ESRF	**Experiment title:** **Determination of redox conditions from the Fe oxidation state of epidote and lawsonite in subducted oceanic crust**	**Experiment number:** ES1275
Beamline: ID16	**Date of experiment:** from: 25/04/2023 to: 29/04/2023	**Date of report:** 05/05/2023
Shifts: 12	**Local contact(s):** Angelika Rosa	*Received at ESRF:*

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Report:

The oxidation state of Fe was evaluated in hydrous Ca-Al silicates – lawsonite and epidote-group minerals (EGM, epidote, clinozoisite, zoisite) using the XANES spectra at the Fe- K-edge. 12 geological samples were chosen from high-pressure / low-temperature metamorphic rocks (blueschist, eclogite) that formed during subduction of oceanic lithosphere. The samples included:

- lawsonite grain mounts with crystals in different orientations: 2 / Franciscan, USA; 1 / Corsica
- lawsonite and garnet in petrographic thin section: 1 / Sivrihisar, Turkey
- lawsonite in thin sections: 2 / New Caledonia
- epidote grain mount with crystals in different orientations: 1 / location unknown
- clinozoisite grain mount with three grains in different orientation: 1 / Pakistan
- zoisite grain mount with crystals in different orientations: 1 / location unknown
- epidote group minerals and garnet in thin section: 3 / New Caledonia

in addition to various reference materials.

In each petrographic thin section and grain mount, we typically analyzed 2-4 distinct crystals of lawsonite or EGM with scans on individual spots or an array of spots in a line across part or all of a crystal to evaluate Fe zoning. In two garnet-bearing samples, we analyzed one garnet in each, including a cross section of a complete garnet grain of ca. 1 mm diameter.

The beam was focused down to 3 x 3 μm^2 using the KB-mirror. The spectra were recorded in fluorescence mode using a SDD detector available from the beamline. The use of a Si (311) double-crystal monochromator together with a small vertical gap of the entrance slit of the KB-mirror revealed unprecedented energy resolution (Fig. 1). The analyses were successful at all Fe contents down to ca. 1 wt% of Fe_2O_3. The analyzed minerals did not show signs of beam damage and we were able to obtain robust, reproducible results. Lawsonite does not exhibit orientation effects, i.e. linear dichroism, but the epidote-group minerals do (Fig. 1). For dipolar transitions, contributions in direction of the linear polarization of the x-ray beam are primarily enhanced (e.g. Waychunas 1990). Both minerals primarily incorporate ferric iron, with ferrous iron in some. The data processing to determine the Fe oxidation state in greater detail as well as the orientation dependence is ongoing.

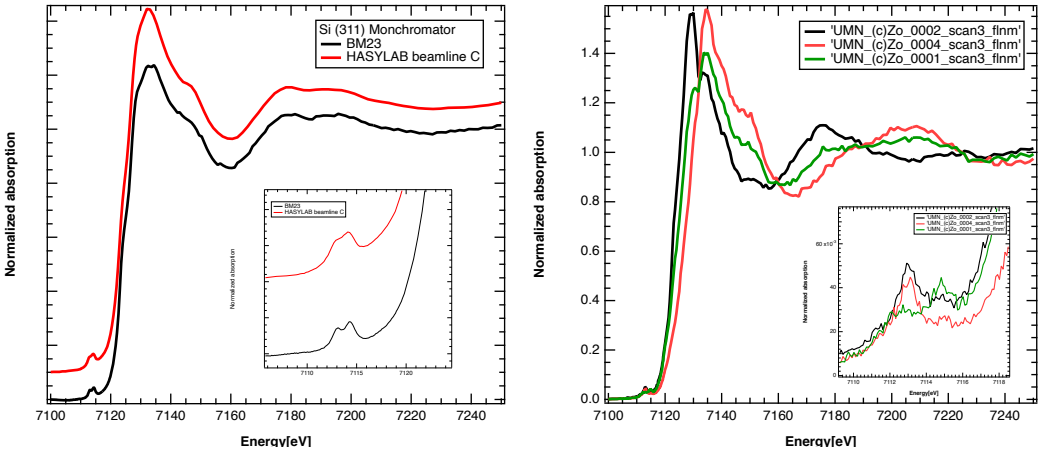

Figure 1: Left: Comparison of spectra of Aegirine (Acmite) taken at different beamlines as indicated, illustrating the energy resolution. Right: Example spectra for EGM grain mount showing variation in pre-edge as a function of crystal orientation. The pre-edge features vary in intensity depending on orientation. Further features at main-edge strongly vary. Crystal orientation was previously determined by electron backscattered diffraction (EBSD).

References:

Waychunas G.E., Brown G.E. Jr. (1990) Phys Chem Minerals, 17, 420-430.

Acknowledgements:
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