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| Shifts: 12 | Local contact(s): Olivier PROUX | |
| Names and affiliations of applicants (* indicates experimentalists): AUFFAN Mélanie* CEREGE DIOT Marie-Ange* CEREGE DOELSCH Emmanuel* CIRAD-CEREGE ROSE Jérôme CEREGE MASION Armand | | |

Report:

Introduction

Ferrihydrite (Fh) is an ubiquitous iron oxyhydroxide discovered in 1971 [1] with a composition commonly given as $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$. Nanosized Fh are characterised by poor crystallinity and high surface area (eg. $270 \text{ m}^2 \cdot \text{g}^{-1}$, [2]). Despite the ubiquity of Fh in natural surface environment and its importance as an industrial sorbent, the nanocrystallinity of this iron oxyhydroxide has hampered accurate structure determination by traditional method. Indeed, the diffraction peaks of Fh are so broad that it is almost impossible to solve the structure. Several structural models have been suggested to describe 2-line Fh and 6-line Fh structure [3-11]. Among the disagreements, we can cite that no consensus has been reached on (i) whether these two materials differ only in domain size or if they exhibit also distinct; (ii) whether these two materials are best described by a single (defective) phase or by a mixtures of phases; (iii) whether iron can be tetra and octahedrally coordinated or only octahedrally coordinated. Recent study [12, 13] suggests a new structural model for ferrihydrite by real-space modeling of the pair distribution function (PDF). The PDF for ferrihydrite synthesized with the use of different routes is consistent with a single phase (hexagonal space group $P6_3mc$; $a = 5.95$ angstroms, $c = 9.06$ angstroms). Moreover, 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. The presence of tetrahedrally coordinated iron in ferrihydrite has been the subject of considerable debate. Whatever the analytical techniques (Electron microscopy, Mössbauer, ...), the existence of tetrahedrally coordinated iron remains inconclusive and the contribution of FeO_4 is not directly demonstrated by PDFs. One of the key point would be the identification of tetrahedral iron.

The local symmetry of iron in Ferrihydrite will be studied by means of $\text{K}\beta$ -detected X-ray absorption spectroscopy. This technique combines high-resolution ($\Delta E \sim 3-4$ eV) fluorescence detection of the $3p$ to $1s$ ($\text{K}\beta$) transition with the X-ray absorption near-edge structure (XANES) at the Fe K-edge.

Experimental details

The experimental set-up installed on BM30b is shown on figure 1 left. Johann's geometry is used for the crystal analyser spectrometer (CAS). The analyzing plane is vertical: the bent crystal, the sample and the detector just above the sample are located on the Rowland circle [14]. Employed as analyzer crystals of the spectrometer are spherically bent Si (440) crystals with a 0.5m radius of curvature [15]. Two crystals were positioned on CA2 and CA3 positions. The overall energy resolution (monochromator + spectrometer) measured from the elastic line is around 3eV at 7.06 keV. This value is slightly higher than the theoretical value of 2.40eV obtained by taking into account from the intrinsic energy resolution of the analyzer, of the aberration due to the Johansson geometry, of the vertical size of the beam on the sample and of the incident beam. Such difference can be due to the lattice distortion of the analyzer induce by the bending.

Experiments were performed in reflexion mode by collecting the $K\beta_{1,3}$ line emitted by the sample (fig. 1 right). Partial Fluorescence Yield X-ray Absorption Spectroscopy (PFY-XAS) was achieved by measuring the energy dependence of the intensity emitted while scanning the incident energy through the Fe K-edge. In order to correct the PFY-XAS spectra from the self-absorption process, acquisition of the XAS spectra in the transmission mode was done simultaneously.

The detector used to collect the fluorescence photons diffracted by the analyzers is a silicon Solid State Detector (Vortex SSD). Its energy resolution around 250eV allows to eliminate any contribution coming from the scattering beam on the crystals (induce mainly by the Compton and Thompson scattering beams and from the Fe- $K\alpha$ fluorescence photons). An helium bag was used to limit the absorbance of air on the 1m long sample-crystal-detector path. The counting ratio was around 1000 cts/s after the edge for all the samples with the two optimized crystals.

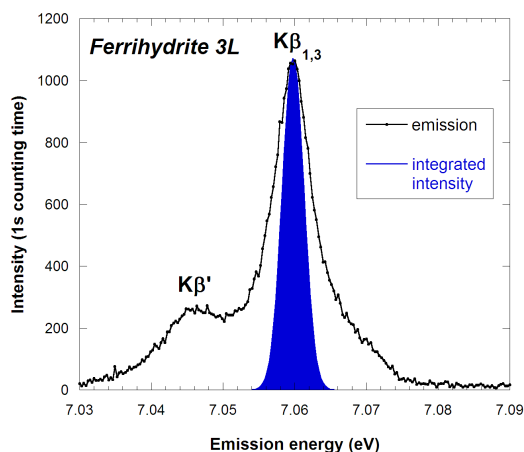
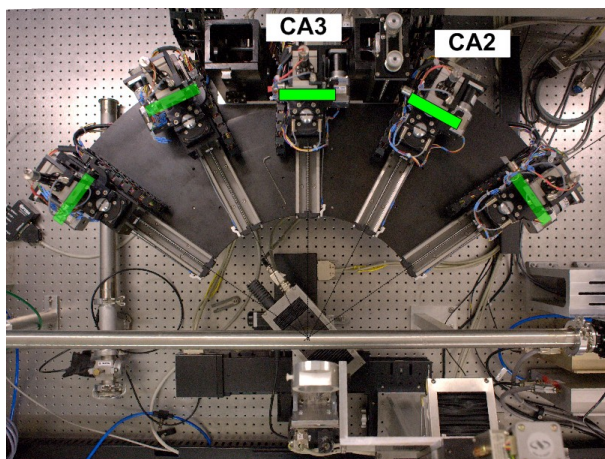


Figure 1. Left: experimental set-up (top-view). The two used positions of the 5 crystals Spectrometer are the 2nd (120°) and the 3rd (90°) ones. Right: X-ray emission spectra of Ferrihydrite 3L obtained with the two crystals (incident energy: 7.2keV).

Results

Among the main requirements for a quantitative determination of changes in the coordination of iron based on variations of the pre-edge features are (1) a high resolution of the spectra so that characteristic features in the pre-edge are well-resolved, (2) a precise isolation of the pre-edge structure from the main edge which requires a proper background subtraction.

Figure 2 clearly shows that in the $K\beta$ -detected XANES spectrum, the intensity of the pre-edge is approximately 2 times 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, which can affect the pre-edge intensity as underlined in previous study [16]. Therefore, $K\beta$ -detected XANES did not overcome this disadvantage of conventional XANES, which means that $K\beta$ -detected XANES are not separated from the main edge.

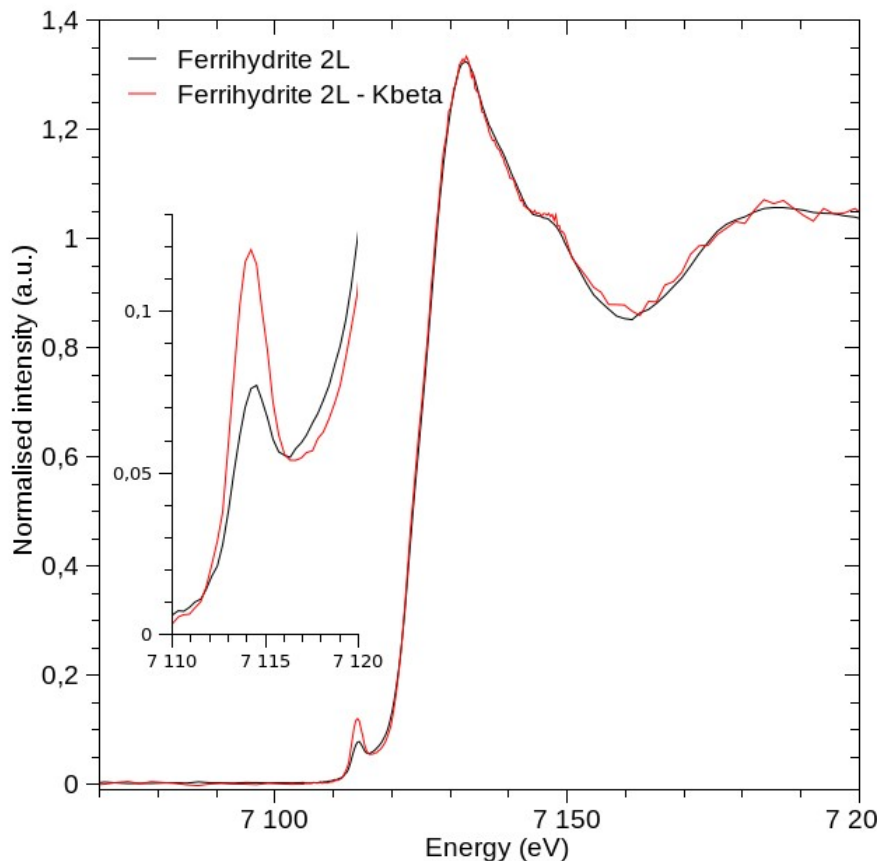


Figure 2 : comparison of the PFY-XAS spectra corrected from the self-absorption process and the XAS spectra in the transmission mode of synthetic ferrihydrite.

The advantage of high resolution $K\beta$ -detected XANES spectroscopy is that it shows spectral features that are sharper than in conventional absorption spectroscopy recorded in transmission mode or by fluorescence detection using a solid-state detector with medium energy resolution (e.g. Ge: $\Delta E \approx 200$ eV). As previously shown [16], authors were able to quantitatively determine the Fe occupying tetrahedral sites in a zeolite framework with $K\beta$ -detected XANES by using appropriate references.

To quantitatively determine the Fe occupying tetrahedral sites in Ferrihydrite, we decided to build a linear combination with appropriate Fe(III) references. We selected FePO_4 as a model since it can be in Fe(III) tetrahedral or octahedral oxygen coordination. Figure 3 shows the $K\beta$ -detected XANES spectra of FePO_4 references: FePO_4 Td exhibits a sharp and strong pre-edge peaks whereas the much weaker prepeak of FePO_4 Oh in octahedral oxygen coordinations is also clearly visible.

The linear combination between FePO4 Td and FePO4 Oh was obtained by mixing the appropriate amounts of each references. This procedure is possible because the pre-edge integrated intensity is proportional to the probability of the $1s \rightarrow 3d$ transitions, which in turn are related to the degree of distortion from the centrosymmetric coordination of the transition metal element. This linear combination was tested with maghemite reference mineral. According to the height of the maghemite prepeak, we calculated the presence of 38% of Fe(III) Td in the structure of this mineral which is very close to the theoretical formula : $[\text{Fe}^{3+}]_{\text{tetrahedral}}[\text{Fe}_{5/3}\text{V}_{1/3}]_{\text{octahedral}}\text{O}_4$ (where V stands for vacancies in the octahedral sublattice).

These promising results for known mineral reference will be used for Ferrihydrite. Data analysis is still in progress.

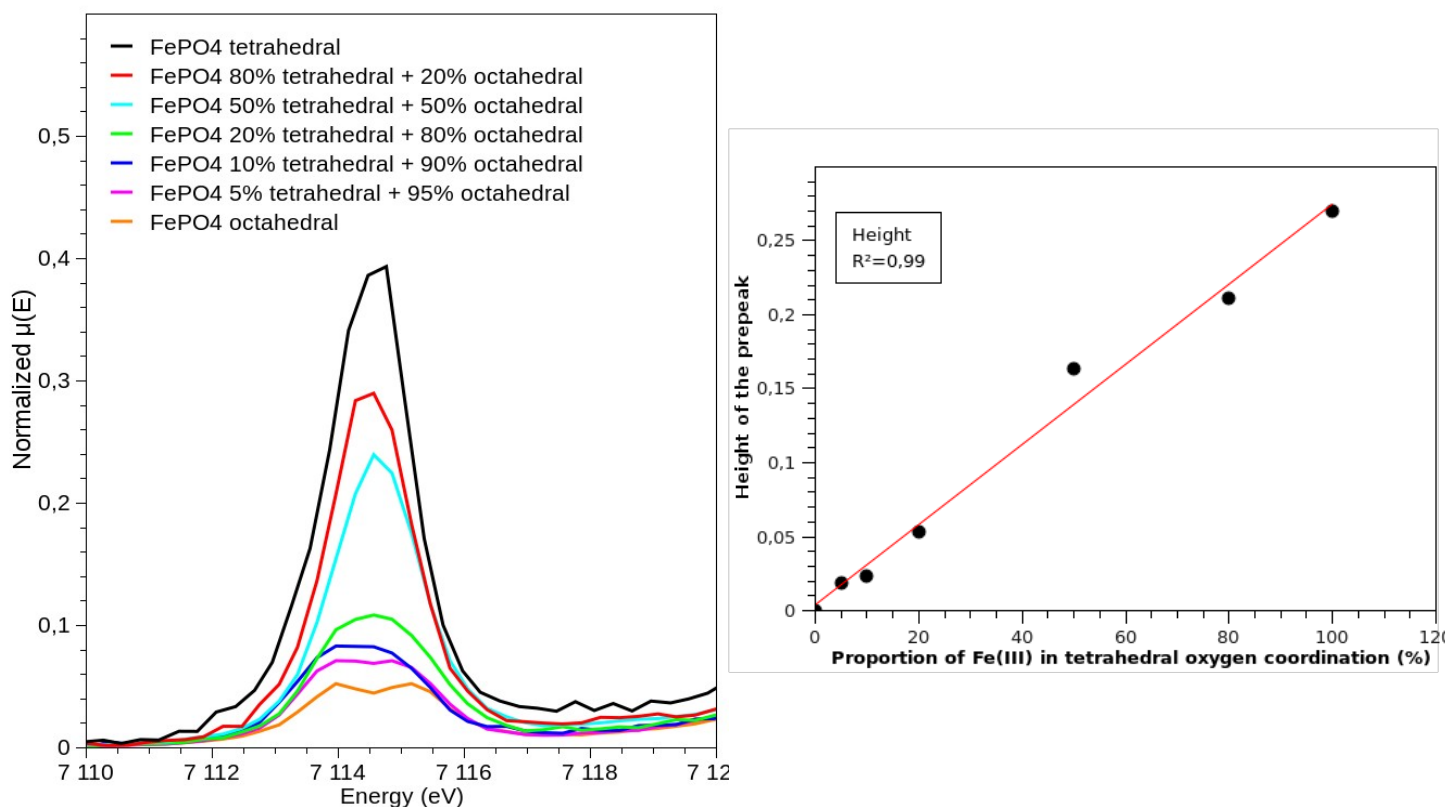


Figure 1. Left: prepeak of FePO4 Td, Oh and mixture references. Right: linear combination between the height of the prepeak and the proportion of Fe(III) in tetrahedral oxygen coordination.

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