



	<b>Experiment title:</b> Probing structural Fe in smectites by polarized resonant inelastic X-ray scattering	<b>Experiment number:</b> 30-02-1103
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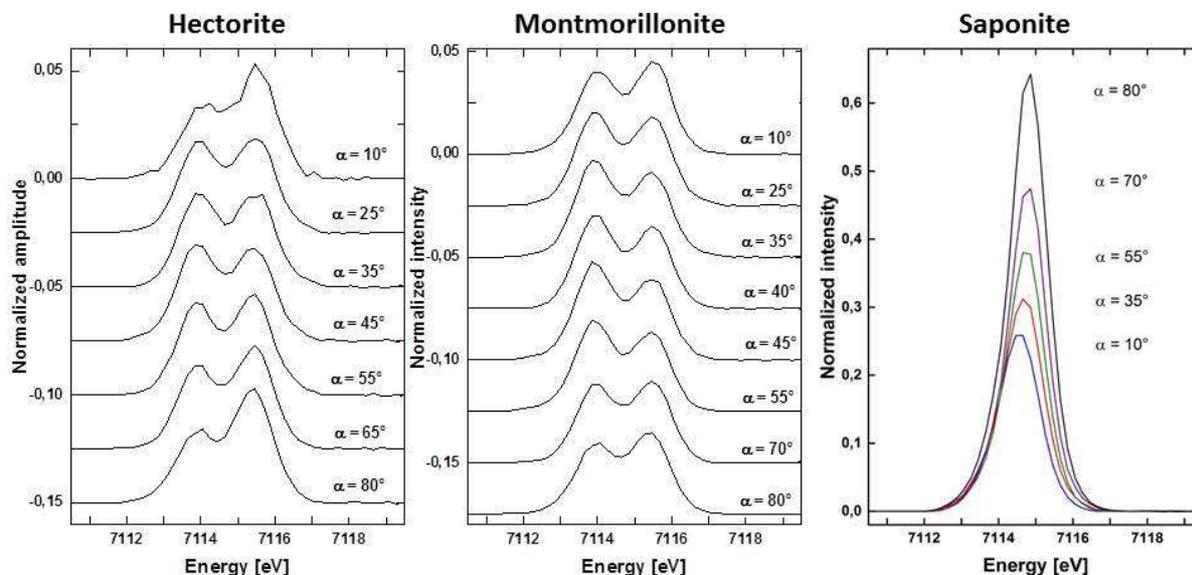
## Scientific background and aim

Smectites (sheet silicates) occurring in nature contain structural Fe, the chemical form of which influences many physicochemical properties such as cation exchange or oxydo-reduction reactivity. Recent Fe *K*-edge polarized EXAFS data on smectite self-supporting films exhibited a dichroic behavior and revealed differences in binding environment in two smectites of contrasted chemical compositions [1]. The angular dependence of the pre-edge features was complex, a likely consequence of the dominant quadrupole nature of the involved  $1s \rightarrow 3d$  transition. These pre-edges features were consistent with an octahedral environment, but the crystal field splitting indicated distinct site symmetry. However, accurate analysis of these features was hindered by relatively limited spectral resolution. In order to get further insights into differences in Fe binding environments, we recorded polarized high-resolution XANES spectra and resonant inelastic X-ray scattering (RIXS) planes at the Fe *K* absorption pre-edge for three smectites prepared as self-supporting films: a hectorite, a montmorillonite and a saponite. In hectorite and saponite, all octahedral sites are filled by  $Mg^{(II)}$  cations. However, in hectorite  $Li^{(I)}$  or  $Fe^{(II,III)}$  substitute for octahedral  $Mg^{(II)}$  and in saponite  $Fe^{(III)}$  substitutes for tetrahedral  $Si^{(IV)}$ . In montmorillonite, only 2/3 of the octahedral sites are occupied by  $Al^{(III)}$  cations, but  $Mg^{(II)}$  or  $Fe^{(II,III)}$  can substitute for octahedral  $Al^{(III)}$ .

## Experiments and results

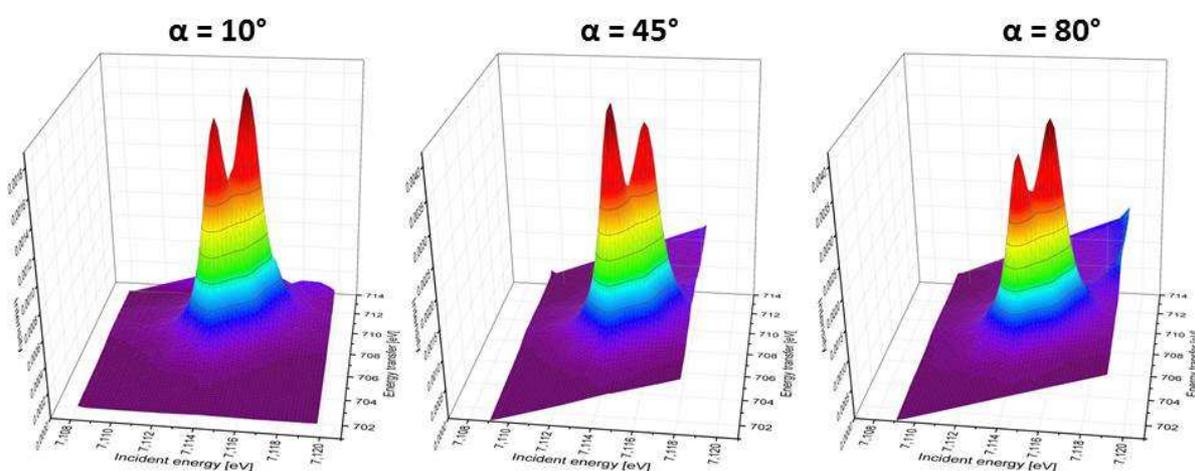
High-resolution polarized XANES and polarized  $1s2p$  RIXS planes at the Fe *K* absorption pre-edge were recorded at the BM30B beamline using a crystal analyser spectrometer. The incoming X-ray beam was monochromatized using Si(220) crystals, the spectrometer was equipped with five Ge(110) crystals and the reflection of the (440) band was recorded using a SDD detector. Various angles ( $\alpha$ ) between the electric field of the X-ray beam and the clay layer plane were selected. High-resolution XANES data were corrected for self-absorption.

For all three smectites, XANES exhibited high angular dependences and contained well-defined isosbestic points. Pre-edge features were extracted after subtraction of the baseline with an exponential function (Figure 1). The pre-edges of hectorite and montmorillonite indicate that Fe is in octahedral coordination, and exhibit clear angular dependences. The ratio of low-energy component ( $t_{2g}$ ) to high-energy component ( $e_g$ ) differs in both samples, but the variation with  $\alpha$  is similar in both samples: it increases from  $\alpha = 10^\circ$  to  $\alpha = 45^\circ$  and then decreases with increasing  $\alpha$  values. This result hints at an electric quadrupole nature of the  $1s \rightarrow 3d$  pre-edge feature. The pre-edge of the saponite contains only one component and is of higher intensity compared to both other samples, indicating that Fe is in tetrahedral coordination. The monotonic intensity increase with  $\alpha$  values hints at an electric dipole character which may arise from metal  $4p$  mixing into  $3d$  orbitals [2].



**Figure 1.** Polarized high resolution Fe K absorption pre-edge features of the three smectites.

Further information of the pre-edge features of the montmorillonite was provided by recording  $1s2p$  RIXS planes (intensity of the energy transfer as a function of the incident energy) at  $\alpha$  values of  $10^\circ$ ,  $45^\circ$  and  $80^\circ$  (Figure 2). All planes contain only two peaks originating from the metal  $3d$  orbital split into  $t_{2g}$  and  $e_g$  orbitals. This result excludes the presence of some tetrahedral Fe, because in that case an additional peak would be expected. The angular dependence of the  $t_{2g}:e_g$  intensity ratio is similar to that in Figure 1: it increases from  $\alpha = 10^\circ$  to  $\alpha = 45^\circ$  and then decreases to  $\alpha = 80^\circ$ . Furthermore, the absence of peak tailing informs that Fe is bound to only one type of ligands (O atoms). Analysis of polarized RIXS data for hectorite will inform whether Fe is bound to only O atoms or to O and F atoms (hectorite contains significant amounts of fluorine). Further work will include calculations of density of states and its decomposition into  $p$  and  $d$  symmetry. The validity of the theoretical model will be tested by comparing with experimental data.



**Figure 2.** Polarized  $1s2p$  RIXS planes at the Fe K absorption pre-edge of the montmorillonite.

### Acknowledgements

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### References

- [1] Finck N. et al. *Phys. Chem. Minerals* **42**, 847-859 (2015).
- [2] Westre T. E. et al. *J. Am. Chem. Soc.* **119**, 6297-6314 (1997).