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1 **Extraction and separation of rare earth elements from hydrothermal metalliferous sediments.**

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18 **Abstract**

19 Rare earth elements (REE) can be efficiently extracted from umbers, ferromanganese metalliferous
20 sediments of the Troodos ophiolite (Cyprus) by simple leaching and selective precipitation, without
21 accumulation of radioactive by-products. Umbers are dominantly composed of amorphous Fe and
22 Mn oxides with minor goethite, quartz and zeolites, and contain 350 – 500 mg.kg⁻¹ of rare earth
23 elements and yttrium (REY), 200 times lower than many of the major REY source ores. To
24 compensate for relatively low grades, a cost-effective extraction process was developed that
25 utilises a weak lixiviant concentration (0.1 – 1.5 N) and short reaction times (5 min to 11 h). Acid
26 solutions recover 70-85% of the initial sample REY content even at 20 °C. By contrast, extraction
27 using ionic solutions of NaCl and ammonium sulphate proved ineffective. Acid recoveries of REY
28 increase by nearly 10% at 70 °C and the use of different acids (HCl, HNO₃, H₂SO₄) yields comparable
29 results. The main impurities in the leachate include Ca and Na at even the weakest acid
30 concentration (0.1 N). However, two-step leaching method greatly reduces concentrations of
31 impurities in the REY-rich liquor, although with REY losses approaching 20%. Purification of the
32 leach liquor via selective precipitation of REY as an oxalate is highly efficient although pH
33 dependent. With maximum REY precipitation (96-99%) occurring between pH 1 and 2, the precise
34 adjustment of pH allows separation of REY from other precipitating impurities (Ca). The maximum
35 purity of the precipitate is achieved at pH 1.1 (> 65%). Strong and consistent fractionation along the
36 lanthanide series observed during the precipitation experiments has been successfully explained
37 using a speciation modelling software (PHREEQC). The uptake of REY by oxalate in the experiments
38 closely follows the bell-shape distribution of REY-oxalate solid complexes stability constant (-log β
39 (RE₂Ox₃.nH₂O)) replicating the fractionation trends observed at pH < 1.1. In addition, the modelling
40 demonstrates that at equivalent REE concentration in solution, oxalate precipitates fractionate REY
41 in the following order: middle REE > light REE >> heavy REE. This ordering and the variable degrees
42 of uptake reflects the interplay of aqueous REY-oxalate complexes (log_{HOx}β₁, oxβ₁ and oxβ₂) with the
43 natural fractionation induced by solid REY-oxalate stability constant distribution. Overall, the
44 combined leaching process and selective oxalate precipitation produces a total enrichment factor
45 ranging between 1400 and 2400 for REY from the sample to the oxalate precipitate in a simple two-
46 step process forming a high-purity end-product of mixed REY.

47 **Keywords:** leaching; metalliferous sediments; oxalate; PHREEQC; rare earth elements; speciation
48 modelling; umbers.

49

51 The perceived supply risk for essential materials used in the development of green energy and other
52 state-of-the art technologies provides motivation to investigate new sources for these raw
53 materials. Many are characterized as “critical”, given supply risks posed by geographic location, the
54 economic and political stability of producing countries, limited possibilities for substitution and
55 currently low-levels of recycling (European Commission, 2014, Graedel *et al.*, 2014). At present, 20
56 raw materials are listed by the European Union as critical. Among these critical elements, the
57 lanthanides and yttrium (REY) form a group of 15 metals (Rollat *et al.*, 2016) essential for the
58 development of applications in the low-carbon energy sector (magnets, low-energy lighting, wind
59 turbines, batteries), industry (catalysis, alloys, oil refining), and other technologies (lasers, optics)
60 (Guyonnet *et al.*, 2015). More than 90% of REY produced worldwide in the last twenty years
61 originated in China, a near monopoly that reflects environmental and economic factors rather than
62 the unequal distribution of REY resources across the world (Weng *et al.*, 2015). Indeed, large
63 primary deposits are known outside China including more than 550 carbonatites/alkaline
64 complexes worldwide (Kanazawa and Kamitani, 2006, Chakhmouradian and Wall, 2012, Jordens *et al.*
65 *et al.*, 2013, Jaireth *et al.*, 2014, Xie *et al.*, 2014, Hoshino *et al.*, 2016).

66 Solvent extraction constitutes the most common treatment of REE-bearing minerals, such as
67 xenotime (YPO_4), bastnäsite ($(\text{Ce,Lu})\text{CO}_3\text{F}$) and monazite ($(\text{RE,Th})\text{PO}_4$) ores, following energy-
68 consuming beneficiation via gravity separation, desliming, magnetic or electrostatic separation and
69 froth flotation (Jordens *et al.*, 2013, Kumar *et al.*, 2014, Xie *et al.*, 2014). The hydrometallurgical
70 process uses strong acid or alkali leaches (sulphuric acid and sodium hydroxide being the most
71 common) at temperatures of 200-400 °C, in a process commonly referred to as cracking (Habashi,
72 2013, Golev *et al.*, 2014). This treatment produces REE-rich leach liquors usually in the range of 1
73 to 40 g.L^{-1} RE_2O_3 with small amounts of impurities (Chi *et al.*, 1995, Abreu and Morais, 2010). REY
74 are separated from co-leached elements by further treatment such as solvent extraction and ion
75 exchange using selective precipitation as carbonates or oxalates by pH adjustment. Rare earth
76 oxalates and carbonates are then roasted to form a mixed RE oxide product ready for sale as a RE
77 alloy known as mischmetal, sent to specialized factories for further separation treatment into
78 individual high purity RE oxides or reduced to pure metal products depending on the required end
79 use (Christie *et al.*, 1998, Golev *et al.*, 2014). The separation of a mixed product into individual
80 elements is inherently difficult due to their very similar chemical behaviour. Multiple methods exist
81 such as selective oxidation/reduction, fractional crystallisation-precipitation, and ion-exchange,
82 though the most effective approach is solvent extraction using organophosphorus compounds (e.g,
83 EDPA, HDEHP, EHEHPA, or TBP) (Abreu and Morais, 2014, Kumar *et al.*, 2014, Xie *et al.*, 2014). All
84 these methods are energy- and material-consuming as they require multiple iterations to obtain a
85 high purity individual rare earth oxides (REO) (Abreu and Morais, 2014).

86 Another problem associated with REY production is the handling of radioactive waste as most REY-
87 rich primary magmatic deposits possess high concentrations of actinides; monazite contains 4-12
88 wt.% Th and although U concentrations are generally low, anomalous content of up to 14 wt.% can
89 occur (Jordens et al., 2013). Uranium and thorium are both concentrated during the beneficiation
90 of REY and the tailings wastes may exhibit high levels of radioactivity after cracking. Co-production
91 of radioactive elements is feasible for the highest U-Th concentration ores, albeit with significant
92 additional costs (Golev et al., 2014). These issues have led to notable pollution in China and
93 Malaysia (Golev et al., 2014, Kolo *et al.*, 2015). For many sites, industrial processing is followed by
94 costly remediation and waste disposal in long-term storage. Significant radioactive element
95 concentrations constitute important economical drawbacks for any new REY exploitation project.

96 Considering the problems associated with magmatic-related REY deposits and despite their
97 abundance, alternative sources of REE more readily beneficiated with low radioactive waste are
98 attracting attention alongside efforts to increase recycling of REY from scrap or end-of-life
99 consumer products. The abundance of neodymium-iron-boron magnets (NdFeB) in cell phones,
100 hard drives and wind turbines forms the major target for this recycling effort with promising results
101 on Nd recovery in the laboratory (Vander Hoogerstraete *et al.*, 2014). In addition, development of
102 REY production from industrial waste or by-products such as red-mud (Ochsenkühn-Petropulu *et al.*,
103 1996, Tsakanika *et al.*, 2004, Qu and Lian, 2013, Liu and Naidu, 2014, Borra *et al.*, 2015, Deady
104 *et al.*, 2016) and coal residue (Rozelle *et al.*, 2016a) has received considerable interest. These
105 formations contain REY-bearing minerals and/or adsorbed REY that are transferred to the wastes
106 during initial ore processing. These wastes constitute a low-grade resource with economically
107 significant tonnage due to the importance and spread of the coal and aluminium industries
108 (Goodenough *et al.*, 2016). Other alternative sources, include sea-floor deposits such as
109 ferromanganese nodules (Fujimoto *et al.*, 2016), hydrogenetic crusts, and marine clays (Kato *et al.*,
110 2011, Menendez *et al.*, 2017) that can have significant REY concentrations (Hein *et al.*, 2013).
111 Although of scientific interest, their relative inaccessibility and need for advanced mining
112 technologies makes their economic exploitation challenging. As an initial approach to establish
113 methods for REY-extraction from such marine formations, here we investigate sub-aerial
114 equivalents of these deposits preserved in ophiolites; slices of ancient oceanic crust now present
115 on-land that provide ease of access and sampling. Given that, the ferromanganese metalliferous
116 sediments of the Troodos ophiolite in Cyprus known as umbers constitute an obvious best choice
117 for study. These deposits represent direct analogue of actual oceanic metalliferous sediments
118 formed in the vicinity of hydrothermal vents (Boyle and Robertson, 1984, Richards and Boyle, 1986,
119 Boyle, 1990, Robertson and Varnavas, 1993a), and have been exploited since classical times for
120 pigments. Nevertheless, to our knowledge no previous work has investigated the processing of
121 these deposits as a potential source of REY.

122 This study investigates the potential recovery of REY from umbers, metalliferous sediments of the
123 Troodos massif in Cyprus, as analogue to numerous oxide-based deposits found on-land that may
124 provide an alternative to magmatic-related REY deposits that currently dominate global supply.
125 Herein, we report the influence of various kinetic parameters such as the nature and concentration
126 of lixiviant, reaction times, temperature and pulp density, on the release of REY during simple and
127 sequential leaching experiments. We also explore in detail the efficiency of oxalate precipitation
128 for the selective extraction of low concentration REY from other impurities present in the leach
129 liquor via pH-dependent experiment and geochemical modelling.

130 **2. Background geology**

131 Umber deposits constitute the basal facies of the sedimentary sequence that accumulated above
132 the extrusive lavas of the Troodos ophiolitic massif, Cyprus. These metalliferous formations resulted
133 from the precipitation and accumulation on the paleo seafloor of Fe and Mn oxides from high
134 temperature hydrothermal solutions in the Tethyan Ocean 91 million years ago (Robertson and
135 Hudson, 1972, Boyle, 1990). Umbers are found interstratified with or overlying the Upper Pillow
136 Lavas of the Troodos ophiolite as lenticular bodies or in shallow depressions of the lava surface.
137 Although there are minor accumulations at multiple levels within the lavas, supra-lava umbers are
138 by far the most abundant and these constitute the basal facies of the Perapedhi Formation,
139 bracketed between the basaltic upper pillow lavas and radiolarian cherts of Campanian age
140 (Robertson and Hudson, 1974). Massive umber deposits can reach thicknesses of 4 m, although
141 most are limited to 1 m. However, records indicate that outcrops up to 35 m thick existed prior to
142 extensive extraction in the Mangaleni quarry (Boyle, 1984) where production peaked at 6000 t.y⁻¹
143 (Morse and Stevens, 1979, Cyprus Geological Survey, 2006). The lateral extent of umber deposits is
144 predominantly controlled by the initial sea floor topography, subsequent preservation from sea
145 floor weathering and more recent anthropogenic activity since Classical to the modern era.

146 Umbers comprise brown Fe-Mn-rich mudstones with an amorphous oxyhydroxides-dominated
147 mineralogy, formed by the accumulation of hydrothermal plume fall-out of Fe-Mn oxyhydroxides
148 (Boyle, 1990). Umber deposits are commonly carbonate-free. Dissolved Fe and Mn from the
149 effluent issued at hydrothermal vents oxidize in contact with bottom seawater to form colloids with
150 strong surface charge that enables the efficient scavenging of dissolved species (Koschinsky and
151 Halbach, 1995, Koschinsky and Hein, 2003). Umbers thus acquired seawater-like REE signatures
152 with concentrations up to ~500 mg.kg⁻¹ total REY (0.06% total REO (TREO) as RE₂O₃) with low
153 concentrations of radioactive elements (average U = 2.4 mg.kg⁻¹ and Th = 2.0 mg.kg⁻¹ (n=59) (Josso,
154 2017); Table 1).

Geochemical composition of supra-lava Umber (n=59)

SiO ₂	17.5 ± 4.5	V	964 ± 220	Ce	41 ± 18
TiO ₂	0.15 ± 0.05	Mo	38 ± 20	Pr	27 ± 12
Al ₂ O ₃	3.7 ± 1.3	As	366 ± 84	Nd	103 ± 30
Fe ₂ O ₃	52.1 ± 7.4	Zn	310 ± 54	Sm	22 ± 6
MnO	10.1 ± 2.6	Ba	1080 ± 553	Eu	5.7 ± 2.6
MgO	1.8 ± 0.5	Rb	21 ± 9	Gd	23 ± 6
CaO	1.7 ± 0.5	Sr	1038 ± 626	Tb	3.7 ± 2.4
K ₂ O	0.6 ± 0.3	Y	98 ± 24	Dy	20 ± 5
P ₂ O ₅	0.8 ± 0.3	Zr	90 ± 23	Ho	4.1 ± 1.3
Co	150 ± 37	Pb	179 ± 69	Er	10 ± 3
Ni	220 ± 57	U	2.4 ± 1	Tm	1.6 ± 1.2
Cu	736 ± 216	Th	2.0 ± 1	Yb	9.0 ± 2.1
Cr	20 ± 9	La	106 ± 29	Lu	1.3 ± 0.2

Major elements are expressed in wt.% ± 2σ

Minor and trace elements are expressed in mg/kg ± 2σ

155

156 Table 1: Typical geochemistry of unaltered supra-lava umbers from the Troodos massif [Josso, 2017].

157 These Fe-Mn oxide formations thus have similar concentrations to the ion-adsorption clay (IAC)
 158 deposits that are mined in southern China ($\Sigma\text{REY} = 300 - 1500 \text{ mg.kg}^{-1}$, (Yang *et al.*, 2013)). By
 159 comparison with the most advanced rare earths projects in Europe, the REY content is 12 to 14
 160 times lower than in the Khibina and Lovozero alkaline complexes of the Kola Peninsula and the
 161 Norra Kärr intrusion in Sweden, respectively 0.7% and 0.59% TREO (Chakhmouradian and Wall,
 162 2012, Guyonnet *et al.*, 2015). However, in contrast with these deposits, umbers possess an
 163 amorphous oxide dominated mineralogy and low concentrations of radioactive elements, and
 164 these may have advantages with regards to the overall extraction and treatment costs of the ore.
 165 Given the low content of targeted elements, it is of prime importance to identify the processing
 166 conditions that maximise the release of REY from umbers. We therefore explore the influence of
 167 major kinetic parameters of a variety of lixiviants used in the REY extractive industry, including acid
 168 and ionic solutions, on the recovery of REY to develop the best recipe for high extraction yields.

169 3. Material and method

170 3.1 Experimental leaching conditions and material

171 Leaching experiments were undertaken to investigate the potential recovery of REY from the
 172 metalliferous sediments. Leaching experiments tested a variety of common inorganic acids, such as
 173 nitric, sulphuric and hydrochloric acid, as well as ion exchange solutions of sodium chloride and
 174 ammonium sulphate, which are widely used in the treatment of IAC deposits in China (Yang *et al.*,
 175 2013). The experiments were designed to test the influence of solution concentration, liquid-to-
 176 solid (LS) ratios, time of reaction, and effect of temperature on the efficiency of REY extraction into

177 the liquid phase. Each factor was studied independently by keeping other parameters constant
 178 (Table 2).

		Tested parameter				Lixiviants	
		Molarity (mol/L)	LS ratio	Time	Temperature	Ionic liquid	Acid
Range	Min	0.05	2	2 min	20°C	NaCl	HNO ₃
	Max	1.75	100	13 h	70°C	(NH ₄) ₂ SO ₄	H ₂ SO ₄
179	When constant	1	25	120 min	20°C		HCl

180 Table 2: Range of experimental parameters and type of lixiviant used in the leaching experiments.

181

182 Batch reactions experiments were performed using 1 to 10 g of powdered samples mixed with the
 183 appropriate volume of lixiviant for the desired pulp density in closed 500 mL Erlenmeyer flasks. The
 184 kinetic influence of temperature on leaching efficiency was investigated at controlled temperature
 185 (40 and 70 °C) by mixing powdered samples and acid solutions (1 N HCl, HNO₃ and H₂SO₄) at 25:1 LS
 186 ratio for 2 h on a heating and stirring plate. The acid solutions were first placed on the hot plate for
 187 1 h to thermally equilibrate prior to insertion in the flask.

188 Sample PJ-CY-2014-91 (Table 3), the primary focus for this study, was recovered south-west of Marki
 189 on the northeastern rim of the Troodos massif. It was chosen from a pool of other samples as
 190 representative of the mean umber composition (n = 59, (Josso, 2017)). The complete sample set
 191 and its geochemistry are presented elsewhere [Josso et al, in prep]. Sample PJ-CY-2014-91 is devoid
 192 of weathering or known alteration affecting some umbers such as silicification or diagenetic
 193 remineralisation that involves removal of Mn and formation of apatite enriched in REY. The sample
 194 was first crushed using a manual press and dried for 48 h at 65 °C. Once dried, the crushed material
 195 was milled in agate pestle and mortar. Quantitative grain size data of the powdered umber were
 196 obtained using a Malvern Mastersizer laser particle size analyser at the National Oceanography
 197 Centre Southampton (NOCS). Two aliquots of the sample were measured in triplicate with good
 198 reproducibility (Supplementary Table 1). After grinding, 90% of the sample size fraction is less than
 199 370 µm in diameter, which constituted the working material for the following leaching experiments.

200

sample PJ-CY-2014-91					
SiO ₂	24.1	Ni	308	Nd	110.1
TiO ₂	0.2	Cu	801	Sm	22.5
Al ₂ O ₃	6.0	Zn	314	Eu	5.6
Fe ₂ O ₃	38.1	Ba	982	Gd	23.3
MnO	12.2	Sr	244	Tb	3.5
MgO	2.4	Zr	115	Dy	20.0
CaO	1.24	Th	4.6	Ho	3.9
K ₂ O	1.2	U	1.5	Er	10.3
Na ₂ O	0.7	Y	97.0	Tm	1.5
P ₂ O ₅	0.5	La	122.5	Yb	9.0
Sc	11.6	Ce	66.3	Lu	1.3
Co	119	Pr	27.0	ΣREY	523.7

201 Table 3: Composition of sample PJ-CY-2014-91 used in leaching experiments. Major elements are expressed
 202 in wt.%, trace elements in mg/kg.

203 **3.2 Oxalate precipitation**

204 The precipitation of REY from a pregnant leach liquor was investigated by the addition of
 205 ammonium oxalate at various pH values. A stock leach solution (SLS) was first produced by the
 206 leaching of 20 g of umber by 600 mL of 1 N HCl over 2 h at laboratory temperature (~21 °C). This
 207 solution was used as a reference material for all further precipitation experiments and its
 208 composition after filtration of the solid residue through 0.45 µm cellulose nitrate membrane filters
 209 is presented in Table 4. For each precipitation experiment, 20 mL of the SLS was transferred into 50
 210 mL Falcon tubes, to which was added 7 mL of a 0.32 N solution of ammonium oxalate
 211 (NH₄)₂C₂O₄·H₂O. The pH of each experiment was then immediately adjusted to the desired pH value
 212 (ranging between 0.85 and 3.15) by the addition of ammonia solution and measured with a Thermo
 213 Scientific Orion pH meter calibrated at laboratory temperature. All reagents used were at least
 214 analytical grade or higher purity. Solutions were left to rest for 5 h and a white precipitate was
 215 observed in all vials after this time. Tubes were then centrifuged and the liquid phase carefully
 216 transferred into pre-weighed HDPE bottles, whereas the precipitate was redigested with 6 N HCl
 217 and transferred to pre-weighed HDPE bottles. Both resulting solutions were analysed by ICP-MS for
 218 major elements, trace elements and REY. A mass balance was undertaken to check the
 219 measurement quality by ICP-MS and assess the experimental workflow. Our results normalized to
 220 the concentration in the stock leach solution show that the mass balance for cumulated solution
 221 and oxalate precipitate is good (90% - 110% of initial mass) for Na, Mg, Al, Ti, Mn, Fe, V, Co and Ba.
 222 Recovery for Ni, Cu, Sr, Y, Zr and REE ranges between 75 and 100% of the initial mass introduced
 223 depending on the element over the range of pH tested. In contrast, the masses of U and K were
 224 constantly found in higher proportions (110-120%) when compared with the initial mass introduced
 225 probably due to higher background noise and measurement precision on these elements. Calcium
 226 shows the greatest variations potentially linked to the formation of insoluble Ca oxalate phases
 227 during the preparation of daughter solutions with 3% nitric acid for ICP-MS analysis. Nevertheless,
 228 these data are of sufficient quality to determine the general phase distribution of each element
 229 during the precipitation of oxalates from the SLS at different pH values.

	Na	Mg	Al	K	Ca	Mn	Fe							
SLS (n=3)	67.4	44.7	24.2	21.6	121.2	100.9	71.3							
Abs. Std. Dev.	1	0.6	0.3	0.3	1.2	0.8	0.5							
	Sc	Ti	V	Co	Ni	Cu	Sr	Y	Zr	Ba	Th	U		
SLS (n=3)	39	684	3597	1105	548	1587	3537	2682	24	3099	32	23		
Abs. Std. Dev.	0.3	4.5	9.5	2.2	3.4	2.2	7.8	4.2	0.2	2.9	0.1	0.1		
	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
SLS (n=3)	3651	653	826	3582	730	186	763	108	624	117	297	37	207	28
Abs. Std. Dev.	3.6	1.3	1.0	2.1	1.0	0.3	0.6	0.2	0.8	0.2	0.3	0.2	0.5	0.2

230 *Major elements expressed in mg/L, trace elements in µg/L*

231 Table 4: Composition of the stock leach solution (SLS) presented as the mean of triplicate and absolute
232 standard deviation

233 **3.3 Analytical procedure**

234 Major, trace and rare earth elements concentrations were determined by inductively coupled
235 plasma mass spectrometry (ICP-MS) using an Element X-series 2 at National Oceanography Centre
236 Southampton (NOCS). Solutions for measurement by ICP-MS were diluted to appropriate total
237 concentrations with a 3% nitric acid solution containing an internal spike with In-Re ($5 \mu\text{g.kg}^{-1}$) and
238 Be ($20 \mu\text{g.kg}^{-1}$). Artificial element standards were produced at 2, 5, 10, 25, 50, 75, 100, 125, 150,
239 175 and $200 \mu\text{g.kg}^{-1}$ and used together with the internal spikes to calibrate the instrument and
240 monitor sample drift corrections. All standard calibration curves display less than 3.5% analytical
241 error with excellent linearity. International rock standards BHVO2, BIR1 and JB3, were run in
242 triplicate as unknown to monitor accuracy of calibration with excellent reproducibility between
243 triplicates (Supplementary Table 2). All analysis for trace and rare earth elements, Mg, Al, Fe and
244 Mn are accurate and fall within the range of published recommended values (Jochum *et al.*, 2005).
245 Sodium was measured in excess by 6% and 3% in BHVO2 and BIR1 respectively, whereas Ca and Ti
246 concentrations were 3% below recommended range in JB3. Measurement reproducibility on
247 international standards was also checked for discrepancies between standards prepared with and
248 without ammonium oxalates to check for matrix effects from the oxalates. Standard dilution to
249 daughter solutions were prepared by including ammonium oxalate matching the final
250 concentration of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ in samples analysed by the ICP-MS. Excellent reproducibility of results,
251 showing less than 5% difference between standards with and without oxalates, indicates the
252 absence of any matrix effects.

253 **3.4 Scanning electron microscopy imaging**

254 Imaging of the oxalate precipitate was obtained by scanning electron microscopy (SEM) at
255 University of Southampton using a Carl Zeiss LEO1450VP. The instrument used an operating voltage
256 of 20 kV and a working distance of 19 mm. The AZtec Energy Software was used for the processing
257 of energy dispersive X-ray spectroscopy (EDS) with a process time of 5 on an average of 3300
258 counts.s⁻¹. Images were collected using a nominal probe current of 800 pA. The leachate was
259 treated with ammonium oxalates and the pH equilibrated with aqueous ammonia. The solution was
260 filtered and the residue washed with deionized water and then deposited onto Al-Cu pellets. The
261 samples were left to dry in an oven at 60°C overnight and C-coated prior to analysis.

262 **3.5 Speciation modelling**

263 A numerical modelling approach, reproducing the conditions of the precipitation experiment was
264 developed to assess rare earth element fractionation results in the oxalate precipitate. Modelling
265 calculations were performed using the hydrogeochemical code PHREEQC version 3.3.9 (Parkhurst

266 and Appelo, 2013) and the thermodynamic data for REE from the Lawrence Livermore National
267 Laboratory (LLNL) database (Delany and Lundeen, 1990). The LLNL database was supplemented by
268 stability constants for the following aqueous RE-oxalate complexes; REHOx^{2+} , REOx^+ , RE(Ox)_2^- from
269 Schijf and Byrne (2001), where “RE” represents any lanthanide (except Pm) and “Ox” abbreviates
270 the oxalate ion $\text{C}_2\text{O}_4^{2-}$. Presently there is no complete set of stability constants for solid RE-oxalate
271 complexes ($\text{RE}_2\text{Ox}_3 \cdot n\text{H}_2\text{O}$). Missing constants were obtained via linear free-energy relationship
272 (LFER) calculations using existing data on RE-oxalate binding (Chung *et al.*, 1998) compared with
273 constants in the NIST database from other complexing agents (Smith and Martell, 2004). Best linear
274 regression was obtained for a Phenol ($R^2 = 0.94$) and used for estimating constants absent in Chung
275 *et al.* (1998) (Supplementary Figure 1).

276 **4. Results**

277 **4.1 Leaching with ion exchange solutions**

278 Leaching experiments using ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$) or sodium chloride (NaCl) at different
279 concentrations (0.05 – 1.75 N) and at a LS ratio high enough for the electrolytes not to be
280 considered a limiting reactant (up to 100:1) are not effective for the leaching of REY from umbers
281 (Figure 1). These solutions generally target the most easily exchangeable cations but the maximum
282 cumulated REY concentration in the leachate represents just 1.3% recovery of the initial REY
283 content of the sample.

284 **4.2 Leaching with acid solutions**

285 Acid-promoted release of REY displays hyperbolic trends of recovery for all kinetic parameters
286 tested (Figure 1). The experiments on acid concentration display curves approaching 80-85%
287 recovery of the initial REY content in the acid leach after levelling off. A threshold concentration
288 (before asymptotic values) is achieved for normality superior to 0.8 N H_2SO_4 , HCl and 0.75 N HNO_3 .
289 Further increases of the normality improve the recovery of REE by only a few percent whereas
290 contaminant concentrations continue to increase. REY recovery levels using HNO_3 are smaller
291 compared with HCl and H_2SO_4 . Although all three are strong acids, there are multiple orders of
292 magnitude difference in their respective dissociation constant ($\text{pK}_a = -6.3, -3$ and -1.4 for HCl, H_2SO_4
293 and HNO_3 respectively) which explains the lower efficiency of HNO_3 .

294 Another important factor influencing REY recovery is the Liquid-to-Solid (LS) ratio, or pulp density.
295 REY yields increase with increasing LS ratio up to 20 with recovery rates of 72%, 83% and 82% for
296 nitric, sulphuric and hydrochloric acid respectively. Further improvements in REY recovery is only
297 minor at higher LS ratios for nitric and hydrochloric acid. In contrast, an improvement of nearly 10%
298 is achieved with sulphuric acid between SL ratio of 20 and 100. This effect can be partly explained

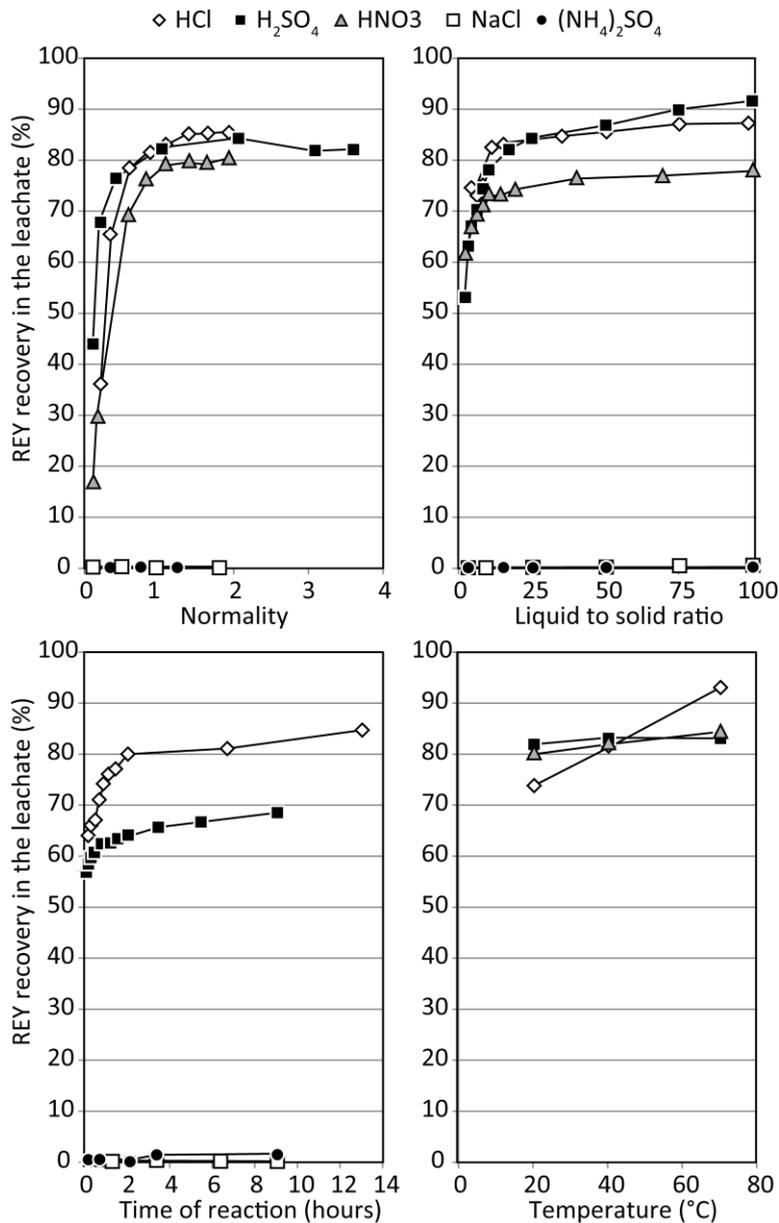
299 by the partial neutralisation of the diluted acid during the reaction with umbers (Ochsenkühn-
300 Petropulu et al., 1996).

301 A threshold reaction time greater than 100 min is observed for the two acids tested here with only
302 minor improvements in REY recoveries for longer leaching times (Figure 1). For HCl, the total
303 recovery increases for the first 2 hours of reaction then levels off, with only a 4% gain in the recovery
304 of REY in the next 11 h of additional reaction time. The reason why the sulphuric acid gave lower
305 yields compared to other tests at equivalent concentration, LS ratio and time of reaction is not
306 known. Nevertheless, during reaction more than 75% of the total recovery was achieved after only
307 15 min for both acids, suggesting rapid reaction kinetics of extraction. However, the major elements
308 recovery continuously increased with reaction time, therefore, shorter reaction times limit the
309 amount of impurities mobilised into the leach liquor.

310 As acid activity increases with temperature, elemental recovery in the leach increases as a function
311 of temperature. Recovery for REY increases by 19% when using HCl as the leaching temperature
312 rises from 20 to 70 °C, ultimately reaching 93% recovery of the initial REY content. However, no
313 improvement in REY recovery is observed when increasing the temperature for the nitric and
314 sulphuric acid leach.

315 These results show that temperature is a key parameter during REY recovery using HCl especially
316 at temperatures of around 70 °C.

317 In all experiments, the recovery of U and Th follow similar trends to the REY but reaching asymptotic
318 recoveries between 20 and 50% for Th and 40 to 70% for U across the range of parameters tested.
319 Despite the discernible mobilisation of these elements, their combined concentrations are below 3
320 mg.kg⁻¹ in all leachates.



321

322 Figure 1: Rare earth element and yttrium recovery in the leaching solution testing the influence of lixiviant
 323 molarity, liquid to solid ratio, time of reaction and temperature.

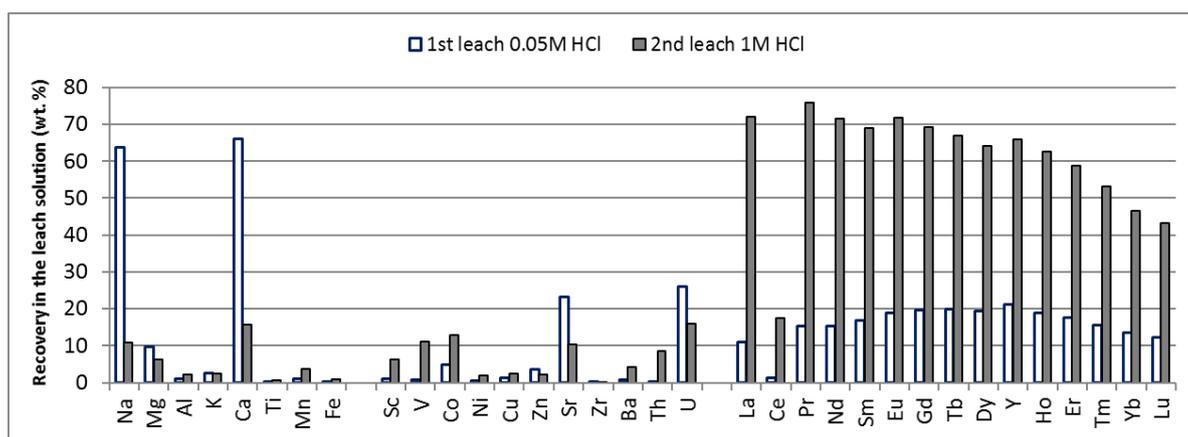
324

325 4.3 Multiple stage leaching conditions

326 Simple leaching experiments recovered > 80% of the initial REY content of the sample with acid
 327 concentrations greater than 0.8 N. Unfortunately, undesirable impurities such as Ca and Na also
 328 display strong leaching efficiencies (40 – 70%) in the weakest acid concentrations.

329 A two-stage leaching process was designed using 0.05 N HCl acid for 1 h in a first stage (L1) to
 330 investigate the possible separation of impurities contained in easily dissolved phases from rare
 331 earth and yttrium. Following centrifuging and extraction of the liquid phase, a 1 N acid solution is
 332 introduced to the sample and allowed to react for another hour on a shaking table (L2).

333 The first leach with weak acid shows that 66% of Ca, 64% of Na and more than 20% of Sr and U
 334 passes into solution (Figure 2). The release of REY in L1 is moderate ranging from 12 to 21% although
 335 the most abundant RE, La and Nd, are amongst the least mobilized. In contrast, yttrium, third most
 336 abundant RE in umbers shows the greatest recovery of the RE during the first stage of leaching
 337 (~21%). In L2, the REY recovery is greater than 65% (up to 76%, with the exception of Ce) for the 3
 338 most abundant REY (La, Nd, Y) whereas the recovery continuously decreases for the heavy REE
 339 (HREE) with only 43% recovery for Lu. Similar trends and levels of recovery were observed for L1
 340 with other weak nitric acid leaching whereas L2 is closer to HNO₃ and HCl recovery trends at higher
 341 molarity although yields are lower by 10 to 20% (supplementary Figure 2).



342

343 Figure 2: Two step leaching experiment on sample PJ-CY-91.

344 Consequently, a two-stage leaching process appears to be a viable way of increasing the purity of
 345 the leach solution containing the dominant fraction of REY by removing 60 - 65% of the main
 346 impurities Ca and Na. These elements are present at less than 15% of their initial concentration in
 347 L2 compared to a single leaching step. However, 13.5% of the sample's REY, equivalent to 19.6% of
 348 the overall inventory of leachable REY, are lost at the L1 stage, which constitutes an important loss
 349 considering the already low concentrations of REY in the umber ores available for recovery.
 350 Although the leaching efficiency for most major elements is below 10% (apart Na and Ca), the mass
 351 of major elements dominate the overall composition of the leachates and highlights that further
 352 steps of purification are needed.

353 Protocols of sequential leaching for nodules and hydrogenetic ferromanganese crusts (Koschinsky
 354 and Halbach, 1995) have already been widely used for the study of trace elements partitioning
 355 between the main mineralogical phases of these marine deposits. Applying this protocol to umbers
 356 yielded no significant REY recoveries for the first 2 leachates using acetic acid and hydroxylamine
 357 hydrochloride (5.8% and 3.9% respectively). Most REY were retrieved in the solution during the
 358 third leach when oxalic acid is employed attacking the dominant amorphous Fe oxide fraction of
 359 umbers. However, although REY recovery was good (53%), impurities, mainly Fe, were far greater

360 than in other leachates previously produced, and the oxalic acid protocol is considered too
361 aggressive for the purpose of this study.

362 **4.4 Purification of the leachate via oxalate precipitation**

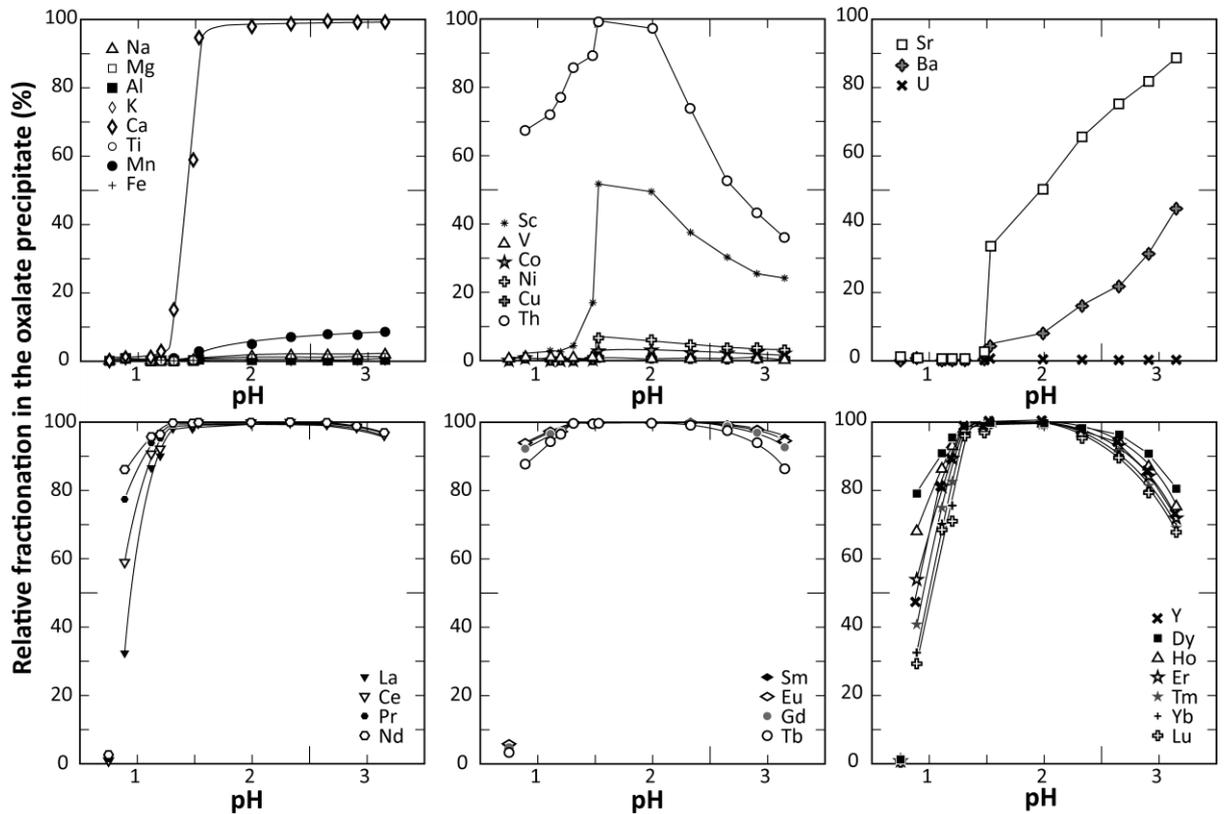
363 The precipitation of REY as an oxalate cake is widely used in industry for the selective extraction of
364 targeted metals (Vander Hoogerstraete et al., 2014, Xie et al., 2014). However, this method is
365 usually applied to leachates of pre-concentrated REY-bearing minerals such as xenotime, bastnäsité
366 or monazite (Xie et al., 2014). These approaches form REY-rich leachates (1 to 40 g.L^{-1}) and limit the
367 amount of impurities in the solution. In contrast to leach solutions produced by the treatment of
368 pre-concentrated REE-bearing minerals, the challenge of this study lies in the initially low rare earth
369 elements concentration of the leach (0.1 - 0.5 g.L^{-1}) and the high concentration of impurities
370 imposed by the non-pre-treatment of minerals for the concentration of a REE-bearing phase. We
371 investigated, as a function of pH, the selective precipitation of RE-oxalate from other elements
372 considered as impurities.

373 **4.5 Elemental partitioning between solution and precipitate in various pH**

374 The distribution of measured element concentrations between the initial leachate and subsequent
375 precipitate is calculated as a mass percentage (Figure 3). Over the range of pH values considered,
376 Na, Mg, Al, K, Ti and Fe do not appear to partition into the solid phase, with less than 1% of the
377 measured mass retrieved in the precipitate for Mg, Al, K and Fe, and < 2% for Na and Ti. Ca shows
378 the greatest variation with no precipitation at $\text{pH} < 1.2$ and nearly complete precipitation achieved
379 with the oxalate at $\text{pH} > 1.5$. The virtually complete precipitation of Ca observed in the pH window
380 1.2 - 1.5 appears to drive most of the other major element variations (Figure 3). Manganese
381 precipitation begins at $\text{pH} = 1.5$ and gradually increases from 0.3% at $\text{pH} = 1.5$, to 8.6% at $\text{pH} = 3.15$.
382 Similar precipitation trends are observed for Ba and Sr that are completely depleted in the
383 precipitate at $\text{pH} < 1.5$, and then strongly and continuously increase as pH becomes less acidic, with
384 up to 45% and 89% mass fraction in the solid for Ba and Sr respectively at $\text{pH} = 3.15$. Scandium, V,
385 Co, Ni, Cu display a similar behaviour with important precipitation occurring at $\text{pH} = 1.5$, although
386 their relative fraction in the solid phase decreases at higher pH values. These patterns (Figure 3)
387 suggest metal co-precipitation with Ca oxalates, the dominant phase of complexation by mass.

388 The partition trends of the REY into the solid show that nearly complete precipitation of rare earth
389 elements with oxalates is achieved between $\text{pH} 1.3$ and 2.3 (Figure 3). Outside of these limits, the
390 fractionation varies along the REE series. In the pH window 0.75 - 1.3 , all REY show increasing
391 affinity for oxalate complexes as a function of increasing pH. However, this fractionation between
392 the solid or liquid phase is not equal across the lanthanides. Uptake within the solid phase increases
393 from La to Eu to then decreases until Lu. In contrast, at $\text{pH} > 2.5$ a decreasing gradient of affinity for

394 the oxalate ligand is observed from light to heavy REE, which suggests a control of the ionic radius
 395 on the complexation of REE with oxalates at pH > 2.3 where light REE are preferentially incorporated
 396 over HREE.



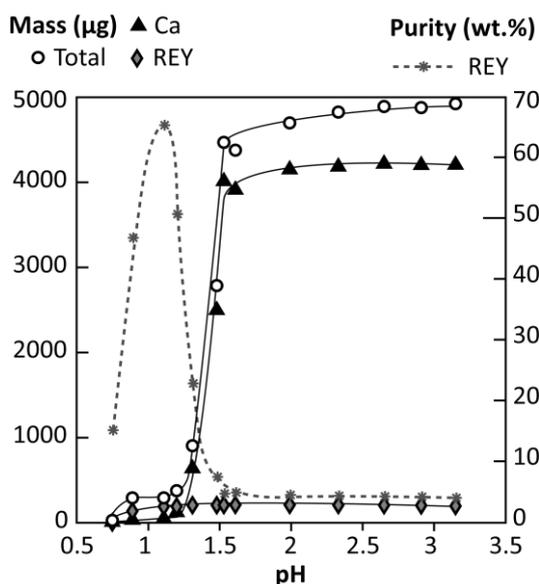
397
 398 Figure 3: Element fractionation in the oxalate precipitate (mass percentage) as a function of pH from the
 399 stock leach solution.

400 4.6 Purity of the precipitate

401 As demonstrated by the mass distribution between solid and liquid phases, the precipitation of
 402 oxalates constitutes an effective stage for the purification of the leach solution. Nearly complete
 403 precipitation of REE can be realized, while most major and trace elements, considered as impurities,
 404 remain in solution. However, these trends do not address the purity of the precipitate, as
 405 substantial differences in mass are not considered in the above results.

406 The purity of the precipitate is analysed as the ratio of the total mass of rare earth and yttrium (REY)
 407 divided by the sum of all measured masses (Figure 4). Disregarding the mass of the oxalates, the
 408 total mass of the precipitate expressed as the sum of all other elements measured in the oxalate
 409 precipitate range from 30 to 4900 µg with Ca making up 70 to 91% of the precipitate at pH > 1.3.
 410 Accordingly, with more than 90% of the total REY mass precipitated from the stock leach solution
 411 at pH > 1.1, the purity increases strongly at lower pH, where mostly REY bind with oxalates to reach
 412 a maximum at pH 1.1. The purity then decreases as Ca, the main impurity, starts to precipitate. The
 413 cumulated masses for all other elements apart from Ca and REY only account for 18 wt.% of the

414 precipitate at pH = 1.1 and less than 10 wt.% above pH 1.3, and is dominated by Mn, Cu, Ni, Na, and
415 Fe.



416

417 Figure 4: Element masses within the oxalate precipitate as a function of pH. The right-hand axis represents
418 the REY fraction or purity of the precipitate (%).

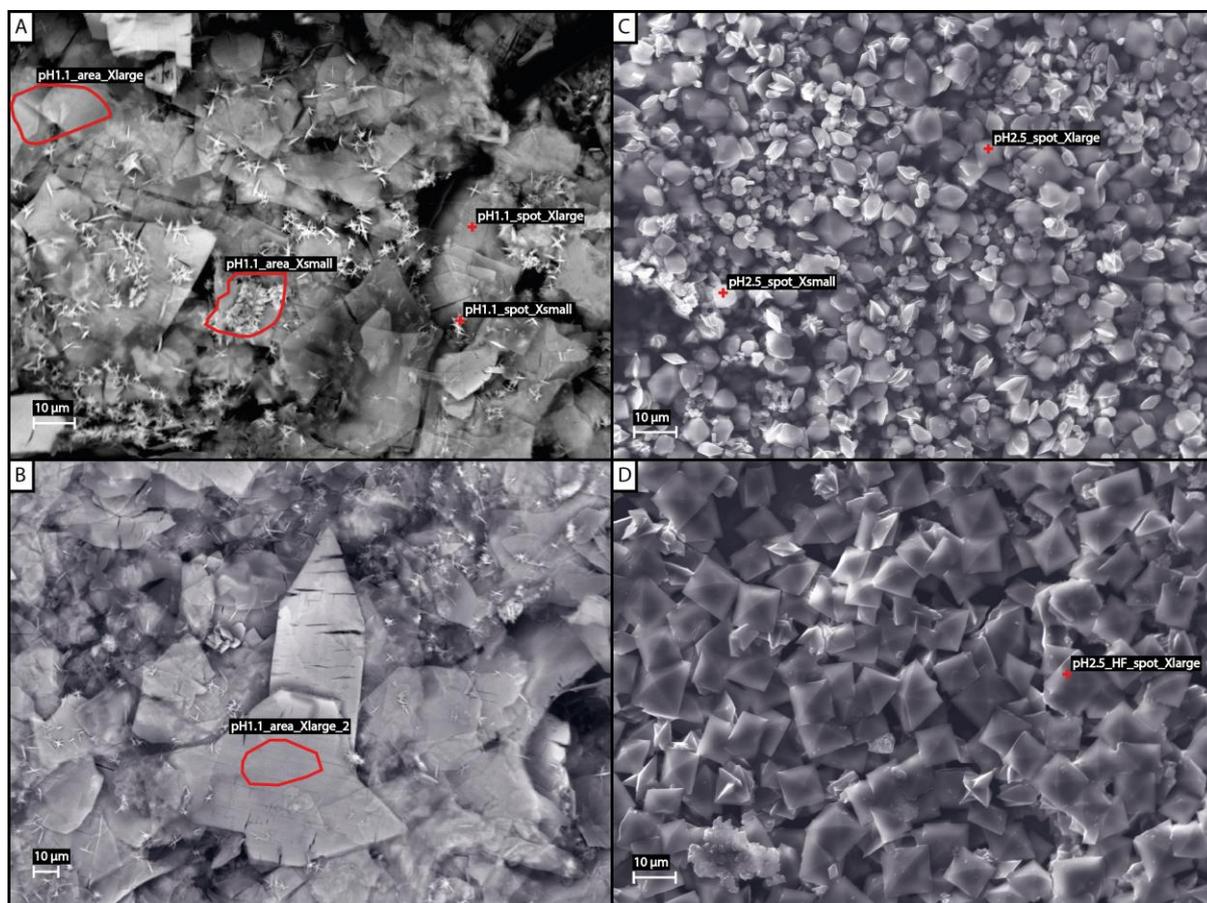
419

420 4.7 Precipitate structures

421 Duplicates of the oxalate precipitation experiments were completed at pH 1.1 and 2.5 for SEM
422 imaging. Two distinct crystal structures are observed between the two experiments, which reflects
423 the difference in composition, notably the Ca content. At pH 1.1, oxalate crystals show platy
424 prismatic and rectangular shapes up to 100 µm with smaller crest-like crystals covering them (Figure
425 5 A and B). Studies of $\text{Ln}_2(\text{C}_2\text{O}_4) \cdot n\text{H}_2\text{O}$ crystal microstructure (Zinin and Bushuev, 2014) have
426 demonstrated crystallization of RE-oxalate in the monoclinic system. Oxalate crystals formed at pH
427 2.5 consist predominantly of small (~10 µm) rhombic bipyramid (Figure 5 C & D). Energy-dispersive
428 X-ray spectroscopy (EDS) data were acquired for bulk areas, zones with specific crystal structure as
429 well as spot analyses. The EDS spectrum and associated chemical data (Figure 6, supplementary
430 table 3 and 4) are in good agreement with previous results on the purity of precipitates deduced
431 from ICP measurements.

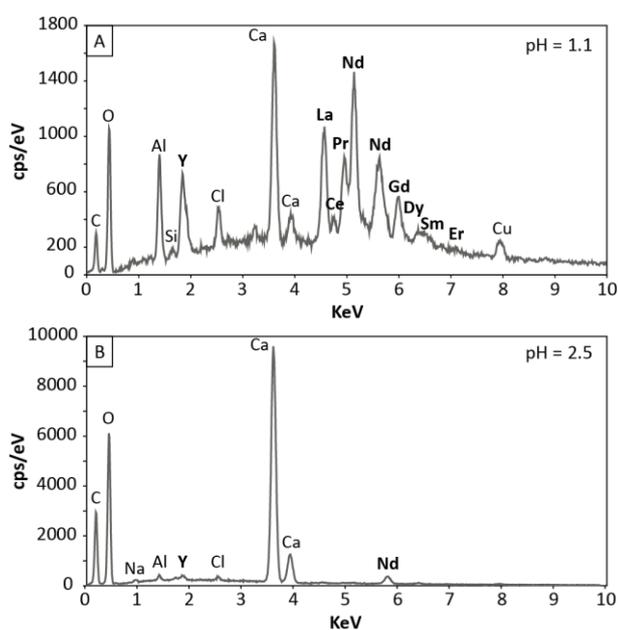
432 The EDS spectra highlight that 9 out of the 15 REY are in detectable range within the oxalate crystal
433 at pH 1.1 whereas only Y, La and Nd, the three most concentrated REY in the experiment are
434 detected in oxalate crystals precipitated at pH 2.5 (Figure 6). The total REY content at pH 1.1 is
435 estimated to represent 85 to 94% of element precipitating with the oxalate. Variations of
436 composition and REY distribution between the different crystals morphologies do not appear to
437 correlate with shape or size. Large and well-formed crystals analysed (area_Xlarge and
438 area_Xlarge2) encompass the range of measured REY concentrations, whereas smaller crystals with

439 a crest-like shape have an intermediate composition (Supplementary Table 3 and 4). At pH 2.5, Ca
 440 dominates the elements co-precipitating with oxalates (78 – 85%) and combined Y, La and Nd
 441 concentration reach a maximum of 7%, in good agreement with ICP-MS results and purity estimates
 442 (Supplementary table 3 and 4).



443

444 Figure 5: Backscatter image of oxalate precipitate at pH 1.1 (A and B) and at pH 2.5 (C and D). Areas and
 445 location of EDS spot analysis are shown on the figure (Supplementary tables 3 and 4).



446

447 Figure 6: EDS spectrum of the oxalate precipitate obtain at pH 1.1 (A) and 2.5 (B). The spectra correspond
448 to the field of view in images A and C of Figure 5. The presence of Al and Cu in measurement (A) reflects the
449 composition of the Al-Cu pellets, these elements are absent of any precise crystal EDS analysis otherwise.
450

451 **4.8 Overall REY recovery and distribution**

452 The stock leach solution used for the oxalate precipitation experiment, corrected for appropriate
453 dilution factors regarding sample PJ-CY-2014-91, contain 406 mg.kg^{-1} REY consisting of 25.2% La,
454 24.7% Nd and 18.5% Y. The recovery rate for individual rare earth elements by the leaching
455 procedure is > 95% for Pr, Nd, Sm, Eu, Gd, Y and Tb, 90% for La, with the recovery of the heavy rare
456 earth elements decreasing with increasing atomic number from Dy (92%) to Lu (65%)
457 (Supplementary Figure 3). The total REY content of the leachate consequently represents a yield of
458 77% of the initial REY content of the umber sample. The greatest loss occurs due to the poor
459 recovery of Ce (30%), which contributes up to 62% of the total REY content not mobilised by
460 leaching. In contrast to the other trivalent REE, Ce is present as Ce^{4+} , which forms acid-resistant Ce
461 oxide complexes (Bau and Koschinsky, 2009).

462 The formation of an oxalate precipitate has been demonstrated to be an efficient way of selectively
463 precipitating REE from the solution and separating them from other impurities with an efficiency
464 strongly dependent on pH. The minimal uptake during precipitation is observed for $\text{pH} = 0.89$
465 (61.5%) and rapidly increases up to $\text{pH} = 1.3$ where precipitation efficiency is > 96% for all REY.
466 Adding the efficiency of oxalate precipitation on the leaching process (85% recovery at 70°C), the
467 REY recovery in the oxalate precipitate relative to the original sample increases from 51% of the
468 initial REY content at $\text{pH} = 0.89$ to 82% for $\text{pH} = 1.3 - 2$. Relative to the impurities that are co-
469 precipitating, the optimal purity for the precipitate is achieved for $\text{pH} = 1.1$ where 76% of the initial
470 REY content of the sample is recovered. Based on these values following optimal leaching and
471 precipitation conditions, the processing of 1 ton of umber with an average 500 mg.kg^{-1} REY would
472 produce an oxalate precipitate containing 380 g of mixed rare earth elements.

473 **4.9 geochemical modelling of REY recovery**

474 **4.9.1 Model conditions and available data**

475 Detailed recovery trends within the oxalate precipitate (Figure 3) have highlighted the strong
476 fractionation that occurs along the lanthanide series at pH values < 1.5. In addition, the decreasing
477 recovery observed at $\text{pH} > 2$ as a function of atomic number constitutes another unexplained
478 observation. Although HREE are present in only minor concentrations in umbers (average $\sum\text{HREE} =$
479 $\sum[\text{Tb-Lu}; \text{Y}] = 147 \pm 34 \text{ mg.kg}^{-1}$, $n = 59$, (Josso, 2017)), they attract the greatest commercial values,
480 which justifies further exploration of the reasons for their less efficient recovery. Furthermore,

481 speciation of oxalic acid as a function of pH (Supplementary Figure 4) shows that the presence of
482 oxalate ion $C_2O_4^{2-}$ is minimal in the pH window considered here, although the precipitation of REE
483 oxalate is observed at pH 0.8 and decreases at higher pH when the activity of Ox^{2-} increases
484 (Supplementary Figure 4 (Chi and Xu, 1998)). To explore these questions, speciation modelling was
485 performed using PHREEQC (Parkhurst and Appelo, 2013) to reproduce the chemistry involved in
486 the precipitation experiments.

487 Following the conditions of the precipitation experiments, the REE contained in the leachate are
488 partitioned between the solution and the precipitate formed after the addition of ammonium
489 oxalate. However, not all oxalate ions will be in the correct ionic form to bind with REY to precipitate
490 and form aqueous complexes that may remain in solution (supplementary Figure 4). Potential
491 aqueous complexes of REY^{3+} and oxalates can be described (Eq. 1 and 2) taking into account the
492 bioxalate (HOx^-) and oxalate (Ox^{2-}) ions such that:

493 Eq. 1: ${}_{HOx}\beta_m = [REY(HOx)_m^{3-m}]$

494 Eq.2: ${}_{Ox}\beta_n = [MOx_n^{3-2n}]$

495 Where ${}_{HOx}\beta_m$ is the m^{th} (order of complexation) stability constant of the bioxalate (HOx^-) ion with
496 any REY^{3+} and ${}_{Ox}\beta_n$ the n^{th} stability constant of oxalate ion (Ox^{2-}) with any REY^{3+} . Schijf and Byrne
497 (2001) showed that one orders of complexation for bioxalate ($m = 1$) and 2 for oxalate ions ($n = 2$)
498 are satisfactory for modelling REY binding behaviour with oxalates in aqueous solution as further
499 orders of complexation are minor.

500 Precipitating REE-oxalate complexes have been reported to form hydrated REY salts (Eq. 3) such
501 that:



503 Although the formation of solid REY oxalates complexes has been considered since the 1950's
504 (Crouthamel and Martin, 1951, Feibush *et al.*, 1958, Bhat and Rao, 1964, Grenthe *et al.*, 1969, Chi
505 and Xu, 1998, Chung *et al.*, 1998, Schijf and Byrne, 2001, Xiong, 2011), a complete set of solubility
506 constants for solid rare earth oxalate remains elusive with no study presenting results for all
507 lanthanides and Y simultaneously under identical experimental conditions. The most complete data
508 set on $REY_2Ox_3 \cdot nH_2O$ complexes are from Bhat and Rao (1964), Chung *et al.* (1998) and Xiong (2011)
509 (Table 5). Although diverging by two log units, two of the sets are consistent in showing increasing
510 solubility constants from La to Gd, with decreasing values along the HREE. This behaviour contrasts
511 with the variations in $\log {}_{Ox}\beta_{1-2}$ for aqueous REY oxalates complexes that show a continuous increase
512 across the lanthanides (Table 5).

513 Although data from Xiong (2011) lack information on HREE, they present a better comparison with
 514 those of Chung et al. (1998) with similar constants for La, Ce and Sm, whereas data from Bhat and
 515 Rao (1964) for La, Nd and Tb are low compared to their direct neighbours suggesting the presence
 516 of potential errors.

517 With relatively complete data over the lanthanide series and consistency with other studies, data
 518 from Chung et al. (1998) are used to estimate missing constants by using linear free-energy
 519 relationships in combination with the NIST databases for critical stability constant (Smith and
 520 Martell, 2004). Best matches were obtained by initially filtering the NIST database by $\log\beta_{La}/\log\beta_{Sm}$
 521 < 1 and $\log\beta_{Gd}/\log\beta_{Yb} > 1$ ratios to match the incomplete convex upwards trends formed by oxalate
 522 data. Accordingly, REE stability constants of 14 acids have been compared with data from Chung et
 523 al. (1998) (Supplementary Figure 1) and best-fit ($R^2 = 0.94$) observed for a phenol (2-Nitroso-1-
 524 Naphtol-8-sulfonic acid) giving the following equation of linear regression to estimate missing
 525 constant for Pr, Tb, Ho, Tm and Yb (Table 5), here exemplified for Pr (Eq. 4):

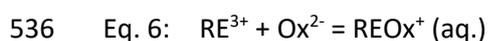
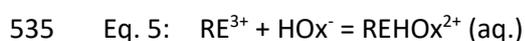
526 Eq. 4: $\text{Log}_{\text{Ox}}\beta_{\text{Pr}_2\text{Ox}_3.\text{nH}_2\text{O}} = -2.232 \text{Log}_{\text{PHENOL}}\beta_{\text{Pr}} - 18.88.$

	$\text{Log}_{\text{HOx}}\beta_1$	$\text{Log}_{\text{Ox}}\beta_1$	$\text{Log}_{\text{Ox}}\beta_2$	$\text{Log}_{\text{Ox}}\beta_{\text{RE}_2\text{Ox}_3.\text{nH}_2\text{O}}$			$\text{Log}_{\text{PHENOL}}\beta$	Calculated $\text{Log}_{\text{Ox}}\beta_{\text{RE}_2\text{Ox}_3.\text{nH}_2\text{O}}$	
	Schijf and Byrne (2001)			Bhat and Rao (1964)	Chung et al, (1998)	Xiong (2011)	Martell and Smith (1982)	LFER linear regression	% diff
Y	2.08	6.66	11.27	-28.91	-29.29	na	na	na	
La	1.92	5.87	10.47	-26.91	-29.22	-29.15	4.70	-29.37	-0.51
Ce	2.43	5.97	10.86	-28.79	-30.40	-30.18	5.04	-30.13	0.88
Pr	2.09	6.25	10.82	-29.64	na	-30.91	5.28	-30.67	
Nd	2.16	6.31	10.82	-29.69	-30.89	-31.57	5.46	-31.07	-0.59
Sm	2.35	6.43	11.08	-30.30	-31.35	-31.59	5.65	-31.49	-0.46
Eu	2.21	6.52	11.09	na	-31.38	na	5.61	-31.40	-0.08
Gd	2.04	6.53	11.10	-29.49	-31.37	-32.31	5.50	-31.16	0.69
Tb	2.29	6.63	11.27	-29.14	na	na	5.33	-30.78	
Dy	1.96	6.74	11.35	-29.44	-30.70	na	5.21	-30.51	0.62
Ho	2.17	6.77	11.41	na	na	na	5.10	-30.26	
Er	2.09	6.83	11.51	-28.82	-30.05	na	5.01	-30.06	-0.06
Tm	2.18	6.89	11.65	na	na	na	4.97	-29.97	
Yb	2.41	6.95	11.75	-28.25	-30.02	na	5.06	-30.17	-0.51
Lu	2.28	6.96	11.77	na	na	na	5.06	-30.17	

527

528 Table 5: Data used in the model to calculate REE speciation between aqueous and precipitating oxalate
 529 complexes. Missing data for solid oxalate complexes were calculated using LFER. Estimations
 530 between the linear regression and available data show at most $\pm 0.9\%$ difference with published
 531 values.

532 The PHREEQC speciation modelling therefore considers the following reactions (Eq. 5 – 8) in
 533 addition to any form of complexation already included within the thermodynamic LLNL database
 534 used calculations:



537 Eq. 7: $RE^{3+} + 2Ox^{2-} = RE(Ox)_2^-$ (aq.)

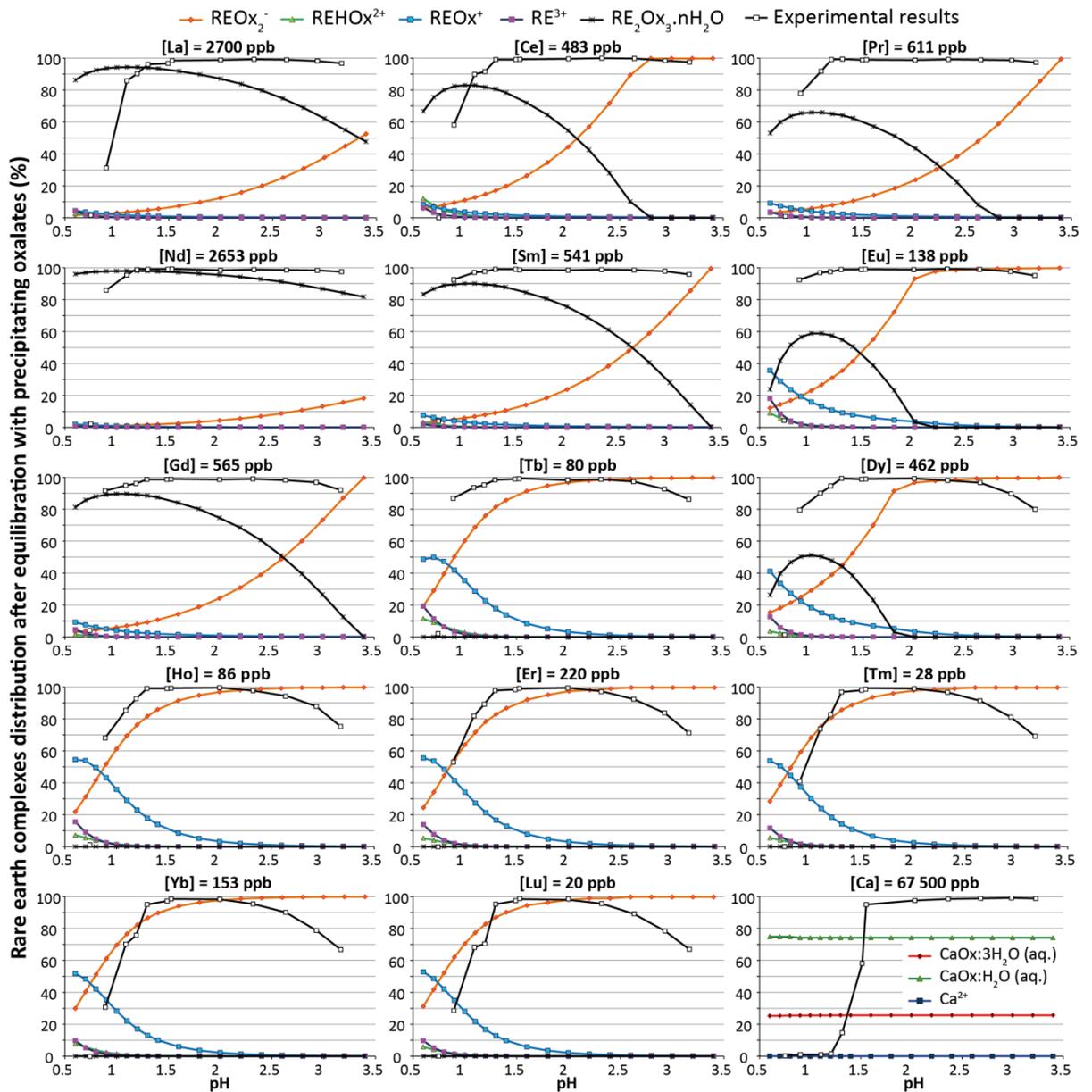
538 Eq. 8: $2RE^{3+} + 3Ox^{2-} + nH_2O = RE_2Ox_3 \cdot nH_2O$ (s)

539 In a similar way to REE, only partial data exists to describe oxalate complexation with other major
540 or trace elements. Some data exists for Ca oxalates complexes (Martell and Smith, 1977, 1982),
541 which is convenient for this study as Ca constitutes the dominant impurity in the REY liquor.
542 Therefore, only the complexation of Ca and the rare earths are taken into account in this simplified
543 model of previous experiments. The model was set up to calculate speciation of each rare earth
544 with the 3 aqueous oxalate complexes and include the kinetic effect of REY-oxalate solid
545 precipitation if saturation was reached.

546 **4.9.2 Model results.**

547 The 5 most abundant complexes present in the results of the model have been selected and are
548 displayed on Figure 7. Combined they account for > 94% of REY complexes at the lowest pH and >
549 99% at pH > 1. Using experimental conditions and complexes calculated from the LLNL database,
550 oxalate-binding dominates REE complexation. Other complexes considered in the calculation such
551 as RE^{3+} and $REOH^{2+}$ are only present in the model at pH < 1 and account for less than 1% of dissolved
552 REE.

553 Speciation calculated using PHREEQC with REE concentrations similar to those in the precipitation
554 experiments displays important differences along the lanthanide series and show divergences with
555 experimental results. In the range of pH and concentrations explored here, the Ca-oxalate
556 complexes considered never reach saturation and remain in solution. In contrast with the
557 experiments, no steep precipitation curve is observed between pH 1.1 and 1.5. Another major
558 difference in the results from the model concerns the total lack of precipitation for Tb, Ho, Er, Tm,
559 Yb and Lu. For these elements, complexation is dominated by aqueous single oxalates at pH < 0.8
560 and then by increasing proportions of double oxalate at more than 90% at pH > 1.6. It is important
561 to note that these 6 elements have some of the lowest concentrations in solution ($[RE] < 220$ ppb).
562 Interestingly, Eu precipitates although its concentration is only 138 ppb. All elements precipitating
563 display convex upward trends of precipitation as a function of pH with a maximum reached for pH
564 0.9 - 1.1 (Figure 7). All these bell-shape curves show diverse degrees of slope inversely related to
565 the concentration of RE in the stock leach solution. These observations suggest a control of both
566 concentration and atomic number in the speciation of REE-oxalates.

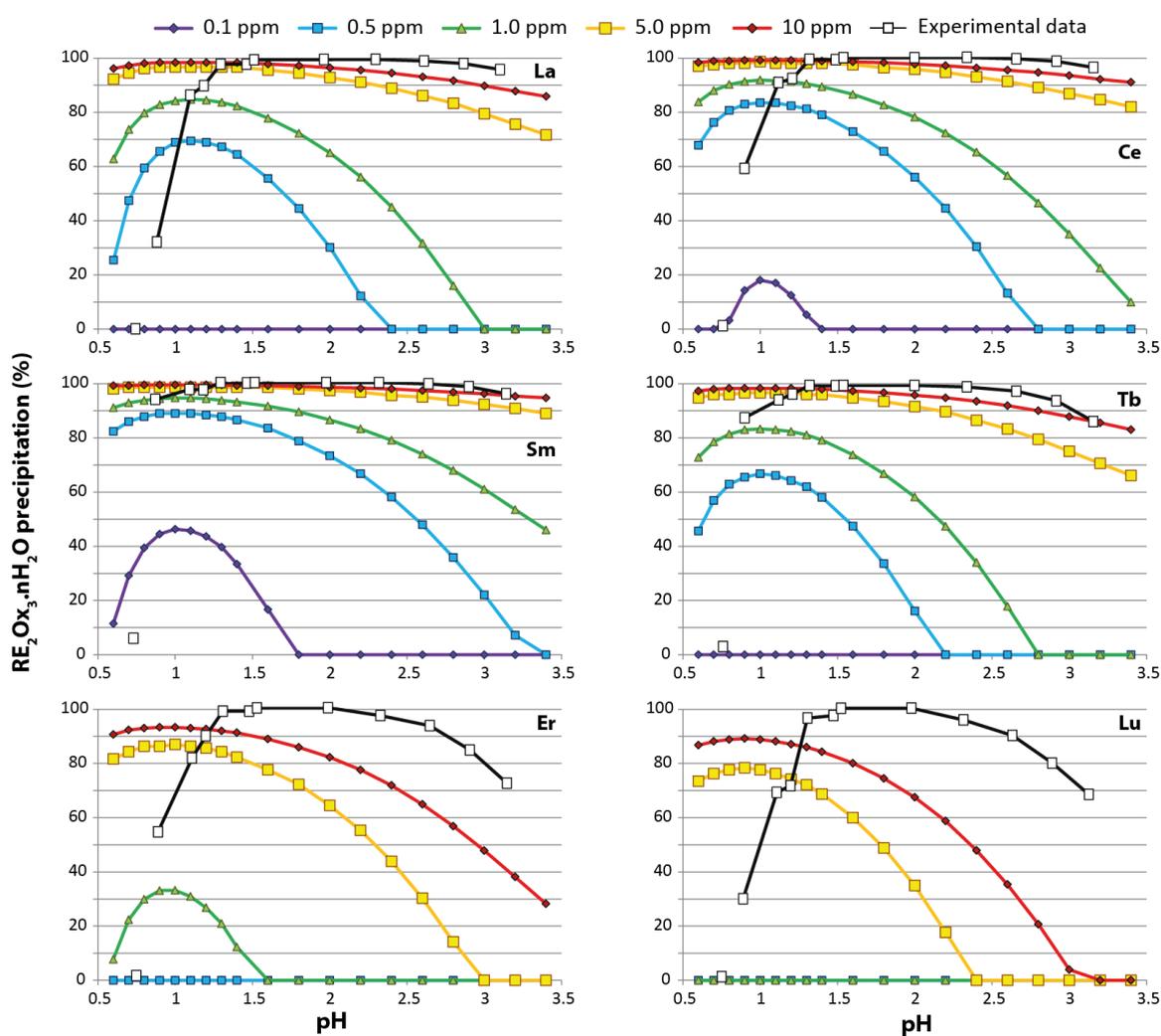


567

568 Figure 7: REE and Ca speciation with oxalate as a function of pH calculated using PHREEQC. Initial
 569 concentrations used replicate the initial experimental design. Experimental results (black line
 570 and white squares) are overlaid for comparison and should be compared with the modelling
 571 of $RE_2Ox_3.nH_2O$ complexes.

572 Accordingly, the modelling was further adjusted to test these hypotheses by calculating the
 573 speciation of all lanthanides in equal concentration at 0.1, 0.5, 1, 5 and 10 $mg.kg^{-1}$. Complete
 574 speciation results for each concentration are available in supplementary Figure 5 to 9. Figure 8
 575 presents the formation of RE-oxalates precipitated at different concentrations for 6 selected rare
 576 earth elements along the lanthanide series. From the following models, the formation of solid RE-
 577 oxalate increases up to pH 0.9 - 1.1 but decreases thereafter. The position of the maximum
 578 precipitation is not constant and evolves from pH 1.1 to 0.9 as a function of increasing atomic
 579 number. In addition, the formation of a precipitate is directly affected by the initial rare earth
 580 concentration in solution. It appears that the formation of middle rare earth oxalate is favoured
 581 against light- and even more so against heavy-rare earth oxalate at equal concentrations. This

582 distribution can be considered as a direct representation of the stability constant $RE_2Ox_3 \cdot nH_2O\beta$ where
 583 constants increase from La to Gd and decrease again through the heavy rare earth elements.
 584 However, although the stability constant of La is the lowest, modelling shows formation of La-
 585 oxalate at potentially lower concentrations than is possible for the heavy rare earths to form solid
 586 complexes. This suggests that the HREE are affected by another parameter that inhibits their
 587 precipitation. Species distribution (supplementary Figure 5 to 9) highlights the increasing
 588 dominance of $REOx_2^-$ aqueous complexes as pH increase up to the point of inhibiting the formation
 589 of solid oxalates. Although the stability constant $ox\beta_2$ increases as a function of the atomic number
 590 ($\log K_2 = 10.5 - 11.7$ from La to Lu) and could account for the decreasing formation in solid oxalates
 591 for HREE by competing in REE binding, this interpretation is counter intuitive considering
 592 $RE_2Ox_3 \cdot nH_2O\beta \gg ox\beta_2$.



593
 594 Figure 8: RE-oxalate precipitation as a function of the initial concentration of REE in the initial solution and
 595 modelling as function of increasing REE concentration. All other parameters are as in the
 596 experiment. Experimental results (black line and white squares) are overlaid for comparison.

597 Although the modelled and experimental trend for the precipitation of REE oxalate do not agree
 598 exactly, the model reproduces some of the observations from the experiments. For example:

- 599 1) The fractionation observed in the recovery from the experiments and the model at pH
600 < 1.1 follows closely the bell-shape of the RE₂Ox₃.nH₂O stability constant
- 601 2) The models show that at equal concentrations, the formation of precipitating RE-
602 oxalate is favoured in the following order: MREE > LREE >> HREE. This trend results
603 from (i) the positive gradient of log $\alpha_{ox}\beta_2$ along the lanthanide series coupled to (ii) the
604 increase of competing species (e.g., dominantly Ca) consuming oxalate ions.
605 Accounting for the initial differences in concentration in the experiment, this explains
606 the decreasing recovery of the HREE observed in the experiment at pH > 2.

607 Under the model conditions, the maximum formation of a REE oxalate precipitate occurs at pH 1,
608 similar to values previously reported for the purification of monazite leach liquor (Salman *et al.*,
609 2014). The species distribution following oxalic acid dissociation (Supplementary Figure 4) shows
610 that Ox²⁻ ions represent less than 0.03% of the total oxalate species distribution at pH 1. In contrast,
611 at pH 3 and above the Ox²⁻ concentration increases steeply and dominates species distribution at
612 pH > 4.2. However, precipitation in the model is low. The dominance of Re₂Ox₃ complexes over
613 aqueous complexes at pH 0.9 - 1.1 can be understood as a constant balance of the system. Free
614 trivalent REE partitioning between the different oxalate complexes follows the magnitude of the
615 stability constants. Therefore RE³⁺ will bind dominantly with Ox²⁻ over HOx⁻ to form a precipitate
616 until Ox²⁻ becomes the limiting reactant. The system therefore balances the equilibrium induced by
617 the decrease of [Ox²⁻] at a fixed pH, by dissociating more oxalic acid into HOx⁻ and Ox²⁻. The newly
618 formed Ox²⁻ ions are therefore readily available for complexation with free RE³⁺ in the solution and
619 precipitate. The cycle carries on balancing until one of the other reactants becomes limiting. The
620 decrease in Re₂Ox₃ at higher pH in favour of aqueous RE-oxalate complexes relates to the increasing
621 competition in oxalate binding from Ca²⁺ which starts to precipitate at pH > 1.1 and is largely in
622 excess over [HOx⁻] and [Ox²⁻]. As pH rises, more oxalate and bioxalate ions bind with Ca over REY
623 due to its much greater abundance in solution; 25 to > 3000 times the REY concentration. Oxalates
624 constitute a chelating agent for REE and usually binds forming bidentate ligand with a ring structure
625 to form precipitates (Hansson, 1970, Rao *et al.*, 2004). The decreasing availability of Ox²⁻ at higher
626 pH due to binding with Ca, prevents the formation of these ring structure and explains the dominant
627 complexation of RE³⁺ as aqueous complexes.

628 The absence of Ca oxalate precipitation in the model may explain the observed difference between
629 REY recovery trends from the model and the experiment at pH > 2. In the experiments, Ca oxalate
630 is the dominant precipitate at pH > 1.5 and REY are included as co-precipitating elements within
631 the newly formed crystals. This may explain why REY recovery trends do not decrease as steeply as
632 in the numerical model. Furthermore, a level of supersaturation of oxalate ion might be needed for
633 the precipitation of a solid phase which is not considered in this model. This parameter might also

634 contribute to the underestimation of the model for RE₂Ox₃ precipitation run at the experimental
635 concentrations.

636 **5. Discussion**

637 **5.2 Leaching efficiency**

638 The use of ionic solutions tested here has proven to be inefficient for the leaching of REY from
639 umbers. Although this method is widely used in China for the treatment of REY adsorbed in clay
640 with economic yields, a similar approach applied here resulted in only 0.3% REY recovery in optimal
641 kinetic conditions. These results highlight a major difference between IAC and umber deposits
642 considering REY location and binding within the deposit. Although REY were initially adsorbed on
643 the surface of Fe and Mn oxides during umber deposition in the Tethyan Ocean, the REY can no
644 longer be considered as easily exchangeable cations and stronger acid conditions are needed for
645 their extraction. This can be partly in response to modifications in the structure and mineralogy of
646 umbers induced by diagenesis of the deposits. Umbers comprise only minor goethite, quartz and
647 zeolite, with amorphous Fe-Mn oxides still dominant suggesting that REY remain bound to the
648 oxides, although they might be incorporated within the oxide matrix following diagenesis and
649 cannot be substituted easily by ions of equivalent size at neutral pH.

650 **5.1 REE leachability**

651 In all acid leaching experiments, the mobilization of REY has been more efficient compared to the
652 recovery of other minor elements scavenged by Fe and Mn oxides. The REY, in all oxidation states,
653 have large ionic radii (0.86 - 1.04 Å), up to 60% larger, when compared to other cations potentially
654 adsorbed like V (0.79 Å), Zn (0.74 Å), Cu (0.73 Å), Ni (0.69 Å) and Co (0.65 Å) in divalent state
655 (Shannon, 1976). This difference in ionic size might account for their ease of extraction compared
656 to these other elements, as they do not fit within the oxide structure as readily as other transition
657 metals.

658 The upper limit for REY recovery, ~80-92% of the total REY content in the original sediment,
659 emphasizes the distinction between REY loosely bound to amorphous oxides and those
660 incorporated within the mineral structure of minor minerals formed during diagenesis such as
661 goethite which are more resistant to the acid leach. The grain size of the material to be leached also
662 constitutes an important parameter to take into account to improve recovery. This parameter can
663 easily be adjusted in a processing plant and the crushing size will have a positive impact on the
664 potential release of REY as the reaction area increases.

665 **5.2 Optimal leaching conditions**

666 Through the experiments carried out in laboratory conditions, all parameters tested indicates a
667 kinetic control over the release of REY in the solution, approaching a maximum of 80 - 92% REY

668 extracted depending on the acid used. Threshold values when approaching asymptotes can be
 669 considered as the lowest conditions of the parameter tested to apply to optimize REY extraction for
 670 each parameter in the most cost-effective way. By implementing beyond threshold leaching
 671 settings of the n experiment within the n+1 test, optimal leaching conditions can be determined for
 672 an optimized REY extraction recipe considering acid concentration, pulp density, time of reaction
 673 and temperature. From the results reported here (Figure 1), it can be estimated that optimal
 674 extraction of REY from umbers can be achieved with either inorganic acid concentrated at 1 N, 70°C,
 675 SL ratio > 10 in 1 h on a shaking table that would give a yield equivalent or superior to 90% of the
 676 initial REY content (Table 6).

	Molarity				LS ratio				Time				Temperature			
	Treshold		Yield		Treshold		Yield		Treshold		Yield		max		Yield	
	M	%	M	%	-	%	-	%	minutes	%	hours	%	°C	%		
HNO ₃	0.75	73	1.75	80	10	73	100	76	X	X	X	X	70	84		
H ₂ SO ₄	0.4	83	1.75	81	20	81	100	92	45	62	9	68	70	81		
HCl	0.75	81	1.75	85	10	82	100	87	120	73	13	77	70	93		

677
 678 Table 6: Rare earth and yttrium yields from acid leaching experiments at the threshold (before asymptotic
 679 inflection) and maximum test parameter values.

680 This leaching process, when compared with industrial processes for the treatment of REY ore from
 681 alkaline rocks, pegmatites or carbonatites is relatively advantageous. It requires only low acid
 682 concentrations and near ambient temperatures, in contrast to cracking methods that employ
 683 concentrated acids and elevated temperatures (> 200 °C), and yields good performance considering
 684 no physical pre-concentration treatment is needed apart from crushing and pulverizing of the ore.
 685 Compared to IAC heap leaching (Vahidi *et al.*, 2016), the process applied for umbers treatment is
 686 relatively similar with an overall comparable efficiency although acid conditions are required.
 687 However, the umber leaching process requires only a few hours, in strong contrast to the 150 - 400
 688 days required for IACs.

689 5.3 From Laboratory to industrial scale

690 The projection of these results obtained in laboratory experiments to the industrial scale should
 691 consider the following adjustments for processing costs reduction and optimization of the plant
 692 economic viability.

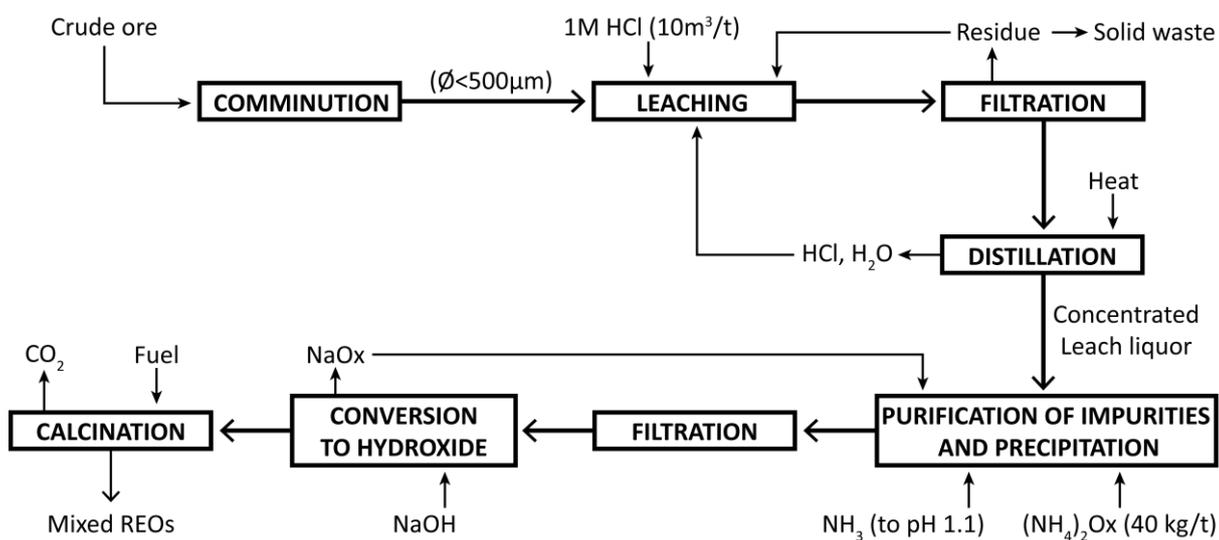
693 Optimal conditions for the leaching of umbers have shown that large volumes of acid are needed
 694 as 10:1 LS ratios are used. Implementing a distillation step following the leaching would allow
 695 recovering hydrochloric acid after condensing to recycle in the next batch (Figure 9). Here, the
 696 additional cost of heating up for distillation is counterbalanced by the significant reduction of
 697 volume of reactant needed on a long-term period. Furthermore, leaching efficiency is improved at
 698 higher temperatures and could therefore benefit from the higher temperature of distilled HCl.

699 Numerical modelling has demonstrated the importance of the initial leach REE concentration for
 700 the precipitation of oxalates. The higher the initial REE concentration the higher the precipitation
 701 efficiency. Therefore, the distillation and associated evaporation would induce an
 702 overconcentration of elements contained in the leach liquor and significantly increase oxalate
 703 precipitation efficiency that in turn would lead to a reduction in oxalate consumption.

704 Similar to HCl recycling, consumption of ammonium oxalate can be greatly reduced if the oxalate
 705 cake is digested by sodium hydroxide (Eq. 9). This reaction allows the conversion of REY oxalate into
 706 hydroxides and formation of sodium oxalate salts (Habashi, 2013) such that:



708 The hydroxides are then calcined to form a mix REY oxide product and the sodium oxalate
 709 reintroduced as a reactant in the precipitation step (Figure 9).



710

711 Figure 9: Optimized workflow of metalliferous sediment processing for the extraction of REY by simple acid
 712 leaching and oxalate precipitation.

713 5.3 Umber deposits as a potential REY resources in Cyprus and beyond

714 Umbers from Cyprus have been quarried extensively for pigments since ancient time and more
 715 recently for cement with a production decreasing from 30,000 tons per year in the late 70's to an
 716 average 6,000 tons per year in the last decade (Morse and Stevens, 1979, Cyprus Geological Survey,
 717 2006). This reduction in umber exploitation is related to both the decrease in the use of umber as
 718 a natural pigment in paint or cement and to the great reduction of available, mineable umber
 719 accumulations. Most umber deposits in Cyprus comprise outcrops limited in size to tens of meters
 720 length for 1 or 2 meters thickness following the original paleo topography of the oceanic floor. Such
 721 outcrops are too dismembered to present any economic potential due to limited availability of the
 722 resource. However, incorporating REY production to the existing processing of umbers could bring
 723 an important value to such exploitation and reduce economic vulnerability by diversifying end-

724 products. This seems to be the strategy employed in a number of alternative deposits whereby REY
725 extraction could be cost-effective from tailings as a by-product after main ore treatment such as
726 processed bauxite (Tsakanika et al., 2004, Qu and Lian, 2013, Ujaczki *et al.*, 2015, Deady et al., 2016)
727 or in coal residue (Rozelle *et al.*, 2016b). However, in the case of umbers, the extraction of REY by
728 acid leaching has to happen as a first step and the residue can be neutralised, dried and sold as a
729 pigment. Indeed, the leaching process using weak acid does not affect the overall mineralogy of
730 umbers as REY are mainly associated with the amorphous oxide phase (Supplementary Figure 10)
731 and the amount of leached Fe and Mn oxides, essential for the pigment quality, remains minor (<
732 3%).

733 Although umbers deposits in Cyprus are now too scarce to be economically viable, similar
734 metalliferous sediment deposits can be found in most ophiolitic sequences preserved on land with
735 significant tonnage to be considered of interest. Potential deposits include the multiple occurrences
736 of umberiferous deposits in Japan, such as the Mineoka Hills (Kenzai Industrial Company), the
737 Kunimiyama deposits in the Chichibu Belt, and the Mugi and Tyujin umbers in the Shimanto belt
738 (Kato *et al.*, 2005a, Kato *et al.*, 2005b). These umber deposits are on average 4 m thick but
739 commonly reach up to 12 m. With respect to Tethyan ophiolites, metalliferous ferromanganese
740 sediments are found in association with many of the Eurasian Tethyan ophiolite complexes, but
741 generally occur as small discrete bodies comparable to umbers in Troodos. Similar deposits are
742 described from the Othris and Pindos Ophiolites (Greece) (Robertson and Varnavas, 1993b), the
743 Kizildag (Hatay) Ophiolite (southern Turkey) (Robertson, 2002), or in the Semail Ophiolite. The
744 application of the hydrometallurgical process developed here for the Troodos umbers could be
745 applied to these deposits given their similar nature, and therefore provide local sources for the
746 production of rare earth metals.

747 **6. Conclusions**

748 Using Umbers, ferromanganese metalliferous sediments from the Troodos Ophiolite, as feedstock,
749 the effectiveness of REY release in a leachate followed by selective precipitation was evaluated
750 under different processing conditions.

751 In contrast to the liberation of REY from many of the current ore feedstock's, the extraction of rare
752 earth elements from umbers by simple leaching using common industrial acids is effective without
753 accumulation of radioactive by-products, and processes can be refined to maximise leaching
754 efficiencies by adjusting acid concentration, temperature, pulp density and time of reaction.
755 Although ionic solutions such as sodium chloride or ammonium sulphate are widely used in China
756 for the treatment of ion adsorption clays, such approaches were not effective for leaching REY,
757 demonstrating that REY could not be considered as easily exchangeable cations in umbers, and that
758 stronger acid conditions are necessary for their extraction. Acid-promoted REY release displays

759 hyperbolic trends of recovery for all kinetic parameters tested. REY constitute the most susceptible
760 elements to the leaching conditions tested with recovery reaching 80-92% of the sample content
761 in optimized conditions. Main impurities included in the leach solutions are Mn, Ca, Fe and Na by
762 weight but Ca and Na show proportionally the highest recovery rate. The leaching stage therefore
763 produces an enrichment factor ranging from 50 to 75 for REY from sample to leach solution. A two-
764 stage leaching process using HCl is an efficient method to separate most of the contaminants (Ca,
765 Na) into the first leach. However, around 20% of the total REY content of the sample is also leached
766 out which represents an important loss given the low purity of the initial ore. Therefore, the
767 valuable improvements in purity of the second leach must be balanced against significant
768 reductions in yields of the targeted elements in the second leach.

769 The use of oxalate is an efficient way of precipitating REY from acid leach liquor with more than
770 96% of the total REY content precipitated between pH 1 and 2. The strong dependence on pH for
771 precipitation of diverse chemical species allows for the selective precipitation of REY from other
772 impurities. The purity is optimal at pH 1.1 as abundant Ca-oxalate precipitates at higher pH. The
773 fractionation observed between the different rare earth elements in the experiment was
774 successfully explained via numeric modelling using PHREEQC: (i) the increasing recoveries from L-
775 to M-REE and decreasing trends towards the HREE at pH < 1.5 follow the solid RE-oxalate solubility
776 constant distribution $-\log \beta (\text{RE}_2\text{Ox}_3 \cdot n\text{H}_2\text{O})$, (ii) the decreasing recovery trends at pH > 2 results from
777 competition with Ca oxalate formation, (iii) the decrease in the recovery is not as steep in the
778 experiment as it is in the model due to co-precipitation of REY with the Ca-oxalate phase or other
779 phases not taken into account in the model. In addition, the model predicts an optimal pH window
780 for the precipitation of REY between 0.9 and 1.1 because of oxalic acid dissociation, availability of
781 Ox^{2-} and lack of competing ions.

782 With REO concentrations reaching 0.06 wt.%, umbers are low grade, and far below concentrations
783 encountered in main magmatic primary deposits. However, REO contents of umber deposits are
784 within the range of concentrations encountered in IAC deposits (Yang et al., 2013) and many active
785 mines from which REE are processed as by-products (Graedel et al., 2014). In contrast to the
786 numerous processing steps of these active REY mines, a REY precipitate of high purity (> 70% REY)
787 can be produced from umber deposits rapidly in only two-steps and with extremely low radioactive
788 content.

789 These experimental results and modelling confirm previous views on the beneficiation potential of
790 deep-sea sediments potential as a REY resource (Kato et al., 2011, Fujimoto et al., 2016, Menendez
791 et al., 2017) as well as red-mud- or coal-processing residue (Qu and Lian, 2013, Deady et al., 2016,
792 Rozelle et al., 2016a) considered as raw polymetallic materials. These results expand the list of
793 potential REY resource available by integrating oceanic hydrothermal metalliferous deposits
794 preserved on-land.

795

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804

805 **References**

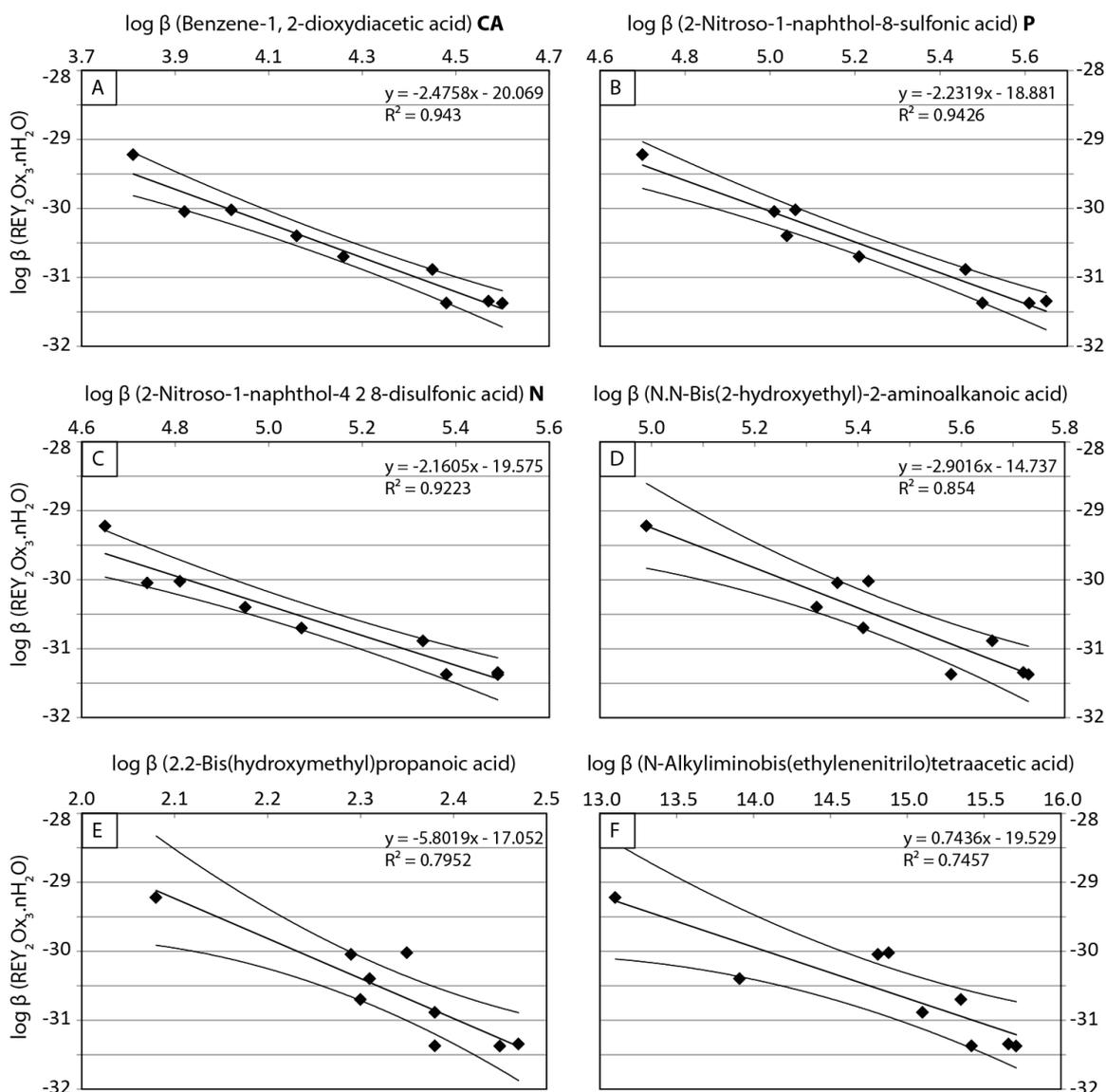
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993

994 Supplementary Figure 1: Linear free-energy relationships for $RE_2Ox_3.nH_2O$ oxalate complexes with various
 995 organic acids. Displayed on graphs are equation of linear regression with R^2 values and 95% CI on the linear
 996 regression.

997

	grain size (μm) per fraction (x %) of the sample								
Sample PJ-CY-91	5%	10%	16%	20%	50%	80%	84%	90%	95%
A1-1	2.3	3.5	5.9	8.6	101.3	279.4	314.7	387.9	486.9
A1-2	2.1	3.3	5.2	7.6	87.9	258.0	292.1	368.7	473.8
A1-3	2.2	3.5	5.9	8.7	99.1	277.4	317.8	432.1	724.5
Avg. 1st aliquot	2.2	3.5	5.7	8.3	95.8	271.5	308.1	391.2	525.6
A2-1	2.5	3.6	5.3	6.8	58.7	224.8	255.3	319.4	539.5
A2-2	2.4	3.6	5.1	6.6	53.0	217.1	250.5	330.2	596.1
A2-3	2.5	3.7	5.5	7.2	59.0	229.3	265.2	380.9	592.5
Avg. 2nd aliquot	2.5	3.6	5.3	6.9	56.9	223.6	256.8	336.7	577.7
Average $\pm \sigma$	2.3 ± 0.1	3.4 ± 0.1	5.5 ± 0.3	7.6 ± 0.8	76.5 ± 20.1	247.7 ± 25.2	282.6 ± 27.2	369.9 ± 37.5	568.9 ± 83.8

998

999 Supplementary Table 1: Grain size measurement (in μm) for two aliquots of sample PJ-CY-91. Values
 1000 represent the maximum size of particles for a fixed fraction of the sample.

1001

All values expressed in mg/kg

	average (n = 3)	BHVO2 ^a	average (n = 3)	BIR1 ^a	average (n = 3)	JB3 ^a
Na	15588 ± 381	15262 - 16100	12513 ± 522	13550	19498 ± 958	20400
Mg	42878 ± 2125	38853 - 43600	57440 ± 1480	54752 - 60300	30818 ± 821	20321 - 34431
Al	69812 ± 3701	70062 - 71600	81122 ± 2005	79244 - 85434	90122 ± 2690	85381 - 94215
K	4696 ± 480	4280 - 5080	266.6 ± 31	198 - 250	6735 ± 489	6000
Ca	80522 ± 2796	78087 - 82440	96502 ± 3421	94000 - 97281	68505 ± 4087	70000
Ti	16405 ± 227	15113 - 27300	5736 ± 74	4875 - 6923	8460 ± 98	8842
Mn	1338 ± 42	1020 - 1432	1383 ± 41	1278 - 1414	1473 ± 49	1263 - 1355
Fe	88263 ± 286	71293 - 83865	84672 ± 4468	68668 - 79900	87855 ± 3379	82500 - 83689
Sc	31.0 ± 0.8	32	41.7 ± 0.7	41 - 45	33.1 ± 0.4	32 - 35.9
Co	43.1 ± 0.6	34 - 56.2	50.0 ± 1.2	41.3 - 64.2	34.5 ± 1.3	24 - 43.3
Ni	118.5 ± 3.3	97.9 - 186	168.2 ± 6.6	116.7 - 249.5	37.6 ± 2.1	32 - 49.1
Cu	130.6 ± 3.6	102 - 168	119.0 ± 4.2	97.3 - 152	193.4 ± 9.4	142 - 196
Sr	427.3 ± 9.7	317 - 438.3	105.7 ± 5.1	90 - 130	442.1 ± 6.2	392 - 452
Y	23.6 ± 1.2	18.8 - 30.4	14.1 ± 0.7	11.28 - 18	23.6 ± 1.1	21.7 - 28.6
Zr	161.2 ± 12.8	124.5 - 195.3	13.4 ± 0.9	4.87 - 32.87	87.5 ± 5.8	86.2 - 110.43
Ba	131.0 ± 5.2	99 - 150	6.4 ± 0.2	0.635 - 17.2	239.8 ± 7.6	217 - 271
La	15.00 ± 0.84	13 - 16.9	0.60 ± 0.03	0.36 - 3.6	8.37 ± 0.40	7.65 - 10.18
Ce	37.80 ± 1.94	32.41 - 45.3	1.90 ± 0.09	1 - 4.44	21.44 ± 0.97	19.5 - 56
Pr	5.27 ± 0.35	4.72 - 5.93	0.37 ± 0.03	0.10 - 0.46	3.21 ± 0.20	3 - 5
Nd	25.11 ± 1.05	22.36 - 28.1	2.46 ± 0.10	1.6 - 3.3	16.17 ± 0.59	14.5 - 17.03
Sm	6.34 ± 0.25	5.14 - 6.9	1.15 ± 0.05	0.8 - 1.24	4.42 ± 0.17	2.95 - 4.83
Eu	2.14 ± 0.11	1.71 - 2.7	0.54 ± 0.03	0.3 - 0.6	1.37 ± 0.07	1.24 - 1.6
Gd	6.41 ± 0.34	4.68 - 7.34	1.94 ± 0.10	0.36 - 3.2	4.81 ± 0.24	3.9 - 5.2
Tb	0.97 ± 0.06	0.72 - 1.08	0.38 ± 0.02	0.22 - 2.28	0.76 ± 0.05	0.65 - 0.94
Dy	5.61 ± 0.31	4.03 - 6.05	2.74 ± 0.14	2.5 - 4	4.85 ± 0.25	3.9 - 4.98
Ho	1.03 ± 0.06	0.7 - 1.12	0.61 ± 0.03	0.34 - 0.64	0.99 ± 0.05	0.82 - 1
Er	2.69 ± 0.16	1.7 - 2.82	1.84 ± 0.11	1 - 1.89	2.86 ± 0.16	2.39 - 2.88
Tm	0.35 ± 0.02	0.26 - 0.42	0.27 ± 0.02	0.14 - 0.3	0.41 ± 0.02	0.34 - 0.59
Yb	2.13 ± 0.13	1.59 - 2.38	1.80 ± 0.10	1.36 - 1.8	2.68 ± 0.14	2.2 - 2.83
Lu	0.30 ± 0.02	0.2 - 0.38	0.28 ± 0.02	0.18 - 0.31	0.40 ± 0.02	0.32 - 0.5
Th	1.30 ± 0.06	1.03 - 3.51	0.05 ± 0.00	0.03	1.34 ± 0.05	1 - 1.42
U	0.45 ± 0.02	0.32 - 0.51	0.02 ± 0.00	0.031	0.52 ± 0.03	0.47 - 0.54

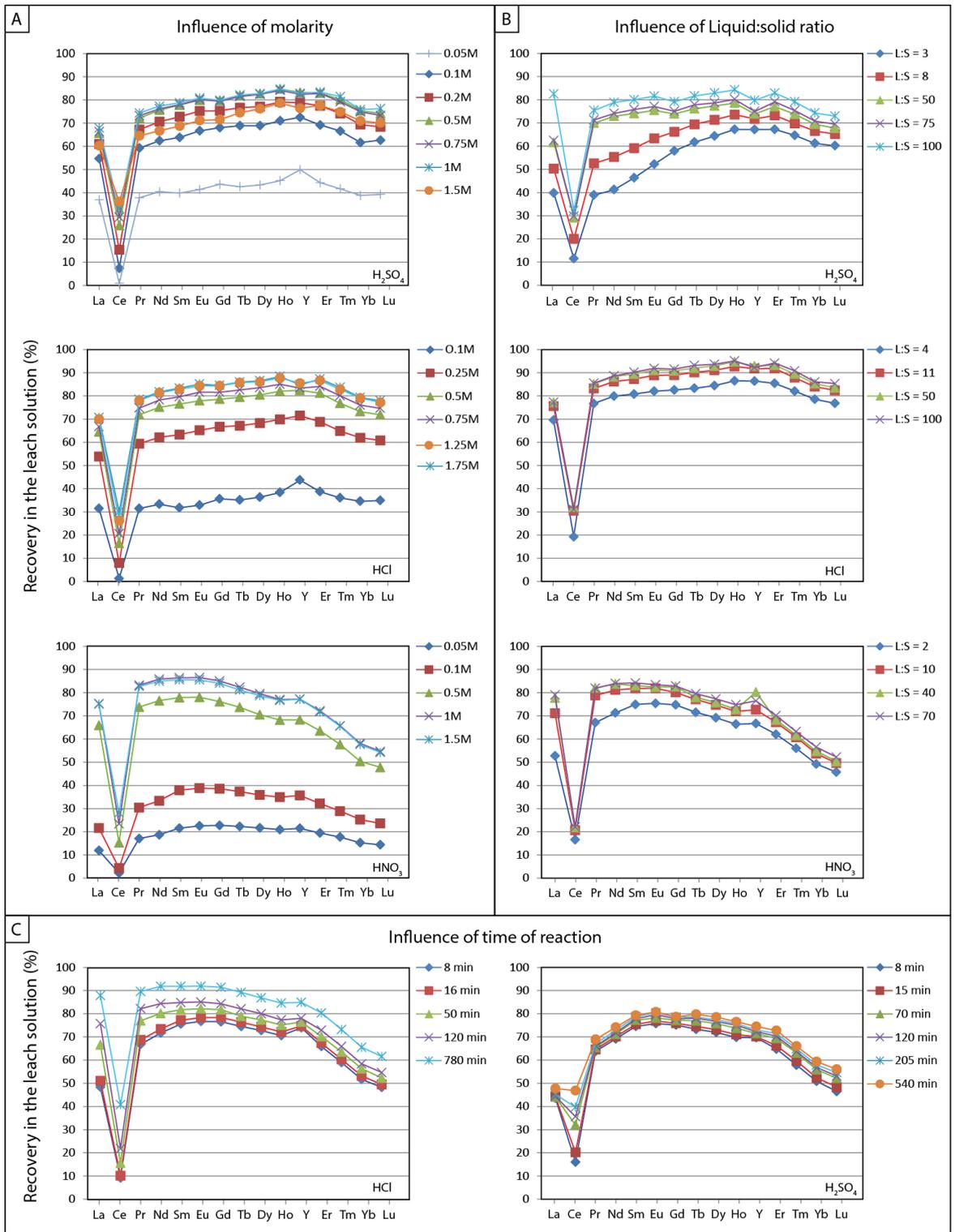
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Standard^a, published values from Jochum et al., [2005]

1003

Supplementary Table 2: Average ± 95 % CI of measured trace element concentration of rock standards run as triplicates and their recommended published values for accuracy and reproducibility checking.

1004



1005

1006 Supplementary Figure 2: Detailed recovery for REY in each leaching experiment.

1007

1008

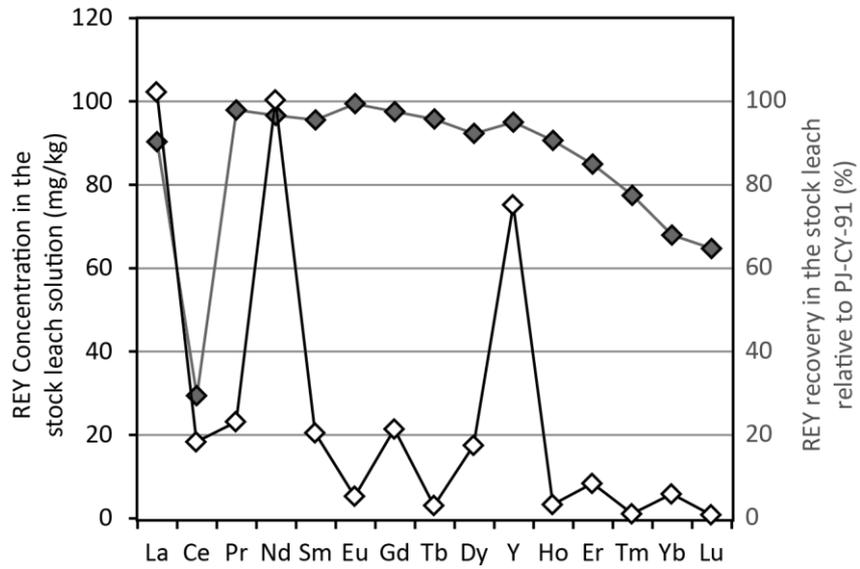
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pH 1.1 no HF treatment						
	Bulk	area_Xlarge	spot_Xlarge	area_Xsmall	spot_Xsmall	area_Xlarge_2
	Wt.% ± σ	Wt.% ± σ	Wt.% ± σ	Wt.% ± σ	Wt.% ± σ	Wt.% ± σ
Si	1.2 ± 0.1	0.9 ± 0.1	-	0.5 ± 0.1	0.5 ± 0.1	-
Cl	1.5 ± 0.1	4.0 ± 0.2	1.7 ± 0.1	1.7 ± 0.1	5.4 ± 0.2	-
K	-	0.5 ± 0.1	-	-	-	-
Ca	6.9 ± 0.2	8.7 ± 0.2	8.9 ± 0.2	5.0 ± 0.1	6.2 ± 0.2	3.7 ± 0.1
Al	3.9 ± 0.3	0.8 ± 0.2	0.9 ± 0.2	0.7 ± 0.2	0.7 ± 0.2	0.7 ± 0.2
Cu	1.0 ± 0.2	-	-	-	-	1.1 ± 0.2
Y	16.6 ± 0.6	15.3 ± 0.6	10.0 ± 0.4	10.8 ± 0.4	11.2 ± 0.5	23.2 ± 0.6
La	16.4 ± 0.5	18.5 ± 0.5	19.5 ± 0.5	19.8 ± 0.4	18.1 ± 0.5	18.0 ± 0.5
Ce	4.0 ± 0.4	4.6 ± 0.4	4.4 ± 0.4	4.9 ± 0.4	4.8 ± 0.4	4.0 ± 0.4
Pr	6.2 ± 0.5	6.1 ± 0.5	6.1 ± 0.5	7.4 ± 0.5	7.2 ± 0.5	5.9 ± 0.5
Nd	25.9 ± 0.6	26.5 ± 0.6	30.2 ± 0.6	29.2 ± 0.5	29.7 ± 0.6	26.3 ± 0.6
Sm	5.5 ± 0.5	5.5 ± 0.5	6.2 ± 0.5	6.9 ± 0.5	5.6 ± 0.5	5.9 ± 0.5
Gd	5.6 ± 0.5	5.3 ± 0.5	6.3 ± 0.5	6.4 ± 0.5	6.5 ± 0.5	5.4 ± 0.5
Dy	3.7 ± 0.5	3.4 ± 0.5	4.2 ± 0.5	5.0 ± 0.4	4.2 ± 0.5	3.9 ± 0.5
Er	1.7 ± 0.5	-	1.7 ± 0.5	1.6 ± 0.5	± 0.0	1.8 ± 0.5
1010 REY	85.6 ± 0.5	85.1 ± 0.5	88.5 ± 0.5	92.0 ± 0.5	87.3 ± 0.5	94.5 ± 0.5

1011 Supplementary Table 3: Energy-dispersive X-ray spectroscopy analysis of the oxalate precipitates at pH 1.1.
1012 Note that EDS analysis were made on a free C and O basis. Area and crystals analysed are displayed in **Error!**
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	pH 2.5 no HF			pH 2.5 with HF treatment	
	Bulk	spot-Xlarge	spot-Xsmall	Bulk	spot_Xlarge
	Wt.% ± σ	Wt.% ± σ	Wt.% ± σ	Wt.% ± σ	Wt.% ± σ
F	-	-	-	5.7 ± 1.4	3.0 ± 0.9
Na	1.1 ± 0.2	1.2 ± 0.2	1.4 ± 0.3	0.0 ± 0.0	0.9 ± 0.2
Cl	0.8 ± 0.1	1.1 ± 0.1	1.3 ± 0.1	2.0 ± 0.1	1.0 ± 0.1
Ca	80.6 ± 0.7	83.7 ± 0.7	84.9 ± 0.7	78.0 ± 1.4	81.9 ± 0.7
Mn	7.4 ± 0.3	7.4 ± 0.3	7.6 ± 0.3	3.0 ± 0.3	7.4 ± 0.3
Al	4.9 ± 0.3	0.8 ± 0.2	0.6 ± 0.1	4.3 ± 0.2	0.9 ± 0.1
Cu	0.6 ± 0.2	-	-	0.8 ± 0.1	-
Sr	0.9 ± 0.3	0.7 ± 0.3	0.0 ± 0.0	-	1.0 ± 0.3
Y	1.0 ± 0.4	1.8 ± 0.4	1.0 ± 0.4	1.2 ± 0.4	1.4 ± 0.4
La	1.5 ± 0.4	1.5 ± 0.4	1.7 ± 0.4	2.9 ± 0.4	2.8 ± 0.4
Nd	1.2 ± 0.4	1.7 ± 0.4	1.4 ± 0.4	2.2 ± 0.5	2.8 ± 0.4
1015 REY	3.7 ± 0.4	5.0 ± 0.4	4.2 ± 0.4	6.3 ± 0.5	7.0 ± 0.4

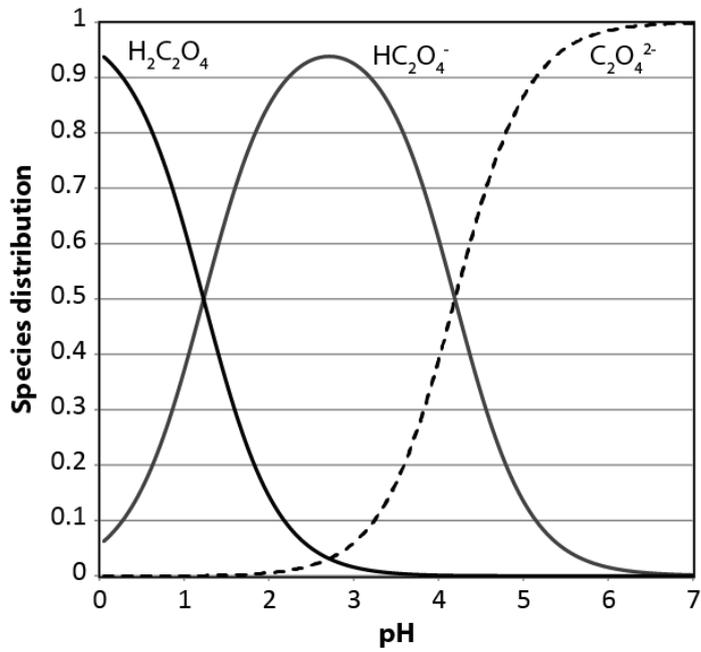
1016 Supplementary Table 4: Energy-dispersive X-ray spectroscopy analysis of the oxalate precipitates at
1017 different pH. Note that EDS analysis were made on a free C and O basis. Area and crystals analysed are
1018 displayed in **Error! Reference source not found..**
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1020

1021 Supplementary Figure 3: REY concentration in the leaching solution (white diamond, scale on the left) and
 1022 the relative elemental recovery from the sample (grey diamond, scale on the right).

1023

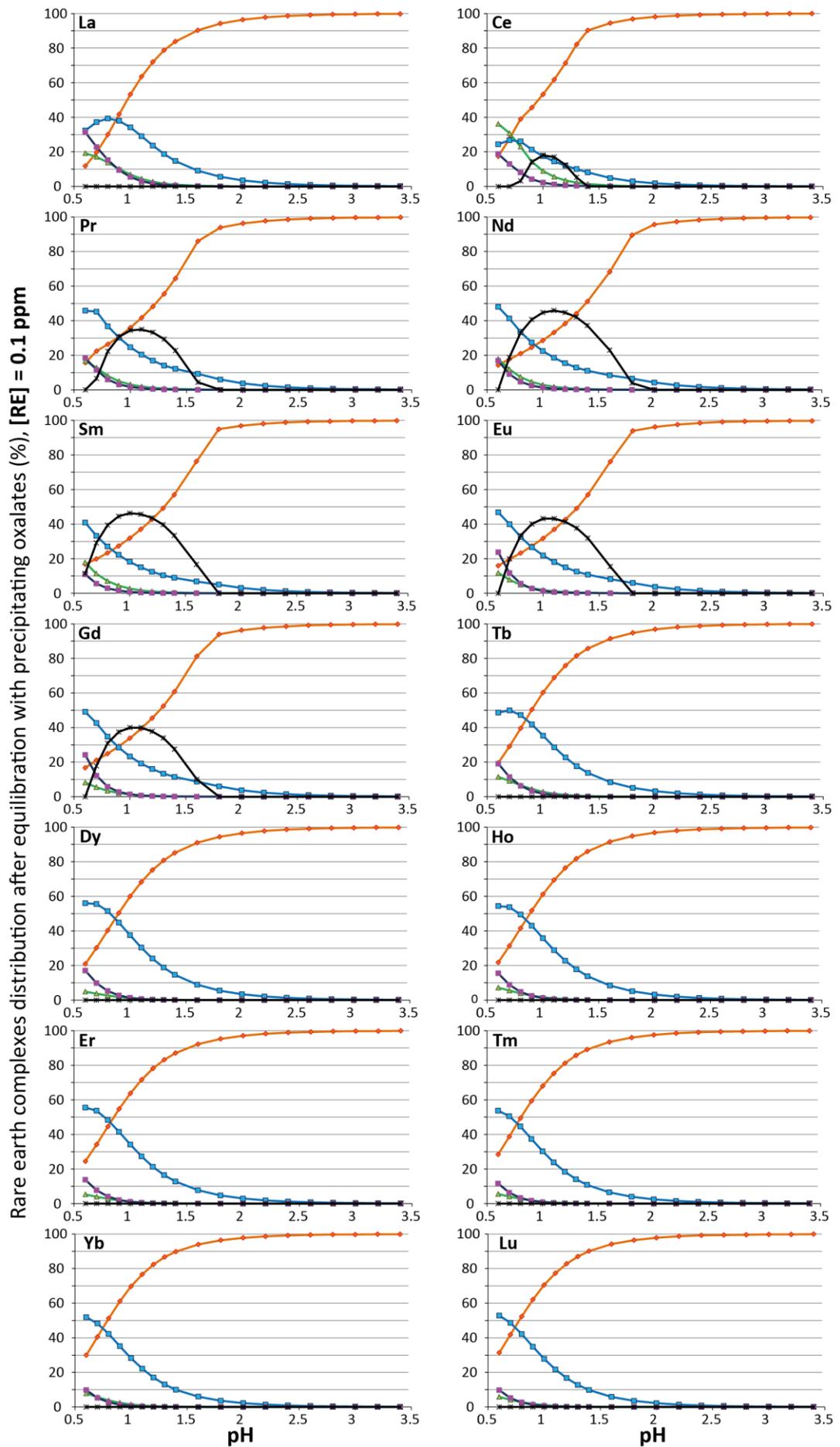


1024

1025 Supplementary Figure 4: Speciation of oxalic acid and conjugate oxalates as a function of pH using acid
 1026 dissociation constant $K_1 = 5.9 \times 10^{-2}$ and $K_2 = 6.4 \times 10^{-5}$ (Chi and Xu, 1998).

1027

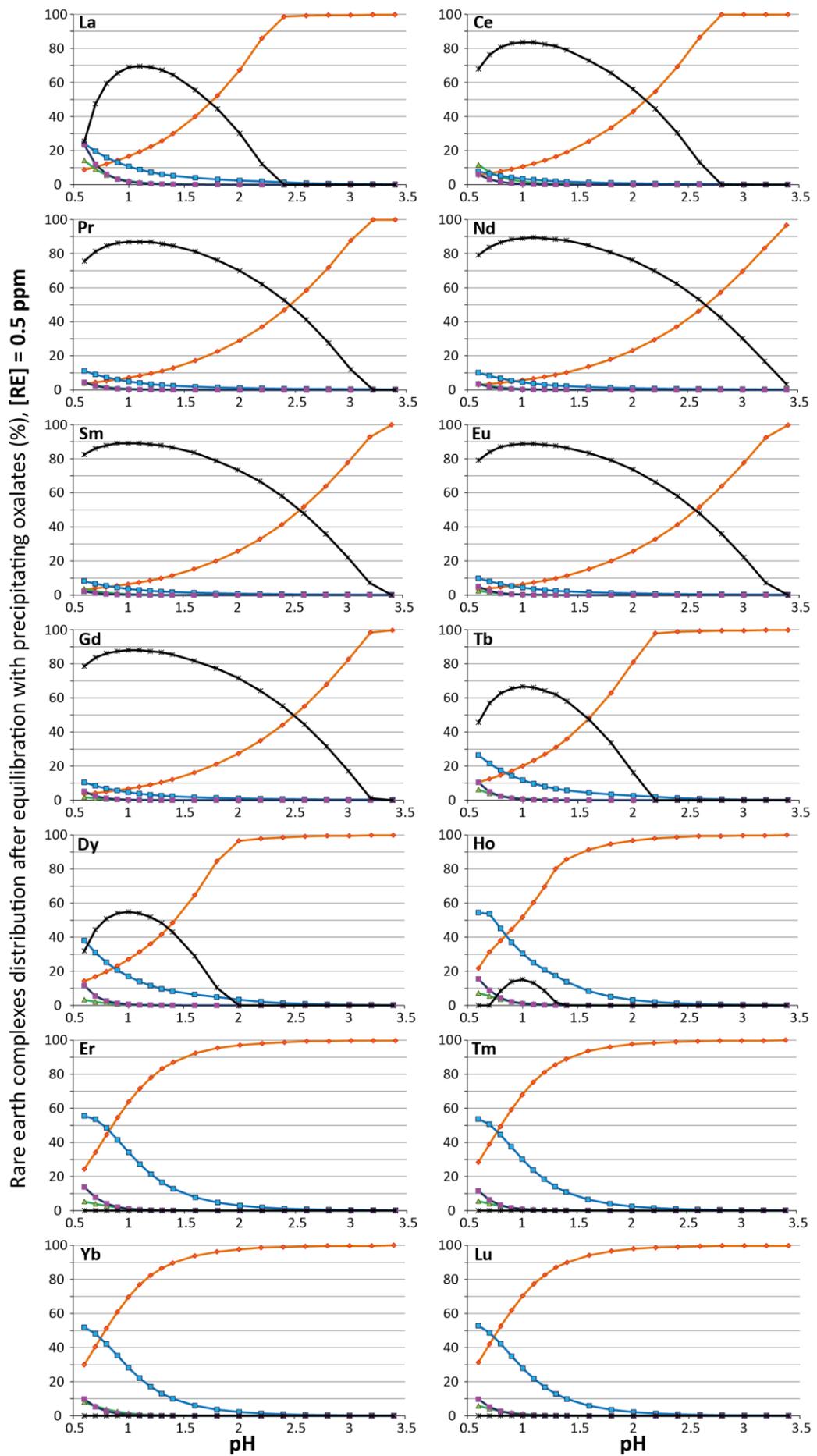
REOx_2^- REHOx^{2+} REOx^+ RE^{3+} $\text{RE}_2\text{Ox}_3 \cdot n\text{H}_2\text{O}$ Experimental results



1028

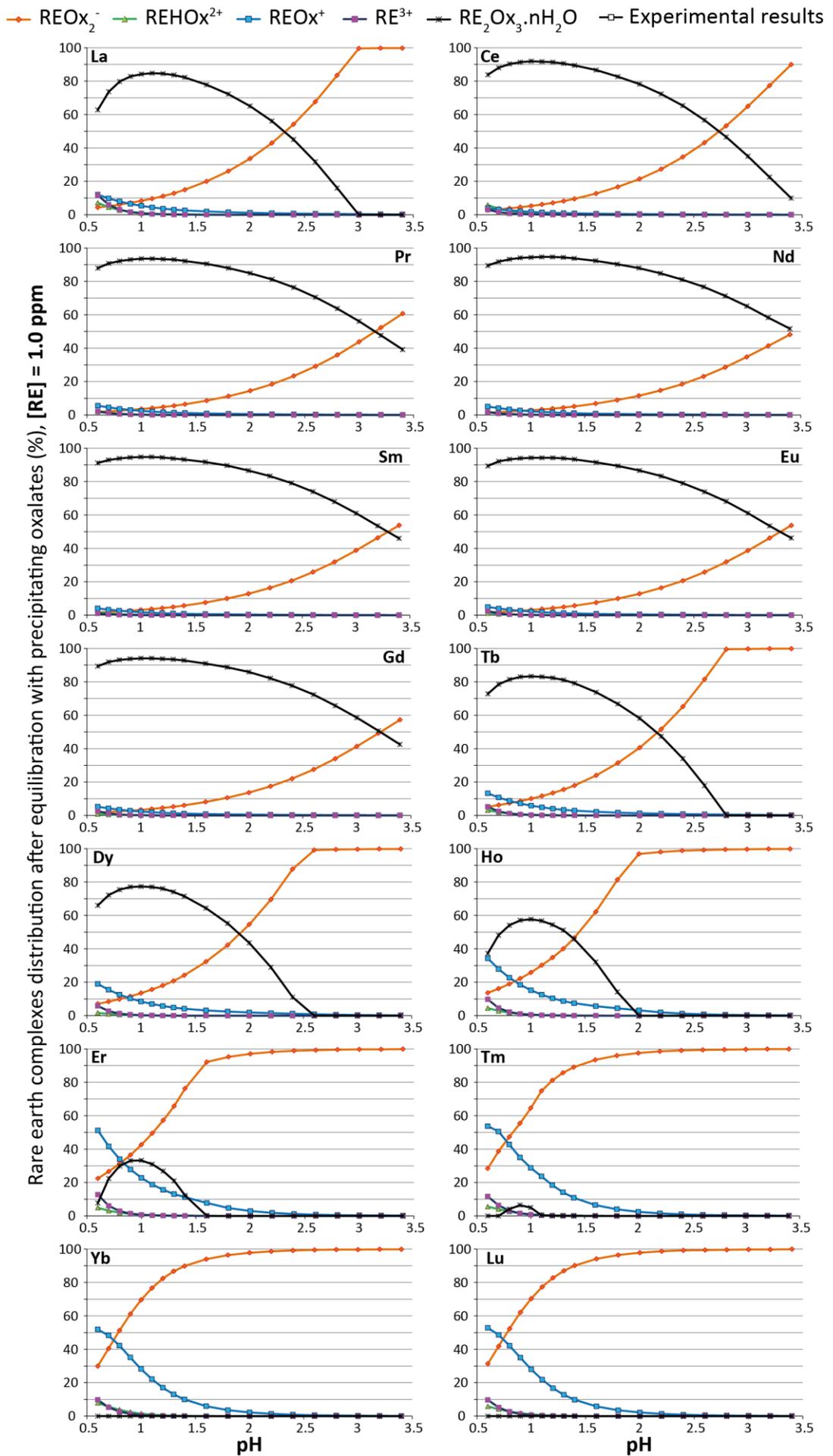
1029 Supplementary Figure 5: REE speciation as a function of pH, [RE] = 0.1 ppm.

—●— REOx_2^-
—▲— REHOx^{2+}
—■— REOx^+
—◆— RE^{3+}
—*— $\text{RE}_2\text{Ox}_3 \cdot n\text{H}_2\text{O}$
—□— Experimental results



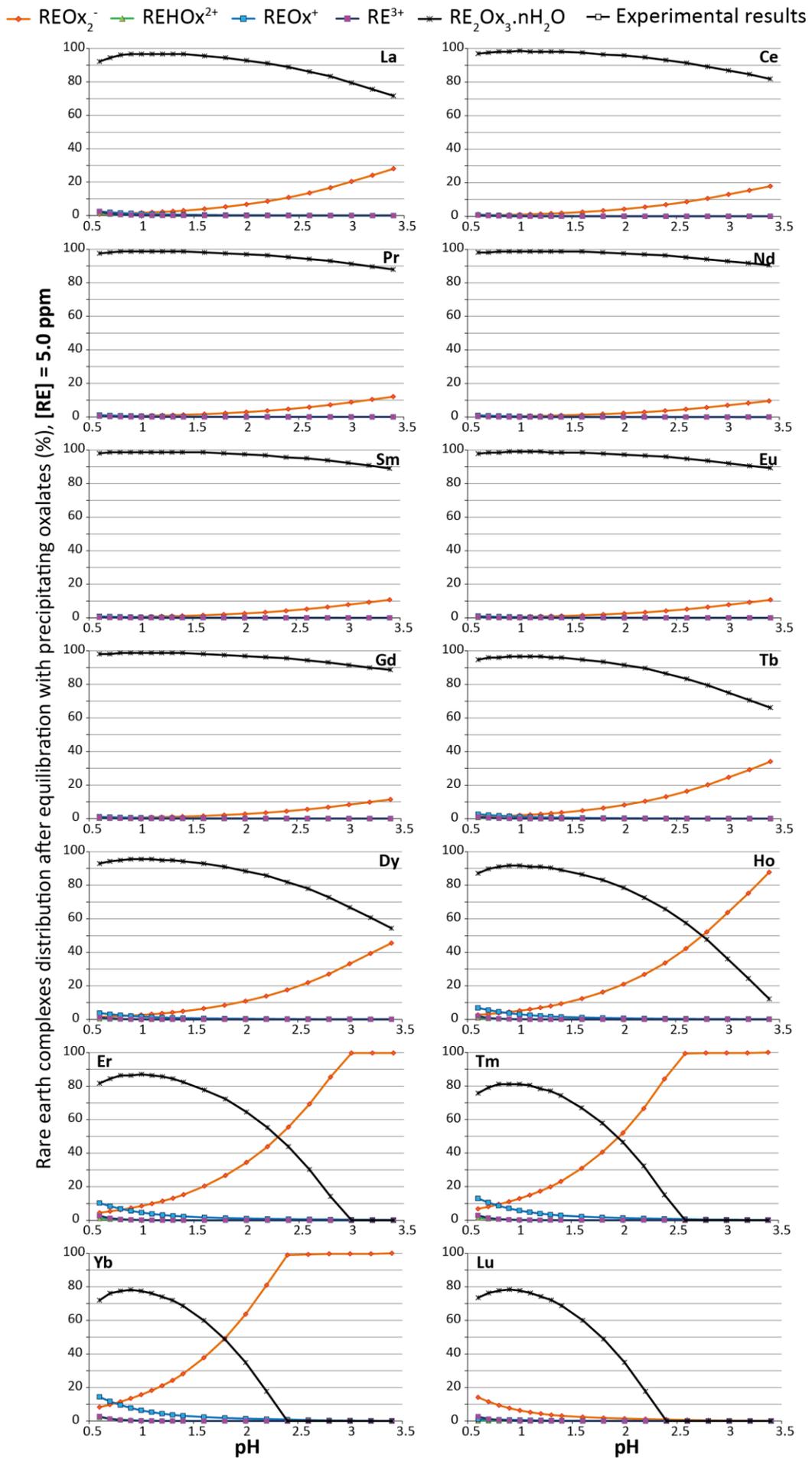
1030

1031 Supplementary Figure 6: REE speciation as a function of pH, [RE] = 0.5 ppm.



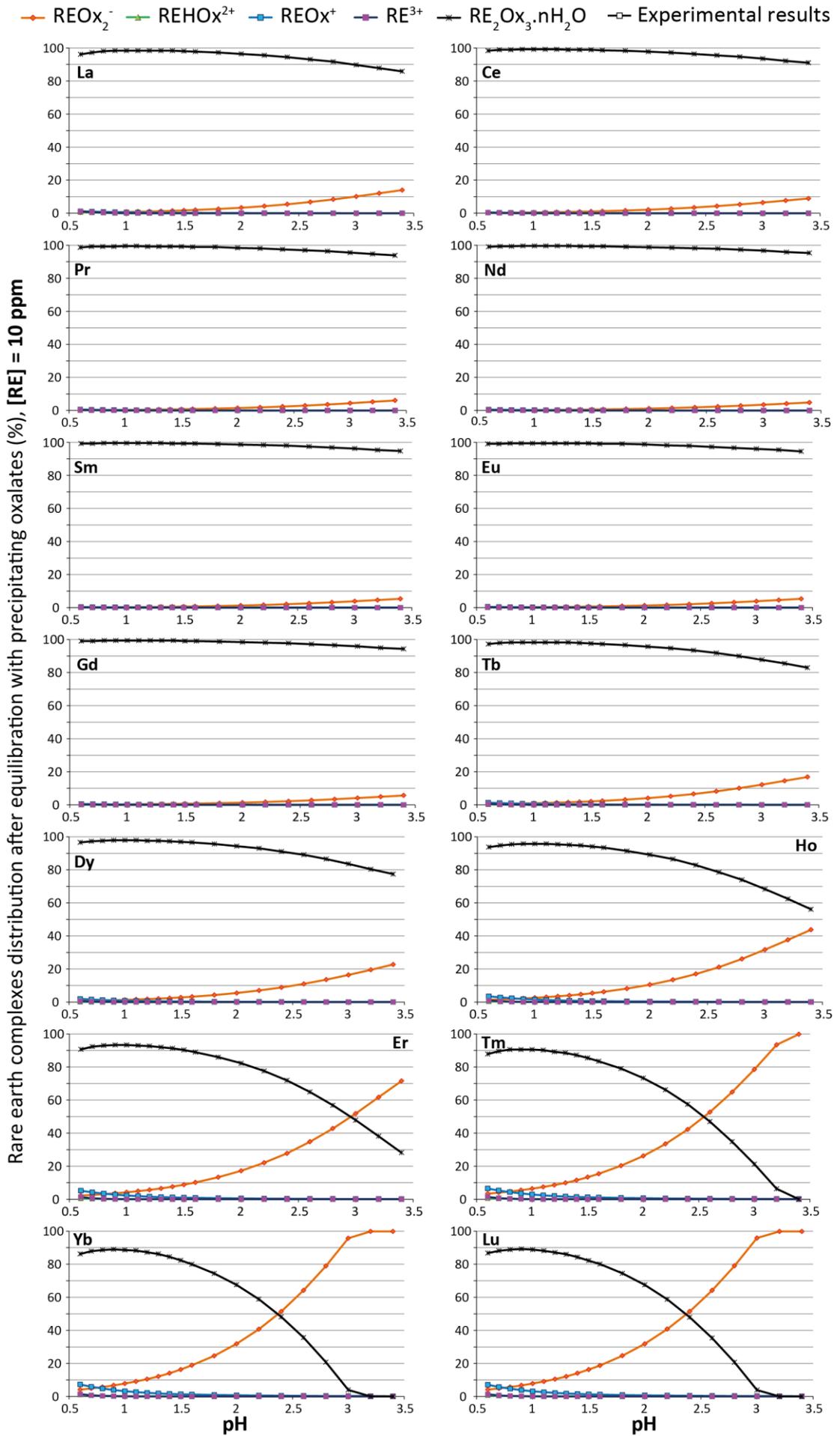
1032

1033 Supplementary Figure 7: REE speciation as a function of pH, $[\text{RE}] = 1.0 \text{ ppm}$.



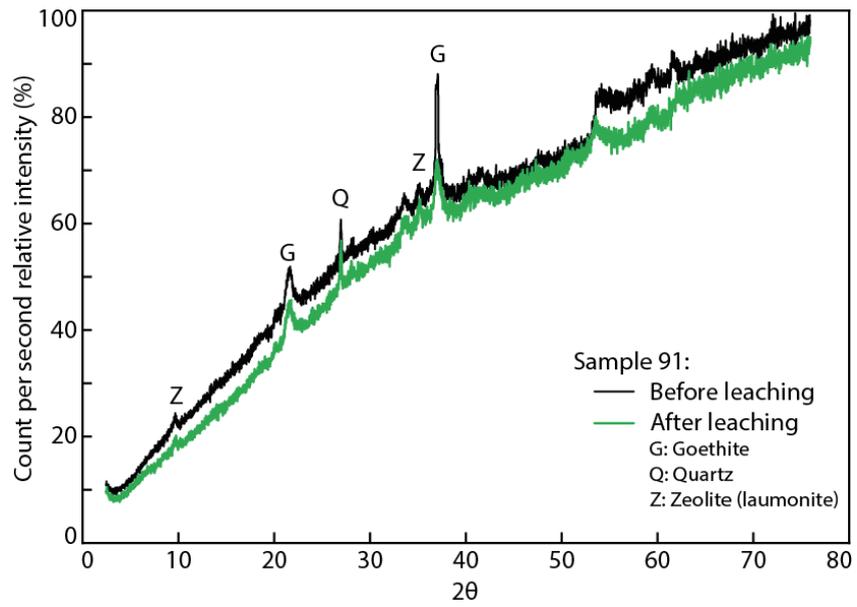
1034

1035 Supplementary Figure 8: REE speciation as a function of pH, $[\text{RE}] = 5.0 \text{ ppm}$.



1036

1037 Supplementary Figure 9: REE speciation as a function of pH, [RE] = 10 ppm.



1038

1039 Supplementary Figure 10: Comparison of X-ray diffraction patterns of sample PJ-CY-2014-91 and the residue
1040 collected after filtration of the leaching experiment using 1M HCl at a liquid to solid ratio of 25, 20°C for 2h.

1041

1042