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Solid and aqueous speciation of yttrium in passive remediation systems of acid mine drainage

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1 Solid and aqueous speciation of yttrium in
2 passive remediation systems of acid mine
3 drainage

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21 **ABSTRACT**

22 Yttrium belongs to the rare earth elements (REE) together with lanthanides and
23 scandium. REE are commonly used in modern technologies, and their limited supply
24 has made it necessary to look for new alternative resources. Acid mine drainage (AMD)
25 is a potential resource since is moderately enriched in REE. In fact, in passive
26 remediation systems, which are implemented to minimize the environmental impacts of
27 AMD, REE are mainly retained in basaluminite, an aluminum hydroxysulfate
28 precipitate. In this study, the solid and liquid speciation and the local structure of
29 yttrium were studied in high sulfate aqueous solutions, basaluminite standards and
30 samples from remediation columns using synchrotron-based techniques and molecular
31 modeling. Pair distribution function (PDF) analyses and ab initio molecular dynamics
32 density functional theory models of the yttrium sulfate solution show that the YSO_4^+ ion
33 pair forms a monodentate inner sphere complex. Extended X-ray absorption fine
34 structure (EXAFS) and PDF analyses show that Y is retained by basaluminite forming a
35 monodentate inner-sphere surface complex at the aluminum hydroxide surface. EXAFS
36 of the column samples show that its signal is represented in more than 75% by the
37 signal of a basaluminite which YSO_4^+ is forming an inner-sphere complex. The atomic
38 vision of the REE configuration in AMD environments could help for a deeper research
39 of the REE recovery from waste generated in the AMD remediation systems.

40

41 INTRODUCTION

42 Yttrium belongs to Rare Earth Elements (REE) group, also composed by lanthanides
43 and scandium. REE are necessary for the development of modern technologies, and
44 specifically, yttrium as important applications, for instance, in fluorescent lamps as
45 phosphors,¹ and in aircraft industry, used in the thermal barrier coatings for jet engines.²
46 The REE increasing demand but low worldwide supply has led to consider REE as
47 critical raw materials boosting searches for alternative resources, such as recycling used
48 stocks or identifying new geological sources of these elements. Because the REE
49 concentrations in acid mine drainage (AMD) are from one to two orders of magnitude
50 higher than the average concentrations in natural waters,³ it may be possible to perform
51 secondary REE recovery from precipitates from AMD neutralization in passive
52 remediation systems. The active systems were developed to minimize the environmental
53 impacts of AMD and they are used worldwide.^{4,5} However, due to the high water
54 content, sludge storage has substantial operational costs and environmental concerns.^{6,7}
55 In contrast, passive remediation systems, which have been developed extensively in
56 recent decades,⁸⁻¹¹ allow the AMD neutralization generating lower amounts of solid
57 waste precipitates. Ayora et al. documented nearly complete aqueous REE retention in
58 two laboratory columns simulating a disperse alkaline substrate (DAS), a passive
59 treatment already implemented in the field, for two highly acidic AMD (SW Spain).^{12,13}
60 The REE were scavenged by basaluminite, a mineral precipitated in the columns, which
61 also presented Y enrichment due to the higher yttrium concentration with respect to the
62 rest of REE in the two treated AMD. Basaluminite, an aluminum oxy-hydroxysulfate
63 ($\text{Al}_4(\text{SO}_4)(\text{OH})_{10}\cdot 5\text{H}_2\text{O}$), precipitates in acidic environments as a consequence of the
64 natural attenuation of the AMD when mixing with more alkaline waters, or due to the
65 induced neutralization of the acid waters, when the solution pH reaches ~ 4 .¹⁴

66 Basaluminite is considered a nanomineral, with a short-range order, around 1 nm of
67 coherent domain size, which is described as layers of Al-octahedra with structural point
68 defects and with the presence of sulfate groups as outer-sphere complexes between the
69 Al layers.¹⁵

70 Similarly to the REE uptake by basaluminite in DAS treatments, Gammons et al.,
71 reported the precipitation of hydrous aluminum oxides accompanied with a decrease in
72 REE concentration from AMD when mixed with natural water.¹⁶ Recently, the scavenge
73 of REE by basaluminite precipitates has been described as a sorption mechanism.¹⁷
74 AMD is characterized to contain high loads of dissolved sulfate and the affinity of REE
75 to form aqueous species with sulfate is very high, the MSO_4^+ aqueous complex being
76 the more abundant in AMD solutions.¹⁸ Sorption of dissolved REE from sulfate-rich
77 waters onto basaluminite is thus described as the sorption of the MSO_4^+ aqueous
78 complex via ligand exchange with a surface site of basaluminite, forming a
79 monodentate surface complex with the Al-octahedron as one proton is released.¹⁷ Here,
80 a structural description of the aqueous YSO_4^+ complex and of the local environment of
81 the surface complex formed upon adsorption onto basaluminite are reported.

82 Most of the previous studies reporting the adsorption mechanisms of REE using X-ray
83 absorption spectroscopy and Extended X-ray Absorption Fine Structure (EXAFS)
84 described the adsorption of free REE ions onto the surface of metal oxides.¹⁹⁻²²
85 However, the AMD environments show a high concentration of dissolved sulfate, which
86 presents high affinity for aqueous REE (M). Thus, the MSO_4^+ aqueous complex is the
87 major REE species in solution and explains that the sorption models of REE in AMD
88 precipitates might be better explained in terms of MSO_4^+ sorption.

89 The structure of the first hydration shell of lanthanides and yttrium has been well
90 characterized.²³⁻²⁸ The coordination number (CN) of the first hydration shell changes
91 from an average of CN ~ 9 oxygen atoms for light REE (LREE La to Pm) to CN ~ 8
92 oxygen atoms for heavy REE (HREE Tb to Lu), with intermediate values for medium
93 REE (MREE Pm to Gd).²⁷ This behavior is explained by the continuous decrease in
94 ionic radii with the atomic number.^{27,29,30} The ionic radius of yttrium is between that
95 those of Ho and Dy, so it is typically considered an HREE with a first hydration shell of
96 CN ~ 8 oxygen atoms. There are several studies describing aqueous complexes of REE
97 with different ligands. REE easily forms inner-sphere complexes with carbonate and
98 phosphate in solution³¹⁻³³ whereas chloride and nitrate forms inner-sphere complexes at
99 concentrations higher than 10 M.^{23,25} In the case of sulfate, no information about the
100 geometry of MSO_4^+ complexes has been reported so far despite their strong binding
101 affinity.¹⁸

102 The objective of this study is to elucidate the structure of Y adsorbed onto basaluminite.
103 Due to its chemical similarities with HREE, this allow us to assume similar structural
104 configuration for this sub-group. Moreover, this element was one of the most
105 concentrated in waste samples allowing performing X-ray absorption spectroscopy
106 experiments. Since the YSO_4^+ aqueous complex is adsorbed onto the mineral,¹⁷ a
107 previous characterization of the geometry of the aqueous complex has been carried out.
108 Finally a quantification of Y-species in basaluminite solids precipitated from AMD
109 treatments has been performed. Structural studies were performed using EXAFS and
110 pair distribution function (PDF) analyses of aqueous and solid samples combined with
111 *ab initio* molecular dynamics (AIMD) simulations of the aqueous YSO_4^+ complexes.

112 Two hypotheses are used to investigate the local structure of the aqueous YSO_4^+ ion
113 pair: (1) an outer-sphere complex, with water located between Y^{3+} and SO_4^{2-} , and (2) an

114 inner sphere complex. In the latter case, two more hypotheses must be considered: (a) a
115 monodentate complex, with one oxygen atom shared between the sulfate and the first
116 coordination sphere of Y^{3+} , and (b) a bidentate complex, with two oxygen atoms shared
117 between the yttrium hydration sphere and the sulfate group.

118 Once the structure of the aqueous solution is fully described, different hypotheses have
119 been considered to interpret the YSO_4^+ surface complexation onto the Al-
120 oxyhydroxysulfate: the formation of (1) a monodentate inner sphere complex, (2) a
121 bidentate mononuclear inner-sphere complex, (3) a bidentate binuclear inner sphere
122 complex.

123 Finally, to determine semi quantitatively the yttrium species in solids from column
124 samples, linear combination fits were performed using the most representative
125 references.

126 MATERIAL AND METHODS

127 Synthetic samples (standards)

128 Different basaluminites doped with Y were prepared for HEXS and EXAFS
129 experiments. To ensure maximum Y incorporation into the solid, sorption and
130 coprecipitation experiments were performed at pH 6,¹⁷ avoiding higher pH values where
131 YCO_3^+ aqueous species could be present.³⁴ A basaluminite sample with sorbed YSO_4^+
132 (B-YSO4-ads) was obtained from a suspension of 1g/L of solid in 0.11 $Y(NO_3)_3 \cdot 6H_2O$
133 and 0.25 M Na_2SO_4 solution for 5 hours at a constant pH of 6. At these conditions, the
134 major species in solution was YSO_4^+ , which is supposedly the aqueous Y specie sorbed
135 on the solid surface.¹⁷ A basaluminite sample coprecipitated with Y (B-Ycop) was
136 obtained using the basaluminite synthesis method adding 1 M $Y(NO_3)_3 \cdot 6H_2O$ in the

137 acid solution of 0.05 M $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (see Chapter S1 of the SI). Basaluminite and
138 nanoboehmite samples with sorbed Y^{3+} (B-Yads and A-Yads, respectively) were also
139 prepared from a suspension of 1 g/L of solid in 0.011-0.11 M $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ solution
140 for 5 hours, and the pH was maintained at ~ 6 at room temperature, respectively (the
141 synthesis protocol is described in detail in Chapter S1 of the SI). At these conditions,
142 the major species of Y is Y^{3+} . In all cases, the suspensions were centrifuged at 4500 rpm
143 for 15 minutes, the supernatant was filtered through 0.2 μm membranes and kept for
144 ICP analysis. The solids were rinsed several times with deionized water and oven dried
145 for 48 hours at a maximum temperature of 40° C.

146 High-energy X-ray scattering (HEXS) and EXAFS experiments of aqueous solutions
147 with Y and YSO_4^+ were carried out. For the HEXS measurements, an aqueous solution
148 of free yttrium ions (Y-sol) was prepared with 0.1 M $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ at pH 3.2, and a
149 solution containing YSO_4^+ as the major aqueous complex (YSO₄-sol) were prepared by
150 mixing equal amounts of 0.2 M $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 0.2 M Na_2SO_4 at pH 3. For the
151 EXAFS measurements, a solution with the free Y^{3+} ion (Y-sol) with a composition of
152 0.01 M $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ at pH 4.6, and the solution of the YSO_4^+ complex (YSO₄-sol) with a
153 composition of 0.01 M $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.01 M Na_2SO_4 at pH 2.9, were prepared,
154 respectively. At these conditions, the major species in solution were Y^{3+} and YSO_4^+
155 (Fig. S1). The yttrium concentrations of the references are listed in Table S1, and a
156 more comprehensive description of the syntheses is given in the Supporting Information
157 S1.

158 Waste samples from column treatments

159 Column samples were collected from two laboratory column experiments of Disperse
160 Alkaline Substrate (DAS), as described in Ayora et al.¹² simulating the remediation
161 systems of the two AMD from the Iberian Pyrite Belt region (SW Spain). The columns
162 (9.6 cm inner diameter and 39 cm in height) consisted in a permeable mixture of grained
163 limestone and wood shavings at a 1:1 weighed ratio. Samples W-MR-C1-4 and W-MR-
164 C1-5 belonged to columns which treated AMD from Monte Romero mine and W-Alm-
165 C3-8 and W-Alm-C3-9 samples belonged to columns which treated leaching of
166 Almagrera mine tailing dam. Y concentration in different AMDs at the inlet ranged
167 from 9 to 42 ppm, and sulfate concentrations 3.5 and 11.7 mg/L. Physical-chemical
168 parameters and water samples were collected every two weeks. Once the treatment
169 finished after 18 weeks, the solid was divided in 2 cm thick slices and dried. The
170 partitioning of Al, Fe and REE was studied by performing a sequential extraction
171 adapted from Torres and Auleda to the solid residues.³⁵ The results showed in Ayora et
172 al. concluded that REE were retained in basaluminite.¹⁰ The W-MR-C1-4, W-MR-C1-5,
173 W-Alm-C3-8 and W-Alm-C3-9 samples were selected from the depth where maximum
174 Al concentration was extracted from the solids, assuming the most enriched in
175 basaluminite solid slice. These waste samples were used for EXAFS measurements and
176 the Y concentrations for these samples are shown in Table S2.

177 Analytical techniques

178 Measurements of the pH values of the initial and final solutions were made with a
179 Crison[®] glass electrode calibrated with buffer solutions of pH 2, 4 and 7. The Al and S
180 concentrations were measured by inductively coupled plasma optical emission
181 spectroscopy (ICP-OES), and the Y concentration was measured by inductively coupled

182 plasma mass spectrometry (ICP-MS). The aqueous speciation and saturation index of
183 the solid phases were calculated with the PHREEQC code³⁶ using the Donnee
184 Thermoddem_V1.10 database³⁷ provided by the Bureau de Recherches Géologiques et
185 Minières (BRGM). Details of the analytical procedures and the database for the REE
186 speciation are described in the Supporting Information S2.

187 The HEXS measurements were performed at the ID31 beamline at the European
188 Synchrotron Radiation Facility (ESRF). The samples were loaded into 1.5 or 2 mm
189 Kapton capillaries, and the HEXS patterns were obtained using a Pilatus3 X CdTe 2M
190 detector. The data correction and generation of structure factors and pair distribution
191 functions were performed with the PDFgetX3 software.³⁸ PDF for aqueous solutions
192 were obtained by subtracting the scattering signal of pure water from the total scattering
193 signal of YSO₄-sol sample and Y-sol sample, respectively. The differential pair
194 distribution functions (d-PDF) for B-Ycop sample were obtained by subtracting the
195 PDF signal of a pure synthetic basaluminite from the PDF of B-Ycop sample.

196 The EXAFS measurements of the samples B-Yads, B-Ycop, A-Yads, Y-sol and YSO₄-
197 sol were performed at the Y K-edge (17.038 keV) at the FAME beamline,³⁹ BM30B at
198 the ESRF. The EXAFS measurements of the B-YSO₄ sample was performed at the Y
199 K-edge (17.038 keV) at CLÆSS beamline (ALBA synchrotron). Atomistic models of
200 YSO₄⁺ and Y³⁺ complexes adsorbed on a basaluminite surface with different initial
201 configurations were employed in the data analysis to extract the Y local order
202 parameters, including the neighbor distances, R, coordination number, N, and Debye-
203 Waller factors, σ^2 . The proportion of Y species present in each waste sample from
204 column treatments was obtained by linear combination fitting (LCF) of the EXAFS
205 spectra using the most representative reference compounds as the basis set. The

206 experimental setup and the details of the data analysis are given in the Supporting
207 Information S3.

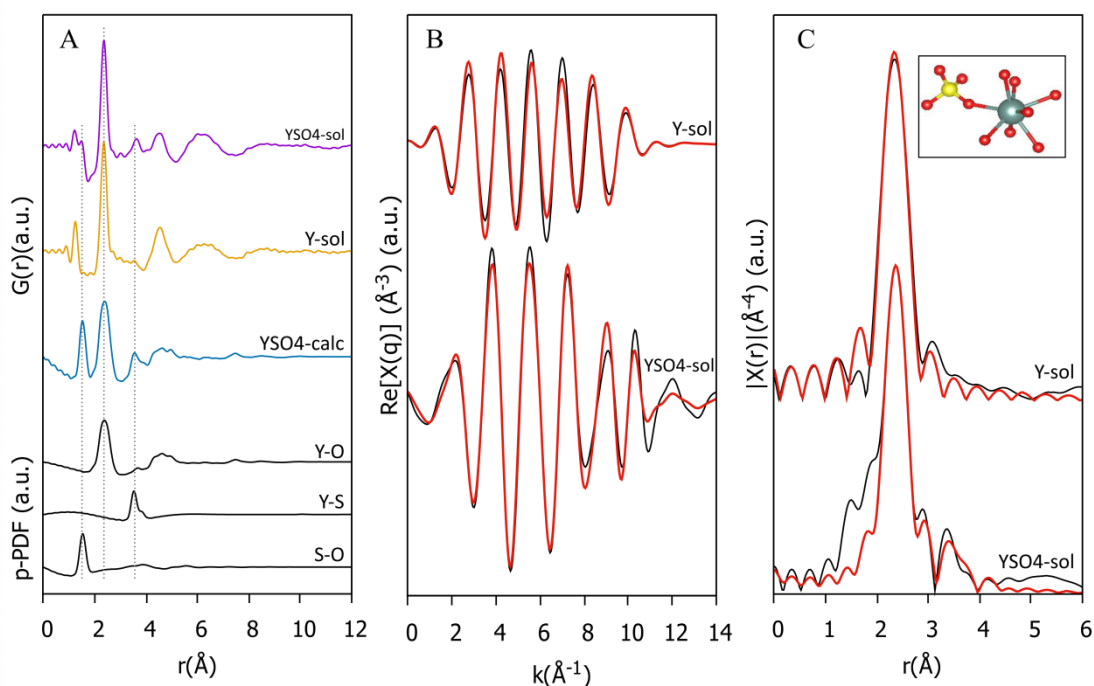
208 The Ab Initio Molecular Dynamics (AIMD) simulations of an aqueous solution of
209 yttrium(III) sulfate were carried out on a Y^{3+} - SO_4^{2-} - OH^- system embedded in a box of
210 61 water molecules. The simulations were conducted with the electronic structure code
211 CP2K/Quickstep code, version 5.1.⁴⁰ CP2K implements density functional theory
212 (DFT) based on a hybrid Gaussian plane wave. The revPBE generalized gradient
213 approximations for the exchange and correlation terms were used together with the
214 general dispersion correction termed DFT-D3.^{41,42} The simulations were carried out for
215 15 ps in the canonical (constant NVT) ensemble to maintain the average temperature at
216 $T = 300$ K. An in-house Python code using DiffPy-CMI was developed to convert the
217 AIMD trajectories to PDF signals.⁴³ Details of the MD simulations are described in S4.

218 **RESULTS AND DISCUSSION**

219 **Geometry of the aqueous complex YSO_4^+**

220 The experimental (YSO4-sol, Y-sol) and theoretical (YSO4-calc) PDFs of the Y-
221 containing aqueous solutions, 0.1 M YNO_3 and YSO_4 , are shown in Fig. 1. Background
222 subtraction of the aqueous samples was performed using a deionized water background,
223 which implies that the experimental PDFs shown here are differential PDFs (water
224 subtracted). The background scale factor was adjusted to minimize the O-O correlation
225 (~ 2.8 Å) in the PDFs. All spectra show an intense peak at 2.37 Å, which corresponds to
226 the Y-O interatomic distances to oxygen in the first coordination shell. The
227 experimental PDF of the YSO4-sol sample shows a small and sharp peak at 1.45 Å that
228 corresponds unequivocally to the S-O interatomic distance in sulfate, and another

229 smaller peak at ~ 3.6 Å, which is absent in Y-sol sample. The DFT-based PDFs obtained
 230 from AIMD simulations of the YSO_4^+ aqueous complex also reproduced this latter
 231 peak. Analyses of the AIMD trajectories show that the 3.6 Å distance between Y and S
 232 is consistent with the formation of a monodentate inner sphere complex (one shared
 233 oxygen) between the coordination shells of the sulfur and yttrium.



234

235 Figure 1. (A) Top: Experimental PDFs of YSO4-sol and Y-sol samples. Bottom:
 236 Simulated (AIMD) PDF (YSO4-calc) and partial PDFs of an YSO_4^+ aqueous complex.
 237 (B) Fourier-filtered signal from 1.8 to 4.2 Å for the EXAFS data. (C) EXAFS FT
 238 amplitude functions of the YSO4-sol sample. Black lines: experimental; red lines: fits.
 239 Simulated (AIMD) PDF and partial PDFs have been multiplied for visualization
 240 purposes: YSO4-cal ($\times 3$), Y-S ($\times 5$) and Y-O and S-O ($\times 2$). Dashed lines indicate the
 241 position of the Y-O, Y-S and S-O bonds in YSO4-sol sample.

242 Fits of the EXAFS spectra of the aqueous solutions were performed using atomistic
 243 models from the AIMD simulations as initial structural models for the generation of the

244 scattering paths. The results yielded an average Y-O distance of 2.37 ± 0.02 Å for the
 245 Y-sol sample and 2.38 ± 0.01 Å for YSO4-sol (Table 1). The intense peak in the FT
 246 function at 2.38 Å for the two aqueous references represents the first solvation shell,
 247 and its asymmetry reveals a distribution of Y-O interatomic distances, as reported
 248 previously by Lindqvist et al.²⁴ The coordination numbers (CN) were 7.6 ± 1.9 and $7.9 \pm$
 249 0.9 for Y-sol and YSO4-sol, respectively, which are close to the expected value of 8 for
 250 HREE. A second shell is visible in the FT of the YSO4-sol sample. It was fitted with a
 251 Y-S distance of 3.50 ± 0.04 Å, similar to that observed in the PDF of the same sample,
 252 and a CN = 1. This corresponds to a monodentate coordination, matching the geometry
 253 obtained from the AIMD simulations. The coordination number CN = 1 was kept fixed
 254 in the EXAFS fitting to increase the stability of the fitting procedure, minimizing the
 255 number of parameters and excessive correlations between them. A multiple scattering
 256 path (Y-S-O) was included and was found to be relevant and to improve the fit. The
 257 fitting parameters matched both the PDF and modeling results and indicated that the
 258 YSO_4^+ aqueous species forms a monodentate inner-sphere complex.

259 Table 1. Modeling parameters of the Y K-edge EXAFS spectra of the 0.1 M YSO_4
 260 aqueous solution (the error is expressed in the parentheses after the last digit).

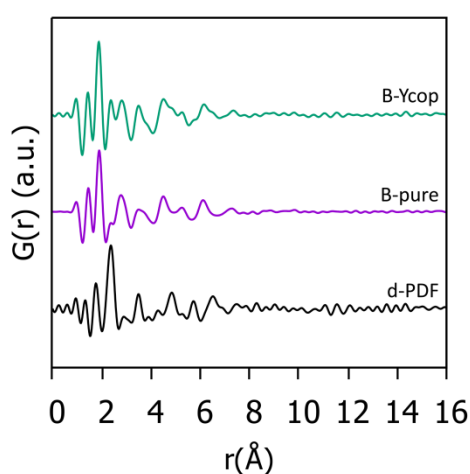
Sample	Neighbor	path	N	σ^2	ΔE_0	R (Å)	Var.	χ^2
Y sol	1 st shell	Y-O	7(2)	0.005(3)	-2(3)	2.37(2)	4	354
Y-SO4 sol	1 st shell	Y-O ₁	7.9(9)	0.007(2)		2.38(1)	8	498
	2 nd shell	Y-S	1 _{fixed}	0.003(6)	-1(1)	3.50(4)		
	3 rd shell	Y-S-O	1 _{fixed}	0.015(19)		3.18(10)		

261 The determined Y-O first shell coordination numbers and interatomic distances are
262 consistent with previous reports describing yttrium coordination shells with $N = 8$ and
263 Y-O distances of 2.36 \AA .^{23,24,28} Likewise aqueous REE carbonate and phosphate
264 complexes,³¹⁻³³ aqueous Y-SO₄ ion-pairs form inner-sphere complexes. This result
265 contrasts with other ligands such as chloride, which hardly forms inner sphere
266 complexes at similar concentrations to those used in this study.²³ Only the formation of
267 monodentate complexation between Dy and NO₃ with a distance of 3.57 \AA has been
268 reported using MD simulations.²⁶

269 **Local order of yttrium adsorbed into basaluminite**

270 HEXS measurements were performed on a pure basaluminite sample (B-pure) and on a
271 sample of basaluminite coprecipitated with Y (B-Ycop). The PDFs are shown in Fig. 2
272 with the differential PDF obtained by subtracting the pure sample from the
273 coprecipitated one. This approach has been previously used to examine the local order
274 of different anions incorporated in poorly crystalline minerals, such as schwertmannite
275 and basaluminite, and the desorption of sulfate from basaluminite when ageing at
276 circumneutral pH values.^{15,46} The PDFs of the two samples are similar and show
277 characteristic basaluminite peaks that correspond to the known interatomic distances (S-
278 O bond at $\sim 1.46 \text{ \AA}$, Al-O bonds at $1.88, 4, 4.8$ and 6 \AA and Al-Al bonds at 3 \AA).^{15,45} The
279 differential PDF shows a main peak at 2.37 \AA , which corresponds to the Y-O distance.
280 This peak matches the distance from Y to the first solvation shell obtained from the
281 EXAFS and PDF of the Y³⁺ and YSO₄⁺ aqueous solutions (Fig. 1). Another peak is
282 present at 1.7 \AA , which is tentatively assigned to a new Al-O distance of the Al-
283 octahedra, due to probable distortions of the basaluminite. The existence of
284 deformations in the structures of mineral nanoparticles upon oxyanion adsorption has
285 been previously observed.^{44,46} A smaller peak appears at 3.48 \AA , which can be

286 tentatively assigned to a Y-S distance, though it is shorter than the Y-S distance
287 reported for the YSO_4^+ aqueous complex (Table 2 and Fig. 1A). This peak may also
288 correspond to a Y-Al interatomic distance, which would be consistent with the
289 formation of an inner-sphere complex, as suggested by Lozano et al.¹⁷ This hypothesis
290 will be tested using different atomistic models for the fitting of the EXAFS data. Other
291 peaks at longer distances are difficult to assign in the absence of a more detailed
292 structural model.

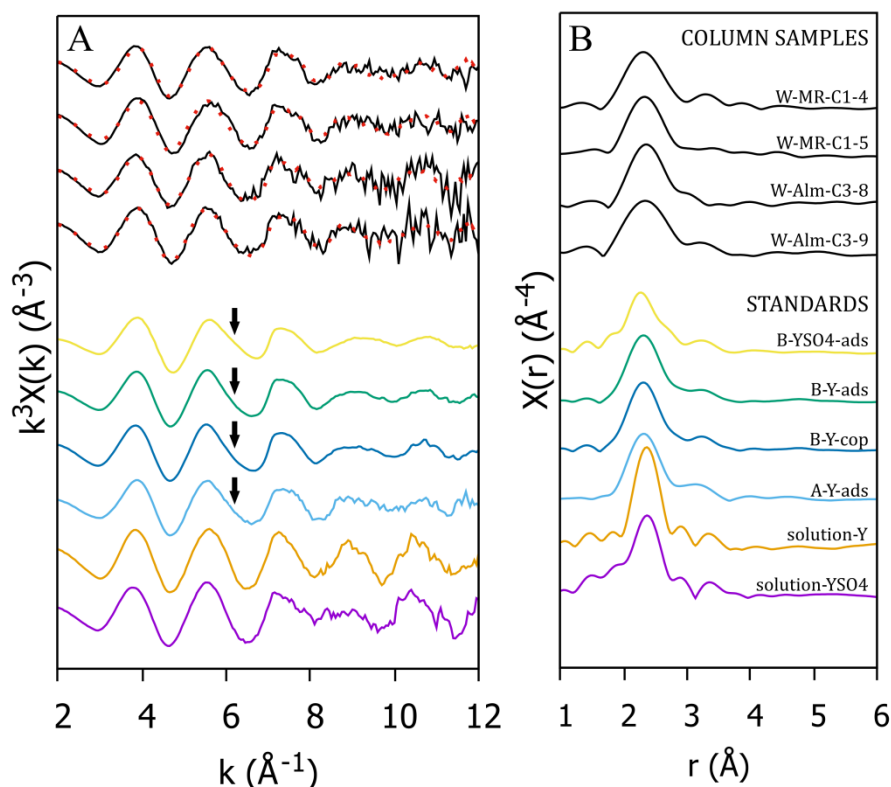


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294 Figure 2. PDFs of basaluminite coprecipitated in the presence of Y (B-Ycop), pure
295 basaluminite (B-pure) and differential PDF (d-PDF). The d-PDF spectrum has been
296 amplified ($\times 3$) for visualization purposes.

297 The k^3 -weighted EXAFS spectra for the solid references B-YSO4-ads, B-Y-ads, B-Y-
298 cop and A-Y-ads (Fig. 3) are indistinguishable and differ from the aqueous Y-sol and
299 YSO4-sol spectra in that a slight oscillation becomes visible at 5-6 \AA^{-1} . In the B-YSO4-
300 ads the dominant Y species in solution is the YSO_4^+ complex. However, in B-Y-ads, B-
301 Ycop and A-Yads, the dominant Y species is Y^{3+} . Still, these four samples show similar
302 spectra. Since the common feature in these three samples is the presence of an Al
303 adsorbent, and this feature agrees with that in the B-YSO4-ads EXAFS spectrum, we

304 hypothesize that the higher frequency observed at $5-6 \text{ \AA}^{-1}$ (arrow in Fig. 3) may be
 305 related to the presence of an Al backscatterer, rather than to a signal from an close
 306 sulfate group. Both Al and S are light atoms with similar atomic numbers ($Z = 13$ and
 307 16 , respectively), which makes their backscattering functions difficult to distinguish via
 308 fitting of the EXAFS signal. These observations lead us to assume that the EXAFS
 309 measurements have poor sensitivity to the presence of Y-S bonds in this system.
 310 However, a contribution from a sulfate shell for the two first samples cannot be ruled
 311 out.

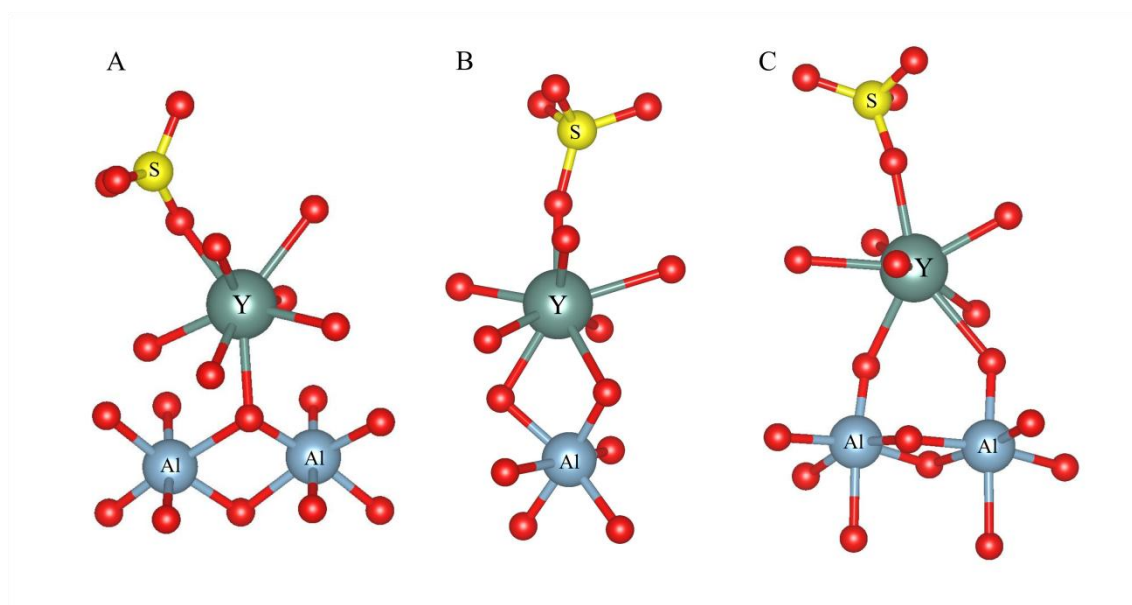


312 [A1]

313 Figure 3. k^3 -weighted EXAFS (A) and FT amplitude functions (B) for four waste
 314 samples from column treatments W-MR-C1-3, W-MR-C1-4, W-Alm-C3-8, and W-
 315 Alm-C3-9 (upper part) and solid standards (basaluminite sorbed with YSO4. (B-YSO4),
 316 basaluminite sorbed and coprecipitated with Y: B-Yads and B-Ycop, respectively) and

317 aqueous solution (free ion and sulfate complex: Y-sol and YSO₄-sol, respectively)
318 (bottom part). The dashed lines in the EXAFS signals of the column samples represent
319 LCF with B-Yads (basaluminite with sorbed yttrium) and YSO₄-sol (solution of Y with
320 SO₄) standards as the most representative references (results in Table 3). The arrows
321 indicate a frequency present in the solid standards.

322 Based on the previous information of the aqueous species and on the thermodynamic
323 model of REE sorption,¹⁷ the B-YSO₄-ads EXAFS signal was fitted with three models
324 of different geometries of the YSO₄⁺ aqueous complex adsorbed onto basaluminite
325 surfaces via inner-sphere complexes (Fig. 4), to obtain an atomistic model
326 representation: (A) a monodentate surface complex; (B) a bidentate mononuclear
327 surface complex and (C) a bidentate binuclear surface complex.



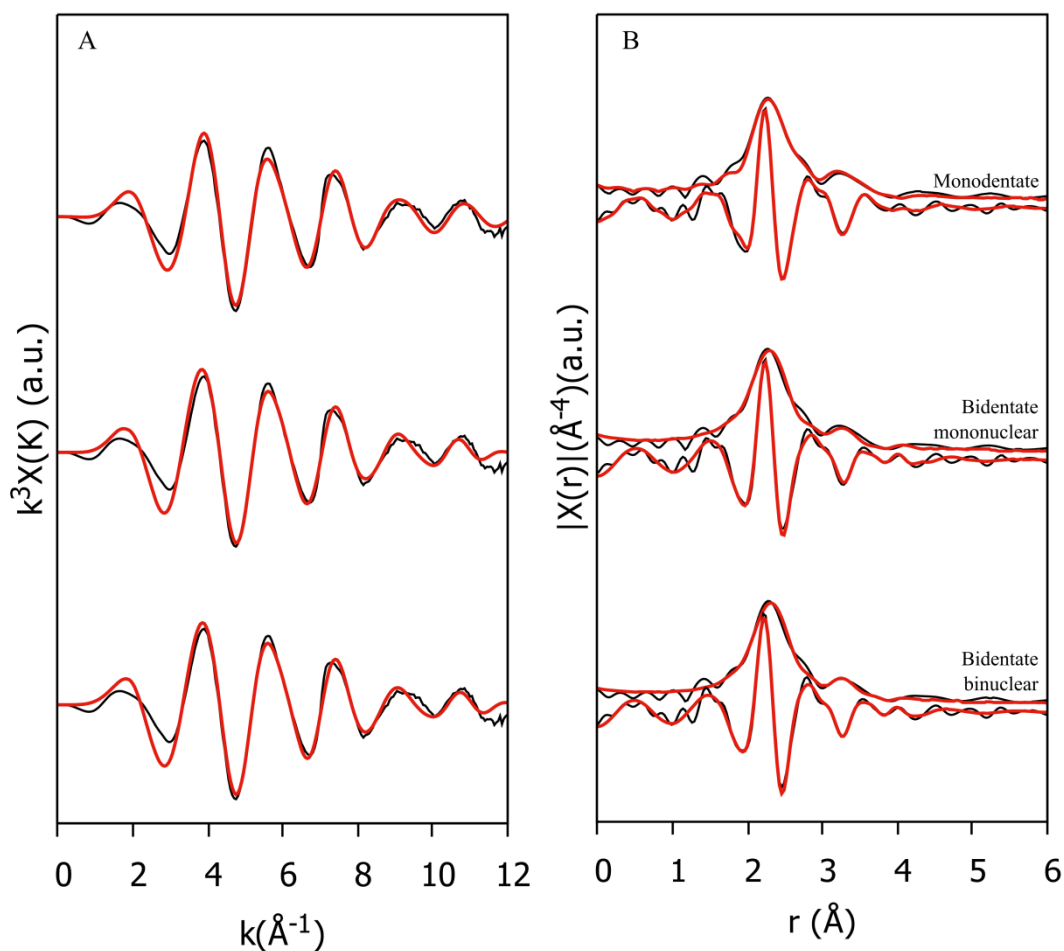
328

329 Figure 4. Atomistic representations of the three models of YSO₄ aqueous complex
330 adsorbed on the basaluminite-water interface. The different atomic positions of YSO₄
331 to octahedral-Al are used to fit the EXAFS signal of the B-YSO₄ sample. The three

332 models show different inner-sphere surface complexes: (A) monodentate, (B) bidentate
333 mononuclear and (C) bidentate binuclear.

334 The EXAFS fits for B-YSO₄-ads for the different models and the calculated parameters
335 are given in Fig. 5 and Table 2, respectively. The first model represents a monodentate
336 inner-sphere surface complex. The coordination number of the shells has been fixed
337 based on information from another sources: The major aqueous species in solution was
338 YSO₄⁺, which, as supported by PDF and DFT data, forms a monodentate aqueous
339 complex. Besides, the thermodynamic model of REE sorption on basaluminite indicated
340 monodentate complexation of the YSO₄⁺ aqueous complex.¹⁷ With this information the
341 fit was performed assuming S and Al coordination numbers equal to 1 and 2,
342 respectively, as it is shown in Fig. 4A. Besides, two oxygen paths were considered due
343 to the Y-O length variation improving the fit. Thus, the fit yielded a first coordination
344 shell with a Y-O distance range between 2.32 and 2.47 ± 0.02 Å with a fix coordination
345 number of 8. The second shell was fitted yielding a Y-Al distance at 3.52 Å with a fixed
346 coordination number of N = 2, and a Y-S distance at 3.33 with a fixed number of N = 1.
347 This result is consistent with the monodentate inner-sphere complex of Y with one
348 oxygen shared with two surface Al sites (Fig. 4A). The second model, the bidentate
349 binuclear inner-sphere complex configuration, gave poorer results without structural
350 significance and with higher χ_v^2 values (Table 2), so it was discarded. The third model
351 was the bidentate binuclear, the first shell was fitted with a coordination number of 10 ±
352 1.31 and a distance of 2.33 Å. The second shell was fitted with a S path yielding an Y-S
353 distance of 3.34 Å with a fix coordination number of N = 1, similar to that for the
354 monodentate hypothesis, and with an Al path with a fixed coordination number of N = 2
355 giving a distance a bit longer, 3.92 Å.

356 Overall, the monodentate inner-sphere surface complex gave the best fit results, which
357 was in accordance to the thermodynamic sorption model. Moreover, the bidentate
358 binuclear inner-sphere surface complexes yielded also a good fit with similar χ^2 values
359 than the monodentate hypothesis, making this configuration also possible (Fig. 4C). In
360 both fits, the distances between Y-S are similar, 3.33, 3.34 Å, which is also observed in
361 the differential PDF of the B-Ycop reference. From the EXAFS data, the presence of a
362 bidentate binuclear surface complex cannot be ruled out. However, the thermodynamic
363 modeling and the EXAFS data both agree on the monodentate surface complex being
364 the one present at the basaluminite-water interface.



365

366 Figure 5. (A) The k^3 -weighted EXAFS spectra at the Y K-edge of the basaluminite with
 367 YSO4 sorbed (B-YSO4 reference) and (B) its Fourier transform amplitude. The
 368 experimental and fitted curves are shown in black and red, respectively.

369 Table 2. Results of the EXAFS fits for B-YSO4 reference. Model 1: monodentate inner
 370 sphere. Model 2: bidentate mononuclear inner sphere. Model 3: bidentate binuclear
 371 inner sphere. Var. indicates independent variables. The best model is indicated with a
 372 star (*). The error is expressed in the parentheses after the last digit.

Model	Neighbor	path	N	σ^2	ΔE_0	R	Var.	χ_v^2
1*	1 st shell	Y-O ₁	6 _{fix}	0.007(1)	-3(2)	2.32(1)	9	338
		Y-O ₂	2 _{fix}	0.004(8)	-3(2)	2.47(2)		
	2 nd shell	Y-S	1 _{fix}	0.008(5)	-3(2)	3.33(4)		
		Y-Al	2 _{fix}	0.012(5)	-3(2)	3.52(5)		
2	1 st shell	Y-O	10 (1)	0.012(2)	-6(2)	2.33 (1)	8	402
	2 nd shell	Y-S	1 _{fix}	0.009(5)	-6(2)	3.88 (5)		
		Y-Al	1 _{fix}	0.006(3)	-6(2)	3.42 (3)		
3	1 st shell	Y-O	10(1)	0.013(1)	-4(1)	2.33(1)	8	334
	2 nd shell	Y-S	1 _{fix}	0.008(3)	-4(1)	3.34(3)		
		Y-Al	2 _{fix}	0.011(5)	-4(1)	3.92(4)		

373

374 The EXAFS of the B-YSO4-ads standard was also fitted with the same three atomistic
 375 models presented in Fig. 4 but without sulfate included (Fig. S2) to analyze the
 376 sensitivity of the fit to the presence of sulfate. The Al-O distances obtained with these
 377 new fits (Table S3) were almost identical to those calculated when including sulfate
 378 shells (Table 2), with the exception in the monodentate inner sphere configuration,
 379 which was a bit longer. Thus, the presence of Al is consistent in the two models, with
 380 and without sulfate. However, the fits obtained with the sulfate group included showed
 381 lower values of the agreement factor (reduced chi-square) (compare Table 2 and Table
 382 S3). This discussion highlights the difficulties of the EXAFS technique to discern the

383 presence of low-Z backscatterers, in particular in disordered systems such as the one
384 present here.

385 These results are consistent with those presented by Rabung et al. where Gd and Lu
386 were shown to adsorb onto γ -Al₂O₃ to form inner sphere complexes.⁴⁷ Lu, which is
387 considered a HREE such as Y, was shown to form a monodentate surface complex with
388 a first shell of 7 atoms and a Lu-O distance of 2.28 Å. The longer Y-O distance found
389 here for Y is consistent with its larger Y ionic radius. However, these authors could not
390 detect any Lu-Al bonds in their EXAFS data. Other sorption studies of Eu onto γ -Al₂O₃
391 showed the formation of both monodentate and bidentate binuclear complexes.²⁰ In
392 contrast to this study and to the results of Rabung et al. on Al oxides, EXAFS studies of
393 lanthanides sorbed onto ferric oxides have shown a predominance of bidentate inner-
394 sphere complexes.⁴⁷ Lu adsorbed onto ferrihydrite at pH \geq 5.5 yielded an Lu-O
395 coordination number of 7 at a distance of 2.30 Å, and a second coordination shell was
396 identified with a Lu-Fe interatomic distance at 3.38 Å. These EXAFS results were
397 complemented by time-resolved laser fluorescence spectroscopy (TRLF) measurements
398 that showed five water molecules surrounding the metal cations, which was interpreted
399 as a bidentate inner sphere complex.²² The similar distance to the second shell found by
400 Dardenne et al.²² and by us in these two different systems can be explained by the
401 smaller size of Lu in comparison to Y, which is compensated for by the longer Fe-O
402 bond distance in comparison to the Al-O bond, making possible a bidentate
403 mononuclear sphere at 3.4 Å in Fe oxides and Al oxides. Another study by Estes et al.
404 reported Eu K-edge EXAFS data of Eu(III) sorbed onto hematite.¹⁹ They observed a
405 decrease in the coordination number of the Eu-O bond from 8 to 5 upon adsorption
406 accompanied by a smaller Eu-Fe bond distance at 3 Å. This result was interpreted via
407 molecular simulations as being due to the formation of an inner sphere bidentate

408 mononuclear surface complex. Such a decrease in the coordination number was not
409 observed in this study; the CN of the Y-O correlation was maintained at $\sim 8 \pm 1$ for both
410 the aqueous and surface complexes.

411 **Identification of Y species in waste samples from AMD treatment**

412 The k^3 -weighted EXAFS of the column samples (upper part) and standards (lower part)
413 and their Fourier transform (FT) envelope functions with corrected phase-shifts are
414 shown in Fig. 3. Visual comparisons of the EXAFS spectra of the column samples
415 reveal a strong similarity between them, suggesting similar local order of Y in all
416 samples. In addition, the EXAFS spectra of the column samples are very similar to solid
417 references (B-YSO4-ads, B-Y-ads, B-Y-cop and A-Y-ads). They have a shoulder at
418 $\sim 6.5 \text{ \AA}^{-1}$, indicating a higher frequency which is absent in the aqueous samples (see
419 arrow in Fig. 3).

420 Based on the PCA analyses (see Chapter S3), the reconstructed spectra indicated that
421 only two components were required to describe the samples (Fig. S4). The two most
422 likely Y species identified by target transformation of the standard spectra, were the B-
423 YSO4-ads and B-Y-ads references (Fig. S5). However, since their EXAFS signals are
424 very similar, LCF of the EXAFS spectra of the waste samples from column treatments
425 was performed using B-YSO4-ads and YSO4-sol (Fig. 3A, upper part) to quantify the
426 proportions of different Y species in the waste samples. The use of these two standards
427 would correspond to YSO_4^+ adsorbed forming inner- and outer-sphere complexes,
428 respectively.

429 The LCF results show that more than 75% of Y adopts a local geometry similar to that
430 of the B-YSO4-ads reference (with the exception of sample W-Alm-C3-8, for which the
431 LCF indicated equal proportion of both YSO4 presented as inner sphere and outer-

432 sphere complexes (Table 3)). The waste samples were selected from the depth where the
 433 major proportion of Al precipitated, assuming basaluminite precipitation. However,
 434 other minor mineral species may have also been precipitated, such as Fe-
 435 oxyhydroxysulfate, due to the presence of small amount of Fe in the solids. Specifically,
 436 samples from Almagrera column (W-Alm-C3-8 and W-Alm-C3-9) presented higher Fe
 437 concentration than samples from Monte Romero treatment. REE can be also scavenged
 438 by amorphous Fe hydroxides in AMD neutralization environments,⁴⁸ so a minor or
 439 almost negligible fraction of Y could be retained by the small proportion of ferric
 440 oxides precipitated in the selected samples, explaining the lower proportion of B-YSO4-
 441 ads.

442 Table 3. Percentages of Y species in the column samples obtained from LCF of the
 443 EXAFS spectra. R-factor and χ^2 are defined in Chapter S3 of the SI.

Standard	C1-4	C1-5	C3-8	C3-9
B-YSO4ads	0.719 ± 0.036	0.867 ± 0.038	0.495 ± 0.059	0.746 ± 0.061
YSO4-solution	0.281 ± 0.069	0.133 ± 0.071	0.505 ± 0.084	0.254 ± 0.085
R-factor	0.14	0.14	0.29	0.30
χ^2	133	154	371	392

444

445 ENVIRONMENTAL IMPLICATIONS

446 The YSO_4^+ aqueous species has been characterized combining PDF analyses of aqueous
 447 solutions and AIMD simulations, confirming the formation of an inner-sphere Y-SO₄

448 ion pair with a monodentate configuration, with an Y-S interatomic distance of 3.5 Å.
449 Results from thermodynamic sorption model describe REE sorption onto basaluminite
450 via sorption of aqueous REESO₄⁺. The use of an atomistic model using this positively
451 charged ion yields the best results for the EXAFS fitting of Y sorbed on basaluminite.
452 However, the EXAFS technique cannot confirm the presence of YSO₄⁺ sorbed into
453 basaluminite by itself, due to the low sensitivity to discern between Al and S neighbors.
454 Rather than this, the EXAFS fitting, together with the PDF, can confirm the strong
455 interaction and the formation of inner-sphere surface complexes of Y onto basaluminite
456 precipitates, via ligand exchange with AlO₆ units of its structure. EXAFS analyses of
457 column waste samples show that most of the Y is retained as the same inner-sphere
458 sorbed species, YSO₄⁺, with a low proportion of YSO₄⁺ in outer-sphere configuration.

459 The description of the local structure of yttrium sorbed onto the basaluminite surface
460 provided here complements the atomic configuration studies of other trace metals, such
461 as As and Se oxyanions.⁴⁴ The chemical similarity between yttrium and other HREE
462 (from Tb to Lu) suggests that similar environments could be present for the other
463 elements of the same group. This fact has important environmental consequences, as the
464 HREE would be strongly sorbed, via covalent bonds, which could result in their long-
465 term immobilization at least until the host phase is dissolved or re-precipitated. A key
466 question emerges about the long-term stability of the complex, particularly with an
467 increase in the solution pH. The structural evolution of pure basaluminite with
468 increasing pH showed its recrystallization onto boehmite, releasing sulfate into the
469 solution.⁴⁵ Previous studies on poorly crystalline Fe phases from AMD such as
470 schwertmannite have shown a release of adsorbed toxic elements during aging due to
471 recrystallization processes.⁴⁹ The occurrence of such processes in REE-doped
472 basaluminite could result in the remobilization of REEs and of other potentially

473 adsorbed toxic elements. The extent to which these processes can occur in natural
474 waters requires further investigation.

475 Further studies on the potential uptake of LREEs by basaluminite are necessary to
476 confirm and/or compare different structural mechanisms to those of their HREE
477 counterpart, as a step to develop separation methods for REEs. These investigations
478 will help to enhance a selective recovery of REE from AMD wastes and thus to
479 generate an economic value of the waste generated during the neutralization of AMD-
480 affected waters.

481 **Associated information**

482 Supporting information. The supporting information contains 1) five chapters with
483 detailed description of synthesis of reference materials, analytical procedures and
484 aqueous speciation calculations, synchrotron experiments and data analyses, molecular
485 dynamics simulations and the Python code used to generate PDF from AIMD
486 simulations; 2) three 3 tables describing samples used for EXAFS measurements and
487 the modeling parameters from EXAFS fitting; and 3) four figures illustrating fitting of
488 EXAFS spectra.

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