Incorporation of Ge in ferrihydrite: Implications for the structure of ferrihydrite

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ABSTRACT

Ferrihydrite is the main form of ferric iron in surficial environments and a key reactive nanoparticle that regulates nutrient availability and the mobility of metal(loid) contaminants, yet its structure is not completely elucidated. Two models exist to date: the “f-phase” in which Fe is fully octahedral and the “akdalaite-model” possessing 20% of the Fe atoms in tetrahedral coordination. In this study, germanium was used as a structural probe to re-examine the validity of the latter model. Germanium-bearing ferrihydrites containing 0.2, 0.6, 1.4, 2.2, 2.9, 3.8, 12, and 15 wt% Ge were synthesized in the laboratory at 25 and 65 °C. X-ray diffraction analyses showed all the precipitates to be six-line ferrihydrite. Semi-quantitative energy-dispersive X-ray microanalyses (TEM) indicate that the precipitates made from solutions having Fe/Ge molar ratios of two and four have Fe/Ge atomic ratios of 3.8–3.9 and 4.4–5.1, respectively, which suggest a limit of Ge uptake in ferrihydrite of about 20 at% relative to total cations. Based on TEM examinations, these high Ge-bearing ferrihydrites are homogenous and consist of equant and plate-like crystallites about 5–6 nm in size. Furthermore, it appears that higher Ge concentrations in solution have no significant effect on the crystallite size, supporting the incorporation of Ge in the ferrihydrite structure. Extended X-ray absorption fine structure (EXAFS) spectroscopy indicated that the Fe atoms in both the low and high Ge-bearing ferrihydrites are in octahedral coordination and that Ge occurs in the ferrihydrite structure by filling the empty tetrahedral sites and coordinating to 4 edge-sharing FeO₆ octahedra through sharing a common oxygen (Ge-O-Fe linkage). Incorporation of the Ge tetrahedra in the ferrihydrite structure requires redistribution of Fe occupancy along the alternating O/OH layers while forming an ordered distribution of octahedral Fe and tetrahedral Ge. The local structure around Ge mimics a Keggin-like motif in two different, yet equivalent, orientations. It appears that the split diffraction peak at 1.46 and 1.51 Å is a characteristic feature of Ge-rich ferrihydrite and suggests that it is a fingerprint of increased order due to significant Ge incorporation in the tetrahedral sites. The findings can be rationalized in terms of the incorporation of Ge in the so-called “f-phase” of the classical ferrihydrite model, and demonstrate the flexibility of the model in terms of accommodating a Keggin-like cluster without the need of imposing unrealistic constraints as in the akdalaite model. Direct comparison of the imaginary parts of the Fourier transforms for ferrihydrite and maghemite further confirms the absence of tetrahedral Fe in ferrihydrite. The absence of tetrahedral Fe substantiates the use of goethite-like or akaganeite-like models to describe the polyhedral structure of ferrihydrite used in modeling sorption reactions at the ferrihydrite-water interface.

Keywords: Ferrihydrite, structure, germanium, iron, tetrahedral iron, EXAFS

INTRODUCTION

Ferrihydrite is a poorly crystalline and metastable nano-sized ferric oxyhydroxide. It is widespread in soils, iron-rich oxidized sediments, acid mine drainage settings, mine wastes, and Fe-rich hydrometallurgical process waters (Jambor and Dutrizac 1998). Because of its small size [i.e., 2–3.5 nm, Eggleton and Fitzpatrick (1988); 1–6 nm, Janney et al. (2000)], its abundance, and the geochemical reactivity of the contained ferric ion, ferrihydrite plays an important role in iron cycling and in controlling nutrient and toxic element mobility and bioavailability in the near-surface environment.

Ferrihydrite has long been considered to be a mixture of defective and defect-free varieties, the so-called “d-phase” and “f-phase” (Drits et al. 1993a; Marchand and Rancourt 2009; Manceau 2009, 2011). More recently, Michel et al. (2007, 2010) proposed a new structural model for ferrihydrite which is single-phase, has a low density of defects, and is isostructural with the mineral akdalaite [Al₉O₈(OH)₂]. Unlike the conventional model (Drits et al. 1993a; Manceau 2011), 20% of the Fe atoms are in tetrahedral coordination in the new model, and octahedra share corners and edges only, without a face-sharing arrangement. The new model received criticism because of its shortcomings in adequately describing the X-ray diffraction, X-ray absorption spectroscopy, and Mössbauer data, and not being in accordance with fundamental crystal-chemical principles (Rancourt and Meunier 2008; Hiemstra and van Riemsdijk 2009; Manceau 2009, 2010, 2011, 2012a).

Recently Song et al. (2010) reported incorporation of Ge in...