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## **Heterogeneous sorption of radionuclides predicted by crystal surface nanoroughness**

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### **ABSTRACT**

Reactive transport modeling (RTM) is an essential tool for the prediction of contaminants' behavior in the bio- and geosphere. However, RTM of sorption reactions is constrained by the surface site assessment. The reactive site density variability of the crystal surface nanotopography provides an “energetic landscape”, responsible for heterogeneous sorption efficiency, not covered in current RTM approaches. Here, we study the spatially heterogeneous sorption behavior of Eu(III), as an analogue to trivalent actinides, on a polycrystalline nanorough calcite surface and quantify the sorption efficiency as a function of surface nanoroughness. Based on experimental data from micro-focus time-resolved laser-induced luminescence spectroscopy ( $\mu$ TRLFS), vertical scanning interferometry (VSI), and electron back-scattering diffraction (EBSD), we parameterize a surface complexation model (SCM) using surface nanotopography data. The validation of the quantitatively predicted spatial sorption heterogeneity suggests that retention reactions can be considerably influenced by nanotopographic surface features. Our study presents a way to implement heterogeneous surface reactivity into a predictive SCM for enhanced prediction of radionuclide retention.

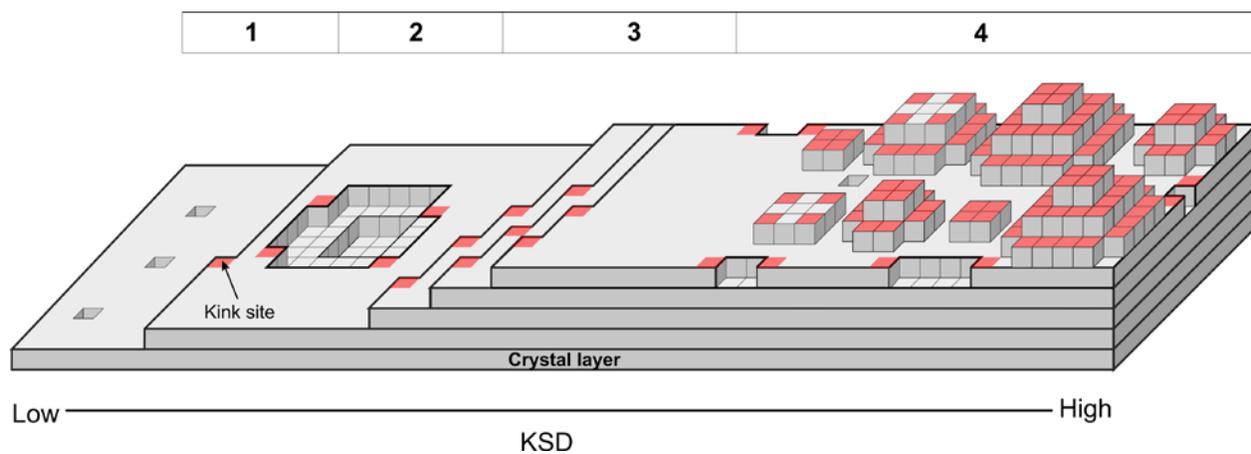
Keywords: Sorption reactions, Crystal surface reactivity,  $\mu$ TRLFS, Surface complexation modeling, Radionuclide migration

## 1 INTRODUCTION

2 The potential migration of actinides constrains the safety assessment of disposal concepts for  
3 nuclear waste in deep geological formations. Such concepts for underground storage facilities  
4 require reliable predictions for 100,000s of years to diagnose potential migration of stored  
5 radionuclides into the biosphere. Reactive transport models are crucial in providing such  
6 predictions and the heterogeneity of physicochemical input values defines the reliability of the  
7 numerical results. A key challenge is the upscaling of the molecular processes to quantify the  
8 radionuclide retention processes, bridging the gap from laboratory scale experiments to large scale  
9 facilities. Molecular mechanistic insights are provided experimentally and analytically by  
10 spectroscopic techniques such as Time-Resolved Laser Fluorescence Spectroscopy (TRLFS)<sup>1, 2</sup>,  
11 and Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS)<sup>3, 4</sup>, and numerically by  
12 molecular dynamic simulations (MD), providing insights into the structure of the adsorbed ions at  
13 specific surface sites<sup>5, 6</sup>. Upscaling and implementing these insights into continuum scale reactive-  
14 transport models is challenging because of the intrinsic variability of surface reactivity at the pore  
15 scale. Typical RTM approaches employ uniform surface parameters such as specific surface area  
16 (SSA) and site density, uniform electrostatic diffuse layer potentials, and simplified uniform  
17 surface protonation models to simulate adsorption processes of radionuclides through various  
18 surface complexation reactions implemented by surface complexation models (SCM)<sup>7-13</sup> to yield a  
19 simple retention coefficient in RTM at the continuum scale<sup>14-16</sup>. Consequently, simplifications such  
20 as the assumption of macroscopically homogeneous behavior<sup>17</sup> as well as surface area  
21 normalizations<sup>18</sup> are commonly applied. These simplifications limit our ability to model and predict  
22 the consequences of varying surface reactivity.

23 Analytically, the recent development of the  $\mu$ TRLFS technique allows us to identify interfacial  
24 speciation with  $\mu$ m-spatial resolution and the very high sensitivity required to investigate surface

25 complexes<sup>19, 20</sup>. This technique revealed heterogeneous sorption behavior of the trivalent actinide  
26 analog Eu(III) on a granite rock surface that cannot be quantitatively explained by mineral type  
27 and composition alone<sup>19</sup>. Consequently, insight into the intrinsic variability of surface reactivity is  
28 required to improve our predictive capabilities of reactive transport processes<sup>21</sup>. The surface  
29 reactivity may depend on several factors, including crystal defects and surface nanotopography as  
30 well as crystal orientation. From an energetic point of view, a dominant factor is the kink site  
31 density (KSD) of the crystal surface.<sup>22</sup> Figure 1 illustrates different nanotopographic configurations  
32 of the crystal surface with specific kink site densities. With increasing KSD, these include (1)  
33 atomically flat terraces with point defects, (2) etch pits walls with steps and kinks resulting from  
34 dissolution processes, (3) surface steps with kinks along cleavage planes, and (4) very rough  
35 surface portions with a multitude of edge and kink sites owing to mechanical treatment (polishing,  
36 grinding, preparation of powdered sample material) of crystalline matter. Previous studies  
37 suggested that increasing KSD results in enhanced surface reactivity for, e.g., sorption<sup>23</sup>.



38  
39 **Figure 1** Schematic representation of nanotopographic characteristics of a crystal surface, showing  
40 (1) an atomically flat terrace with point defects, (2) an etch pit wall with steps and kinks, (3) surface  
41 steps with kinks due to crystal cleavage, and (4) a very rough surface due to mechanical treatment  
42 such as polishing. Kink sites are marked in the red color and the kink site density increases from  
43 left to right in this scheme.

44 Here, we investigate the sorption of Eu(III) on calcite to experimentally exemplify the variability  
45 of surface reactivity as a function of surface nanotopography of monomineralic but polycrystalline  
46 collector surfaces during sorption processes. Eu(III) serves as a luminescent probe with excellent  
47 spectroscopic properties<sup>24</sup> and a chemical analogue for the trivalent actinides, some of which  
48 (Am(III), Pu(III)) determine the radiotoxicity of nuclear wastes over 100,000s of years. Calcite was  
49 selected as one of the most widely distributed mineral phases in the earth's crust, with demonstrated  
50 importance for the migration of radionuclides<sup>25</sup> and other contaminants in the geosphere<sup>26</sup>, by both,  
51 the complexation reactions at the mineral surface<sup>27, 28</sup> as well as incorporation processes within the  
52 crystal lattice.<sup>25, 29</sup> Due to the presence of only a single mineral phase in this study, we can exclude  
53 mineralogical effects and instead focus on the surface energy variability induced by crystallography  
54 or topography. Our strategy is the quantitative mapping of surface sorption efficiency data,  
55 including information about speciation and hydration of Eu(III) using  $\mu$ TRLFS<sup>19</sup>. These data are  
56 correlated with surface nanotopography maps from vertical scanning interferometry and crystal  
57 orientation data from electron backscatter diffraction (EBSD) analysis. The spatially-resolved  
58 information allows us to parameterize an improved SCM using surface nanoroughness data that  
59 account for heterogeneities in crystal surface energy, and which makes it possible to predict  
60 heterogeneous sorption behavior. The modeling results were validated using experimental data  
61 from  $\mu$ TRLFS.

## 62 **METHODS**

63 **Experimental setup.** Two calcite samples were utilized to investigate the effect of the different  
64 nanotopographical endmembers on the sorption efficiency of Eu(III) on the crystal surface. One  
65 sample was a polished calcite crystal with a high density of edge and kink sites due to its rough  
66 surfaces (manufacturer: KORTH Kristalle GmbH, Altenholz, polished along (10-14), the other is  
67 a cleaved calcite surface (calcite island spar, Chihuahua, Mexico, WARD's 46E1438) with varying

68 degrees of step densities analyzed by VSI. The two samples were exposed to  $10^{-6}$  M aqueous  
69 [ $^{152}\text{Eu}$ ] $\text{Eu}(\text{NO}_3)_3$  in 0.1 M NaCl solution [at pH 7.5 by immersing their surface upside down in the  
70 solution for 15 minutes. No alterations of the surface topography are detected using interferometry  
71 microscopy surface analysis. The sorption was quantified via autoradiographic imaging using a  
72 BAS-IP SR storage phosphor screen that was read out with a pixel size of 25  $\mu\text{m}$  after exposure  
73 using an Amersham Typhoon Biomolecular Imager (GE Lifesciences). Absolute concentrations  
74 were yielded by calibration of the image in ImageJ using a series of europium standards of known  
75 concentration.

76 As a second step, the investigations were then expanded to a more realistic system with respect to  
77 calcite-bearing host rocks. Another sorption experiment was performed using polycrystalline  
78 calcite. A cylindrical drilled marble sample (diameter: 1.5 cm, length: 1 cm, Großsoelk, Austria,  
79 composition: calcite (95 wt. %), quartz (< 2 wt. %), muscovite (< 1 wt. %), phlogopite (< 1 wt. %)  
80 and ore minerals (<1 wt. %) <sup>30</sup>, was polished using an oil-based mono-crystalline diamond  
81 suspension (crystal size: 50 nm) and partially masked with a layer of 550 nm of gold <sup>31</sup> as a height  
82 reference for surface analysis at the nanometer scale. To identify the crystallographic orientation  
83 of the crystal grains in the sample surface a grid of 200 x 150 points (resolution: 10  $\mu\text{m}$ ) was  
84 analyzed with EBSD using a Zeiss NVision 40 scanning electron microscope equipped with a  
85 Bruker eFlash<sup>Hr</sup>- detector and a QUANTAX CrystAlign EBSD-System (acceleration voltages:  
86 10kV, beam current: 2.5nA). <sup>32</sup> First, to provide a surface roughness variability similar to what is  
87 expected in natural systems after diagenetic reactions, a dissolution experiment was performed by  
88 reacting the sample surface with air-equilibrated, aqueous 2.2 mM  $\text{Na}_2\text{CO}_3$  at pH 8.8 for 1 hour  
89 using a custom-made flow-through cell (cell volume: 300  $\mu\text{L}$ , flowrate: 30 mL/h). The  
90 experimental conditions are identical to those described in the literature for studying dissolution  
91 kinetics of calcite surfaces at far-from-equilibrium conditions <sup>22</sup>. Second, a batch europium sorption

92 experiment was conducted by immersing the sample surface into a solution of  $10^{-5}$  mol/L  $\text{Eu}(\text{NO}_3)_3$   
93 and 0.1 mol/L NaCl with a pH value of 8.5 for 24 hours. In this step, the larger concentration and  
94 longer sorption period were made necessary to enable the  $\mu\text{TRLFS}$  studies<sup>19, 20</sup>. The sample was  
95 then rinsed with the background solution and dried. Spatially resolved information on the europium  
96 sorption efficiency and the adsorbed species was gained using  $\mu\text{TRLFS}$  mapping of a  $0.5 \text{ mm} \times$   
97  $1.5 \text{ mm}$  subsection with a spatial resolution of  $20 \text{ }\mu\text{m}$ .

98 The surface topographies of all the samples were analyzed using a Sensofar S neox white-light  
99 vertical scanning interferometer equipped with Nikon DI interferometry objectives for  $20 \times$ ,  $50 \times$ ,  
100 and  $100 \times$  magnifications (see SI, Table S1 for detailed specifications).

101  **$\mu\text{TRLFS}$ .**  $\mu\text{TRLFS}$  measurements were conducted with a setup designed in-house as described in  
102 Molodtsov et al. 2019<sup>19</sup>. The laser beam was provided by a pumped (Surelite SL I-20 @ 355 nm,  
103 Continuum) dye laser (NarrowScan @ Exalite 389/398 1:1 mix, Radiant Dyes). The pulse energy  
104 was set to approximately  $20 \text{ }\mu\text{J}$  to prevent possible laser ablation. The wavelength was fixed at 394  
105 nm to maximize the light absorption of  $\text{Eu}^{3+}$  ( ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$  transition) resulting in higher sensitivity  
106 for luminescence detection<sup>24</sup>. The laser beam was focused by a 50x long-distance objective  
107 (MLWD-50X, Newport) to a spot with approximately  $20 \text{ }\mu\text{m}$  in diameter. The sample surface was  
108 aligned to the focal plane of the laser beam with a z-stage (KT-RS60, Zaber) and then scanned in  
109 a  $20 \text{ }\mu\text{m}$  grid with an x-/y-stage (M-423 driven by TRB25CC and controlled with CONEX-CC,  
110 Newport). The gathered luminescence light was redirected to the detector (Shamrock SR303i  
111 spectrograph combined with DH320T-18U-63 iCCD camera, Andor) to collect the full spectral  
112 information in each data point. Spectra were measured with 100 accumulations over 5 seconds in  
113 total with a gate width and exposure time of the iCCD of 10 ms. To evaluate the data a python-  
114 based software (picroTRLFS EVAL, HZDR) was used. The spectra were analyzed with respect to  
115 the peak areas of the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  ( ${}^7\text{F}_1$ ) and  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  ( ${}^7\text{F}_2$ ) transitions and their fluorescence decays

116 after applying a linear background correction. The fluorescence intensity (sum of peaks  ${}^7F_{1+} + {}^7F_2$ )  
117 is correlated to the number of Eu(III) atoms and therefore corresponds to the sorption efficiency.  
118 The sorption efficiency of each pixel was calculated by normalizing the peak sum by the highest  
119 measured luminescence signal. The luminescence peak ratio ( $F_2/ F_1$ ) corresponds to the sorption  
120 strength and also serves as a distinguishing indicator for speciation because the  $F_2$  peak is a  
121 hypersensitive electric multipole transition, and its intensity reacts strongly to changes in Eu(III)'s  
122 chemical surroundings, while the  $F_1$  peak as a magnetic dipole transition is mainly unaffected.<sup>24</sup>  
123 Lifetimes of the luminescence decays were recorded in several selected data points. The  
124 luminescence decay patterns could be reconstructed by bi-exponential decay functions with a fixed  
125 long lifetime of 3600  $\mu$ s, which represents the well-known lifetime of the  $\text{Eu}^{3+}$  incorporation  
126 species into the crystal lattice of calcite.<sup>25</sup> This fixation is useful because the long-lived species  
127 usually have a quite low luminescence intensity, which is therefore much more affected by  
128 background correction uncertainties. As a result, the short lifetime can then be determined much  
129 more reliably. In some cases, the observed luminescence decay pattern was described by a mono-  
130 exponential decay function for residual-minimization purposes. The resulting lifetimes were then  
131 correlated to the number of remaining water molecules  $n(\text{H}_2\text{O})$  in the first coordination sphere of  
132  $\text{Eu}^{3+}$  by the empirical equation<sup>33,34</sup>:

$$133 \quad n(\text{H}_2\text{O}) \pm 0.5 = \frac{1.07}{\tau} - 0.62, \quad (1)$$

134 where  $\tau$  denotes the measured luminescence lifetime (in a unit of ms). The value of  $n$  can range  
135 from zero (incorporation) up to nine remaining water molecules (fully hydrated  $\text{Eu}^{3+}$  aquo ion).  
136 Intermediate amounts of water molecules left correspond to inner sphere complexation of the  $\text{Eu}^{3+}$   
137 ion, here sorption to the calcite surface.

138 **Sorption data analysis.** Areas of different quantities of sorption were identified in the  
139 autoradiogram of the polished and cleaved samples and representative high-resolution topography

140 images were recorded. The sorption data on the polycrystalline calcite material from  $\mu$ TRLFS with  
141 a pixel size of 20  $\mu\text{m}$  were cross-referenced with different grains (A-J) identified by EBSD. The  
142 grains were ordered with increasing europium sorption (see Figure S1) and Student t-tests were  
143 performed to analyze statistically significant differences in europium sorption ( $p=0.05$ ). The data  
144 from neighboring grains with no statistically significant differences were combined into single  
145 datasets. This created four combined datasets with statistically significant differences in europium  
146 sorption efficiency, AF, IJHG, EDC, and B (in order of increasing europium sorption, see Table  
147 S2 and S3). Of the four datasets the grains with the most available data points – A, I, D, and B (in  
148 order of increasing europium sorption) – were chosen for a more detailed correlative analysis of  
149 the europium sorption and surface nanoroughness. VSI maps of each grain were measured and Sq  
150 values, the root mean square deviation or the standard deviation of the height data, of 20  $\mu\text{m} \times 20$   
151  $\mu\text{m}$  pixels were extracted from the images and correlated with the  $\mu$ TRLFS sorption data.  
152 For a more detailed investigation, the 20  $\mu\text{m} \times 20 \mu\text{m}$  pixels were each divided into subpixels with  
153 a smaller field of view (FOV) down to a maximum of 64 subpixels with a minimum FOV of  $2.5 \times$   
154  $2.5 \mu\text{m}^2$  which were analyzed according to their Sq value. The applied minimum FOV size of  
155 topographic data utilized for the calculation of the Sq parameter is limited by the spatial resolution  
156 and consecutive bisection algorithm used. The resulting datasets of Sq values were then averaged  
157 for every original pixel to mitigate the influence of larger structures such as scratches and holes in  
158 the crystal surface on the Sq-data (note that averaging the Sq values of the subpixels and measuring  
159 one Sq value for the whole pixel will give different results, with a higher influence of extreme  
160 values with the latter approach). These converged datasets were then correlated with the europium  
161 sorption efficiency. In a separate analysis different Sq ranges were investigated for their correlation  
162 with the sorption efficiency by only averaging the subpixels with Sq values in the ranges of 0-5  
163 nm, 5-10 nm, 10-50 nm, and >50 nm (see Figure S2).

164 **Numerical model.** According to the lifetime analysis, we utilized the surface complexation  
165 reactions to describe  $\text{Eu}^{3+}$  adsorption on the calcite surface in a short time experiment. Therefore,  
166 the SCM was developed using the aqueous speciation reactions and surface complexation reactions  
167 in Table S4. The SCM is an electrostatic double-layer model<sup>11,13</sup> in which the net surface charge  
168 balances the net charge in the diffuse layer<sup>7</sup>. The identical site density and specific surface area  
169 (SSA) are 5 sites/nm<sup>2</sup> and 0.262 m<sup>2</sup>/g, respectively<sup>28</sup>. The chemical reactions were calculated using  
170 PHREEQC v3.5<sup>7</sup> with the Nagra/PSI Chemical Thermodynamic Database<sup>35</sup>. The SCM results were  
171 validated using measured sorption efficiency data from Zavarin et al. 2005<sup>28</sup> (Figure S3 in SI).

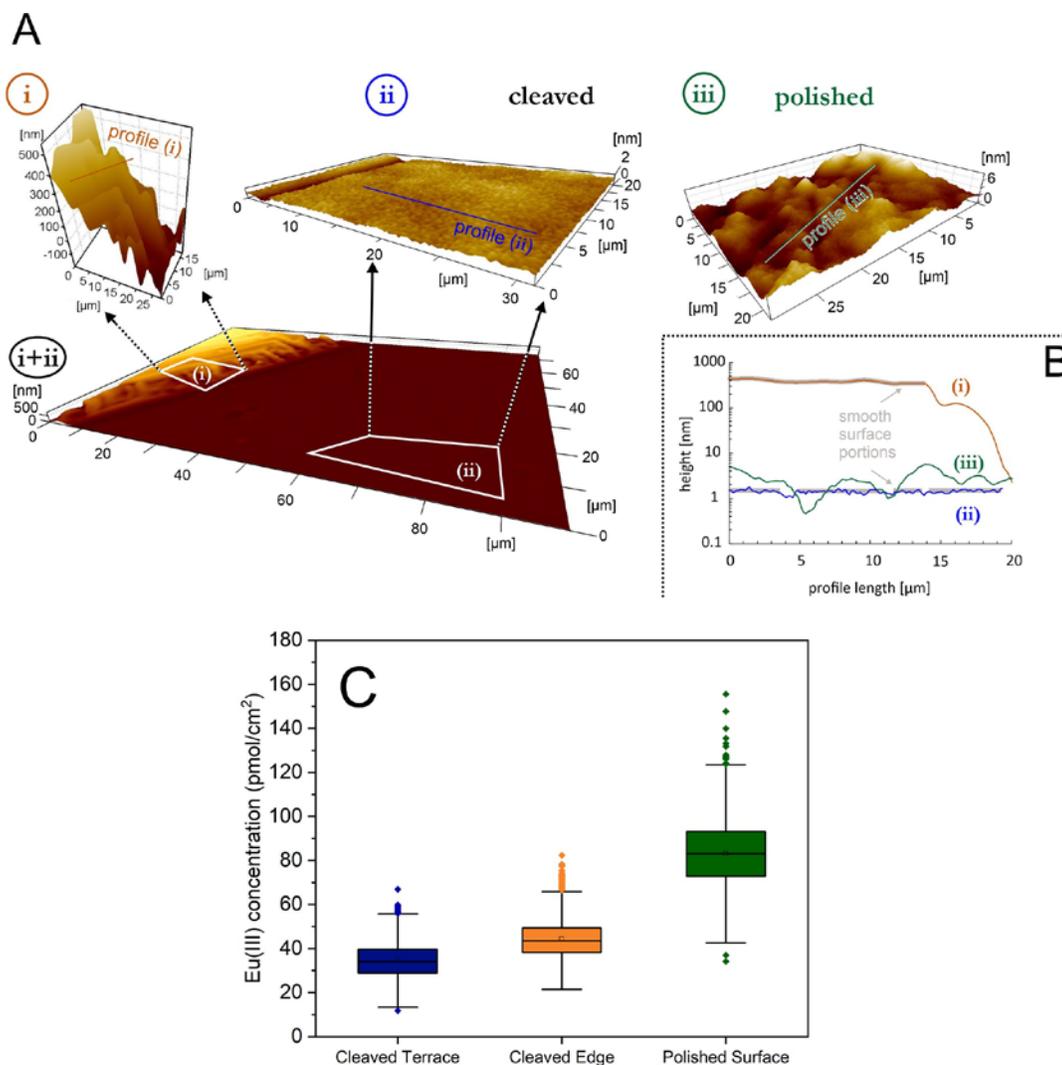
172 **Parametrization of the predictive model.** The topographical data for the predictive model is  
173 obtained from phase shifting interferometry (PSI) measurement with a high spatial resolution of 46  
174 nm × 46 nm. The Sq value of each pixel is calculated at a 0.46 × 0.46 μm<sup>2</sup> FOV using 10 × 10  
175 pixels of the surface topography data. Since the averaged Sq value is sensitive to the FOV, the  
176 calibration curve for the predictive modeling was adapted for the higher resolution. Based on the  
177 experimentally validated correlation of the optimized slope  $\alpha$  with the FOV of the Sq value for ROI  
178 I and II (Figure S4 in SI),  $\alpha$  was set to 0.03 for the predictive modeling. See below for a detailed  
179 discussion of these procedures. The use of a slope not specifically optimized for the surface in  
180 question may cause deviations in the prediction of the sorption efficiency, however, the predicted  
181 spatial sorption patterns and their trends with the evolution of the surface are valid.

## 182 **RESULTS AND DISCUSSION**

183 **Calcite nanotopography effects on Eu(III) sorption.** The influence of surface topography on  
184 sorption efficiency was studied using calcite crystal samples with different topographies that  
185 allowed us to isolate the effects of specific surface features. The use of single-crystal samples  
186 allowed us to study specific structural endmembers, i.e. very low KSD to very high KSD, even  
187 though the exact KSDs are not accessible to measurement. Figure 2 shows the surface topographies

188 of a cleaved and a polished calcite crystal (I) and the absolute concentrations of sorbed Eu(III) in  
189 a cleaved edge area (A), a cleaved terrace (B), and a fine-polished surface (C) (II). The polished  
190 crystal surface (C, Figure 2I) exhibits a highly nanorough surface that consists of a high amount of  
191 kink sites due to the fine polishing (cf. Figure 1 surface 4) producing a surface that may be linked  
192 to a powder sample. On the surface of the cleaved sample, two distinct structural features can be  
193 observed: distinct steps (A) that contain various degrees of steps according to the height difference  
194 (cf. Figure 1 surface 3) and flat terraces (B) in between the steps that can be made up by the large  
195 flat areas with a low amount of step density and point defects (cf. Figure 1 surface 1). Figure 2II  
196 shows the different concentrations of sorbed europium that the surface features A, B, and C lead  
197 to, as quantified by autoradiography. The highest amount of sorbed Eu(III) can be observed on the  
198 polished sample with a highly nanorough surface while the cleaved terrace with an approximately  
199 flat surface exhibits the lowest one, with the edge structure falling in between.

200 The observed heterogeneous sorption behavior suggests a variability of surface reactivity that  
201 reflects a heterogeneous distribution of crystal surface energy that can be quantified by surface  
202 topography analysis. The surface energy strongly depends on the number of surface building blocks  
203 such as kink sites and step edges<sup>17</sup>. A previous study<sup>22</sup> investigated heterogeneous surface reactivity  
204 and the probability of variations in kink site density. Additional literature data<sup>36, 37</sup> confirm the  
205 importance of the surface kink sites as the dominating intrinsic factor of enhanced surface reactivity  
206 during, e.g., dissolution and precipitation reactions. We thus hypothesize that such surface energy  
207 distribution affects the sorption efficiency, as suggested by kinetic Monte Carlo simulations (KMC)  
208 at the atomic scale<sup>38</sup>. Moreover, a molecular dynamics (MD) study investigating the reactivity of  
209 the calcite-water interface shows the number of surface reactive sites for adsorbing water molecules  
210 is higher at rough surface positions with kink sites and step edges compared to the flat surface  
211 portions with no surface roughness<sup>5</sup>.



212

213 **Figure 2.** (A) surface topographies of cleaved calcite surface ((i) and (ii)) and polished calcite

214 surface (iii). (i) shows a stepped edge due to cleaving with an overall height of about 500 nm. (ii)

215 shows a flat cleavage plane with a maximum height of ~2 nm due to a single scratch along the

216 otherwise flat surface. Note the different exaggerations of the z scale compared to the x and y scale

217 of the maps (i-iii). (B) shows height distributions of the profile lines (i), (ii), and (iii). (C) Box-

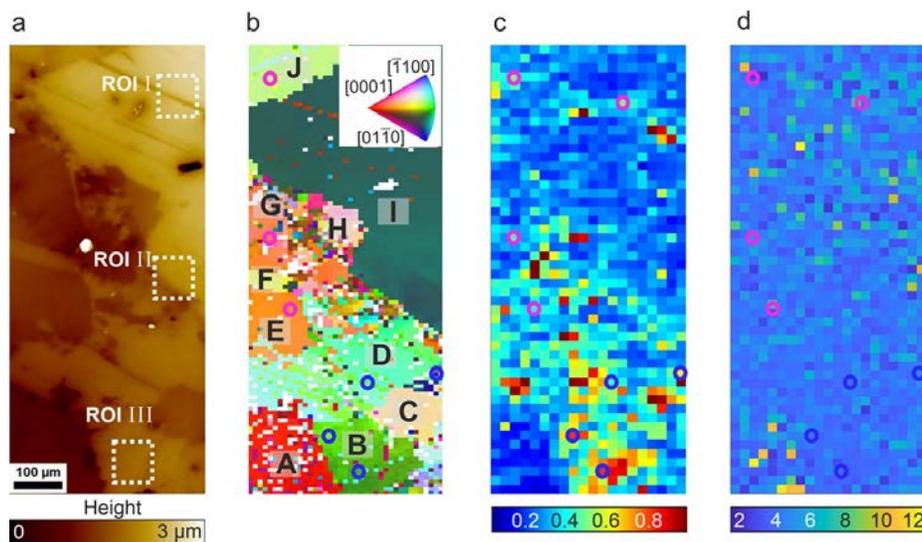
218 Whisker plots of the measured absolute concentrations of sorbed Eu(III) among the areas (i), (ii),

219 and (iii). The quantitative concentration trend indicates the effect of crystal surface nanotopography

220 (cf. Fig. 1) on sorption efficiency.

221 **Heterogeneous sorption of Eu(III) on polycrystalline calcite.** Now, we investigate the surface  
222 of polycrystalline calcite towards variability in sorption efficiency. Figure 3 shows an overview of  
223 the investigated calcite crystal surface maps including (a) the surface topography, (b) crystal  
224 orientations of the polycrystalline calcite material, (c) normalized sorption efficiency including  
225 selected spots where fluorescence lifetimes were collected, and (d) speciation distribution. The  
226 surface is composed of multiple crystal grains with diameters of about 10  $\mu\text{m}$  to several 100  $\mu\text{m}$   
227 with varying crystal orientation. The sorption efficiency was determined based on the total  
228 luminescence intensity of Eu(III) as described in the methods section. The luminescence intensity  
229 reveals a heterogeneous distribution of the Eu(III) sorption, even within single crystal faces,  
230 varying by a factor of around 10 between lowest and highest concentrations. Several grains show  
231 statistically significant differences in sorption efficiency, however, no correlation between crystal  
232 orientation and sorption efficiency is found (see below and SI). An analysis of the ratio of the  ${}^5D_0$   
233  $\rightarrow {}^7F_2$  and  ${}^7F_1$  luminescence transitions and lifetimes of the excited states provides information on  
234 the speciation of Eu(III) on the sample surface, as they are influenced by the bond strength<sup>24</sup> and  
235 the number of water molecules<sup>33</sup> in the first coordination sphere of the excited europium (see SI  
236 for detailed analysis of luminescence lifetime and speciation). In contrast to the heterogeneously  
237 distributed sorption efficiency, the mapping of the  ${}^7F_2/{}^7F_1$  peak ratio which is correlated to  
238 speciation (Figure 3d) shows a mostly homogeneous distribution. Most pixels exhibit peak ratios  
239  $\sim 5$ , indicating that the dominant speciation of Eu(III) is surface sorption or incorporation species.  
240 A few pixels show a peak ratio of seven or above, but only where the luminescence intensity is  
241 very low, which leads to larger uncertainties in the determination of the peak ratios.  
242 The measured lifetimes at selected surface sites (see Figure 3c, circles) are shown in the SI (Table  
243 S5). We generally find two distinct lifetimes: A short lifetime, which correlates to  $\sim 2$   $\text{H}_2\text{O}$  in the  
244 coordination sphere of Eu(III) and a longer lifetime which indicates a complete loss of hydration.

245 The short lifetime in combination with the typical peak ratio discussed above can be interpreted as  
 246 an inner-sphere surface sorption complex that has been previously reported<sup>25, 39</sup>. This species is  
 247 only present where the luminescence intensity is high and can be considered to be the major fraction  
 248 of Eu on the mineral surface. The long lifetime and thus complete loss of hydration suggest  
 249 incorporation into the calcite lattice<sup>25</sup>. The species appears homogeneously distributed over the  
 250 whole surface, albeit always only in low quantities. As Eu is a common impurity in natural  
 251 calcites<sup>40</sup>, and because it seems unlikely that incorporation occurred in the short duration of our  
 252 experiments<sup>29</sup> we interpret this species as Eu(III) incorporated into the natural calcite before our  
 253 experiments. We can then conclude that as a first approximation the Eu(III) sorption efficiency is  
 254 heterogeneously distributed over the surface, but the dominant species is the same inner sphere  
 255 complex throughout.

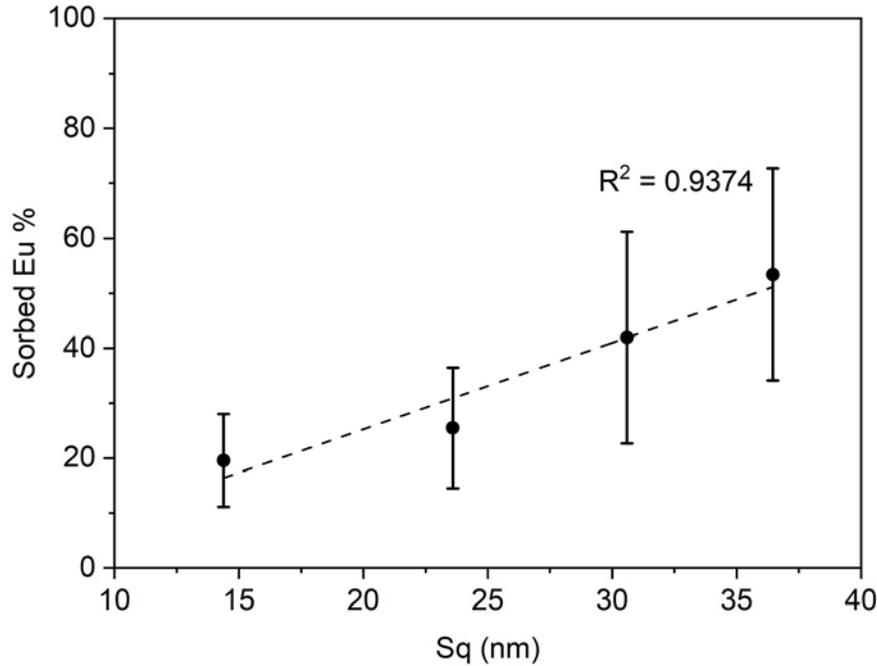


256  
 257 **Figure 3.** Correlative microscopy of (a) Surface height map, field-of-view (FOV) size = 1 mm ×  
 258 0.4 mm; ROIs I-III refer to three representative sub-regions for model validation (see Figure 6).  
 259 (b) Crystal orientation map based on EBSD data, different colors represent specific crystal  
 260 orientations, see the legend in Figure S1 for details. (c) Normalized sorption efficiency (normalized  
 261  $F_1 + F_2$   $\mu$ TRLFS peak sum) with lifetime data points marked with a hollow dot in blue (high

262 intensity) and purple (low intensity), spatial resolution:  $20\ \mu\text{m} \times 20\ \mu\text{m}$ . **d**, Peak ratio  $F_2/F_1$ ,  
263 indicating speciation/bonding strength, spatial resolution:  $20\ \mu\text{m} \times 20\ \mu\text{m}$ .

264 **Surface nanoroughness parametrization replaces the SSA parametrization towards**  
265 **improved surface complexation modeling.** The two datasets of the cleaved and polished surface  
266 illustrate the influence of the surface nanotopography is as a major factor for the measured Eu(III)  
267 sorption variability (Fig. 2). At the nanometer scale, the spatial configuration surface building  
268 blocks defines the surface reactivity and, thus, the sorption efficiency<sup>23</sup>. Nanoroughness can be  
269 considered a proxy to quantify the occurrence of such surface building blocks. In order to quantify  
270 surface roughness, we select the Sq parameter, the root-mean-square (r.m.s.) deviation of the  
271 surface height<sup>41</sup> calculated from the surface topography data, to test its suitability to explain the  
272 observed heterogeneous sorption efficiency. Parameter Sq quantifies the height variability more  
273 reliably<sup>42</sup> than the arithmetic average roughness Sa. Additionally, we tested the potential use of the  
274 surface area ratio parameter,  $S_{\text{dr}}$ , as a proxy parameter, see Figure S6 in SI.

275 For the polycrystalline calcite sample, we identify four datasets of different grains, AF, IJHG, EDC,  
276 and B by  $\mu\text{TRLFS}$  with statistically significantly different Eu(III) sorption (see Table S2 & S3).  
277 The crystal orientation within these datasets varies widely with no discernable trend (see Figure  
278 S1). No correlation between crystal orientation and Eu(III) sorption efficiency has been found.  
279 Furthermore, no correlation between the sorption efficiency and the absolute sample height exists  
280 as regions of distinctly different absolute surface heights show similarly low sorption efficiencies  
281 (see Figure 3a and c). Grain-specific data (grains: A, B, D, and I) of the sorption efficiency of  
282 Eu(III) versus the average Sq roughness of the grain surfaces show a linear correlation ( $R^2 = 0.94$ ),  
283 cf. Figure. 4, proving the Sq parameter as a suitable proxy for surface reactivity. Note that effects  
284 of crystal orientation may result in a variability of surface nanoroughness, encompassed in the  
285 roughness parameter.



287  
 288 **Figure. 4.** Normalized amount of europium sorption efficiency based on  $\mu$ TRLFS data collected  
 289 on grains A, I, D, and B as a function of the Sq roughness of the grain surface.

290 For a more detailed site-specific investigation as well as for testing the potential use of  
 291 topographical features for parametrization of the numerical approach, the sorption efficiencies of  
 292 all pixels of the four different grains with statistically significant different Eu(III) sorption  
 293 efficiencies were correlated with the Sq value of the field-of-view of each pixel (Figure 5a). Each  
 294 pixel covers an area of  $20 \mu\text{m} \times 20 \mu\text{m}$  (in accordance with the Eu sorption data resolution), which  
 295 is equivalent to  $200 \times 200$  pixels of the surface topography data shown in Figure 3a. Based on these  
 296 115 data points (Figure 5a), only a weak correlation ( $R^2 = 0.16$ ) between Eu sorption efficiency  
 297 and Sq value can be identified. Overall, the data seems to be distributed between two regimes, i.e.,  
 298 one regime shows a larger increase of Eu sorption with elevated Sq values up to 40 nm (red color  
 299 area in Figure 5a), the other regime shows a strong effect of Sq on Eu sorption, mostly covering  
 300 low includes elevated Sq values up to 80 nm with minor or no correlation with Eu sorption

301 efficiency (blue color area in Figure 5a). A closer look at the VSI images reveals that in the latter  
302 case, the Sq values are strongly influenced by larger surface structures, such as scratches or holes.  
303 These features have a large impact on the Sq value but do not appear to significantly impact Eu(III)  
304 sorption. Thus, to deconvolve the two regimes (large structures vs. nanoscale roughness) we  
305 gradually reduced the field of view for the Sq value calculation down to a minimum of  $2.5 \times 2.5$   
306  $\mu\text{m}^2$  using consecutive bisection to divide each pixel into a maximum of 64 subpixels, resulting in  
307 64 Sq values for each original pixel. Averaging these sub-pixel Sq values for each original pixel  
308 results in a new Sq value for each pixel at a  $2.5 \times 2.5 \mu\text{m}^2$  FOV, and the impact of the larger  
309 structures is reduced due to the averaging procedure. The mitigation of the influence of the larger  
310 structures is warranted by a more detailed analysis of the correlation between sorption efficiency  
311 and Sq values. A separate analysis of subpixels in the ranges of  $< 5$  nm, 5-10 nm, 10-50 nm, and  $>$   
312 50 nm was performed. These ranges were chosen to characterize different surface building blocks:  
313 The range of 0-10 nm reflects the critical nanoroughness of the surface, the intermediate range is  
314 typical for smaller holes left by the EBSD process and dissolution etch pits (10-50 nm), and the  
315 range  $> 50$  nm corresponds to large scratches and holes due to the sample preparation. A correlation  
316 of the chosen Sq ranges with the sorption efficiency shows correlations only for the first three  
317 ranges, i.e., 0 - 50 nm. No correlation was found for Sq values above 50 nm, justifying the de-  
318 emphasis of larger structures by the averaging procedure in the previously described (see  
319 Figure S2). Mechanistically, this indicates that specific nm-sized surface building blocks such as  
320 steps and kinks are the main drivers of the increased sorption efficiency.

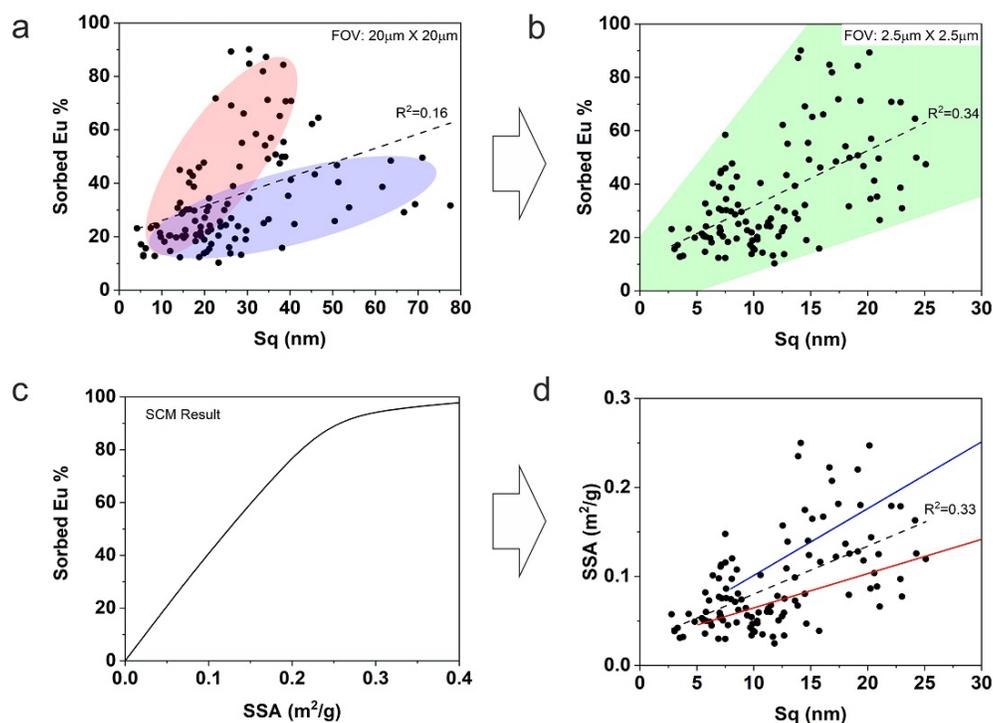
321 Using the newly calculated Sq values for each pixel, we see an increase of the coefficient of  
322 determination ( $R^2$ ) (see SI Figure S5), resulting in a linear correlation at a FOV of  $2.5 \times 2.5 \mu\text{m}^2$   
323 with  $R^2 = 0.34$  (Figure 5b) corresponding to a Pearson's correlation coefficient  $r$  of 0.58. While  
324 this may appear low, we like to point out that an  $r$  of 0.58 is considered to reflect a rather strong

325 effect for datasets with a large influence of other randomly distributed influences<sup>43</sup>. The motivation  
326 of our investigations is to test the predictive power of Sq as a proxy parameter in a polycrystalline  
327 system that inherently reflects a combination of several variables. The important prediction of the  
328 safety of a nuclear waste repository needs model parameter validation in a realistic system to avoid  
329 oversimplification. The data showing a visible spread, nevertheless, the point cloud envelopes a  
330 cone of possible linear relationships between Sq and Eu sorption efficiency. This general  
331 correlation is potentially and locally affected by several other factors that cause a decreased  
332 coefficient of determination for the overall pixel-by-pixel correlation when compared to the  
333 averaged grainwise correlation. Influencing factors may include the crystal orientation, the  
334 contribution of intrinsic Eu to the  $\mu$ TRLFS signal, the still present impact of larger structures on  
335 the Sq value, and effects of unspecific Eu(III) precipitation and calcite dissolution during the  
336 sorption experiment. This leads to slightly different valid slopes in different areas of the sample.  
337 Furthermore, assuming slightly increased Eu sorption signals due to the presence of incorporated  
338 natural Eu and slightly exaggerated Sq values due to large topographic features for the outliers  
339 would shift the highest Eu sorption data and highest Sq values to lower values. This would result  
340 in a tendency of narrowing the spread of the cone of possible linear relationships (see Figure S7  
341 for illustration). Possible corrections and improvements will be the subject of future investigations.  
342 For this study, we choose the linear regression of all data points as the most parsimonious solution  
343 to establish a correlation between sorption efficiency and surface nanoroughness. However, while  
344 these results provide a quantitative link between surface nanoroughness and sorption efficiency,  
345 they cannot be implemented into standard SCM approaches directly. Instead, these models rely on  
346 the specific surface area (SSA) and site density (SSD) to quantify the available surface sorption  
347 sites interacting with aqueous species at the solid/liquid surface. Typically, SCMs include a  
348 description of the electric double layer (e.g. the Gouy-Chapman model<sup>44</sup>) and conventional mass

349 action laws for intrinsic chemical reactions at the surface,<sup>45</sup> but adsorption is ultimately treated as  
350 an interaction of metal ions with functional groups uniformly distributed on the surface.  
351 Consequently, heterogeneous sorption variabilities as observed in our experiment and previously  
352 reported in our previous work<sup>19,20</sup> cannot be modeled by this standard approach. These variabilities  
353 are based on heterogeneously distributed affinities of cations for distinct positions on the calcite  
354 surface<sup>46</sup>, which are interpreted to be related to the variable amount of coordinated water molecules  
355 and Ca-O bond lengths<sup>47</sup> on the different positions of the crystal surface. These underlying affinity  
356 variations hold true beyond our specific system, for example, an investigation of the interaction  
357 between CO and a Cu surface demonstrated the CO-Cu binding energies at surface defects like  
358 steps or kinks to be systematically larger than at the terraces<sup>48</sup>. In general, cations preferably form  
359 surface complexes with the typically undercoordinated functional groups at the position of surface  
360 defects<sup>49</sup>.

361 In surface complexation modeling, the SSD reflects the total surface sites per unit surface area  
362 ( $\text{nm}^2$ ), and the SSA reflects the total surface area per unit mass of mineral, which is typically  
363 measured using the BET method<sup>50</sup>. The BET-measured surface area shows a dependence on the  
364 surface topography of the solid surface, which is linearly correlated with a surface roughness factor  
365 , i.e., the ratio of the measured (rough) surface area to the projected (smooth) area<sup>51</sup>. In order to  
366 implement spatial variability of the total number of surface sites based on variations of SSD and/or  
367 SSA owing to surface roughness variability into an SCM, one could either modify the SSA and fix  
368 SSD or vice-versa or modify both at the same time. We choose to vary the SSA and keep the SSD  
369 constant, supported by a strong linear correlation of the interpolated surface area and the Sq value  
370 (see Figure S8 in SI). As we have established a correlation between surface nanoroughness Sq and  
371 sorption efficiency, linking the Sq of our sample to its SSA should enable us to implement the  
372 observed interfacial heterogeneity into a predictive model. An SCM was set up (see SI for details)

373 to establish a quantitative relationship between the Eu sorption efficiency and SSA (Figure 5c).  
374 Ultimately, we aim to link our experimental data to literature data using surface data collected by,  
375 e.g., BET adsorption techniques. Thus, the concept utilizes a modification of the SSA parameter  
376 based on the bulk literature data as a starting point. An opposite choice of varying SSD and keeping  
377 SSA constant would yield identical results (see Figure S9) as the process is mathematically  
378 equivalent. This allows us to quantitatively link SSA and Sq pixel by pixel (Figure 5d) by cross-  
379 referencing the experimental sorption efficiency data (Figure 5b) and the model result (Figure 5c).  
380 The quantitative trends in Figs. 5b and d exhibit consistent trends with the investigations of both  
381 KMC<sup>38</sup> and MD<sup>5</sup> approaches, which confirms the validity of using surface nanoroughness data as  
382 a proxy for the intrinsic crystal surface energy, which has a significant impact on sorption  
383 efficiency. Therefore, we utilize this linear trend between SSA and Sq to parameterize a predictive  
384 SCM with the assumption that the SSA has a monotonically increasing linear relationship with Sq  
385 values.

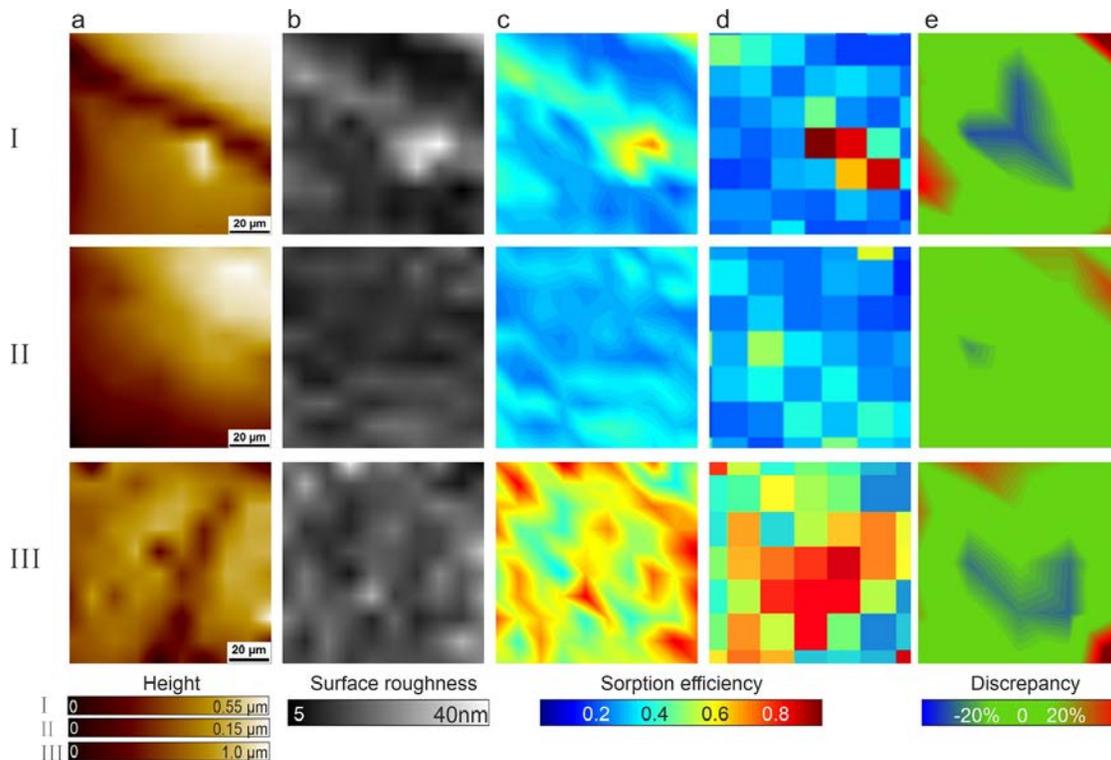


386

387 **Figure 5.** Quantitative correlation between SSA (model) and Sq (experiment) based on  
388 experimental data analysis and SCM results. **a,** The scatter plots of measured sorption efficiency  
389 versus Sq at a  $20 \times 20 \mu\text{m}^2$  FOV. **b,** The scatter plots of measured sorption efficiency versus Sq at  
390  $2.5 \times 2.5 \mu\text{m}^2$  FOV (right). **c,** SCM results of sorption efficiency versus SSA based on the reactions  
391 and thermodynamic data in Table S4. **d,** A scatter plot of SSA versus the averaged Sq at a  $2.5 \times$   
392  $2.5 \mu\text{m}^2$  FOV. The SSA of each point is calculated by the sorption efficiency through the  
393 quantitative curve in Figure 2c. The correlation between SSA and Sq shows a linear curve (gray  
394 dashed line) with a coefficient of determination,  $R^2 = 0.33$ . The red solid line and blue solid line  
395 represent the calibration curves used to parameterize the SCM for model validation in ROI I, II,  
396 and III, respectively. See text for detailed discussion.

397 **Improved SCM parametrization and model validation.** The quantitative relationship between  
398 Sq and SSA derived in the previous section is now used to parameterize a spatially resolved SCM  
399 using experimentally determined nanoroughness data. Based on the quantitative analysis in Figure  
400 2, we derive the slope of the linear function of SSA vs. Sq as  $\alpha$ , with  $\alpha = 0.0054$ . The ROIs I, II,  
401 and III in Figure 1a are selected as representative regions with available VSI-measured surface  
402 topography and sorption data from  $\mu\text{TRLFS}$  for model validation. Based on the surface topography  
403 of the ROIs (Figure 6a), the corresponding surface roughness maps (Figure 6b) were calculated  
404 with a pixel resolution of  $10 \mu\text{m} \times 10 \mu\text{m}$  by averaging the Sq value of  $2.5 \mu\text{m} \times 2.5 \mu\text{m}$  sub-pixels.  
405 We then use the quantitative relationship between Sq and SSA as reflected in  $\alpha$  to calculate the  
406 SSA of each  $10 \mu\text{m} \times 10 \mu\text{m}$  pixel in the three ROIs and, from that, the Eu sorption (Figure 6c).  
407 Naturally, the SCM results of the SSA parameterization are very sensitive to the value of  $\alpha$  and the  
408 spread of the cone of possible linear relationships is wide. Consequently, we performed a sensitivity  
409 analysis to optimize the value of  $\alpha$  for every ROI. Optimized  $\alpha$  values were obtained for the  
410 individual ROIs by maximizing the fit of the modeled Eu sorption in each ROI with the

411 corresponding experimental values (Figure S10). This yielded different calibration curves for each  
412 ROI which are plotted in Figure 5d and fall well within the spread of the experimental data, with  
413 ROI III exhibiting a steeper slope (blue line with  $\alpha = 0.0075$ ) than the other two (red line with  $\alpha =$   
414  $0.0038$ ). The SSA modification via Sq parametrization allows us to model similar sorption trends  
415 in all three cases. In general, a quantitative comparison of model results (Figure 6c) with the  
416 measured data (Figure 6d) shows good agreement within a 20% discrepancy between model and  
417 experiment (Figure 6e). In particular, the model underestimates the highest Eu sorption values in  
418 ROI III, which may be caused by Eu impurities of the natural calcite crystals, as indicated by the  
419 fluorescence lifetime measurement at this point of the sample (see SI Table S5, point 12/48). In  
420 contrast to typical SCM approaches that employ a simple uniform SSA value<sup>9, 10</sup>, this modified  
421 SSA based on Sq analysis allows for the investigation of spatially resolved retention variability  
422 based on the variability of crystal surface energy<sup>17</sup>. Choosing the right  $\alpha$  will be critical in the  
423 feasibility of this approach for predictive modeling and more research needs to be devoted towards  
424 the clarification of the varying influences on the relationship between surface topography and  
425 surface energy variation.



426  
 427 **Figure 6.** SCM validations in ROIs I, II, and III. **a**, surface topography, spatial resolution =  $10 \mu\text{m}$   
 428  $\times 10 \mu\text{m}$ ; **b**, averaged surface roughness ( $S_q$ ) at a  $2.5 \mu\text{m} \times 2.5 \mu\text{m}$  FOV, spatial resolution =  $10$   
 429  $\mu\text{m} \times 10 \mu\text{m}$ ; **c**, SCM results of sorption efficiency, spatial resolution =  $10 \mu\text{m} \times 10 \mu\text{m}$ ; **d**,  
 430 normalized experimental results of sorption efficiency measured using  $\mu\text{TRLFS}$  techniques, spatial  
 431 resolution =  $20 \mu\text{m} \times 20 \mu\text{m}$ ; **e**, the ratio of model vs. experimental sorption efficiency. Green color  
 432 represents a range of  $\pm 20\%$  discrepancy, red color: overestimation, blue color: underestimation.

433 **Predicting radionuclide sorption evolution.** As a next step, we explore the potential of our  
 434 improved parameterization approach to predict heterogeneous sorption on the crystal surface of an  
 435 independent set of experimental data. Figure 7 shows two surface topography maps, measured  
 436 using phase shifting interferometry (PSI) of a calcite single crystal after 120 minutes (a I) and 135  
 437 minutes (a II) of etching, respectively, representing the crystal surface evolution during dissolution.  
 438 From the topographical data (Figure 7a), we again derived the  $S_q$  values, here with a spatial  
 439 resolution of  $0.46 \mu\text{m} \times 0.46 \mu\text{m}$  (Figure 7b), use  $S_q$  to derive the SSA with the previously

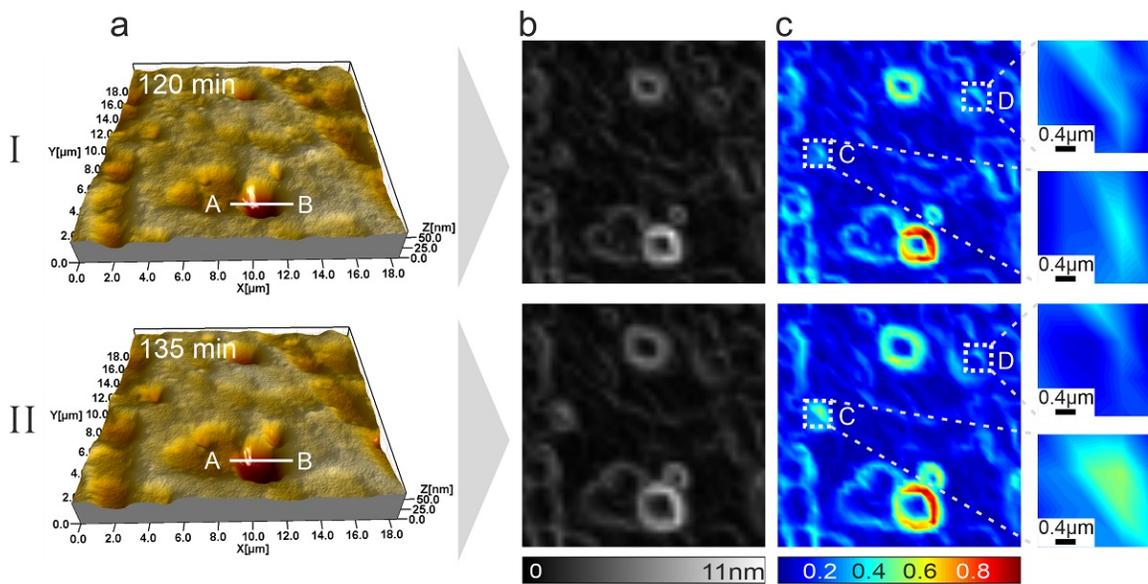
440 determined value for  $\alpha$ , adapted for the higher resolution (see Figure S4), and predict heterogeneous  
441 Eu(III) sorption (Figure 7c) based on our novel SCM parameterization approach.

442 A first important finding from this prediction is that Eu(III) is preferably adsorbed at surface steps  
443 which exhibit higher nanoroughness and kink site densities. In contrast, flat terraces and nearly flat  
444 bottoms of the surface pits are predicted to show lower adsorption. For the widening of etch pits  
445 on the surface, such as in cross-section A-B in Figure 7, the areas of high surface roughness move  
446 outwards with the evolution of the etched pit, resulting in a redistribution of the preferred sorption  
447 areas. Another finding with important implications for the evolution of the overall surface  
448 efficiency is that the sorption efficiency varies with the evolution of surface topography beyond  
449 just a spatial redistribution of the preferred sorption sites. As an example, ROI C shows an overall  
450 increase of the  $S_q$  value due to the etching which goes along with a 160% increase in sorption  
451 efficiency. This enhanced sorption efficiency as a result of the evolving surface structure may be  
452 linked to an increase in surface steps and kinks<sup>17</sup> by etching. In contrast to the enhanced sorption  
453 efficiency in ROI C, the sorption efficiency of ROI D exhibits a 25% reduction, linked to a reduced  
454  $S_q$  due to the removal of surface features by etching. Such behavior is explained by locally  
455 contrasting surface step arrangement on a reacting crystal surface. One situation is a constant  
456 number and density of single height steps on the crystal surface. The other situation is the formation  
457 of step bands due to surface step bunching, resulting in a locally enhanced step density<sup>52</sup>.

458 The overall sorption efficiency of the entire domain and its evolution over time depends on the  
459 balance between such subareas. Thus, SSA parameterization via surface nanoroughness in SCM  
460 analysis may provide a tool to predict the evolution of radionuclide sorption caused by the changes  
461 in surface building blocks. Consequently, the detailed quantitative insight into retention variability  
462 gained by this approach may provide a more accurate description of sorption at the pore scale  
463 contributing to an enhanced predictive capability on the core scale and beyond. An experimental

464 validation of such high-resolution modeling is not yet possible using current analytical approaches  
 465 with limited spatial resolution. Nevertheless, the mechanistic background of specific crystal surface  
 466 portions showing enhanced kink site densities (Figure 1) and, thus, elevated sorption uptake (Figure  
 467 2) provides an opportunity for the validation of such modeling approaches. Consequently, the  
 468 numerical results predict potential pattern evolution of reacting surfaces and offer opportunities for  
 469 applications.

470



471  
 472 **Figure 7.** Prediction of the evolution of sorption efficiency for two high spatial resolution data,  
 473 based on PSI techniques reflecting evolving surfaces at 120 min and 135 min dissolution reaction  
 474 time. Surface area =  $18.5 \mu\text{m} \times 18.5 \mu\text{m}$ . **a**, surface topography, spatial resolution =  $0.046 \mu\text{m} \times$   
 475  $0.046 \mu\text{m}$ . **b**, surface roughness (Sq), spatial resolution =  $0.46 \mu\text{m} \times 0.46 \mu\text{m}$ . **c**, SCM results of  
 476 sorption efficiency, spatial resolution =  $0.46 \mu\text{m} \times 0.46 \mu\text{m}$ . ROI A-B shows the sorption  
 477 preference at surface steps rather than the flat terrace. ROIs C and D show the enhanced and  
 478 reduced sorption efficiency due to the changes in surface topography by etching, respectively.

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