|	**Experiment title:** Iron speciation in natural serpentine polymorphs : relations between nano-, and micro-structures	**Experiment number**: HS-4780
Beamline: BM23	**Date of experiment**: from: 21/11/2012 to: 26/11/2012	**Date of report**: 26/02/2013
Shifts: 17	**Local contact(s)**: Manuel Munoz	*Received at ESRF:*
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Report:

    The goal of this project was to characterize relationships between the crystal chemistry of the serpentine minerals and their microstructures. The chrysotile variety is known to have a cylindric microstructure with a winding of the silicate sheets around the tetrahedral layer, while the lizardite variety has a flat texture and the antigorite variety shows periodic reversal of the slightly curved sheets. Serpentine theoretical formula is $Mg_3Si_2O_5(OH)_4$, which could also be written $(Mg,Fe^{2+},Fe^{3+},Al)_3(Si,Al,Fe^{3+})_2O_5(OH)_4$ depending on cationic substitution. The amount of iron ranges between around 0.5 and 4 wt.%. However, it was already shown that chemical composition alone cannot explain the occurrence of the different variety of serpentines. Therefore, we aimed at understanding the links between the microstructures of serpentines and speciation of iron. Based on the Fe-K pre-edge information, a first step of this study consists of determining the average valence of iron in the minerals. Then, XANES and EXAFS spectra are used to derive the average coordination number of iron and possibly to characterize its second-neighbor environment (e.g., check for eventual Fe-clustering effects).

    A set of 31 magnetite-free samples from the Muséum National d'Histoire Naturelle (MNHN, Paris) have been studied during the run. Laboratory Raman and XRF
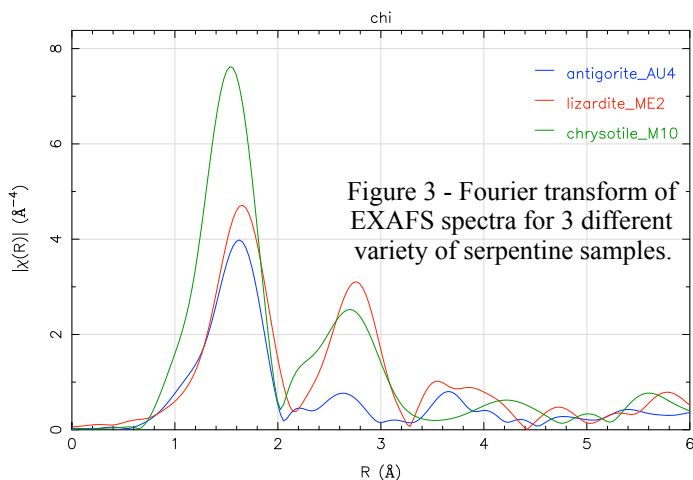
Figure 1 - Normalized XANES spectra of the complete series of samples.
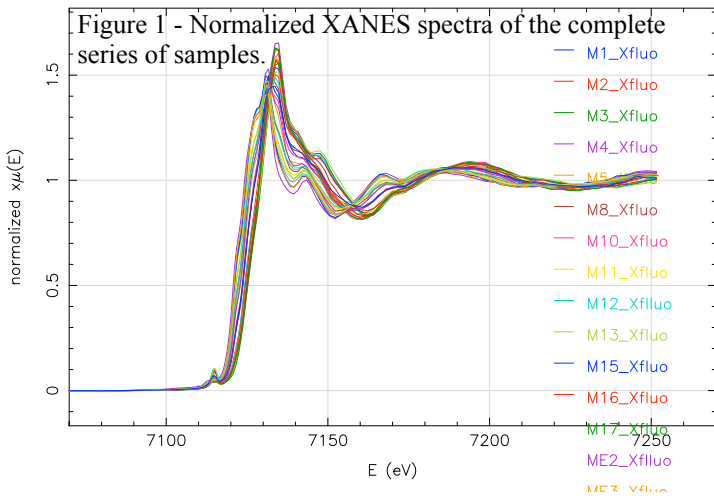
characterization were performed prior these measurements to characterize, respectively, the variety of serpentine, and it chemical composition. Data are still under reduction, but preliminary results show a clear variability in the XANES signatures (see Figure 1). The variations observed cannot be alone attributed to valence changes (changes in pre-edge and edge position) since the white line region and the first EXAFS oscillation also show important contrasts.

The pre-edge analysis reveals the main trends for each variety of serpentine, although some exceptions are observed (Figure 2). Pure ferrous iron is not observed in these samples. Iron in chrysotiles and antigorites is mostly 6-fold coordinated. In contrast, lizardite samples contain mostly ferric iron, and a significant part of it could be 4-fold coordinated. However, the high intensities observed for these pre-edges might also result from strong distortions of the octahedral sites.

Figure 2 - Pre-edge centroid analysis.
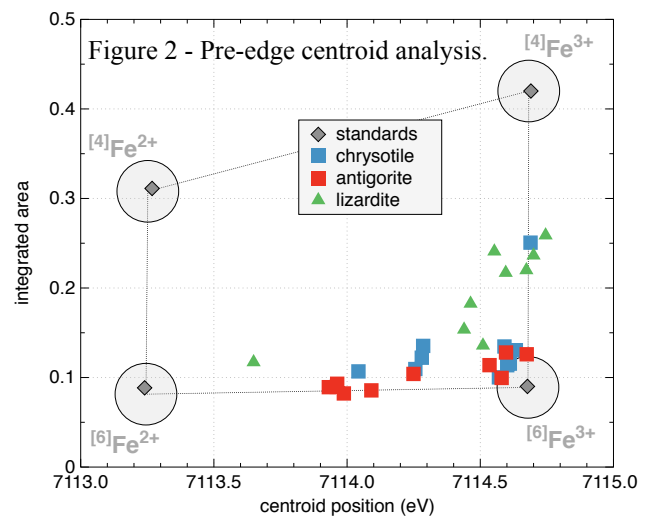
The next steps of this study consist of 1) investigating and understanding the different shapes observed for the white-lines, based on *ab-initio* XANES calculations; 2) investigating possible correlations between pre-edge and XANES information; 3) reducing the EXAFS information to derive both, the first- and second-neighbor environment around Fe. Preliminary data reduction also shows strong contrasts between the different varieties of serpentine (see Figure 3). Finally, cationic substitution mechanisms will be proposed to explain the microstructures observed for serpentines. This work is still in progress.

Figure 3 - Fourier transform of EXAFS spectra for 3 different variety of serpentine samples.