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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 $Fe^{3+}_{tet.}/Fe^{3+}_{oct.}$ ratio similar to that of maghemite. Neither of the two first arguments is convincing, and, instead of assessing the presence of $Fe^{3+}_{tet.}$ ions, XAS clearly points towards the absence of $Fe^{3+}_{tet.}$, 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_{13} polymers (Keggin-type structure), containing 1 $Al_{tet.}$ 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 åkaganeite, which contains no $Fe^{3+}_{tet.}$ (Gonzales-Calbet and Alario Franco, 1982). Similarly, each time chemists heat boehmite to get spinel-type aluminas (γ-, δ-, θ-, η-Al_2O_3), they do not question the absence of $Al^{3+}_{tet.}$ in boehmite (see, e.g., Coke *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° 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 $Fe^{3+}_{tet.}$ 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

Table 1. Pre-edge spectra decomposition of ferrihydrite and reference compounds (Lorentzian parameters).

Material	Pre-edge Int.	L1		L2		L3		L4		L5	
		Energy	Int.	Energy	Int.	Energy	Int.	Energy	Int.	Energy	Int.
$FePO_4$[1]	210	7112.1	210	—	—	—	—	—	—		
Hematite[2]	59	—	—	7111.2	25	7112.4	44	7113.5	17	7114.9	14
Goethite[1]	47	—	—	7111.3	21	7112.6	38	7113.9	12	7115.8	14
Maghemite 30% $Fe_{tet.}$[3]	77	7112.1	57	7111.3	15	7112.6	27	—	—	—	—
6-line Fh. 0% $Fe_{tet.}$	48	—	—	7111.5	27	7112.4	36	7113.7	7	7115.2	6
36% $Fe_{tet.}$[3]	48	7112.1	72	7111.3	13	7112.6	24	7113.9	8	7115.8	9
2-line Fh. 0% $Fe_{tet.}$	42	—	—	7111.4	25	7112.3	32	7113.7	6	7115.2	3
36% $Fe_{tet.}$[3]	42	7112.1	72	7111.3	13	7112.6	24	7113.9	8	7115.8	9

Spectra of 6-line and 2-line ferrihydrite have been fitted assuming 0% and 36% of tetrahedral Fe. Int. = normalized intensity × 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.

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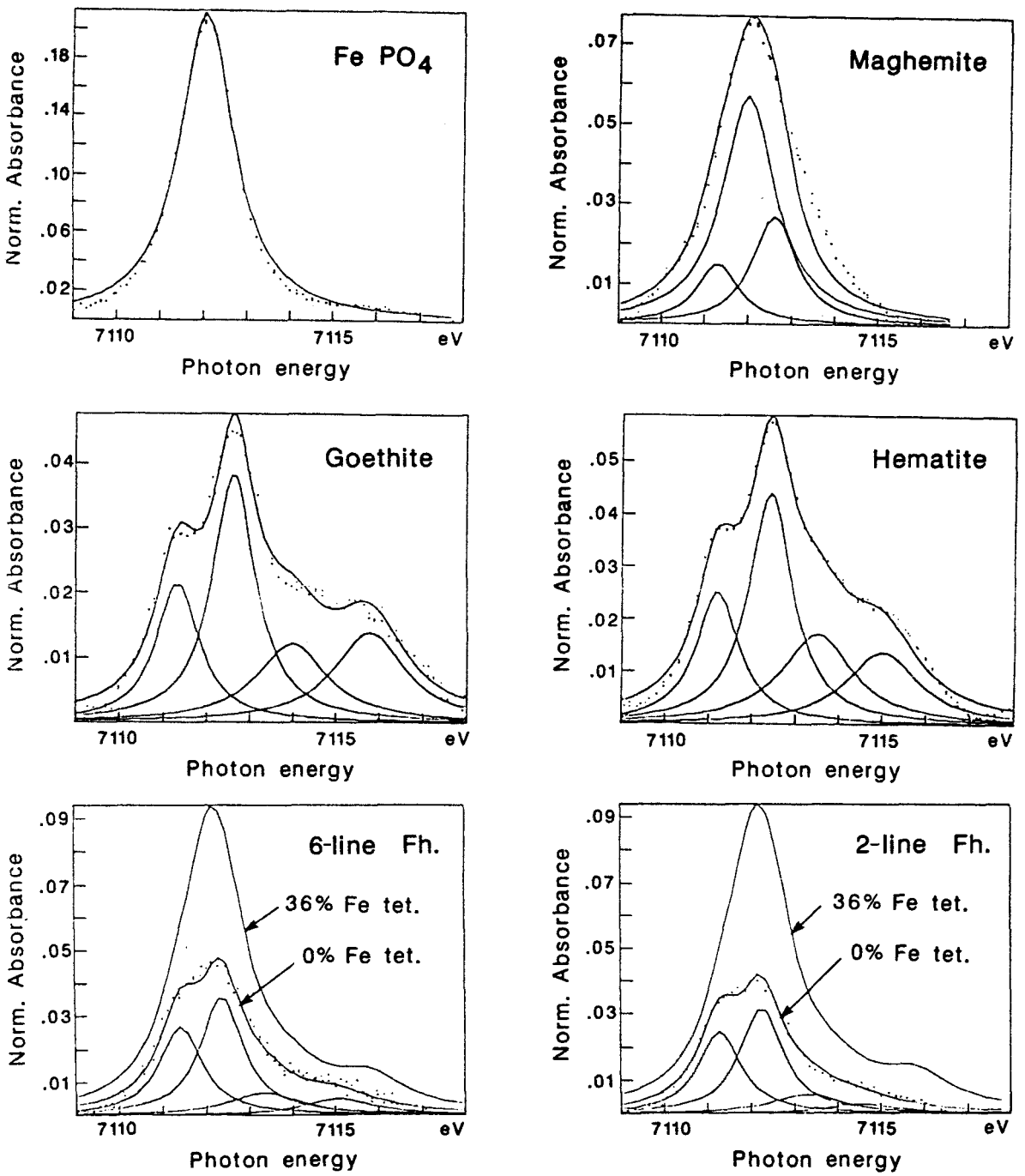


Figure 1. Normalized X-ray absorption pre-edge spectra of ferrihydrite samples and reference Fe oxides recorded on a X-ray synchrotron beam. Intensity of spectrum of maghemite is between those of $Fe^{3+}_{tet.}$ and $Fe^{3+}_{oct.}$ reference compounds, confirming the intracrystalline Fe-site distribution (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

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gaussian line of 50-eV width strongly diminishes the normalized intensity of the pre-edge spectrum. Because of this experimental broadening, the normalized absorbance of the $FePO_4$ pre-edge spectrum of Eggleton and Fitzpatrick (1988) is as weak as 3–5% instead of 21%, if recorded using synchrotron radiation (Table 1).

The analysis of the spectra has no physical meaning; in no spectroscopic methods are site occupancies obtained by deriving spectra. Accurate crystal chemical information can be obtained only by fitting spectra with fundamental components. In absorption edge spectra, such a fitting must be performed on *normalized absorbance* spectra, after background removal, as has been done for several minerals (Bonnin *et al.*, 1985; Calas and Petiau, 1983; Dräger *et al.*, 1988; Manceau and Calas, 1986; Manceau *et al.*, 1987; Calas *et al.*, 1984; Roe *et al.*, 1984; Waychunas, 1987; Brown *et al.*, 1988). None of these requirements were fulfilled by Eggleton and Fitzpatrick (1988). Finally, their row-absorption spectrum of 6-line ferrihydrite was closer to goethite than to maghemite. A correct spectral interpretation should have suggested either the absence of $Fe^{3+}_{tet.}$, as in goethite, or the presence of $Fe^{3+}_{tet.}$, as in maghemite. In either case, the presence of 30% $Fe^{3+}_{tet.}$ can be concluded without assuming a large amount of 4-fold Fe in goethite.

Combes (1988) analyzed the pre-edge spectra of a large collection of natural and synthetic ferric hydrous gels, including a 6-line ferrihydrite synthesized by the method of Towe and Bradley (1967), similar to the one of Eggleton and Fitzpatrick (1988). The intensity and shape of those spectra were similar to those of goethite and hematite, and Combes (1988) concluded, for all of their samples, an absence of $Fe^{3+}_{tet.}$. To illustrate the above comments the normalized pre-edge spectra of a 2-line and a 6-line ferrihydrite are shown in Figure 1 for synchrotron radiation. These two natural ferrihydrite materials were characterized by Schwertmann and Fischer (1973), and Carlson and Schwertmann (1981), and possess XRD patterns identical to those published by Eggleton and Fitzpatrick (1988) (Figure 2). The pre-edge intensity of $FePO_4$ ($Fe^{3+}_{tet.}$) is about four times that of hematite and goethite (Combes *et al.*, 1989a, 1989b, and Table 1). Both the intensity and the structure of ferrihydrite spectra are close to those of goethite and clearly distinct from those of maghemite. Spectral simulations of 2-line and 6-line ferrihydrites show that adding 36% $Fe^{3+}_{tet.}$ (the amount suggested by Eggleton and Fitzpatrick, 1988) strongly enhances the intensity of the pre-edge spectrum, which then looks like that of maghemite. These results strongly support the absence of 4-fold coordinated Fe. Given the reliability of our spectral decompositions (Table 1), the detection limit of 4-fold iron is 5–7%.

As a final note, in agreement with Schneider (1988), we believe that the presence of $Fe^{3+}_{tet.}$ in ferritin has not 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.

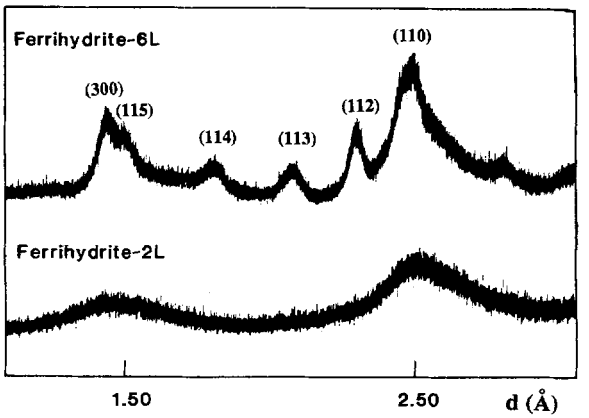


Figure 2. X-ray powder diffraction patterns for 2-line and 6-line ferrihydrite samples.

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