The Structure of Ferrihydrite, a Nanocrystalline Material

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Despite the ubiquity of ferrihydrite in natural sediments and its importance as an industrial sorbent, the nanocrystallinity of this iron oxyhydroxide has hampered accurate structure determination by traditional methods which rely on long-range order. Here we uncover the atomic arrangement by real-space modeling of the pair distribution function (PDF) derived from direct Fourier transformation of the total x-ray scattering. The PDF for ferrihydrite synthesized using different routes is consistent with a single phase (hexagonal spacegroup P6₃mc; a = ~5.95, c = ~9.06 Angstroms). In its ideal form, this structure contains 20% tetrahedrally and 80% octahedrally coordinated iron and has a basic structural motif closely related to the Baker-Figgis δ-Keggin cluster. Real-space fitting indicates structural relaxation with decreasing particle size and also suggests that second-order effects such as internal strain, stacking faults and particle shape contribute to the PDFs.

Ferrihydrite is ubiquitous in many near-surface environments (1, 2) and is routinely used in industrial applications such as in direct coal liquefaction and metallurgical processing (3, 4). It occurs in pristine soils and sediments as the precursor to hematite (5) and often in areas contaminated by acid mine drainage. Due to its extremely high surface area and reactivity, ferrihydrite plays a significant role in the sequestration of contaminants from groundwater and streams through adsorption and coprecipitation. As such, it is also manufactured for use as a scavenger of heavy metals and metalloids during the treatment of wastewaters and in remedial activities. It also forms the inorganic core of ferritin, an iron storage protein that plays a key role in controlling the levels of iron in plants, animals, and microbes (6).

Even with the considerable attention given to the chemical and physical properties of ferrihydrite in prior research, there is no consensus on the crystal structure of this mineral. The primary impediment to the development of a definitive structural determination is the size of individual ferrihydrite crystallites which are typically <10 nm (nanocrystalline). With regard to structure, most of the disagreement centers on the possible presence of multiple structural phases and the local environment of iron (7–10), and has implications for understanding its reactivity, magnetic properties, and overall chemical composition. No single formula is widely accepted for ferrihydrite and this is attributed to variable water content and a lack of a known crystal structure (11). Ferrihydrite is commonly designated as “2-line” or “6-line” on the basis of the number of poorly defined, broadened maxima observed in x-ray diffraction (XRD) patterns. Determining a starting structural model for this phase is particularly challenging because ferrihydrite has no known well-crystalline counterpart that can be synthesized in the laboratory or found in nature. We recently showed that the short- and intermediate-range ordering in synthetic nanocrystalline ferrihydrite is consistent for scattering domain sizes ranging from 2 to 6 nm, and therefore the structure of ferrihydrite appears to be single phase (12). This result contradicts some prior studies (7–10) and is fundamentally different from the current multi-phase structure model that is increasingly cited for this phase.

Synthetic ferrihydrite with three distinct average coherent scattering domain sizes of approximately 2 (Fhyd2), 3 (Fhyd3), and 6 nm (Fhyd6) were synthesized and evaluated as part of this study (13). Structural analysis using the PDF method involves a comparison between PDFs generated from the experimental scattering data and those calculated from structural models [(14) for review]. A highly constrained “Rietveld-like” refinement can be performed on a properly normalized PDF in which the unit cell dimensions, atomic positions, displacement, occupancies, and other model-dependent parameters are varied to improve the fit between the observed and calculated PDF (15). The starting model best describing the distribution of interatomic distances in ferrihydrite is isostructural to the mineral akdalaite (Al₁₀O₄(OH)) (16, 17) and was identified by using the few positions of the most identifiable Bragg features in the XRD patterns. Based on the real-space fitting results, we contend
that the structure of ferrihydrite with domain sizes ranging from 2 to 6 nm can be adequately described by a single phase model with the hexagonal spacegroup P6\textsubscript{3}mc and a unit cell with average dimensions of \(a = 5.95\ \text{Å}\) and \(c = 9.06\ \text{Å}\) (Fig. 1). On the basis of this structure in its ideal form the chemical formula for ferrihydrite is \(\text{Fe}_{10}\text{O}_{14}(\text{OH})_2\). Thermal analysis strongly suggests the presence and particle size dependence of additional surface-bound water (12). Although the structure of ferrihydrite can be satisfactorily described by a periodic model (Fig. 2), residuals in the fitting results suggest that second-order effects such as disorder, surface relaxation, internal strain, defects (e.g., stacking faults), particle shape (18), and/or inter-particle correlations may also contribute to the experimental PDFs. Misfits in the region between 2.5 and \(6\ \text{Å}\) (Fig. 2, A to C) are reminiscent of those found in a similar study of \(\gamma\text{-Al}_2\text{O}_3\), where differences are attributed to nanometer-sized domains (\(\sim 1\ \text{nm}\)) reflecting stacking faults in the matrix (19).

The basic structural motif of the model, which is closely related to the Baker-Figgis \(\delta\)-Keggin cluster (20), consists of 13 iron atoms and 40 oxygens (Fig. 3). The central tetrahedrally coordinated Fe is connected via \(\mu_4\)-oxo bridges to twelve peripheral octahedrally coordinated Fe atoms arranged in edge-sharing groups of three. The 2-to-6 nm ferrihydrite nanoparticles can then be described as a 3-dimensional packing of these clusters with adjacent clusters connected by a common pair of edge-shared octahedra, forming \(\mu_4\)-oxo bridges from the three \(\mu_2\)-OH groups \textit{cis} to each of the \(\mu_4\)-oxo centers in the bare cluster. This arrangement creates a cubane-like moiety corresponding to four edge-shared Fe octahedra (Fig. 1). Fitting results indicate that some parameters such as unit cell dimensions and occupancies change systematically as the average domain size decreases from 6 nm to 2 nm for Fhyd6 and Fhyd2, respectively. Additionally, the degree of distortion of the Fe1 polyhedra varies as indicated in part by the change in the refined \(z\)-parameter for the O1 site, but despite these differences, the cluster-like structural motif remains. Such changes could reflect the occurrence of stacking defects or internal strain in the structure but are not fully understood at present.

This structure in its ideal form consists of 20\% \(\text{FeO}_4\) and 80\% \(\text{FeO}_6\) polyhedra. However, the Fe2 and Fe3 sites show a decrease in occupancy with decreasing particle size whereas no particle size dependent changes are observed for the fully occupied Fe1 site. This trend might reflect an overall increase in disorder resulting from the change in ratio of Fe atoms near the surface versus interior with decreasing particle size (21). These surface regions of ferrihydrite are anticipated to be predominantly octahedrally coordinated given the overall topology of the structure presented and the unlikely existence of coordinatively unsaturated Fe at the hydrated surfaces. The refined parameters for each sample are available in the supporting online text.

The presence of tetrahedrally coordinated iron in ferrihydrite has been the subject of considerable debate. Previous estimates based on a variety of techniques have ranged from 0\% to \(\sim 40\%\), approximately the same amount found in maghemite (\(\gamma\text{-Fe}_2\text{O}_3\)), and even up to 100\% (22–24). In a recent study using electron energy loss spectroscopy (EELS) to evaluate the effects of electron beam damage to ferrihydrite, Pan \textit{et al.} (25) observed the reduction of \(\text{Fe}^{3+}\) to \(\text{Fe}^{2+}\) and a migration of Fe from octahedral to tetrahedral sites with increasing electron dose. These results highlight how investigations carried out under the high vacuum of the transmission electron microscope may cause significant, and perhaps undetected, changes to occur in a sample. Such changes must now be considered when evaluating the most current and increasingly cited multi-phase model for ferrihydrite that was purportedly confirmed using electron nanodiffraction (7, 8). Pan \textit{et al.} estimate, by linear extrapolation to very low electron dose (1 electron nm\(^{-2}\)), that tetrahedrally coordinated \(\text{Fe}^{3+}\) could be absent from the pristine structure of ferrihydrite and only appears due to electron beam damage. However, this is a minimum estimate. Peak fitting of the energy loss spectrum recorded at the lowest measured electron dose (3 x \(10^7\) electron nm\(^{-2}\)) indicates that at this dose as much as 25 ±15\% of the total iron in the mineral is tetrahedrally coordinated \(\text{Fe}^{3+}\) (26).

Mössbauer studies performed at temperatures as low as 4.2 K by our group and others (27) show spectra completely split magnetically and appearing as sextets. Although this behavior does not rule out the existence of discretely different iron sites, the existence of 4-coordinated iron remains inconclusive (28). Future Mössbauer studies at sub-liquid He temperatures may prove useful for further resolving this debate as was demonstrated in a study of a structurally-related Fe\(\text{13}\) cluster ((C\(\text{H}_3\text{N}^+\))\text{[Fe}_{13}\text{F}_{26}\text{(OCH}_3\text{)}_3\text{O}_4\]) \(\text{CH}_3\text{OH-4H}_2\text{O}\) (29).

Whether a 2 nm (i.e., \(\sim 30\) unit cells) or even a 6 nm plate-like particle can be described using a periodic model is debatable. It has been argued that a particle with maximum dimensions of only several nanometers and possessing significant disorder may itself be described by a single large super cell. The satisfactory fit obtained by the single phase defect-free unit cell for ferrihydrite in the present study does not support this view. Synthetic ferrihydrite samples with average coherent scattering domain sizes ranging from 2 to 6 nm can be described by a single phase periodic structure that does not require multiphase, size-dependent models (16). The proposed structure model for ferrihydrite does not address the positions for H-sites. However, we anticipate that, with the iron and oxygen framework established, neutron total...
scattering studies on deuterated ferrihydrite will provide a complete model.

Quantitatively evaluating the structures of materials that exhibit coherent periodicity only on length scales of the order <10 nm and are sensitive to changes under vacuum represents a considerable challenge for conventional diffraction methods and electron imaging techniques. Although ab initio structure determination of nanocrystalline materials is in its infancy (30), domain-limited PDFs from total scattering data to very high reciprocal space values (i.e., ≥25 Angstroms⁻¹) provide a map of interatomic distances, which can be fitted with competing structure models [e.g., (31)]. Such models may appear to be quite similar in terms of short range ordering (i.e., distances of 1 to 5 Angstroms) but are distinguishable over intermediate-range length scales (i.e., 5 to 20 Angstroms) due to differences in overall topology. Although it is not possible to demonstrate the uniqueness of a successful model, a solution which is consistent with the experimental PDF over 20 Angstroms, or more, provides strong confidence in the result. Traditional structure solution in well-ordered periodic materials relies on the interpretation of sharp Bragg reflections to derive an initial unit cell. This conventional approach is generally not feasible for nanocrystalline materials like ferrihydrite due to the lack of discernable Bragg reflections in diffraction patterns dominated by broad diffuse scattering. This diffuse component results not only from extremely small coherent scattering domain sizes, but also from surface relaxation, strain, and complex disorder which often distinguishes the structures of nanocrystalline materials from their bulk counterparts (32). Thus, the interpretation of the broad diffuse diffraction patterns of nanometer-sized crystals through observation of structural details in real space via the pair distribution function method provides the best means of discrimination between existing, and potentially closely related models.

References and Notes
12. F. M. Michel et al., Chemistry of Materials 19, 1489 (2007).
13. Materials and methods are available as supporting material on Science Online.
16. Further details available on Science Online.
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Supporting Online Material
www.sciencemag.org/cgi/content/full/1142525/DC1
SOM Text
Fig. S1
Tables S1 and S2
Crystallographic Information Files
References

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Fig. 1. Polyhedral representation of the hexagonal unit cell for ferrihydrite. The bonded atoms (shown in yellow) define a cubane-like moiety that connects the basic structural motif of the model.

Fig. 2. G(r) or the PDFs for Fhyd6 (A), Fhyd3 (B), and Fhyd2 (C) plotted to 20 Å (gray x) with the refined fit of the model overlain (solid black) for each. Difference plots are shown immediately below.

Fig. 3. Polyhedral representation of the ideal ferrihydrite structure viewed along the c axis. The central FeO₄ tetrahedra are surrounded by 12 FeO₆ octahedra.