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Critical evaluation of the revised akdalaite model for ferrihydrite

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Abstract

The defect-free akdalaite model (fhyd6) for six-line ferrihydrite (6Fh) derived from a pair distribution function (PDF) analysis of high-energy X-ray scattering (HEXS) data was revised (model ferrifh) by Michel et al (2010) using data from a sample produced by heating two-line ferrihydrite (2Fh) at 175 °C for 8 h in the presence of citrate. We show here that the scattering pattern for this sample is similar if not the same as that for hydromaghemite, which in turn is a mixture of maghemite (γ-Fe_2O_3), hematite and 6Fh. As in the case of fhyd6, the PDF of ferrifh was regressed using the structure of the weakly hydrated phase akdalaite [$Al_{10}O_{14}(OH)_2$] after substituting Fe for Al as a starting model. We show that the ferrifh model is implausible for the following reasons. (1) It is derived from a sample, ferrifh, that appears to be hydromaghemite, not pure 6Fh. (2) It has 20% tetrahedral Fe, a coordination that had been eliminated previously using XANES, Mössbauer, and EELS spectroscopies. (3) 75% of the Fe octahedra have shared edge lengths considerably longer than the shortest unshared edges in violation of Pauling's distortion rule. (4) Three tetrahedral Fe-O bonds are longer than three octahedral Fe-O bonds, inducing significant polyhedral distortions. And (5) the calculated composition [$Fe_{10}O_{14}(OH)_2 \cdot 1.2H_2O$] disagrees with literature data on weight loss from dehydration for 6Fh.

We present an alternative interpretation of the histogram of Fe-Fe distances up to 3.7 Å obtained from the PDF of the fhyd6 ferrihydrite as a mixture of local structures of goethite/akaganeite (α/β-FeOOH) and feroxyhite/hematite (δ-FeOOH/α-Fe_2O_3). Within this interpretation Fe only occupies octahedra that are bonded to each other by faces, edges, or double-corners. This polyhedral connectivity is confirmed experimentally by analysis of the EXAFS spectra of six-line ferrihydrites measured at room and liquid helium temperature. The Fe-Fe pairs from EXAFS data are described reasonably well by a mixture of approximately 70% feroxyhite (containing some nanohematite) and 30% akaganeite, without resorting to other phases. This set of evidence indicates that HEXS data are consistent with the Drits model for ferrihydrite (Drits et al. 1993a).

Keywords: Ferrihydrite, diffraction, HEXS, PDF, EXAFS, structure, oxyhydroxide, nanoparticle