Evaluation of surface complexation parameters for Eu^{3+} on muscovite and orthoclase

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Sorption on mineral surfaces of sediments is an important retardation process for radionuclides to be considered in safety assessments for radioactive waste repositories.

This study deals with sediments of the overburden at Gorleben site that are mainly composed of tertiary and quaternary sands and clays [1]. A bottom-up approach is chosen to describe the sorption of Eu^{3+} (as homologue for trivalent actinides) on each single mineral phase of a representative sediment. Orthoclase and muscovite are important constituents of the sediment significantly contributing to the overall distribution coefficient.

The scope of the study is the assessment of surface complexation parameters by applying the geochemical speciation model PhreeqC, Version 2.17 which is coupled with the parameter-estimation code UCODE_2005. Since relevant data were missing for the sediment constituents orthoclase and muscovite batch experiments are performed for the parameter estimation. Establishing solid/liquid ratios of 1/20 and 1/80 the minerals are suspended in 0.01 M $NaClO_4$. Subsequently pH values ranging between 6 and 9 are employed in the suspensions over a period of several weeks. Eu^{3+} concentrations of 10^{-5} M, 10^{-6} M, 10^{-7} M, and 10^{-8} M are applied, whereat a chemical equilibrium between Eu^{3+} and the mineral is reached within 24 h.

PhreeqC and UCODE are used to acquire protolysis constants via a diffuse double layer model from measured titration curves. In the second step the basic required parameters, i.e. logK-values for selected surface reactions, the surface site density, and the specific surface area are iteratively determined by fitting the experimental data.

To simulate Eu-sorption on a representative sediment (10% muscovite, 10% orthoclase, 80% quartz) the derived surface complexation model is applied to a corresponding experimental data-set. Results show good reproduction of the data, hence, backing up a robust parameter set.

[1] Klinge *et al*. (2002) *Geologie und Hydrogeologie des Deckgebirges über dem Salzstock Gorleben*, Z. angew. Geol. **2**, 7-15.

Molecular fossils and the late rise of eukaryotes and oxygenic photosynthesis

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Hydrocarbon biomarkers are the molecular fossils of natural products such as lipids and pigments. They can yield a wealth of information about early microbial ecosystems and are particularly valuable when preserved in > 1 billion-year-old (Ga) sedimentary rocks where conventional fossils are often lacking. Therefore, in 1999, the detection of traces of biomarkers in 2.5 to 2.7 Ga shales from Western Australia [1, 2] was celebrated as a breakthrough. The discovery, which was later confirmed by several independent studies, led to far-reaching conclusions about the early evolution of oxygenic photosynthesis [2] and ancestral eukaryotes [1]. However, here we present new data based on the carbon isotopic composition of solidified hydrocarbons [3] and the spatial distribution of liquid hydrocarbons within the original 2.5 and 2.7 Ga shales [4] that demonstrate that the molecules must have entered the rocks much later in Earth's history and therefore provide no information about the Archean (>2.5 Ga) biosphere or environment.

The elimination of the Archean biomarker data has immense implications for our understanding of Earth's early biosphere. 2α-methylhopanes have been interpreted as evidence for the existence of cyanobacteria at 2.7 Ga, about ~300 million years before the atmosphere became mildly oxygenated in the Great Oxidation Event (GOE; between 2.45 and 2.32 Ga). Now, the oldest direct fossil evidence for cyanobacteria reverts back to 2.15 Ga, and the most ancient robust sign for oxygenic photosynthesis becomes the GOE itself. Moreover, the presence of steranes has been interpreted as evidence for the existence of ancestral eukaryotes at 2.7 Ga. However, without the steranes, the oldest fossil evidence for the domain falls into the range ~1.78-1.68 Ga. Recognition that the biomarkers from Archean rocks are not of Archean age renders permissive hypotheses about a late evolution of oxygenic photosynthesis, and an anoxygenic phototrophic origin of the vast deposits of Archean banded iron formation.

[1] Brocks *et al*. (1999) *Science* **285**, 1033-1036. [2] Summons *et al*. (1999) *Nature* **400**, 554-557. [3] Rasmussen *et al*. (2008) *Nature* **455**, 1101 - 1104. [4] Brocks (2011) *Geochim. Cosmochim. Acta, in press*.