

Title:

Application of X-ray Absorption Spectroscopy in Earth and Environmental Sciences

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X-ray Absorption Spectroscopy (XAS) is indispensable in Earth and environmental analysis because it allows insight to structures on a molecular level. XAS has extended its applications from a bulk technique towards extracting chemical state information at high spatial resolution, and benefits from recent detector developments accessing structural information also for diluted systems. Modern accelerators with low emittance and focused intense synchrotron beams have provided the basis for methodological improvements, but high photon flux densities come along with challenges such as preventing irradiation induced changes in samples. The benefit of solving scientific questions in Earth and environmental research by applying recent methodological developments will be demonstrated and limitations discussed.

Earth and environmental samples are rarely homogeneous and require investigations of large sample areas with sufficient spatial resolution to record heterogeneities and to achieve reasonable significances for research sites. X-ray fluorescence mapping is essential to localize elements of interest for subsequent determination of their structural and chemical states but does not use beam-time efficiently in its classical step-scan mode. Continuous sample movement and recording XRF signals on-the-fly with low gate-time-electronics enable mapping of larger areas within reasonable time. Step-scan and fast XRF-mapping were applied to bulk low-ppm-Tl-containing rocks showing that Tl L $\alpha$ -fluorescence-emission is still detectable at 0.025 s gate-time. Good energy resolution of SDD-detectors at high count-rates enable Tl L3-edge XAS on areas with high Fe, Zn and As concentrations. Further applications could be detection and speciation of critical metals in ores and their processing residues.

Tracking of redox-states or detecting minor fractions of element species in heterogeneous samples is often fragmentary because it is hardly possible to record XANES spectra seamlessly across the sample area with a micro-beam. Full-field-transmission XAS could be in certain cases an alternative to measure distribution of element speciation all-over the sample [1,2]. A setup of a CCD-detector with scintillator-optics enables e.g. at 12.5x1.1 mm<sup>2</sup> beam size simultaneously recording of 550000 spectra at 5x5  $\mu$ m<sup>2</sup> spatial resolution. Sample requirement is a slice sufficiently thin to adapt transmission ideally to 0.01< $\mu$ d<1.5 for the element of interest. Candidates for full-field chemical-state imaging are e.g. transition metals of elevated concentrations. Fe-speciation-imaging in tidal sand-concretions and other rock types will be presented.

Metal sorption on mineral surfaces can trigger their transformation from harmful into less toxic species, but speciation changes in many cases during probing with synchrotron beam. The effects of metal concentration, photon flux density, temperature and sample matrix on spectral changes during irradiation has been studied for Cr(VI) adsorption on clay minerals as an example. A broad bending-magnet beam (6E9 ph/mm<sup>2</sup>/s/100mA) allowed recording of undisturbed XAS spectra. The increasing rate of Cr(VI) reduction at higher photon flux densities (e.g. 3.8E12 ph/mm<sup>2</sup>/100mA) could neither be compensated by a less radiosensitive environment nor by cooling to LN<sub>2</sub> temperature and 15 K which may not give access to undisturbed spectra at small unique sample areas.

[1] Meirer, F. et al. (2011), J. Synchrotron Rad. 18, 773–781

[2] Mangold S., et al. (2013) Journal of Physics: Conference Series **430**, 012130