



Experiment title: Redox state and location of vanadium and chromium in magnetite and silicate glasses : implications for crystal chemistry and geochemistry of V and Cr.

Experiment number:
CRG
30-02-724

Beamline: BM 30	Date of experiment: from: 4 march 2005 to: 8 march 2005	Date of report: 7-10-05 <i>Received at ESRF:</i>
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Report:

The Cr surrounding in glasses and crystalline references was investigated using Cr K-edge XANES and EXAFS fluorescence detection. Due to the environmental impact of chromate groups in glasses, a goal was to study the redox state. We want also to determine the local structure around Cr and in various glasses, as a fonction of glass composition (alkali alumino borate, silicate and boro-silicate glasses) and synthesis conditions.

Cr K-edge XANES spectra of Cr-alum and potassium bichromate were recorded as Cr(III) and Cr(VI) references, respectively. Alum (Cr(III)) pre-edge splitting structure is resolved into 2 apparent compounds in good agreement with ligand-field theory, thanks to energy resolution. Bichromate spectrum is characterised by a single intense pre-edge transition (figure 1).

Glass spectra have been recorded under the same conditions. As main Cr redox states are only III and VI, Cr(VI) /total Cr can be estimated using a linear combination of the Cr-K edge pre-edge structures of the two crystalline references.

For example, a soda silicate glass sample synthesized in air and containing 1% Cr has been studied. Its Cr(VI) /total Cr proportion has been evaluated between 40 and 45%. (figure 2). Other samples have been studied in order to determine the influence of glass composition and synthesis conditions. Pre-edge analysis is well suited to quantify the proportion of chromate groups in multicomponent glass, for Cr total concentration down to 1000 ppm or less, and for chromate proportion as less as a few percents.

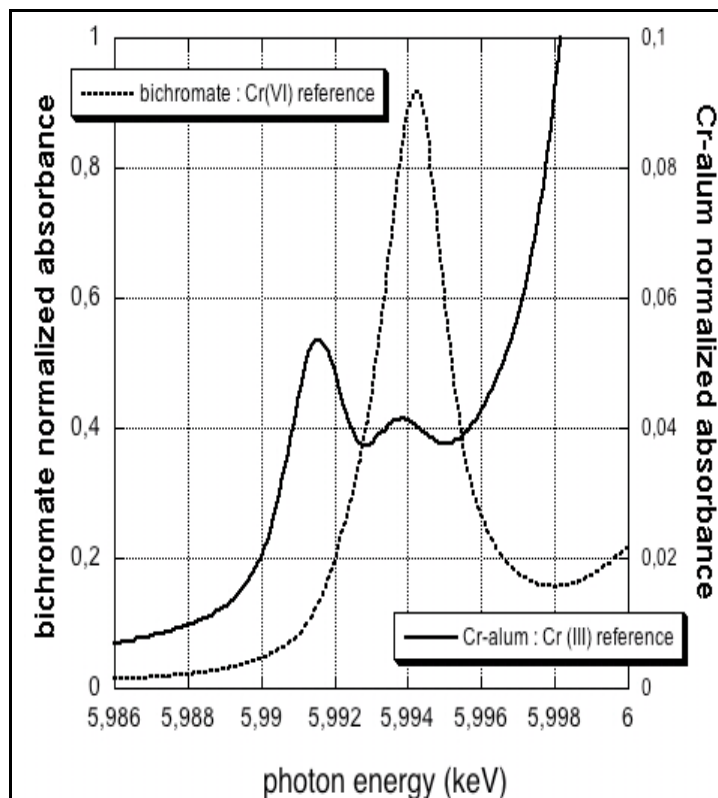


Figure 1 : Cr K-edge XANES spectra in the region of pre-edge of Cr(III) and Cr(VI) crystalline reference compounds. Absorption spectra are normalized to the atomic absorbance. Note double scale.

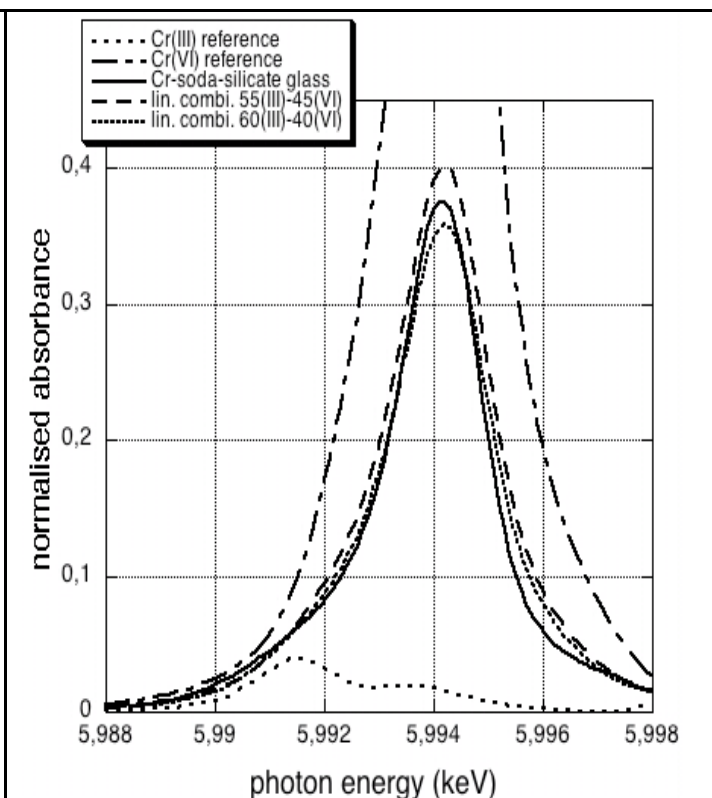


Figure 2 : Cr K-edge XANES spectra in the region of pre-edge of Cr(III) and Cr(VI) crystalline references and Cr-soda-silicate glass. Absorption spectra are normalised to the atomic absorbance and background subtracted. Linear combinations of reference spectra indicate the relative proportion of the two oxydation states.