ESRF	**Experiment title:** INVESTIGATION OF THE HIGH-TEMPERATURE BEHAVIOR OF TRANSITION ELEMENTS IN NATURAL MELTS	**Experiment number**: CH-**769**
Beamline: **ID 26**	**Date of experiment**: from: 28/10/1999 to: 2/11/1999	**Date of report**: 21-02-2000
Shifts: **18**	**Local contact(s)**: Pierre-E. PETIT	*Received at ESRF:*

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Report:

We collected among the highest resolved pre-edge spectra ever collected on any beamline on a series of more than 60 model compounds of Ni and Fe. The impressive quality of the pre-edge information obtained on ID26 supercedes our previous SSRL pre-edge set of data, collected also in 1999. Because of the excellent signal-to-noise ratio, the deconvolution of such features is also much more constrained and significant understanding of these 1s -> 3d/4p transitions was possible. We found that the centroids of the pre-edges for Fe(II) and Fe(III) are separated by 1.4 eV, which allows a coarse determination of the oxidation state of Fe in unknown compounds, based on pre-edge centroid position. However non-linear variations of the pre-edge are complex and require special care (Wilke et al, 2000). At the Ni K-edge, we performed also a resolution analysis of the ID26 beamline (Farges et al., 2000).

In glasses and melts to 1300°C, we collected numerous pre-edge, XANES and EXAFS spectra as planned. Because we studied so far mostly model compounds, we started reducing the data for these glasses and melts only in early 2000. Thanks to several improvements done at ESRF (such as titanium slots), the thermal stability of the furnace has been greatly improved. The main problems encountered was the noisy answer of the pin-diode detector to the black body radiation. We solved this problem by adding several aluminium foils in front of the diode.

Fe. We observed, however, evidence for the presence of 5-coordinated Fe(II) and 4-coordinated Fe(III) in a wide number of melts, synthetic and natural. All *in-situ* experiments at high temperature showed an slight oxidation of Fe, which do not allowed to study accurately ferrous iron in melts (postponed to 2000). The high number of quick-EXAFS scan collected around the glass transition temperature (near 700°C in tonalite) will also allow to understand this major structural transition in much better details than previously taught.

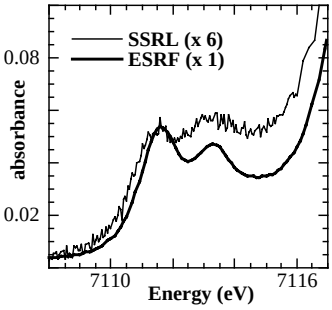

Fig. 1 — Fe K-edge XANES spectra of Fe(II) in the rare trigonal bipyramid (grandiderite) collected at SSRL 4-3 (grey, average of 6) and ESRF ID26 (black, x 1).

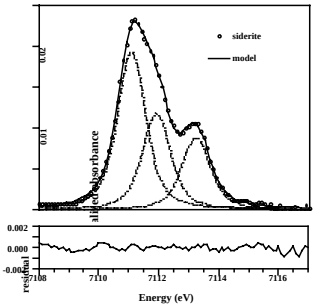

Fig. 2 — Fe K-edge pre-edge spectra of Fe(II) in siderite (Oh) showing clearly the 3d crystal-field splitting predicted by the theory.

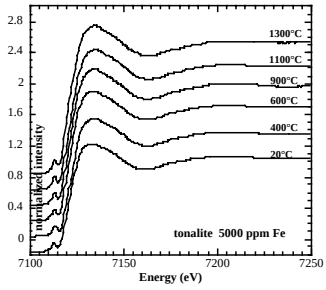

Fig. 3 — Fe K-edge XANES of tonalite glass and melt to 1300°C (data is under reduction).

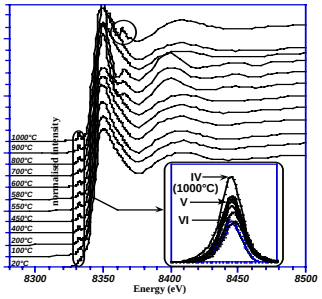

Fig. 4 — Ni K-edge XANES spectra of NS2 glass with 2000 ppm Ni to 1000°C and its pre-edge (inset).

Ni. Thanks to a thorough analysis of model compounds, we found that the position and the normalized height of the Ni pre-edge varies considerably with the coordination number of Ni (details are in Farges et al., 1999). Among the various glasses and melts we studied, we will present here the case of the sodium disilicate ($Na_2Si_2O_5$ or NS2) containing 2000 ppm nickel (Figure 4). Up to ~580°C (glassy state), Ni remains 5-coordinated. Between 580 and 800°C, Ni undergo a coordination change to 6, with a XANES spectra that recall that for crystalline NiO (supercooled liquid domain of NS2 corresponding to the stabilization of NiO). Above 800°C, the sample reaches the molten state and Ni-coordination decreases from 6 to 4. A well different behavior was observed for NS3 and an albite composition for which we tried to correlate with optical spectroscopy data. Two papers have already been submitted.

Paper submitted from these runs :

Farges F., Brown Jr. G.E., Petit P.-E., and Munoz M. (2000) Transition elements in water-bearing silicate glasses/melts. Part I. A high resolution and anharmonic analysis of Ni coordination environments in crystals, glasses, and melts. Geochimica and Cosmichimica Acta (submitted 1/2000).

Wilke M., Farges F., Petit P.-E., and Brown GE, Jr. (2000) Oxidation state and coordination of Fe in minerals: an Fe *K* XANES spectroscopic study. American Mineralogist (submitted 2/2000).

Conferences/posters at meetings :

Farges F., Wilke M. and Petit P.-E. (2000) Fe redox determinations in minerals using XANES spectroscopy. Meeting EMPG (Bergamo, April 2000, submitted).

Petit P.-E., Farges F and Wilke M. (2000) Determination of the iron oxidation state in Earth materials using high-resolution pre-edge information. Meeting XAFX XI (Japan, August 2000, to be submitted).

Wilke M., Farges F., Petit P.E., Behrens H., Burkhardt D. and Brown G.E. Jr. (1999) Effet de l'eau sur l'environnement du fer dans les verres silicatés. Meeting GDR "Verres" (Montpellier, Nov. 99).
Wilke M., Farges F., Behrens H., Burkhard D. and Petit P.E. (2000) The local environment of Fe in dry and water-bearing silicate glasses. Meeting EMPG (Bergamo, April 2000, submitted).