

1 **Y(III) sorption at the orthoclase (001) surface measured by X-ray reflectivity**

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20 **ABSTRACT**

21 Interactions of heavy metals with charged mineral surfaces control their mobility in the
22 environment. Here, we investigate the adsorption of Y(III) onto the orthoclase (001) basal
23 plane, the former as a representative of rare earth elements and an analogue of trivalent actinides
24 and the latter as a representative of naturally abundant K-feldspar minerals. We apply *in-situ*
25 high-resolution X-ray reflectivity to determine the sorption capacity and molecular distribution
26 of adsorbed Y species as a function of Y^{3+} concentration, $[Y^{3+}]$, at pH 7 and 5. With $[Y^{3+}]$
27 ≥ 1 mM at pH 7, we observe an inner-sphere (IS) sorption complex at a distance of ~ 1.5 Å from
28 the surface and an outer-sphere (OS) complex at 3–4 Å. Based on the adsorption height of the
29 IS complex a bidentate, binuclear binding mode, in which Y^{3+} binds to two terminal oxygens is
30 proposed. In contrast, mostly OS sorption is observed at pH 5. The observed maximum Y
31 coverage is max. $\sim 1.3 Y^{3+}/A_{UC}$ (A_{UC} : area of the unit cell = 111.4 \AA^2) for all investigated pH
32 values and Y concentrations, which is in the expected range based on the estimated surface
33 charge of orthoclase (001).

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35 **KEYWORDS:** solid liquid interface, rare earth elements, sorption, crystal truncation rod,
36 resonant anomalous X-ray reflectivity, feldspars

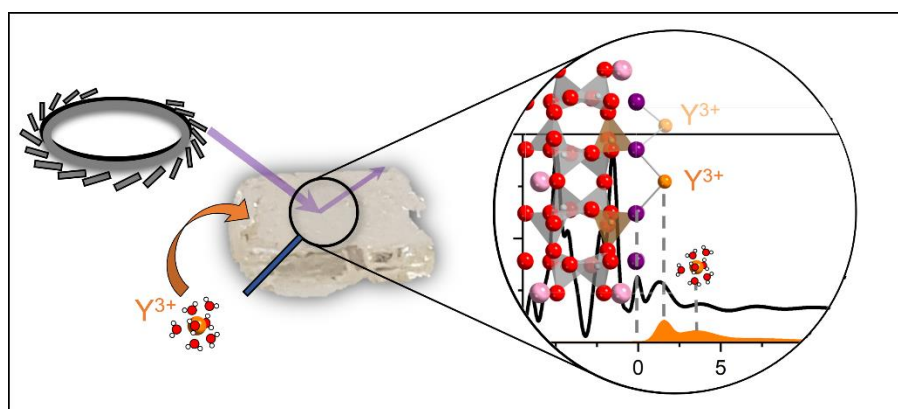
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38 **Synopsis statement:** (approximately 20 words)

39 The study provides a molecular-scale insight into the facet-specific sorption of Y(III) on
40 orthoclase (001).

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42 **TOC:**



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46 **1 Introduction**

47 Heavy metal contaminants are of concern due to their high risks to ecological systems and
48 human health. One group of heavy metals that has been of special interest in the last few decades
49 are rare earth elements (REE), which are essential for modern electronic devices, especially
50 those developed for green technologies.^{1,2} Increased demand and use of REEs has led to
51 significant increases in the environmental pollution caused by REE mining, recycling, and
52 electronic waste disposal³⁻⁸, resulting in negative health effects such as oxidative stress in living
53 organisms.⁹⁻¹¹ Especially acid mine drainage leads to high REE concentrations in the
54 environment, with total REE concentrations as high as 17 mg/L at a wide range of pH values
55 from 2 to 7.5.^{8,12-15}

56 The mobility of REEs in the environment is largely controlled by their interactions with mineral
57 surfaces.^{16,17} Many studies have been carried out to assess the retention potential of major rock-
58 forming minerals, such as quartz¹⁸⁻²⁰ and micas²¹⁻²⁶ for trivalent heavy metals M(III), including
59 REEs and trivalent actinides. The impact of pH, metal concentration, and ligands on the
60 adsorption was investigated and models have been developed to predict the fate of REEs.^{23,27,28}
61 Mechanistically, studies of ion adsorption on muscovite mica showed that multivalent ions tend
62 to adsorb farther from the mineral surface,²⁹⁻³¹ which is related to multivalent ions' ability to
63 retain water molecules. Some ions, for example Al(III)³² and some actinides like Pu(III/IV)³³
64 and Th(IV)²⁶, polymerize at the interface to form secondary-phase thin films or nanoparticles.
65 Another naturally abundant group of minerals are feldspars,³⁴ which are composed of a
66 negatively charged 3D framework of oxygen-bridged aluminosilicate tetrahedra, usually
67 compensated by K⁺, Na⁺, or Ca²⁺. Some studies are available on the sorption of trivalent heavy
68 metals on feldspars,³⁵⁻³⁸ most of which use mineral powder samples. For example, our group
69 has recently studied the sorption of REEs (Eu, La, Lu, Nd, Y) as well as Am(III) and Cm(III)
70 on K-feldspar powders. By combining batch sorption experiments and time-resolved laser-
71 fluorescence spectroscopy (TRLFS), a generic surface complexation model was developed to

72 predict the retention of REEs and trivalent actinides.³⁶ A bidentate coordination for the sorption
73 complex was assumed for this model but could not be verified by the available experimental
74 data.

75 While studies using mineral powder samples give a solid basis for determination of
76 thermodynamic parameters for surface complexation reactions,³⁹⁻⁴¹ the development of realistic
77 reactive transport models requires an understanding of facet-specific reactivity,⁴² the influence
78 of surface roughness,^{38,43,44} and solid-liquid ratios more similar to those in natural systems.
79 Orthoclase (KAlSi_3O_8), a common polymorph of K-feldspar, has a monoclinic crystal structure
80 ($a = 8.56 \text{ \AA}$, $b = 12.99 \text{ \AA}$, $c = 7.19 \text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 116^\circ$)⁴⁵ with perfect cleavage planes along
81 the (001) and (010) orientations, which are commonly exposed in natural systems.⁴⁶ An
82 illustration of the (001) surface is given in the Supporting Information (Figure S1 in SI). Each
83 unit cell of the (001) surface is terminated by a layer of four aluminosilicate tetrahedra pointing
84 out of the surface plane and exposing terminal oxygens (TOs). There are two symmetry-distinct
85 sites of TOs in the orthoclase (001) unit cell, referred to as TO1 and TO2. Two symmetry-
86 equivalent TO1s and two TO2s are located in the middle and the border of the unit cell,
87 respectively (Figure S1). The TOs are typically hydrolyzed in aqueous solution and are
88 (de)protonated depending on the conditions in the aqueous solution, e.g. pH and ionic strength,
89 causing a pH-dependent surface charge of orthoclase. Furthermore, the orthoclase (001) surface
90 has two cavities that are occupied by K^+ , which can be released in contact with water,^{47,48}
91 leading to an additional contribution of $2 e^-/A_{\text{UC}}$ (A_{UC} : area of the unit cell, $A_{\text{UC}}(001) = 111.4$
92 \AA^2) to the maximum surface charge.

93 Due to its perfect cleavage plane, the orthoclase (001) surface is well suited for investigations
94 of molecular-scale processes, including mineral dissolution⁴⁷⁻⁵⁰ and ion sorption.^{38,51} For the
95 latter, spectroscopy and X-ray scattering techniques allow the discrimination of different
96 sorption modes, which are usually divided based on differences in the degree of adsorbate
97 hydration. Inner-sphere (IS) complexes show a partially removed hydration shell, while for

98 outer-sphere (OS) and extended outer-sphere sorption complexes the first or multiple
99 intervening hydration layers are preserved.⁵²

100 Studies of ion adsorption on the orthoclase (001) surface report that alkali ions (e.g., Rb⁺, Cs⁺)
101 undergo a cation exchange with K⁺ from the top layer of the mineral surface and adsorb as an
102 IS complex in the K⁺ cavities.^{51,53} In contrast, experimental and theoretical studies show that
103 alkaline earth ions (Sr²⁺, Ca²⁺, Mg²⁺) form mainly OS complexes due to their relatively stronger
104 hydration.^{51,54} Molecular dynamic simulations investigated the hydration structure of the
105 orthoclase (001) and (010) surfaces⁵⁵ and sorption of U(VI)O₂²⁺ thereon,⁵⁶ and report a
106 transition from an OS to a monodentate IS complex, and eventually to a bidentate, mononuclear
107 IS coordination.

108 Additionally, we recently investigated the impact of nanoscale surface roughness on the
109 sorption of Cm(III) on an individual K-feldspar crystal of the (001) orientation using spatially
110 resolved luminescence spectroscopy.³⁸ We find that the surface reactivity depends upon the
111 topographic variation of the K-feldspar surface. Therefore, models describing reactivity based
112 only on sorption studies using mineral powders with uncontrolled defect densities are
113 insufficient for robust environmental transport predictions. While the previously applied
114 spectroscopy is sensitive to changes in the hydration and gives spatially resolved information
115 about the interfacial speciation, it cannot give insight in the molecular scale interfacial structure,
116 e.g., different binding modes of adsorbed species. The structure and binding mode of a complex
117 will, however, directly affect how strongly the adsorbed ion is retained by the interface and is
118 required to establish thermodynamic models of the sorption process. Consequently, we aim to
119 directly determine such interfacial structures by investigating the truly intrinsic reactivity of an
120 ideal defect-free surface by applying surface-sensitive and element-specific high-resolution X-
121 ray reflectivity to get a deeper insight in the sorption structure.

122 2 Materials and Methods

123 2.1 Mineral Substrate and Sample Preparation

124 Gem-quality orthoclase single crystals (transparent with slightly yellow discoloration) were
125 purchased from The Arkenstone Company (mined in Itrongay, Madagascar). The crystals were
126 cleaved, rinsed with deionized water (DIW), and stored in a solution of 0.1 M NaCl at pH 7 to
127 prevent contamination or dissolution.⁵⁷ Solutions containing 0.1–10 mM YCl₃ were prepared
128 by dissolving the salt in DIW under atmospheric conditions. The pH value was adjusted by
129 addition of small amounts of 0.01 and 0.1 M HCl or NaOH.

130 Two different orthoclase (001) crystals (cleaved from the same specimen) were used for the
131 sorption experiments. One crystal was used to explore the impact of dissolved Y³⁺ ion
132 concentration, [Y³⁺]. The chosen concentration are in the range of, but not limited to the values
133 found in water samples at REE mining sites (< 17 mg/L).^{8,12–15} The first crystal was reacted in
134 a solution of 0.1 mM YCl₃ (= 8.9 mg/L) at pH 7 for 18 h of equilibration, after which X-ray
135 reflectivity (XR) was measured. Due to a relatively low surface coverage, two samples at higher
136 Y concentrations were measured. The same crystal used for the experiments at 0.1 mM Y³⁺ was
137 transferred into a solution at a higher [Y³⁺] = 1 mM at the same pH, reacted for additional 18 h,
138 and XR was measured again. While the Y concentrations are relatively high our previous work
139 on the adsorption of REEs and trivalent actinides on K-feldspar powder showed that a change
140 of metal concentration (in the investigated range of nM–mM) leads only to a shift in the
141 adsorption edge, but not to a change in the molecular adsorption structure.³⁶ Therefore, insights
142 obtained at higher Y concentrations are still transferable to REE concentrations related to heavy
143 metal contaminated sites (up to 17 mg/L¹³).

144 A similar experimental approach was chosen for the second crystal, where the impact of pH
145 was investigated at a fixed [Y³⁺] = 10 mM. After initial reaction at pH 5, XR was measured,
146 and the crystal was then transferred to a 10 mM YCl₃ solution at pH 6.9 (for simplicity referred

147 to as pH 7) and remeasured. These two chosen pH values are based on the beginning of the
148 sorption edge on K-feldspar powders obtained in the previous study and overlap
149 environmentally relevant pH values in stream waters in tailing of REE mines (4.5–7.5).^{8,12,13}
150 Speciation calculations (Visual Minteq, Database NIST46, Critically Selected Stability
151 Constants of Metal Complexes: Version 8.0) for the experimental conditions (10 mM YCl_3 at
152 pH 6.9) show a saturation index of +0.361, suggesting a slight oversaturation of $Y(OH)_3$.
153 However, precipitation of Y-containing solid phases was not observed visually during the
154 preparation of the solutions. In addition, no evidence for crystalline precipitates was observed
155 (either as oriented precipitates that would lead to Bragg peaks that are superimposed on the
156 specular rod, or as randomly oriented precipitates that would appear as "powder rings" that
157 would appear in the background signals) during X-ray measurements.

158

159 2.2 X-ray Reflectivity Experiments

160 We used two variations of high-resolution X-ray reflectivity. The first one is specular crystal
161 truncation rod (CTR) diffraction, a type of surface X-ray diffraction.⁵⁸ CTRs are continuous
162 lines of scattering intensity perpendicular to surfaces and are several orders of magnitude
163 weaker than Bragg peaks. Specular CTR analysis enables the determination of the total
164 electron-density profile of the mineral/water interface. The second method is resonant
165 anomalous X-ray reflectivity (RAXR),⁵⁹ which is element-specific and probes the interfacial
166 distribution of a specific element.

167 *CTR and RAXR experiments.* X-ray data were measured at beamline 13-ID-C
168 (GeoSoilEnviroCARS) at the Advanced Photon Source (APS) at Argonne National
169 Laboratory.⁶⁰ A thin-film cell⁶¹, containing a reacted orthoclase crystal (see above) with its
170 cleaved (001) surface exposed, was filled with ~50 μ L of sample solution and closed with a
171 7.5 μ m Kapton film, holding the crystal in place while maintaining a thin layer (several μ m) of

172 the solution on the crystal surface. To minimize any solution evaporation through the Kapton
173 window, and therefore changes in $[Y^{3+}]$ during the measurement, an additional Mylar dome
174 filled with water-saturated He was placed on the sample cell. Potential beam-induced alteration
175 of the mineral surface was monitored by repeatedly measuring smaller parts of the CTR and
176 RAXR data throughout the entire measurement. No significant changes were observed.

177 The incident X-ray beam was collimated using a pair of 1-meter-long Si mirrors in Kirkpatrick-
178 Baez geometry, and the final size was adjusted by slits to a size of 0.05–0.25 x 0.5–1.0 mm²
179 with an average flux of $\sim 10^{12}$ photons per second at the sample position. The scattering data
180 was measured in the horizontal plane using a Newport six-circle diffractometer and a Dectris
181 PILATUS 100K 2D pixel array detector.⁶²

182 Specular CTR data were measured with an X-ray energy of 14.0 keV that is far from the Y K-
183 edge (17.038 keV, determined by X-ray absorption spectroscopy of a sample in fluorescence
184 mode). CTR measures the X-ray reflectivity signal, $R(q)$, as a function of momentum transfer
185 magnitude, q (0.3–6.0 Å⁻¹), which is related to the scattering angle 2θ through the relation:

$$186 \quad q = 2 \cdot |\vec{k}| \cdot \sin\left(\frac{2\theta}{2}\right) = \frac{4\pi}{\lambda} \cdot \sin\left(\frac{2\theta}{2}\right) \quad (\text{Eq. 1})$$

187 Here, \vec{k} is the wave vector with $|\vec{k}| = 2\pi/\lambda$ and λ ($= 0.886$ Å) is the X-ray wavelength.

188 Element-specific structural information is obtained from RAXR spectra that probe X-ray
189 reflectivity signal (at 10–11 different fixed values of momentum transfer) as a function of X-
190 ray energy through the X-ray absorption edge of the resonant element. Here the Y(III) K
191 absorption edge is at 17.038 keV. Data analysis requires the determination of resonant
192 anomalous dispersion terms $f'(E) + if''(E)$, which were obtained by the measurement of X-
193 ray absorption spectroscopy (XAS) from one of the samples using a SII Vortex ME4

194 fluorescence detector, followed by a Kramers-Kronig transformation. More details are provided
 195 in the literature.^{22,63}

196 *XR Data Analysis*. Here, only a brief description of XR data analysis is given, and more details
 197 can be found in Section 2 of the SI and in the literature.^{58,64,65} The reflectivity R of a given
 198 interfacial structure is proportional to the squared value of the structure factor modulus F and
 199 can be calculated from the atomic scattering factors $f_j(q)$:

$$200 \quad R(q) \sim |F(q)|^2 = \left| \sum_j c_j f_j(q) \cdot \exp(iqz_j) \cdot \exp\left(-\frac{(qu_j)^2}{2}\right) \right|^2 \quad (\text{Eq. 2})$$

201 Individual atomic layers in Eq. 2 are expressed as j Gaussian peaks with an occupancy c_j ,
 202 distance from the surface z_j , and a root-mean-square (rms) width u_j . The model structure
 203 consists of the orthoclase bulk structure, an interfacial layer ($d_{001} = 6.484 \text{ \AA}$)⁴⁵, and several
 204 layers of adsorbed species including water molecules. Each data set is analyzed by simulating
 205 the reflectivity for a given structural model and optimizing the model parameters using a least-
 206 squares fitting routine based on the scaled χ^2 and R-factor (see Section 2 in SI). The CTR data
 207 then reveal a total electron density profile in the direction normal to the orthoclase (001) surface.

208 The analysis of the resonant data followed a similar approach. Each RAXR spectrum, $R(q, E)$ at
 209 a fixed q , is calculated from the total structure factor F that is the sum of a non-resonant
 210 component (F_{NR}), which is known from the CTR analysis, and a resonant structure factor F_R :

$$211 \quad R(q, E) = |F(q, E)|^2 = |F_{NR}(q) + F_R(q, E)|^2 \quad (\text{Eq. 3})$$

$$212 \quad F_R(q, E) = (f'(E) + if''(E)) \cdot \sum_j c_j \cdot \exp(iqz_j) \cdot \exp\left(-\frac{(qu_j)^2}{2}\right) \quad (\text{Eq. 4})$$

$$213 \quad F_R(q, E) = (f'(E) + if''(E)) \cdot A(q) \exp(i\Phi(q)) \quad (\text{Eq. 5})$$

214 In equation 4 and 5, F_R is defined as the product of $f'(E) + if''(E)$ and the partial resonant
215 structure factor of the resonant atom. Using this expression, the parameters describing the
216 distribution of the resonant species (Y^{3+}) is obtained by least-squares optimization.

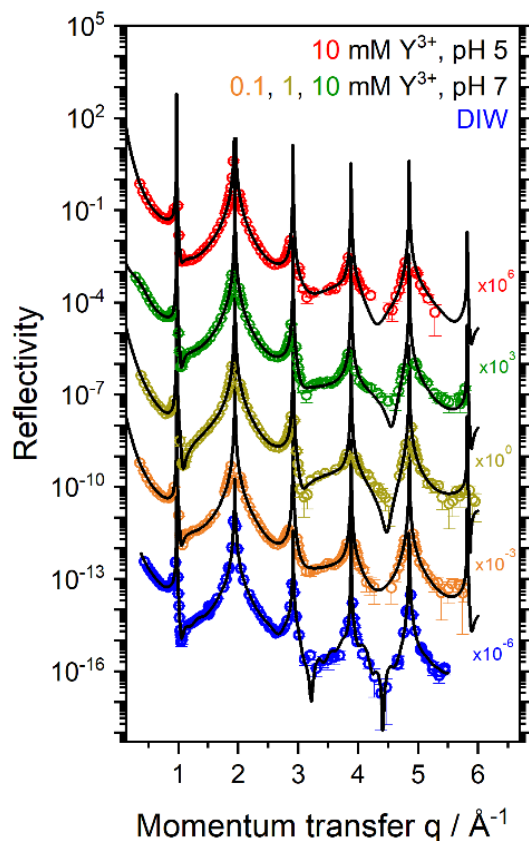
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218 **3 Results & Discussion**

219 **3.1 Reflectivity Data**

220 *CTRs*. First, the impact of Y^{3+} concentration ($[Y^{3+}] = 0.1 - 10$ mM) at $pH = 7$ on the adsorption
221 on orthoclase (001) was investigated by CTR. The measured data are displayed in **Figure 1**.
222 Generally, the non-resonant reflectivity of all samples is very similar to that of the previously
223 published CTR data of the orthoclase (001)–water interface.⁶⁶ At $q < 3 \text{ \AA}^{-1}$, the reflectivity for
224 the samples containing Y^{3+} is slightly lower than that for orthoclase in DIW, while the
225 differences for $q = 4-5 \text{ \AA}^{-1}$ are mostly within the statistical uncertainty of the datapoints. When
226 comparing the reflectivity between the datasets at 0.1 and 1 mM Y^{3+} , which were measured on
227 the same crystal, the observed changes in the reflectivity signal are most pronounced at the
228 higher $[Y^{3+}]$, which is likely due to an increasing amount of adsorbed Y^{3+} on the surface.

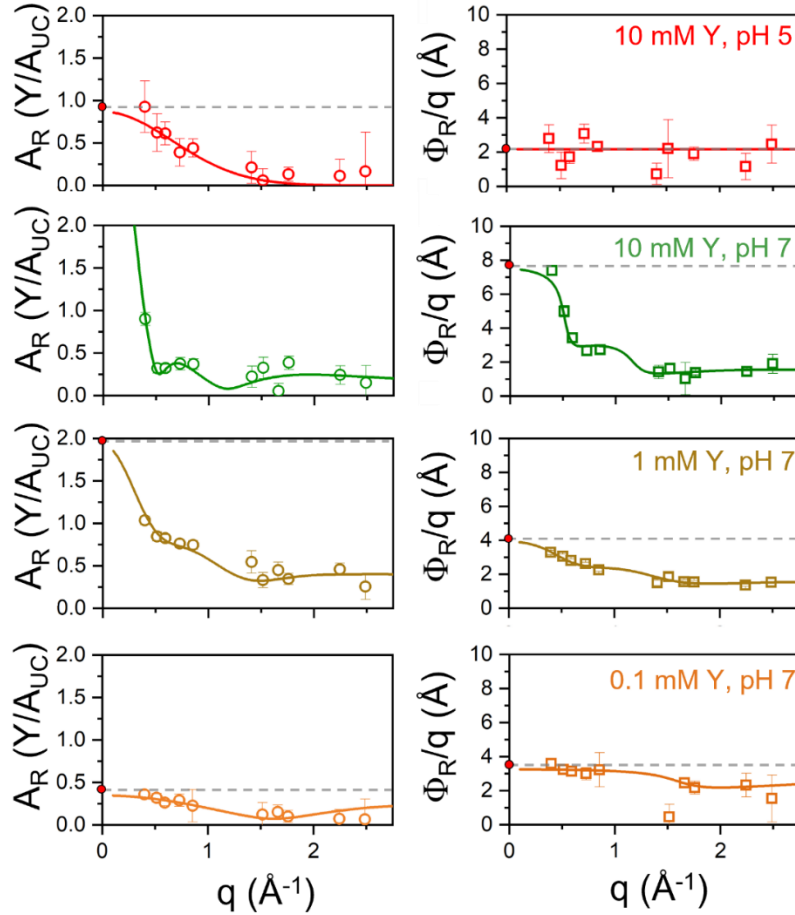
229 The sorption of Y^{3+} was also investigated at two pH values (5 and 7, **Figure 1**). These pH values
230 were chosen based on our previous powder study, which showed significant changes in sorption
231 quantity and structure within this pH range.³⁶ The observed trends in the variation of the CTR
232 intensity for the two investigated pH values are similar to those for the aforementioned Y^{3+}
233 concentration series, i.e., decreasing reflectivity for $q < 3 \text{ \AA}^{-1}$.



234

235 **Figure 1.** Non-resonant specular X-ray reflectivity of orthoclase (001) surfaces reacted with
 236 Y^{3+} -containing solutions at pH 5 and 7 at three different Y^{3+} concentrations (0.1, 1, and 10 mM)
 237 displayed using a vertical offset given next to each data set. For comparison the previously
 238 reported reflectivity data for the orthoclase (001) surface in DIW is added in blue.⁶⁶
 239

240 *RAXR spectra.* RAXR measurements were performed to probe the adsorbed distribution of Y^{3+}
 241 at the orthoclase (001) surface. All samples show RAXR modulations at the Y(III) X-ray
 242 absorption edge at 17.038 keV (Figures S3 and S4 in SI), showing larger differences between
 243 the samples than observed in the CTR data. A model-independent analysis of the RAXR spectra
 244 was used to obtain the amplitude A_R and phase Φ_R of the partial resonant structure factor (after
 245 Eq. 5, **Figure 2** symbols).⁶⁷ Also shown in **Figure 2** is the q -dependent variation of A_R and
 246 $\Phi_R(q)/q$ (lines) calculated from the best-fit models of the RAXR spectra (model-dependent
 247 analysis, cf. **Table 1**).



248

249 **Figure 2.** Amplitudes $A_R(q)$ (left) and phase $\Phi_R(q)/q$ (right) of the element-specific partial
 250 structure factors F_R as a function of momentum transfer q determined by model-independent
 251 (data points) and model-dependent (solid lines, cf. **Table 1**) analyses of RAXR spectra. The
 252 average sorption height \bar{z} and total Y coverage θ_{tot} of the adsorbed Y distribution can be
 253 estimated from the values of $A_R(q)$ and $\Phi_R(q)/q$ in the limit of $q \rightarrow 0$. The determined values
 254 based on best-fit models are indicated by dashed lines and filled, red dots.
 255

256 Two primary characteristics of the Y-distribution can be inferred directly from the RAXR
 257 spectra: the Y-coverage and its average height. The total coverage θ_{tot} can be estimated by the
 258 asymptotic value of $A_R(q)$ in the limit of $q \rightarrow 0$.⁶⁷ From this we observe that θ_{tot} increases with
 259 increasing $[Y^{3+}]$ from ~ 0.4 to $> 1 Y^{3+}/A_{UC}$ for $[Y^{3+}] = 0.1, 1, \text{ and } 10 \text{ mM}$ at pH ~ 7 (**Figure 2**
 260 left panel). The average Y^{3+} sorption height \bar{z} can be estimated by the value of $\Phi_R(q)/q$ in the
 261 limit of $q \rightarrow 0$ (i.e., $\bar{z} \approx \frac{\Phi(q)}{q} \Big|_{q \rightarrow 0}$).⁶⁷ The data suggest that $\bar{z} \sim 3\text{--}4 \text{ \AA}$ at $[Y^{3+}] = 0.1$ and 1 mM
 262 at pH 7 (**Figure 2**, right panel), values that are both small and similar in magnitude, suggesting
 263 an adsorption mode close to the surface. This result indicates that the Y^{3+} uptake differs between

264 the two samples (0.1 to 1 mM Y^{3+}), but no significant modifications in adsorbed ion speciation
265 are observed, supporting the transferability of the observed speciation information to lower
266 metal concentrations.

267 When [Y^{3+}] is further increased to 10 mM, the adsorbed Y^{3+} is located on average farther from
268 the surface, which can be seen from an increase of $\Phi_R(q)/q$ from $\sim 3\text{--}4$ Å to ~ 8 Å. At 10 mM
269 Y^{3+} at pH 5, an intermediate coverage of $\sim 1 Y^{3+}/A_{UC}$ is observed and \bar{z} is ~ 2 Å, which indicates
270 that Y^{3+} adsorbs on average closer to the surface at the lower pH. At first glance, this could be
271 interpreted as a larger amount of IS sorption for this condition. However, a detailed analysis of
272 the speciation at pH 7 (described below) indicates the existence of multiple species, and
273 therefore, the conclusion that Y^{3+} adsorbs generally closer to the surface at low pH is
274 misleading.

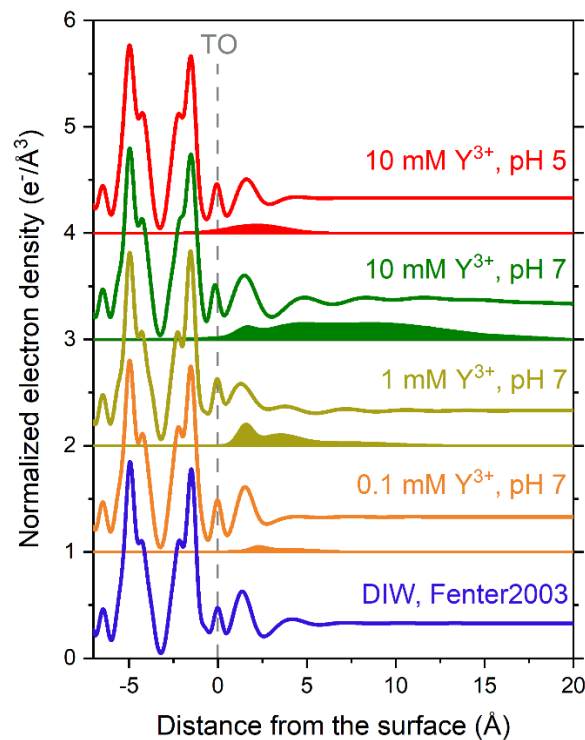
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276 3.2 Interfacial Structures and Adsorption Speciation of Y

277 The measured CTR and RAXR data were analyzed to extract the total and Y-specific vertical
278 electron density profiles of the orthoclase (001)–solution interface. The interfacial total electron
279 density profiles of the models that reproduced the CTR data best are displayed in **Figure 3**
280 (lines). Their structural parameters are summarized in Table S1 in the SI. The best-fit models
281 of the orthoclase–water interface all show surface-normal electron density profiles with an
282 ideally terminated surface orthoclase unit cell, the TOs at $z \sim 0$ Å, followed by a well-defined
283 peak, which is located for all samples at a distance of 1.3–1.6 Å. This peak, which is similar to
284 the one reported for the orthoclase (001)–water interface by Fenter et al.⁶⁶, can be attributed to
285 adsorbed water, which shows oscillatory features at larger distances up to ~ 7 Å from the
286 orthoclase surface.⁶⁸

287 An important aspect of the structure for interpretation of the surface charge is the coverage of
288 the outermost K^+ -ions. The experimental data could only be fitted satisfactorily when the

289 occupancy of the top K layer was reduced to a partially occupied layer, which is consistent with
 290 exchange of Na^+ against K^+ during storage of the crystals in NaCl and/or the release of Na^+/K^+
 291 from the mineral when the surface becomes hydrated.⁶⁶ A more detailed description of the
 292 influence of this parameter on the fit is given in Section 5 in the SI. In brief, the best-fit models
 293 were obtained for a half occupied top K layer, corresponding to an occupancy of $\sim 1 \text{ K}_{\text{top}}/\text{A}_{\text{UC}}$
 294 (see Tables S1 and S4 in SI). However, CTR is not an element-specific technique, and therefore
 295 it is not possible to distinguish between Na^+/K^+ and H_3O^+ in the top layers. This leads to the
 296 conclusion that the $c(\text{K}_{\text{top}})$ values given in Tables S1 and S4 are likely overestimated and
 297 provide only a lower limit for the K^+ release for an estimation of the surface charge ($1\text{--}2 \text{ e}^-$
 298 $/\text{A}_{\text{UC}}$) caused by cation exchange.



299

300 **Figure 3.** Best fit models of CTR and RAXR data of Y^{3+} adsorbed to orthoclase (001). The
 301 total electron density profiles (lines) and Y^{3+} contributions (filled areas) are displayed with a
 302 vertical offset of $1 \text{ e}^-/\text{Å}^3$ for each sample. The interfacial structure of orthoclase (001) in DIW
 303 (blue) was adopted from Fenter et al. for comparison.⁶⁶ TO marks the terminal oxygen groups,
 304 which are defined as crystal surface ($z = 0 \text{ Å}$, unrelaxed positions) in our structural model.

305

306 *Adsorbed Y speciation at pH 5.* The electron density profiles of adsorbed Y^{3+} are displayed as
307 filled areas in **Figure 3**. A summary of the parameters of the best-fit models of the RAXR data
308 is provided in **Table 1**. The best fit ($\chi^2 = 0.93$) Y distribution at 10 mM Y^{3+} at pH 5 is described
309 with a single broad peak with an occupancy of $0.86 \pm 0.22 Y^{3+}/A_{UC}$ centered at $2.2 \pm 0.2 \text{ \AA}$.
310 Other more complex models (e.g., with 2-peak adsorption structures) were explored for but did
311 not yield better fit results (see Section 4.1 in SI). Interestingly, this adsorbed structure is very
312 similar to the findings of a previous study on the adsorption of Sr^{2+} on orthoclase (001), for
313 which an adsorbed amount of $0.74 \pm 0.04 Sr^{2+}/A_{UC}$, centered at $2.00 \pm 0.05 \text{ \AA}$ under similar
314 experimental conditions (10 mM $SrCl_2$, pH 5.3) was observed (note that for comparison we
315 recalculated the literature coverages because values in the previous study were reported for $\frac{1}{2}$
316 of the orthoclase unit cell).⁵¹ This species was interpreted to be mainly an OS complex, with a
317 possible small contribution of IS, but the distinction between these scenarios was beyond the
318 experimental resolution of the data. Therefore, at pH 5 the adsorbed Y^{3+} species can be
319 interpreted to be mainly OS, which is consistent with the previous prediction from the surface
320 complexation models for K-feldspar powders.³⁶ One possible explanation for the poorly defined
321 sorption structure at this pH may be the physical separation of the two K^+ cavities, which are
322 mainly responsible for the surface charge at pH 5. In contrast to IS complexes, OS species are
323 expected to have a higher mobility and therefore less kinetic hindrance for (partial)
324 de/rehydration, allowing less-ordered adsorption in an intermediate position between the two
325 K^+ sites.

326

327 **Table 1.** Measured Y(III) coverages (θ_{tot}) by RAXR, as well as details of the best fit models of
 328 RAXR spectra of orthoclase (001) samples reacted in a solution of 0.1–10 mM YCl_3 at pH 5
 329 and 7.

[Y] (mM)	0.1	1	10	10
pH	7	7	7	5
θ_{tot} (Y/A _{UC})	0.43(15)	1.82(84)	5.3(19)	0.86(22)
IS Species				
z_1 (Å)	-	1.54(6)	1.56(14)	-
c_1 (Y/A _{UC})	-	0.55(8)	0.28(4)	-
u_1 (Å)	-	0.30*	0.30*	-
OS Species				
z_2 (Å)	2.26(26)	-	-	2.17(20)
c_2 (Y/A _{UC})	0.11(3)	-	-	0.86(22)
u_2 (Å)	0.30*	-	-	1.52(33)
z_3 (Å)	3.74(40)	3.43(32)	4.11(18)	-
c_3 (Y/A _{UC})	0.32(12)	0.72(34)	0.60(30)	-
u_3 (Å)	1.66(62)	1.04(33)	1.29(48)	-
Additional Species				
z_4 (Å)	-	7.0(17)	8.67(45)	-
c_4 (Y/A _{UC})	-	0.55(42)	4.4(16)	-
u_4 (Å)	-	2.5(14)	4.09(56)	-
Goodness of Fit				
χ^2	1.06	0.99	1.06	0.93
R-factor (%)	4.4	3.5	1.6	3.0

330 θ_{tot} : Total coverage (in Y/A_{UC}), z : height (Å) from the orthoclase surface, c : occupancy
 331 (Y/A_{UC}), and u : rms width (Å) of the Gaussian peaks. *fixed value. Errors are reported in
 332 brackets.
 333

334

335 *Adsorbed Y speciation at pH 7.* In contrast, the variation of $A_R(q)$ and $\Phi_R(q)/q$ for the samples
 336 at near neutral pH clearly indicate the presence of multiple adsorbed Y^{3+} species. The Y electron
 337 density at the lowest investigated $[Y^{3+}]$ (0.1 mM, **Figure 3**) is broadly distributed and is
 338 described by two peaks, one at 2.3 ± 0.3 Å and the other at 3.7 ± 0.4 Å, with a total Y coverage
 339 of 0.43 ± 0.15 Y/A_{UC}. The first peak has a similar distance from the surface as the species
 340 described above for pH 5. Therefore, it probably represents here also an OS species with a small
 341 contribution of an IS complex, which cannot be distinguished from the OS species at such small
 342 amounts.

343 Higher coverages are obtained at 1 and 10 mM Y^{3+} . The first peak is located at a distance of
344 $\sim 1.55 \pm 0.10$ Å from the TO planes for both samples. This value indicates that the first hydration
345 shell of the Y^{3+} aquo ion (2.36 Å)⁶⁹ was partially removed and therefore this peak represents an
346 IS complex. The rms width of this species was fixed at a small value (0.3 Å) to represent a well-
347 defined adsorption height. The IS complex has a rather small (< 30 % of θ_{tot}) contribution to
348 the overall Y electron density with a coverage of < 0.6 Y^{3+}/A_{UC} (cf. **Table 1**). A second peak is
349 located at larger distances from the orthoclase surface, centered at ~ 3 – 4 Å from the TOs. The
350 observed distance is between the radii of the first and second hydration shells (2.36 and
351 4.40 Å)⁶⁹ of the Y^{3+} aquo ion, and would therefore be consistent with an OS sorption complex.
352 This distance is slightly larger than distances of the OS complex found at low pH, but in good
353 agreement with values reported for OS complexes of Y^{3+} on muscovite (4.1 – 4.3 Å).⁷⁰
354 The fit quality for the datasets at 1 and 10 mM YCl_3 at pH 7 was improved by including a third
355 species (see Section 4.2 in SI). This additional species is characterized by its large and poorly
356 defined distance from the surface extending up to large distances (10 – 20 Å) from the surface.
357 While for 1 mM Y^{3+} this species still has a low occupancy (0.55 ± 0.42 Y/A_{UC}), at 10 mM Y^{3+}
358 a large quantity of adsorbed Y of 4.42 ± 1.56 Y/A_{UC} is present in this form. Although only one
359 RAXR spectrum, at lowest measured $q = 0.4$ Å⁻¹, indicates the very high Y coverage of
360 > 1 Y/A_{UC} for the dataset at 10 mM (see **Figure 2**), the very broad distribution of Y electron
361 density is supported by three data points in the phase plot ($q < 0.6$ Å⁻¹), making the fit results
362 reasonably robust.

363 It should be noted that the experimental conditions for the 1 and 10 mM solutions were close
364 to the solubility limit of $Y(OH)_3$ (see Experimental section for details). The sample surface was
365 mounted on the diffractometer vertically, meaning that precipitates would not deposit onto the
366 crystal surface by sedimentation. However, precursors of the hydroxide phase in the solution
367 could be attracted to the surface, depending on their charge. In addition, it cannot be excluded
368 that locally increased $[Y^{3+}]$ concentrations at the interface induced a heterogeneous formation

369 of an amorphous $\text{Y}(\text{OH})_3$ surface precipitate, causing the large contribution of this species to
370 the Y electron density. However, the CTR data do not show any evidence for any crystalline
371 precipitates on the orthoclase (001) surface.

372 It should be pointed out here that the estimated \bar{z} in the $\Phi_{\text{R}}(q)/q$ plot (cf. **Figure 2** right) was
373 larger at pH 7 ($> 3 \text{ \AA}$) than at pH 5 ($\sim 2 \text{ \AA}$), which could be misinterpreted as adsorption species
374 moving farther away from the mineral surface with increasing pH. However, this is only
375 partially true since \bar{z} represents the average height of adsorbed Y species. While at pH 5, only
376 one OS species is observed and therefore \bar{z} matches z given in **Table 1**, this is not the case for
377 the sample at pH 7, where several species are present. The contribution of additional species
378 far away from the surface at pH 7 leads to the observed \bar{z} of $\sim 8 \text{ \AA}$. However, the detailed
379 analysis of the RAXR data shows the presence of a well-defined IS complex (1.55 \AA), which is
380 in fact adsorbed closer to the surface than the OS complex (2.17 \AA) found at pH 5.

381 *Y coverage.* The obtained total and species-specific coverages are summarized in **Table 1**.
382 Overall, Y coverages at pH 7 increase as expected from 0.43 ± 0.15 to 1.82 ± 0.84 and
383 $5.30 \pm 1.90 \text{ Y}^{3+}/\text{A}_{\text{UC}}$ with increasing Y^{3+} concentration of 0.1, 1, 10 mM Y^{3+} , respectively. An
384 increase of the pH value also leads to a strong increase of the total Y coverage at 10 mM Y^{3+}
385 from $0.86 \pm 0.22 \text{ Y}^{3+}/\text{A}_{\text{UC}}$ at pH 5 to $5.30 \pm 1.90 \text{ Y}^{3+}/\text{A}_{\text{UC}}$ at pH 7. The error bars of the
386 coverages are relatively large, especially for samples with high coverages. This is mostly caused
387 by the large uncertainty of the species at large distances from the surface. Therefore, we
388 conservatively estimate the adsorbed Y^{3+} coverage as a range using the sum of the IS and OS
389 coverages, i.e., $0.4 - 1.2 \text{ Y}/\text{A}_{\text{UC}}$. The additional Y sorbed farther from the surface than the IS
390 and OS complexes may be due to the initial onset of precipitation (cf. additional species in
391 **Table 1**). The trends in Y^{3+} uptake identified for changes in pH and $[\text{Y}^{3+}]$ are consistent with
392 the trends described in previous studies on K-feldspar powder, which show increased sorption
393 with increasing metal concentration and pH.³⁵⁻³⁷

394

395 **3.3. Structure of the Inner-Sphere Sorption Complex**

396 X-ray reflectivity was used to gain insight into the sorption structure of Y(III) on the orthoclase
397 (001) surface. An IS complex at a distance of ~ 1.5 Å from the TO plane was identified based
398 on the RAXR results. From this observation certain binding geometries of the IS complex can
399 be excluded (see Section 6 in SI for illustrations): (1) No Y electron density was found for $z < 0$,
400 indicating that direct cation exchange at the K^+ site, similar to the previously reported
401 mechanism for Rb^+ ,⁵¹ is not observed in the case of Y^{3+} . Although the ionic radius of Y^{3+} is
402 smaller ($Y^{3+}_{CN9} = 107.5$ pm, $Rb^+_{CN9} = 163$ pm),⁷¹ its large and strongly bound hydration shell
403 presumably makes cation exchange in the K^+ cavity energetically unfavorable. (2) A tridentate
404 or even higher denticity of the sorption complex is unlikely to form on the orthoclase (001)
405 surface. The distances between the TOs are large ($5.10 - 8.54$ Å, see Figure S1 in SI), which
406 would lead to very long Y-O bond lengths in the sorption complex. (3) A bidentate,
407 mononuclear sorption complex, as observed for UO_2^{2+} experimentally for orthoclase powder⁷²
408 and theoretically (MD simulations) also for the (001) surface⁵⁶ seems unreasonable, since each
409 aluminosilicate tetrahedron has only one TO on the (001) surface and therefore, the second
410 bond would correspond to a bridging oxygen. Based on the observed average sorption height
411 of ~ 1.5 Å, a bidentate, mononuclear sorption complex would require a very asymmetric
412 sorption complex with an unrealistically long bond to the bridging oxygen of 3.8 Å (Figure S9
413 in SI) as compared with the typical Y-O distance of $\sim 2.2-2.5$ Å observed in many Y-containing
414 oxides.^{73,74} (4) Last, a monodentate, mononuclear sorption complex, in which Y^{3+} forms a
415 chemical bond with one of the TOs, with a relatively short Y-O bond length of ~ 1.5 Å also
416 seems unlikely (Figure S10 in SI).

417 The results presented in this study therefore suggest that the Y binding motif is a bidentate,
418 binuclear sorption complex in one of two surface locations: (A) with Y^{3+} located between the
419 two symmetry-equivalent TO1s (Site A, $d(TO1-TO1) = 3.72$ Å) in the middle of the (001) unit

420 cell shown in Figure S11, or (B) between TO1 and TO2, with $d(\text{TO1-TO2}) = 5.10 \text{ \AA}$ (Site B,
421 Figure S12 in SI). Considering the vertical distance from the TO layer of $\sim 1.5 \text{ \AA}$, simple
422 geometric calculations can estimate the Y-O bond length in such a triangular complex, resulting
423 in values of 2.46 \AA for Site A and 3.05 \AA for Site B. In particular, the value for Site A is in the
424 same range as observed for IS sorption complexes of lanthanides and Am(III) on $\gamma\text{-Al}_2\text{O}_3$ and
425 clay minerals ($2.28\text{--}2.50 \text{ \AA}$)⁷⁵, making this binding geometry the most plausible. However,
426 further studies will be needed to support this suggestion with experimental data. This could for
427 example be achieved by the measurement of off-specular X-ray reflectivity data, which could
428 identify laterally ordered structures and therefore, enable the determination of a three-
429 dimensional binding geometry of sorption complexes.^{76,77}

430

431 **3.4. Orthoclase Surface Charge and Compensation by Adsorbed Ions**

432 The results presented in this study enable insights into the orthoclase surface charge, which
433 originates from two different sources: (1) The pH-independent release of K^+ from the surface
434 layer, which was observed to be between $\sim 50\text{--}100 \%$ of the $2 \text{ K}_{\text{top}}/\text{A}_{\text{UC}}$. Therefore, the
435 contribution of this source of charge can be estimated to be $\sim 1\text{--}2 \text{ e}^-/\text{A}_{\text{UC}}$, which corresponds to
436 $-0.14\text{--}0.28 \text{ C/m}^2$. (2) A pH-dependent surface charge of the $4 \text{ TOs}/\text{A}_{\text{UC}}$ that can be deprotonated
437 at high pH, theoretically leading to an additional $4 \text{ e}^-/\text{A}_{\text{UC}}$ if they were to fully deprotonate.
438 Considering these two factors, the charge of orthoclase (001) can theoretically be as high as 6
439 $\text{e}^-/\text{A}_{\text{UC}}$ or -0.84 C/m^2 , which is much higher than reported values for crystallographic planes of
440 other common mineral phases, e.g. -0.02 C/m^2 for calcite (104)⁷⁸, -0.11 C/m^2 for quartz (101)
441 at pH 9.8⁷⁹ or -0.34 C/m^2 for the muscovite (001) basal plane.²⁵ While the high surface charge
442 of orthoclase (001) induces a high potential to retain cationic species, the theoretical maximum
443 surface charge is probably not achieved due to electrostatic repulsion between the negative
444 charges.

445 In more detail, at pH 5 only ~30 % of surface TOs are expected to be deprotonated, indicating
446 that the contribution of pH-dependent surface charge will be small ($\sim 1 e^-/A_{UC}$, see Section 7 of
447 SI).^{36,51} Under these conditions higher quantities of species that keep large parts of their
448 hydration shell, i.e. OS species, are observed. It can therefore be concluded that in the case of
449 orthoclase the negative surface charge is an important driving force to replace water molecules
450 from the coordination sphere and form IS complexes. The coverage at pH 5 is $0.86 Y^{3+}/A_{UC}$,
451 which can compensate as much as $2.58 e^-/A_{UC}$. At pH 7, ~60 % of the TOs are deprotonated
452 and therefore their contribution to pH-dependent surface charge is more significant ($\sim 2.4 e^-$
453 $/A_{UC}$). The estimated total surface charge at pH 7 is $\sim 3.4\text{--}4.4 e^-/A_{UC}$ and the theoretical amount
454 of adsorbed Y^{3+} needed for surface charge compensation is $\sim 1.13\text{--}1.47 Y^{3+}/A_{UC}$. The RAXR
455 results for the sample at 1 mM Y^{3+} at pH 7 show a total uptake of $1.27 \pm 0.42 Y^{3+}/A_{UC}$ (not
456 considering the contribution of species 3 for the reasons mentioned in Section 3.2), which is in
457 the expected range and indicates full compensation of the estimated surface charge.
458 It is interesting that a monolayer of the bidentate IS complex with the proposed structure that
459 has two equivalent bidentate sites/ A_{UC} would theoretically lead to a maximum IS coverage of
460 $2 Y^{3+}/A_{UC}$. However, the RAXR data clearly show that in fact the coverage of the IS complex
461 is relatively low, with values of $< 0.6 Y^{3+}/A_{UC}$, meaning that only ~ 30 % of available bidentate
462 sites are occupied by IS complexes.

463

464 **3.5. Current Understanding of Adsorption of Trivalent Heavy Metal Ions on** 465 **Feldspars**

466 *Batch sorption studies.* At this point, a comparison to available literature studies provides a
467 comprehensive view on the adsorption of trivalent heavy metal ions on K-feldspar. First, our
468 study was able to shed light on the molecular structure of the formed IS complex. The single
469 type of bidentate IS complex found here is consistent with spectroscopic results reported in our

470 previous study using K-feldspar powder, in which one type of IS complex and its two hydrolysis
471 forms (which would be indistinguishable for X-ray reflectivity) were identified.³⁶ Moreover,
472 for surface complexation modeling of the K-feldspar powder, a bidentate coordination of the
473 IS complex was assumed based on the fact that this is often described to be the most common
474 case⁸⁰ and yielded reasonable and robust results. Our newest findings on the sorption structure
475 support this assumption and underline the robustness and reliability of the developed surface
476 complexation model, confirming that molecular level studies on single-crystal model systems
477 can be employed to understand powder studies. The major difference is found in the ratio of IS
478 to OS species, which depends strongly on the ratio of available adsorption sites to metal ions in
479 solution. Powder studies usually show higher amounts of IS sorption due to the large excess of
480 surface area of the mineral powder leading to 100 % metal uptake from solution.

481 *Single crystal studies.* The results can also be compared to the only study available for sorption
482 of Cm^{3+} on macroscopic K-feldspar crystals,³⁸ combining autoradiography for quantification of
483 Cm uptake and TRLFS for structural investigations of the sorption complexes. Although the
484 comparability is limited due to differences in metal concentration (1 μM Cm^{3+} vs. 0.1–10 mM
485 Y^{3+}), measurement mode (*ex situ* for TRLFS, where sample preparation partially desorbs OS
486 sorption complexes,^{21,81} and *in situ* for (XR), and surface roughness, a few general similarities
487 and differences can be identified: (1) The observed total coverages from both analysis
488 techniques are in the same order of magnitude. TRLFS reported $\sim 0.3 \text{ Cm}^{3+}/\text{nm}^2$ at pH 5.5 and
489 $\sim 1.4 \text{ Cm}^{3+}/\text{nm}^2$ at pH 7 for areas of ‘smooth’ surface topography and the adsorbed amount of
490 Y^{3+} found by RAXR is $\sim 0.84 \text{ Y}^{3+}/\text{nm}^2$ at pH 5 and $\sim 0.4 - 1.3 \text{ Y}^{3+}/\text{nm}^2$ at pH 7 (not considering
491 the species at large distance from the surface), depending on $[\text{Y}^{3+}]$. (2) Regarding the speciation
492 of adsorbed Y^{3+} , Demnitz et al. report a continuous distribution of adsorbed Cm species with
493 1–9 remaining H_2O in the Cm^{3+} hydration shell. This observation is consistent with the broad
494 distribution of Y electron density observed here. TRLFS identifies weak IS sorption (7–8

495 remaining H₂O) as the dominant species at both investigated pH values. This species is probably
496 consistent with the species that we interpreted as OS species (9 H₂O) in this study. The change
497 in sorption height caused by removing 1 or 2 water from the hydration shell is probably difficult
498 to differentiate by XR. Consistent with the IS complex observed at 1 and 10 mM Y(III) at pH
499 7 here, Demnitz et al. find a larger contribution of species with < 4 remaining hydration water
500 molecules with increasing pH.³⁸

501 *Comparison to other mineral phases.* The described sorption behavior can be put into context
502 with other mineral phases. For example, the sorption of Y on orthoclase (001) at pH 5 seems to
503 be similar to the sorption of multivalent cations on muscovite (001).^{31,70} While the surface
504 charge of muscovite (001) is mostly pH-independent and therefore the impact of pH on the
505 adsorption of ions is small, this is not true for orthoclase (001). While the surface charge of
506 muscovite (001) is mostly pH-independent and therefore its impact on the adsorption of ions is
507 small, this is not true for orthoclase (001).

508 The additional contribution of deprotonated TOs to the overall surface charge leads to the
509 increased formation of well-ordered IS complexes of Y³⁺ on orthoclase (001) at near neutral
510 pH. Therefore, the maximum retention of Y³⁺ by orthoclase ($\theta_{\text{tot}} = 1.72 \text{ Y}^{3+}/\text{nm}^2$) is higher than
511 by muscovite ($\theta_{\text{tot}} = 1.28 \text{ Y}^{3+}/\text{nm}^2$) at the same metal concentration (1 mM). The sorption
512 behavior found for orthoclase at near neutral pH is in fact more similar to the adsorption
513 behavior known for oxide mineral rutile (110) (TiO₂), that adsorbs Y³⁺ predominantly as a
514 tetradentate IS sorption complex.⁸²

515 The results reported in this study clearly demonstrate a very high potential for orthoclase (001)
516 to retain Y³⁺ ($\theta_{\text{tot}} = 2.86 \mu\text{mol}/\text{m}^2$). This appears to be caused by its two sources of surface
517 charge, release of K⁺ and pH-dependent surface site deprotonation. On a fundamental level, we
518 can make a connection between the source of surface charge and dominant sorption speciation.
519 When the orthoclase surface charge is mainly caused by release of cations from the crystal

520 structure, multivalent ions have been observed to adsorb predominantly in the form of OS
521 complexes.⁵¹ In contrast, IS complexes on orthoclase are preferably formed when surface sites
522 are deprotonated. Orthoclase is unique in this context as its dominant source of surface charge
523 changes with pH. While cation release and OS sorption are found close to the point of zero
524 charge (i.e., pH ~ 2.5³⁶), surface site deprotonation and subsequent IS adsorption are found on
525 orthoclase (001) for near-neutral and alkaline pH values (> 6).

526

527 **3.6. Environmental Implications**

528 Our results improve the current understanding of the retention of trivalent heavy metal ions by
529 K-feldspars on the molecular level. This and previous work showed the high potential of
530 feldspars to retain trivalent heavy metal ions, by an increasing amount of IS sorption with
531 increasing pH.^{36,37} The consistency between this study and previous works supports the
532 applicability of the models developed for K-feldspar powders to macroscopic orthoclase
533 crystals, and therefore to more realistic scenarios, which certainly are in between the two
534 extremes studied: mineral powders and gem-quality single crystals. This work shows that the
535 formed molecular species appear to be similar for mineral powders and mineral crystals over
536 large concentrations range, but the total coverage and the ratio of IS to OS species differ due to
537 the different ratio of available sorption sites to metal ions in the aqueous phase.

538 Therefore, the molecular level findings of this study can be transferred to lower metal
539 concentrations,⁸³ as they will be present in the environment, for example at REE acid mine
540 drainage sites.^{8,12-15} Although the orthoclase (001) cleavage plane investigated here may not be
541 representative for all naturally existing crystal orientations, it will present a significant extent
542 of the exposed surface area.⁸⁴ In consequence, the basal planes control adsorption of cations,
543 despite the presence of other more energetically favorable sites, as was previously shown in a
544 computational study on muscovite mica.⁴³ Overall, the results presented here are therefore

545 closely related to phenomena occurring in some natural systems, e.g. a crystalline rock fracture
546 exposing mm-sized feldspar grains, while providing molecular level structures which can be
547 used to derive reaction equations required for the correct thermodynamic description of the
548 sorption process.
549

550 **Associated content**

551 Supporting Information. Structure of Orthoclase (001) Surface, Experimental Details and Data
552 Analysis of XR Data, Full XR Data Sets and Model Parameters, Alternative Models for RAXR
553 Data, Discussion on Impact of Occupancy of Top K layer, Illustration of (im)possible Binding
554 Motifs of Inner-Sphere Complex, Calculation of Site Deprotonation of Orthoclase (001).

555

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