

ME840

Report

In order to determine by the XANES technique the oxidation state of Cr and the $\text{Cr}^{2+}/\text{Cr}^{3+}$ ratio in Earth materials, which is so important from a geophysics perspective, reference spectra are crucial.

Chromium oxides exist in a range of oxidation states with known coordination environment hence they are very useful to serve as reference materials. The oxidation state of the chromium oxides has been determined by wet chemical analysis on quenched materials and the phase diagram subsequently calculated (Toker et al., 1991; Wilhelmi, 1968). However, due the fact that Cr^{2+} ions are rare and unstable in terrestrial minerals *in situ* observation becomes almost unavoidable. Furthermore, the oxidation state determined from quenched materials does not necessarily correspond to the one present at high temperature because of the possibility of disproportionation or charge-transfer reactions on cooling (Berry and O'Neill, 2004; Berry et al., 2003).

As a consequence, a high temperature induction furnace has been designed and constructed for *in situ* X-ray spectroscopic experiments under controlled atmospheric conditions and high temperatures. The multi-purpose chamber design allows working in forward backscattering, normal fluorescence and transmission mode for synchrotron X-ray absorption and emission spectroscopy. Before the XANES experiments, tests were done in the laboratory on the proper working of the furnace and of the multi-wavelength pyrometer.

Fluorescence-yield XANES spectra at the Cr *K*-edge were collected at the ID26 beamline. Highly pure chromium metal was used as a starting material and the different stability fields of the calculated phase diagram for chromium oxide were investigated by changing both temperature and atmospheric conditions. The oxygen pressure P_{O_2} or redox potential inside the furnace was imposed by CO/CO₂ gas mixtures using computer-driven Bronkhorst mass-flow controllers. According to the reaction $\text{CO}_2 \rightarrow \text{CO} + 1/2 \text{O}_2$ the ratio of CO and CO₂ accurately defines the partial pressure of oxygen. The used flow rates of CO and 1% CO₂ in He were between 27 and 100 ml/min. XANES spectra were collected *in situ* at $\log P_{\text{O}_2}$ s between -10 and -11.3 and temperatures in the range 1550 to 1750°C. A multi-wavelength pyrometer was used as a non-contact temperature probe.

In figure 1 some selected XANES spectra normalized to the edge jump are displayed. The use of XANES spectroscopy to determine the redox state and coordination number of transition metal cations generally relies on the analysis of the pre-edge features observed at the low energy side of the edge. Their intensity and energy depend on the valence state and site symmetry of the metal cation. In figure 2 the pre-edge features for some selected spectra are shown. In the analysis of the pre-edge features, a baseline subtraction was performed by fitting an arctangent function on the edge. The pre-edges were fitted by a sum of pseudo-Voigt functions. A clear relation has been found between the integrated intensity vs centroid position and the oxidation state. Furthermore, this work shows that the used setup is of particular interest to study liquid metals, alloys and other electrically conductive materials at extreme conditions.

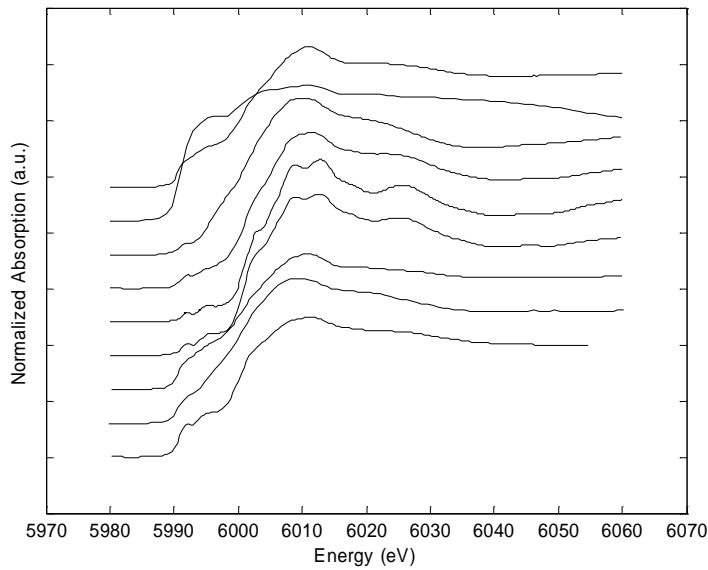


Figure 1: Some selected normalized Cr K-edge XANES spectra

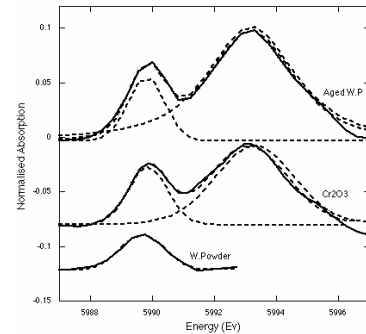


Figure 2: Some selected pre-edge peaks after baseline subtraction

References

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