ESRF	**Experiment title: INVESTIGATION OF THE HIGH-TEMPERATURE BEHAVIOR OF TRANSITION ELEMENTS IN NATURAL MELTS**	**Experiment number**: CH-769
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Shifts: 15	**Local contact(s)**: Pierre-Emmanuel PETIT	*Received at ESRF:*

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Report:

Proposal CH-769 - 1999 Activity Report

Ni-model compounds. The first part of the data processing consists in studying the pre-edge of XAFS spectra. Then, we will be interested in EXAFS oscillations (examination in progress) in order to characterize thermal dilations of the connections Ni-O which take place when the temperature evolves.

Before starting to study glasses and the silicate melts of high temperature, we studied various model compounds where nickel is in tetrahedral, octahedral or trigonal bipyramidal sites, i.e. in IV, VI or V coordinated (see figure 1 below). By studying pre-edge more precisely, we could note that their position and their intensity are considerably affected by the changes of coordinated number (see figure 2 below).

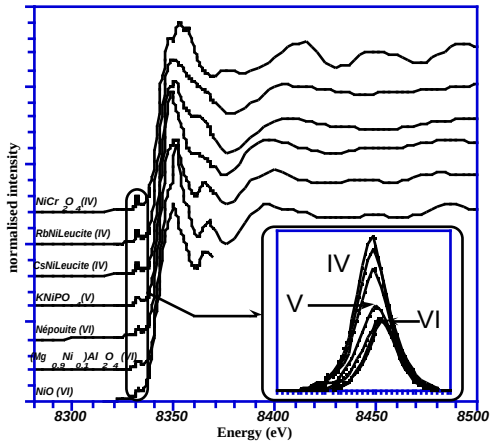

Fig.1 – XANES of various model compounds. Pre-edge check well that nickel is IV, V or VI coordinated according to case's.

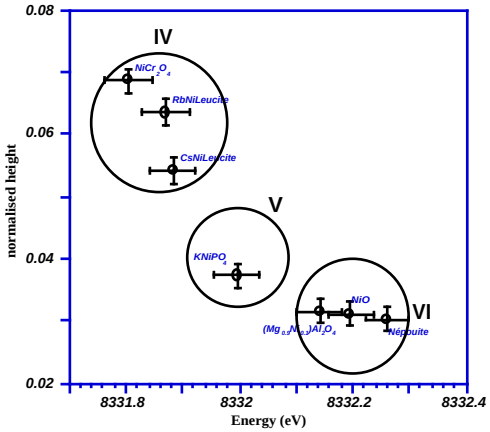

Fig. 2 – Positions and intensities of pre-edge maxima for various model compounds.

We then made a study in temperature on the KNiPO4 compound. Indeed, in this compound nickel is V coordinated and consequently are well connected with glasses as well as with silicate melts. Figure 3 below presents the whole of spectra XAFS obtained during the rise in temperature. Pre-edge study lets clearly appear that nickel passes from V to IV coordinated when the temperature reaches 1000°C. Moreover, figure 4 shows that with quench, nickel is in two types of sites (tetrahedral and trigonal bipyramidal).

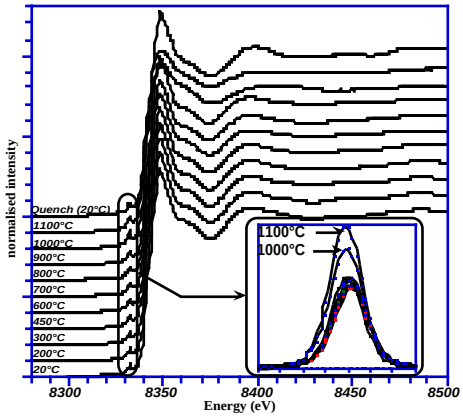

Fig.3 – KNiPO4 XANES in temperature. Pre-edge show that nickel passes from V to IV coordinated number starting from 1000°C.

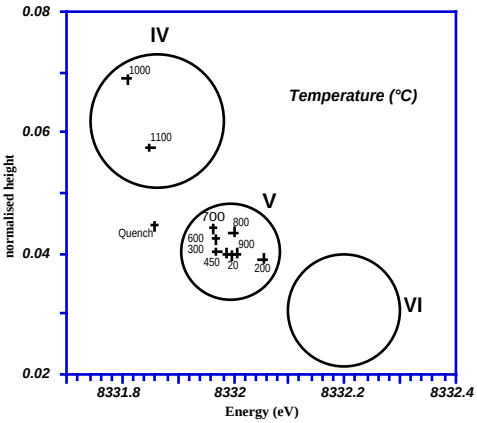

Fig.4 – Positions and intensities of pre-edge of KNiPO4 during the rise in temperature and after quench.

Ni-glasses. Many glasses were studied. Here the example of the sodium disilicate with 2000 ppm nickel. We could notice interesting structural modifications during the rise in temperature. Figures 5 and 6 below present the whole of the XANES obtained thus that the precise positions of pre-edge maxima.

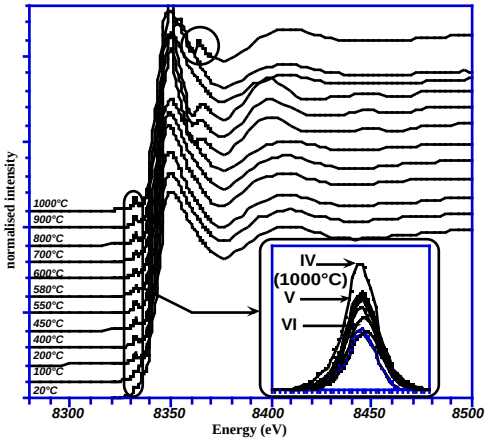

Fig.5 – XANES of the sodium disilicate with 2000 ppm nickel in temperature. Pre-edge show passages in IV, V and VI coordinated number according to the temperature.

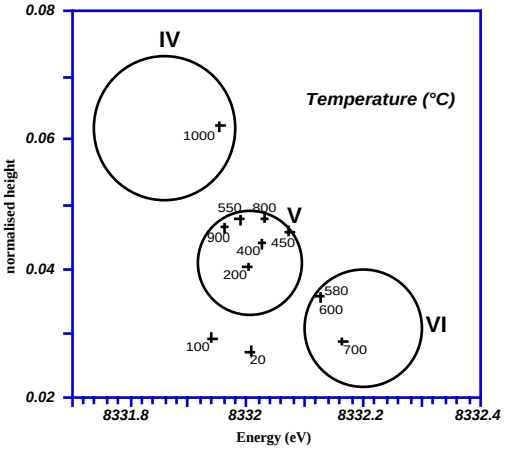

Fig.6 – Positions and intensities of pre-edge maxima for sodium disilicate to 2000 ppm nickel. Many changes of coordinated number takes place during the change of the temperature.

To 100°C, nickel is in V and VI coordinated sites. This is probably with the phenomenon of quench during the synthesis of the sample. Then nickel passes entirely in V coordinated number until 580°C. This level we could notice a change of coordinated number. Indeed, the temperature of vitreous transition is reached, and glass is then with the state of liquid in superfused which allows a recrystallization. Nickel thus passes in VI coordinated number. Then, starting from 800°C the compound is completely molten and nickel is again V coordinated, as in its vitreous state. Then finally, we could note a new change of coordinated number when the temperature reaches 1000°C. Nickel passes then in IV coordination number. This stage, we reached the real state of nickel in the magma. However we can notice that, on figure 5, spectrum XANES with 1000°C presents defects which limit us when one tries to increase the temperature. However, we could identify the cause of this problem. They were flashes of lights caused by the heating wire. We could note that by putting a simple aluminium foil in front of the detector, this phenomenon was largely attenuated.

Moreover, the objetif one of our study being to identify the behavior of nickel in the magmas in-situ, it will be necessary to work thereafter, at high temperature, but also with high pressure (5 kbars approximately).

Paper submitted from these runs :

Farges F., Gordon E., Brown Jr., 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 in crystals, glasses and melts. Geochimica et Cosmochimica Acta (submitted November 1999).