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3 Curium, and Europium onto Muscovite

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13 Abstract

14 For a safe enclosure of contaminants, for instance in deep geological repositories of 15 radioactive waste, any processes retarding metal migration are of paramount importance. 16 This study focusses on the sorption of trivalent actinides (Am, Cm) and lanthanides (Eu) to the surface of muscovite, a mica and main component of most crystalline rocks 17 18 (granites, granodiorites). Batch sorption experiments quantified the retention regarding 19 parameters like pH (varied between 3 and 9), metal concentration (from 0.5 µM Cm to 20 10 μ M Eu), or solid-to-liquid ratio (0.13 and 5.25 g·L⁻¹). In addition, time-resolved laser 21 fluorescence spectroscopy (TRLFS) using the actinide Cm(III) identified two distinct 22 inner-sphere surface species. Combining both approaches allowed the development of a robust surface complexation model and the determination of stability constants of the 23 24 spectroscopically identified species of $(\equiv S-OH)_2M^{3+}$ (logK^{\bullet} -8.89), $(\equiv S-O)_2M^{+}$ $(\log K^{\circ} - 4.11)$, and $(\equiv S-O)_2MOH$ ($\log K^{\circ} - 10.6$), with all values extrapolated to infinite 25 26 dilution. The inclusion of these stability constants into thermodynamic databases will 27 improve the prognostic accuracy of lanthanide and actinide transport through 28 groundwater channels in soils and crystalline rock systems.

29

30 Keywords: mica, trivalent actinides, retardation, TRLFS, Diffuse Double Layer
31 Model

32

33 Highlights:

- 34 Multi-method approach to study trivalent actinide sorption onto muscovite
- 35 First spectroscopic verification of surface species of trivalent actinides on muscovite
- 36 Reliable surface complexation model based on spectroscopically verified speciation

38 TOC Graphic:



41 1. Introduction

42 Hazardous waste from a manifold of sources must be confined from the ecosphere, and 43 specifically from entering the food chain. Prominent examples are metal ore mining and 44 processing, fertilizer production, nuclear power generation, geothermics, decommissioning of 45 industrial installations, and most branches of consumer good production. To safely dispose of 46 such contaminants for long periods is a huge challenge and of great societal concern. In the 47 case of radioactive waste, safe isolation for 1 million years is demanded by German law to be 48 considered in safety assessments (NEA, 2006). Engineered barriers are usually expected to fail 49 in their protection functions after thousands of years, after which the influx of groundwater will 50 mobilize toxic materials and potentially introduce such species into the water table. In case of 51 radioactive waste, and with the ability for mineralogical formations to retain mobile species, this has led to the consideration of deep geological storage as the most viable option in many 52 53 countries, such as Russia, Japan, USA, and Germany (Blyth et al., 2009; Ojovan et al., 2019; 54 Vokál et al., 2010). The selection and characterization of a suitable multi-shell encapsulation 55 system (including the host rock) requires serious consideration to prevent transfer of 56 radionuclides into the ecosphere.

57 Granitic rock is one such formation (BGE, 2020; Laverov et al., 2016; Oy, 2012; Yamamoto 58 et al., 2013) and consists predominantly of quartz, feldspar, and mica in varying ratios. Studies 59 conducted on the immobilization characteristics of complete mineral assemblies will generate 60 information on a specific granite only; alterations in composition may however alter 61 performance between samples. With mechanistic understanding of the sorbing capabilities of 62 individual mineral phases a more universal approach can be generated, further improving 63 predictions for retardation capabilities within complex rock assemblies (Stockmann et al., 64 2017).

65 Minor actinides Americium and Curium, but also Plutonium, contribute significantly to the total radiotoxicity of spent nuclear fuel and are expected to occur in their trivalent oxidation 66 67 state under the strongly reducing conditions developing over time in a deep geological 68 repository. As Pu(III) is a big challenge for experimental designs, many sorption studies have 69 focused on Am(III) and Cm(III), as well as an inactive rare earth analogue Eu(III) - all of them 70 keeping their oxidation state even under oxidizing conditions. Here, interactions with mineral 71 phases such as feldspars (J. Neumann et al., 2021; Stumpf et al., 2006b), clays (Hartmann et 72 al., 2011; Schnurr et al., 2015; Stumpf et al., 2004), and aluminum (Huittinen et al., 2009) and

73 iron oxides (Stumpf et al., 2006a) as well as guartz (García et al., 2019) are of highest 74 importance. Surface complexation models (SCM) for actinide sorption have also been 75 developed for some of these systems. In a brief overview, quartz was reported to display two 76 distinct adsorbed species ((=S-O)₂HEu⁺ between pH ~3.5 and 6 and (=S-O)₂EuOH as pH 77 increases) that vary in immobilization contribution dependent on ionic strength (García et al., 78 2019). Feldspar minerals have been reported to display as many as four distinct surface species $((\equiv S-OH)_2M^{3+}, (\equiv S-O)_2M^+, (\equiv S-O)_2MOH \text{ and } (\equiv S-O)_2M(OH)_2), \text{ verified utilizing both SCM}$ 79 and spectroscopy (J. Neumann et al., 2021; Stumpf et al., 2006b). 80

81 Mica minerals, such as muscovite, as major components of granitic rock, have been the focus 82 of several studies investigating their retention potential towards radionuclides. Some 83 investigations also covered effects of counter-ions on sorption of trivalent metal ions (Lee et 84 al., 2013; Neumann et al., 2022; Pan et al., 2017; Yan et al., 2013), of co-ions on nano particle formation of tetravalent actinides (J Neumann et al., 2021), or speciation on U(VI) sorption 85 86 (Arnold et al., 2006; Richter et al., 2016). Most of these studies used large single crystals as 87 substrates, however, and hence there is still a distinct lack of a fundamental understanding of 88 sorption of trivalent actinides (An(III)) and a realistic set of species required to parametrize 89 respective SCMs to close gaps in thermodynamic databases (Richter, 2015). With the 90 utilization of µTRLFS, sorption of trivalent actinides has been discovered to mainly occur 91 along mineral grain boundaries (Blyth et al., 2009; Demnitz et al., 2022; Molodtsov et al., 2021, 92 2019) in natural granite samples, including those of the mica mineral fractions. Muscovite is a 93 mica mineral that is both abundant and chemically analogous to illite, and weathering processes 94 of this mineral cause the formation of many other clay minerals and colloidal species (Jackson et al., 1948). For example, muscovite is a major component of a variety of soils (Anand and 95 96 Gilkes, 1987; Wilson, 2004) and also (22 %) of the mineralogical matrix at the Grimsel Test 97 Site (GTS) (Degueldre et al., 1989; Soler and Mäder, 2010), an underground research 98 laboratory facility in a crystalline rock formation in Switzerland, used for research projects 99 related to radioactive waste disposal. In situ experiments conducted in a fracture zone at the 100 GTS showed that transport of trivalent actinides (Am, Cm, and Pu) occurred mainly colloid-101 mediated, in particular through their adsorption to mobile clay colloids (Geckeis et al., 2004; 102 Möri et al., 2003). It, therefore, seems imperative that the behavior of muscovite will be pivotal 103 for an overarching model describing the long-term mobility of disposed (radio-)toxic waste 104 compounds. Hence, this work strives for the formulation of a SCM for the sorption of 105 An(III)/Ln(III) to the surface of muscovite based on a sound molecular-level understanding of the interfacial speciation. As the data situation with respect to metal cation sorption onto other micas (biotite, chlorite, phlogopite, glauconite) is similarly disappointing, any muscovite sorption model may at least be indicative or serve for scoping calculations also for such systems.

110 The information derived from such studies will help improve the accuracy of reactive transport models, such as the 'Smart K_d-concept' (Stockmann et al., 2017), which is a modern 111 112 and robust approach to simulate contaminant transport through complex geochemical systems. 113 The premise behind this concept is the computation of distribution coefficients (K_d values) 114 based on sorption equilibria for each relevant ion-mineral combination in a comprehensive and 115 competitive manner. Such calculations exploit the mechanistic understanding casted into 116 validated surface complexation and ion exchange models. Then, it is easy to perform these 117 computations for a wide range of physicochemical parameters, generating multidimensional 118 matrices. They, in turn, are used in reactive transport codes for a more reliable prediction of 119 contaminant transport through ground water pathways within the host rock, taking into 120 consideration localized geochemical conditions and decreasing the computational costs for 121 each simulation (Stockmann et al., 2017).

122 This study combines sorption experiments (pH edges and isotherms) with TRLFS investigations in the exploration of trivalent actinide (Am, Cm) and lanthanide (Eu) sorption to 123 the surface of muscovite. In a next step, SCMs are generated with and without the 124 125 implementation of spectroscopically observed species. The finally selected species set with 126 respective reaction constants are valuable expansions to thermodynamic databases. Namely, 127 they allow for a more realistic description of actinide immobilization by muscovite (e.g. as a 128 major constituent of granitic rock). Thus, our approach provides robust thermodynamic data 129 based on molecular level speciation derived from spectroscopic investigations. Due to the use 130 of multiple trivalent actinides and lanthanides the data are nonetheless generic and can be used 131 to describe the interaction of any trivalent f-elements with muscovite mica. The resulting 132 increased modelling accuracy for long-term safety assessments aids in the selection of sites 133 suitable for deep geological storage of radioactive waste.

134 2. Materials and Methods

135 2.1. Materials

For all sorption experiments, NaCl was purchased from Sigma-Aldrich and HCl and NaOH (Sigma-Aldrich) were used for pH adjustments. An ²⁴³Am stock solution (in 0.01 M HCl) was diluted for batch contacts, a stock solution of ²⁴⁸Cm in 1 M HClO₄ was diluted for TRLFS experiments, and EuCl₃·6H₂O (99.9%, abcr Chemie) was used for batch sorption experiments. Milli-Q water was produced via ultrafiltration (membraPure, Astacus²) and its resistance was measured to be > 18 MΩ.

142 Synthetic muscovite mica sheets (V1 quality, AFM standard 25×75 mm) were supplied by 143 Ted Pella, Inc (Redding, California, USA). The mineral sheets were crushed into platelets by a 144 tungsten carbide ball mill (Fritsch Pulverisette 7 Planetary Micro Mill), then sieved to a size 145 fraction of 20 – 63 µm via dry vibrational sieving (Fritsch Pulverisette 7 sieve). The crystal 146 structure of the mineral was analyzed using Powder X-Ray Diffraction (PXRD, Rigaku 147 MiniFlex600 and the PDXL software suite) and elemental composition was analyzed using 148 X-Ray Fluorescence Analysis (XFA, PANalytical, Axios^{mAX}, Rh X-Ray Source).

Muscovite mica (KAl₂(AlSi₃O₁₀)(OH)₂) is a phyllosilicate. It displays a TOT layered structure, with an aluminum octahedral layer (O) 'sandwiched' between two silicate tetrahedral layers (T), and a potassium interlayer between sheets. As many common phyllosilicate minerals contain a range of transitional metals, XFA was used for the determination of the mineral's iron concentration (1.9%, Table S1), which is relevant for the interpretation of the TRLFS results (see below).

The specific surface area (SSA, $18.1 \text{ m}^2 \text{ g}^{-1}$) was measured using N₂-BET analysis 155 (Quantachrome ASiQwin QuadraSorb) and the surface binding site density (SSD, 156 2.61 sites nm⁻²) was obtained from literature (Arnold et al., 2001). Zeta potential measurements 157 158 of the muscovite powder were conducted by first generating a range of 20 samples with a solid:liquid ratio (SLR) of 0.15 g L⁻¹ and [NaCl] of 0.1 M, and pH adjustments were conducted 159 160 by addition of negligible quantities of 1, 0.1, or 0.01 M HCl or NaOH. Suspensions were 161 equilibrated over a 48-h period in an end-over-end agitator, before surface charge 162 measurements were taken by zeta-potential measurements (Malvern Company, Zetasizer Nano 163 ZS). Respective results are reported within the supplemental information (Figure S1).

164 2.2. Sorption Experiments

165 2.2.1. Batch sorption experiments - pH edges. Eu(III) batch sorption experiments were conducted by the generation of mineral suspension with an SLR of either 1 or 3 g L^{-1} and metal 166 concentrations of 10 or 0.5 µM Eu(III). All sorption experiments with Eu were performed 167 168 under atmospheric conditions. The investigated metal concentrations represent typical REE 169 concentrations measured for waste water of REE mining sites (up to 80 µM and lower) 170 (Grawunder et al., 2014; Hao et al., 2016; Merten et al., 2005). Expected concentrations for 171 trivalent actinides in the vicinity of a nuclear waste repository are significantly lower 172 (Keesmann et al., 2005; Zhao et al., 2016). The chosen SLR and metal concentrations 173 correspond to site occupancies of ≤ 18 % (see section 3 in SI for further explanation) assuming 174 a bidentate binding mechanism, at which (surface) precipitation is not expected for $pH \le 8$ 175 (Table S2). The background electrolyte concentration was set to 0.1 M NaCl to maintain 176 constant ionic strength and the pH of each suspension was altered by addition of negligible 177 quantities of 1, 0.1, or 0.01 M NaOH or HCl. Samples were prepared as singlets. After pH 178 adjustment, suspensions were equilibrated for > 48 h by end-over-end agitation in ambient 179 conditions ($25 \pm 1^{\circ}$ C).

180 Scoping calculations with PhreeqC and the ThermoChimie TDB (version 10a (Blanc et al., 181 2015; Giffaut et al., 2014; Grivé et al., 2015)) were performed to estimate the amount of Eu 182 potentially transforming into secondary solid phases. The maximum [Eu] considered was 183 10⁻⁵ mol/L, in the pH edge experiments at pH 6, beyond which sorption will reduce the Eu 184 content in the aqueous phase significantly. Here, only Eu(OH)₃(am) and Eu(OH)CO₃·0.5H₂O were assumed relevant as any formation of well-crystalline minerals within only five days and 185 186 at ambient temperatures is implausible. The saturation indices for the two solids were -5.62187 and -5.81, respectively. Therefore no precipitation is expected from a theoretical point of view 188 and indeed no secondary phase formation was observed in any sorption experiment.

²⁴³Am experiments were undertaken in a similar manner (SLR of 3 $g \cdot L^{-1}$ and [Am³⁺] of 10 μ M), but in a nitrogen glovebox for radiation protection reasons, and agitation was conducted on an orbital shaker. For all sorption samples, post contact pH of the suspension was measured prior to centrifugation for 20 min (3.46 g), and afterwards three aliquots of the supernatant were taken for analysis of remaining metal concentration via ICP-MS (PerkinElmer LAS; NexION 350X). Displayed error bars represent the standard deviation of
the triple ICP-MS measurement. The quantitative information from the Cm(III) TRLFS results
was also considered here.

197 2.2.2. Sorption isotherm experiments. Sorption isotherm experiments were conducted in a 198 similar manner to the batch sorption experiments, however a static pH (pH \sim 7) was decided upon, to minimize mineral dissolution and ensure complete uptake of available Eu^{3+} (> 90 %, 199 see Figure S3 in SI for details). Deviating from the usual isotherm philosophy, $[Eu^{3+}]$ was kept 200 201 constant at 1.5 µM in order to alleviate concerns of the precipitation of amorphous Eu(OH)3 or 202 Eu(OH)CO₃ \cdot 0.5H₂O. The respective saturation indices are -3.55 and 0.26, computed as outlined under section 2.2.1. Assuming no sorption, this would translate into a maximum of 203 204 about 45% of initial Eu being theoretically precipitated as Eu(OH)CO₃·0.5H₂O.

Instead of varying [Eu], the SLR was altered between 0.13 and 5.25 g·L⁻¹, corresponding to a site occupancy of ~0.75% and ~50%. The minimal SLR investigated (0.13 g·L⁻¹) provided a maximum of ~50% theoretical site occupancy (Lützenkirchen and Behra, 1996), also minimizing the risk of surface precipitation.

209 Mineral suspensions were equilibrated over 48 h in D.I. water before addition of electrolyte 210 solution and pH equilibration (where pH was adjusted as above). After pH remained steady 211 over a 24 h period, suspensions were spiked with a Eu(III) stock solution. If a pH drift was 212 observed during the reaction time, it was adjusted back to the desired pH and contacted until 213 the pH remained stable (± 0.05) for a minimum of 48 h. Equilibrated suspensions were 214 centrifuged and analyzed in the same manner as those within the batch sorption experiments.

215 Sorption isotherm data were fit to three common two-parameter models. In brief, the 216 <u>Freundlich model is described by the following equation (Dada et al., 2012; Ho et al., 2002):</u>

$$q_e = a_F C_e^{bF} \tag{Eq. 1}$$

It contains two constants, the relative adsorption capacity, a_F and the heterogeneity factor or intensity of binding, b_F (both unitless) (Dada et al., 2012); where a value of ≥ 1 alludes to multilayer sorption, ≤ 0 alludes to irreversible binding, and $1 > b_F > 0$ describes the homogeneity (the higher the value the more heterogeneous, potentially displaying multiple bound species).

221 With respect to the Langmuir isotherm:

$$q_e = \frac{q_m a_L c_e}{1 + a_L c_e} \tag{Eq. 2}$$

the monolayer sorption equilibrium constant is given by a_L (L·m²·mol⁻¹), and the value of q_m (mol·m⁻²) relates to the equilibrium sorption capacity (Ho et al., 2002).

Lastly, we applied the <u>Dubinin-Radushkevich (D-R)</u> model (Ho et al., 2002):

$$q_e = q_D exp\left(-B_D\left(RT \cdot ln\left(1 + \frac{1}{c_e}\right)\right)^2\right)$$
(Eq. 3)

, which describes both, the homogeneous binding capacity $(q_D, mol \cdot m^{-2})$ and the energies of binding E (kJ·mol⁻¹), and therefore further mechanistic information (B_D):

$$E = \frac{1}{\sqrt{2B_D}} \tag{Eq. 4}$$

, where sorbent-sorbate interactions can be elucidated ($E < 8 \text{ kJ} \cdot \text{mol}^{-1}$ equates to physisorption/ outer-sphere sorption (Van der Waals interactions), $8 \text{ kJ} \cdot \text{mol}^{-1} < E < 16 \text{ kJ} \cdot \text{mol}^{-1}$ equates to intermediate cases and $E > 16 \text{ kJ} \cdot \text{mol}^{-1}$ equates to chemisorption/ inner-sphere sorption (Bulai et al., 2009).

231 2.3. Time-Resolved Laser-Induced Fluorescence Spectroscopy (TRLFS)

For structural investigations, the actinide Cm(III) was used as a luminescent probe at a 232 concentration of 0.5 μ M at an SLR of 3 g L⁻¹ in the pH range 4.5 – 7.5. The sample preparation 233 was performed within a glove box under nitrogen atmosphere for radiation safety reasons. A 234 235 pulsed (5 – 8 ns) Nd:YAG OPO laser system (Powerlite Precision II 9020) coupled with an OPO (PANTHER EX OPO, Continuum, USA) was used for excitation of the sample, at the 236 most intense adsorption line (${}^{8}S_{7/2} \rightarrow {}^{6}I_{11/2}$) of Cm(III) at 396.6 nm, within a quartz cuvette. 237 The luminescence was collected using an optical fiber and transferred to a 300 lines/mm grating 238 239 polychromator (Andor Kymera-328I-C) and CCD Camera (iStar DH320T-18U-63). A delay 240 between the laser pulse and luminescence measurement of 1 µs was generated (DG535 Digital 241 Delay Generator, Stanford Research Systems, Inc.) for protection of the detector from intense 242 pulses.

With increasing complexation of Cm(III), a red-shift of the emission band with respect to the Cm(III)-aquo ion (593.8 nm) is observed. Therefore, from the spectral deconvolution of emission spectra the Cm(III) speciation can be obtained, with the band positions of single 246 component spectra giving information about their chemical environment. With the change in 247 the emission band, also a shift of the absorption maximum of each species is observed. 248 Therefore, the efficiency of the luminescence excitation is reduced. To deduce the relative 249 abundances of the distinct chemical species, their contribution to the overall speciation needs 250 correction by relative fluorescence intensity (FI) factors (Edelstein et al., 2006). Furthermore, 251 the lifetime of this luminescence is also highly dependent on the hydration shell of Cm(III), 252 and with analysis of this lifetime the number of waters within the hydration shell can be 253 determined (Kimura et al., 1996).

254 There are, however, limitations of this approach to speciation determination. The first of which 255 is that both the Cm aquo ion and its outer-sphere sorption complex will return the same 256 emission spectra, as neither species display alteration of the inner hydration sphere; the second 257 is that with the presence of transition metals (specifically iron) in the mineral sample, relaxation 258 processes will quench the luminescence by non-radiative energy transfer (Hartmann et al., 259 2008). This quenching process will decrease the reliability of both lifetime analysis and FI 260 calculation. FI factors for mineral sorption species can, however, be calculated from the 261 species' band position using the relationship described in Eibl *et al.* (Eibl et al., 2019).

262 2.4. Surface Complexation Modelling (SCM)

263 The determination of the surface complexation parameters was conducted through coupling the 264 geochemical speciation software PhreeqC (version 3.6.2.15100, (Charlton and Parkhurst, 2011; 265 Parkhurst and Appelo, 2013) and the parameter estimation code UCODE 2014 (version 1.004 266 (Poeter et al., 2014)). A diffuse double layer model was applied (Dzombak and Morel, 1990). For aqueous speciation of Eu(III), Cm(III), and Am(III) as well as mineral dissolution 267 268 thermodynamic data, the ThermoChimie PhreeqC TDB (version 10a (Blanc et al., 2015; Giffaut et al., 2014; Grivé et al., 2015)) was used. The surface of muscovite was considered to 269 270 contain one generic functional group (surface site \equiv S-OH) with protolysis values pK_a taken 271 from literature (Arnold et al., 2001), i.e. valid at their experimental ionic strength of 0.1 M, 272 being identical to the one in this work:

$$\equiv S-OH + H^+ \rightleftharpoons \equiv S-OH^+_2 \qquad pK_1 = 6.06 \qquad (Eq. 5)$$

$$\equiv S-OH \rightleftharpoons \equiv S-O^- + H^+ \qquad pK_2 = -7.81 \qquad (Eq. 6)$$

273 An overview of the thermodynamic parameters used in the SCM is given in Table 2.

275 **3. Results**

276 **3.1. Batch Sorption Experiments**

277 3.1.1. Aqueous speciation. The aqueous speciation of each system (Am(III), Cm(III) and 278 Eu(III)) were calculated at experimentally relevant conditions using PhreeqC (see section 5 in SI). M^{3+} is the predominant species in all data series up to a pH of ~7.5, where it is overtaken 279 by hydrolysis products $(M(OH)^{2+} \text{ or } M(OH)^{+}_{2})$. Between pH ~8.5 – 10, $M(OH)_{2}^{+}$ is the most 280 281 dominant species in each case before being overtaken by M(OH)₃ at pH 10.5 for Eu(III). As 282 we have limited the pH range to pH < 9, the neutral species can thus be neglected. The 283 introduction of carbonate changes the speciation slightly, especially under alkaline pH 284 conditions, with the MCO_3^+ complex being dominant for pH 8 – 8.5. As experiments with 285 Am(III) were conducted under exclusion of atmospheric CO₂, any influence of carbonate 286 complexation should be visible as differences between the Eu(III) and Am(III) data in this pH 287 range. Moreover, carbonate complexation - in solution or as a ternary complex on the muscovite surface – should be easily identifiable by Cm(III) TRLFS (Kim et al., 1994; Marques 288 289 Fernandes et al., 2010).

3.1.2. *pH edges*. The sorption data of Eu(III) and Am(III) (spectroscopically observed Cm(III) sorption data has been also included) are reported on the surface of muscovite flakes (< 63 μ m). In order to gain insight into site occupancy effects on the sorption edge, two SLR (1 and 3 g·L⁻¹) and two concentrations ([Eu³⁺] = 0.5 and 10 μ M) were investigated, with an extension to Am(III) (10 μ M [M³⁺], SLR of 3 g·L⁻¹) and Cm(III) (0.5 μ M [M³⁺], SLR of 3 g·L⁻¹). The percentage immobilization as a function of pH is given in **Figure 1**.



Figure 1: Batch sorption data (symbols), underlaid by the calculated speciation by the developed SCMs (cf. section 3.3, solid lines), for the sorption of Am(III) and Eu(III) to the surface of muscovite flakes (< 63μ m) in the given experimental conditions. Additionally, retention of Cm(III) based on spectroscopic investigations is plotted for comparison (cf. section 3.2). Reported error bars represent the uncertainty of triplet ICP-MS measurements and are smaller than the plotted symbols.

304 Eu(III) immobilization on muscovite begins at pH ~5 and reaches 100 % by a pH of ~6.5 (Figure 1). The obtained sorption edges show a small shift towards lower pH with decreasing 305 306 maximum site occupancy (Figure 1, left to right). One noticeable deviation is observed for the 307 spectroscopically derived Cm(III) data (see below) at highest pH values (pink symbols in 308 Figure 1, right). While both Am(III) and Eu(III) reach a plateau at 100% immobilization at pH 309 ~6.5, the plateau for Cm(III) begins at the same pH but only reaches ~90% immobilization, 310 which is likely caused by the presence of ~ 10 % outer-spherical bound Cm. This is because it 311 is impossible to distinguish outer-sphere complexes from the aquo ion by TRLFS due to the 312 lack of changes in the first hydration shell of Cm. The data for Eu(III) measured in normal 313 atmosphere and the Am(III) data measured under N2 atmosphere are identical within the 314 precision of the measurement, suggesting no influence of carbonate on the sorption process. A 315 confirmation of this assumption on the molecular level will, however, have to rely on 316 spectroscopic data.

317 3.1.3. Sorption isotherms. The isotherm data is plotted in Figure 2 with q_e (equilibrium 318 concentration of Eu(III) adsorbed on the mineral surface, mol·m⁻²) as a function of C_e

- 319 (equilibrium solution phase concentration of Eu(III), adjusted for available mineral surface
- area, mol· L^{-1} ·m²). This data plot is combined with fitted Langmuir, Freundlich, and D-R isotherms.



Figure 2: Equilibrium isotherm of Eu(III) sorption to the surface of muscovite (pH 7 ± 0.05 , 1.5 μ M Eu(III)), with respective fits to Langmuir, Freundlich, and D-R isotherm models. Reported error bars represent the uncertainty of triplet ICP-MS measurements and are smaller than the plotted symbols.

Sorption of Eu(III) to muscovite displays an initially steep isotherm profile, indicative of strong sorption. Beyond a C_e of $2.0 \cdot 10^{-6}$ mol m⁻² this profile begins to display a gentler slope, while not levelling out completely. This alteration in isotherm profile is coupled with a slow approach to adsorption saturation of the surface, as extraction efficiency decreases from 100% to ~90% (Figure S3). The values generated by fitting the isotherm data to the models (cf. section 2.2.2.) are reported within **Table 1**.

Table 1: The three common two-parameter models for the description of the isotherm data obtained within this study. Errors given are calculated from the square root of the diagonals of the covariance matrix and correspond to two standard deviations.

Model	Parameter	Value	
Freundlich	\mathbf{a}_F	2 ± 1.10^{-4}	
	\mathbf{b}_F	0.48 ± 0.06	
	\mathbb{R}^2	0.970	
Langmuir	$a_L/(L.m^2)\cdot mol^{-1}$	$5\pm1\cdot10^5$	

	$q_m / \text{mol} \cdot \text{m}^{-2}$	$6.7 \pm 0.8 \cdot 10^{-7}$	
	\mathbb{R}^2	0.972	
D-R	$q_D / \text{mol} \cdot \text{m}^{-2}$	$1.0 \pm 0.4 \cdot 10^{-5}$	
	\mathbf{B}_D	$3.3\pm 0.4\!\cdot\!10^{-9}$	
	E / $kJ \cdot mol^{-1}$	12.3 ± 0.6	
	\mathbb{R}^2	0.972	

330 The sorption data were reasonably well-fit to all three models ($R^2 \ge 0.97$). The fits to the 331 Freundlich isotherm relate to a strong binding mechanism (b_F of 0.48), leading to the 332 determination that within the site occupancy range studied, no surface precipitation or 333 cooperative binding (multi-layer) mechanism was apparent.

334 The Langmuir model returns an equilibrium sorption capacity q_m of $6.7 \pm 0.8 \cdot 10^{-7}$ mol·m⁻²,

335 which slightly exceeds the maximum equilibrium concentration of adsorbed Eu(III) (qe) on the

336 mineral surface covered by our measurements ($\sim 6.0 \cdot 10^{-7}$ mol·m⁻²). Despite this extrapolation

337 of the experimental data the Langmuir model is still a reasonable descriptor of the data at hand.

338 In stark contrast, the homogeneous binding capacity q_D for the D-R isotherm is $1.0 \pm 0.4 \cdot 10^{-5}$ mol·m⁻² and is based on a much larger extrapolation of this data (see orange 339 curve in Figure 2), leading to very tentative reliance on this model. In other words, the result 340 341 of our isotherm analysis overestimates the amount of sorption, since the homogeneous binding 342 capacity is 2-3 times larger than the total number of available sorption sites according to the SSD used in our SCM (2.61 sites \cdot nm⁻² corresponding to 4.33 \cdot 10⁻⁶ mol·m⁻² (Arnold et al., 343 344 2001)). It is possible that a contribution of outer-sphere species leads to the high value of q_D as outer-spherically bound species do not occupy specific sorption sites. The E value determined 345 346 from the D-R isotherm model of 12.3 kJ·mol⁻¹ is in between the typical energies of 347 physisorption and chemisorption, which can be interpreted as a combination of both processes, 348 consistent with the interpretation of the value for the homogeneous binding capacity.

In short, while details vary between different isotherms, all models describe a strong, heterogeneous binding mechanism. Both the Freundlich and Langmuir isotherms describe a process that occurs in the absence of any precipitation. This, in conjunction to a high heterogeneity factor and a D-R binding energy between physisorption and chemisorption, leads to the allusion of multiple reactions causing sorption of Eu(III) onto the surface of muscovite. With these assumptions in mind, it can be assumed that there is a combination of both outersphere (physisorption) and inner-sphere sorption (chemisorption) mechanisms creating themeasured sorption profiles.

357

358 3.2. Time-resolved laser-induced fluorescence spectroscopy (TRLFS)

359 By TRLFS measurement using the luminophore Cm(III), we are able to gain insight into the speciation and potentially the sorption mechanism of An(III)/Ln(III) on muscovite. As the 360 position of the ${}^{6}D_{7/2} \rightarrow {}^{8}S_{7/2}$ luminescence band shifts depending on the chemical environment 361 362 of Cm(III), the peak deconvolution of the measured Cm emission spectra enables the 363 identification of the present species and their quantitative contributions to the overall speciation (Eibl et al., 2019; Huittinen et al., 2012; Stumpf et al., 2001). With this information, further 364 365 deductions can be made upon the mechanisms of sorption of An(III)/Ln(III). The spectra 366 utilized in deconvolution, residual spectra after deconvolution, and deconvoluted single 367 component spectra are plotted in Figure 3. Due to the iron content of the muscovite samples (Table S1), the signal-to-noise ratio of the emission spectra was relatively low. And, while 368 369 lifetimes can be derived from our data, they do not contain the structural information with 370 respect to the number of water molecules in the Cm's first coordination sphere, due to the 371 excess quenching effect of structural Fe.



Figure 3: Emission spectra of Cm sorbed to the surface of muscovite between pH 4.6 and 7 (left) and the single component spectra (right) deconvoluted for each species within this study (solid, lines) underlaid by the respective single component spectra for Cm(III) adsorbed on K-feldspar deconvoluted within Neumann et al. (J. Neumann et al., 2021) (translucent lines).

374 In addition to the Cm(III) aquo ion, a minimum of two distinct species were required in order 375 to minimize the residual spectra (Figure 3 left, black) after deconvolution. These species have 376 been assigned as an inner-sphere surface complex (SC) of Cm(III) (SC2, $(\equiv S-O)_2M^+$, peak at ~598 nm) and its hydrolysis species (SC3, (\equiv S-O)₂MOH, peak at ~603 nm), by referencing 377 378 similar studies on K-feldspar (J. Neumann et al., 2021), illite/montmorillonite (Schnurr et al., 2015), and kaolinite (Huittinen et al., 2012, 2010). Deconvolution of individual species' spectra 379 380 became difficult, due to the simultaneous occurrence of multiple species, overall low signal 381 quality, as well as a potential small contribution (< 5%) of a fourth species. Therefore, 382 deconvolution was conducted based on single component spectra available in the literature for 383 the sorption of Cm(III) on another alumina-silicate mineral, K-feldspar (J. Neumann et al., 384 2021). These spectra are shown as translucent lines in Figure 3 (right).



Figure 4. Comparison of the Cm(III) speciation determined through spectroscopic measures (symbols) and the speciation calculated from the surface complexation models of this study (SCM-A and SCM-B, lines). OS: outer-sphere species.

386

387 The peak deconvolution resulted in a quantitative species distribution (Figure 4), which was

388 corrected by FI values (aquo ion: 1.0, SC2: 0.54, SC3: 0.29, (J. Neumann et al., 2021)). The

389 contribution of spectroscopically indistinguishable Cm aquo ion/outer-sphere species (SC1,

390 Figure 4, left) decreases steeply from 100 % at pH ~5 to 10% at pH ~6, from here there is a

391 steady decrease to > 5% beyond pH 7. As discussed above, complete uptake is observed in 392 batch sorption experiments under identical experimental conditions. Therefore, the observation 393 of a small amount of fully hydrated Cm can be interpreted as a constant contribution of outer-394 spherically bound Cm to the speciation.

395 The species designated SC2 (Figure 4, middle), present from pH ~5 and higher, is assumed to 396 be analogous to the bidentate inner-sphere sorption species reported for the K-feldspar, 397 $(\equiv$ S-O)₂M⁺, displaying a gentle onset, reaching a relative abundance of ~40 % at pH ~6. Parallel to the formation of SC2 its first hydrolysis product, (≡S-O)₂MOH (SC3, Figure 3, right), is 398 399 formed and reaches a maximum relative abundance of ~70 % by pH 7, being the most abundant 400 of the spectrally observable species. There is no evidence of carbonate complex species in 401 solution or on the mineral surface. At those pH values where relevant carbonate concentrations 402 would be expected most Cm(III) has already been adsorbed to the surface. Consequently 403 dissolved carbonate complexes can only play a minor role and are not observed 404 spectroscopically. Ternary surface complexes involving carbonate should exhibit larger red 405 shifts (> 606 nm) (Marques Fernandes et al., 2010), than were found in our experiments. Due 406 to the low signal-to-noise ratio we cannot unambiguously conclude that such species do not 407 form, but it appears evident that they are at most minor species under these conditions.

408 **3.3.** Surface Complexation Modelling (SCM)

409 The surface complexation model was developed utilizing two distinct methods, building on 410 each other. Both models have in common that they postulate bidentate species, because the 411 entropic effect should favor the formation of bidentate complexes (Wang and Giammar, 2013). 412 The first modelling approach (SCM-A) is stepwise, increasing the number of surface species, 413 in order to both describe the batch sorption data and minimize the total number of surface 414 species. It is empirical as it does not take into account specific spectroscopic information. 415 Consequently, SCM-A was initially attempted with a single surface species, increasing the complexity of the system as additional species were included. Stoichiometry of each species 416 417 was based upon the aqueous speciation within the pH region of the conducted batch sorption 418 experiments (Figure S2).

The second modelling approach (SCM-B) further expands the SCM-A basis. It incorporates spectroscopically observed species in combination with the batch sorption data for the formation of the initial species estimation within the model. The comparison of both models to experimental data is shown in **Figure 1**. Modelled species and their corresponding log K values 423 are reported in **Table 2**. The nomenclature denotes the level of hydrolysis of sorbed Eu(III),

424 with SC1 being the potential outer-sphere complex not releasing any protons upon formation.

425 SCM-A, i.e. the model without consideration of the spectroscopic data, showed that two distinct 426 species were sufficient to describe the experimental batch sorption edges of Eu(III) and 427 Am(III), (Figure 1). These two major species were assigned as a) an outer-sphere species 428 (SC1), dominating the surface speciation until pH ~6 (Figure S6). However, when comparing 429 the experimentally observed and simulated contributions of these two species (Figure 4), it 430 becomes obvious that there are major deviations, in particular SCM-A overestimates 431 dramatically the amount of outer-sphere sorption, which can be easily seen by the orange line 432 in Figure 4 left, which displays the sum of Cm aquo ion and outer-sphere sorption. Including 433 additional surface complexes within the model led to either the repression of these species to 434 an abundance of zero throughout the fitting, or failure of the modelling process to determine a 435 suitable fit at all. This behavior illustrates the necessity to provide speciation data derived 436 independent from the modelling process, which is why we include the spectroscopically 437 obtained speciation in the next step.

Table 2: Surface complex formation constants of M(III) adsorbed on muscovite, determined via SCM within this study (upper/lower 95% confidence level). The last column gives the values extrapolated to infinite dilution based on Davies, 1962:

Species	Complex formation	logK (SCM-A)	logK (SCM-B)	logK ^e (SCM-B)*
SC1	$2 \equiv \text{S-OH} + \text{M}^{3+} \rightleftharpoons (\equiv \text{S-OH})_2 \text{M}^{3+}$	8.57 (8.72/8.42)	7.93 (8.28/7.57)	8.89 (9.24/8.53)
SC2	$2 \equiv S-OH + M^{3+} \rightleftharpoons (\equiv S-O)_2M^+ + 2 H^+$	-5.32 (-5.06/-5.58)	-4.86 (-4.81/-4.92)	-4.11 (-4.06/-4.17)
SC3	$2 \equiv S-OH + M^{3+} + H_2O \rightleftharpoons$ $(\equiv S-O)_2MOH + 3 H^+$	-	-11.3 (-11.2/-11.5)	-10.6 (-10.5/-10.8)

438 * For calculations only model SCM-B should be used!

With the incorporation of the spectroscopically determined speciation, i.e. SCM-B, the upper region of the modelled sorption edge is shifted to slightly lower pH. Both models were capable of describing both inner- and outer-sphere surface complexes. However, considering spectroscopic data, SCM-B also incorporated SC3, see Figure 4 (purple lines). Consequently, the abundance of SC2 was greatly reduced in place of SC3.

445 **4. Discussion**

The sorption edges recorded for Am(III), Cm(III), and Eu(III) overlap with regards to similar 446 447 suspension conditions, reaffirming the assumptions of analogous behavior of An(III)/Ln(III) 448 (Lee et al., 2006). While the directly comparable analysis of Am(III) and Eu(III) reproduced 449 identical sorption edges, there is a slight discrepancy between those of Am(III)/Eu(III) and 450 Cm(III). This is caused by the two different experimental approaches and the fact that 451 differentiation between Cm aquo ion and outer-sphere complexes within the TRLFS data is 452 impossible. With an inclusion of the spectroscopic data, all three site occupancies are well 453 described by the SCM.

454 The aqueous speciation of each An(III)/Ln(III) (e.g. hydrolysis or carbonate complexation, 455 Figure S2) appears to have little effect on the sorption behavior, although spectroscopic data shows that hydrolysis does occur at the interface. The transition from M³⁺ to MOH²⁺ or MCO₃⁺ 456 in solution occurs between pH 7 and 8, while sorption in each case begins already at or below 457 458 pH 5, reaching near completion by pH 6. Previous studies have noted sorption occurring earlier 459 and reported contributions by outer-sphere sorption at the lower pH values (Pan et al., 2017; 460 Yan et al., 2013). This feature is less apparent within this study (~ 10% based on the difference 461 between TRLFS and batch experiments), as Cm-TRLFS returned spectrally observable 462 sorption (inner-sphere) within all pH regions that had also displayed sorption within the batch 463 experiments (Figure 4 and S4). The spectroscopically derived speciation of Cm(III), however, 464 suggests that outer-sphere complexes do contribute to Cm's speciation albeit in limited 465 quantities.

The fit of the sorption raw data to a variety of isotherm models provided a rather consistent picture. With reference to the Freundlich isotherm results, the heterogeneity factor obtained ($b_F = 0.48 \pm 0.06$) is indicative of a monolayer system, which is in agreement with the reasonable fit towards the Langmuir isotherm model. This value for b_F is, however, skewed closer towards a heterogeneous binding mechanism. Coupled with the variation from the previously determined Langmuir sorption constant (at a higher pH (Yan et al., 2013)) and a

472 high D-R free energy of binding (12.3 ± 0.6)

473 kJ·mol⁻¹), a strong indication for multiple mechanisms is provided. This coincides nicely with

the independent spectral indication of both inner- and outer-sphere complexes contributing to

- 475 this sorption process. Thus, these three isotherm models have all acted in support of
- 476 assumptions corresponding directly to previous understanding of the muscovite system, where
- 477 multiple species are bound to the surface (Pan et al., 2017; Yan et al., 2013).

478 Although the batch sorption data is generally well reproduced by SCM-A, a comparison to the 479 spectroscopically derived speciation clearly shows that the abundance of the outer-sphere 480 sorption complex is greatly overestimated by this model (Figure 4). Consequently, an inclusion of spectroscopic information (SCM-B approach) led to the identification of one more surface 481 482 species than dictated within SCM-A. Observation of single component Cm(III) TRLFS spectra 483 displayed a discrepancy between inner-sphere sorption species and batch sorption edge, which 484 was used for the determination of an outer-sphere species. The deconvoluted, single component 485 spectra align well with the spectra previously determined for K-feldspar (J. Neumann et al., 486 2021), emphasized as they are underlaid within Figure 3; alluding to close parallels to the 487 surface speciation between the two alumino-silicate mineral phases.

488 The formation of a similar surface bound Cm(III) species ($\sim 597 - 599$ nm) has been noted between pH 4 and 7 for many alumino-silicate minerals (Huittinen et al., 2012; J. Neumann et 489 490 al., 2021; Schnurr et al., 2015), with this species appearing at a higher wavelength (~601 nm) 491 and at pH \sim 5 for guartz and for alumina minerals (Kupcik et al., 2016; Rabung et al., 2006). 492 Other studies have postulated secondary hydrolysis species ($\sim 605 - 607$ nm) at pH > 8 493 (Huittinen et al., 2012; Kupcik et al., 2016; J. Neumann et al., 2021; Rabung et al., 2006) and 494 ternary surface complexes (~610 nm) at pH values of 10 and higher (Huittinen et al., 2012). 495 While neither were observed in appreciable amounts within this study, there is the potential for 496 a low abundance (5 %) of a secondary hydrolysis species SC4 (Figure S4), also in our system, 497 however outside of the experimentally investigated range.

From spectroscopic data it is observed that inner-sphere sorption of Cm(III) to the surface and the formation of surface-bound $Cm(OH)^{2+}$ coincide. This species, SC3, swiftly becomes the dominant surface species, and remains so throughout the pH region studied; this occurs despite the low concentration of aqueous $Cm(OH)^{2+}$.

502 As would be expected with the inclusion of this data, and as has been previously observed (J. 503 Neumann et al., 2021), the approach taken in SCM-B results in a model that displays a better 504 agreement with the spectroscopically observed speciation of Cm(III), while still reproducing 505 the sorption edges with similar accuracy. Thus it is clear that SCM-B is significantly closer to 506 reality than SCM-A. Although the level of description of total sorption is comparable, the 507 extrapolative capability of SCM-B should be much more dependable. To verify that statement, 508 independent sets of sorption data have been tested with experimental parameter ranges 509 differing from those in this study.

511 Model Validation

512 For the validation of the models, two previously reported datasets for sorption of lanthanides 513 Nd(III) and Eu(III) to the surface of muscovite flakes were compared with prognostic PhreeqC calculations of the currently developed SCM, utilizing the experimental conditions outlined 514 with each dataset. The first of the two datasets is from a doctoral thesis of C. Richter (Richter, 515 516 2015). From this thesis, the immobilization of Nd(III) by a muscovite powder (particle size 30 $-400 \,\mu\text{m}$, 10 % montmorillonite, SSA = 0.66 m²/g (Britz, 2018; Richter, 2015)) is plotted as 517 518 a function of pH and has been directly compared to SCM-A and SCM-B from this study in 519 Figure 5.



Figure 5: Sorption data of Nd(III) to the surface of muscovite in suspension reproduced from (Richter, 2015) (experimental conditions given in each figure) combined with blind prediction sorption curves utilizing the SCM-A and B approaches from this work.

521 SCMs developed in this work excellently reproduce the data obtained from this thesis, in particular for points along the top and middle of the sorption edge above pH ~4.5. Both models 522 523 in each case created a reasonable approximation of the edge, independent of An(III)/Ln(III), 524 ionic strength, or SLR. However, it is difficult to make assumptions about the description of 525 the low pH region of each sorption edge. This agreement of the model derived from 526 Am(III)/Cm(III)/Eu(III) data with Nd(III) sorption data thus not only validates the SCM 527 derived here, but again reaffirms the robust nature of the analogy between Ln(III) and An(III) 528 exploited here and in many other investigations.



Figure 6: Sorption data of Eu(III) to the surface of muscovite in suspension reproduced from Pan *et al.*, 2017 (experimental conditions given in each figure, muscovite flake size: 45 μ m, SSA: ~8.9 m²·g⁻¹) underlaid by the sorption determined by the developed SCM-A and B.

531 The Eu(III) sorption edge of an analogous study, comparing the effects of counter ions on the 532 sorption of Eu(III) to the surface of muscovite by Pan et al. (2017), has been digitized and is displayed in Figure 6, again underlain with the respective PhreeqC simulations (SCM-A and 533 534 SCM-B). In this case, however, neither SCM was capable of describing the data satisfactorily. 535 It can be seen that the sorption edge is less steep than predicted by the model. This could 536 potentially be caused by the larger site occupancy in the study of Pan et al., 52 % (as opposed 537 to the maximum of max. ~30 % studied here), which may lead to a higher contribution of outer-538 sphere sorption, especially at low pH, where the least number of deprotonated sites are 539 available. Another factor relates to a potential inability for our models to describe a relationship 540 between sorption and ionic strength, as the batch sorption experiments only covered one 541 specific ionic strength of 0.1 M. This ionic strength was sufficient for the anticipated 542 application cases for crystalline rocks and soils, where higher ionic strengths are unlikely to 543 occur. However, additional experiments would be necessary when dealing with various clay 544 rocks where higher salinity can be expected, as well as for crystalline rock layers in immediate 545 contact with salt rocks. In such cases, a switch from the Diffuse Double Layer SCM to a 546 Constant Capacitance SCM may be necessary as the latter one is more suitable for higher 547 salinities (Hayes et al., 1991).

549 **5.** Conclusions

- 550 Here we report the sorption of trivalent europium, americium, and curium by muscovite mica
- using a multi-method approach, consisting of batch sorption experiments, TRLFS, and SCM.
- 552 Sorption is low (< 5 %) up to pH 5 but shows a strong increase up to completion around pH 6.
- 553 All sorption pH edges can be reproduced adequately with only two surface complexes (SCM-
- 554 A), one outer- and one inner-sphere species.
- 555 However, Cm(III) TRLFS revealed the sorption structure on the molecular level and three 556 sorption species were identified: an outer-sphere complex ($\sim 10\%$) at low pH (pH < 6), an 557 inner-sphere complex ((\equiv S-O)₂M⁺), and its subsequent hydrolysis species ((\equiv S-O)₂MOH), 558 which form at the same pH. The improved thermodynamic model SCM-B is more realistic and 559 thus more robust with respect to extrapolation beyond the boundary conditions of these 560 experiments, as was proven by modelling independent literature data. SCM-B, therefore, 561 delivers surface complexation parameters (cf. Table 2) that are added to the sorption database 562 of the Smart K_d-concept (Stockmann et al., 2017).
- 563 Sorption isotherms delivered thermodynamic parameters of the sorption reaction and support 564 the modelled binding mechanisms. All findings imply great similarities to sorption on K-565 feldspar regarding sorption quantity and structure.
- 566 Overall, the SCM developed within this study will aid in developing transport models for rare 567 earth elements and trivalent actinides in the environment, whenever aqueous media play an 568 essential role. This is relevant for a broad variety of applications, such as safety assessments 569 for nuclear waste repositories, where adsorption of trivalent actinides to mobile clay colloids 570 may increase radionuclide transport. Beyond that the results of this study are also relevant for 571 NORM problems associated with geothermal power generation as well as environmental 572 prevention and remediation measures connected to ore mining and milling, but also rare earth 573 element hydrometallurgy, and recycling.

574

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