Fe-model compounds. In 1999, we collected among the highest resolved pre-edge spectra to date, collected on any beamline on a series of more than 50 model compounds of Ni and Fe. In 2000, we focused on Fe (see previous report on Ni).

Based on an experimental deconvolution analysis (Kosarev, 1990 - see also Loeffen and Pettifer, 1979 for another applicayion of these methds) that we modified slightly to consider also core-hole lifetime, a spectral resolution for this beamline could be determined at the Fe-, and Ni K-edges (~ 1.5 and 1.6 eV, respectively: Farges et al., 2000, Wilke et al., 2000). The quality of the pre-edge information supercedes our previous SSRL pre-edge information. Because of the good spectral qualities of ID26, it has been possible to collect high quality pre-edges around Fe in unusual environments (square pyramid, trigonal bipyramids) because Fe is relatively diluted in such structures (less than 1 wt.%: grandidierite, vesuvianite), making the collection of high resolution pre-ege spectra difficult at SSRL. Because of the excellent signal-to-noise ratio, the deconvolution of such features is also much more constrained and singificant understanding of these 1s -> 3d/4p transitions was possible. Also, we made a statistical study of the percentage of Gaussain/Lorentzian in the pseudo-Voigt shape of these features and found an average of 49 %, which is close to teh value commonly adapted in previous studies.

We found that the centroids of the pre-edges for Fe(II) and Fe(III) are separated by 1.4 eV, whch allows a coarse determination of the oxidation state of Fe in unknown compounds, based on pre-edge centroid position. We also did an extensive study of mechanical mixtures between 4, 5 and 6-coordinated Fe(II) and Fe(III) and found most pre-edges for the mixtures to vary non-linearly with the iron redox state. Therefore, we preconise a cautious analysis of the pre-edge information we ensure an careful determination of the iron redox state. This study was the goal of a paper submitted in February 2000 to the "American Mineralogist".
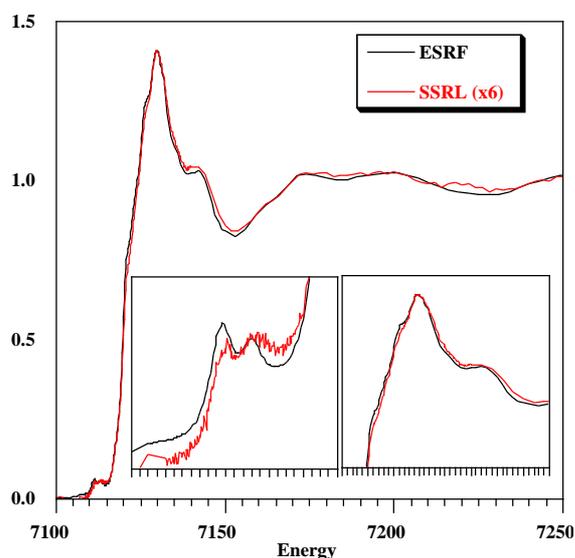

Fig. 1 — Fe K-edge XANES spectra of Fe(II) in the rare trigonal bipyramid (grandiderite) collected at SSRL (grey, average of 6) and ESRF (black, x 1). Gains in resolution and in signal are obvious.
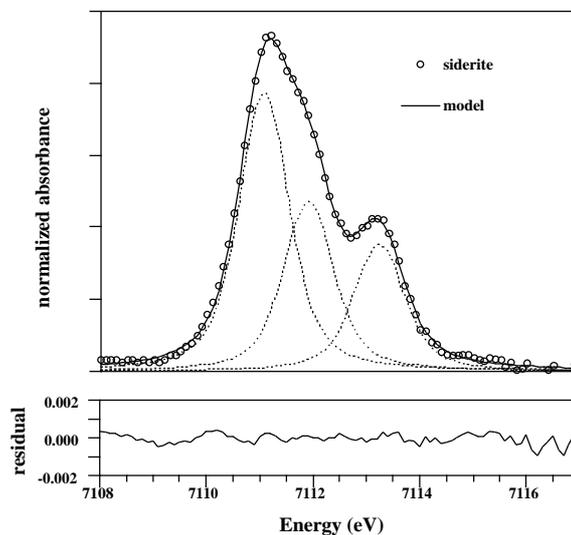
Fig. 2 — Fe K-edge pre-edge spectra of Fe(II) in siderite (regular octahedron) showing clearly for the first time the crystal-field splitting of 3d levels into 3 e_g/t_{2g} sub-levels, as predicted by the theory (Westre et al., 1997).

Fe-glasses. We collected a bunch of pre-edge, XANES ad EXAFS in glasses and melts to 1300°C. Because it took a lot of time to reduce the data for model compounds, we

still are reducing the data for these samples. Thanks to several improvements done at ESRF (such as titanium slots), the thermal stability of the furnace has been greatly improved. A convenient low voltage/high current power supply was also builded which controls the furnace from the user's hutch. We are currently re-calibrating all cables, thermocouples and heating elements for the possible continuation of these experiments in 2000. The fluorescence mode has proven to be efficient, as expected, as self-absorption effects (Goulon et al., 1983) were monitored by varying the angle between the beam and the sample. The main problems encountered were : (1) the strong answer of the pin-diode detector to the black body radiation, and the nitrogen flux inside the furnace which was not reducing enough. The first problem is solved by adding several aluminium foils and the second by the use of a nitrogen/hydrogen mixture (99%:1%), which is commonly used to welding metal pieces. We are testing this gas right now to check its reducing conditions, but the lack of direct XAFS measurement to estimate the redox state of Fe limits our investigations.
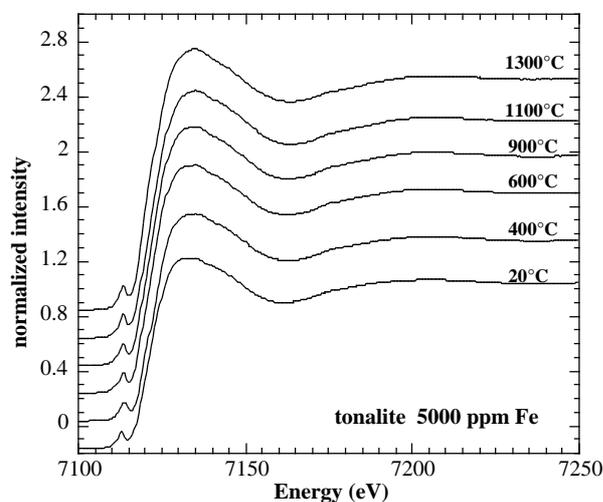

Fig. 3 — Fe K-edge XANES of tonalite glass and melt to 1300°C (data is under reduction).
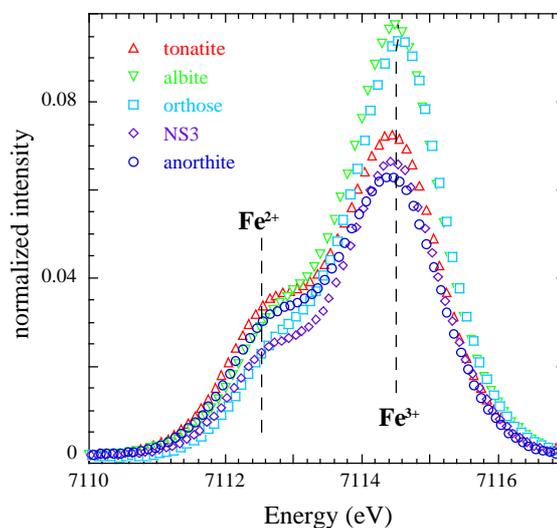
Fig. 4 — pre-edge spectra of various glasses.

We observed, however, evidence for the presence of 5-coordinated Fe(II) and 4-coordinate Fe(III) in a wide number of glasses, 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. The high number of quick-EXAFS scan collected around the glass transition temperature (near 700°C in tonalite) will also allow to understand this transition in much better details than previously taught. We are lacking a detailled analysis of the EXAFS spectra for model compounds with temperature. Our previous LURE data for fe in model compounds to 2000°C is limited in k-space to 6 $\mathring{A}^{-1}$ (collected in dispersive EXAFS in 1994 with D. Andrault).

Paper submitted from these runs :
   Wilke M., Farges F., Petit PE, and Brown GE, Jr. (2000) Oxidation state and coordination of Fe in minerals:
   an Fe *K* XANES spectroscopic study. American Mineralogist (submitted 2/2000).
Conference at meetings :
   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. Congrès GDR verres (Montpellier, Novembre 99).
Related paper (SSRL data) :

Wilke M., Farges F., Behrens H. et Burkhardt D. (1999) The effect of water on the local environment of Fe in silicate glasses: Deutsche Mineralogische Gesellschaft Meeting (Vienne, Autriche, octobre 1999). *Europ. J. Mineral.* 11(1), 244.