

## X-ray microspectroscopic investigations of Ni(II) uptake by argillaceous rocks of the Boda Claystone Formation in Hungary

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One of the main aspects for evaluating the safety case of a potential radioactive waste repository in a deep geological formation is to understand and quantify the geochemical and physical processes that influence the mobility of the radionuclides in the geochemical environment imposed by the host rock. This information is needed to make reliable predictions of the long-term retardation behaviour of radionuclides. The present study focuses on the interaction of a key radionuclide with the Boda Claystone Formation (BCF) of the planned high level radioactive waste repository in Hungary. BCF is rich in illite and hematite. The aim is to identify the mineral phases responsible for the uptake of Ni by BCF, and to investigate the uptake mechanisms of radionuclides on clays and other minerals present in the host rock.

Small pieces of selected BCF core hole samples from a depth of 540 m were prepared as thin sections and equilibrated with NiCl<sub>2</sub> solutions at pH = 7.05 in a 0.1 M NaCl background electrolyte. Combined  $\mu$ -XRF/XAS/XRD measurements were performed at HASYLAB Beamline L (Hamburg, Germany) and  $\mu$ -XRF/XRD at the ANKA FLUO Beamline (Karlsruhe, Germany).  $\mu$ -XRF maps were recorded from pre-selected areas of the samples, using a step size comparable to the beam size (20  $\mu$ m at HASYLAB and 5  $\mu$ m at ANKA) and 1 s counting time per pixel. The elemental maps served as a basis for selection of small areas of interest where  $\mu$ -XRD images were collected by a CCD detector. The  $\mu$ -EXAFS measurements were measured in fluorescence mode at HASYLAB Beamline L, at 20  $\mu$ m lateral resolution for certain points of interest.

The distribution maps indicate that Ni is mainly associated to K- and Fe-rich phases.  $\mu$ -XRD analyses with a 5  $\mu$ m beam diameter indicate that the composition of the argillaceous rock matrix on the micro-scale agree well with the mineral composition of the clay rich areas obtained by bulk-XRD measurements. The good correlation of Fe with K is mainly caused by the high K content in illite (a K-rich 2:1 clay mineral). Micro-EXAFS investigations demonstrated that inner-sphere complexation of Ni occurred to clay minerals. At higher Ni concentrations (10<sup>-3</sup> M Ni) surface precipitation processes prevailed. The formation of Ni precipitated phases such as Ni-phylosilicates has important geochemical implications because layered silicates are stable minerals in mildly acidic to basic pH conditions and can irreversibly bind metals in waste and soil matrices. The uptake of contaminants on mineral surfaces forming inner-sphere complexes strongly reduces the mobility of metals in the geosphere. The results of the analyses demonstrated that for Ni(II) the clay mineral illite is an effective sink in the BCF sample.

## Tracing Euxinia in Ancient Oceans with molybdenum

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Elevated molybdenum (Mo) concentrations in organic-rich sediments are a characteristic feature of deposition in sulfidic waters. A comparative study of modern sediment cores from more than 200 marine sites worldwide show that all euxinic basins display >25 ppm Mo [1]. Conversely, all organic-rich sediments with >25 ppm Mo are deposited from a permanently or intermittently sulfidic water column. We show that this last observation can now be determined in <30 seconds using handheld X-Ray absorption Fluorescence spectroscopy (HH-XRF). The new tool enables euxinic classification in the field.

The Mo enrichment process in euxinic settings is expected based on the critical role that aqueous H<sub>2</sub>S plays in breaking Mo=O double bonds when soluble MoO<sub>4</sub><sup>2-</sup> forms reactive Mo sulfides [2]. However, we have identified Neoproterozoic euxinic settings based on Fe-speciation indicators [3] with only small sedimentary Mo enrichments [4]. The Fe speciation technique is unlikely to give false-positive identifications of euxinia, and the question remains what controlling factors could have obstructed the Mo enrichment process at that time.

First, we speculate that the Mo supply to the basins was particularly slow. However, the Mo enrichment process takes place today even in settings with low Mo supply, whether limited by basinal restriction and a slow deepwater renewal rate (e.g. Black Sea) or low Mo load in the source waters of only (e.g. 10 nM in Lake Cadagno).

We have established a one-box model for the oceanic Mo cycle, where Mo burial rates are linked 1st order with respect to ambient Mo reservoir. It shows that seawater Mo concentrations, today 105 nM, never decreased below modern riverine values (~6 nM). Hence, a low seawater inventory is insufficient to obstruct the Mo enrichment process in settings with supply comparable to Lake Cadagno, but a combination of both widespread euxinia (lowering seawater Mo inventory) and basinal restriction (lowering basinal Mo relative to open ocean) could potentially compromise Mo enrichment in the Neoproterozoic sediments.

This illustrates how expansion of oceanic euxinia derived from our models rests on a rigorous understanding of the key factors involved in the removal pathway of Mo from oxic surface waters to euxinic sediments. We discuss how laboratory and field-based studies elucidate which factors, other than H<sub>2</sub>S, could influence the Mo burial pathway in the past. Overall, we illustrate the linkage between studies of modern euxinic systems and reconstructions of global-scale ocean conditions of the past.

[1] Lyons et al. (2009) *Annu. Rev. Earth Planet Sci.* **37** 507-534 [2] Erickson and Helz (2000) *GCA*, **64** 1149-1158; Dahl et al. (2012) *in prep.* [3] Canfield et al. (2008) *Science*, **321** (5891) 949-952. [4] Dahl et al. (2011) *EPSL*, **311** (3-4), 264-274