	Experiment title: Determination of the redox state of vanadium in magnetites synthesized under specific oxidizing conditions.	Experiment number: EC-391
Beamline: ID26	Date of experiment: from: 24 september 2008 to: 01 october 2008	Date of report: 13-03-09 <i>Received at ESRF:</i>
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Report

Previous preliminary works have shown the coexistence of V^{3+} and V^{4+} in natural titanomagnetite samples from layered intrusions (Balan et al. 2006). Therefore, the pre-edge XANES spectroscopy of V in titanomagnetite can provide useful information about the redox conditions prevailing during rock-forming processes. We investigated in a previous project the fO_2 and V^{4+}/V^{3+} ratio fluctuations at different length scales in the giant magmatic chamber of Bushveld, where vanadium is encountered in meter-thick discrete layers of magnetite (Bordage et al., in prep). The goal of this project was to get a better understanding of the relation between the V^{4+} content and the fO_2 conditions in this layered intrusion by investigating the vanadium redox state in magnetite samples synthesized under controlled oxidizing conditions.

Eighteen samples of synthesized magnetites have been studied. They correspond to nine different conditions (fO_2 and temperature) of synthesis with analysis performed on powders and bulk material. XRD, SEM and electron microprobe measurements have been performed prior to X-ray spectroscopic measurements. The size of the X-ray beam is $250\text{ }\mu\text{m} \times 60\text{ }\mu\text{m}$, which is reasonable for the investigation of petrographic samples displaying relatively large grain sizes (mm). Each spectrum has been measured by accumulating about 30 spectra recorded in the quick scan mode, between 5460 eV and 5515 eV. Additional

spectra have been measured up to 5815 eV in order to properly normalize the XANES spectra to the edge jump.

Because of the proximity of the Ti $K\beta$ (4931 eV) and V $K\alpha$ (4952 eV) fluorescence lines, the study of the natural titanomagnetites samples require the use of the high energy-resolution emission spectrometer (Ge(331) crystal analyser) installed on the ID26 beam line. This is particularly important because the intense Ti fluorescence from the titanomagnetite matrix has to be filtered out to obtain high-quality pre-edge spectra of vanadium. In order to compare the present results with the previous measurements, this particular configuration of ID26 beam-line, which provided us excellent spectra with a high signal/noise ratio, was needed.

We observe identical XANES features for the synthesized and natural samples (Figure 1), meaning that the vanadium has the same crystallographic environment in all samples. We detect small but significant variations of pre-edge intensity among the investigated samples (Figure 2). The pre-edge features are also really similar between natural and synthesized samples. It confirms the coexistence of two vanadium speciations in the synthetic samples. A proper thermodynamic modelling of vanadium incorporation in magnetite's, based on XAS observations, is under progress.

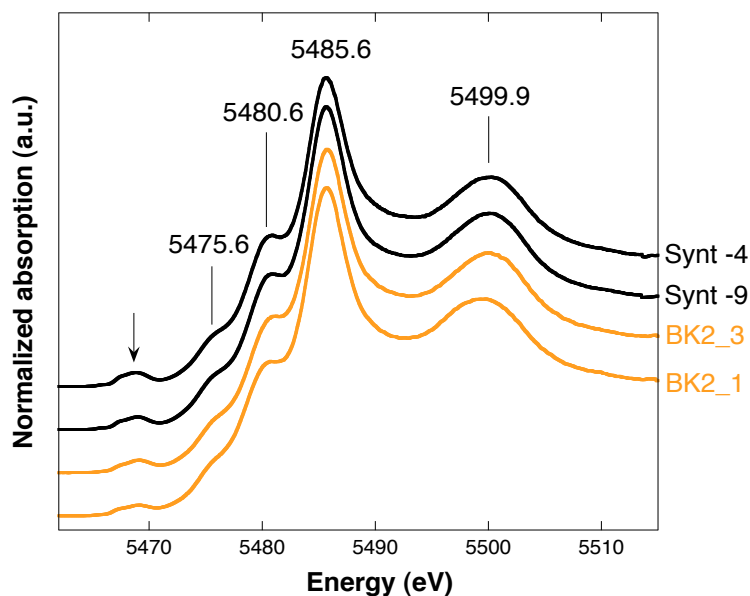


Figure 1: Normalized K edge spectra of 2 natural (orange) and 2 synthesized (dark) magnetites.

Figure 2: Evolution of the pre-edge of the HERFD-XAS spectra of the titanomagnetites (with the V^{3+} reference spectra at the bottom)

