ESRF

Experiment title:
Speciation of Zinc in Soils in Relation to Soil Type

Experiment number:
01-01-708

Beamline:
BM 26

Date of experiment:
from: 02.03.2007 to: 06.03.2007

Date of report:
05.01.2008

Received at ESRF:

Shifts:
12

Local contact(s):
Dr. S. Nikitenko

Names and affiliations of applicants (* indicates experimentalists):

Dr. Andreas VOEGELIN*
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:

Beamtime for this experiment was requested in April 2005, but only allocated in March 2007. Therefore, the measurements finally carried out (Cr K-edge XAS spectroscopy) deviated from those originally proposed.

Near edge structure of different Cr(III) reference phases

Chromium (Cr) is a versatile metal used in a plethora of industrial processes. The extensive use of Cr during several decades entailed however severe environmental problems mainly connected to hexavalent Cr (Cr^{VI}) which is toxic to a variety of plants and animals even at low concentrations. Studies dealing with the biogeochemistry of chromium must permit a reliable speciation of the compound under investigation. This speciation needs to go beyond the determination of the oxidation state (having pronounced influences on toxicity and mobility) and must allow for differentiating between different Cr^{III} phases (the exact specitaiton determines geochemical reactivity, e.g. towards a possible reoxidation by Mn^{IV}-oxides). The method of choice to obtain such information is EXAFS spectroscopy. The information content in the EXAFS is however intrinsically limited (e.g. regarding 3D arrangements) and EXAFS spectra with a good enough signal-to-noise ratio are not allways obtainable form environmetal samples (low concentrations, interferences). Thus a promissing approach to improve the fingerprinting capabilities of XAFS and to further constrain structural interpretation is to combine EXAFS with a detailed analysis of the near-edge features in the x-ray absorption spectra. As there is no unique understanding of this near edge structure, research on its origins in complex systems has to be based on both, explorative measurements and computational methods.
At BM26 we have measured the XANES and the EXAFS of a variety of Cr reference samples varying in their composition and the degree of crystallinity and polyhedral linkage. Figure 1 shows a selection of XANES spectra; good signal quality has been achieved (beside low frequency noise of unknown origin in some EXAFS spectra). The single spectra show variations in the EXAFS, the XANES and the pre-edge structures (Fig. 1) depending on crystallinity, molar fraction of Cr, aging time, and the presence of organic

and inorganic ligands. These data are currently combined together with results form emission spectroscopy (RXES at ID26) and quantum chemical modeling (StoBe, FEFF) to improve our understanding of the correlation between structure and spectral features. Results will be summarized and published in international high ranking journals.

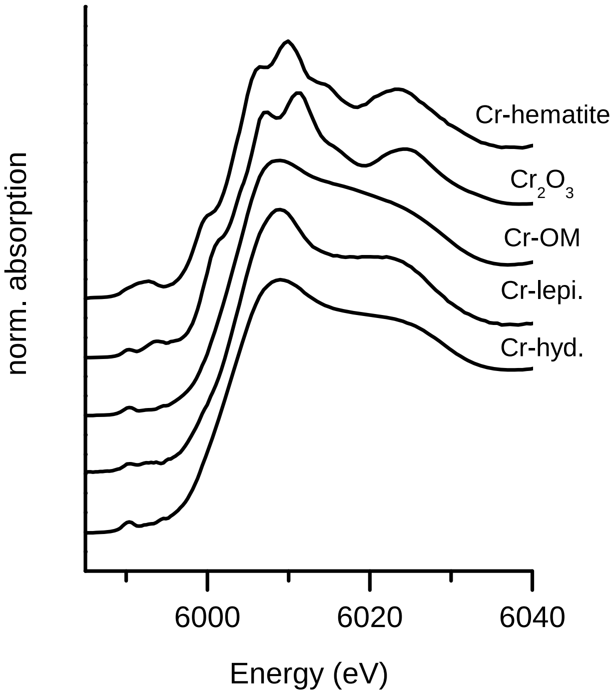

Figure 1: Normalized XANES of a selection of Cr reference samples: Cr-hyd.: amorphous Cr-hydroxide; Cr-lepi: 1%-Cr-susbtituted Lepidocrocite (γ-FeOOH); Cr-OM: Cr-complexed with organic matter.

Acknowledgements:

We acknowledge the DUBBLE Beamline at the European Synchrotron Radiation Facility for the provision of beamtime at the beamline BM26 and would like to thank Dr. Serge Nikitenko for his assistance.

Publications:

Frommer, J., Nachtegaal, M., Czekaj, I., and Kretzschmar, R., Absorption and resonant X-ray emission spectroscopy of poorly crystalline chromium-hydroxides. XAS08 workshop, PSI, October **2008**.

Frommer, J., Nachtegaal, M., Czekaj, I., Weng, T.-C., Kretzschmar, R., X-ray absorption and emission spectroscopy of Cr(III) (hydr)oxides: Analysis of the K pre-edge region, **in preparation**.