



	Experiment title: <i>Electronic and topologic structure of Cr (III) in different oxides and hydroxides</i>	Experiment number: EC 243
Beamline: ID-26	Date of experiment: from: 03/10/2007 to: 09/10/2007	Date of report: 05/01/2009
Shifts: 18	Local contact(s): Dr. Tsu-Chien WENG	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Jakob FROMMER* Prof. Dr. Ruben KRETZSCHMAR Department of Environmental Sciences, Institute of Biogeochemistry and Pollutant Dynamics, Swiss Federal Institute of Technology, ETH Zurich, CHN, Universitätstr. 16, CH-8092 Zurich, Switzerland Dr. Maarten NACHTEGAAL* General Energy Research Department, Laboratory for Energy and Materials Cycles, Paul Scherrer Institute, PSI, CH-5232 Villigen, Switzerland		

Report:

Background

In this project we investigated the structural significance of spectral features before the main X-ray absorption K-edge of Chromium (Cr). To this end we analyzed a series of crystalline Cr(III) oxyhydroxide and oxide reference compounds varying in the nearest metal type (either Cr or Fe) and in the degree of octahedral polymerization. These reference phases were namely: active chromium hydroxide (ACH, containing isolated hydrogen-bridged Cr-octahedra), grimaldiite (α -CrOOH, containing edge-sharing Cr-octahedra), 5%-Cr-substituted hematite (α -Fe₂O₃; face-, edge-, and double-corner-sharing octahedra; the bulk of the metals surrounding Cr are Fe atoms), and 5%-Cr-substituted goethite (α -FeOOH; edge- and double-corner-sharing octahedra the bulk of the metals surrounding Cr are Fe atoms).

Methods and Results

At the beamline ID-26 of the ESRF we collected 1s2p RXES planes and high energy resolution fluorescence detected (HERFD) XANES spectra (Cr K α_1 fluorescence line) at the Cr-K-edge for all reference samples. This was done with a Rowland circle spectrometer (Ge(422) crystal). The HERFD-XANES spectra and the 1s2p-RXES planes are provided in Figure 1 and 2, respectively.

We found that the pre-edge of Cr(III) in (hydr-)oxides can be divided into transitions of localized and of delocalized nature [1]. Among other experimental observations also the peak dispersion in the RXES-plane is an indication for the proposed assignment. The non-local transitions [2] show a pronounced sensitivity to the degree of octahedral polymerization and to the next-nearest metal type. These transitions are therefore a promising and complementary source of structural information in geochemical research and related fields.

Progress of evaluation

The results of this study served as a basis for the preparation of two manuscripts [3, 4]. The manuscripts will be submitted to high-ranking peer-reviewed journals. Parts of the results were in addition presented at an international conference [5].

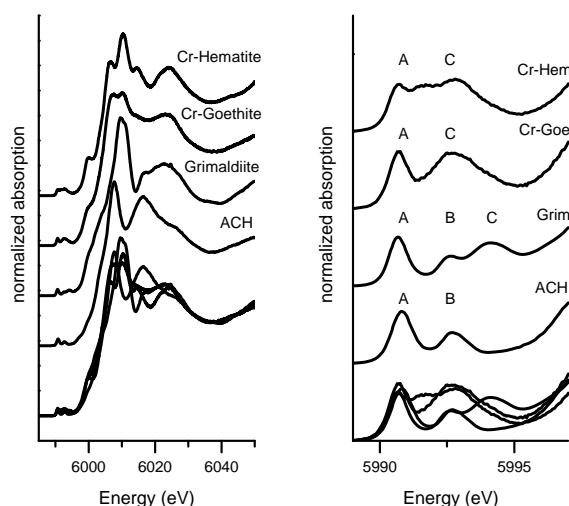


Figure 1: Left: normalized HERFD-XANES spectra of the reference samples. Right: Enlarged view of the pre-edge region. At the bottom an overplot of all spectra is shown.

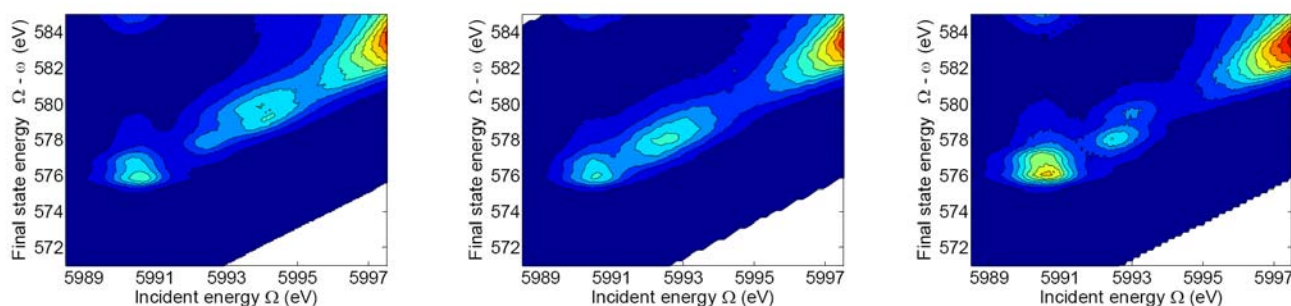


Figure 2: 1s2p RXES planes of (from left to right) grimaldiite, Cr-substituted goethite, and ACH. The normalized intensity is shown. The ACH RXES plane shows a minor contribution of Cr(VI) due to beam-induced oxidation during the analysis.

Acknowledgement

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References

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