Geophysical Research Abstracts, Vol. 10, EGU2008-A-07695, 2008 SRef-ID: 1607-7962/gra/EGU2008-A-07695 EGU General Assembly 2008 © Author(s) 2008



Redox state of vanadium in the titanomagnetite layers of the Bushveld complex

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Vanadium oxidation state ranges from divalent to pentavalent in terrestrial magmatic systems, which makes it a valuable geochemical indicator, providing useful information on the oxygen fugacity in magmatic processes (Sutton et al., 2005). Vanadium does not form ore minerals by itself but is extracted from V-rich titanomagnetite ($Fe_{3-x}Ti_xO4$) cumulates in the upper part of layered basic intrusions. In particular, the largest vanadium ore deposit in the world is the Bushveld Complex (South Africa) where vanadium is encountered in meter-thick discrete layers of massive titanomagnetite. The redox state of vanadium (V^{4+}/V^{3+} ratio) in these natural samples would provide important information about the physical-chemical conditions prevailing during the formation of these layers, which are still poorly known.

The pre-edge features of the V K-edge X-ray absorption spectra can be used to determine the oxidation state of vanadium in natural and synthetic samples (Giuli et al., 2004; Sutton et al., 2005; Balan et al., 2006) The energy and relative intensity of these features indeed depend on the valence state and site symmetry of the transition element cation (Calas and Petiau, 1983). Here we performed Resonant Inelastic X-ray Scattering (RIXS) measurements at the V K-edge. Compared with conventional Xray absorption measurements in fluorescence mode, this experimental set-up leads to a significant sharpening of the pre-edge features and filters out the strong fluorescence of Ti from titanomagnetite (Glatzel and Bergmann, 2001). We will present the results of a RIXS study on a detailed vertical sampling of the main magnetite layer of the Bushveld complex. In these V-rich samples (c.a. 1.5 wt. % V_2O_3), the proportion in V^{4+} varies between 7 and 14 mol. %. The vertical variations in the V^{4+}/V^{3+} ratio follow the fluctuations of oxygen fugacity determined from the hematite-magnetite equilibrium (Lepage, 2003). This observation suggests that the V^{4+}/V^{3+} ratio in titanomagnetite is affected by the sub-solidus cooling history of the rock.

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