Effects of the Background Electrolyte on Th(IV) Sorption to Muscovite Mica

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ABSTRACT

The adsorption of tetravalent thorium on the muscovite mica (001) basal plane was studied by X-ray crystal truncation rod (CTR), and resonant anomalous X-ray reflectivity (RAXR) measurements and alpha spectrometry in the presence of perchlorate background electrolytes LiClO₄, NaClO₄, and KClO₄ ([Th(IV)] = 0.1 mM, I = 0.1 M or 0.01 M, pH = 3.3 ± 0.3). RAXR data directly reveal a strong influence of the background electrolyte on the actinide sorption. No significant Th adsorption was observed in 0.1 M NaClO₄, i.e., the Th coverage $\theta(\text{Th})$, the number of Th per unit cell area of the muscovite surface ($A_{\text{UC}} = 46.72 \text{ \AA}^2$), was $\leq 0.01 \text{ Th}/A_{\text{UC}}$, whereas limited uptake ($\theta(\text{Th}) \sim 0.04 \text{ Th}/A_{\text{UC}}$) was detected at a lower ionic strength (I = 0.01 M). These results are in stark contrast to the behavior of Th in 0.1 M NaCl which showed a coverage of 0.4 Th/A_{UC} (Schmidt et al., 2012a). Th uptake was also influenced by the electrolyte cation. Weak adsorption was observed in 0.1M KClO₄ ($\theta(\text{Th}) \sim 0.07 \text{ Th}/A_{\text{UC}}$) similar to the results in NaClO₄ at lower ionic strength. In contrast, strong adsorption was found in 0.1 M LiClO₄, with $\theta(\text{Th}) = 4.9 \text{ Th}/A_{\text{UC}}$, a ~10-fold increase

compared with that previously reported in NaCl. These differences are confirmed independently by *ex situ* alpha spectrometry, which shows no measurable Th coverage in 0.1 M NaClO₄ background in contrast to a large coverage of 1.6 Th/A_{UC} in 0.1 M LiClO₄. The CTR/RAXR analyses of Th-LiClO₄ show the sorption structure consisting of Th species that are broadly distributed, centered at heights of 4.1 Å and 29 Å distance from the interface. Neither the very large distribution height of the second species nor the high coverage can be explained with (hydrated) ionic adsorption, suggesting that the enhanced uptake is presumably due to the formation and sorption of Th nanoparticles.

1 INTRODUCTION

Thorium is a primordial ($t_{1/2}({}^{232}\text{Th}) = 1.4 \times 10^{10}$ y) member of the actinide series that occurs naturally in considerable amounts (11 ppm in the earth's crust). Thorium is the largest, chemically "softest", and least polarizing tetravalent cation, and as such least likely to undergo hydrolysis and subsequent condensation reactions (Baes and Mesmer, 1976; Burgess, 1978). The stable [Rn]⁰ electron configuration of Th(IV) also prevents any redox chemistry, and in aqueous solution only the tetravalent state of thorium is stable (Wickleder et al., 2011). Nevertheless, Th solution chemistry, while simpler than for the other actinides, still requires careful accounting for complexation, hydrolysis, and subsequent oligomerization. These reactions and their thermodynamics have been studied in great detail (Baes et al., 1958; Brown et al., 1983; Ekberg et al., 2000; Felmy et al., 1991; Knope and Soderholm, 2012; Knope et al., 2011; Neck et al., 2002; Rand et al., 2008; Ryan and Rai, 1987; Walther et al., 2008; Wilson et al., 2007), and it has become increasingly clear that condensation reactions can significantly impact Th(IV) solution chemistry, even at relatively low pH and low Th concentration.

There is a wide range of studies aiming to quantify the sorption of Th on various natural and synthetic minerals (Guo et al., 2005; Jakobsson, 1999; Landa et al., 1995; Li and Tao, 2002; Rojo et al., 2009; Sharma et al., 2009; Sharma et al., 2006; Sheng et al., 2008; Talip et al., 2009; Zhang et al., 2006). Several studies have attempted to gain a more mechanistic understanding through the use of advanced spectroscopic techniques (Östhols, 1995; Östhols et al., 1997), or surface complexation modelling (Reiller et al., 2005). However, little attention is usually given to the choice of background

electrolyte. Many studies are performed in NO_3^- media (Guo et al., 2005; Li and Tao, 2002; Reiller et al., 2005; Sharma et al., 2009; Sharma et al., 2006; Sheng et al., 2008; Talip et al., 2009; Zhang et al., 2006), presumably due to its relevance in chemical-separations processes and its ubiquitous presence in groundwater. Studies in ClO_4^- media are also commonly found (Jakobsson, 1999; Östhols, 1995; Östhols et al., 1997; Reiller et al., 2005; Rojo et al., 2009). Only one study (Jakobsson, 1999) investigated sorption reactions for multiple background electrolytes, namely NaCl and NaClO_4 (in this case on TiO_2 substrates). The reaction is found to be independent of ionic strength and an effect of the change of media was not discussed.

The adsorption behavior of tetravalent Th on muscovite mica has been observed from NaCl media using alpha spectrometry and resonant anomalous X-ray reflectivity (RAXR) (Schmidt et al., 2012a). The study finds that sorption occurs in two distinct regimes. At low concentrations ($[\text{Th}] = 1 \times 10^{-6} - 1 \times 10^{-3}$ mol/L, pH = 3.2) sorption can be described by a Langmuir-type sorption isotherm that yields a sorption constant of $\log K_0 = 6.6 \pm 0.2$ and a maximum coverage of $\theta_\alpha = 0.21$ Th/ A_{UC} (number of Th atoms per area of the unit cell). At higher concentrations ($[\text{Th}] \geq 2 \times 10^{-3}$ mol/L) a steep increase in surface coverage is observed (i.e. $\theta_\alpha > 2$ Th/ A_{UC}), well beyond the amount of Th required for surface charge compensation ($\theta = 0.25$ Th/ A_{UC}). These results were speculated to be due to an oligomerization reaction of Th(IV) at the mineral-solvent interface. A similar, though more pronounced reaction has been observed for plutonium at the same interface (Schmidt et al., 2013). Specular X-ray reflectivity and RAXR at the muscovite (001) – 1×10^{-4} mol/L Th(IV) solution (i.e., within the “Langmuir regime”) interface revealed that Th(IV) adsorbs dominantly as a hydrated extended outer sphere complex (Lee et al., 2010; Schmidt et al., 2012a). This Th species is distributed broadly with an average height ~ 10 Å, too large to be either an inner or outer sphere sorption complexes, which would be expected at ~ 2 Å and ~ 4 Å, respectively. (Lee et al., 2010) The coverage found in the *in situ* RAXR experiments ($\theta_{\text{RAXR}} = 0.4$ Th/ A_{UC}) was slightly larger than what was found in the *ex situ* alpha spectrometry quantification. This difference may result from the washing step, applied prior to *ex situ* alpha spectrometry, which can remove some weakly-bound Th from the surface. The θ_{RAXR} value is larger than the amounts needed for the compensation of the muscovite

78 surface charge (i.e., 0.25 or 0.33 Th/A_{UC} for Th⁴⁺ or trivalent Th species, respectively, the two major
79 Th species in the bulk solution), indicating that adsorbed Th overcompensates the mineral's surface
80 charge.

81 Here, we demonstrate that Th sorption at the muscovite–water interface is strongly influenced by
82 the choice of background electrolyte (NaCl, LiClO₄, KClO₄, and NaClO₄). Sorption was studied at the
83 molecular level by surface X-ray reflectivity and was independently quantified by alpha spectrometry.
84 For geochemical studies the use of a background electrolyte is intended to provide a constant ionic
85 strength for the studied reaction and ideally should not interfere with the reaction in any other way.
86 For this reason perchlorate salts, particularly sodium perchlorate NaClO₄, are frequently chosen, due
87 to the perchlorate ion's very weak coordination strength with nearly all cations. However, recent
88 results highlight that even minor changes in the background electrolyte composition can drastically
89 alter the reactivity of a mineral surface (Hofmann et al., 2014). In this study, trace concentrations of
90 NO₃⁻ in a predominantly ClO₄⁻ background electrolyte significantly changed the surface morphology
91 of calcite, which in turn affected the uptake of Eu(III) at the interface. These effects were observed
92 even at very low nitrate concentrations (as low as 10⁻⁶ mol/L). The adsorption of Th to the muscovite
93 basal plane from a NaCl solution was recently shown to be relatively simple, with a single extended
94 outer sphere sorption complex dominating the adsorbed speciation of Th (Schmidt et al., 2012a), thus
95 providing an ideal case for testing the influence of the background electrolyte on sorption reactions of
96 strongly hydrated ions in the limit where only adsorption can occur without any morphological
97 changes to the surface.

98 Moreover, a recent study found a potential mechanism for the surface-mediated formation of
99 Pu(IV)-oxo-nanoparticles from an ostensibly Pu(III) solution (Schmidt et al., 2013). In this work the
100 formation of the polymers is attributed to the presence of low concentrations of Pu(IV) in equilibrium
101 with Pu(III). The considerably increased Pu concentration at the interface, it is speculated, then leads
102 to the polymerization of those relatively minor quantities of Pu(IV). Even though the analogy of Th
103 and Pu is known to be limited (Wilson, 2011), the absence of redox chemistry for Th allows to

determine whether the polymerization reaction observed for Pu(III) is associated to Pu redox reactions, or specific to tetravalent actinides.

2 EXPERIMENTAL DETAILS

2.1 Sorption experiments and uptake quantification

Summarized in Table 1 are details of the aqueous Th speciation in both 0.1 M NaCl (Schmidt et al., 2012a) and 0.1 M NaClO₄ background electrolyte solutions, modeled using data from the OECD-NEA (Rand et al., 2008) and NAGRA/PSI thermodynamic databases (Hummel et al., 2002) with additions from other experimental data (Choppin and Jensen, 2011; Neck and Kim, 2001; Walther et al., 2008). The Calculations were performed using the PHREEQC solution modeling suite (version 2.17, (Parkhurst and Appelo, 1999)) and are representative of the speciation of Th in the bulk solution.

The calculated Th speciation is similar in both solutions. The most apparent difference is the lack of Th-ClO₄⁻ complexes in NaClO₄ compared to a significant fraction of mono-chloro-complex (30.7%) in NaCl. To our knowledge, no complexation has been reported between Th and ClO₄⁻. The absence of Th-ClO₄⁻ complex data leads to an increase of the concentrations of not only the Th aquo ion (14% → 22%) but also the hydrolyzed species ThOH³⁺ (44% → 63%) and Th(OH)₂²⁺ (3.5% → 6.8%). A parallel increase in the formation of the dimer complex, Th₂(OH)₅³⁺, is observed (0.19% → 0.34%). It remains a minor species in the system, and all other oligomers contribute even less to the speciation under the condition. Note, that the existence of a ThCl³⁺ complex is suggested based on thermodynamic calculations (Schmidt et al., 2012a) using the most recent update of the NEA thermodynamic database (Rand et al., 2008) but its existence in solution could not be verified spectroscopically (Rothe et al., 2002). If no chloro-complexation occurs in the NaCl system, a Th speciation identical to the speciation described for NaClO₄ in Table 1 would be expected. No change in speciation is expected with the different cations (Li⁺, Na⁺, K⁺) based on thermodynamic data, and calculations for all perchlorate media yield identical results. For both NaCl and NaClO₄ systems, the average charge of all Th species in the bulk solution (+2.70 and +2.75, respectively) is lower than the nominal +4 charge.

Table 1. Calculated solution speciations. $[\text{Th}]_{\text{tot}} = 1.0 \times 10^{-4}$ mol/L, pH = 3.2, 1×10^{-1} mol/L NaCl (left) and 1×10^{-1} mol/L NaClO₄ (right).

Species (0.1 M NaCl)	Conc. [mol/L]	%	Species (0.1 M NaClO ₄)	Conc. [mol/L]	%
ThOH ³⁺	4.4×10^{-5}	43.6	ThOH ³⁺	6.3×10^{-5}	62.8
ThCl ³⁺	3.1×10^{-5}	30.7	Th ⁴⁺	2.2×10^{-5}	21.7
Th ⁴⁺	1.4×10^{-5}	13.9	$[\text{Th}(\text{CO}_3)_2(\text{OH})_2]^{2-}$	8.0×10^{-6}	8.0
$[\text{Th}(\text{CO}_3)_2(\text{OH})_2]^{2-}$	8.0×10^{-6}	8.0	Th(OH) ₂ ²⁺	6.8×10^{-6}	6.8
Th(OH) ₂ ²⁺	3.5×10^{-6}	3.5	Th ₂ (OH) ₃ ⁵⁺	3.4×10^{-7}	0.3

The coverages of ²³²Th sorbed on the muscovite (001) basal plane from NaClO₄ and LiClO₄ media were measured using alpha spectrometry (Schmidt et al., 2012a; Wilson et al., 2010). Samples were reacted with the Th solution overnight, quickly rinsed, first with a solution of the background electrolyte (to remove excess, non-sorbed Th), and subsequently with deionized water (DIW) (to remove excess background electrolyte, which would precipitate upon drying), and left to dry in air. This washing procedure can remove weakly-adsorbed species (Lee et al., 2013a; Lee et al., 2013b), and therefore the adsorbed cation coverage measured by this *ex situ* alpha spectrometry can be smaller than that measured by *in situ* RAXR (see 2.5).

Signals were collected from an area of 79 mm² defined by the aperture ($\emptyset = 10$ mm) in the stainless steel mask with 31.2 % of the instrumental efficiency. All experiments were performed using ²³²Th. Due to its relatively low activity (i.e., with a half-life of 1.41×10^{10} y), data were measured typically at very low count rate compared to those measured using more highly-active isotopes. For example, a surface coverage of 10^{-10} mol/cm² ²³²Th, or 0.36 Th/A_{UC}, results in a signal of $\sim 11.4 \pm 3.4$ counts with a counting time of 108 h (388,800 s). Therefore, the ²³²Th coverage measured by alpha spectrometry serves mainly as a qualitative indicator of whether Th sorption occurs.

2.2 Muscovite substrates

Muscovite $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH},\text{F})_2$ is a phyllosilicate with a tetrahedral-octahedral-tetrahedral (TOT) layer structure, which is also a common building block of many clay minerals. Each TOT layer in muscovite has a structural negative charge of $1e^-$ per area of the unit cell, $A_{\text{UC}} = 46.72 \text{ \AA}^2$, corresponding to $0.021 e^-/\text{\AA}^2$. The K^+ ions, which are located between the TOT layers and compensate the layer charge in the bulk crystal, are exposed upon cleavage of the muscovite lattice and removed when the cleaved surface is immersed in water (Israelachvili and Wennerstrom, 1996; Pashley, 1981, 1982).

V1 quality muscovite crystals (clear, hard, of uniform color, nearly flat, free of all stains, foreign inclusion, cracks, and other similar defects, $12.7 \times 12.7 \times 0.2 \text{ mm}^3$) from the Asheville-Schoonmaker Mica Company were used for all but one experiment. For the Th-ClClO_4 experiment (see below) thicker crystals had to be used for practical considerations. For this purpose round V1-quality mica crystals ($\varnothing = 10 \text{ mm}$) with a thickness of 2mm were obtained from Electron Microscopy Sciences. In all cases, the (001) basal plane is nearly atomically flat and the geometrical crystal surface can be considered identical to the reactive surface, i.e. 161 mm^2 , or 79 mm^2 , respectively. The lattice spacing perpendicular to the (001) plane was found to be within the range of $19.97 \pm 0.02 \text{ \AA}$ for the samples similar to the value from the literature ($19.956 \pm 0.003 \text{ \AA}$) (Schlegel et al., 2006). Errors for the lattice parameters of individual samples are significantly smaller.

No significant interfacial roughness was observed by X-ray reflectivity, which is typical for muscovite in aqueous conditions (Cheng et al., 2001; Fenter et al., 2010; Lee et al., 2007; Schlegel et al., 2006). Dissolution of the muscovite substrate is expected to be negligible for the experiments (Lee et al., 2010; Lee et al., 2009). Based on the dissolution rates published by Oelkers and coworkers (Oelkers et al., 2008) the expected release of Al^{3+} from a $12.7 \times 12.7 \text{ mm}^2$ sample at $\text{pH} = 3.2$ over 2h will be below 10^{-11} moles. According to these calculations less than 0.001 monolayers of the substrate will dissolve within the duration of the experiment, in good agreement with the lack of observable interfacial roughness.

2.3 X-Ray reflectivity experiments

To probe the influence of both anions and cations on the sorption behavior of the non-redox-active actinide, and to isolate trends in the observed effects, four background electrolyte media were tested: NaClO₄ at two different concentrations, LiClO₄, and KClO₄. In addition, an experiment was conducted in which a NaCl solution was replaced by NaClO₄ after sorption had occurred. The samples and their respective solution conditions are listed in

Table 2.

Table 2. Details for the experimental solution conditions for all samples discussed in this work

Designation	Electrolyte	I	pH	c(Th(IV))
Th-NaCl ^a	NaCl	0.1M	3.2	0.1mM
Th-hiNaClO ₄	NaClO ₄	0.1M	3.2	0.1mM
Th-loNaClO ₄	NaClO ₄	0.01M	3.2	0.1mM
Th-ClClO ₄	NaCl/ NaClO ₄	0.1M	3.2	0.1mM
Th-LiClO ₄	LiClO ₄	0.1M	3.5	0.1mM
Th-KClO ₄	KClO ₄	0.1M	3.5	0.1mM

^a From (Schmidt et al., 2012a)

The sample preparation procedure was identical for all samples except the exchange experiment Th-ClClO₄. Solutions were prepared from ²³²Th stock solutions (in HNO₃) by appropriate dilution with the respective background electrolyte. No pH adjustments were performed to avoid inducing local changes in Th chemistry, e.g. leading to oligomerization or precipitation. Consequently, pH values vary slightly throughout the series.

Freshly cleaved mica crystals were suspended in the Th solution overnight for the sorption reactions. Afterwards the crystals were removed from the solution, quickly mounted in a thin-film cell for X-ray reflectivity measurements, and covered with 20 µl of the reaction solution. The liquid film was then enclosed with a 7.5 µm-thick Kapton® film and the cell was closed with two additional Kapton® domes for containment. This setup has been described in more detail previously (Schmidt et al., 2012b). For the exchange experiment with sample ThClClO₄ the sorption reaction was performed in NaCl background media under the same conditions as described above. We use a second, previously described cell for X-ray scattering experiments with radioactive samples (Schmidt et al.,

2011) to change the background electrolyte *online*. The sample was mounted in the cell's sample compartment, and covered with the NaCl reaction solution. As in the other cell, the solution was enclosed using a thin Kapton® film, and radioactive containment was achieved using two domed layers of Kapton®. The liquid container of the cell was filled with a solution of equivalent pH and ionic strength in NaClO₄, without added Th(IV), to allow the exchange of solutions during the experiment.

2.4 X-ray reflectivity measurements

The combination of crystal truncation rod (CTR) measurements and resonant anomalous X-ray reflectivity was applied to probe elemental distributions in the near-surface regime *in situ*, ranging in height from sub-monolayer adsorption structures to extended (few nm wide) distributions, with a high spatial resolution (i.e., <1 Å). In particular, the RAXR technique has element specificity with reasonably good detection limit in estimating the atomic coverage at an interface (Lee et al., 2013c; Schmidt et al., 2012a). For example, ion coverages as low as ~0.03 atoms/A_{UC} have been measured on muscovite with an area of the unit cell of 46.72 Å² (Lee et al., 2010). These characteristics make surface X-ray diffraction a powerful and versatile tool for geochemical systems (Fenter, 2002; Park et al., 2006), in particular when studying complex multi-species systems (Catalano et al., 2008; Lee et al., 2010; Lee et al., 2013c; Schmidt et al., 2013). Detailed reviews on the methods can be found in the literature (Feidenhans'l, 1989; Fenter et al., 2007; Park and Fenter, 2007; Robinson and Tweet, 1992).

All X-ray reflectivity (XR) measurements were performed at the GeoSoilEnviroCARS undulator beamline 13-ID-C at the Advanced Photon Source (APS), with a beam size of 0.05 – 0.25 mm horizontally and 0.5 – 1.0 mm vertically with a typical flux of ~10¹² photons/s. For some experiments the beam was partly defocused and collimated by slits in order to prevent chemical changes induced by the X-ray beam. No beam induced effects were observed. Specular reflectivity data were collected by reflecting the incident beam from the sample surface and detecting the reflected beam using a Dectris PILATUS 100K 2D pixel array detector (Eikenberry et al., 2003). For CTR measurements (i.e., non-resonant XR) the incident photon energy E (typically 18 keV) was fixed at a value well away from the Th L_{III} absorption edge (16.3 keV). The reflected intensity was recorded as a function of the momentum transfer q oriented along the surface normal direction (i.e., specular reflection condition).

RAXR data were collected by scanning the energy through a 600 eV range centered on the Th L_{III} edge at selected values of q . System stability was verified by periodically returning to designated conditions and checking reproducibility. Two datasets (Th-hiNaClO₄ and Th-NaCl) were also reproduced using different crystals and at a different beamline (6-ID-B at the Advanced Photon Source).

The anomalous dispersion terms required for analyzing the RAXR data, as well as determining the exact absorption edge position of the studied Th sample under the given conditions were derived from fluorescence X-ray absorption near-edge structure (XANES) measurements collected on the same samples in grazing-incidence mode using an SII Vortex ME4 X-ray fluorescence detector and applying a difference Kramers-Kronig transform (Cross et al., 1998; Fenter et al., 2010).

2.5 X-Ray reflectivity data analysis

The CTR measurement defines the total interfacial electron density, including that from water and adsorbed ions. CTR data were fit by applying a parameterized structural model consisting of the ideal muscovite substrate lattice, the interfacial region, and bulk water. The interfacial region includes the structural relaxation of atoms in the two top unit-cell layers of the muscovite surface and the presence of near-surface species such as adsorbed species and water. The distribution of each adsorbed species is described as a Gaussian peak, whose structure factor is expressed as:

$$F = \sum_j c_j f_j(q) \exp(iqz_j) \exp\left[-\frac{q^2 u_j^2}{2}\right] \quad (1)$$

where $f_j(q)$ is the atomic scattering factor and c_j , z_j , and u_j are the occupancy, height from the surface, and rms width of the j^{th} atom, respectively. Bulk water was expressed by a layered water-model (Cheng et al., 2001; Schlegel et al., 2006). The quality-of-fit of each model was characterized by a scaled χ^2 and an R-factor (see Electronic Annex (EA) for details).

The Th contribution to the electron density profile was determined by resonant anomalous X-ray reflectivity. Procedures for RAXR data fitting are described in detail in the literature (Fenter et al., 2007; Park and Fenter, 2007). For several samples (see below) we were limited to qualitative comparison of results, using our previous study of Th sorption on muscovite (Schmidt et al., 2012a) as

a reference, due to the very low population of Th at the interface. Data processing of the RAXR spectra followed the procedures described earlier.

In a first step, semi-quantitative constraints on the elemental distribution were established (Fenter et al., 2007; Park and Fenter, 2007). The systematic variations in the resonant modulations' amplitude $A_R(q)$ and phase $\Phi_R(q)$ are obtained from a model-independent analysis of the RAXR spectra. The relationship between the amplitude and phase and the partial structure factor of resonant atom at the interface can be written as:

$$A_R(q) \exp[i\Phi_R(q)] = \sum_j c_j \exp\left(-\frac{q^2 u_j^2}{2}\right) \exp(iqz_j) \quad (2)$$

where c_j , u_j , and z_j are the occupancy, rms width and average height of Th species j , respectively. The surface loading is estimated as $\sum_j(c_j) = \theta$ using the amplitude in the limit of $q \rightarrow 0$, while the $q \rightarrow 0$ limit for $\Phi_R(q)/q$ corresponds to the average height of the elemental distribution (Park and Fenter, 2007). Additional information can be obtained from inspection of the q -dependence of the resonant amplitude and phase, such as the vertical width of the distribution and the relative heights of multiple distinct adsorption species, if any (Park and Fenter, 2007). This model-independent approach is partially limited in its accuracy by the absence of data near $q = 0$, yet it is helpful in that it provides an unbiased initial constraint that can be used to build a model for the model-dependent RAXR analysis.

The structural model for the Th distribution will be based on least-squares fitting of the RAXR data with a model composed of individual Gaussian peaks (Fenter et al., 2007). The resonant structure factor is expressed as

$$F_R(q) = (f'(E) + if''(E)) \sum_j c_j \exp(iqz_j) \exp\left[-\frac{q^2 u_j^2}{2}\right] \quad (3)$$

where $f'(E)$ and $f''(E)$ are the anomalous dispersion terms of the resonant element, in this case Th.

3 RESULTS

3.1 Uptake measurements

As a first step, uptake of Th from 0.1 M LiClO₄ and NaClO₄ solution was quantified by alpha spectrometry. In the Th-LiClO₄ system ([Th] = 1.0×10^{-4} mol/L, pH = 3.3 ± 0.3 , 0.1 M LiClO₄) ²³²Th coverage was 1.6 ± 0.3 Th/A_{UC} (= 0.14 µg/cm²). This coverage is significantly larger than seen in 0.1 M NaCl media, 0.15 Th/A_{UC}, using the same technique (Schmidt et al., 2012a).

Alpha spectrometry was not able to detect a ²³²Th coverage above background (detection limit approx. 0.1 Th/A_{UC}) from the 0.1 M NaClO₄ background electrolyte solution (Th-hiNaClO₄), in contrast to the previous results obtained from a NaCl solution (0.15 ± 0.02 Th/A_{UC}) (Schmidt et al., 2012a). These measurements are constrained by the low specific activity of ²³²Th, as described in 2.1. A better understanding of the Th sorption at the muscovite basal plane in this system can be obtained from RAXR measurements, which are not only capable of detecting lower Th concentrations at the interface, but also provide insight into its vertical distribution (i.e. its speciation) at the interface. Yet, the absence of detectable signal is in agreement with the RAXR findings (see the next section). Nevertheless, these results demonstrate the surprising sensitivity of Th uptake at the muscovite surface to the choice of electrolyte and motivated the more extensive measurements described below to understand this observation.

290

291 Figure 1. Selected resonant anomalous X-ray reflectivity data (black circles) measured from the
 292 muscovite (001) surface for the samples in Table 2. Each spectrum represents the variation of the
 293 specular reflectivity measured as a function of photon energy, E , at a different fixed momentum
 294 transfer, q ($\text{\AA}^{-1}$), as indicated. Spectra are normalized to the non-resonant structure factor F_{NR} as
 295 $(|F_{\text{tot}}(q, E)|^2 / |F_{\text{NR}}(q)|^2)$, where F_{tot} and F_{NR} are total and non-resonant structure factors, respectively, and
 296 offset vertically for clarity (offset given in brackets for each spectrum). The blue lines show the
 297 calculated intensities from the best-fit models, where applicable. The green dashed lines are results
 298 from model-independent analysis and may serve as a guide-to-the-eye. Note that the y-axis scale for
 299 Th-LiClO₄ (e) is about twice larger than the others.

300 The RAXR data measured in various electrolyte conditions (Figure 1) are visually different from
 301 one another, indicating that the thorium–muscovite interaction is influenced by the choice of
 302 electrolyte. Small modulations are observed for Th-KClO₄ and Th-IoNaClO₄ whereas no discernible

modulations are observed for Th-hiNaClO₄. In contrast, the RAXR spectra of Th-LiClO₄ show significantly larger modulations than those of the other systems (note the difference in y-axis scale for Th-LiClO₄ from the others in Fig. 1) that are substantially larger than those observed in the Th-NaCl reference system. The data in this reference system were fit with a partially-overlapping two-peak model describing a broadly distributed extended outer sphere sorption species of Th (Schmidt et al., 2012a). Since the fractional modulation observed in the RAXR spectra are proportional to the adsorbed Th coverage, these data immediately indicate that Th adsorption on muscovite is a strong function of the choice of electrolyte, consistent with the alpha spectrometry measurements.

The total coverages of Th at the muscovite–water interface were estimated using the model-independent RAXR analysis (Park and Fenter, 2007). A complete lack of modulations for Th-hiNaClO₄ indicates that there is no significant coverage of the resonant atom registered at the reflecting interface, $\theta(\text{Th-hiNaClO}_4) \cong 0$. At 0.01 M NaClO₄ concentration, small modulations are visible for data at $q = 0.19$ and $0.28 \text{ \AA}^{-1}$. The estimated Th coverage, $\theta(\text{Th-loNaClO}_4) \sim 0.04 \text{ Th/A}_{\text{UC}}$, is ten times smaller than that from NaCl media (Schmidt et al., 2012a). Th-KClO₄ shows similar behavior with modulations that are significantly weaker than those observed in NaCl, with $\theta(\text{Th-KClO}_4) \sim 0.07 \text{ Th/A}_{\text{UC}}$. By comparison, the Th coverage for Th-LiClO₄, $\theta(\text{Th-LiClO}_4) \sim 5 \text{ Th/A}_{\text{UC}}$, is more than one order of magnitude higher than those measured in the other ClO₄[−] systems.

3.2.1 Structural model Th-LiClO₄

The RAXR data collected in 0.1 M LiClO₄ were analyzed using a model-dependent approach to obtain the vertical distribution of Th species sorbed at the interface. The same type of full structural analysis was not possible for the other ClO₄[−] systems because the observed RAXR signals were too weak.

The best fit structural model for the Th-LiClO₄ RAXR is presented in Figure 2. This includes both the total electron density profile (black line) and the Th-specific electron density (blue). The Th-specific electron density distribution in 0.1 M NaCl (Schmidt et al., 2012a) is shown in a black dotted line for comparison. The Th distribution in Th-LiClO₄ consists of two broad layers at $\sim 4.1 \text{ \AA}$ and $\sim 29 \text{ \AA}$, respectively, indicating the coexistence of two Th sorption modes. The derived Th distribution

model has fairly small statistical uncertainty (i.e., 1σ errors are indicated as an orange band in Figure 2), and reproduces the experimental data (RAXR quality-of-fit: $\chi^2 = 5.1$, $R = 3.8\%$). The first Th layer is closer to the surface than the extended outer sphere complex observed for Th-NaCl (Schmidt et al., 2012a). It covers the range of adsorption heights typically occupied by sorption complexes of hydrated and partly hydrated cations (Lee et al., 2010). The second peak is broader and reaches up to 50 Å height from the surface. This distribution is similar to what has been observed upon adsorption (Schmidt et al., 2012b) and formation (Schmidt et al., 2013) of Pu nanoparticles on the muscovite–water interface, but the coverage of Th is smaller than those of Pu in the adsorbed nanoparticles (4.9 Th/A_{UC} compared to 9.9 and 10.8 Pu/A_{UC}, respectively).

Figure 2. Interfacial structure of Th-LiClO₄. Total electron density (ED) profile derived from CTR (solid black line) and Th electron density distribution derived from RAXR (blue area, uncertainty in electron density is shown in orange). The Th-specific ED profile measured for Th-NaCl (Schmidt et al., 2012a) is also plotted (dashed black line) for comparison. The electron density is normalized by that of bulk water $\rho(\text{bulk water}) = 0.33 \text{ e}^-/\text{\AA}^3$. The average height of muscovite surface oxygens is set to be $z = 0 \text{ \AA}$.

3.3 Crystal truncation rods

To understand the immense differences in the sorption behavior of Th, we have to take into consideration how the background electrolyte changes the conditions at the muscovite (001) basal plane. The CTR data and total electron density profiles for all background electrolytes are shown in Figure 3. A summary of all constituents of the models can be found in Table S2 and S3 in the EA.

351

352 Figure 3. Total electron density derived from CTR for all background electrolytes. Plots are offset
 353 for clarity and the corresponding sample name is indicated in the figure. The electron density (ED) is
 354 normalized by that of bulk water $\rho(\text{bulk water}) = 0.33 \text{ e}^-/\text{\AA}^3$. The average height of muscovite surface
 355 oxygens is at $z = 0 \text{ \AA}$. Black dashed lines indicate the bulk water ED.

356 The electron density profiles (Figure 3) – with the exception of Th-LiClO₄ – show great similarity
 357 near the muscovite-electrolyte interface. Two peaks close to the interface can be found in all electron
 358 density profiles, for the NaClO₄ samples these are found at identical positions at 2.0 and 4.0 $\text{\AA}$
 359 distance from the surface, for Th-KClO₄ they are shifted towards smaller distances from the interface
 360 at 1.7 and 3.1 $\text{\AA}$, with one additional peak at 5.7 $\text{\AA}$. Both Th-loNaClO₄ and Th-hiNaClO₄ show a weak
 361 broad feature in their respective ED distributions, centered at 12.7 and 11.7 $\text{\AA}$, with the ED
 362 approaching the value of bulk water at $\sim 20 \text{\AA}$. In both cases the broad peak contributes little to the total
 363 ED, $\sim 7 \%$ above bulk water ED for Th-loNaClO₄ and $\sim 6 \%$ for Th-hiNaClO₄. The coverage of
 364 adsorbed species is larger for Th-loNaClO₄ than for Th-hiNaClO₄, consistent with the trends observed
 365 in the RAXR spectra.

The electron densities observed near the muscovite surface are generally similar to that identified previously for muscovite in electrolyte solutions of simple ions, with two layers that are observed close to the interface. The structural details are, however, different: The adsorbed water appears closer to the interface at 1.3 Å and 2.5 Å (Cheng et al., 2001), compared to 2.0 Å and 4.0 Å in NaClO₄ samples and 1.7 Å and 3.1 Å for Th-KClO₄. The peak positions are also different upon sorption of Na⁺ in the absence of Th(IV), where the first adsorbed layer was found at 1.2 Å and 2.4 Å with a third species at 5.2 Å for Na⁺. The electron density profile for Th-KClO₄ is similar to the one found for K⁺ adsorption in the absence of Th (Fig. 4), yet the structural details vary. For K⁺ in the absence of Th, layers at 1.9 Å, 3.3 Å, and 5.4 Å have been reported (Lee et al., 2012). The positions of the peaks are reasonably close to each other, but the peak intensities are consistently larger in the presence of Th(IV). This is consistent with co-adsorption of K⁺ with small quantities of Th, as indicated by the RAXR results presented here.

Figure 4. Total electron density derived from CTR for K⁺ samples. Electron density (ED) is normalized by that of bulk water $\rho(\text{bulk water}) = 0.33 \text{ e}^-/\text{\AA}^3$. Electron density profiles for Th-KClO₄ (red line, this work), muscovite in 3 mM KCl (black dashed line, (Lee et al., 2012)), and muscovite in deionized water (dotted blue line, (Cheng et al., 2001)) are shown. Uncertainties in the ED profiles for Th-KClO₄ (light red area) and 3mM KCl on muscovite (grey area) are shown as well.

The total electron density profile derived from the CTR data for Th-LiClO₄ is plotted in Figure 2d (solid black line). The structure differs substantially from the profiles discussed in the previous

paragraphs. It includes several sharp features overlapped with an intense broad peak within $\sim 15 \text{ \AA}$ from the surface. These are followed by a broad structured peak centered at $\sim 27 \text{ \AA}$, which slowly declines to the electron density of bulk water at a distance of $50 \text{ \AA}$ from the interface. That is, a primary difference between these data with respect to the others is the presence of a significant enhancement of the electron density near the interface, with a magnitude of the density that can only be explained by the adsorption of large amounts of Th.

3.4 Exchange experiments NaCl/NaClO₄

Figure 5. Amplitude of the element-specific partial structure factors of Th(IV) adsorbed at muscovite (001)–aqueous solution interface determined by model-independent (data points) analyses of RAXR spectra for the samples of the NaClO₄/NaCl exchange experiment: a) after adsorption of Th from NaCl, b) 1h after replacing NaCl by NaClO₄, c) 8h after replacing NaCl by NaClO₄. Dashed lines are guides-to-the-eye, and may facilitate extrapolation to $q \rightarrow 0 \text{ \AA}^{-1}$.

The reversibility of the effect of sodium perchlorate on Th(IV)'s sorption behavior was tested by comparing selected RAXR scans after Th(IV) adsorption from 0.1 M NaCl media, with those from the same sample after one and eight hours in 0.1 M NaClO₄. The scans are shown in the EA in comparison to the low- q RAXR spectra measured in NaCl medium (Figure S4). The spectra measured before exchanging the background electrolyte are similar to the previously reported spectra measured under the same condition (Schmidt et al., 2012a), confirming their reproducibility. The coverage estimated

from the amplitude of the RAXR spectra by model-independent analysis (Figure 5) matches the coverage found previously for Th adsorption from NaCl media, i.e. $\theta(\text{Th}) = 0.4 \text{ Th}/A_{\text{UC}}$ (Schmidt et al., 2012a).

Having established reproducibility in the NaCl systems, the sample was flushed with several mL of 0.1 M NaClO₄ solution without added Th and left to react for eight hours. After one hour of reaction we observed ~30 % decreases in the RAXR signal amplitude at $q = 0.15 - 0.38 \text{ \AA}^{-1}$ (Figure 5). The reduction of amplitude indicates partial removal of sorbed Th from an initial coverage of $0.4 \text{ Th}/A_{\text{UC}}$ to approximately $0.33 \text{ Th}/A_{\text{UC}}$. There is no change in the q -dependent variation of the resonant amplitude, suggesting that the distribution remained unchanged. Eight hours after flushing with NaClO₄ solution the spectra show that the resonant amplitude at the lowest q value was unchanged, but that the amplitude decreases with increasing q . This suggests that while the coverage has not changed significantly, the speciation has changed, likely to a broader, less organized Th distribution. The desorption process is slow, and it was not possible to achieve complete removal of Th(IV) within the time allotted for the experiment (~10 h).

In the previous Th-NaCl study (Schmidt et al., 2012a) quick removal of about 60% of Th had been found by comparison of the Th coverage obtained *in situ* by RAXR ($0.4 \text{ Th}/A_{\text{UC}}$) and after flushing with NaCl solution and deionized water by alpha spectrometry ($0.15 \text{ Th}/A_{\text{UC}}$). Consequently, 30% removal over eight hours in NaClO₄ would suggest that desorption is actually slower in NaClO₄ than in NaCl, although it should be cautioned that the experiments are not entirely comparable.

4 DISCUSSION

4.1 Anion effect

The present data offer insight into background electrolyte effects on the sorption behavior of tetravalent Th on the muscovite (001) basal plane at slightly acidic solution pH (3.3 ± 0.3). The reference point for this discussion will be the previously observed behavior of Th adsorption from 0.1 M NaCl solution, which leads to the formation of an extended outer sphere sorption complex of

Th(IV), with a coverage $\theta(\text{Th}) = 0.4 \text{ Th}/A_{\text{UC}}$ (Schmidt et al., 2012a). This sorption structure is distinct from that observed in the other studied electrolytes.

The most unexpected differences in thorium's reactivity with respect to muscovite in 0.1 M NaCl are observed in 0.1 M NaClO₄ (Th-hiNaClO₄). Through this relatively simple change in anion of the background electrolyte, the sorption of Th(IV) to muscovite is effectively inhibited. Note that the duplicate measurements of these two experiments as mentioned in Section 2.4 yielded the same results (data not shown). The total ED profile obtained from CTR shows that Th and/or perchlorate still affect the interfacial structure. The adsorbed water structure is clearly different from the structure found upon adsorption of Na⁺ from NaCl solution in the absence of Th(IV) (Lee et al., 2012) with peaks shifted to larger distances from the interface. In addition, a broad feature at a distance close to the sorption height of the Th extended outer sphere complex (11.7 Å compared to 10.1 Å) is found. The peak is however very weak, and if it is related to Th adsorption the amount of adsorbed Th is diminutive (The peak contributes electron density equivalent to $\sim 0.3 \text{ H}_2\text{O}/A_{\text{UC}}$, or $\sim 0.06 \text{ Th}/A_{\text{UC}}$ if all electron density originates from Th). The effect is observed to a lesser extent at lower ionic strength of NaClO₄ (Th-loNaClO₄; I = 0.01 M). RAXR modulations were detected, proving that a small amount of Th has adsorbed at the interface, but the coverage is nearly ten times lower ($\theta(\text{Th}) \sim 0.04 \text{ Th}/A_{\text{UC}}$) than for Th-NaCl. A model-independent analysis (see EA) implies a broad distribution of Th(IV) at the interface with a very low coverage.

Table 3. Thorium coverages θ , measured by RAXR.

Sample $\theta(\text{Th}/A_{\text{UC}})$	Th-LiClO ₄ 4.9	Th-KClO ₄ ~ 0.07	Th-loNaClO ₄ <0.04	Th-hiNaClO ₄ n.d.	Th-NaCl 0.4
Sample $\theta(\text{Th}/A_{\text{UC}})$	Exch. Exp. (0h) ~ 0.4	Exch. Exp. (1h) ~ 0.33	Exch. Exp. (8h) ~ 0.33		

4.2 Cation effect

Our results show that the choice of cation introduced with the background electrolyte has a significant effect on the Th(IV) sorption as well. A very similar Th coverage is found in 0.1 M KClO₄ (Th-KClO₄) compared to 0.01 M NaClO₄ (Th-loNaClO₄). For Th-KClO₄ the coverage is $\sim 0.07 \text{ Th}/A_{\text{UC}}$, meaning that sorption is still about five times weaker than from NaCl solution.

However, this indicates that K^+ has a positive effect on the adsorption of Th relative to Na^+ in ClO_4^- media, where under otherwise identical solution composition (Th-hi $NaClO_4$) no significant Th sorption was observed.

A substantial change in Th reactivity also is observed upon adsorption from $LiClO_4$ background (Th- $LiClO_4$). Here, uptake (i.e., $\theta(Th) = 4.9 \text{ Th}/A_{UC}$ in 0.1 M $LiClO_4$) is increased markedly beyond the observed uptake from $NaCl$ media ($0.4 \text{ Th}/A_{UC}$ in 0.1 M $NaCl$). In this system, there appears to be no inhibitory effect from the presence of perchlorate on Th uptake to the muscovite surface in contrast to those in $NaClO_4$ and $KClO_4$ systems. The observed Th(IV) structure consists of two broad distributions, which can be interpreted as Th in adsorbed Th-nanoparticles and larger aggregates of Th-nanoparticles. The presence of Th(IV) sorption complexes as minor species cannot be ruled out. Pu(IV)-oxo-nanoparticles have been shown to form at the muscovite basal plane from Pu(III) solutions under similar conditions (Schmidt et al., 2013). Finding a similar mode of nanoparticle formation from Th(IV) solutions suggests that the same mechanism is applicable for tetravalent actinides independent of previous redox reactions. We can assume that the interfacial concentration of Th(IV) is larger in this experiment than the concentration of Pu(IV), which was only a minor species in the previous experiments (Schmidt et al., 2013). However, the observed Th coverage is lower than the Pu coverage ($4.9 \text{ Th}/A_{UC}$ compared to $9.9 \text{ Pu}/A_{UC}$) and the extent of the Th distribution is smaller ($z_{max}(Th) < 50 \text{ \AA}$; $z_{max}(Pu) < 80 \text{ \AA}$), which indicates that the driving force for the formation of Th-nanoparticles at the interface appears to be smaller, most likely due to Th(IV) being chemically softer and thus less prone to hydrolysis than Pu(IV).

Results from alpha spectrometry suggest that the particles may be partially removable. Uptake quantification performed *ex situ* after two flushing steps finds a significantly smaller coverage of $\theta_\alpha = 1.6 \pm 0.3 \text{ Th}/A_{UC}$ than the $\theta_{RAXR} = 4.9 \text{ Th}/A_{UC}$ found by RAXR. The plutonium nanoparticles reported previously were not desorbed by similar flushing steps, and RAXR and alpha spectrometry found matching coverages in these experiments (Schmidt et al., 2013; Schmidt et al., 2012b). For Th extended outer sphere complexes, however, it has been demonstrated that the sorption reaction is partly reversible (Schmidt et al., 2012a).

4.3 Potential mechanisms for background electrolyte effects

There are two possible pathways for how the presence of Li^+ could influence the formation of the Th(IV) nanoparticles: by increasing the uptake of Th(IV) at the interface, or by catalyzing the formation of Th oligomers in solution. The adsorption isotherm measured for Th(IV) in the presence of NaCl shows a stark increase in Th coverage at concentrations larger than 10^{-3} mol/L to more than $2 \text{ Th}/\text{A}_{\text{UC}}$, well beyond what is required for charge compensation. The increase has been associated with a surface precipitation reaction, even though all Th solid phases were undersaturated (Schmidt et al., 2012a). The precipitate has not been characterized, and the chemical state of Th(IV) at the interface at these higher concentrations remains unclear. On the other hand it was shown for Pu adsorption at the muscovite basal plane that the high interfacial concentrations in a charge compensating layer are sufficient to induce polymerization of even minor quantities of Pu(IV) in a solution of ostensibly Pu(III) (Schmidt et al., 2013). In these experiments small quantities of tetravalent Pu in a solution of trivalent Pu in contact with air lead to the formation of Pu(IV)-oxo-nanoparticles at the interface, in part due to the enhanced concentration of plutonium in the near-interface regime. Atomic force microscopy confirms that plutonium is present as discrete nanoparticles. Thorium's tendency to hydrolyze and polymerize is less pronounced than plutonium's (Knope and Soderholm, 2012), thus it is expected that Th only begins to polymerize at higher interfacial concentrations. Therefore the central question appears to be to understand what factors control the interfacial Th concentration and consequently allow it to become sufficiently high for nanoparticle formation at the interface.

A partial explanation for the cation effect may be found in the competitive adsorption behavior of Th and the “inert” background electrolyte, which is closely connected with their relative hydration energies. Li is the smallest alkali metal ion and has the corresponding largest hydration energy, and it decreases systematically within the group. Accordingly, recent results (Lee et al., 2012) have demonstrated that the adsorption enthalpy of these cations has a distinct non-monotonic dependence along the alkali series, where Li is more weakly bound than the heavier alkali cations (e.g., Rb, and Cs). From this, it was inferred that it adsorbs on the muscovite surface as an outer-sphere species, while Rb and Cs, for instance, are known to adsorb preferentially as IS species. Therefore a possible

explanation for the observed cation effect on the Th sorption behavior is that the difference in the background cation speciation and adsorption enthalpies may influence the adsorption structure and coverage of Th by ability of the alkali cation to compete with Th for adsorption. This observation is fully consistent with the observed systematic trend of an increasing Th coverage (at 0.1 M background electrolyte concentration) in the presence of KClO_4 vs. LiClO_4 . What is not expected within this model is the negligible adsorption of Th in the presence of NaClO_4 at this concentration. A further test of this idea could be obtained by additional Th adsorption studies at higher background electrolyte concentrations. This picture predicts that Th precipitation would be inhibited for all background electrolytes, but with a threshold concentration for inhibition that decreases from Li through K due to the different adsorption enthalpies.

Lithium may also have an impact on the solution chemistry of Th. Lithium has been shown to enhance the formation of nanoparticles and oligomers of several actinides, amongst others Th and Pu (Knope and Soderholm, 2012; Soderholm et al., 2008). Hence, it is conceivable that the aqueous speciation of Th is modified in the presence of lithium towards a larger prevalence of oligomeric species. However, our interface-specific experiments do not probe the bulk solution speciation and no effect of lithium on bulk speciation has been documented in the available databases (Rand et al., 2008). There is some indication that lithium does not increase the formation of oligomers in chloride media, and does in fact hamper the underlying hydrolysis reaction with respect to sodium and potassium (Milic, 1981). In conclusion, additional research into the dependence of the aqueous speciation of Th on the background electrolyte will be required to resolve this question.

The effect of the anion is more challenging to understand. The comparison of the otherwise identical samples Th-NaCl and Th-hiNaClO₄ clearly shows that the presence of ClO_4^- reduces the uptake of Th(IV) to the mica basal plane with respect to that in Cl^- media. A direct involvement of the perchlorate ion by complexation to the cation would reduce its charge and cause increased uptake at the interface, as more Th would be required to compensate the surface charge. Also, no inner sphere complexation of Th(IV) by ClO_4^- has been observed and no complexation constants are reported (Rand et al., 2008). Complexation of Th with ClO_4^- can thus be ruled out as primary cause of the

observed perchlorate effect. Also important to consider is the capacity of an ion to “make or break” water structure beyond its formal hydration shell (Marcus, 2009), with their relative influences expressed through the Hofmeister series (Hofmeister, 1888). Here, the electrolyte effect is not directly on the adsorbing cation, but rather sorption would be affected indirectly through differences in the water structure around the cation or on the interface. The theory as presented in the review by Marcus (Marcus, 2009) considers both Cl^- and ClO_4^- to be “structure breaking” ions, but the effect is considered much stronger for ClO_4^- than for Cl^- , so a possible explanation for the observed effects would be that the water structure at the interface or around Th(IV) is disturbed in a way that decreases the tendency for Th(IV) to adsorb. However, the observed behavior of the cations of the background electrolyte contradicts the systematics demonstrated in (Marcus, 2009). According to the study, Li^+ is a “structure making” ion, Na^+ is a borderline case, and K^+ is “structure breaking”. Consequently, if breaking the water structure inhibits the adsorption of Th(IV), uptake of Th(IV) should follow the trend $\text{Li}^+ > \text{Na}^+ > \text{K}^+$, and no adsorption should be observed for Th- KClO_4 as is the case for Th- hiNaClO_4 . While Li^+ appears to follow this trend and significantly increases Th(IV) uptake (see discussion above), Th(IV) uptake is in fact increased for Th- KClO_4 compared to Th- hiNaClO_4 and even Th- loNaClO_4 . In addition, the total ED profiles derived from CTR (see Figure 3 and EA) show similar water layering close to the interface, nearly independent of the electrolyte. The theory of structure making and breaking ions is mainly built on data from biological systems (Hofmeister, 1888) and from ionic solutions at fairly high ionic strengths (Marcus, 2009), where such weak effects can be observed. It is then not surprising that under more dilute geochemical conditions other interactions, e.g. complexation or adsorption competition, may dominate.

The reversibility experiments show that the perchlorate effect on the Th adsorption is very slow, once Th(IV) has adsorbed to the interface from NaCl media. After one hour of reaction time with NaClO_4 background no significant change occurs, and even after eight hours the adsorption structure has not changed dramatically. We cannot unambiguously assign the observed partial desorption to the change in background electrolyte in these experiments. The flushing solution did not contain Th(IV), hence partial desorption is expected to occur. (Schmidt et al., 2012a) Still, it appears reasonable to

conclude that the effect of the perchlorate ion on the sorption reaction occurs prior to the adsorption step, and is less (or not at all) effective once sorption has happened.

5 CONCLUSION

The present results demonstrate that the sorption behavior of tetravalent Th onto the muscovite (001) basal plane shows unexpected and strong sensitivity to the background electrolyte. Comparing to the Th-NaCl system, we can differentiate two distinct regimes for the effects of perchlorate media: a sorption inhibition regime for Th-hiNaClO₄ and to a lesser extent Th-loNaClO₄ and Th-KClO₄, and a sorption enhancement effect for Th-LiClO₄. Both effects have been observed and quantified by RAXR and alpha spectrometry. It was possible to exclude complexation reactions, and chaotropic effects of the ions (Hofmeister series), as the underlying mechanism of the effect. While the effect of the background electrolyte cation might be explained by competitive adsorption (due to the different adsorption enthalpies of K vs. Li, for instance), this explanation is not necessarily unique. A straightforward deduction a single mechanism, especially as regards to the role of anions, is as yet not possible and will require further studies. It is plausible that the identified effects are in fact not the consequence of a single mechanism, but a convolution of several effects in solution and at the interface. That notwithstanding, the presented data draw attention to the importance of ionic effects on (geo-)chemical reactions, given the large differences between the most commonly applied electrolytes – NaCl and NaClO₄ – in this system.

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