A disordered whole-nanoparticle model for 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*. (2007, 2010) proposed a structural model for ferrihydrite in place of the long-accepted model by Drits *et al*. (1993). The *Drits* and *Michel* models each achieve arbitrarily good agreement with, respectively, XRD and PDF data, but not with both. Because X-ray scattering methods have a growing role in structural studies of nanoscale materials, it is essential to understand the origin of this apparent paradox. Here we present a novel structural analysis of total X-ray scattering data acquired from 6-line ferrihydrite. We generated candidate whole-nanoparticle models of ferrihydrite composed of a two-phase *Drits* model, the *Michel* model, or 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.

Nanoparticles based upon the *hybrid* structure converged to give better agreement to the experimental total scattering data than was attained for nanoparticles based upon either the *Michel* or *Drits* models. RMC models that incorporated tetrahedrally coordinated iron sites achieved better matches to the data than RMC models with face-sharing octahedra. Long-range vacancy disorder was essential for optimum fits to the scattering data, highlighting the advantage of whole-nanoparticle models in place of unit cell models. The RMC-derived structures do not satisfy all experimental constraints, but our results suggest a route to achieving better descriptions of this, and other, defective nanomaterials.

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

Sequence of phase transitions in calcite biominerals, mapped with 20 nm resolution, and their energetics

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We will show data from 20nm-resolution synchrotron photoelectron spectromicroscopy and microcalorimetry, demonstrating that in sea urchin biominerals the first mineral deposited is hydrated amorphous calcium carbonate (ACCH2O), which rapidly transforms into ACC, which slowly transforms into calcite [1]. The same process occurs abiotically, but it takes seconds to crystallize, whereas in the animal it takes days, hence the above phase transitions are highly bio-regulated. The energetics [2], spatial distribution of phases, and time-evolution [3] of this complex process will be presented, with particular emphasis on the role of SM50 [3], a protein that appears to stabilize ACCH2O in vitro, and may have this function in vivo [4].

[1] Y Politi *et al*. (2008) *PNAS*. [2] AV Radha *et al*. (2010) *PNAS*. [3] YUT Gong *et al*. (2012) *PNAS*. [4] CE Killian *et al*., work in progress.

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