NEW DATA AND A REVISED STRUCTURAL MODEL FOR FERRIHYDRITE: COMMENT

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

Eggleton and Fitzpatrick (1988) proposed a new structural model for ferrihydrite having 35% tetrahedral and 65% octahedral Fe. According to Eggleton and Fitzpatrick (1988), the presence of 4-fold coordinated Fe was mainly based upon three distinct results: (1) Goncharov et al. (1978) recognized the presence of 4-fold Fe in solution; (2) the first product that forms on heating ferrihydrite is maghemite; (3) X-ray absorption spectroscopy (XAS) indicates a Fe$^{3+}$/Fe$^{2+}$ ratio similar to that of maghemite. Neither of the two first arguments is convincing, and, instead of assessing the presence of Fe$^{3+}$ ions, XAS clearly points towards the absence of Fe$^{3+}$, if it is recorded and analyzed in correct conditions.

The first argument implies that, if present, 4-fold coordination would be preserved from the solution to the formation of ferric gels, such as ferrihydrite. Contradictory examples are well known: at low hydrolysis ratio, Al-bearing solutions possess only Al$^{4+}$ polymers (Keggin-type structure), containing 1 Al$^{4+}$ among 13 Al atoms; this tetrahedral contribution disappears as hydrolysis is completed (Akitt et al., 1972; Bottero et al., 1987). Furthermore, unlike Goncharov et al. (1978), most authors agree that Fe is exclusively 6-fold coordinated in solutions and ferric gels (see, e.g., the reviews of Schneider and Schwyn, 1987; Flynn, 1984; Magini, 1977; Van der Giessen, 1968).

The second argument assumes that phase transformations preserve site occupancies. Maghemite may also form by the thermal decomposition of akaganeite, which contains no Fe$^{3+}$ (Gonzales-Calbet and Alario Franco, 1982). Similarly, each time chemists heat boehmite to get spinel-type aluminas (γ-, δ-, θ-, η-Al$_2$O$_3$), they do not question the absence of Al$^{4+}$ in boehmite (see, e.g., Cocker et al., 1984; Léonard et al., 1967). Finally ferrihydrite aged at moderate temperature (92°C) directly transforms to hematite instead of maghemite (Johnson and Lewis, 1983). The appearance of maghemite between 250°C and 600°C reported in the work of Eggleton and Fitzpatrick (1988) might also have been due to the diffusion of 6-fold coordinated Fe to vacant tetrahedral sites, as is known for the formation of spinel-type aluminas. As pointed out by Eggleton and Fitzpatrick (1989), however, "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 ..."; there is some futility of trying to derive structural information from the thermal behavior of a solid.

The only direct evidence of the presence of Fe$^{3+}$ in ferrihydrite stems from the analysis of XAS, but the quality of spectra presented by Eggleton and Fitzpatrick (1988) was insufficient to allow any conclusive finding; the interpretations had no firm physical basis and thus must be regarded as speculative. A correct spectral resolution, necessary to analyze absorption edge

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<td>FePO$_4$</td>
<td>210</td>
<td>7112.1</td>
<td>210</td>
<td>7112.4</td>
<td>25</td>
<td>7113.5</td>
<td>17</td>
<td>7114.9</td>
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<td>7115.8</td>
<td>14</td>
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<tr>
<td>Hematite</td>
<td>59</td>
<td></td>
<td></td>
<td>7111.2</td>
<td></td>
<td>7112.4</td>
<td>44</td>
<td>7113.9</td>
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<td>14</td>
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<td>Goethite</td>
<td>47</td>
<td>7111.3</td>
<td>21</td>
<td>7112.6</td>
<td>38</td>
<td>7113.9</td>
<td>12</td>
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<td>14</td>
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<td>Maghemite 30% Fe$_{6tet}$.</td>
<td>77</td>
<td>7112.1</td>
<td>57</td>
<td>7112.6</td>
<td>27</td>
<td>7113.7</td>
<td>7</td>
<td>7115.2</td>
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<td>6-line Fh. 0% Fe$_{6tet}$.</td>
<td>48</td>
<td>7111.5</td>
<td>27</td>
<td>7112.4</td>
<td>36</td>
<td>7113.7</td>
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<td>7115.2</td>
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<td>36% Fe$_{6tet}$.</td>
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<td>25</td>
<td>7112.3</td>
<td>32</td>
<td>7113.7</td>
<td>7</td>
<td>7115.2</td>
<td>6</td>
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<tr>
<td>2-line Fh. 0% Fe$_{6tet}$.</td>
<td>42</td>
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<td>13</td>
<td>7112.6</td>
<td>24</td>
<td>7113.9</td>
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Spectra of 6-line and 2-line ferrihydrite have been fitted assuming 0% and 36% of tetrahedral Fe. Int. = normalized intensity \( \times 1000 \); line L1 = tetrahedral component, FWHM = 1.45 eV; lines L2, L3 = octahedral components, FWHM = 1.2 eV (after Combes et al., 1989a, 1989b); lines L4, L5 = octahedral components, FWHM = 2.0 eV (after Combes et al., 1989a, 1989b).

1 After Coombes et al. (1989a).
2 After Coombes et al. (1989b).
3 Spectrum has been fitted with a linear combination of FePO$_4$ and goethite lines.
Figure 1. Normalized X-ray absorption pre-edge spectra of ferrihydrite samples and reference Fe oxides recorded on a X-ray synchrotron beam. Intensity of spectrum of maghemite is between those of Fe$_{3+}$ and Fe$_{3+}^{2+}$ reference compounds, confirming the intracrystalline Fe-site distribution (Table 1).

spectra, may be achieved only by using synchrotron radiation. The resolution thus reached is as low as 1.2–1.3 eV at the FeK-absorption edge using a Si (511) monochromator (Combes et al., 1989a, 1989b). This experimental resolution is to be compared with that given by Eggleton and Fitzpatrick (1988), 50 eV (full width), which is rather broad to resolve spectral features of about 2-eV width (Table 1). Furthermore, because of the closeness of the main edge, the convolution of the whole X-ray absorption edge spectrum with a
been firmly established. Whatever the coordination may be, a structural analogy between the structures of ferrihydrite and ferritin, a metallo-protein, has never been shown. To our knowledge, no direct link exists between thermal analysis (differential thermal, thermal gravimetric), transmission electron microscopy, selective chemical dissolution, surface area measurements, and magnetic properties and the local structure of highly disordered materials, nor transition-metal coordination environments. Only by using adequate structural analytical tools (e.g., extended X-ray absorption fine-structure spectroscopy and X-ray absorption near-edge spectroscopy), can the local order, the only preserved structural scale of poorly ordered compounds, be elucidated.

REFERENCES

A. MANCEAU

J.-M. COMBES

G. CALAS

Laboratoire de Minéralogie-Cristallographie
Université Paris 6 et 7
CNRS UA09
Tour 16, 2ème étage
4 Place Jussieu
75252 Paris Cedex 05, France


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