

## **Impact of carbonate on the sorption of Eu(III) and Cm(III) on clay minerals: A combined experimental and theoretical study**

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Compacted argillaceous rock formations are discussed in different countries as potential host rocks for deep geological repositories for nuclear waste. Trivalent actinides show a strong retention by clay minerals in dilute as well as in high ionic strength solutions. The presence of competitive ligands however may lead to a significant sorption reduction [1]. Thus, a detailed study of the impact of strong complexing anionic ligands, such as carbonate, on the sorption processes is required for a comprehensive assessment of the retention capabilities of clay rocks for trivalent radionuclides.

The present work is a multi-method study on the sorption of Eu(III) and Cm(III) on montmorillonite and illite at different ionic strengths (0.1, 1.0, 3.0 M, NaCl) and two CO<sub>2</sub> partial pressures (pCO<sub>2</sub>=10<sup>-3.3</sup>, 10<sup>-2</sup> bar). The work includes batch experiments, time resolved laser fluorescence-, vibrational side-band- and surface-sensitive vibrational spectroscopy, as well as model calculations (2SPNE/CE) and quantum-chemical calculations (DFT, MD simulation).

The results show, that the presence of carbonate leads to a distinct decrease of the log  $K_d$  values in the alkaline pH range, which has been observed already earlier [1]. However, a slightly increased sorption of Eu(III) is found at mildly acidic pH. The origin of this effect is determined as the formation of the two ternary  $M(\text{CO}_3)_n^{3-2n}$  (M = Eu(III), Cm(III); n = 1,2) carbonate species at the clay mineral edges. Hereby, the first CO<sub>3</sub><sup>2-</sup> ligand coordinates to both the mineral surface and the sorbed metal ion simultaneously, acting as an additional stabilizing anchor. Using the two determined surface species, the surface complexation was modelled with a parameterized 2SPNE/CE surface complexation model to describe experimental sorption data.

[1] Marques et al. Radiochim. Acta (2008), 96, 691-698

*Acknowledgement: This work was partly funded by the collaborative German BMWi funded GRAZ project.*