



Experiment title: Redox state and location of vanadium and chromium in magnetite : crystallographical and geochemical implications.

Experiment number:
ME-1120

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Report:

The main goal of the project was to investigate the redox state and location of V in natural and synthetic magnetite samples to better understand the mechanisms controlling its incorporation in magnetite, which is the most important vanadium ore. Nine natural vanadium-bearing magnetite samples of various origin and five synthetic samples corresponding to various fO_2 have been analysed. Several compounds with known V oxidation state and coordination number were used as standards: tsavorite (3+, octahedron), lavrovite (3+, octahedron), cavansite (4+, pentacoordinated), vanadyle sulfate (4+, octahedron), descloizite (5+, tetrahedron) and Na_3VO_4 (5+, tetrahedron).

Most magmatic samples of V-bearing magnetite correspond to Ti-magnetite, with up to 10 wt.% Ti, whereas the V concentration is generally below 2 wt.%. Therefore, the Ti fluorescence (Ti K edge at 4966 eV and $K\alpha$ emission at 4931 eV) makes it very difficult to obtain XAS spectra at the V K-edge (5465 eV) using its $K\alpha$ line (4952 eV) with a conventional experimental configuration. The emission spectrometer installed on the ID26 beam line, using a Ge 331 crystal analyser, made it possible to record the spectra by selecting the V $K\alpha$ fluorescence line. This unique experimental configuration provided us with excellent spectra, with almost no baseline and a very good resolution (Figure 1 & 2).

The change in pre-edge intensity as a function of the redox state of V (Figure 1) makes it possible to unambiguously determine the redox state of V in the samples. In the natural magnetite samples, the V is mostly trivalent (Figure 2). However and interestingly, some variations are observed among the series of investigated samples, depending on their

geochemical characteristics. In addition, very similar spectra are obtained for some synthetic and natural samples (Figure 2), supporting the use of experimental petrology experiments to explain the high concentration of V observed in specific natural magnetites.

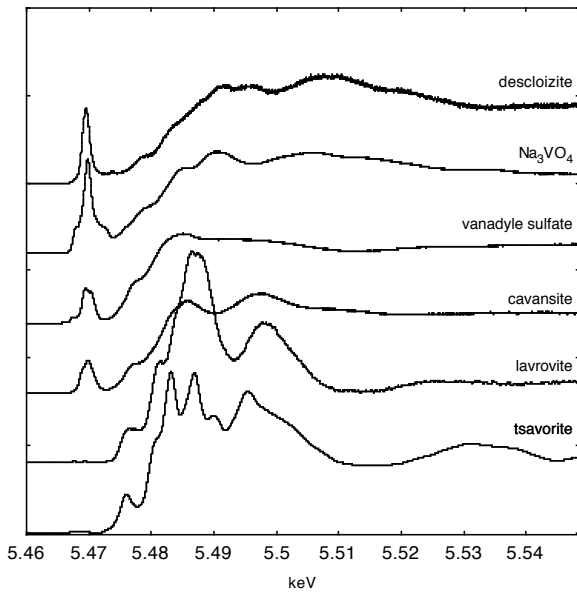


Figure 1: XANES spectra of reference samples. Note the very good resolution and the change in pre-edge intensity as a function of V valence state.

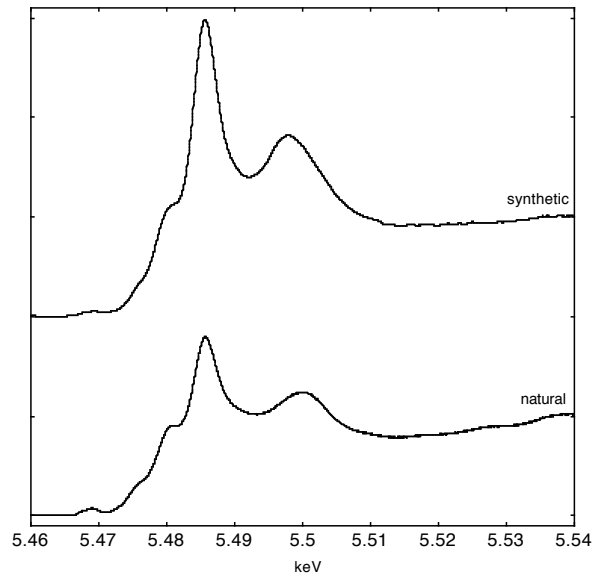


Figure 2: Representative XANES spectra of a natural and a synthetic Ti-magnetite sample. Note the similarity of both spectra and the low intensity of the pre-edge features indicating that V is mostly trivalent.