

Sorption of Lanthanides and trivalent actinides on montmorillonite in the presence and absence of carbonate

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The fate of released RNs in a deep geological radioactive waste repository is primarily controlled by sorption/desorption processes onto mineral surfaces. Clay minerals are major constituents in both the man-made engineered barriers and in the argillaceous host rock formations currently being considered for a deep high level radioactive waste (HLW) repository in Switzerland. In the near-field of HLW repositories, reducing conditions are expected to prevail and the RNs are present in their lowest oxidation states. Trivalent actinides such as Am(III), Cm(III) and Pu(III) make a significant contribution to the radiotoxicity of HLW. In natural environments, the predominant aqueous phase reactions of lanthanides and trivalent actinides (Ln/An(III)) are hydrolysis and complexation with dissolved inorganic ligands, such as carbonates. Such complexation reactions could potentially decrease the metal ion sorption and thus increase the migration rates of these RNs.

The sorption of Ln/An(III) on montmorillonite in the absence and presence of dissolved carbonate was investigated by a combination of different approaches. Batch sorption experiments, surface complexation modelling, Time-Resolved Laser Fluorescence Spectroscopy (TRLFS) and Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy were applied to investigate the uptake of Ln/An(III) on montmorillonite at low surface loadings ($\leq 3 \text{ mmol}\cdot\text{kg}^{-1}$). The macroscopic sorption experiments showed that the presence of carbonate leads to a pronounced decrease of Ln/An(III) uptake on montmorillonite. Modelling the experimental data with the 2SPNE SC/CE sorption model under the assumption that carbonate complexes do not sorb, clearly under predicted the experimental data, suggesting the formation of ternary Ln/An(III)-carbonate surface complexes. In order to verify this assumption, EXAFS and TRLFS were applied. The differences in the TRLFS spectra obtained for samples in the presence and absence of carbonate *i.e.* red-shift of excitation and emission spectra, as well as the increase of fluorescence lifetimes, unambiguously showed the influence of carbonate, and were fully consistent with the formation of Ln/An(III)(III) surface species involving carbonate complexes. The EXAFS parameters derived by fitting the spectra of the carbonate free sample were consistent with bond lengths from Am-O and Am-Si/Al backscattering pairs, and clearly indicated that An(III) forms inner sphere complexes at the montmorillonite surface. The EXAFS parameters obtained by fitting the spectra of the sample prepared in the presence of carbonate was consistent with the formation of an An(III) complex at the montmorillonite surface with 1 to 2 carbonate groups. The application of EXAFS and TRLFS clearly supported the macroscopic sorption experiments and modeling results and confirmed the formation of ternary Ln/An(III)-CO₃ complexes at the montmorillonite surface.

Comparison of grain size and BET surface area trends in modern glacial and non-glacial fluvial sediments as a proxy for deep-time climate

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Chemical and physical weathering in sediments is highly contingent upon erosion rates and climatic variables (temperature and precipitation). Sediment grain size and surface area also impose critical controls on mineral-water reaction rates, where finer grain sizes are correlated to higher surface areas and thus increased chemical weathering, even in glacial environments [1]. However, sediment surface area is generally not evaluated or reported for natural systems. Here we document grain size and BET surface area trends within the mud fraction ($< 63 \mu\text{m}$) of proximal fluvial sediments in a cold-arid, glacial (Clark Glacier Stream, Wright Valley, Antarctica) and a warm semi-arid, non-glacial (Blue Beaver Creek, Wichita Mountains, Oklahoma) environment. Both systems are of similar basin drainage size (40 km²), relief (360-465 m), and bedrock lithology (granitoid).

In the polar glacial transect, the mud fraction coarsens with distance along transect, with a corresponding decrease in BET surface area, indicating rapid dissolution of fines. In the non-glacial transects, grain size decreases downstream while surface area increases, reflecting precipitation of clay-sized weathering products. Aqueous chemistry of stream water samples collected simultaneously with stream sediments supports the conclusion that silicate dissolution dominates in the glacial environment, whereas incongruent chemical weathering of silicate phases is predominant in the non-glacial environment. The occurrence of opposing trends within climatically distinct settings indicates that the production and fate of fine-grained sediments may be diagnostic of glacial and non-glacial regimes and potentially evident in the rock record. Additionally, systematic quantification of sediment surface areas provides critical constraints on evaluating the effect of chemical weathering on modern and deep-time global carbon cycles.

[1] Anderson (2005) *Geomorphology* **67**, 147-157.