochella et al., 2008). In soils, the natural nano-oxide fraction creates a reactive surface area of 3–30 m^2/g soil (Hiemstra et al., 2010). This number may look modest, but only a few m^2/g may easily represent a reactive surface area of one million m^2 or more in a soil pedon of just 1 m^2. It illustrates the potential of nanoparticles to react in nature.

Ferrihydrite (Fh) or hydrous ferric oxide (HFO) is a well-studied, but yet enigmatic nano Fe(III) oxide material (Dzombak and Morel, 1990; Jambor and Dutrizac, 1998; Hochella et al., 2008). When freshly precipitated in lab or field, the particles are extremely small, in the order of 2–3 nm (Janney et al., 2000; Cismasu et al., 2011), and the reactive surface area is correspondingly very high (Davis and Leckie, 1978). From a practical and theoretical perspective, these particles are of interest for soil and geochemists, for aquatic and marine chemists, for environmental scientists and engineers (Davis et al., 1978; Pichler et al., 1999; Swedlund and Webster, 1999; Fukushi and Sato, 2005; Eusterhues et al., 2008; Hiemstra et al., 2010), as well as for mineralogists, colloid, surface, and computational chemists, and for material scientists (Manceau and Gates, 1997; Jansen et al., 2002; Michel et al., 2007; Rancourt and Meunier, 2008; Pinney et al., 2009; Rossberg et al., 2009; Harrington et al., 2011; Xu et al., 2011; Peak and Regier, 2012). It is highly relevant to know the surface structure of Fh because insight in its ion adsorption

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behavior cannot be well-developed without a proper view on the surface structure (Hiemstra and Van Riemsdijk, 1996). Surface structure and composition are not only very relevant for understanding ion complexation in terrestrial and aquatic systems, but this is also highly relevant for comprehending mineral phase stability of Fe oxides in nature (Fukushi and Sato, 2005; Navrotsky et al., 2008; Majzlan, 2011), iron storage in organisms (Kim et al., 2008; Michel et al., 2010b), and biogeochemical processes such as oxidation of greenhouse gasses (Beal et al., 2009).

A variety of structural models has been suggested for Fh as recently reviewed by Harrington et al. (2011) and Manceau (2011). In 2007, a new structure for Fh with δ-Keggin entities has been proposed (Michel et al., 2007). Synchrotron-based High-Energy X-ray total Scattering (HEXS) was used, basically collecting information on the distribution of neighboring atoms, described with the Pair Distribution Function (PDF). Fh contains, besides Fe in hexa-coordination, also Fe in tetrahedral coordination, and is isostructural with akdalaite ($Al_{10}O_{14}(OH)_2$) (Yamaguchi et al., 1964; Hwang et al., 2006). The crystallographic characteristics of Fh have been pointedly discussed (Drits et al., 1993; Jansen et al., 2002; Michel et al., 2007; Rancourt and Meunier, 2008; Hiemstra and Van Riemsdijk, 2009; Pinney et al., 2009; Manceau, 2010, 2011; Michel et al., 2010a; Harrington et al., 2011; Maillot et al., 2011; Mikutta, 2011; Xu et al., 2011; Peak and Regier, 2012).

According to Michel et al. (2010a), the structure of Fh is particle size dependent and has two end members. The largest particles (diameter d ~7–9 nm) are supposed to be defect-free and have been called 'FerriFh' ($Fe_{10}O_{14}(OH)_2$). These are formed upon aging from freshly-precipitated two-line Fh (2LFh), supposing to be highly defect resulting in a water rich mineral core. However, recently it is has been shown that 2LFh can be largely dehydrated without significant changes in the mineral structure (Xu et al., 2011) reaching the composition of ideal Fh ($Fe_{10}O_{14}(OH)_2$) having a OH/Fe ratio of only 0.2 (Xu et al., 2011). This observation strongly questions a mineral core with a large number of defects that can dehydrate while basically maintaining the mineral structure. Moreover, it challenges OH-rich models for Fh such as the model of Drits et al. (1993).

Small (2.5 nm) Fh nanoparticles consist of only about 200 Fe atoms. The majority of the Fe atoms is also part of the surface as an "inter-phase". This reality is easily overlooked in the structural analysis of 2LFh. In fact, surfaces are the key for understanding Fh. Our hypothesis is that the polyhedral composition of the surface differs fundamentally from that of the mineral core and that this inter-phase concept can be linked to the observed particle size-dependency of the PDF (Michel et al., 2010a). Here, we will elucidate the surface structure and composition of Fh, developing a quantitative surface depletion (SD) model. Our analysis enables for the first time assessment of the type and number of reactive sites on the Fh surface and, additionally, a first estimation of the corresponding proton affinities and point of zero charge (PZC). Our results also show that the mineral core of Fh is essentially defect-free for all Fh particles and that the size-dependent variation is surface driven.

2. MINERAL AND SURFACE STRUCTURE

2.1. Mineral structure and stability

According to Michel et al. (2010a), the ideal structure for Fh consists of three types of Fe sites (Fe1, Fe2, Fe3). The first two types of Fe ions (respectively 60% and 20%) are hexa-coordinated and the last one (20%) is tetrahedrally coordinated. In the Fh structure, a δ-Keggin moiety can be recognized having a tetrahedral Fe (Fe3) in the center (Fig. 1).

Fh can be built (Fig. 2) from horizontal sheets with Fe1 octahedra (yellow) sandwiched by octahedral Fe2 (dark blue) and tetrahedral Fe3 (light blue). Since Fe(III) does not fit well in a tetrahedron, we propose that the Fe3 polyhedron is only stable in the mineral core while it is depleted from the surface and therefore, from the Fh particles as a whole. If surfaces are involved, the depletion will be most significant for the smallest Fh particles, in line with the PDF analysis (Michel et al., 2010a), showing the strongest depletion of Fe3 for the smallest particles.

Simultaneously, the PDF analysis (Michel et al., 2010a) shows a similarly large depletion for Fe2, suggesting also a lower stability for Fe2 octahedra at the surface. Less stability may be due to the strong asymmetry in its coordination sphere, having three exceptionally short bonds and three exceptionally long Fe–O bonds. For 2LFh, the bond length difference is about 24 pm while for six-line Fh (6LFh), the asymmetry is even larger, i.e. about 36 pm. This contrasts with the distances in the Fe1 octahedron that differ only 8 pm or less.

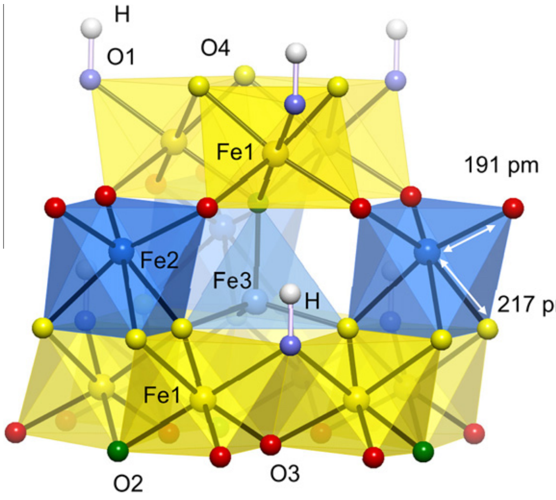

Fig. 1. Keggin moiety as a part of the Ferrihydrite (Fh) structure. Two sheets with edge-sharing Fe1 octahedrons (yellow) are fixed together by three octahedral Fe2 (dark blue) and one tetrahedral Fe3 (light blue) in the middle. Four types of oxygens can be distinguished (O1, O2, O3, and O4). O1 binds a proton (Pinney et al., 2009). In Fh, the Fe2 octahedrons are strongly distorted, which will affect its stability if present at the surface of an Fh particle (see text). The Fe–O distances in the Fe2 octahedron are for 2LFh (Harrington et al., 2011). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)