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NEW DATA AND A REVISED STRUCTURAL MODEL FOR FERRIHYDRITE: REPLY

Key Words—Coordination, Crystal structure, Ferrihydrite, Iron, Thermal analysis, X-ray absorption edge spectroscopy.

We thank Manceau *et al.* (1990) for their comments and the interest they have shown in our paper (Eggleton and Fitzpatrick, 1988) and more particularly for prompting further examination of the ferrihydrite structure. Some of the points raised by Manceau *et al.* (1990) are welcomed in that they provide us with the opportunity to clarify and further emphasize the important features of our original communication. We do not, however, agree with all their remarks. In their concluding remarks they state: "It is only by using adequate analytical tools (e.g., extended X-ray absorption fine-structure spectroscopy and X-ray absorption near-edge spectroscopy), that the local order, the only preserved structural scale of poorly ordered compounds, will be elucidated." We agree that adequate analytical tools should be used and for this reason we used a range of techniques including X-ray powder diffraction (XRD), thermal analysis (DTA and TGA), transmission electron microscopy (TEM), X-ray absorption edge spectra, selective chemical dissolution, surface area measurements and magnetic susceptibility. Moreover, we made it quite clear that our interpretations were tentative and could be refined by data obtained from other specialized techniques. In our paper we also tried to emphasize that the structure of a ferrihydrite material might depend on the method of preparation (p. 122, end of discussion section). Our approach, therefore was (1) to use several techniques, (2) to describe in detail the methods of preparation, and (3) carefully and specifically to publish the XRD, DTA, TGA, and X-ray absorption edge curves of the products of these detailed methods of formation. Manceau *et al.* (1990) unfortunately did not give the details of their methods of preparation nor did they include the XRD curves from those preparations. They do refer to two papers which as yet have not been published.

Some of their comments on our thermal analyses interpretations and discussion are based on misunderstanding of our argument. When cubic close-packed (CCP) γ-phase oxyhydroxides of Al and Fe dehydroxylate on heating, they transform to the CCP γ-oxide phase (e.g., boehmite to spinel or lepidocrocite to maghemite). The α-phase hexagonal close-packed (HCP) oxyhydroxides (e.g., goethite), however, dehydroxylate on heating to α-phase HCP oxides (e.g., hematite is generally formed, unless some reduction of Fe^{3+} also occurs during the thermal dehydroxylation, in which case the magnetic CCP magnetite is formed here also). Therefore, the important observation we emphasized was the appearance of maghemite as an intermediate stage during the heating of ferrihydrite and that this transformation indicated the presence in this ferrihydrite of an oxygen packing arrangement different from simple hexagonal close-packing.

The observation that at least some ferrihydrite transformed first to a spinel-type structure we interpreted as supporting the concept that ferrihydrite did not have the Towe and Bradley (1967) defect-hematite structure, in which Fe is present in octahedral sites only and anions are in hexagonal closest packing. Certainly, the presence of tetrahedral ferric iron in a heating product does not prove tetrahedral ferric iron the precursor, but it does require an explanation. Manceau *et al.* (1990), however, quoting Johnson and Lewis (1983), stated that "aging ferrihydrite at moderate temperature (92°C) directly transforms to hematite instead of maghemite." In contrast and rather unexpectedly we detected both maghemite and hematite after heating our ferrihydrite samples between 250° and 600°C (see combined DTA, TGA, XRD data in Figures 1 and 8 on pp. 114 and 120, respectively). We also observed double exotherms on the ferrihydrite DTA pattern, which had been observed before by several workers (e.g., Towe and Bradley, 1967; Karim, 1984; Lewis and Schwertmann, 1980). Furthermore, Manceau *et al.* (1990) stated, "Diffusion of 6-fold iron to vacant tetrahedral sites requires higher temperatures." Thermal transformations between the various iron oxyhydroxide and oxide phases are complex and may depend on the structure of the original phase, crystal size, and heating rates (see Mackenzie, 1970, 1972; Rooksby, 1961). The relatively low-temperature transition of our ferrihydrite samples to maghemite supports our contention that the structure contains tetrahedral Fe^{3+}.

Manceau *et al.* (1990) also mentioned åkaganeite (β-FeOOH) and boehmite (γ-AlOOH) in their argument regarding the thermal decomposition of minerals. We specifically synthesized the ferrihydrite samples under conditions (i.e., in the absence of Fe^{2+}, Cl^-, and Al^{3+} ions) so as to avoid the formation of other minerals, such as åkaganeite, lepidocrocite, and boehmite. It is important to note that no mineral other than the specified 2- or 6-line ferrihydrite was detected in the unheated samples by any of the above-mentioned techniques. Their comments concerning our thermal transformation evidence for the presence of 4-fold co-

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ordinated Fe do not contradict nor add to those expressed in our paper. Manceau *et al.* (1990), however, do point out that "the appearance of maghemite between 250° and 600°C reported in the work of Eggleton and Fitzpatrick (1988) might also have originated from the diffusion of 6-fold coordinated Fe atoms to vacant tetrahedral sites as known for the formation of spinel-type aluminas." If this were so, it would suggest that the precursor (ferrihydrite) did not have hexagonal close packed oxygens. Changes in close packing during heating can be detected by thermal and XRD methods. Furthermore, Cardile (1988) obtained Mössbauer spectroscopic data on our synthetic samples that cannot be adequately explained by Fe^{3+} being present in one environment and pointed out a ". . . varied environment surrounding Fe^{3+} within the ferrihydrite."

Manceau *et al.* (1990) correctly pointed out some of the inherent limitations associated with our interpretations based on X-ray absorption edge spectroscopy. We recognize that some of the variance reported in our X-ray absorption edge spectroscopy data may be due to the use of a modified instrument, and for this reason stated (p. 121) "The X-ray absorption edge spectrum reported here, although of low resolution . . . ." After private communication with Dr. Manceau, we did not use the term EXAFS. In context, we noted that maghemite and ferrihydrite gave similar spectra and were different from those of hematite and $FePO_4$ (Figure 7 on page 120). We do not claim to be seeing 2-eV-wide features with our 50-eV full width resolution; our features are about 20 eV apart.

We emphasized in our paper that the model for the ferrihydrite structure, which includes tetrahedral ferric iron, was the XRD work, not the X-ray absorption spectroscopy (see our discussion, page 121). Manceau *et al.* (1990) appear to have overemphasized our conclusion on other results (e.g., Goncharov's work, heating experiments, and the absorption spectra), when in fact we said that these "point toward" it (our page 120, top of column 2). We used these results to support the XRD conclusion. It should also be emphasized that our paper dealt with important "properties" associated with ferrihydrites, such as differences between 2- and 6-line ferrihydrites (Table 1, page 115), regarding for example, color, weight loss, and selective chemical dissolution analyses using NH_4-oxalate extractions (e.g., to determine composition), surface areas and crystal diameters (e.g., to determine aggregation and reactivity), thermal, and magnetic properties.

In our view, none of the proposed models for the structure of ferrihydrite, which range from all tetrahedral to all octahedral Fe^{3+} has been proven or disproven (e.g., see recent paper by Cardile, 1988). All models must be retained therefore, along with those proposed for cores of ferritin macromolecules, until incontrovertible evidence rules out one, or all of them.

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