

Sorption of trivalent rare earth elements on calcite

S. PESCHEL^{1*}, M. SCHMIDT¹, S. HOFMANN²,
J. E. STUBBS³ AND P. J. ENG³

¹Institute of Resource Ecology, Helmholtz-Zentrum Dresden-Rossendorf, 01328 Dresden, Germany (*correspondence: s.peschel@hzdr.de)

²Institute of Nuclear Waste Disposal, Karlsruhe Institute of Technology, 76021 Karlsruhe, Germany

³Center of Advanced Radiation Sources, University of Chicago, Chicago, IL 60637, USA

Transuranic elements with their long half-lives and high radiotoxicity are subject of intensive research because of their importance in long term safety assessments of nuclear waste disposal. There, also calcite plays a significant role. It has the potential to adsorb ions at its surface and substitute guest ions into its crystal lattice. Recently Hofmann et al. [1] showed that the sorption of trivalent ions can be affected by the anion of the background electrolyte. Atomic force microscopy and time-resolved laser fluorescence spectroscopy indicated that in presence of NaNO₃ a "gel-like layer" with lower crystallinity but unknown composition forms on the surface of the calcite crystal, in which the Eu(III) is incorporated. Here, the rare earth element Y served as a nonradioactive homologue to trivalent Am and Cm, as its ionic radius and chemical behavior are similar.

We used two X-ray reflectivity techniques, crystal truncation rod (CTR) measurements and resonant anomalous X-ray reflectivity (RAXR). These techniques yield the overall electron density near the interface and the distribution of the resonant element therein. The experiments were run *in situ*, with the mineral surface in contact with a thin solution layer. Freshly cleaved (along the (104) plane) calcite crystals are reacted with 10⁻⁷ M Y(III) over a course of ~ 170 hours. We can detect low quantities of adsorbed Y [$\sim 0.05 \text{ Y}/A_{\text{UC}}$ ($A_{\text{UC}} =$ area of the calcite unit cell $\sim 20.20 \text{ \AA}^2$)] on the calcite surface with an average height of $\sim 3 \text{ \AA}$. Y(III) appears to be present as at least two distinct species. In a second step the sample is flushed with calcite saturated solution containing 10 mM NaNO₃. After approx. 20 min Y is no longer detectable, and consequently must have desorbed from the surface entirely. CTR experiments with different contact times with NaNO₃ show that nitrate quickly affects the water sorption structure on calcite. The formation of the "gel-like layer" (Hofmann et al. [1]) is slower, and its formation can be verified after 14 days of exposure to NaNO₃.

[1] Hofmann et al. (2014), *Geochim. Cosmochim. Acta* **125**, 528-538