

Behaviour of Zr/Hf and Y/Ho ratios during transition between seawater column and deep-sea brines

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During the oceanic cruise Mamba 2011 in the Eastern Mediterranean Sea seawater, biogeochemistry of the oxic layers and of the underlying anoxic deep-sea brines was studied. In order to extend the knowledge of processes occurring at oxic-anoxic interface in seawater, Zr/Hf ratio, coupled for the first time with Y/Ho and lanthanide behaviour, was investigated. Lanthanides and especially Y/Ho ratio are considered powerful probes of geochemical processes and a coherent behaviour with respect to Y/Ho was shown by the Zr/Hf ratio in several geochemical systems [1]. Observed covariance of Zr/Hf ratio with respect to dissolved Mn and Fe in anoxic brine, suggest that Zr was preferentially scavenged on MnO₂ surfaces under oxic conditions and the same process occurred for Hf onto FeOOH. These data confirm the observed behaviour in pore water studies [2] and extend the knowledge of Zr and Hf reactivity also onto Mn-oxides.

Different is the Y/Ho behaviour that correlates with dissolved Fe content, especially in brine from Tyro basin but not with Mn content, neither in brines, nor in oxic seawater. The observed lack of correlation observed among Y/Ho and Zr/Hf with respect Fe and Mn contents in seawater is probably due to the delivery of detrital materials in shallowest water layers.

[1] Bau (1996) *Contrib. Miner. Petrol* **123**, 323–333.

[2] McKelvey (1994) *PhD Thesis*, Univ. British Columbia.

The role of multicomponent diffusion and electromigration for reactive transport in porous media

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Aqueous diffusion is the dominant mass transport process in low permeability formations or in the absence of significant advection. There are systems in which electrostatic interactions between diffusing molecules strongly affect the apparent diffusion coefficients. Neglecting electromigration may lead to the inability of reactive transport models to adequately simulate diffusion dominated transport and to properly reproduce key phenomena such as mineral dissolution and precipitation [1]. An application for which electrochemical migration plays a significant role is the electrokinetic remediation of contaminated groundwater. Electrokinetic remediation is based on controlled application of low intensity direct current through the soil between electrodes. The change of redox condition induced near the electrodes shifts the thermodynamic conditions and ionic mobility with the goal to decontaminate the soil.

The formulation for numerical modeling of reactive transport including multicomponent diffusion and electromigration will be presented and preliminary results from simulations of electrokinetic remediation of metal contaminated soils will be discussed.

This modelling effort evaluates the importance of feedback mechanisms between electromigration, applied electric current, and homogenous and heterogeneous reactions in the aqueous phase and attempts to integrate the simulated response with observed geochemical data.

[1] Galíndez, J. M. & Molinero, J. (2010) On the relevance of electrochemical diffusion for the modeling of degradation of cementitious materials. *Cement & Concrete Composites* **32**, 351–359.