



Experiment title: Fluctuations of redox conditions in a giant magmatic chamber : XANES spectroscopy of vanadium in magnetites from the Bushveld Complex

Experiment number:
EC-172

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Report:

Our previous works at ESRF have shown the coexistence of V^{3+} and V^{4+} in natural titanomagnetite samples from layered intrusions. Therefore, the pre-edge XANES spectroscopy of V in titanomagnetite can provide useful information about the redox conditions prevailing during rock-forming processes. The goal of this project was to investigate the fO_2 fluctuations at different length scales in the giant magmatic chamber of Bushveld, where vanadium is encountered in meter-thick discrete layers of magnetite. In particular, it is important to determine whether the V^{4+}/V^{3+} depends on magmatic or later subsolidus processes.

Eleven thin sections of rock have been investigated, corresponding to a detailed vertical sampling of the main magnetite layer of Bushveld. SEM and electron microprobe measurements have been performed prior to X-ray spectroscopic measurements. For each thin sections, X-ray absorption spectra have been recorded on about 5 different points. The size of the X-ray beam is $250 \mu m \times 60 \mu m$, 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 $K\alpha$ (4931 eV) and V $K\alpha$ (4952 eV) fluorescence lines, this study required 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. This specificity of the ID26 beam-line provided us with excellent spectra, displaying a high signal/noise ratio (Figure 1). It was therefore possible to detect significant variations of pre-edge among the investigated thin sections. In contrast, the spectra recorded at the scale of a single thin section were very similar. The change in pre-edge intensity makes it possible to unambiguously determine the redox state of V in the samples, confirming the occurrence of tetravalent vanadium in the titanomagnetite samples. Depending on the sample, the proportion of V^{4+} varies between 7 and 14 mol. % (Figure 2) and the observed fluctuations can be correlated to petrological observations.

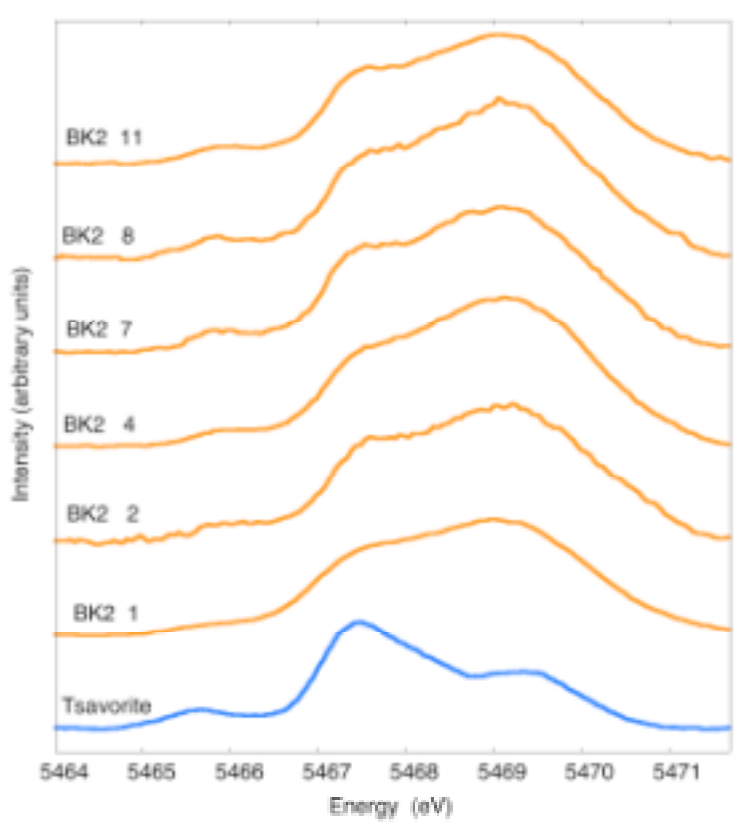


Figure 1: Selected RIXS pre-edge of vanadium in the investigated samples (V^{3+} reference spectra at the bottom)

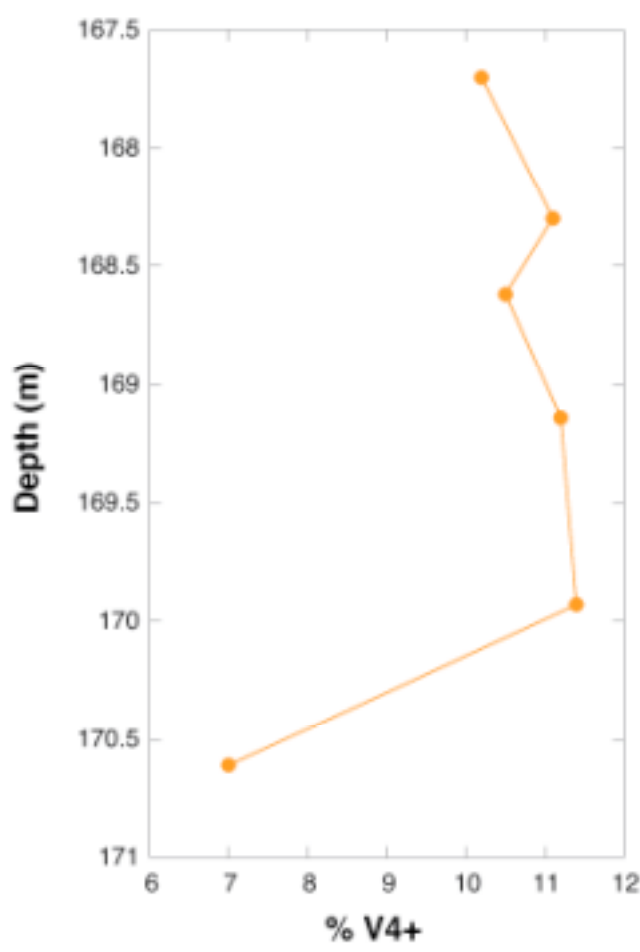


Figure 2: Vertical evolution of the V^{4+} fraction in titanomagnetite