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1 Molecular-level speciation of Eu(III) adsorbed on a migmatized gneiss
2 as determined using μ TRLFS

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9 Abstract

10 The interaction of Eu(III) with thin sections of migmatized gneiss from the Bukov Underground
11 Research Facility (URF), CZ was characterized by microfocus time-resolved laser-induced
12 luminescence spectroscopy (μ TRLFS) with a spatial resolution of $\sim 20 \mu\text{m}$, well below typical grain
13 sizes of the material. By this approach, sorption processes can be characterized on the molecular level
14 while maintaining the relationship of the speciation with mineralogy and topography. The sample
15 mineralogy was characterized by powder X-ray diffraction and Raman microscopy and the sorption was
16 independently quantified by autoradiography using ^{152}Eu . Representative μ TRLFS studies over large
17 areas of multiple mm^2 reveal that sorption on the heterogeneous material is not dominated by any of the
18 typical major constituent minerals (quartz, feldspar, and mica). Instead, minor phases such as chlorite
19 and prehnite control the Eu(III) distribution, despite their low contribution to the overall composition of
20 the material, as well as common but less studied phases like Mg-hornblende. Especially prehnite shows
21 high a sorption uptake as well as strong binding of Eu to the mineral surface. Sorption on prehnite and
22 hornblende happens at the expense of feldspar, which showed the highest sorption uptake in a previous
23 spatially-resolved study on granitic rock. Similarly, sorption on quartz is reduced, even though only low
24 quantities of strongly bound Eu(III) were found here previously. Our results illustrate how competition
25 of mineral surfaces for adsorbing cations drives metal distribution in heterogeneous systems.

26 1. Introduction

27 The safe disposal of highly radioactive nuclear wastes – mainly spent nuclear fuel from commercial
28 energy production, but also waste streams from nuclear fuel reprocessing and military applications – is
29 a worldwide challenge. In the case of water intrusion into a deep geological disposal facility, interactions
30 with the solid phases of the surrounding barrier system will control the migration of the nuclear waste
31 components into the biosphere by being responsible for the major retention mechanisms.¹ Consequently,
32 a sound understanding of these interactions of relevant radionuclides and mineral phases on the
33 molecular level is a prerequisite for any safety assessment to allow reliable prediction over 100,000s of
34 years.

35 Among the constituents of nuclear waste, plutonium and the minor actinides (Np, Am, and Cm) are of
36 particular safety concern, due to their very high radiotoxicity over long periods of time. Especially ^{241}Am
37 and ^{243}Am ($t_{1/2} = 432 \text{ a}$ and $7,370 \text{ a}$, respectively) and ^{239}Pu ($t_{1/2} = 24,110 \text{ a}$), dominate the radiotoxicity
38 of spent nuclear fuel over hundreds of thousands of years.² Americium behaves mostly lanthanide-like
39 in solution and is essentially always trivalent under environmental conditions in aqueous solutions, but
40 also Pu is expected to occur in its 3+ oxidation state under the strongly reducing, oxygen free conditions
41 of a nuclear waste repository in a deep geological formation.^{1,3,4} Here, we use Eu(III) as an analogue for
42 these elements to make use of its outstanding luminescence properties⁵ for microfocus time-resolved

43 laser-induced luminescence spectroscopy (μ TRLFS).⁶ Europium(III)'s ionic radius is nearly identical to
44 its direct homologue Am(III) as well as Pu(III) [$r_{\text{ion}}^{\text{VI}}(\text{Eu}^{3+}) = 94.7 \text{ pm}$, $(\text{Am}^{3+}) = 97.5 \text{ pm}$, $(\text{Pu}^{3+}) = 100.0$
45 pm]⁷ and their chemical behavior is generally comparable,⁸ also with respect to their interaction with
46 mineral phases.^{9,10}

47 Crystalline rock is a possible host rock formation for nuclear waste repositories. Some countries have
48 already decided to construct their disposal facility for highly-radioactive nuclear waste in granite,^{11,12}
49 while others are considering crystalline rock in general as a preferred option.¹³⁻¹⁷ Consequently, many
50 studies have addressed the retention of relevant radionuclides on granite^{6,18-21} and its components.²²⁻³⁰
51 Such studies are complicated by the inherent heterogeneity of the material. They will contain at least the
52 three most common main components (quartz, feldspar, and mica) to varying degrees, and a plethora of
53 additional minor mineral phases. For single component studies to be used in safety assessment, it has to
54 be assumed that all effects observed for the single components are additive, which overlooks
55 competition between the materials as well as structural aspects, such as grain boundaries and surface
56 topography. Studies addressing the heterogeneous system as a whole, on the other hand, are often purely
57 quantitative, while mechanistic studies are rarely capable of clearly assigning molecular sorption
58 mechanisms to a specific mineral component of the heterogeneous system.

59 Single component studies of the sorption of trivalent actinides, lanthanides, or rare earth elements are
60 available for quartz,²³⁻²⁵ feldspars,^{22,27,30,31} and micas,^{26,28,29} as well as several of the minor phases, e.g.
61 apatite.³²⁻³⁴ On both, quartz and feldspar, sorption occurs first as a bidentate inner-sphere sorption
62 complexes around mildly acidic pH values, which are then gradually hydrolyzed at higher pH. The initial
63 sorption step occurs at pH ~ 4.5 and hydrolysis begins after pH ~ 6.0 , around pH = 7.5 complete retention
64 is observed on both minerals. Some feldspar studies report slight variations in the pH edge²⁷ or
65 speciation³⁰ depending on the type of cation in the Na/K/Ca-feldspar. On quartz, additionally, the
66 formation of ternary surface complexes with silicate released by the mineral has been reported in the
67 alkaline pH range (pH > 9.0).²⁴ A similar process may also occur on K-feldspar at yet higher pH ($>$
68 10).³⁰ Micas show different behavior depending on their composition. Biotite exhibits strongly ionic
69 strength dependent ion exchange in its interlayer as the main interaction mechanism with trivalent metal
70 cations, which begins at acidic pH ~ 2.5 and reaches its maximum already at pH ~ 3.5 .²⁰ There is no
71 structural characterization of the sorption complexes to unambiguously distinguish inner- and outer-
72 sphere complexes, but the pH and ionic strength dependency suggests mainly outer-sphere sorption. In
73 contrast, interaction with muscovite is *via* external surfaces instead of the interlayer.²⁹ Sorption also
74 begins at acidic pH ~ 3.0 , and is initially mainly outer-sphere sorption as well as extended outer-sphere
75 sorption.^{26,28} Sorption increases over a much wider pH range and becomes mostly independent of ionic
76 strength at pH > 7.0 , indicating a transition to an inner-sphere sorption mode.²⁸ It can be shown that the
77 formation of inner-sphere complexes begins at pH ~ 5.0 ; for Y^{3+} it was shown that at pH 5.5 three

78 species, inner-, outer-, and extended outer-sphere sorption complex co-exist on the muscovite (001)
79 basal plane.²⁶

80 These studies on model systems containing only one mineral phase are essential to understand the
81 interaction with these minerals at a high level of detail, but they cannot accurately describe the behavior
82 of the system as a whole. For instance, studying separate mineral phases cannot reveal how sorption of
83 Eu^{3+} on one mineral affects its sorption on the other phases, or what effect surface features such as grain
84 boundaries, crystallite orientation, and topography have on the sorption process.^{18,19,35,36} Here, studies
85 of the whole system are required, ideally with spatial resolution to avoid the loss of connection between
86 mineral phase and speciation described above. Several microscopic studies using a variety of techniques
87 are available in the literature. Many studies focus on the quantitative distribution of radionuclides and
88 their analogues,²¹ often resorting to co-location with other elements to derive additional
89 information.^{20,37,38} For example, Eu^{3+} sorption on granite was studied by electron probe micro analysis
90 (EPMA) and laser-ablation ICP-MS (LA-ICP-MS)^{20,21} at low to neutral pH. Both studies show a
91 heterogeneous distribution, mostly on biotite, which is affected by its topography and surface alteration
92 during the sorption process. The dominance of sorption on biotite was expected based on the pH of the
93 experiments and the sorption behavior on the pure phase. However, additional observations could not
94 have been obtained in such studies, such as an accumulation of the metal ions at grain boundaries
95 between quartz and feldspar.²⁰ A drawback of both techniques, EPMA and LA-ICP-MS is, that no
96 information regarding the speciation at the interface can be obtained, which would be required to
97 extrapolate the sorption behavior to other environmental conditions than the ones chosen for these
98 studies.

99 More recently, spatially-resolved studies of the speciation of Eu^{3+} on granitic rocks as a whole system
100 have become available. Ishida et al. applied luminescence imaging and combined it with Eu^{3+}
101 luminescence lifetime measurements to obtain chemical information [time-resolved laser-induced
102 luminescence microscopy (TRLFM)].³⁹ The assignment of species was then achieved by fingerprinting
103 the decay profiles with previously measured single component data. The study finds heterogeneous
104 sorption distributions on all components of the studied granite, which exhibit a wide range of lifetimes,
105 except on biotite, where only the aquo ion was found. A drawback of the imaging approach is the lack
106 of actual spectral information. While luminescence lifetimes bear information on the hydration state of
107 Eu^{3+} , its luminescence spectra can be used to directly reveal speciation information based on the intensity
108 ratio of the two main transitions in the spectra, ($^5\text{D}_0 \rightarrow ^7\text{F}_1$) and ($^5\text{D}_0 \rightarrow ^7\text{F}_2$). The former is a magnetic
109 dipole transition, barely affected by chemical changes around the luminescing ion, while the latter is a
110 “hypersensitive” electric dipole transition, which will strongly increase in intensity when Eu^{3+} 's ligand
111 field changes.⁵ Generally, larger band ratios ($^5\text{D}_0 \rightarrow ^7\text{F}_2$)/($^5\text{D}_0 \rightarrow ^7\text{F}_1$) (in the following F_2/F_1 for short)
112 point to stronger binding to Eu^{3+} .⁵ This is exploited for μTRLFS : instead of imaging luminescence
113 intensity of a large area, the sample is scanned through the focal point of a laser beam and the whole

114 luminescence spectrum is recorded in each point and supplemented with lifetime measurements in select
115 points. This process is significantly slower than TRLFM but allows unambiguously distinguishing
116 between strongly bound species at the interface and those more weakly associated. Using this approach,
117 we recently showed, that all main components of a granite rock from Eibenstock, Germany interact
118 heterogeneously with Eu^{3+} .⁶ This means that the Eu^{3+} distribution and speciation varies, both from
119 mineral grain to mineral grain and within a single mineral grain. Interestingly, sorption was significantly
120 higher on feldspar than on quartz, while the sorption strength was reversed as evidenced by very high
121 F_2/F_1 ratios on quartz. The study also found deviating behavior at several grain boundaries, which
122 showed increased sorption at reduced bond strength compared to the adjoining mineral grains.

123 Here, we present an investigation of the sorption of Eu(III) on a much more complex migmatized gneiss
124 from the Bukov underground research facility, Czech Republic. The formation is being investigated for
125 its suitability as a host rock for a future repository for Czech nuclear wastes,¹⁵ and related formations on
126 the German side of the border are equally under investigation.⁴⁰ As such, it is of utmost importance to
127 characterize its retention properties under as realistic conditions as possible, while still obtaining
128 molecular scale information. A thin section of the material was prepared, and characterized regarding
129 its mineralogy by Raman microscopy and subsequently sorption and speciation of Eu(III) were
130 characterized with 20 μm spatial resolution by μTRLFS . The results are verified by an independent
131 sorption quantification (although with slightly lower spatial resolution), using autoradiography. We aim
132 to identify the mineral components responsible for the retention of Eu(III) in this rock and to characterize
133 the sorption mechanisms on the molecular level to assess the effectiveness of this retention. By
134 comparison with the previous results on Eibenstock granite, we also aim to reveal the impact of mineral-
135 mineral competition on the quantity and speciation of adsorbed cations.

136 2. Materials and Methods

137 2.1 Sample preparation

138 A drill core was obtained from the Underground Research Facility Bukov (Bukov URF), which is built
139 in 600 m depth of a rock formation at the south end of the Rožná uranium deposit in Czech Republic,
140 close to Brno. The geology of the site is further described in the SI, Page S1. The laboratory is used to
141 test the suitability of this rock formation as a repository for high-level nuclear waste. A piece of this
142 drill core was used to produce thin-sections with (20×20) mm x 150 μm in size, which are glued onto
143 microscopy slides and finally polished. Polishing (Logitech polisher) was performed with a suspension
144 of diamonds 1 μm and 3 μm in diameter, respectively, in ethanediol. The sample was washed with
145 ethanol and deionized water (MilliQ, 18.2 M Ω), before the reaction with the Eu^{3+} solution.

146 For the μTRLFS and autoradiography measurements the thin-section was brought into contact with a
147 Eu^{3+} solution containing the radioactive isotope ^{152}Eu (15 ml of 5×10^{-5} M [^{152}Eu] Eu^{3+} ($A \approx 17$ kBq) with

148 0.1 M NaCl background electrolyte). The pH was adjusted to 7.5 by adding NaOH and HCl. That pH
149 was chosen, because sorption reaches its maximum in the pH edge experiments, while homogeneous
150 precipitation of Eu solids is still very low. These findings are based on batch sorption experiments,
151 which are described in more detail in the SI, Page S1 and Figure S1. To conduct the sorption experiment,
152 the sample was put upside down in a watch glass to avoid any sorption on the backside of the sample,
153 which would lead to interfering signals in the autoradiography measurement. The watch glass was filled
154 with the europium solution, so that the liquid surface was covering the whole sample on the mineral side
155 for 5 days. Liquid levels were readjusted on a daily basis. After the sorption experiment the sample was
156 washed gently with MilliQ water (18.2 MΩ) to avoid precipitation.

157 2.2 Powder X-ray Diffraction

158 Different parts of the drill core were thoroughly pulverized using a McCrone mill. The powder X-ray
159 diffraction data was collected on a Bruker D8 Advance powder diffractometer in a Bragg-Brentano
160 geometry. CuK α radiation and Lynx Eye XE detector were used. The data was collected in the angular
161 range 4-80° of 2 Θ with a 0.015° step and 0.8 sec time per step. The qualitative phase analysis was
162 performed using the Diffrac.Eva 4.1 program (Bruker AXS, Germany, 2015) with the help of the PDF-
163 2 database. Subsequently, the semi quantitative phase analysis was performed by the Rietveld method⁴¹
164 using the Topas 5 (Bruker AXS, Germany, 2014) software suite. The results of both analyses are shown
165 in the SI, Figure S2 and S3. The crystal structures of mineral phases used in the refinement were obtained
166 from the ICSD database (FIZ Karlsruhe, Germany, 2018). During the Rietveld refinement, only the scale
167 factors, unit-cell parameters, and size of coherent-diffracting domains were refined. A correction for
168 preferred orientation was applied for selected mineral phases (e.g. biotite, K-feldspar, labradorite).
169 Limits of detection vary in the range 0.2-0.5 wt%.

170 2.3 Raman microscopy

171 Before sorption experiments were conducted, Raman mappings of the mineralogy were determined for
172 the unloaded thin section and a (3×4) mm² ROI was chosen based on the presence of many visually
173 different features (used as an indicator for different mineral phases). A grid of (20×20) μm^2 was used
174 resulting in around 26000 single Raman spectra. These spectra were evaluated with a Python-based
175 software (pycroTRLFS EVAL, HZDR, Germany) regarding their peak positions and compared to
176 spectra from the RRUFF database to identify the mineral phases.⁴² Representative measured spectra
177 compared to reference spectra are available in the SI, Figure S4. Spectra were measured with a LabRAM
178 ARAMIS (Horiba, Japan) Raman microscope combined with a 532 nm cw-laser (50 mW). Slit and pin-
179 hole diameter were set to 200 μm . Spectral resolution was set by a 600 lines/mm grating.

180 2.4 μ TRLFS

181 μ TRLFS measurements were performed with a specially designed setup, which was already described
182 in our previous work.⁶ Briefly, A laser beam (Surelite SL I-20 @355 nm pump laser, Continuum with
183 NarrowScanK @Exalite 389/398 mix dye laser, Radiant Dyes) was coupled into the setup by a dichroic
184 mirror (490 nm cut-off wavelength, Thorlabs). The redirected beam was then focused onto the sample
185 by an objective (HCX APO 10 \times , Leica). The sample was placed on an XYZ motorized stage (Newport).
186 The emitted luminescence is collected and collimated by the focusing objective, passes the dichroic
187 mirror and is focused by a second lens (achromatic, f = 100 mm, Thorlabs) onto the tip of a light guide.
188 The light guide was connected to a spectrometer (Shamrock SR303i spectrograph with DH320T-18U-
189 63 iCCD camera, Andor, UK) for detection. A lower laser pulse energy of around 20 μ J was used to
190 avoid laser ablation on the sample. A 300 l/mm grating was used in the polychromator and a delay of 1
191 μ s after the laser pulse with a gate width of 10 ms was chosen, to protect the detector from laser light
192 and collect the entire luminescence emission, respectively. In total around 6700 single luminescence
193 spectra were recorded in the three chosen μ TRLFS ROIs.

194 The luminescence of the two main emission transitions of Eu³⁺ (⁵D₀ \rightarrow ⁷F₁) and (⁵D₀ \rightarrow ⁷F₂) was
195 evaluated by a Python-based software (pycroTRLFS EVAL, HZDR, Germany) by first applying a linear
196 background correction for each peak and then integrating both peaks separately spectrum by spectrum.
197 The sum of intensities (F₁+F₂) and the intensity ratio (F₂/F₁) were then assigned to the coordinates of the
198 spectra, which results in a mapping of the sorption uptake (total luminescence intensity, F₁+F₂) and
199 speciation or sorption strength respectively (peak ratio, F₂/F₁). It should be noted here that comparisons
200 of the luminescence intensity are contingent on the absence of quench processes, as could be induced
201 by e.g. iron. In the minerals with a high Fe content (see below) this will effectively lead to complete
202 extinction of the luminescence signal, but other parts of the sample may also be affected. Typically, the
203 presence of quenchers in addition to water can be derived from the detection of lifetimes shorter than
204 the aquo ion's lifetime (see below), but lifetimes measurements are only available in select points.

205 Lifetime analysis of the luminescence decay was done point by point at selected pixels. For this, spectra
206 were measured with varying time delays relative to the laser pulse, got background corrected and the
207 total luminescence intensity was approximated by mono-, bi- or tri-exponential decay curves depending
208 on convergence and residuals to obtain the lifetime values. The lifetimes were then used to calculate the
209 corresponding number of water molecules remaining in the first coordination sphere of Eu³⁺ with the
210 following empirical equation.⁴³⁻⁴⁵

$$n(\text{H}_2\text{O}) \pm 0.5 = \frac{1.07 \text{ ms}}{\tau[\text{ms}]} - 0.62 \quad \text{Eq. 1}$$

211 The Eu³⁺ aquo ion has nine water molecules in its hydration sphere.⁴⁵⁻⁴⁷ When measuring surface-
212 bound species, a coordination number of nine indicates an outer-sphere (OS) sorption species with no
213 loss of the hydration sphere. A lower number of water molecules indicates inner-sphere (IS) sorption,
214 with a partial loss of the hydration sphere and a direct bond between Eu³⁺ and the surface. Low values

215 of $n = 1-3$ can be interpreted as a surface (SF) incorporation species with Eu^{3+} partially imbedded into
216 the mineral surface.^{32,48,49} A total loss of hydration indicates full incorporation into the mineral, which
217 likely stems from intrinsic Eu^{3+} impurities of the natural material, due to the short duration of our
218 experiments.

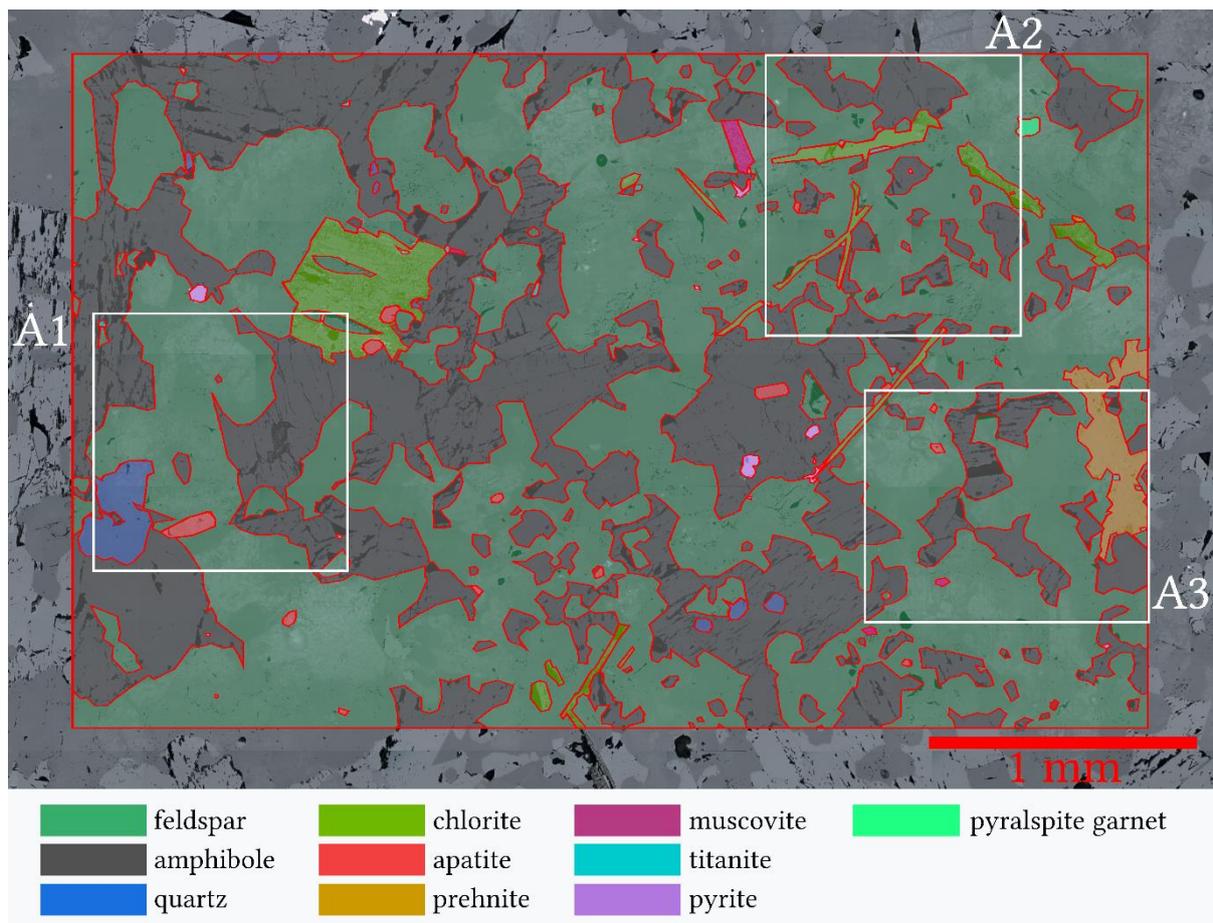
219 2.5 Autoradiography

220 To conduct the autoradiography measurements the loaded sample was placed on a BAS-IP MS image
221 plate (GE Lifesciences) and put into a light-tight aluminum cassette to press both on top of each other,
222 separated by a plastic wrap to avoid contamination. After exposure of the image plate at different
223 positions over several time frames, it was read out using an Amersham Typhoon Biomolecular Imager
224 (GE Lifesciences) with a pixel size of $10\ \mu\text{m}$. The data of the 120 min exposure time was chosen for
225 further analysis due to the highest dynamic range. The actual resolution is expected to be lower than the
226 $10\ \mu\text{m}$ read-out. One reason is the isotropic radiation combined with the distance between sample and
227 image plate due to the plastic wrap. Scattering by the foil and the backscattering from the surface will
228 additionally lower the effective resolution.

229 3. Results

230 3.1 Mineralogy

231 The PXRD measurements show, that the Bukov sample is mainly composed of feldspar, amphibole,
232 quartz and mica (feldspar: 44.8 wt% plagioclase, 0.7 wt% alkali-feldspar; amphibole: 30.3 wt%
233 Mg-hornblende; quartz: 13.5 wt%; and mica: 9.2 wt% biotite and 1.5 wt% chlorite, on average over
234 three fractions of the sample). Based on a former study, the Bukov rock is classified as migmatized
235 amphibole-biotitic paragneiss to migmatized biotitic paragneiss with amphibole.⁵⁰ The Bukov rock is
236 characterized by a distinctive mineralogical heterogeneity and spatial variability. For simplicity, we will
237 refer to the material as migmatized gneiss in the following. A detailed qualitative analysis of the PXRD
238 spectra shows additional minor minerals like prehnite, apatite and kaersutite as another member of the
239 amphibole mineral group. This macroscopic mineralogy just serves as a starting point for the mineral
240 phase identification with Raman microscopy of a region of interest (ROI) on a thin-section of the Bukov
241 migmatized gneiss.



242

243 Figure 1: Raman-based mineralogy and μ TRLFS-ROIs (white rect.) with feldspar, amphibole, quartz,
 244 chlorite, apatite, prehnite, muscovite, titanite, pyrite, and pyralspite garnet mineral grains separated by
 245 red grain boundaries.

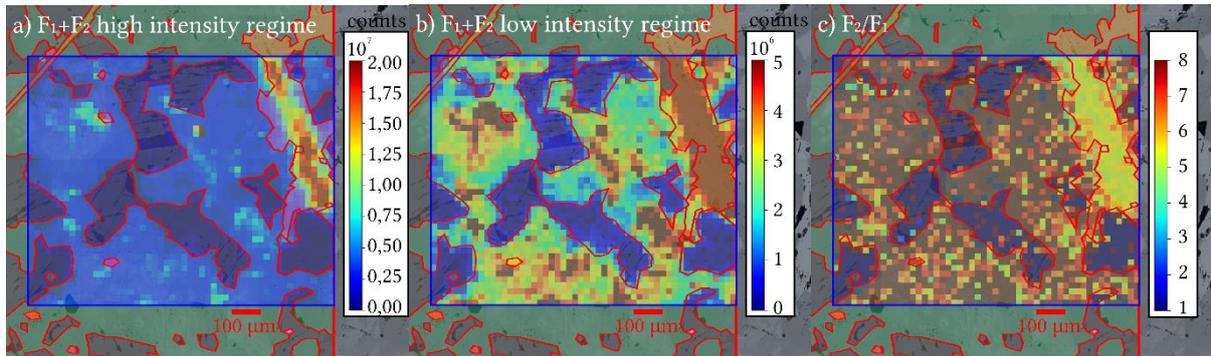
246 In Figure 1 the Raman-based mineralogy of the ROI is shown along with μ TRLFS-ROIs A1 to A3
 247 marked in white. As expected, most of the ROI is covered with the main minerals already identified by
 248 PXRD. Additionally, titanite, pyrite, and pyralspite garnet could be identified. Mineral grains identified
 249 as chlorite could also be a mix of biotite and chlorite, as the Raman spectra are not definitive, but the
 250 needle-like morphology is more common for chlorite.^{51,52} As most of these secondary minerals are not
 251 identified by the quantitative PXRD analysis, the total amount should be low on average. Within the
 252 area marked in red in Figure 1, the mineral composition by area is 58.1 % feldspar, 36.4 % amphibole,
 253 3.0 % chlorite, 1.0 % prehnite, 0.9 % quartz, 0.3 % apatite, 0.2 % muscovite, 0.1 % pyrite, 0.1 % titanite
 254 and 0.1 % pyralspite garnet. Titanite forms only tiny mineral grains, which are hardly visible in the
 255 mineralogy; the spectral identification is nonetheless reliable.

256 3.2 μ TRLFS: Local Eu^{3+} speciation and sorption uptake

257 To investigate the sorption behavior of Eu^{3+} , in contact with Bukov migmatized gneiss, three ROIs,
 258 which contain most of the identified minerals, were measured with μ TRLFS and evaluated regarding
 259 the sorption uptake and speciation as already explained in the methods section. In the following

260 μ TRLFS-ROI A3 mappings will be presented in detail, while A1 and A2 mappings and all lifetimes can
261 be found in the SI, Figure S5, S6 and S7. The following discussion will take all ROIs into account.

262



263 Figure 2: μ TRLFS mappings of ROI A3 of sorption uptake (F_1+F_2) in the high (a) and low intensity
264 regime (b) and speciation (F_2/F_1) (c) with highlighted grain boundaries in red

265 In Figure 2 the μ TRLFS mappings of ROI A3 are visualized. The sorption uptake is shown with two
266 different intensity regimes, so that the differences in areas with a low luminescence intensity can be
267 identified better. For all of the ROIS the luminescence intensity distribution is mostly correlated with
268 the crystal grains and the intensities between different mineral grains can vary from lowest to highest
269 by a factor of 100. Additionally, to this inter-grain variation of the sorption uptake also distinct intra-
270 grain variations can be observed, especially on feldspar, with intensities varying by a factor of 10.
271 Prehnite, which is located on the upper right of the mapping (cp. Figure 1), has the highest observed
272 luminescence intensities within all ROIs. Apatite (A1, A3) has a nearly as high sorption uptake as
273 Prehnite. On amphibole grains, the luminescence intensity is very low, but a Eu^{3+} signal is still
274 detectable, while grain boundaries to feldspar partially show a higher sorption uptake (A1). The same
275 grain boundary effect can also be observed in the case of the quartz mineral grain (A1). On pyrite,
276 titanite and chlorite there is no Eu^{3+} luminescence detectable, due to the high Fe content in these minerals
277 quenching Eu^{3+} luminescence.

278 In Figure 2 c) the speciation mapping of ROI A3 is shown as a distribution of luminescence peak ratios,
279 F_2/F_1 . Prehnite not only has the highest sorption uptake, but also the highest evaluable peak ratio of 5 to
280 6 within all ROIs, which is homogeneously distributed over the whole grain. This indicates strong
281 binding over the whole mineral grain surface. On feldspar we typically find slightly lower peak ratios
282 of 4 to 5, where luminescence intensity is high. In the areas of low overall intensity, the F_1 peak becomes
283 indistinguishable from the background, which precludes a numerical analysis. The F_2 band is still
284 prominent in these areas, which suggests fairly high band ratios. The peak ratios on apatite are also hard
285 to quantify. In this case the F_1 band overlaps with luminescence of non- Eu^{3+} fluorophores. The spectral
286 fingerprint of Eu^{3+} is still evident, but an evaluation of the band ratio becomes impossible.
287 Representative spectra of feldspar hot spots and bulk, prehnite and apatite are shown in the SI, Figure
288 S8. Minerals with a very low luminescence intensity like quartz, amphibole, or chlorite cannot be

289 evaluated regarding their peak ratio. Here it is noteworthy that in our previous study⁶, luminescence
 290 intensity on quartz was also relatively low but still well sufficient for a band ratio analysis.

291 Table 1: Species identified on each mineral based on lifetime analysis and the number of
 292 corresponding water molecules in Eu³⁺'s first coordination sphere. Uncertainties represent distribution
 293 of values determined on multiple spots wherever possible.

Mineral	<i>n</i> (H₂O)	<i>Species</i>
Apatite	0.4 ± 0.5	<i>Intrinsic incorporation</i>
	2.8 ± 0.9	IS sorption
Feldspar	3.1 ± 0.5	SF incorporation (common)
	5.1 ± 0.5	IS sorption (interm.)
	7.3 ± 0.5	IS sorption (rare)
	0.2 ± 0.3	<i>Intrinsic incorporation</i>
Prehnite	5.8 ± 1.0	IS sorption
	2.5 ± 0.8	SF incorporation
	9.0 ± 0.9	OS sorption
	0.2 ± 0.2	<i>Intrinsic incorporation</i>
Pyralspite garnet	1.4 ± 0.3	SF incorporation
	0.0 ± 0.1	<i>Intrinsic incorporation</i>
Quartz*	0.4 ± 0.4	<i>Intrinsic incorporation</i> (likely into feldspar)

294

295 In Table 1 all identified species based on a total of 44 lifetime measurements are listed (see SI, Figure
 296 S7 and Table S1 for locations and determined lifetimes). Omitted mineral phases showed too low
 297 luminescence intensity for reliable lifetime analysis. Taking the F₂F₁ band ratios into account, we can
 298 use the number of water molecules remaining in the first coordination sphere of Eu³⁺ to identify the type
 299 of sorption complexes formed on each mineral. On feldspar we find a total of four different species, a
 300 surface incorporation species, two inner-sphere sorption complexes differing in their degree of
 301 hydration, and an incorporation species. The latter must be Eu³⁺ intrinsically present in the mineral, as
 302 an incorporation process seems unlikely in the short duration of our experiments. This is corroborated
 303 by the observation that this species is present over the whole surface of the mineral and appears most
 304 prominently where the total luminescence intensity is low. The inner-sphere sorption species show a
 305 wide distribution of hydration with 3, 5, or 7 water molecules remaining in the hydration spheres,
 306 respectively. The species with only three remaining water molecules is by far the most common,
 307 accounting for more than 70% of the inner-sphere complexes, while around 20% exhibit five water
 308 molecules and only ~7% maintain the highest number of water molecules. In our previous study,⁶ the

309 same incorporation species was also identified, as well as the IS complex with seven remaining water
310 molecules. However, on K-feldspar in Eibenstock granite, this IS complex was dominating the Eu^{3+}
311 speciation and any other IS complex was too minor to be identified. The grain boundaries between
312 feldspar and amphibole, which showed increased sorption of Eu^{3+} relative to bulk amphibole, also reveal
313 a feldspar-like speciation, confirming that here amphibole is likely covered by a thin layer of feldspar.

314 On prehnite we can also identify four different species, three sorption complexes and Eu^{3+} intrinsically
315 incorporated into the mineral. Sorption occurs as both, IS sorption characterized by lifetimes
316 corresponding to hydration by about six water molecules and as a surface incorporation species⁹ with
317 shorter lifetimes corresponding to 1.5 to 3.5 coordinating water molecules. Both modes of surface
318 bonding appear with similar frequency, which explains the homogeneous distribution of band ratios on
319 prehnite (Figure 2c). Close to the mineral grain boundaries, also very short lifetimes, which belong to
320 the Eu^{3+} aquo ion were determined, albeit with relatively large uncertainties. This would indicate an
321 outer-sphere sorption mechanism for these areas.

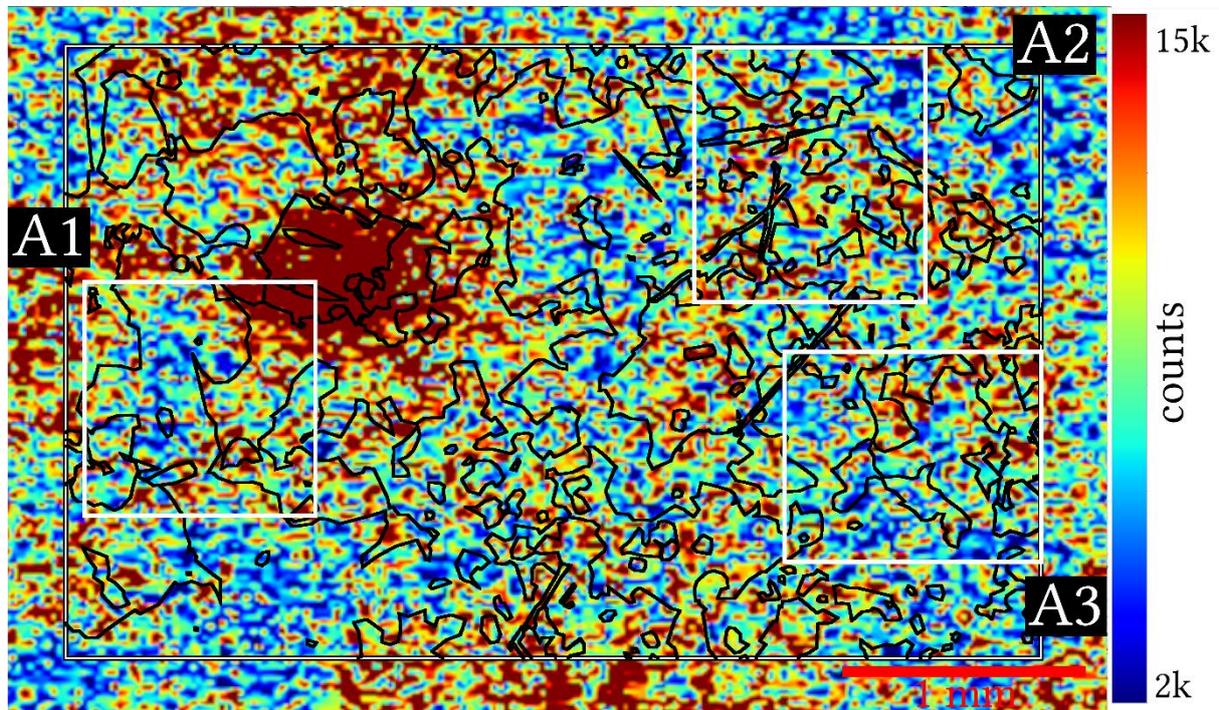
322 Two lifetimes can be determined on apatite, corresponding to complete loss of hydration and
323 coordination by three water molecules, respectively. Here again, interpretation of the data is complicated
324 by overlap with luminescence unrelated to Eu^{3+} . This impurity luminescence has a very similar lifetime
325 as the long-lived Eu^{3+} species, which leads to a large uncertainty in the determination of this lifetime.
326 As discussed for incorporation into feldspar, we assume most incorporation to be unrelated to our
327 experiments, but rather intrinsic Eu^{3+} (representative spectra are shown in the SI, Figure S9). However,
328 incorporation of Eu^{3+} into apatite has been shown to occur rapidly under some conditions (see below).³²
329 The second species can be interpreted as a surface (SF) incorporation species, due to its relatively low
330 number of bound water molecules.

331 On quartz lifetime determination was only possible close to the grain boundary with feldspar, where the
332 luminescence intensity was slightly higher. The species we identify here is a fully dehydrated
333 incorporation species, with a spectral fingerprint matching that of the incorporation species in feldspar,
334 once again confirming that these grain boundaries exhibit layering of two minerals. Therefore, these
335 lifetimes cannot be considered typical of the speciation of Eu^{3+} on quartz grains in Bukov migmatized
336 gneiss. On pyralspite we once again find only surface incorporation and intrinsic incorporation into the
337 bulk of the mineral.

338 3.3 Autoradiography: Eu^{3+} sorption uptake comparison

339 Autoradiography allows us to independently quantify the sorption of Eu^{3+} on the migmatized gneiss
340 surface. The method is not affected by luminescence quenching by transition metals and hence all
341 minerals can be considered and the use of radioactive ^{152}Eu ensures that only Eu from our sorption
342 experiments is detected (as opposed to intrinsically incorporated Eu). The autoradiogram (Figure 3) was

343 recorded for the same ROI that was used for the mineral identification with a nominally similar
344 resolution ($\sim 10\ \mu\text{m}$) as μTRLFS . Due to the specific conditions of the measurement, the actual resolution
345 is however significantly lower ($\sim 100\ \mu\text{m}$).



346

347 Figure 3: Autoradiogram of the same ROI as used in Figure 1 with highlighted μTRLFS ROIs (white
348 rectangles)

349 Radiographically, the chlorite grain on the upper left (cp. Figure 1) exhibits the highest Eu^{3+} deposition
350 in the whole ROI. Other chlorite grains also show high sorption uptake, but not as prominent as the
351 largest grain. Sorption is somewhat lower on amphibole and prehnite, which exhibit very similar
352 sorption capacities. Sorption on feldspar is significantly lower than on the previously mentioned
353 minerals. There is no observable difference between feldspar, quartz, and apatite. All the other minerals,
354 which only occur as very small grains cannot be reliably evaluated due to the low resolution of the
355 method. As the autoradiogram is noisy, especially in those regions with a lower sorption uptake, an
356 absolute quantification of the Eu^{3+} was not feasible, but a relative sorption uptake can be determined:
357 chlorite $>$ amphibole \approx prehnite $>$ feldspar \approx quartz \approx apatite.

358 The sequence of mineral reference agrees with the μTRLFS findings, with the notable exceptions of
359 chlorite and amphibole, which are not accessible to μTRLFS measurements due to their high Fe
360 contents. As mentioned in the experimental section, other discrepancies may arise from the significantly
361 lower resolution of the autoradiography measurement due to the isotropic radiation and scattering by
362 the plastic wrap and the surface itself.

363 3.2 Discussion

364 The sorption behavior of Eu^{3+} on Bukov migmatized gneiss can be briefly summarized as follows.
365 Quantitatively, the overall sorption uptake is controlled by chlorite, amphibole, and prehnite, with only
366 low sorption on feldspar and quartz. We can only obtain speciation information where μTRLFS is not
367 affected by quenching by e.g. iron or very low luminescence intensities. Here, we find relatively strong
368 inner-sphere complexes on feldspar, but also on prehnite, where additional surface incorporation was
369 observed. On quartz, no characterization was possible due to the very low Eu^{3+} sorption on its surface.
370 Sorption on apatite appears to be quite high, but an interpretation is complicated by additional
371 luminophores in the natural material. Nevertheless, the species can be tentatively identified as a surface
372 incorporation species and fully incorporated Eu^{3+} . The incorporated Eu^{3+} is most likely intrinsic⁵³ and
373 not a consequence of the sorption experiment, although some studies suggest rapid incorporation into
374 apatite is possible.³²

375 These findings illustrate the complexity of sorption processes on natural materials and particularly shed
376 light on the effect of mineral competition on sorption processes, as becomes clear when comparing the
377 distribution of Eu^{3+} on Bukov migmatized gneiss to the previously determined distribution on
378 Eibenstock granite.⁶ The previously investigated system had a significantly simpler composition of only
379 K-feldspar, quartz, and biotite. It quickly becomes clear that the mineral phases that dominate retention
380 of Eu on Bukov migmatized gneiss were not present in Eibenstock granite, which affects the interaction
381 with the mineral phases present in both rocks.

382 This is most obvious for feldspar, where the competition affects the quantity of adsorbed Eu^{3+} , which in
383 turn affects its speciation. In the previous study on Eibenstock granite, feldspar was the main surface for
384 metal retention especially at high pH. Here, on the other hand, feldspar exhibits low to medium Eu^{3+}
385 sorption and is clearly outcompeted by other phases, according to both autoradiography and μTRLFS .
386 At the same time, sorption to feldspar has become stronger, as evidenced by the lower number of water
387 molecules (and hence larger number of surface coordinating groups) in Eu's first coordination sphere.
388 On Eibenstock granite feldspar, typically ~7 water molecules remain with adsorbed Eu^{3+} , corresponding
389 to mono- or bidentate binding to the surface. While we find the same species on feldspar in Bukov
390 migmatized gneiss, the larger fraction of adsorbed Eu^{3+} is coordinated by 3 or 5 water molecules, which
391 indicates a higher coordination number from the surface. In addition, surface incorporation with only 1-
392 2 remaining water molecules is observed. Apparently, binding to feldspar in Bukov migmatized gneiss
393 only occurs at preferential sites offering strong binding by multiple surface groups, which presumably,
394 goes along with a low reversibility of the sorption process. As sorption on feldspar in Bukov gneiss is
395 low, the weaker sorption sites, which dominated sorption on feldspar in Eibenstock granite, are rarely
396 occupied. Thus, the weakly bound IS complex identified on Eibenstock granite is almost completely
397 replaced by sorption on more preferable mineral phases like prehnite or chlorite. A similar effect though
398 with lower sorption uptake overall can be seen on quartz, where sorption was low, but the sorption
399 interaction was fairly strong on Eibenstock granite. This was interpreted as a preferential occupation of

400 defect sites, which can bind through multiple surface sites. Through the competition with prehnite,
401 chlorite, and hornblende, sorption on quartz is nearly completely suppressed in this study, to such an
402 extent that a characterization of Eu^{3+} 's speciation on quartz was no longer possible.

403 The observed changes in speciation appear to lead to the preferred occupation of sorption sites with very
404 low number of water molecules remaining with Eu^{3+} , strong IS complexes or even surface incorporation
405 species. It seems reasonable to assume that the formation of such species will require surface defects, as
406 an atomically flat mineral surface without kinks or steps would not be able to provide six or even eight
407 binding groups. As the spatial resolution of our experiments is, however, significantly larger than these
408 atomic defects, the observed speciation must be a consequence of an increased density of defects in the
409 areas, where such strong sorption modes dominate. This connection between surface topography and
410 sorption preference and speciation should be investigated in more detail.

411

412 3.3 Environmental Implications

413 This study proves once more the importance of sorption studies on whole natural rock samples at the
414 molecular level. The interaction with mineral phases controls the mobility of contaminants and
415 radionuclides at contaminated sites and technical installations, such as a deep geological repository for
416 nuclear waste. Safety assessment and remediation strategies for such sites frequently rely on reactive
417 transport modelling based on thermodynamic constants derived from sorption studies. As our results
418 demonstrate, the speciation and sorption uptake will depend on the combination of mineral phases
419 present and sorption on one phase may significantly change the amount of adsorbed Eu^{3+} on another.
420 Where multiple types of binding sites exist, this competition will also affect the speciation of the
421 adsorbed cation. This type of behavior cannot be studied in single phase systems but must be
422 investigated in systems as close to reality as possible. Single phase model studies will of course remain
423 important as the foundation necessary for the understanding of more complex systems.

424 One such system was here identified in prehnite, which may be a highly relevant mineral phase for the
425 retention of trivalent actinides, such as Am^{3+} from nuclear wastes, in repositories located in crystalline
426 rock. It is known to be a fracture filling material⁵⁴⁻⁵⁶ and will exhibit accessible surfaces in contact with
427 a presumed water flow path through the material. Our results indicate prehnite may serve as an effective
428 barrier for the transport of radionuclides in this scenario, but detailed and quantitative studies are to the
429 best of our knowledge absent from the literature. The situation for the other mineral phases, which
430 control the retention of Eu^{3+} in our study is similar; also, for chlorite and Mg-hornblende data on their
431 retention potential is very limited, both thermodynamically and on the molecular level.

432 To expand the applicability of our findings to a broader range of scenarios such detailed studies on the
433 model systems will be required. In addition, attempts must be made to accurately reproduce

434 spectroscopically verified distributions of Eu^{3+} on natural rock using surface complexation modelling
435 and reactive transport calculations, which would allow to better evaluate both, the quality of current
436 models and the relevance of our molecular scale information on the larger scale.

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571 Supporting Information

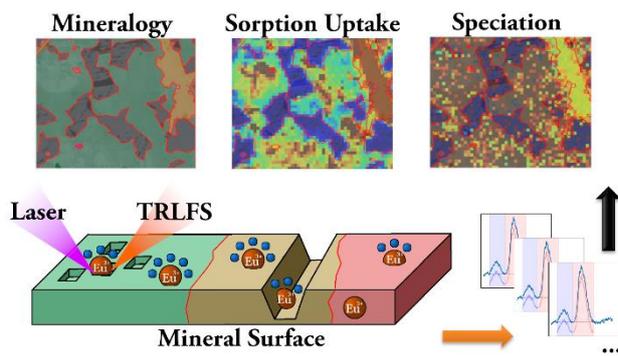
572 Excerpt of the URF Bukov geology; Batch sorption data and sample preparation; PXRD data; Raman
573 reference spectra; μ TRLFS mappings of A1 and A2 of sorption uptake (F_1+F_2) and speciation (F_2/F_1);
574 detailed lifetime data and locations; Representative spectra for the most important non-quenching
575 mineral phases; Delayed spectra of apatite and feldspar

576 Additional Information

577 Competing interests: The authors declare no competing interests.

578

579 TOC graphic



580

581 Synopsis: Spatially-resolved spectroscopy revealed the mechanism of uptake of Eu(III) on a complex

582 natural crystalline rock sample.