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Potential of ligand-promoted dissolution at mild pH for the selective recovery of rare earth elements in bauxite residue

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Abstract

In a context of overexploitation of natural resources, a circular economy and particularly the extraction of resources from secondary sources, are essential to sustain a number of key technologies including renewable energies. Among secondary sources, bauxite residue contains critical elements including rare earth elements (REEs) (712mg/kg). We investigated the use of soft and selective dissolution protocols at mild pHs (2-6) as an alternative to pyro- and hydrometallurgy for the recovery of REEs through ligand-promoted dissolution. This approach depends on the detailed characterization of the waste and the speciation of targeted elements. We assessed dissolution using low molecular weight organic acids (LMWOAs) and their conjugate bases. Citric acid/citrate showed satisfactory dissolution of REEs (up to 50% of light REEs) up to a pH of nearly 5, while tartaric acid/tartrate showed the best dissolution selectivity (enrichment factor up to 21.5 compared to Fe, Al and Ti). Almost no heavy REEs were dissolved in any of the conditions tested, probably due to the high chemical stability of their bearing phases. Indeed, heavy REEs were found as discrete phosphate particles.

Synopsis

Ligand-promoted dissolution, an interesting mechanism for the development of selective recovery processes of REEs from bauxite residue in mild pH conditions.

56 **Introduction**

57 The world population has increased fivefold since the 1900s, leading to overexploitation of
58 the Earth's primary resources. Metals are one of these resources, particularly the critical
59 metals used in modern technologies (smartphones, electronic compounds, wind turbines,
60 permanent magnet, electric cars, etc.) because of their unique physical and chemical
61 properties¹. These critical elements combine high economic value (in terms of end-use
62 applications) and high risk of disruption in supplies due to limited reserves and geopolitical
63 considerations^{2,3}.

64 Among these metals, rare earth elements (REEs), including lanthanides, yttrium (Y) and
65 scandium (Sc), are among the most critical in Europe. Global consumption increased from 80
66 000 tons of rare earth oxides in 2000 to 140 000 tons in 2019¹. REEs are often separated into
67 two subgroups according to their different physico-chemical properties: La, Ce, Pr, Nd, Sm,
68 Eu and Gd are classified as light rare earth elements (LREEs) and Tb, Dy, Ho, Er, Tm, Yb,
69 and Lu are classified as heavy rare earth elements (HREEs). Yttrium and Sc are often
70 included in the REE group because of their similar physico-chemical properties. Although Sc
71 often behaves differently than other REEs, partly due to its smaller radius (for example, it can
72 replace iron in goethite⁴). Yttrium behavior is very similar to that of HREEs (similar ionic
73 radii and valence state).

74 Most REEs are produced in China, which accounts for 86% of world production (average
75 2012-2016, EU report 2020), and is also the world's largest consumer and exporter⁵. REEs
76 are almost entirely produced by extraction from natural ores, mostly using controversial
77 methods with negative sanitary (radioactivity, corrosivity) and environmental impacts
78 (water/soil contamination)⁶. This mining industry is also a particularly big consumer of
79 energy, water, and chemicals, and produces effluents and solid wastes that are intentionally or
80 accidentally released into the environment⁶. In this context, there is an urgent need to find
81 alternatives for the production of REEs to reduce (i) the supply risk and (ii) the environmental
82 and sanitary impacts associated with their extraction.

83 In circular economy, mining and industrial wastes represent secondary REE resources that are
84 largely under-exploited partly because of the low cost of extracting REEs from natural ores
85 and the lesser quality of secondary sources compared to natural ones. However, given the
86 strong pressure on these metals, mining secondary sources may become a sustainable source
87 of REEs in the near future. Among secondary sources, bauxite residues (BR), also known as
88 red mud when hydrated, are an attractive source of REEs. BR is an industrial waste resulting

89 from the extraction of alumina from natural bauxite rocks using the Bayer process (soda
90 leaching). For example, a Jamaican residue contains up to 2,500 mg/kg of REEs ⁷ which is
91 about 10 times higher than the natural abundance of REEs in the Earth's crust ⁸. Extracting
92 REEs from BR is a real economic and environmental challenge. Existing processes, usually
93 based on the leaching of REEs from BR, use strong mineral acids such as hydrochloric, nitric,
94 or sulfuric acids ^{9,10}. During acidification, proton-promoted dissolution digests most of the
95 matrix with poor REE selectivity, requires post-leaching purification steps, and produces large
96 quantities of hazardous acidic liquid and solid wastes.

97 The use of low molecular weight organic acids (LMWOAs) as alternatives to the strong acids
98 traditionally used in hydro- or pyro-metallurgy, has been less studied, partly due to their lower
99 leaching efficiency. Leaching efficiency reported in the literature using LMWOAs rarely
100 exceeds 50% for LREEs and 65% for HREEs ^{11,12} (*see SI in SI*) whereas strong acids usually
101 dissolve 80-90% of REEs ¹³. However, although less efficient, leaching with LMWOAs
102 involving ligand-promoted dissolution has other advantages that deserve more attention with a
103 view to designing more sustainable extraction strategies. In particular, ligand-promoted
104 dissolution is expected to be more selective (i.e., to require fewer extraction steps and to
105 produce less waste) and can be performed at more neutral pH (hence producing non-acidic
106 solid and liquid wastes). However, developing such processes requires a better understanding
107 of the speciation of the REEs, the identification of the bearing phases in the matrix, which we
108 investigate here. In particular, ligand-promoted dissolution depends to a great extent on the
109 specific affinity of LMWOAs for the surface of minerals and for the element in solution,
110 which will be strongly affected by pH.

111 The aim of our study was to investigate the potential of ligand-promoted dissolution for the
112 selective leaching of REEs in BR in mild conditions. We performed multi-scale
113 characterization of the BR including the speciation of REEs (chemical composition,
114 mineralogy, particle size, elemental distribution, speciation), and assessed the effects of a
115 number of experimental variables including the nature of the LMWOAs and pH on
116 dissolution efficiency and selectivity. For the first time, speciation of HREEs in bauxite
117 residue has been described at the bulk scale and pH-dependent dissolution behavior has been
118 reported. In light of these results, ligand-promoted dissolution mechanisms are discussed with
119 a view to improving dissolution selectivity and yield in future work.

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123 **Material and methods**

124 **Material**

125 The BR we studied came from Bouc-Bel-Air (South of France). It was produced and collected
126 in February 2019 and stored in sealed plastic containers at ambient temperature until required.
127 The fresh BR was sampled immediately after the chemical extraction of alumina (Bayer
128 process) from bauxite, a lateritic deposit, originating from Guinea (West Africa). Before the
129 experiments, the BR was dried at 60-70 °C for 2 days, manually ground in an agate mortar,
130 sieved to 125µm and homogenized using an orbital shaker before use. The effect of different
131 BR grinding methods on dissolution efficiency was further studied and is presented in SI (*see*
132 *S2 in SI*)

133

134 **Characterization of the bauxite residue**

135 **Chemical composition.** Four samples of the same dry and ground BR were mineralized using
136 the alkaline fusion method: 100 mg of BR and 500 mg of dry lithium tetraborate (flux) were
137 mixed and heated at 1 000 °C in an oven. The resulting fusion bead was dissolved in 40ml of
138 nitric acid (1N). The final solutions were diluted in 2% nitric acid at a dilution factor of 200
139 and trace elements and minor elements including REEs were analyzed with a Perkin Helmer
140 300X quadrupole ICP-MS for, while major elements were analyzed with a Perkin Elmer ICP-
141 OES Optima 4300 DV. The results (concentration in mg/kg) are expressed along with the
142 average and the standard deviation of the 4 samples.

143 **Mineralogy of the bauxite residue.** X-Ray diffraction was performed at 40 kV and 40mA on
144 a Panalytical X'Pert Pro θ - θ diffractometer equipped with a rear monochromator and a cobalt
145 anticathode ($K_{\alpha} = 1.79\text{\AA}$). Scans were made between 5° and 75° (2 θ) with a step size of
146 0.033°. The sample was rotated at 15 rpm during analysis to improve the statistics.

147 **Spatial distribution of REEs.** Scanning electron microscopy coupled with EDX analysis
148 (SEM-EDX) and Nano X-Ray Fluorescence (Nano-XRF) microscopy were performed to
149 assess the spatial distribution of the REEs in the BR. For the SEM-EDX analysis, a BR pellet
150 was prepared with 5g of BR dispersed in 25mL of ultrapure water, centrifuged at 2061xg for
151 15 minutes and dried to remove excess salts. The process was repeated 3 times. SEM was
152 carried out at 30kV using a Zeiss GeminiSEM 500 SEM equipped with an EDAX Octane
153 Silicon Drift Detector (129 eV energy resolution for Manganese) at Aix-Marseille University.
154 Nano X-Ray Fluorescence microscopy (nano-XRF) experiments were performed at the
155 Nanoscopium hard X-ray nanoprobe beamline of Soleil Synchrotron (Saint-Aubin, France).

156 Dry and washed BR was homogeneously dispersed on Kapton tape for analysis. The
157 monochromatic X-ray beam energy was set at 18.3keV with a gap size of 150 x 60nm,
158 focused with a Kirckpatrick-Baez nano-focusing mirror. A fast continuous scanning
159 technique was used to obtain elemental mapping with an integration time of 40ms per pixel. Y
160 was located at the nano scale with the fluorescence K-emission line at 14.9 keV. A dead time
161 correction was applied to each pixel. Elemental maps were extracted from the hyperspectral
162 maps, including Y (K_{α} 14.96 keV), Fe (K_{α} 6.40 keV), Ti (K_{α} 4.51 keV), Yb (L_{α} 7.42 keV) and
163 Er (L_{β} 7.81 keV). Elemental mapping was performed by selecting an ROI of energy centered
164 on the emission line on the XRF spectra using PYMCA software (background subtraction,
165 calibration, fit (*see S3 in SI*)). Possible correlations were further investigated by calculating
166 the Pearson coefficient on the nano-XRF maps.

167 **Yttrium speciation.** X-ray absorption spectra (XAS) at Y K-edge (17.038 keV) were
168 recorded by the P65 undulator beamline at the Deutsches Elektronen-Synchrotron (Hamburg,
169 Germany). Incoming photon flux energy was modulated using a Si(111) double crystal
170 monochromator and higher harmonics were suppressed using Rh-plane mirrors. The data were
171 collected in continuous mode with a beam size of $0.3 \times 1.5 \text{ mm}^2$. Samples were prepared as
172 pure pellets (50mg) for BR, or as diluted pellets with polyvinylpyrrolidone for model
173 compounds. For the latter, the quantity of the sample was calculated to get $\Delta\mu_{\text{theoretical}}=1$. Each
174 spectrum was measured at 20K to prevent beam damage. The BR sample was measured in
175 fluorescence mode with a Hitachi/Vortex 4-pixel silicon drift detector (SDD), One spectrum
176 represented an average of 3 to 6 scans of Y reference compounds and 30 scans of the BR
177 sample, depending on the concentration of Y and the noise level. Energy was calibrated using
178 reference Y metal foil. E0 (absorption edge) was defined at 17038eV at the gap between the
179 two maximum points of the first derivative. Calibration, normalization and averaging data
180 were performed using Athena software ¹⁴.

181 A library of Y reference compound spectra was used to identify Y species in BR. It consisted
182 in commercial references: yttrium oxide (Y_2O_3 ; Acros Organics), yttrium carbonate
183 ($\text{Y}(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$; Alfa Aesar), natural minerals (xenotime, YPO_4), and model compounds
184 synthesized in the laboratory (crystallized and amorphous Y phosphates, Y hydroxide, Y-
185 adsorbed on montmorillonite, (*see S4 in SI for synthesis protocols*). Least square linear
186 combination fitting (LCF) of the XANES (X-ray Absorption Near Edge Spectroscopy) region
187 was performed over an energy range of -50eV to +200eV around E0 using Athena software.
188 The residual factor of LCF was calculated as follows: $R = (\sum(\mu_{\text{exp}} - \mu_{\text{fit}})^2) / \sum(\mu_{\text{exp}})^2$ using
189 Athena software. At each step of the fitting, an additional reference spectrum was added if the

190 two following conditions were true: the R factor decreased by 20% or more and the additional
191 reference contributed 10% or more Y species. The uncertainty of this LCF method was
192 estimated at $\pm 15\%$ ¹⁵.

193 **Dissolution with LMWOAs.** Three LMWOAs (citric, tartaric, and oxalic acids) and their
194 conjugated bases were tested. The molecular structures of LMWOAs are similar with a short
195 carbon chain (C₂-C₆), carboxylic acid functions (-COOH) and similar pKa. The complexing
196 reagents used were citric acid (>99%), di-hydrated trisodium citrate (99%), di-hydrated oxalic
197 acid (98%), mono-hydrated di-ammonium oxalate (>99%), L (+)-tartaric acid (99.5%), and
198 tetra-hydrated potassium tartrate (<99%). The dissolution experiments consisted in two 48-h
199 sequential experiments performed in triplicate at a liquid/solid ratio (L/S) of 50 (0.8g of dried
200 and hand-ground BR in 40ml of complexing solution at 0.1mol/L). Forty-eight hours consist
201 in the time needed to reach a steady-state dissolution for most elements (*see S5 in SI*). The
202 complexing solution was renewed 48 hours after the solid phase was separated by
203 centrifugation (6 133 x g). To increase the pH from 2 to 9, the organic acids used were mixed
204 with their conjugated base at different ratios (citric acid and citrate for example, (*see S6 in*
205 *SI*)). The total concentration of complexing reagents (LMWOAs and their conjugate base)
206 was maintained at 0.1M. During dissolution, the solutions were stirred on a Heidolph REAX
207 20 1-16 RPM mechanical rotary shaker (14 rpm), at room temperature. pH was measured
208 regularly with a HI 2550 Multiparameter pH/ORP/°C/EC/TDS/NaCl Bench Meter. In the
209 literature (*see SI in SI*), leachate is typically separated from the solid residue using 0.22µm or
210 0.45µm filters. Here, ultrafiltration (3kDa=1-2nm) of the leachate insured that there were no
211 suspended particles in the solution by separating only dissolved species or small organic-
212 metal complexes. The filtered solutions were diluted by a factor of 20 or 40 and analyzed
213 using both ICP-OES and ICP-MS.

214 The results are presented with their dissolution percentage (concentration of the dissolved
215 element in mg/kg divided by the concentration in the BR in mg/kg, converted into
216 percentage). Selectivity was calculated with the enrichment factor (EF) according to the
217 following equation:

$$218 \quad EF = \frac{\frac{\sum[REEs] (dissolved)}{\sum[Fe,Al,Ti] (dissolved)}}{\frac{\sum[REEs](BR)}{\sum[Fe,Al,Ti](BR)}} \quad (\text{Equation 1})$$

219 Where *dissolved* stands for the concentrations of element in the filtered solution (mg/kg) and
220 *BR* for the concentrations of the element in the original material (mg/kg). EF stands for the
221 enrichment of REEs, Y and Sc in the 3 most concentrated elements (Fe, Al, Ti) in BR.

222 **Dissolution with nitric acid.** A dissolution experiment with a mineral acid was performed for
223 comparison with ligand-promoted dissolution. Two concentrations of HNO₃ (0.1M, 0.05M)
224 were used to target low and close to neutral pH (pH_{mix}=2 and 5.3 respectively). The
225 dissolution protocol used was the same as that used for dissolution with LMWOAs described
226 above.

227

228 **Results and discussion**

229 **Characterization of initial BR**

230

231 **Chemical composition and mineralogy**

232 The chemical composition and the mineralogy of BR is presented in *Table 1* and in SI (*S7*).
233 BR was mainly composed of Fe (33wt%), in the form of hematite (α -Fe₂O₃) and goethite (α -
234 FeOOH) followed by Ti (5.41wt%) as rutile (TiO₂) and Al (3.91wt%) as gibbsite (Al(OH)₃).
235 Calcium is present as calcite (CaCO₃). Two silicate phases were identified: cancrinite
236 (Na₆Ca₂CO₃, Al₆Si₆O₂₄·2H₂O) and katoite (Ca₃Al₂(SiO₄)_{3-x}(OH)_{4x}, x=1.5 to 3). This is
237 consistent with the literature on BR composition and mineralogy: Fe and Al are usually the
238 two main concentrated elements, but their concentration varies considerably depending on the
239 origin, the type of the bauxite (lateritic or karstic)^{7,16}, the Al extraction treatment conditions
240 (pH, temperature, reagents) and the storage time^{17,18}. Together, reviews^{17,19,20} by *Xue et al.*
241 *2016*, *Gräfe, Power, and Klauber 2011* and *Snars and Gilkes 2009*, and the estimation by the
242 *International Aluminum Institute (IAI)* and the *European Aluminum Association (EAA)* in
243 2014, suggest that Fe₂O₃ comprises from 7% to 72wt% of the residue, Al₂O₃ 2% to 33wt%,
244 TiO₂ 1% to 23 wt%, CaO 0% to 14 wt% and SiO₂ 5% to 30 wt%. Aside from Al and Fe, the
245 mineralogy we observed is consistent with the literature¹⁷. Other inorganic phases reported in
246 other studies including perovskite (CaTiO₃), sodalite (Na₄(Si₃Al₃)O₁₂Cl), diaspore (AlO(OH))
247 or magnetite (Fe₃O₄) were not detected in our BR sample^{21,22}.

248 The total amount of REEs, including Y and Sc in the BR studied here was 712.6mg/kg. The
249 most concentrated REEs were Ce (220.7mg/kg), Y (121.2mg/kg), La (105.9mg/kg) and Sc
250 (75.2mg/kg). The concentration of REEs in BR reported in the literature is highly variable
251 (*see S8 in SI*). The main variations in the concentration of REEs are explained by the origin of
252 the bauxite deposit: karstic-type bauxites (12% of the global bauxite deposits mostly located
253 in Europe) are usually richer in REEs than lateritic-type bauxites (88% of the global bauxite
254 that can be found in Guinea, India or Australia for example). In this study, the BR was

255 produced from a lateritic deposit (in Guinea, West Africa) using the Bayer process. No
 256 particular anomalies were observed according to the PAAS-normalized REE pattern (*see S9*
 257 *in SI*).

258

259 **Table 1 : Chemical composition of the BR for REEs, Sc, Y, and major elements (average \pm**
 260 **standard deviation). Concentrations in the Earth's crust were taken from Kabata-**
 261 **Pendias 2011.**

REEs	BR Concentration (mg/kg DW)	Earth's crust (mg/kg DW)
Sc	75.2 \pm 1.7	16-30
La	105.9 \pm 2.0	30
Ce	220.7 \pm 3.2	60
Pr	21.0 \pm 0.3	8.2
Nd	72.1 \pm 0.9	28
Sm	16.7 \pm 0.2	4.7
Eu	3.1 \pm 0.1	1.2
Gd	16.7 \pm 0.2	5.4
Tb	3.1 \pm 0.1	0.6
Dy	21.3 \pm 0.4	3.7
Ho	4.6 \pm 0.1	0.8
Er	14.4 \pm 0.5	2.8
Tm	2.2 \pm 0.1	0.5
Yb	15.2 \pm 0.3	2.2
Lu	2.3 \pm 0.1	0.3
Y	121.2 \pm 3.0	20-33
Total REEs	712.6\pm13.1	168-200

Majors	Mass (%)	Equivalent oxide (%)
Fe	33.03 \pm 0.61	47.22 \pm 0.87 (Fe ₂ O ₃)
Ti	5.41 \pm 0.05	9.02 \pm 0.08 (TiO ₂)
Al	3.91 \pm 0.23	7.39 \pm 0.43 (Al ₂ O ₃)
Ca	2.95 \pm 0.20	4.13 \pm 0.28 (CaO)
Si	1.43 \pm 0.12	3.06 \pm 0.26 (SiO ₂)
P	0.17 \pm 0.02	0.77 \pm 0.07 (PO ₄)

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263

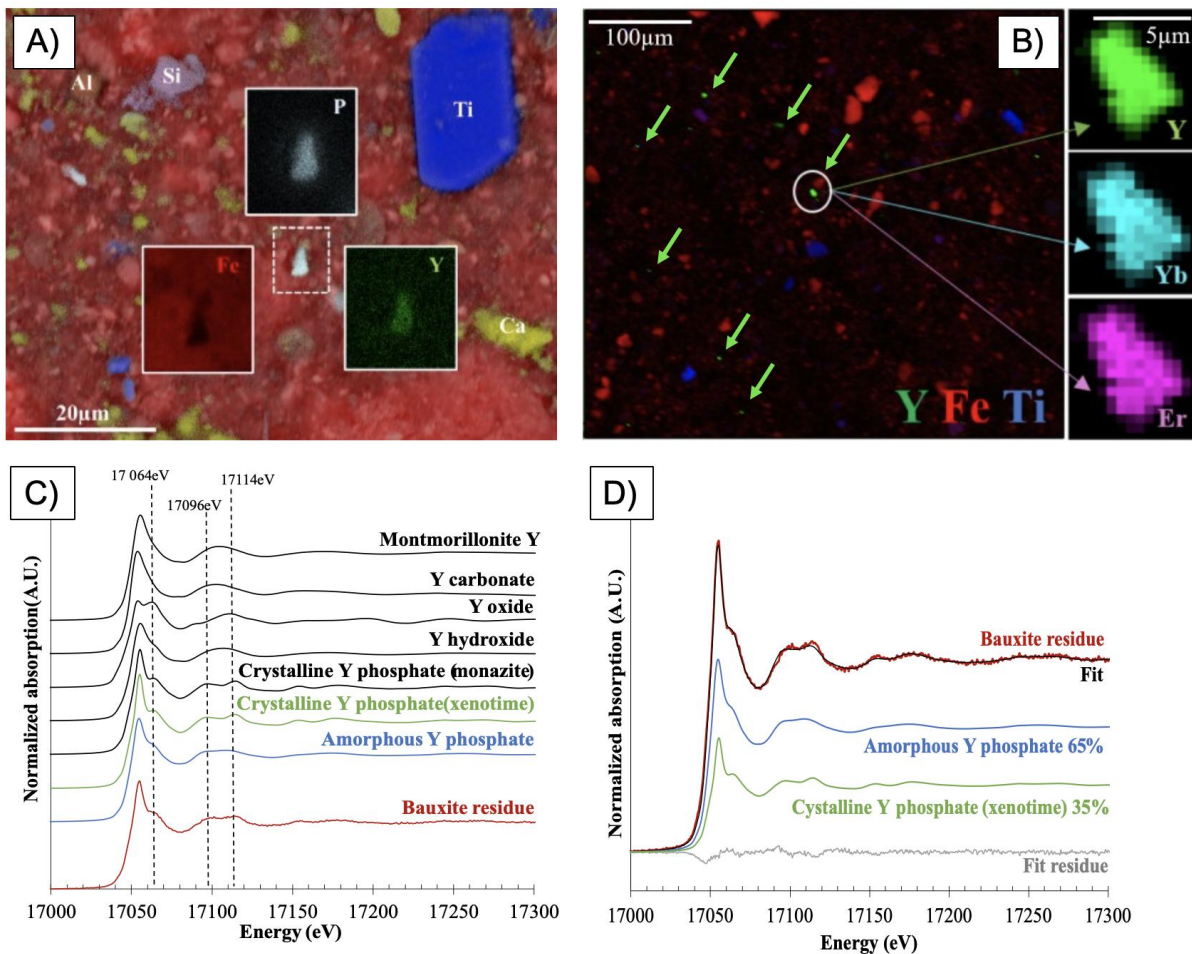
264

265 **Spatial distribution of REEs in BR**

266 Elemental mapping with SEM-EDX confirmed the prevalence of Fe in our BR matrix (*Figure*
 267 *1A*). Discrete particles rich in Al (dark blue), Si (red), Ti (pink) and Ca (cyan) were also
 268 observed confirming the results of bulk analysis and the mineralogy observed by XRD. The

269 detection of REEs was very challenging because of (i) their relatively low concentration
 270 (especially HREEs), and (ii) the overlap between their L_{α} fluorescence emission lines with the
 271 K_{α} emission lines of Ti, Cr and Fe (regarding LREEs). However, few Y-rich particles (white)
 272 were observed with SEM-EDX (*Figure 1A*). Y was not correlated with Al, Fe, Ti, Si and Ca
 273 but co-localized with P (light blue). This co-localization raises the hypothesis that Y and P
 274 could exist as yttrium phosphates (YPO_4). Indeed, Y commonly occurs in phosphate minerals
 275 (such as monazite, xenotime) in nature and forms very stable phases. At this stage, no other
 276 REEs were detected by SEM-EDX.

277



278

279 **Figure 1:** (A) Combined elemental map obtained by SEM-EDX showing the spatial
 280 correlation between Al, Si, Ti, Fe, Ca, Y and P in BR sample (30kV, pixel=71.11nm). (B)
 281 Combined elemental map obtained by nano-XRF showing the distribution of Fe, Ti, Y, Yb,
 282 Er in BR sample, (1px = 1 μm for the large image, 1px = 400nm for small images). (C)
 283 Bulk XANES spectra of BR and model compounds at the Y K-edge and (D) LCF performed
 284 with Athena software (R-factor=0.0009)(right).

285

286 Deeper investigation of the spatial distribution was performed at the SOLEIL synchrotron
287 with using nano-XRF which is more sensitive than that of SEM-EDX. In agreement with
288 SEM, nano-XRF revealed several Y-rich particles (*Figure 1B*) of $4.9 \pm 1.9 \mu\text{m}$ ($n=24$) not
289 associated with major elements (Fe, Ti, Al, Si, Ca) but co-localized with other REEs,
290 especially HREEs, as expected (Gd, Er, Yb). LREEs (La, Ce, Nd) were also investigated but
291 were not detected, probably because their signals are hidden by the intense XRF emissions of
292 Ti, Cr and Fe. P was not detected either because of the limited sensitivity of the beamline for
293 the detection of P $K\alpha$ emission lines. At this low energy (2.01keV), fluorescence signal is
294 strongly absorbed by the air before reaching the detector, unlike in SEM-EDX analysis, which
295 is performed under vacuum.

296 The Pearson coefficient was calculated for some trace elements (Y, Yb, Gd, Er, Cu, U, Th)
297 and for major elements (Fe, Ti) on the Y-rich area (Inset in *Figure 1B*) (*Figure S2, SI*). A
298 correlation was observed ($\text{Coef} \geq 0.70$) for the HREEs (Gd, Er, Yb) and Y, but also for other
299 elements of interest present at low concentrations such as Cu, U and Th. Fe and Ti were not
300 correlated with these elements. To confirm our hypothesis that Y forms YPO_4 phases,
301 probably associated with HREEs in BR, Y speciation was investigated at the bulk scale.

302

303 **Y speciation in BR**

304 The bulk XAS spectrum (*Figure 1C*) obtained for the BR sample closely resembled spectra
305 corresponding to synthesized Y phosphates (amorphous and crystallized monazite), and
306 xenotime (natural and crystalline phosphate mineral). The spectra of these model compounds
307 were characterized by specific features, i.e., a shoulder at 17064eV in the white line and the 2
308 features at 17096eV and 17114eV. The amorphous Y phosphate had less pronounced features.
309 Linear combination fitting (LCF) confirmed that the Y speciation in BR was YPO_4 (*Figure*
310 *1D*) in agreement with the Y/P spatial correlation previously identified with SEM-EDX. The
311 best fit was obtained using a mixture of crystalline and amorphous YPO_4 (35% xenotime and
312 65% amorphous).

313 These results concerning HREEs are consistent with those obtained in the study by *Vind and al.*
314 (2018)¹⁶ where Y, Gd, Dy and Er were found to be co-localized at the particle scale using an
315 Electron Probe Micro Analyzer (EPMA) and EDX methods as xenotime/churchite-kind phases
316 (yttrium phosphate). Observed in a karstic BR, these microscale particles were slightly smaller
317 (2-3 μm) than the ones observed in our study. Our study thus confirms for the first time at the
318 bulk scale, observations performed at small scale. It is likely that we only observed the biggest
319 particles and missed a large fraction of sub-micron particles, potentially amorphous (1 μm pixel

320 on the big map in *Figure 1B*). The distributions of REEs and Y observed here as well as by
321 *Vind and al. (2018)*¹⁶ confirm that BR is potentially an ideal matrix for developing selective
322 dissolution of HREEs since it is concentrated in accessible particles and not associated with
323 major elements.

324

325 **Dissolution of REEs using LWMOAs**

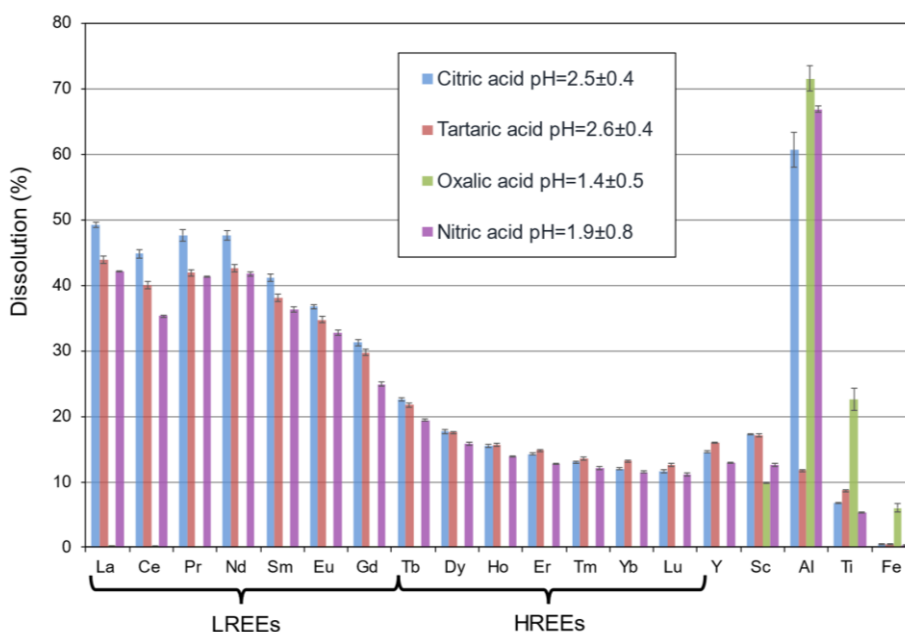
326 **Ligand-dependent dissolution**

327 It has been shown that aliphatic acids (citric acid, oxalic acid, succinic acid, malic acid, etc.)
328 produced by organisms such as plants, fungi and bacteria are good candidates for the recovery
329 of REEs from REEs/Y-rich phosphate minerals (apatite and monazite), particularly citric acid
330²³⁻²⁵. Some of these organic acids have also been identified in the literature as biomolecules
331 capable of selectively solubilizing REEs from BR (*Table S1, S1*).

332 *Figure 2* shows the fraction of dissolved elements (REEs, Y, Sc and major elements Al, Ti,
333 Fe) after two-step sequential extraction (2x48 h) for three organic acids that have known
334 affinity for REEs (citric, tartaric, and oxalic acids) and nitric acid. Citric and tartaric acids
335 exhibit quite similar behavior that is very different from that of oxalic acid. Citric acid
336 dissolves more LREEs and Al. It can extract up to 49% of LREEs and 12% of HREEs.
337 Tartaric acid dissolves slightly more HREEs, Y, Sc, Ti and Fe. More interestingly, it dissolves
338 Al poorly in comparison with citric acid, which might be of interest in terms of selectivity.
339 This can be explained by the lower affinity of tartrate for Al compared to citrate (log K= 5.32
340 and 7.98 respectively). Finally, no REEs were measured in solution in the oxalic acid
341 experiment, unlike Al, Ti, Sc, and a small amount of Fe. This was not surprising since oxalic
342 acid is often used in industrial processes to precipitate the REEs as insoluble metal-oxalate
343 complexes²⁶⁻²⁹. In our study, it was not possible to quantify the amount of REEs that reacted
344 with oxalic acid.

345 In the citric and tartaric acid systems, LREEs (La to Sm) were better dissolved than HREEs
346 (Ho to Lu, Y and Sc) and the dissolution of Eu to Dy was intermediate. Two hypotheses may
347 explain this trend: (i) the stability constants of ligand-REEs complexes are lower for HREEs
348 than for LREEs for a given speciation, (ii) LREEs and HREEs have different speciation and
349 consequently different affinities for the extractant. The second hypothesis is more likely, in
350 view of the speciation data collected in our study and in the study by *Vind and al. (2018)*¹⁶. In
351 addition, stability constants reported in the literature show either a continuous increase with Z
352 or close values for LREEs and HREEs (*see S10 in S1*)^{30,31}, which is not consistent with our
353 first hypothesis.

354 For the sake of comparison, a similar experiment was performed using nitric acid. Nitric acid
 355 is usually described in the literature as one of the most efficient inorganic lixiviants for
 356 leaching of REEs from BR under very acidic conditions ($\text{pH} < 0.5$)^{10,11,32}. At $\text{pH} 1.9 \pm 0.8$
 357 (0.1M HNO_3), the recovery yields were slightly lower but close to those obtained with citric
 358 and tartaric acids at $\text{pH} = 2.5 \pm 0.4$ and 2.6 ± 0.4 . We hypothesize that at these relatively low pH,
 359 proton-promoted dissolution is the dominant mechanism for the dissolution of REEs.
 360 However, in the presence of LMWOAs, ligand-promoted dissolution is also probably
 361 involved in the dissolution of LREEs, which may explain the slightly better dissolution
 362 efficiency of REEs by citric and tartaric acids compared to HNO_3 treatment. However, at this
 363 stage, it is difficult to dissociate the two mechanisms taking place with LMWOAs. The
 364 potential effect of the ligand-promoted dissolution was studied by performing similar
 365 experiments at higher pH at which proton-promoted dissolution is negligible.



366
 367 **Figure 2 : Dissolution of REEs, Fe, Al and Ti with citric acid, tartaric acid, oxalic acid, and**
 368 **nitric acid (2x48 h, 0.1mol/L, L/S=50).**

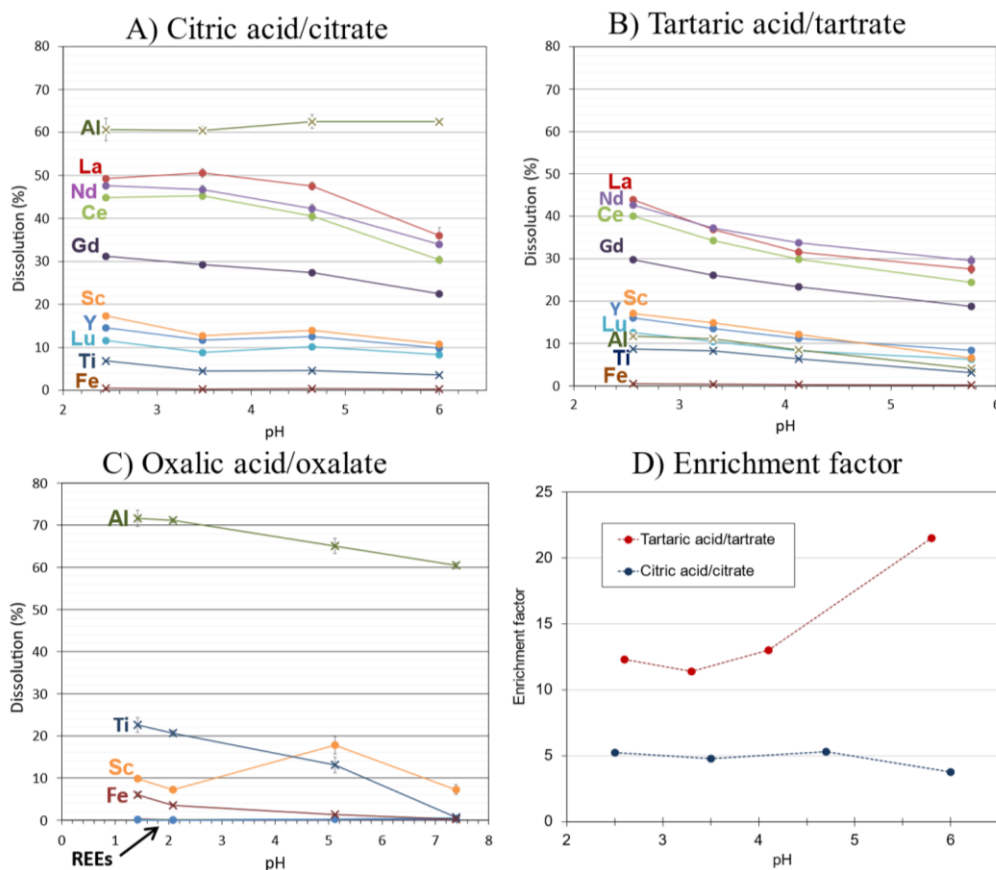
369 **pH-dependent dissolution**

370 To further decipher the role of ligand-promoted dissolution, a set of dissolution experiments
 371 was performed at different pH. pH was controlled by varying the acid/conjugate base ratio.
 372 The better dissolution of LREEs compared to HREEs observed above at pH 2.5 with citric
 373 acid and at 2.6 with tartaric acid was also observed at all the pH tested using the citric
 374 acid/citrate and tartaric acid/tartrate systems.

375 Regarding the citric acid/citrate system, similar dissolution was obtained from pH 2.5 to 4.7
 376 before a significant drop at pH 6 (Figure 3A). The average dissolution of Al is 61%, with low
 377 variability among the pH range investigated here. Ti and Fe dissolution were low (%Ti<6%,
 378 %Fe<1%) and decreased toward alkaline pH.

379 The tartaric acid/tartrate system behaved differently from the citric acid/citrate system with a
 380 decrease in the dissolution of REEs with increasing pH (Figure 3B). However, the major
 381 elements including Al were poorly dissolved compared to in the citric acid/citrate system. Al
 382 dissolution did not exceed 12% (pH=2.6±0.4), only 9% of Ti, and less than 0.5% of Fe were
 383 dissolved.

384 As mentioned earlier, oxalic acid is known in the literature as an efficient complexing and
 385 precipitating agent for REEs at acidic pH²⁶⁻²⁹. Consequently, no REEs or Y dissolution was
 386 measured (Figure 3C) regardless of the pH in the oxalic acid/oxalate system
 387 (%REE,Y<0.5%). A fraction of REEs probably precipitated with oxalate and was therefore
 388 not detected in the supernatant. Interestingly, Sc was partly dissolved with optimal extraction
 389 at pH=5.1±1.6 (%Sc=18%) which confirms the difference in the chemical behavior of this
 390 element from that of other REEs. Between 60% and 70% of the Al was dissolved at pH< 7.5
 391 and Ti dissolution increased from 13% at pH=5.1±1.6 to 22% at pH=1.4. More Fe was more
 392 dissolved with oxalic acid than with the other organic ligands (%Fe>3.5% for pH<2).



394 **Figure 3 : Dissolution of REEs, Sc, Y, Al, Ti, and Fe with (A) citric acid/citrate, (B) tartaric**
395 **acid/tartrate, and (C) oxalic acid/oxalate as a function of pH (2x48h, L/S=50, 0.1mol/L).**
396 **(D) Selectivity (expressed by the enrichment factor) for the dissolution with citric**
397 **acid/citrate and tartaric/tartrate acid.**

398 Although less efficient at mild pH than the citric acid/citrate system, the tartaric acid/tartrate
399 system is interesting in terms of selectivity, especially related to Al. To quantify the
400 selectivity of REE dissolution, an enrichment factor (EF) towards the 3 main elements was
401 calculated (*Figure 3D*). Despite slightly lower recovery yields, tartaric acid was found to be
402 more selective for REEs than citric acid regardless of the pH: $EF_{\text{citric acid}}=3.8$ to 5.3 and
403 $EF_{\text{tartaric acid}}=11.4$ to 21.5 for $2.5 < \text{pH} < 6$. The enrichment factor was similar regardless of the
404 pH, except at pH=6 for tartaric acid where selectivity reached maximum.

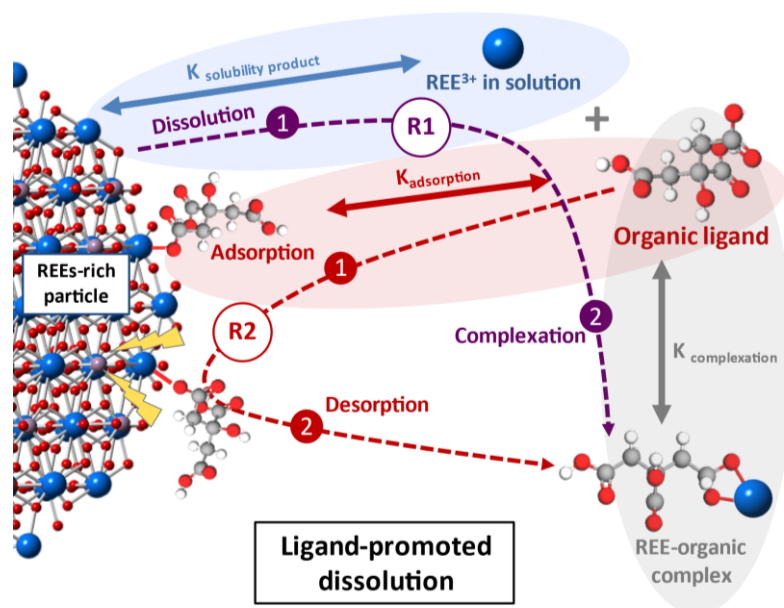
405

406 **Dissolution mechanisms**

407 To better understand the mechanisms involved as a function of pH, recovery yields were
408 measured using HNO_3 at 0.05M to reach a pH of 5.3 (*see S11 in SI*). In this condition, there
409 was no dissolution of REEs, Y or Sc unlike in the citric/citrate and tartaric/tartrate systems at
410 similar pH. This experiment confirms that at such mild pH, ligand-promoted dissolution is the
411 main driver of the dissolution of REEs.

412 Two routes for ligand-promoted dissolution may exist, as illustrated in *Figure 4*. Based on the
413 observations we made in this study for HREEs, we hypothesize that HREEs are hosted in a
414 phosphate matrix. LREEs on the other hand are suspected to be concentrated within particles
415 with varying chemistries¹⁶. The first route (R1 in *Figure 4*) is controlled by (i) the dissolution
416 of the REE-hosting mineral defined by the solubility product constant K_{sp} and (ii) the affinity
417 of the dissolved species for the organic ligand defined by the complexation constant
418 $K_{\text{complexation}}$. The complexation of free REE^{3+} ion by organic ligands will shift the first
419 equilibrium towards dissolution of REE-hosting mineral.

420 The second route (R2 in *Figure 4*) is controlled by the affinity of the organic ligand for the
421 surface of the REE-hosting mineral present in BR ($K_{\text{adsorption}}$) and its ability to weaken the
422 bonds that bind surface atoms to the particle and that will eventually break to form a complex
423 in solution.



424

425 **Figure 4 : Conceptual diagram of the chemical mechanisms involved in the dissolution of**
 426 **REEs in bauxite residues with organic ligands.**

427 As a result of these processes, dissolution may be affected by a number of parameters
 428 including the solubility product of the different phases that comprise the BR, the affinity of
 429 the LMWOAs for soluble REEs and particle surfaces. For the latter, pH is a key parameter
 430 that controls the dissociation of LMWOA protons (pK_a) and the surface charge of the
 431 mineral.

432 Therefore, improving dissolution efficiency requires a good understanding of dissolution
 433 mechanisms, which, in turn requires a good knowledge of the physico-chemical properties of
 434 the matrix. To give an example, the poor dissolution of HREEs in our case could be explained
 435 by their speciation. The REE-phosphates observed in our study are known to be very stable
 436 (poorly soluble, $K_{sp}=10^{-24.75}$ to $10^{-26.43}$ for REEs and Y)³³ which will limit dissolution (route 1)
 437 and prevent the release of the REE-organic ligand complex (route 2). Further improvement of
 438 the process for HREEs should focus on identifying other organic ligands that have a high
 439 affinity for phosphate minerals (either for the HREEs or for the phosphate function) in order
 440 to favor route 2 since route 1 seems unfavorable in the presence of REE-phosphate (*Figure 4*).
 441 The better dissolution yield of LREEs compared to HREEs was probably due to the
 442 occurrence of LREEs phases that are less chemically stable (e.g. higher solubility product
 443 (route 1) or less energetic release of REE-organic ligand complex (route 2)) than the HREEs-
 444 phosphates observed in our study. Although the speciation of LREEs seems to differ from that

445 of HREEs¹⁶, the host LREEs-phases are still not known, and work is now underway to
446 characterize it.

447

448

449 **Conclusion**

450 Rather than focusing on maximum dissolution efficiency, which is the primary objective of
451 past studies on the dissolution of REEs from BR, our study aimed at investigating the
452 potential of ligand-promoted dissolution for the selective dissolution of REEs under mild pHs.
453 In the citric acid/citrate system, similar recovery yields were obtained at pH ranging from 2.5
454 to 4.7. Although slightly less efficient, the tartaric acid/tartrate system displayed interesting
455 dissolution selectivity with enrichment factors comparable to those of Al, Fe and Ti reaching
456 up to 21.5. Unlike in strong mineral acid, it is therefore possible to dissolve REEs at mild pH
457 with relatively good selectivity.

458 Understanding ligand-promoted dissolution mechanisms in the optic of improving the
459 efficiency and selectivity of REE dissolution requires a good knowledge of the BR matrix,
460 which was investigated in our study. LREEs were recovered better than HREEs most
461 probably because of the difference in speciation in the BR. Yttrium was found as 4.9 μm
462 YPO_4 particles. HREEs co-localized with Y and, given the analogy between Y and HREEs,
463 the latter probably form mixed phosphate phases. Although the formation of discrete particles
464 of Y and HREEs appears favorable for selective dissolution, the very high chemical stability
465 of these phosphate phases probably explains the poor recovery yields of Y and HREEs. LREE
466 speciation is still not clear, although the literature reports LREEs (La, Ce, Nd) embedded in
467 ferrotitanate phases, and minor amounts in carbonate and phosphate phases¹⁶. Despite
468 measurement challenges, work is now underway to identify the LREE-bearing phases. In any
469 case, we hypothesize that their speciation is more favorable for their recovery using
470 LMWOAs. The case of Sc is probably not favorable for selective dissolution since it has been
471 shown to be strongly associated with iron phases⁴. As an example, in a previous study, we
472 showed that Sc can replace Fe in the goethite structure making dissolution selectivity
473 impossible to address for this element⁴.

474 Several options will be investigated in future studies to improve dissolution efficiency and
475 selectivity, in particular for HREEs. One possibility is to favor route 2 of the mechanisms
476 described in *Figure 4* by selecting appropriate organic ligands that have a stronger affinity for
477 REE-rich phases than the LMWOAs tested in the present study. In this regard, understanding

478 the effect of ligand composition and structure (e.g. nature and number of functional groups,
479 the presence of an hydroxyl group in α -, β - or γ -hydroxy acids, pKas, etc.) on the dissolution
480 of REE-rich phases can help in the choice of more appropriate ligands in the optic of
481 enhanced dissolution yield and selectivity. In addition, the use of organic molecules produced
482 by living organisms will also be explored. It includes highly selective organic molecules
483 produced specifically to recover REEs by methylotroph bacteria such as lanmodulin³⁴⁻³⁶ but
484 also other molecules produced by plants, bacteria or fungi than are known to dissolve
485 phosphates and/or REEs in soil (siderophores³⁷⁻³⁹, formic acid, succinic acid, malic acid,
486 amino acids...) ^{23,25,40-46}. In this regard a better knowledge of plants and microorganisms
487 developing in BR deposits may be particularly informative for selecting appropriate bio-
488 inspired extraction strategies⁴⁷⁻⁴⁹.

489
490 Although poorly investigated compared to conventional hydrometallurgy, we believe that
491 selective dissolution using ligand-promoted dissolution is a promising approach for the design
492 of sustainable extraction processes of various critical elements from a variety of secondary
493 sources. In a circular economy, this approach makes it possible to decrease pressure on
494 natural resources, to limit the number of extraction steps and to minimize the production of
495 hazardous wastes.

496
497 **Supplementary information:** Complementary literature, additional experimental details
498 including synthesis protocols, additional results including XRF spectra analysis, granulometry
499 experiments and nitric acid dissolution. The document is available online.

500
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514

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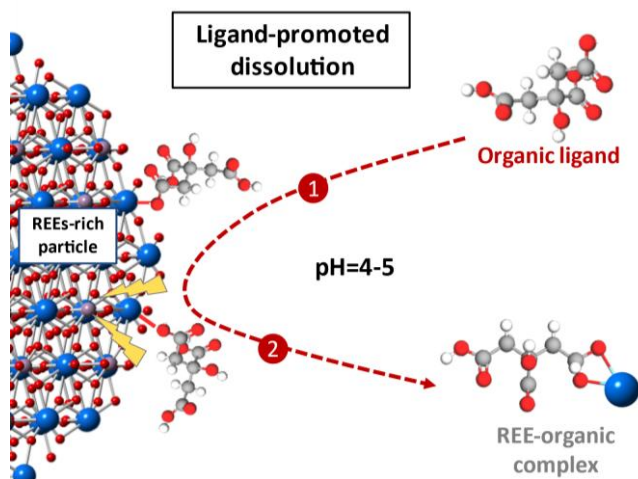
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