

## A disordered nanoparticle model for 6-line ferrihydrite

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### ABSTRACT

Much of the bioavailable and geochemically reactive iron in aerobic, circumneutral settings is frequently found in the form of nanoscale particles of a hydrated iron(III) oxyhydroxide phase known as ferrihydrite. Developing useful structural descriptions of defective nanophases such as ferrihydrite has long posed significant challenges. Recently, Michel et al. (2007, 2010) proposed a structural model for ferrihydrite in place of the long-accepted model of Drits et al. (1993). Both models reproduce to high accuracy certain forms of X-ray scattering data from powdered ferrihydrite. However, discrepancies remain that we hypothesized are due to forms of structural disorder not easily represented by existing models. To test this hypothesis, we performed a novel structural analysis of total X-ray scattering data acquired from 6-line ferrihydrite. We generated three candidate whole-nanoparticle models of ferrihydrite composed of a two-phase *Drits* model, the *Michel* model, and a *hybrid* phase based on a single-phase *Drits* model that incorporated tetrahedral Fe sites, creating a lattice in which the *Michel* model was one of many possible topologies. We implemented a reverse Monte Carlo (RMC) approach to explore alternative configurations of iron occupancies plus structural disorder, and to refine the nanoparticle structure using both the reciprocal and real-space forms of the X-ray scattering data. We additionally used oxygen *K*-edge X-ray absorption spectroscopy to semi-quantitatively assess the ratio of protonated:non-protonated oxygen sites in an iron(III) oxides. This analysis provides independent evidence for a significantly lower OH:O stoichiometric ratio for ferrihydrite than for goethite, further constraining the RMC models.

The *hybrid* structure model gave better agreement to the experimental total scattering data than nanoparticles based upon either the *Michel* or *Drits* models. Models that incorporated tetrahedrally coordinated iron sites consistently achieved better matches to the data than models containing face-sharing octahedra. Long-range vacancy disorder was essential for optimum fits to the scattering data, highlighting the utility of whole-nanoparticle models in place of unit-cell models with random distributions of iron vacancies. The RMC-derived structures do not satisfy all experimental constraints on composition and structure. Nevertheless this work illustrates that a suitably constrained RMC method applied to whole-nanoparticle models can be an effective approach for exploring disorder in nanocrystalline materials.

**Keywords:** Nanoparticle structure, reverse Monte Carlo, total X-ray scattering, pair distribution function