Protonated nanoparticle models of 6-line ferrihydrite

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Ferrihydrite is a probably the most widespread and environmentally important natural inorganic nanoparticle, composed of defective nanocrystals of hydrous iron(III) oxide. Recently, Michel *et al* [1,2] proposed a structural model for ferrihydrite in place of the long-accepted model by Drits *et al* [3]. Despite the excellent agreement between the *Michel* model and experimental pair distribution function (PDF) analysis of ferrihydrite samples, X-ray diffraction data are not perfectly reproduced. We hypothesized that the discrepancies were due to structural disorder not easily captured by a single-unit cell model. We implemented a reverse Monte Carlo (RMC) approach to explore structural disorder in whole-nanoparticle models, including alternative configurations of iron occupancies plus displacement disorder. We refined the nanoparticle structure using both the reciprocal and real-space forms of the X-ray scattering data. The RMC-derived disordered nanoparticles gave better agreement to the experimental total scattering data than was attained for nanoparticles based upon either the *Michel* or *Drits* models [4].

We are seeking to determine whether the RMC-derived structures may be used as realistic whole-nanoparticle models of ferrihydrite. A step towards this goal is the generation of atomistic models that are stable in molecular dynamics (MD) simulations and can be used to study hydration and aggregation phenomena. A challenge for this effort is the correct protonation of oxygen atoms. Because proton positions cannot be determined from X-ray scattering data, we applied an algorithm based on bond strength analysis. We will discuss the results of the protonation approach, and the insights that whole-nanoparticle models may confer for understanding the structure of highly disordered minerals.

[1] Michel, F.M. *et al* (2007) *Science* **316**, 1726-1729. 7 [2] Michel, F.M. *et al* (2007) *Proc. Nat. Sci. Am.* **107**, 2787-2792 [3] Drits, V.A., *et al* (1993) *Clay Minerals* **28**, 185-207 [4] Gilbert, B., *et al* (2013) *Am. Min.* **98**, 1465-1476