

Combining Batch Experiments and Spectroscopy for realistic Surface Complexation Modelling of the Sorption of Americium, Curium, and Europium onto Muscovite

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1 **Combining Batch Experiments and Spectroscopy for realistic**
2 **Surface Complexation Modelling of the Sorption of Americium,**
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)
17 to the surface of muscovite, a mica and main component of most crystalline rocks
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 μM Eu), or solid-to-liquid ratio (0.13 and 5.25 $\text{g}\cdot\text{L}^{-1}$). 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
23 robust surface complexation model and the determination of stability constants of the
24 spectroscopically identified species of $(\equiv\text{S-OH})_2\text{M}^{3+}$ ($\log K^\circ -8.89$), $(\equiv\text{S-O})_2\text{M}^+$
25 ($\log K^\circ -4.11$), and $(\equiv\text{S-O})_2\text{MOH}$ ($\log K^\circ -10.6$), with all values extrapolated to infinite
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:**

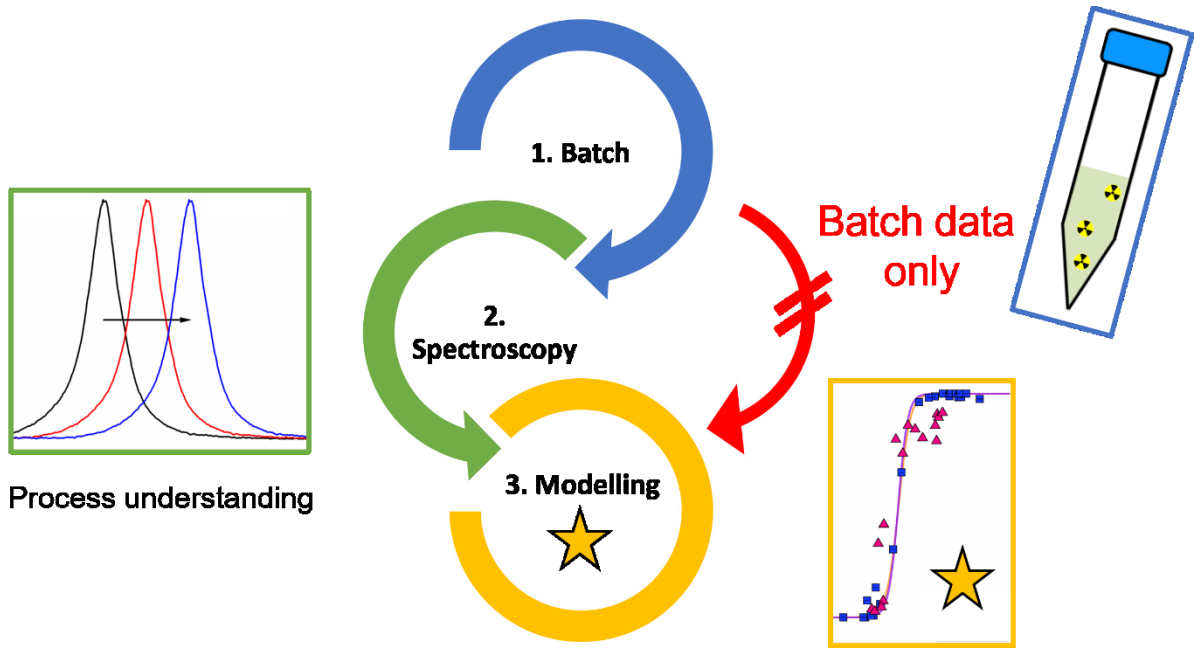
34 - Multi-method approach to study trivalent actinide sorption onto muscovite

35 - First spectroscopic verification of surface species of trivalent actinides on muscovite

36 - Reliable surface complexation model based on spectroscopically verified speciation

37

38 TOC Graphic:



39

40

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,
52 this has led to the consideration of deep geological storage as the most viable option in many
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
66 total radiotoxicity of spent nuclear fuel and are expected to occur in their trivalent oxidation
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 quartz (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 ($(\equiv\text{S-O})_2\text{HEu}^+$ between pH ~ 3.5 and 6 and $(\equiv\text{S-O})_2\text{EuOH}$ 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
79 ($(\equiv\text{S-OH})_2\text{M}^{3+}$, $(\equiv\text{S-O})_2\text{M}^+$, $(\equiv\text{S-O})_2\text{MOH}$ and $(\equiv\text{S-O})_2\text{M}(\text{OH})_2^-$), verified utilizing both SCM
80 and spectroscopy (J. Neumann et al., 2021; Stumpf et al., 2006b).

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
85 formation of tetravalent actinides (J Neumann et al., 2021), or speciation on U(VI) sorption
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
95 et al., 1948). For example, muscovite is a major component of a variety of soils (Anand and
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

106 the interfacial speciation. As the data situation with respect to metal cation sorption onto other
107 micas (biotite, chlorite, phlogopite, glauconite) is similarly disappointing, any muscovite
108 sorption model may at least be indicative or serve for scoping calculations also for such
109 systems.

110 The information derived from such studies will help improve the accuracy of reactive
111 transport models, such as the ‘Smart K_d -concept’ (Stockmann et al., 2017), which is a modern
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 TRIFS
123 investigations in the exploration of trivalent actinide (Am, Cm) and lanthanide (Eu) sorption to
124 the surface of muscovite. In a next step, SCMs are generated with and without the
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

136 For all sorption experiments, NaCl was purchased from Sigma-Aldrich and HCl and NaOH
137 (Sigma-Aldrich) were used for pH adjustments. An ^{243}Am stock solution (in 0.01 M HCl) was
138 diluted for batch contacts, a stock solution of ^{248}Cm in 1 M HClO_4 was diluted for TRLFS
139 experiments, and $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%, abcr Chemie) was used for batch sorption experiments.
140 Milli-Q water was produced via ultrafiltration (membraPure, Astacus²) and its resistance was
141 measured to be $> 18 \text{ M}\Omega$.

142 Synthetic muscovite mica sheets (V1 quality, AFM standard 25×75mm) 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).

149 Muscovite mica ($\text{KA}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$) is a phyllosilicate. It displays a TOT layered
150 structure, with an aluminum octahedral layer (O) ‘sandwiched’ between two silicate tetrahedral
151 layers (T), and a potassium interlayer between sheets. As many common phyllosilicate minerals
152 contain a range of transitional metals, XFA was used for the determination of the mineral’s
153 iron concentration (1.9%, Table S1), which is relevant for the interpretation of the TRLFS
154 results (see below).

155 The specific surface area (SSA, $18.1 \text{ m}^2 \text{ g}^{-1}$) was measured using N_2 -BET analysis
156 (Quantachrome ASiQwin QuadraSorb) and the surface binding site density (SSD,
157 $2.61 \text{ sites nm}^{-2}$) was obtained from literature (Arnold et al., 2001). Zeta potential measurements
158 of the muscovite powder were conducted by first generating a range of 20 samples with a
159 solid:liquid ratio (SLR) of 0.15 g L^{-1} and $[\text{NaCl}]$ of 0.1 M, and pH adjustments were conducted
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
166 conducted by the generation of mineral suspension with an SLR of either 1 or 3 g L⁻¹ and metal
167 concentrations of 10 or 0.5 μM Eu(III). All sorption experiments with Eu were performed
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 ≤ 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 ± 1°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
185 were assumed relevant as any formation of well-crystalline minerals within only five days and
186 at ambient temperatures is implausible. The saturation indices for the two solids were -5.62
187 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.

189 ²⁴³Am experiments were undertaken in a similar manner (SLR of 3 g·L⁻¹ and [Am³⁺] of
190 10 μM), but in a nitrogen glovebox for radiation protection reasons, and agitation was
191 conducted on an orbital shaker. For all sorption samples, post contact pH of the suspension was
192 measured prior to centrifugation for 20 min (3.46 g), and afterwards three aliquots of the
193 supernatant were taken for analysis of remaining metal concentration via ICP-MS

194 (PerkinElmer LAS; NexION 350X). Displayed error bars represent the standard deviation of
195 the triple ICP-MS measurement. The quantitative information from the Cm(III) TRLFS results
196 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 ~ 7) was decided
199 upon, to minimize mineral dissolution and ensure complete uptake of available Eu^{3+} (> 90 %,
200 see Figure S3 in SI for details). Deviating from the usual isotherm philosophy, $[\text{Eu}^{3+}]$ was kept
201 constant at 1.5 μM in order to alleviate concerns of the precipitation of amorphous $\text{Eu}(\text{OH})_3$ or
202 $\text{Eu}(\text{OH})\text{CO}_3 \cdot 0.5\text{H}_2\text{O}$. The respective saturation indices are -3.55 and 0.26, computed as
203 outlined under section 2.2.1. Assuming no sorption, this would translate into a maximum of
204 about 45% of initial Eu being theoretically precipitated as $\text{Eu}(\text{OH})\text{CO}_3 \cdot 0.5\text{H}_2\text{O}$.

205 Instead of varying $[\text{Eu}]$, the SLR was altered between 0.13 and 5.25 $\text{g} \cdot \text{L}^{-1}$, corresponding to
206 a site occupancy of ~0.75% and ~50%. The minimal SLR investigated (0.13 $\text{g} \cdot \text{L}^{-1}$) provided a
207 maximum of ~50% theoretical site occupancy (Lützenkirchen and Behra, 1996), also
208 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 Freundlich model is described by the following equation (Dada et al., 2012; Ho et al., 2002):

$$q_e = a_F C_e^{b_F} \quad (\text{Eq. 1})$$

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

221 With respect to the Langmuir isotherm:

$$q_e = \frac{q_m a_L c_e}{1 + a_L c_e} \quad (\text{Eq. 2})$$

222 the monolayer sorption equilibrium constant is given by a_L ($\text{L} \cdot \text{m}^2 \cdot \text{mol}^{-1}$), and the value of q_m
 223 ($\text{mol} \cdot \text{m}^{-2}$) relates to the equilibrium sorption capacity (Ho et al., 2002).

224 Lastly, we applied the Dubinin–Radushkevich (D-R) model (Ho et al., 2002):

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

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

$$E = \frac{1}{\sqrt{2B_D}} \quad (\text{Eq. 4})$$

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

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

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

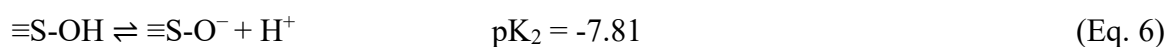
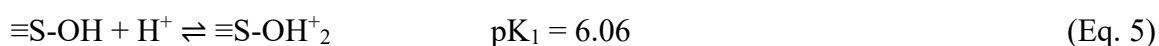
243 With increasing complexation of Cm(III), a red-shift of the emission band with respect to the
 244 Cm(III)-aquo ion (593.8 nm) is observed. Therefore, from the spectral deconvolution of
 245 emission spectra the Cm(III) speciation can be obtained, with the band positions of single

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).
267 For aqueous speciation of Eu(III), Cm(III), and Am(III) as well as mineral dissolution
268 thermodynamic data, the ThermoChimie PhreeqC TDB (version 10a (Blanc et al., 2015;
269 Giffaut et al., 2014; Grivé et al., 2015)) was used. The surface of muscovite was considered to
270 contain one generic functional group (surface site $\equiv\text{S-OH}$) 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:



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

274

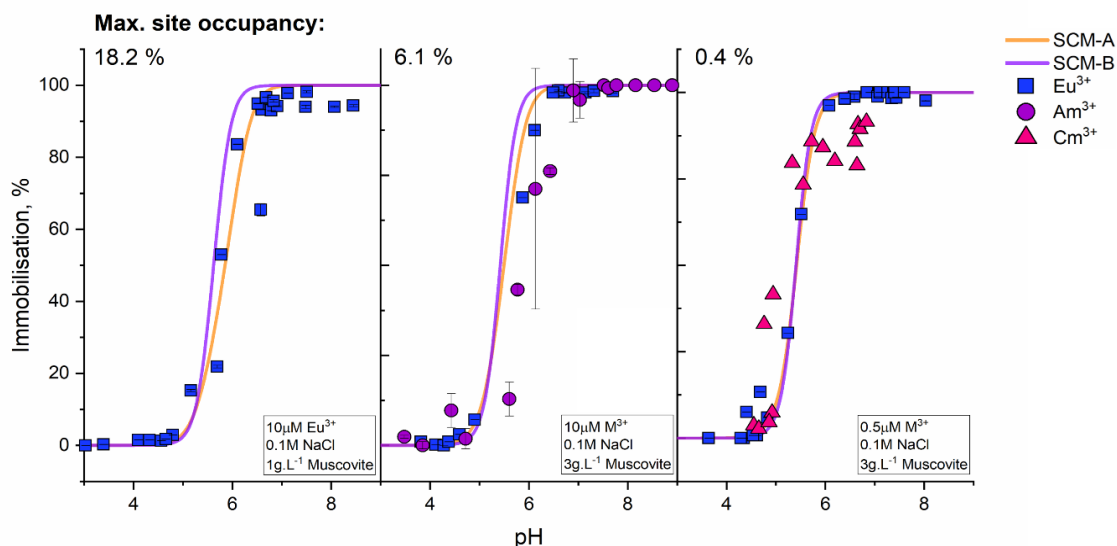
275 **3. Results**

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
279 SI). M^{3+} is the predominant species in all data series up to a pH of ~ 7.5 , where it is overtaken
280 by hydrolysis products ($M(OH)^{2+}$ or $M(OH)^{+}_2$). Between pH $\sim 8.5 - 10$, $M(OH)^{+}_2$ is the most
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 CO_2 , 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
288 muscovite surface – should be easily identifiable by Cm(III) TRLFS (Kim et al., 1994; Marques
289 Fernandes et al., 2010).

290 *3.1.2. pH edges.* The sorption data of Eu(III) and Am(III) (spectroscopically observed Cm(III)
291 sorption data has been also included) are reported on the surface of muscovite flakes ($< 63 \mu m$).
292 In order to gain insight into site occupancy effects on the sorption edge, two SLR (1 and
293 $3 g \cdot L^{-1}$) and two concentrations ($[Eu^{3+}] = 0.5$ and $10 \mu M$) were investigated, with an extension
294 to Am(III) ($10 \mu M [M^{3+}]$, SLR of $3 g \cdot L^{-1}$) and Cm(III) ($0.5 \mu M [M^{3+}]$, SLR of $3 g \cdot L^{-1}$). The
295 percentage immobilization as a function of pH is given in **Figure 1**.

296



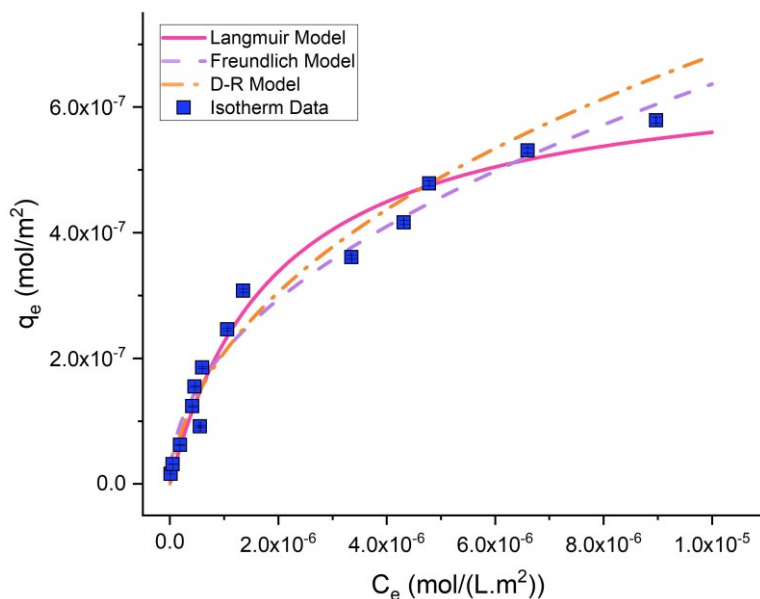
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298 **Figure 1:** Batch sorption data (symbols), underlaid by the calculated speciation by the
 299 developed SCMs (cf. section 3.3, solid lines), for the sorption of Am(III) and Eu(III) to the
 300 surface of muscovite flakes ($< 63 \mu\text{m}$) in the given experimental conditions. Additionally,
 301 retention of Cm(III) based on spectroscopic investigations is plotted for comparison (cf. section
 302 3.2). Reported error bars represent the uncertainty of triplet ICP-MS measurements and are
 303 smaller than the plotted symbols.

304 Eu(III) immobilization on muscovite begins at $\text{pH} \sim 5$ and reaches 100 % by a pH of ~ 6.5
 305 (**Figure 1**). The obtained sorption edges show a small shift towards lower pH with decreasing
 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 $\sim 90\%$ immobilization,
 310 which is likely caused by the presence of $\sim 10\%$ 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 N_2 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, $\text{mol}\cdot\text{m}^{-2}$) as a function of C_e

319 (equilibrium solution phase concentration of Eu(III), adjusted for available mineral surface
 320 area, $\text{mol}\cdot\text{L}^{-1}\cdot\text{m}^2$). This data plot is combined with fitted Langmuir, Freundlich, and D-R
 321 isotherms.



322

Figure 2: Equilibrium isotherm of Eu(III) sorption to the surface of muscovite ($\text{pH } 7 \pm 0.05$, $1.5 \mu\text{M}$ 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.

323 Sorption of Eu(III) to muscovite displays an initially steep isotherm profile, indicative of strong
 324 sorption. Beyond a C_e of $2.0 \cdot 10^{-6} \text{ mol m}^{-2}$ this profile begins to display a gentler slope, while
 325 not levelling out completely. This alteration in isotherm profile is coupled with a slow approach
 326 to adsorption saturation of the surface, as extraction efficiency decreases from 100% to $\sim 90\%$
 327 (Figure S3). The values generated by fitting the isotherm data to the models (cf. section 2.2.2.)
 328 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 | a_F | $2 \pm 1 \cdot 10^{-4}$ |
| | b_F | 0.48 ± 0.06 |
| | R^2 | 0.970 |
| Langmuir | $a_L / (\text{L}\cdot\text{m}^2)\cdot\text{mol}^{-1}$ | $5 \pm 1 \cdot 10^5$ |

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

329

330 The sorption data were reasonably well-fit to all three models ($R^2 \geq 0.97$). 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 $6.7 \pm 0.8 \cdot 10^{-7} \text{ mol}\cdot\text{m}^{-2}$,
 335 which slightly exceeds the maximum equilibrium concentration of adsorbed Eu(III) (q_e) on the
 336 mineral surface covered by our measurements ($\sim 6.0 \cdot 10^{-7} \text{ mol}\cdot\text{m}^{-2}$). 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
 339 $1.0 \pm 0.4 \cdot 10^{-5} \text{ mol}\cdot\text{m}^{-2}$ and is based on a much larger extrapolation of this data (see orange
 340 curve in Figure 2), leading to very tentative reliance on this model. In other words, the result
 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
 343 SSD used in our SCM (2.61 sites $\cdot\text{nm}^{-2}$ corresponding to $4.33 \cdot 10^{-6} \text{ mol}\cdot\text{m}^{-2}$ (Arnold et al.,
 344 2001)). It is possible that a contribution of outer-sphere species leads to the high value of q_D as
 345 outer-spherically bound species do not occupy specific sorption sites. The E value determined
 346 from the D-R isotherm model of $12.3 \text{ kJ}\cdot\text{mol}^{-1}$ 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.

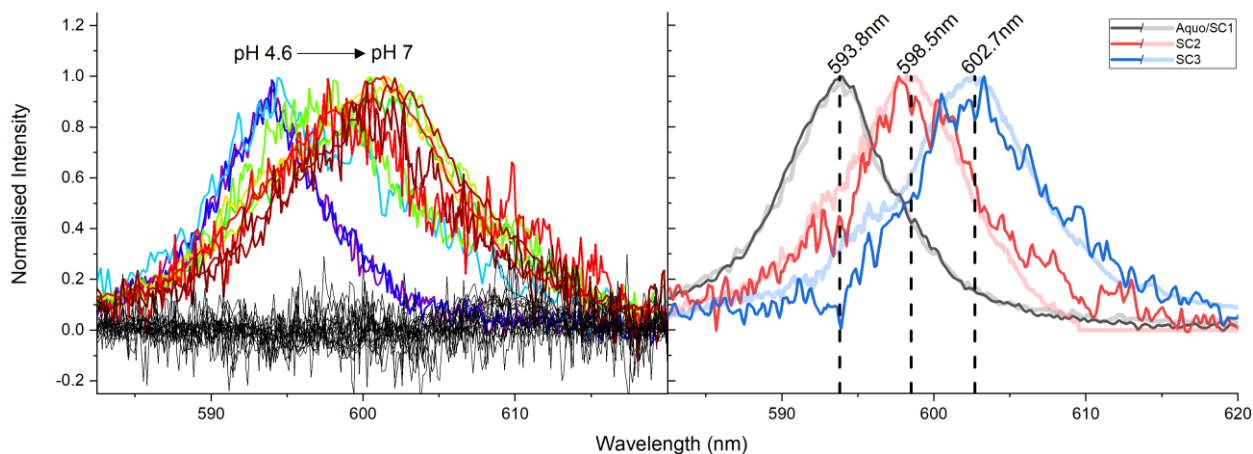
349 In short, while details vary between different isotherms, all models describe a strong,
 350 heterogeneous binding mechanism. Both the Freundlich and Langmuir isotherms describe a
 351 process that occurs in the absence of any precipitation. This, in conjunction to a high
 352 heterogeneity factor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

355 sphere (physisorption) and inner-sphere sorption (chemisorption) mechanisms creating the
356 measured 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
360 speciation and potentially the sorption mechanism of An(III)/Ln(III) on muscovite. As the
361 position of the ${}^6D_{7/2} \rightarrow {}^8S_{7/2}$ luminescence band shifts depending on the chemical environment
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
364 (Eibl et al., 2019; Huittinen et al., 2012; Stumpf et al., 2001). With this information, further
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
368 (Table S1), the signal-to-noise ratio of the emission spectra was relatively low. And, while
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.

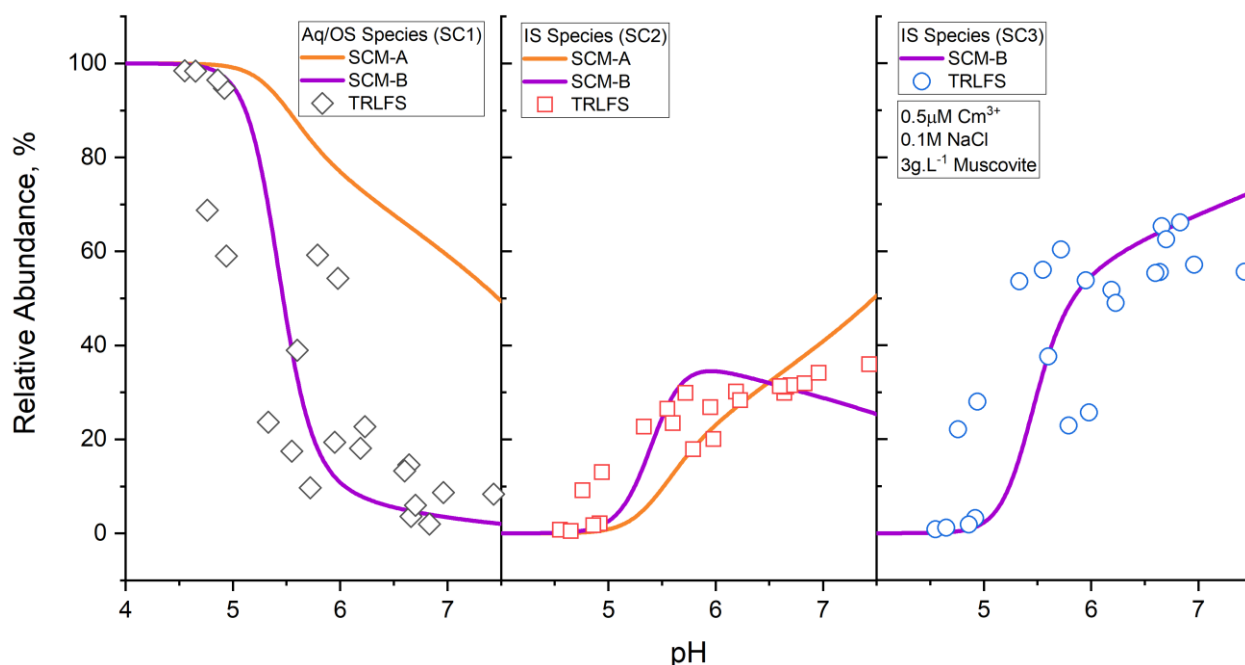


372

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).

373

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, $(\equiv\text{S-O})_2\text{M}^+$, peak at
 377 ~ 598 nm) and its hydrolysis species (SC3, $(\equiv\text{S-O})_2\text{MOH}$, peak at ~ 603 nm), by referencing
 378 similar studies on K-feldspar (J. Neumann et al., 2021), illite/montmorillonite (Schnurr et al.,
 379 2015), and kaolinite (Huittinen et al., 2012, 2010). Deconvolution of individual species' spectra
 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).



385

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 $(\equiv\text{S-O})_2\text{M}^+$, displaying a gentle onset, reaching a relative abundance of ~40 % at pH ~6. Parallel
398 to the formation of SC2 its first hydrolysis product, $(\equiv\text{S-O})_2\text{MOH}$ (SC3, **Figure 3**, right), is
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
416 complexity of the system as additional species were included. Stoichiometry of each species
417 was based upon the aqueous speciation within the pH region of the conducted batch sorption
418 experiments (Figure S2).

419 The second modelling approach (SCM-B) further expands the SCM-A basis. It incorporates
420 spectroscopically observed species in combination with the batch sorption data for the
421 formation of the initial species estimation within the model. The comparison of both models to
422 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 ^o (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 | $2 \equiv\text{S-OH} + \text{M}^{3+} \rightleftharpoons (\equiv\text{S-O})_2\text{M}^+ + 2 \text{H}^+$ | -5.32 (-5.06/-5.58) | -4.86 (-4.81/-4.92) | -4.11 (-4.06/-4.17) |
| SC3 | $2 \equiv\text{S-OH} + \text{M}^{3+} + \text{H}_2\text{O} \rightleftharpoons (\equiv\text{S-O})_2\text{MOH} + 3 \text{H}^+$ | - | -11.3 (-11.2/-11.5) | -10.6 (-10.5/-10.8) |

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

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

444

445 **4. Discussion**

446 The sorption edges recorded for Am(III), Cm(III), and Eu(III) overlap with regards to similar
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
456 shows that hydrolysis does occur at the interface. The transition from M^{3+} to MOH^{2+} or MCO_3^+
457 in solution occurs between pH 7 and 8, while sorption in each case begins already at or below
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.

466 The fit of the sorption raw data to a variety of isotherm models provided a rather consistent
467 picture. With reference to the Freundlich isotherm results, the heterogeneity factor obtained
468 ($b_F = 0.48 \pm 0.06$) is indicative of a monolayer system, which is in agreement with the
469 reasonable fit towards the Langmuir isotherm model. This value for b_F is, however, skewed
470 closer towards a heterogeneous binding mechanism. Coupled with the variation from the
471 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 $\text{kJ}\cdot\text{mol}^{-1}$), a strong indication for multiple mechanisms is provided. This coincides nicely with
474 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
481 of spectroscopic information (SCM-B approach) led to the identification of one more surface
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 overlaid 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 (~597 – 599 nm) has been noted
489 between pH 4 and 7 for many alumino-silicate minerals (Huittinen et al., 2012; J. Neumann et
490 al., 2021; Schnurr et al., 2015), with this species appearing at a higher wavelength (~601 nm)
491 and at pH ~5 for quartz and for alumina minerals (Kupcik et al., 2016; Rabung et al., 2006).
492 Other studies have postulated secondary hydrolysis species (~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.

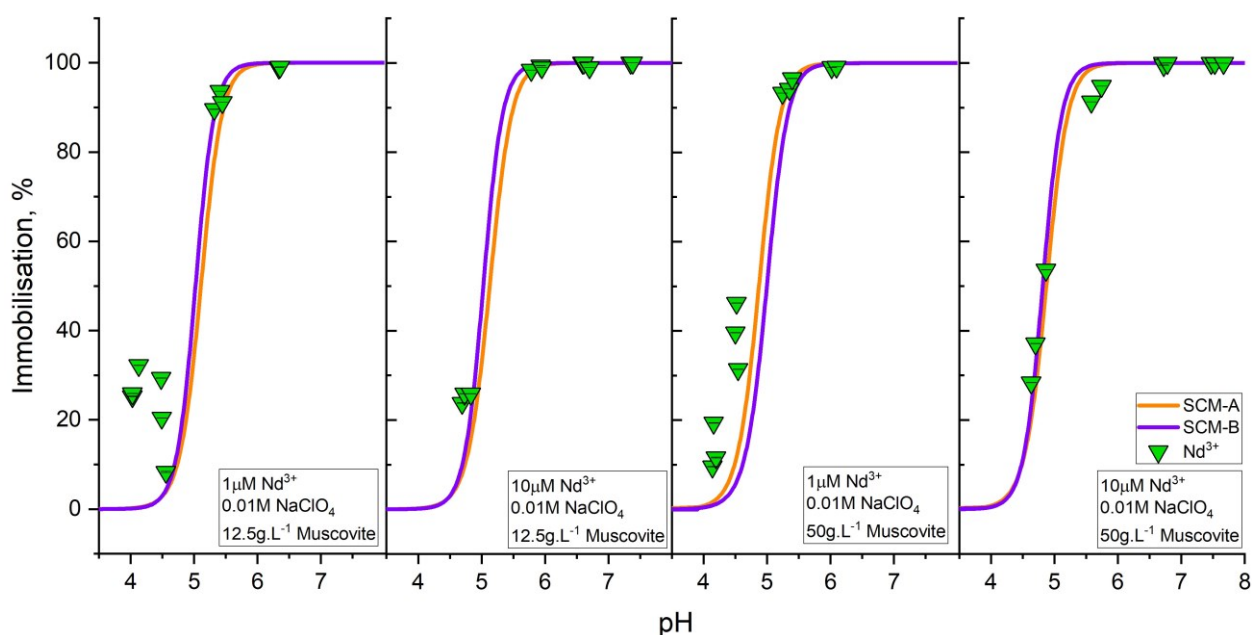
498 From spectroscopic data it is observed that inner-sphere sorption of Cm(III) to the surface and
499 the formation of surface-bound Cm(OH)²⁺ coincide. This species, SC3, swiftly becomes the
500 dominant surface species, and remains so throughout the pH region studied; this occurs despite
501 the low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

510

511 **Model Validation**

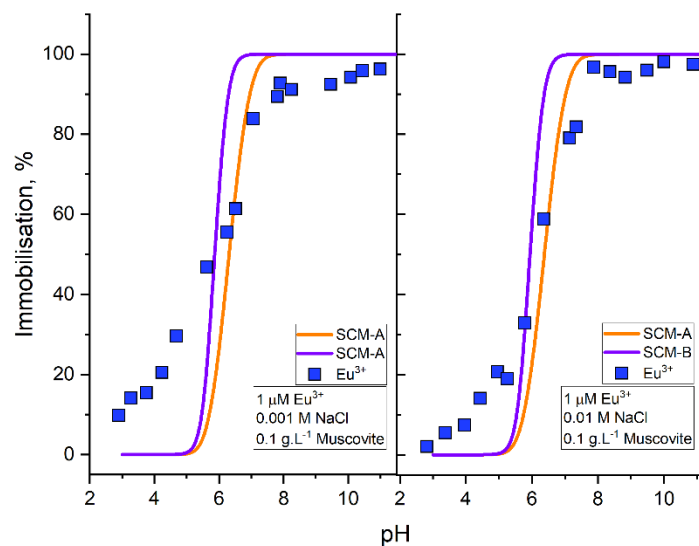
512 For the validation of the models, two previously reported datasets for sorption of lanthanides
513 Nd(III) and Eu(III) to the surface of muscovite flakes were compared with prognostic PhreeqC
514 calculations of the currently developed SCM, utilizing the experimental conditions outlined
515 with each dataset. The first of the two datasets is from a doctoral thesis of C. Richter (Richter,
516 2015). From this thesis, the immobilization of Nd(III) by a muscovite powder (particle size 30
517 – 400 μm , 10 % montmorillonite, SSA = 0.66 m^2/g (Britz, 2018; Richter, 2015)) is plotted as
518 a function of pH and has been directly compared to SCM-A and SCM-B from this study in
519 **Figure 5**.



520

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
522 particular for points along the top and middle of the sorption edge above pH ~4.5. Both models
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.



530

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 μm , SSA: $\sim 8.9 \text{ m}^2 \cdot \text{g}^{-1}$) overlaid 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
 533 displayed in **Figure 6**, again overlain with the respective PhreeqC simulations (SCM-A and
 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).

548

549 **5. Conclusions**

550 Here we report the sorption of trivalent europium, americium, and curium by muscovite mica
551 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 (~10%) at low pH (pH < 6), an
557 inner-sphere complex ($(\equiv\text{S-O})_2\text{M}^+$), and its subsequent hydrolysis species ($(\equiv\text{S-O})_2\text{MOH}$),
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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578

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