

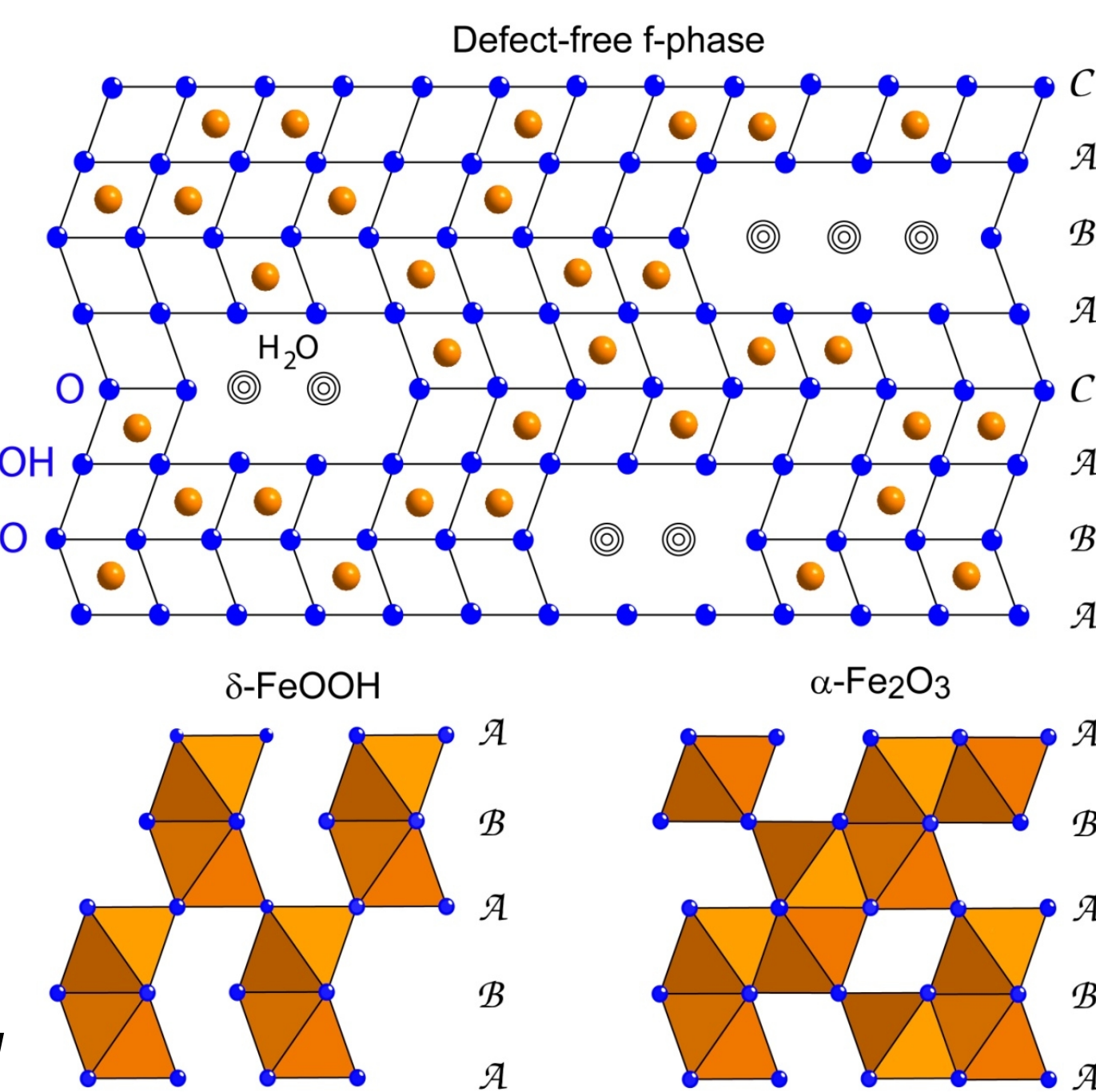
Ferrihydrite Nanoparticles : New Perspectives ?

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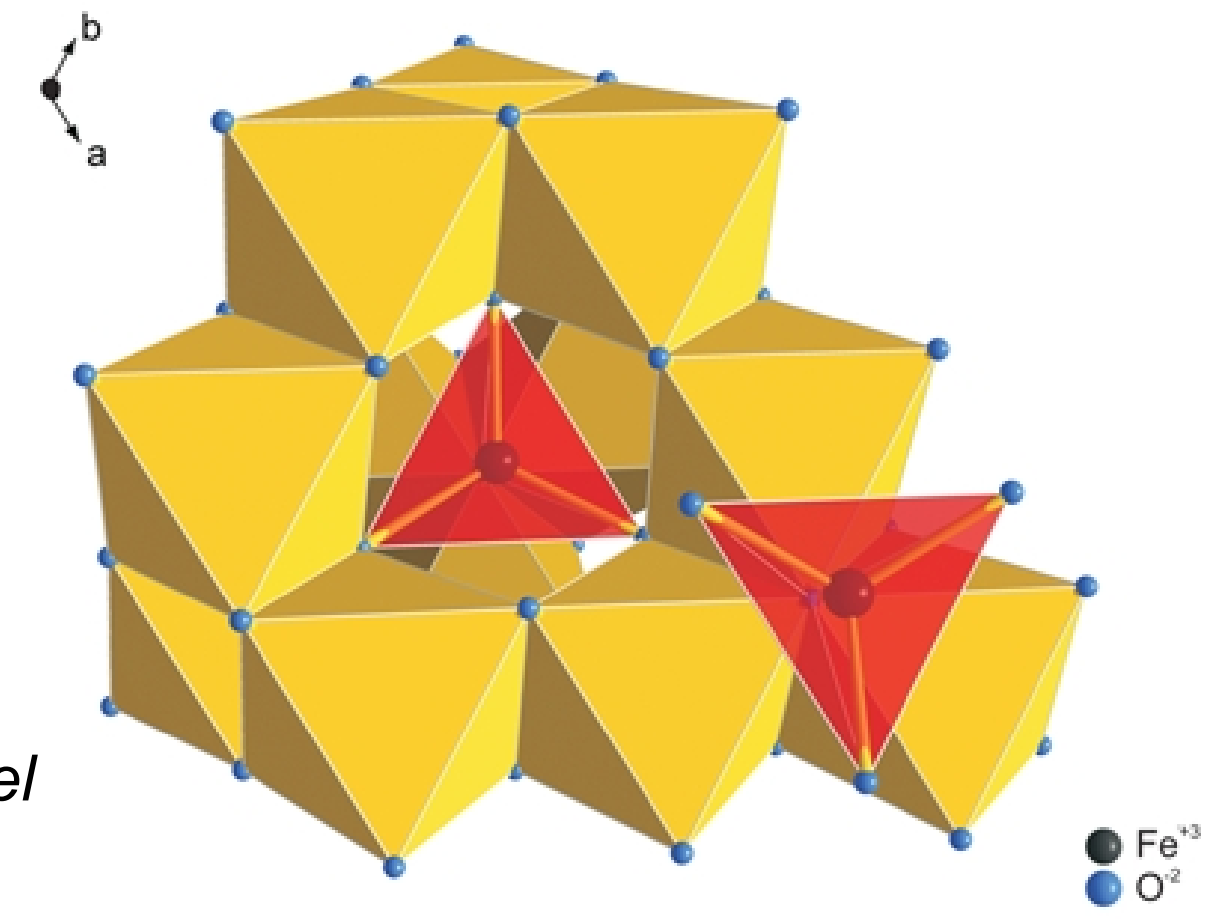
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Context

Ferrihydrite (Fh) is an ubiquitous iron oxyhydroxide [1] characterized by a poor crystallinity and a high specific surface area (eg. 270 m².g⁻¹, [2]). The nanocrystallinity of Fh has hampered accurate structure determination by traditional method. Several models have been suggested to describe 2- and 6-lines Fh structures [3-11].



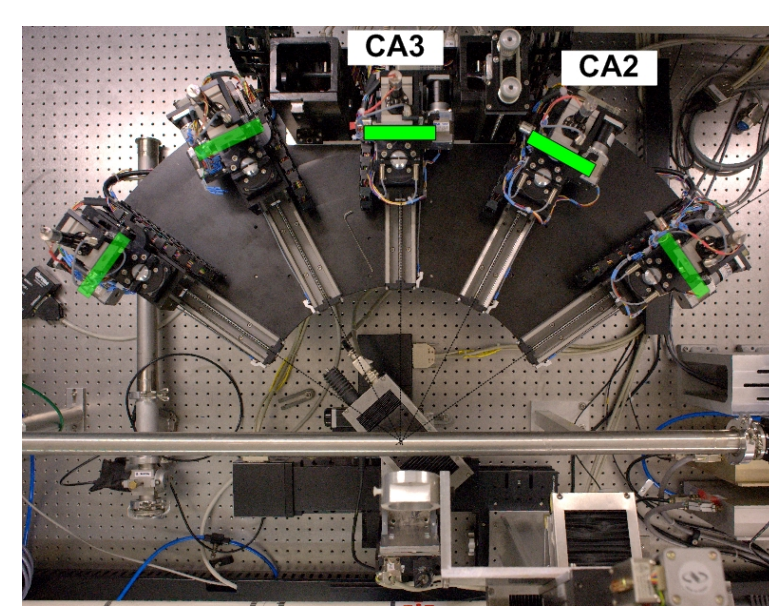
Recent studies [12-13] propose a new structural model for Fh by real-space modelling of the pair distribution function (PDF). The model is consistent with a single phase ($P6_3mc$) containing 20% tetra (T_d) and 80% octahedrally (O_h) coordinated Fe.



But the presence of T_d coordinated iron in Fh has been the subject of considerable debate. Their existence remains inconclusive and their contribution is not directly demonstrated by PDFs.

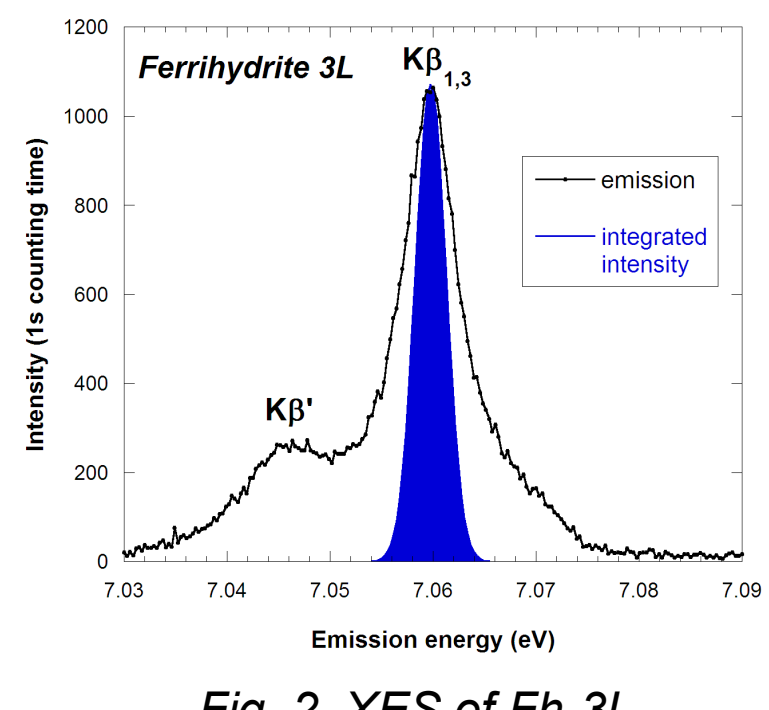
Ferrihydrite and reference compounds

Synthetic Fh were formed with \neq coherent scattering domain sizes: 2 (Fh-2L), 3 (Fh-3L), and 6 nm (Fh-6L). Mixtures of $FePO_4$ where Fe(III) is in T_d or O_h sites have been used in order to investigate the presence of T_d coordinated iron in Fh. Fe(III) model compounds were also studied: hematite, lepidocrocite, and maghemite.



PFY-XANES measurements

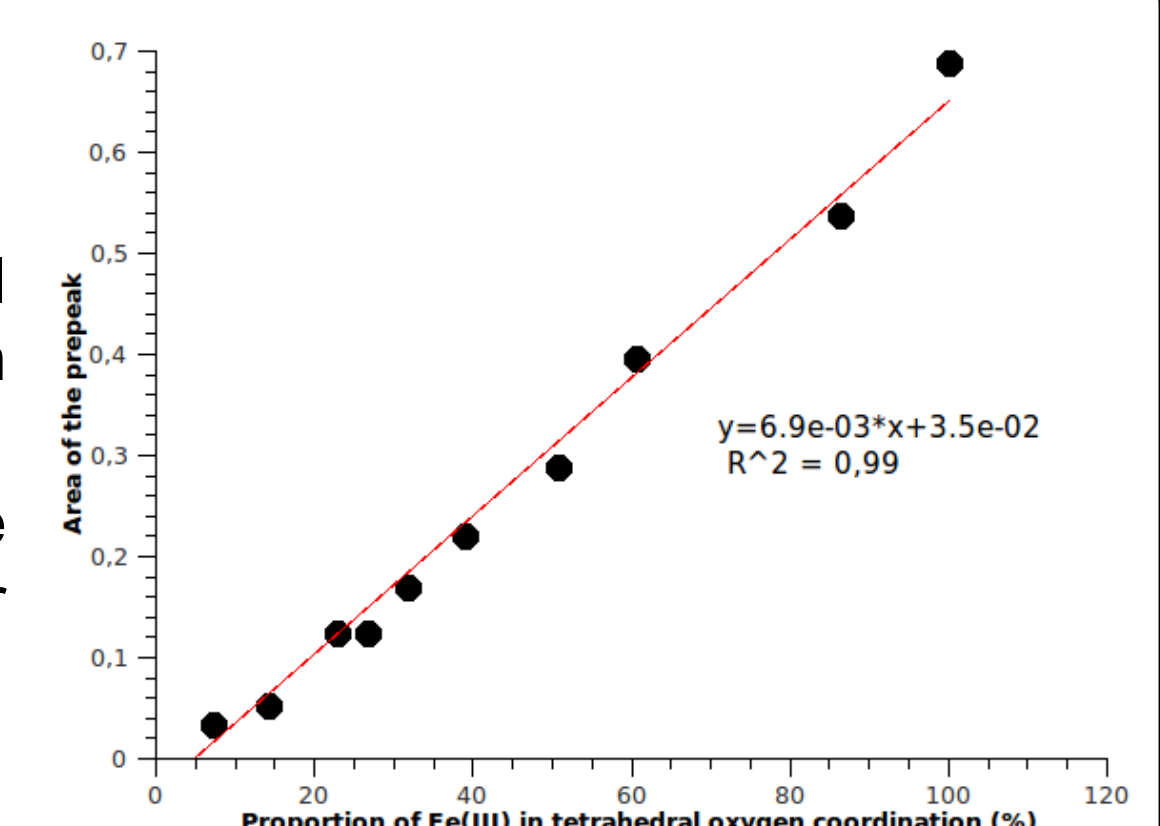
Johann's geometry is used for the crystal analyser spectrometer. The bent crystal, the sample and the detector just above the sample are located on the Rowland circle [15]. Crystals are spherically bent Si (440) crystals with a 0.5 m radius of curvature [16]. The overall energy resolution is ~ 3 eV at 7.06 keV. Partial Fluorescence Yield X-ray Absorption Spectroscopy (PFY-XAS) was achieved by measuring the energy dependence of the $K\beta_{1,3}$ emission line (Fig. 2). PFY-XAS spectra were corrected from the self-absorption process using the transmission XAS spectra.



1st hypothesis: Fe is either in Oh or Td sites

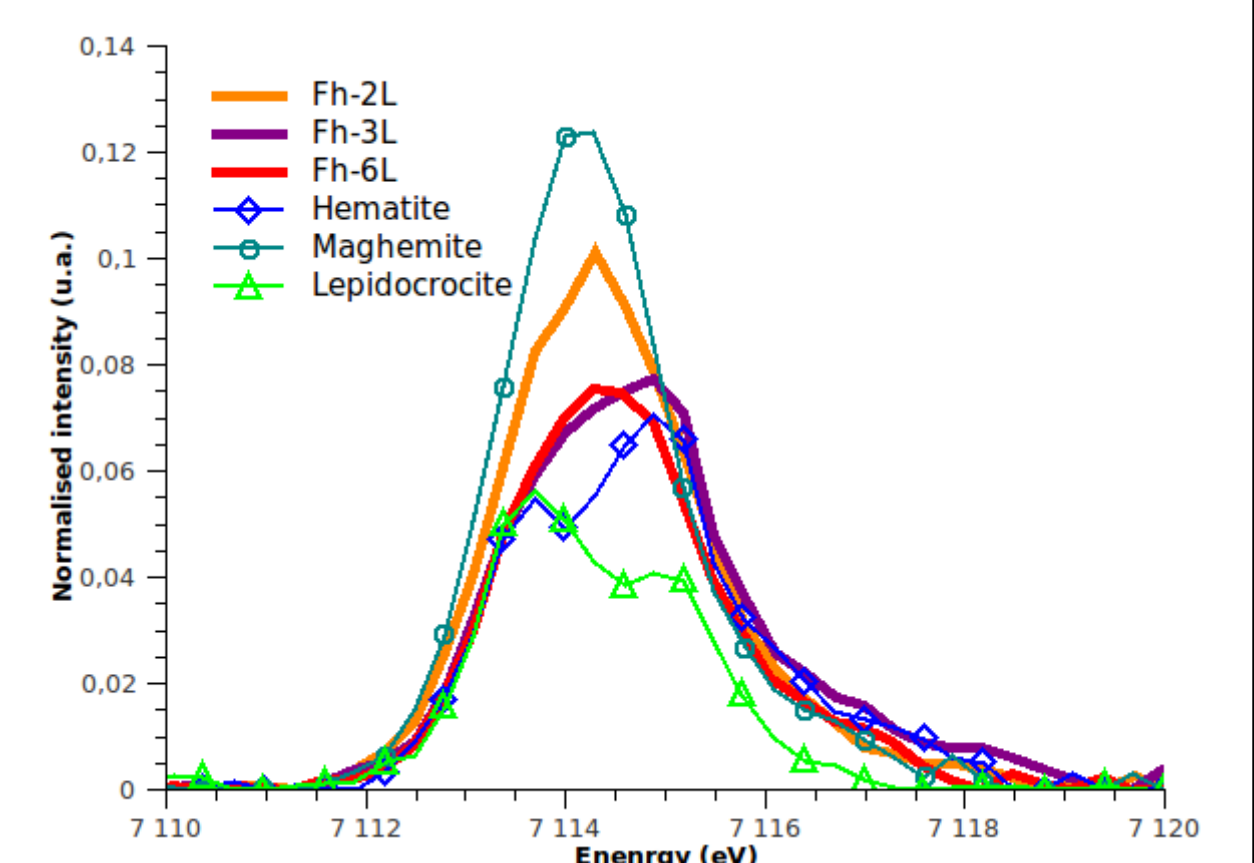
To quantitatively determine the Fe occupying tetrahedral sites in Ferrihydrite, we build a linear combination with appropriate $FePO_4$ references.

By using linear combination (Fig. 5), we can estimate the proportion of Fe(III) in tetrahedral coordination : $\sim 15\%$ for Fh-2L and $\sim 7\%$ for Fh-6L.



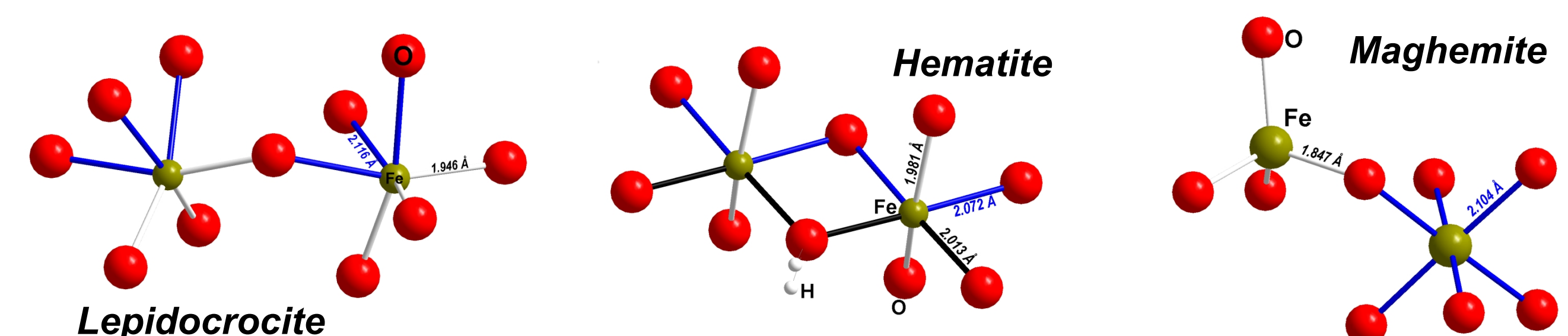
2nd hypothesis: Fe is in distorted Oh sites

A small modification in the prepeak intensity may arise from variations in the Fe-O bond distances. On fig. 6 are reported $K\beta$ -detected prepeak of iron oxide model compound and Fh.



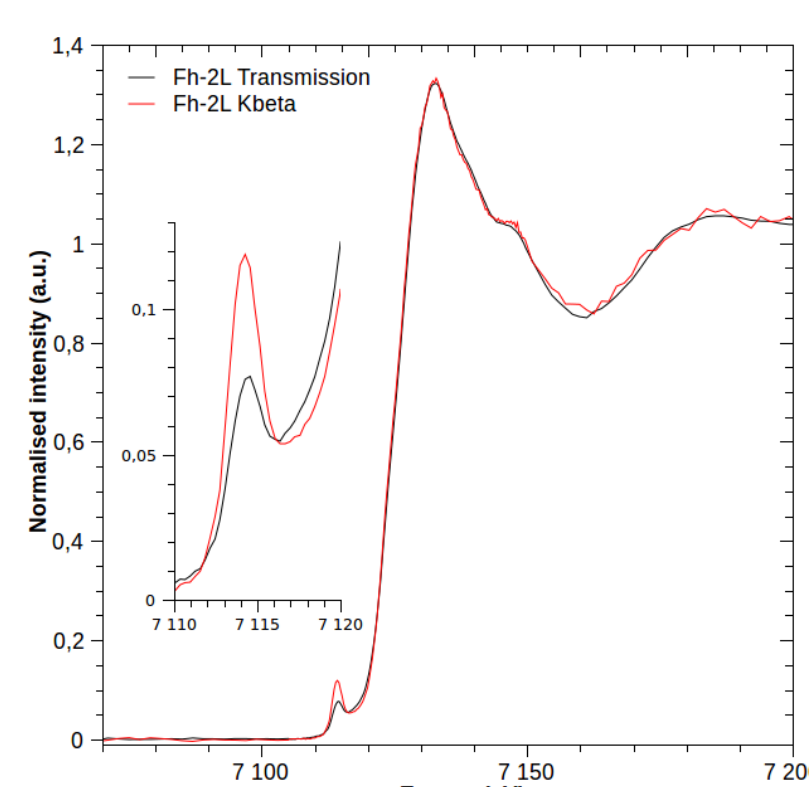
The height of Fh-3L and Fh-6L prepeak is similar to those of hematite ($\alpha-Fe_2O_3$) which contains Fe(III) in non-perfect octahedral oxygen coordination.

The height of Fh-2L prepeak is between hematite and maghemite prepeaks. Maghemite is an iron oxide ($\gamma-Fe_2O_3$) with 33% of Fe(III) in tetrahedral oxygen coordination.

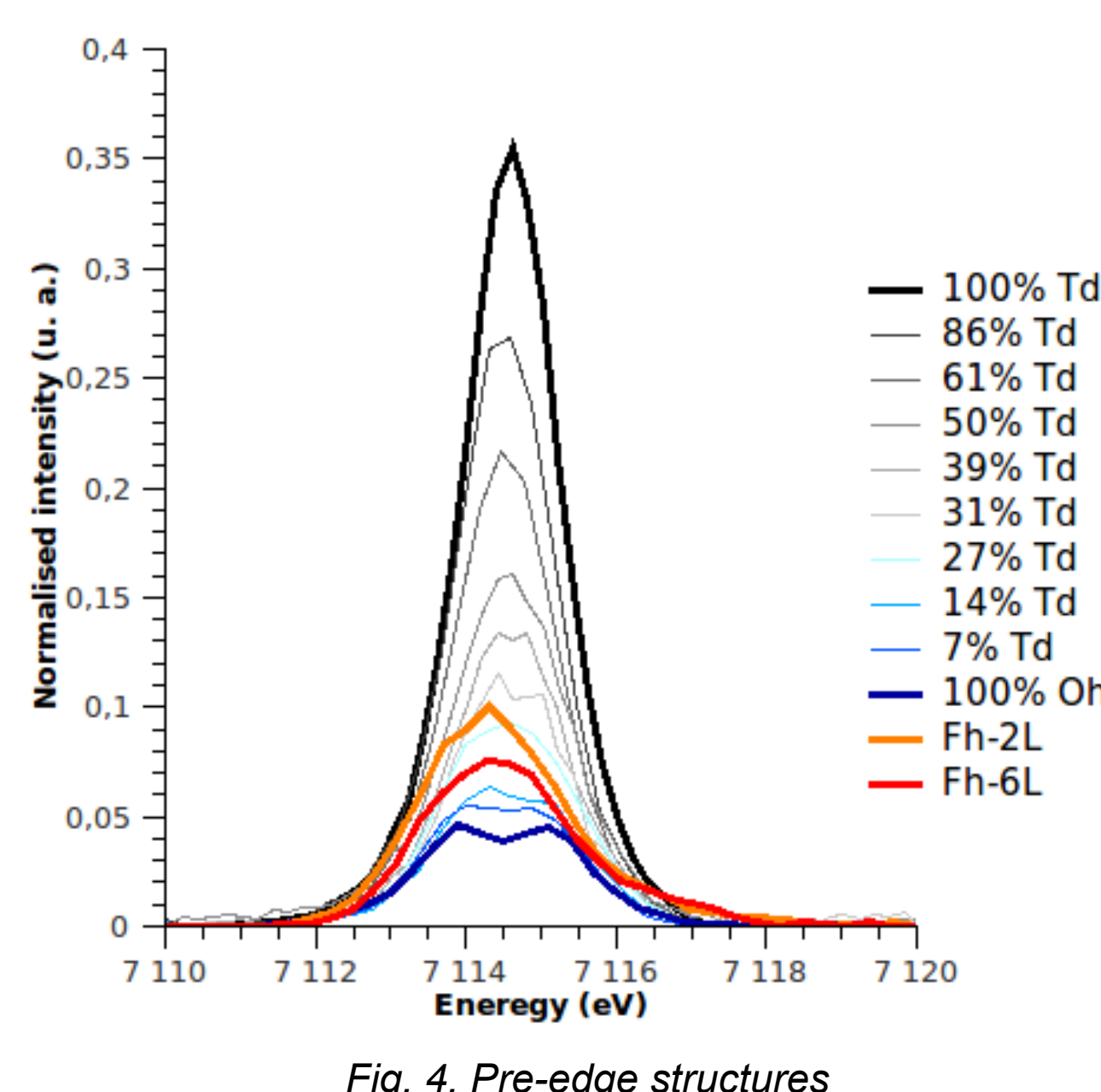


Interest of PFY-XANES measurement

Among the main requirements for a quantitative determination of changes in the coordination of iron are (1) a high resolution of the spectra, (2) a precise isolation of the pre-edge structure from the main edge which requires a proper background subtraction. Fig. 3 clearly shows that in the PFY-XANES spectrum, the intensity of the pre-edge is approximately twice higher than in the conventional XANES spectrum. But to isolate the pre-edge of $K\beta$ -detected XANES, a subtraction by a cubic spline will be necessary. This procedure was applied to all the spectra.



As shown in Fig. 4, $FePO_4 \cdot T_d$ exhibits a sharp and strong pre-edge peaks whereas the much weaker prepeak of $FePO_4 \cdot O_h$ is also clearly visible. Pre-edge structures of Fh are slightly higher than the one of $FePO_4 \cdot O_h$. Moreover, there is a small difference in the height of the prepeak of Fh-2L and Fh-6L.



Fe is not purely in O_h sites in ferrihydrite

Conclusion

The height of Fh-3L and Fh-6L prepeaks could be explained by the presence Fe in non-perfect octahedral oxygen coordination. For Fh-2L, the presence of T_d coordinated iron ($\sim 15\%$) can be supported by the present study. This is consistent with the findings of Michel et al. [12], who detected 20% T_d in the Fh.

On going research

We propose to validate or not the presence of tetrahedrally coordinated iron at the various precipitation stages of Fh by varying the hydrolysis ($[OH^-]/[Fe]$) ratio from 0.5 to 3. One of the key point would be the identification of T_d iron in-situ during the synthesis. Calculations will be also performed to check all the possible models.

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