ESRF	**Experiment title:** Determination of Th(IV) uptake mechanisms onto hectorite using polarized EXAFS	**Experiment number**: ME-740
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Report: Aims of the experiment and scientific background

The underlying goal of the experimental efforts at the Laboratory for Waste Management at the Paul Scherrer Institute is to understand the processes controlling the uptake (sorption) and release (desorption) of safety relevant radionuclides in (underground) nuclear waste repositories. The flow of ground water through a repository can potentially result in the release of radionuclides from waste matrices. The released radionuclides can then be transported through engineered barrier systems (cement and clay barriers) and the surrounding geosphere (often clay rich settings) and potentially harm environmental quality. The release of radionuclides can be considerably retarded due to interactions with clay minerals. Thus, a detailed molecular level understanding of sorption mechanisms of radionuclides in clay systems is of fundamental importance for safety assessment for nuclear waste repositories. Smectitic clay minerals are abundant in the environment and major components of sedimentary rock formations considered as waste sites. From a chemical view point, radionuclides and other metal ions can sorb on edge sites and/or interlayer sites of smectites. The planar sites result from isomorphic substitution in the octahedral and tetrahedral sheets, and edge sites are due to broken Al/Mg-OH and Si-OH bonds at the sites of the clay mineral.

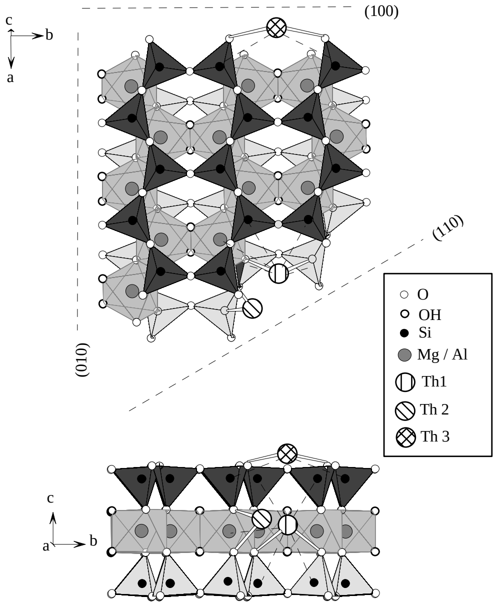

Fig. 1: Three possible Th surface complexes (Th1-Th3) bounded to the montmorillonite surface.

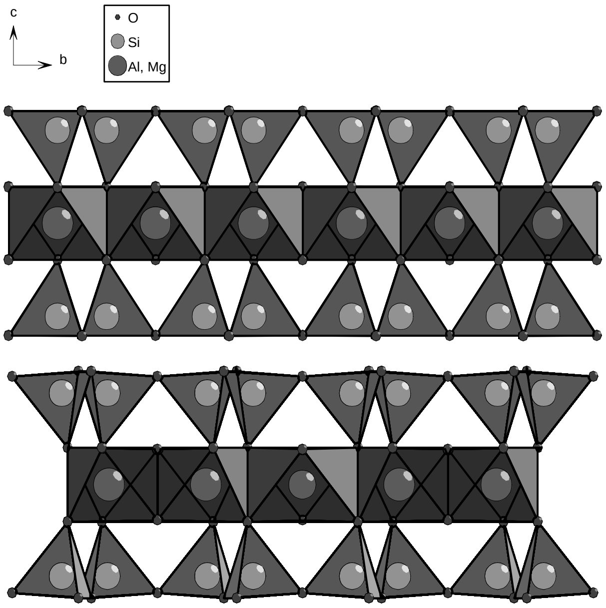

Fig. 2: Representation of the hectorite (top) and montmorillonite (bottom) structure.

Using a combination of powder EXAFS and P-EXAFS we recently investigated the uptake of Ni(II) and Th(IV) onto montmorillonite (1-3). The Ni study showed a strong P-EXAFS dependency and the formation of a Ni-phyllosilicate-like phase at elevated pH and Ni concentrations (1). At near neutral pH and low Ni concentrations the formation of Ni inner-sphere mononuclear surface complexes located at the edges of montmorillonite platelets was observed using P-EXAFS (2). In the Th/montmorillonite system, however, the P-EXAFS dependency was only negligible (3). It was speculated in the Th/montmorillonite study that the absence of a P-EXAFS dependence is caused by the formation of a wide variety of Th surface complexes which are bound to the montmorillonite surface in different configurations and bond angles (e.g. Th1-Th3, Fig. 1). Instead of this hypothesis it could be argued that the absence of a P-EXAFS dependency in the Th/montmorillonite uptake system is caused by the corrugated clay structure of montmorillonite. This corrugated montmorillonite structure is caused by unoccupied octahedral positions (Fig. 2). To investigate whether the corrugated clay structure is responsible for the absence of a P-EXAFS dependence the uptake of Th onto hectorite was examined in this study. Trioctahedral clays like hectorite are lacking vacancies in the octahedral sheets and are consequently highly ordered and uncorrugated clays with a flat basal plane (Fig. 2) (4), and can therefore be considered as “model” clays for uptake experiments.

Experiments + Results

The samples were prepared by adding Th to a montmorillonite suspension (pH 3, 0.3 M $NaClO_4$). After 7 days of reaction time the suspensions were filtrated and highly oriented self supporting clay films were prepared. Th L_{III}-edge fluorescence P-EXAFS spectra were recorded for incident beam angles of α = 10, 35, and 80 degrees (α = the angle between the electric field vector and the plane of the self-supporting film) using a 13-element solid state detector. The k^3-weighted P-EXAFS spectra of Th treated self-supporting clay films for a Th loading of 25 μmol/g and 3 μmol/g are shown in Fig. 3 and 4. The figures illustrate that the P-EXAFS spectra of the clay films have no significant polarization dependence although the self-supporting clay films were well orientated. In P-EXAFS measurements backscattering pairs in the in-plane direction are strongly attenuated when the X-ray polarization vector is parallel to film plane. Therefore, the lack of a P-EXAFS dependency indicates that Th is not sorbed to the hectorite in the continuity of the octahedral sheet in a single surface complex. A mixture of surface complexes which all have bonds to Si that form different angles would severely decrease the P-EXAFS angular dependence. It is therefore possible that there is a series of similar complexes in which Th polyhedra bridge to the hectorite surface in such a manner that the average angle of Th-O and Th-Si pairs with respect to the c* direction (β) is ~54.7°. At this particular β-angle polarized and powder EXAFS spectra are identical and would eliminate any angular dependence in P-EXAFS measurements. We could therefore demonstrate that the uptake of Th onto montmorillonite and hectorite is similar and in particular that the uptake of Th is not affected by the corrugated montmorillonite structure.

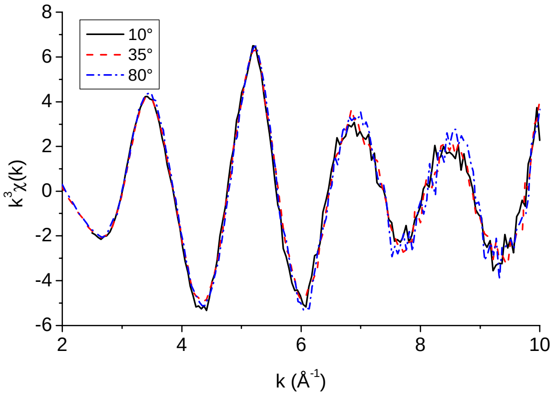

Fig. 3: k^3-weighed Th L_{III}-edge EXAFS spectra at beam angles of 10, 35 and 80 degrees for 25 μmol/g Th sorbed onto hectorite.

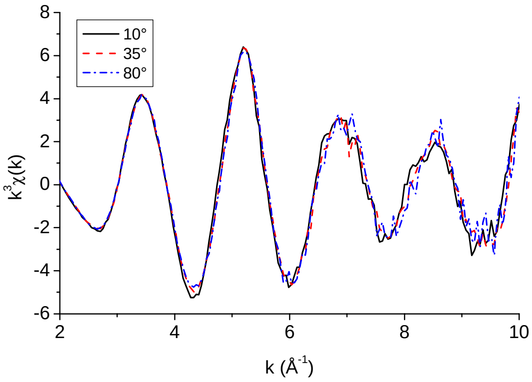

Fig. 4: k^3-weighed Th L_{III}-edge EXAFS spectra at beam angles of 10, 35 and 80 degrees for 3 μmol/g Th sorbed onto hectorite.

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4. Güven, N., "Smectites.", *in* "Hydrous phyllosilicates (exclusive micas)" Vol. 19, 1988.