



**HAL**  
open science

## Geochemical signatures of rare earth elements and yttrium exploited by acid solution mining around an ion-adsorption type deposit: Role of source control and potential for recovery

Haiyan Liu, Huaming Guo, Olivier Pourret, Zhen Wang, Maohan Liu, Weimin Zhang, Zebing Li, Bai Gao, Zhanxue Sun, Pierre Laine

### ► To cite this version:

Haiyan Liu, Huaming Guo, Olivier Pourret, Zhen Wang, Maohan Liu, et al.. Geochemical signatures of rare earth elements and yttrium exploited by acid solution mining around an ion-adsorption type deposit: Role of source control and potential for recovery. *Science of the Total Environment*, 2022, 804, pp.150241. 10.1016/j.scitotenv.2021.150241 . hal-03340094v2

**HAL Id: hal-03340094**

**<https://hal.science/hal-03340094v2>**

Submitted on 10 Sep 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

**Geochemical signatures of rare earth elements and yttrium exploited by acid  
solution mining around an ion-adsorption type deposit: role of source control  
and potential for recovery**

1 Haiyan Liu<sup>1,2,\*</sup>; Huaming Guo<sup>3,\*</sup>; Olivier Pourret<sup>4,\*</sup>; Zhen Wang<sup>1,2</sup>; Maohan Liu<sup>1,2</sup>;  
2 Weimin Zhang<sup>1,2</sup>; Zebing Li<sup>1,2</sup>; Bai Gao<sup>1,2</sup>; Zhanxue Sun<sup>1,2</sup>; Pierre Laine<sup>4</sup>

3 <sup>1</sup> *School of Water Resources and Environmental Engineering, East China University  
4 of Technology, Nanchang 330013, P. R. China*

5 <sup>2</sup> *State Key Laboratory of Nuclear Resources and Environment, East China University  
6 of Technology, Nanchang 330013, P. R. China*

7 <sup>3</sup> *School of Water Resources and Environment, China University of Geosciences  
8 (Beijing), Beijing 100083, P.R. China*

9 <sup>4</sup> *UniLaSalle, AGHYLE, Beauvais, France*

10 \* **Corresponding author:** Haiyan Liu, Huaming Guo, Olivier Pourret

11 418 Guanglan Road, Jingkai District, Nanchang, P. R. China (**H. Liu**);

12 29 Xueyuan Road, Haidian District, Beijing, P. R. China (**H. Guo**)

13 19 rue Pierre Waguet-BP 30313, 60026 Beauvais, France (**O. Pourret**)

14 E-mail address: hy\_liu@ecut.edu.cn (H. Liu); hmguo@cugb.edu.cn (H. Guo);

15 olivier.pourret@unilasalle.fr (O. Pourret)

16

---

17 **Abstract:** Elevated concentrations of rare earth elements and yttrium (REE+Y) in  
18 acid mine drainage (AMD) attract worldwide attention. However, the source and  
19 control of REE+Y distribution patterns in AMD remain unclear. Water, rock, sediment,  
20 and sludge samples were collected from an ion-adsorption deposit site to investigate  
21 REE+Y concentrations and distributions. The heavy REE (HREE)-enriched patterns  
22 of the AMD resulted from preferential desorption of HREE in the clay-rich sediment  
23 strata, from which the REE+Y were ion-exchanged by an in-situ underground  
24 leaching process using ammonium sulfate brine. Free ions and sulfate complexes  
25 preserved REE+Y patterns and facilitated REE+Y mobility in the AMD leachate  
26 system. High concentrations of REE+Y occurred in the AMD, and decreased  
27 progressively through nitrification-denitrification and coagulation-precipitation  
28 procedures in a water treatment plant. Concentrations of REE+Y were one to three  
29 orders of magnitude higher in AMD than those in groundwater, and were negatively  
30 correlated ( $r^2 = -0.72$ ) with pH (3.8 to 8.7), suggesting that an acid desorption from  
31 minerals contributed the REE+Y to the AMD from the source rock. Normalized  
32 REE+Y patterns showed enrichments of HREE over light REE (LREE) and negative  
33 Ce anomaly. The distribution patterns were relatively constant for all water samples,  
34 despite their huge difference in REE+Y concentrations. This suggested a limited  
35 impact of preferential precipitation of LREE over HREE on REE+Y fractionations  
36 during neutralization. The potentially recoverable LREE and HREE were calculated  
37 to range between 1.12 kg/day and 3.37 kg/day, and between 1.29 kg/day and 3.76  
38 kg/day, respectively. The findings reported in this study lends promise for efficient

39 REE+Y recovery from AMD.

40 **Keywords:** Lanthanide; Acid mine drainage; Water-rock interaction; Fractionation;

41 Critical metals

42

---

## 43 1. Introduction

44 Global demand of rare earth elements and yttrium (REE+Y) to support  
45 technology has increased in the past two decades (Haxel et al., 2002; Van Gosen et al.,  
46 2014), leading to increased production of rare-earth oxides (U.S. Geological Survey,  
47 2021). China sustains 98% of global REE+Y demand with an ion-exchange processed  
48 clay deposit in southern China as a major supplier for middle REE (MREE) and heavy  
49 REE (HREE) (Alonso et al. 2012). The REE+Y were mainly mined via heap leaching,  
50 and this technology produced a large amount of acid mine drainage (AMD) and mine  
51 tailings (Liu et al., 2019b). The AMD potentially migrating into subsurface  
52 environments imposed severe REE+Y contamination to soils, waters, and crops (Liu  
53 et al., 2019a; Liu et al., 2020). The thus increased REE+Y emissions to the  
54 environment have caused worldwide concerns (Vaziri Hassas et al., 2021; Ayora et al.,  
55 2016).

56 Acid mine drainage is generated through oxidation of sulfides (e.g., pyrite)  
57 contained in target strata upon ADM has acidic pH and contains elevated sulfate and  
58 metal(loid)s (Nordstrom and Alpers, 1999; Gimeno et al., 2000; Nordstrom et al.,  
59 2015). The highly polluted AMD has been considered a severe environmental  
60 problem posing great risks to the environment near the exploited mine. This issue is  
61 of global concern (e.g., in China, Vietnam, Australia, India and Spain) (Akcil and  
62 Koldas, 2006; Marquez et al., 2018, and references therein). AMD could be treated by  
63 passive natural attenuation like microbial activity, or by active technology requiring  
64 external input of energy and material to maintain in continuous operation (Johnson

---

65 and Hallberg, 2005). However, both technologies have drawbacks such as bioclogging  
66 and scaling problems resulting from mineral precipitation for the former, and costly  
67 and time-consuming processing for the latter (Léon et al., 2021).

68 Acid mine drainage has also been shown to contain high levels of REE+Y  
69 (Verplanck et al., 2004; Moraes and Ladeira, 2021). Owing to their spectroscopic and  
70 magnetic properties, the REE+Y have been widely used in clear energy producing,  
71 medical diagnosis, and other applications (Wall, 2014; Van Gosen et al., 2014). This  
72 has resulted in increased demand of REE+Y for the world's market. Therefore,  
73 seeking alternative sources of REE+Y (esp. HREEs: Dy, Tb, Eu and Yb) is an  
74 important need for development of recovery technology in many countries  
75 (Binnemans et al., 2013).

76 REE+Y recovery from AMD and its sludges were investigated by a number of  
77 studies (Stewart et al., 2017; Vass et al., 2019; Zhang and Honaker, 2020). Previous  
78 research at various mine sites showed that the REE+Y concentrations in AMD were  
79 several orders of magnitude higher than the median values of near-neutral mine  
80 waters (Ayora et al., 2016). The normalized REE+Y patterns were characterized by  
81 MREE enrichment over LREE and HREE. Some studies showed LREE- (Bozau et al.,  
82 2004) and HREE- (Medas et al., 2013) enriched normalized patterns in AMD as well.  
83 Other studies reported that AMD was depleted in LREE (Gammons et al., 2003;  
84 Sharifi et al., 2013; Migaszewski et al., 2014).

85 In spite of the known normalized REE+Y patterns in AMD systems, the  
86 underlying mechanism regulating the formation of the patterns is poorly understood.

---

87 Considering the extremely low concentrations of REE+Y in rainwater (Zhang and Liu,  
88 2004; Zhu et al., 2016), REE+Y are ultimately sourced from water-rock interactions.  
89 Preferential leaching of REE-bearing solids was proposed for causing the enrichment  
90 patterns (Sun et al., 2012; Wallrich et al., 2020, and references therein). In this  
91 framework, REE+Y-enriched mineral phases should be present in the bulk solid  
92 samples. Indeed, sequential extraction of strata rocks showed that the REE content  
93 was related to carbonate and aluminosilicate minerals (Worrall and Pearson, 2001).  
94 After being removed by ion-exchange, the rock samples were extracted sequentially  
95 with acidic solutions buffered at pH 1.6, 3.6, and 5.5, to simulate the formation  
96 process of AMD, showing that the sequential extracts had similar REE patterns to  
97 those of AMD (Worrall and Pearson, 2001). Results of Worrall and Pearson's (2001)  
98 experiments further demonstrated that REE signatures in acidic water were a mixture  
99 of leachates of various sedimentary mineral components, suggesting that REE+Y  
100 enrichment patterns for AMD were of source-control. Furthermore, the conservative  
101 behavior of REE+Y in the acidic solutions had accounted for their long-distance  
102 transport (Verplanck et al., 2004). However, other studies indicated that  
103 process-derived reactions such as fractionation by colloidal complexes (Åström and  
104 Corin, 2003), adsorption-desorption on surface coatings (Åström, 2001), differences  
105 in solutes complexation (Dia et al., 2000), and preferential precipitation of certain  
106 REE during formation of secondary minerals (Elderfield et al., 1990; Leybourne et al.,  
107 2000) were responsible for the deviating REE+Y enrichment patterns. A recent study  
108 suggested that the roles of geology in controlling REE+Y distribution and patterns in

---

109 AMD might be complicated by geochemical, biological and environmental factors  
110 (León et al., 2021). The coherent properties and predictable behavior of REE+Y make  
111 them ideal tracers of clastic sediment transport (Taylor and McLennan, 1988),  
112 water-rock interactions (Worrall and Pearson, 2001), and mixing processes (Liu et al.,  
113 2017a). The unique properties of REE+Y constitute therefore an opportunity to study  
114 the source, origin, fate and transport of AMD, which is important in addressing the  
115 mechanisms of AMD formation and contamination.

116 The hypotheses for this study were: (i) high REE+Y concentrations occur in  
117 AMD where elevated metal, sulfate and ammonium concentrations co-occur, (ii) local  
118 lithology in relation to acidification-enhanced desorption and scavenging by  
119 secondary minerals controls REE+Y distribution patterns in AMD, and (iii) the  
120 REE+Y inventory of AMD is potentially recoverable upon pH neutralization by  
121 implementing appropriate treatment options. The objectives of this study were to: (i)  
122 investigate the concentrations and distributions of REE+Y in an AMD system (i.e.  
123 water, rock, sediment, and sludge), (ii) characterize the geochemical controls of  
124 REE+Y sources and fractionation patterns in AMD, and (iii) assess the potential of  
125 REE+Y recovery from AMD.

## 126 **2. Methods and materials**

### 127 2.1 Regional hydrogeological settings

128 The mining site (longitude: 114°47'28", latitude: 24°54'25") is located in the  
129 Jiangxi province, southern China (Fig. 1), and has a subtropical monsoon climate. The  
130 temperature ranges from 39°C to -3.1°C (recorded historically), with an annual



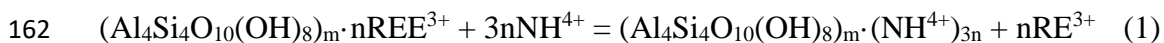
---

131 average of 19.7 °C. Precipitation ranges from 1058 to 2190 mm (annual average 1608  
132 mm), dominating from April to July (accounts for 60%). Annual evaporation is 1497  
133 mm (1349 to 1619 mm), intensely occurring in July and August. The drainage basin  
134 has five main rivers that are connected to the tributaries of Dongjiang River running  
135 from south to north with an annual average flow rate of 14 m<sup>3</sup>/s.

136 Late Cretaceous to Quaternary strata outcrop in the mine area, of which  
137 Cambrian, Devonian and Jurassic strata are exposed in most areas and are distributed  
138 primarily in the eastern and southern part of the study area. The mine is hosted in  
139 Jurassic to early-Cretaceous igneous rocks, which cover a total area of 360 km<sup>2</sup>. The  
140 main rocks are micaceous granite, porphyry granite, monzonitic granite, and diorite  
141 (Yang et al., 2013). The REE+Y are concentrated in two types of micaceous granite,  
142 namely muscovitic granite and biotitic granite, where HREE and LREE have distinct  
143 distribution patterns in their weathered layers (Yang et al., 2013). The HREE  
144 accounted for 75 to 89 wt.-%, with an average value of HREE/LREE of 4.4 in the  
145 weathering regoliths of muscovitic granite. The average HREE proportion was 61%,  
146 and the HREE/LREE value was 1.6 for the biotitic granite counterpart. The thickness  
147 of the strongly-weathered regolith layer ranges from 5 to 25 m with a corresponding  
148 mineral inventory of mainly quartz, feldspar and mica.

149 Groundwater in the mine area is mainly hosted in the fissure network of  
150 medium-grain micaceous granite and largely belongs to the phreatic water type. The  
151 hydrochemical facies include Ca-SO<sub>4</sub>, Ca-SO<sub>4</sub>-HCO<sub>3</sub>, Ca-Cl, and Ca-HCO<sub>3</sub>-Cl type  
152 waters with total dissolved solids (TDS) ranging from 17 to 170 mg/L.

153 Heap and pond leaching was used previously as an active mining technology at  
154 this mine site. However, it has been banned by Chinese government due to great  
155 vegetation damage. In-situ leaching is currently done by injecting acidic ammonium  
156 sulfate solution through wells drilled into the sedimentary ore deposit. The acidic  
157 leachate solution containing the dissolved metals pumped out poses environmental  
158 risks as well. Ammonium has been reported to exceed the threshold recorded in  
159 groundwater quality standard (Liu et al., 2019b). The main REE leaching mechanism  
160 as shown by Eq. (1) is an ion-exchange reaction with ammonium ( $\text{NH}_4^+$ ) from clay  
161 minerals in the sedimentary deposit (Chi and Liu, 2019):



163 Although not AMD in sensu-stricto, the acidic mine waters recovered from this  
164 solution mining process are termed AMD as well in the following. A sewage treatment  
165 plant (STP) was established at the mine site to process the acid efflux from the mine.  
166 The STP technology mainly consists of three procedures, which are (i)  
167 nitrification-denitrification to remove ammonium, (ii) coagulation-precipitation to  
168 remove metals, and (iii) dilution of treated water with original mine water. Finally, the  
169 mixture is discharged into rivers down-stream.

## 170 2.2 Sample collection

171 Sixteen water samples were collected in July 2020. Among them, five were  
172 AMD samples (MW1 to 5), six were effluents of STP undergoing  
173 nitrification-denitrification treatment procedures (NDT1 to 6), four were effluents  
174 going through coagulation-precipitation treatment processes (CPT1 to 4), and one was

---

175 water sample collected from a local groundwater (GW) well in a village near the mine.  
176 All water samples were filtered with 0.22  $\mu\text{m}$  pore size cellulose acetate membranes.  
177 Samples for cation and trace element analysis were stored in 50 mL high-density  
178 polyethylene (HDPE) bottles and were acidified to  $\text{pH} < 2$  with  $\text{HNO}_3$ . Samples for  
179 anion analysis were stored in HDPE bottles without acidification. Samples for DOC  
180 analysis were sampled in 30 mL amber glass bottles and acidified to  $\text{pH} < 2.0$  by  
181 admixing 1:9 (v/v)  $\text{H}_2\text{SO}_4$ . Samples for REE+Y analysis were sampled in 500 mL  
182 HDPE bottles following an acidification with  $\text{HNO}_3$ . Sampling locations are shown in  
183 Fig. 1.

184 Two rock samples (R1 and R2) were sampled from the outcrop. Three surface  
185 sediment samples (MW1-SS, MW2-SS and MW3-SS) were collected from the  
186 locations where mine water samples (MW1, 2, and 3) were taken (Fig. 1). The surface  
187 sediment samples were collected down to a depth of about 30 cm below land surface.  
188 Sludge samples (MW4-SG, MW5-SG and CPT1-SG) were taken from the bottom  
189 precipitates of the settling pond and creek bed, while NDT2-SG and NDT3-SG were  
190 sludge samples collected by using a vacuum hose that was deployed to the bottom of  
191 a huge container having a depth of about 6 m. All the rock, sediment and sludge  
192 samples were stored in clean plastic bags.

### 193 2.3 Analytical methods

194 Physicochemical parameters of the water samples, including temperature, pH,  
195 electrical conductivity (EC), and redox potential, were measured with a HI 9828  
196 portable multi-meter (HANNA, Woonsocket, RI, USA). To minimize the influence of

---

197 atmospheric contact, the monitoring probe was immersed in an in-line flow cell where  
198 water was pumped through constantly. Physiochemical data were recorded in the field  
199 once stabilized. Alkalinity was titrated immediately in the field by using a Model  
200 16900 digital titrator (HACH, Loveland, USA). Redox sensitive components such as  
201 total Fe, Fe(II), NH<sub>3</sub>-N, NO<sub>2</sub>-N, and S<sup>2-</sup> were quantified using a portable UV/VIS  
202 spectrophotometer (HACH, DR2800). This device was calibrated with holmium oxide  
203 filter and holmium oxide wavelength standard solution.

204 Anions were analyzed by a lab-based ion chromatography system (ICS2000,  
205 Dionex, Thermo Fisher Scientific, Waltham, USA). Cations and trace elements were  
206 determined by using inductively coupled plasma optical emission spectrometry  
207 (ICP-OES iCAP6300, Thermo Fisher Scientific, Waltham, USA) and inductively  
208 coupled plasma mass spectrometry (ICP-MS 7500C, Agilent Technologies, Santa  
209 Clara, USA), respectively. Six standard solutions, diluted from stock standards (AR,  
210 Tanmo Quality Inspection Technology, China), were used to calibrate the instrument.  
211 Only the standard curves with correlation coefficient ( $r^2$ ) better than 0.9999 were used  
212 for subsequent analysis. The results were verified with replicate samples to ensure an  
213 analytical precision better than 5%.

214 Analysis of REE+Y concentrations were performed by employing two different  
215 single-collector inductively coupled plasma sector field mass spectrometry  
216 instruments (ICP-SFMS ELEMENT XR and ELEMENT 2, Thermo Fisher Scientific,  
217 Bremen, Germany) based on the protocol published by Rodushkin et al. (2018). A  
218 cation exchange resin (AG 50W-X8, 200 to 400 dry mesh size, Bio-Rad laboratory

---

219 AB, Solna, Sweden) was used for the preconcentration of REE+Y. Prior to use, the  
220 resins were immersed in 14 mol/L HNO<sub>3</sub> overnight and were cleaned with deionized  
221 water. A 2 mL low-density polyethylene (LDPE) column was loaded with the  
222 prepared resins, and 4 mL 14 mol/L HNO<sub>3</sub> (AR, Sinopharm, China), 8 mL deionized  
223 water and 4 mL 9.5 mol/L HCl (AR, Sinopharm, China) were loaded sequentially for  
224 conditioning. Finally, a 200 mL sample was introduced into the pre-conditioned  
225 column and the retained REE+Y were eluted with 4 mL 0.5 mol/L HCl. By this  
226 method, a 50-fold preconcentration was achieved. The REE+Y recovery ranged  
227 between 90% and 103%. Calibration and quality control samples were prepared in 2%  
228 nitric acid with a stock solution. A medium resolution mode (MR, m/Δm  
229 approximately 5400) was set up for monitoring the isotopes <sup>146</sup>Nd, <sup>147</sup>Sm, <sup>151</sup>Eu, <sup>163</sup>Dy,  
230 <sup>165</sup>Ho, and <sup>172</sup>Yb, and a high resolution mode (HR, m/Δm approximately 12000) was  
231 used for monitoring the isotopes <sup>139</sup>La, <sup>140</sup>Ce, <sup>141</sup>Pr, <sup>157</sup>Gd, <sup>159</sup>Tb, <sup>166</sup>Er, <sup>169</sup>Tm, and  
232 <sup>175</sup>Lu, as suggested by Wilkin et al. (2021). The detection limits were 0.1 ng/L for Lu,  
233 0.2 ng/L for Eu, and 0.5 ng/L for other REE and Y. One ng/L In solution was used as  
234 internal standard to check for the mass bias. Interferences of BaO<sup>+</sup> on the <sup>151</sup>Eu and  
235 <sup>153</sup>Eu isotopes were corrected automatically by setting up a correction measure during  
236 analysis. Briefly, we run ~100 μg/L Ba and determine the peak area of the Eu isotope  
237 being monitored. During a run of samples, Ba (without calibration) was monitored  
238 and the results were applied for a correction. The analytical precision of replicate  
239 samples of REE+Y were generally better than 8%.

240 Bulk composition analysis of sediment and sludge samples were carried out

---

241 using a  $\text{LiBO}_2\text{-LiB}_4\text{O}_7$  fusion and X-ray fluorescence (XRF ARL Advant X), and after  
242 dissolving the glass disks by dilute nitric acid also by ICP-OES and ICP-MS. Mineral  
243 compositions in sediment and sludge were determined by X-ray diffraction (XRD D8  
244 advance, Bruker) with a  $\text{CuK}\alpha$  radiation. Diffraction patterns were scanned at  $2\theta$  of  
245  $20^\circ$  to  $70^\circ$  and a step size of  $0.02^\circ$ . Minerals having content greater than 5 wt.-% of  
246 the bulk solid were thus identified.

247 Solid samples and suspended matter filtered out of aqueous solutions were  
248 examined additionally by using scanning electron microscopy (SEM) (NovaNano  
249 450, Fei Czech, Co., Ltd.).

#### 250 2.4 Modelling approach

251 Speciation calculations were performed using the hydrogeochemical code  
252 PHREEQC version 3.4 (Parkhurst and Appelo, 2013) with the Nagra/PSI database  
253 (Hummel et al., 2002). Stability constants of REE complexation to major anions (e.g.  
254  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ , and  $\text{NO}_3^-$ ) were incorporated into the database from  
255 literature (Table S1) (Supporting Information). For example, constants for  
256  $\text{REE}(\text{CO}_3)_2^-$  and  $\text{REECO}_3^+$  were taken from Luo and Byrne (2004), and those for  
257  $\text{REESO}_4^+$  were taken from Schijf and Byrne (2004). Surface complexations of REE  
258 onto iron oxyhydroxides were considered as previously done by Liu et al. (2017b), in  
259 which the relevant formation constants and detailed modelling procedures were  
260 provided. Statistical tests were performed using Grapher (version 10.0) and IBM  
261 SPSS Statistics (version 19.0) programs.

### 262 3. Results

---

### 263 3.1 Water chemistry

264 Major ion concentrations and physicochemical parameters are compiled in Table  
265 S2. Results revealed that mine waters (MW1 to 5) had pH values between 3.8 and 4.2.  
266 A slight increase in pH (4.1 to 4.9) was observed for NDT samples (NDT1 to 6). The  
267 CPT samples had pH values  $> 7$  (7.4 to 8.7), and the GW sample's pH was 6.5.  
268 Generally, pH values increased from the regions nearest to the mine site to  
269 downstream of the STP facility.

270 All water compositions are shown on a Piper plot for comparison (Fig. 2). The  
271 TDS ranged between 95 and 562 mg/L (average 363 mg/L) with the lowest values in  
272 GW. Before passing through the STP (i.e., samples MW 1 to 5), cation compositions  
273 were predominated by  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , and  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  were the dominant anions,  
274 while  $\text{Cl}^-$  concentrations were  $< 5$  mg/L. Water types thus determined for MW 1 to 5  
275 were Ca/Mg- $\text{SO}_4$  and Ca/Mg- $\text{HCO}_3/\text{SO}_4$ . Over the CPT pathway (CPT 1 to 4), the  
276 major cation composition shifted towards  $\text{Na}^+$  predominance (52 to 104 mg/L),  
277 followed by  $\text{Mg}^{2+}$  (23 to 26 mg/L) and  $\text{Ca}^{2+}$  (31 to 48 mg/L), while the dominant  
278 anion was  $\text{HCO}_3^-$  ( $>156$  mg/L), hydrochemical type for these samples being  
279 Na-Ca/Mg- $\text{HCO}_3$ . This type of water continued downstream near the village (CPT 4),  
280 approximately 1 km downstream from the STP. The NDT samples showed a coherent  
281 water type of Mg-Na-Ca- $\text{HCO}_3$ - $\text{SO}_4$ . The GW collected from the village was of  
282 Na- $\text{HCO}_3$  water type.

283 Total dissolved Fe ( $\text{Fe}_T$ ) concentration ranged from 0.23 to 0.48 mg/L (average  
284 0.31 mg/L) in MW samples, while it dramatically decreased to a range of 0.05 to 0.20

---

285 mg/L (average 0.08 mg/L) after passing through the NDT procedure. A further  
286 decrease in  $Fe_T$  concentration occurred in water which went through the CPT (0.03 to  
287 0.07 mg/L, average 0.06 mg/L). The lowest  $Fe_T$  concentration was observed in GW  
288 (0.006 mg/L, i.e. near detection limit). Ferrous presumably dominated the Fe species  
289 in MW and NDT water samples due to the high  $Fe_T$  concentrations. For CPT and GW  
290 samples, Fe(II) concentrations were below detection limits, with an exception of CPT  
291 4 which had a  $Fe_T$  concentration of 0.02 mg/L (Fig. 3a).

292 Total dissolved Al ( $Al_T$ ) concentration ranged between 3.04 and 5.64 mg/L  
293 (average 4.7 mg/L), and between 1.77 and 2.57 mg/L in MW and NDT samples,  
294 respectively. Concentrations of  $Al_T$  decreased to  $< 0.3$  mg/L in CPT samples. No  $Al_T$   
295 could be detected in GW. Total dissolved Mn concentrations were generally higher in  
296 MW samples ( 2.00 to 5.36 mg/L, average 3.09 mg/L), as compared to those in NDT  
297 (2.14 to 2.61 mg/L, average 2.45 mg/L) and CPT (1.14 to 2.12 mg/L, average 1.63  
298 mg/L) samples. Other trace element concentrations, including Pb, Zn, Sr, Rb, and U,  
299 all decreased substantially after the CPT procedure (Fig. 3b).

### 300 3.2 Aqueous REE+Y distribution patterns

301 Total concentrations of REE+Y ( $\Sigma REE+Y$ ) in water samples are presented in  
302 Table S3. The  $\Sigma REE+Y$  concentrations ranged from 3.84 to 4.33 mg/L (average 4.11  
303 mg/L), and from 1.67 to 2.97 mg/L (average 2.21 mg/L) in MW and DNT samples,  
304 respectively. These values were up to two orders of magnitude higher than the  
305  $\Sigma REE+Y$  concentrations of CPT samples (0.07 to 0.19 mg/L, average 0.12 mg/L), and  
306 were more than three orders of magnitude higher than the  $\Sigma REE+Y$  concentrations in



307 GW sample (5.3 µg/L, Fig. 3a).

308 Upper continental crust normalized REE+Y patterns were characterized by  
309 HREE enrichment over LREE and negative Ce ( $Ce/Ce^* = Ce_{UCC}/(La_{UCC} \times Pr_{UCC})^{0.5}$ )  
310 (Fig. 4). The average normalized  $(Yb/Nd)_{UCC}$  ratio (as a fractionation measure) was  
311 higher in CPT samples (10.23) as compared to MW (7.11), NDT (7.76), and GW  
312 (5.70) samples. The Ce anomaly was  $< 0.3$  with an exception of GW ( $Ce/Ce^* = 0.37$ )  
313 (Table S3). Positive Y anomaly ( $(Y/Ho)_{UCC}$ ) was observed in MW (1.14 to 1.53,  
314 average 1.29) and NDT (1.21 to 1.36, average 1.33) samples. Value of  $(Y/Ho)_{UCC}$   
315 was  $> 1.70$  for CPT samples, and was 1.39 for the GW sample.

### 316 3.3 Modelling results

317 Free ( $REE^{3+}$ ) and sulfate ( $REESO_4^+$ ) complexes dominated lanthanide species in  
318 MW and NDT samples (Figs. 4b and d). The LREE tended more to be associated with  
319  $SO_4^{2-}$ , while the HREE were dominantly present as free ions. The average proportion  
320 of La occurring as  $REESO_4^+$  was 48%, and 36% for Lu. Carbonate ( $REECO_3^+$  and  
321  $REE(CO_3)_2^-$ ) and nitrate complexes ( $REENO_3^+$ ) were  $< 5\%$  in proportion of all  
322 lanthanide species. The lanthanides in CPT samples were calculated mainly in  
323 carbonate complex forms of  $REECO_3^+$  and  $REE(CO_3)_2^-$  that accounted for 73% to  
324 98% for La and 89% to 99% for Lu. Free ions made up 6% for La and  $< 1\%$  for Lu  
325 (Fig. 4f). Lanthanides in the GW sample were predicted to occur as free ions,  
326  $REECO_3^+ + REE(CO_3)_2^-$ , and  $REESO_4^+$ . The proportions of these three species were  
327 predicted to be 49% to 79%, 5% to 34%, and 7% to 15%, respectively (Fig. 4h).  
328  $REENO_3^+$  mostly accounted for  $< 2\%$  of total lanthanide speciation. The other

---

329 potential species, including hydroxyl and chloride complexes, were < 1% in the water  
330 samples.

### 331 3.4 Geochemical and mineralogical properties of solids

332 The rock samples were dominated by SiO<sub>2</sub> (66 to 68 wt.-%), while Al<sub>2</sub>O<sub>3</sub> was the  
333 second most abundant component (9 to 18 wt.-%), followed by Fe<sub>2</sub>O<sub>3</sub> (4 to 7 wt. %)  
334 (Table S4). Composition of surface sediment samples ranged from 61 to 76 wt. % for  
335 SiO<sub>2</sub>, 10 to 3 wt. % for Al<sub>2</sub>O<sub>3</sub>, and 2 to 5 wt. % for Fe<sub>2</sub>O<sub>3</sub>. Other metal oxides were  
336 generally < 6 wt. %. For the sludge samples, SiO<sub>2</sub> contents ranged from 60 to 67  
337 wt. %, Al<sub>2</sub>O<sub>3</sub> from 15 to 18 wt. %, and Fe<sub>2</sub>O<sub>3</sub> from 3 to 12 wt. %. Other metal oxides  
338 were < 5 wt.%.

339 Contents of ΣREE+Y in sludge samples ranged between 0.80 mg/kg and 44.74  
340 g/kg (average 19.95 g/kg). Those values were much higher than the ΣREE+Y contents  
341 of rock (0.33 to 0.85 g/kg, average 0.66 g/kg) and sediment samples (0.35 to 0.43  
342 g/kg, average 0.39 g/kg) (Table S5). UCC-normalized REE+Y patterns showed that  
343 all samples were enriched in HREE relative to LREE and had negative Ce anomaly.  
344 The (Yb/Nd)<sub>UCC</sub> values ranged from 6.14 to 9.14, from 3.51 to 5.83, and from 1.08 to  
345 2.10 in sludge, sediment and rock samples, respectively (Table S5). Normalized  
346 REE+Y patterns of sludge and sediment samples showed an increasing upward trend  
347 from La to Sm, and a relatively flat trend from Tb to Lu (Fig. 5). On the other hand,  
348 REE+Y patterns for rock samples showed a slightly increasing trend with atomic  
349 numbers, indicating that a higher degree of HREE enrichment over LREE occurred  
350 for sludge and sediment samples as compared to rock samples. The Ce anomaly

---

351 ranged from 0.18 to 0.63, and from 0.61 to 0.79, in sludge and sediment samples,  
352 respectively. Rock samples showed weakly negative Ce anomalies ( $Ce/Ce^* \sim 0.98$ )  
353 (Table S5).

354 SEM imaging of filter residuals showed that the mine waters contained many  
355 suspended aggregate particles with diameters larger than 0.22  $\mu\text{m}$ . This was more  
356 commonly observed in CPT samples as compared to MW samples (Fig. S1).  
357 Sediment samples contained clastic textures on the surfaces with length  $< 1 \mu\text{m}$  (Fig.  
358 S2). On the surfaces of sludge samples, needle-like and burr-like shapes occurred with  
359 shorter length than those observed in sediment samples (Fig. S2).

360 Results of XRD show that quartz (56% to 68%), muscovite (7% to 11%),  
361 kaolinite (8% to 14%), feldspar (both albite ( $\text{NaAlSi}_3\text{O}_8$ ) and microcline ( $\text{KAlSi}_3\text{O}_8$ ),  
362 10% to 14%), schwertmannite ( $< 5\%$ ), and ferrihydrite ( $< 5\%$ ) were present in the  
363 sediment samples (Fig. S3). For sludge samples, quartz was determined to account for  
364 27% to 47%, feldspar 10% to 27%, and schwertmannite 15% to 24%. Other minerals  
365 mostly showed contents  $< 5\%$ .

## 366 **4. Discussion**

### 367 4.1 Geochemical characteristics

368 The average values of REE concentrations in the acid mine waters were several  
369 orders of magnitude higher than those in natural near-neutral waters (Ayora et al.,  
370 2016). Specifically, the average total REE ( $\Sigma\text{REE}$ ) concentrations in our samples  
371 (0.003 to 2.18 mg/L, average 0.94 mg/L) were comparable to the values reported by  
372 Liu et al. (2019a) (up to 10.86 mg/L, average 1.14 mg/L) found for the same study

---

373 area. The MW samples showed higher  $\Sigma\text{REE}+\text{Y}$  concentrations than NDT, CPT and  
374 GW samples. With MW water moving downstream the processing line,  $\Sigma\text{REE}+\text{Y}$   
375 concentrations decreased (Fig. 3a). Trends of Fe, Al, and Mn concentrations were  
376 similar to those of  $\Sigma\text{REE}+\text{Y}$  concentrations (Fig. 3a), indicating that REE+Y exhibited  
377 similar behavior to these metals. Indeed, the Fe, Al and Mn concentrations were  
378 positively correlated with  $\Sigma\text{REE}+\text{Y}$  concentrations, with correlation coefficients ( $r^2$ )  
379 of 0.61 ( $p < 0.01$ ), 0.86 ( $p < 0.01$ ), and 0.43 ( $p < 0.01$ ) (Fig. 6a), respectively,  
380 indicating that REE+Y behaved more like Al than Mn or Fe. The positive correlation  
381 indicated intense leaching of these cations and a close association of REE+Y with Fe,  
382 Mn and Al in particulate phases (Zhou et al., 2012).

383 Samples with higher  $\Sigma\text{REE}+\text{Y}$  concentrations also contained relatively higher  
384  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  concentrations (Table S2 and S3). Although a poor positive  
385 correlation was observed between  $\text{SO}_4^{2-}$  and  $\Sigma\text{REE}+\text{Y}$  concentrations ( $r^2 = 0.18$ ,  $p =$   
386 0.1) (Fig. 6a), the predominance of  $\text{SO}_4^{2-}$  in total anions could be observed in MW  
387 samples (Fig. 2). This was largely due to the use of ammonium sulfate as an in-situ  
388 extractant for REE+Y mining (Liu et al., 2019b). Similarly, anthropogenic pumping of  
389 ammonium sulfate would account for the high  $\text{NO}_3^-$  concentrations, and the relatively  
390 constant  $\text{NO}_3^-$  concentrations in CPT samples demonstrated that nitrification reactions  
391 occurred under these conditions. It should be noted that, in addition to Fe, Al, Mn,  
392  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ , high concentrations of  $\text{NH}_3\text{-N}$  (mostly  $>10$  mg/L) were found to  
393 co-occur with REE+Y in AMD. The  $\Sigma\text{REE}+\text{Y}$  occurrence was therefore attributed to  
394 geochemical characteristics of source deposit as well as anthropogenic alterations.

---

## 395 4.2 Origin and mobility of REE+Y

396 Previous investigations of AMD suggested that REE+Y originated from leaching  
397 of acid soils (Åström, 2001). Other studies attributed REE+Y source to dissolution of  
398 REE+Y-bearing minerals in host rocks (Pérez-López et al., 2010; Cánovas et al., 2020;  
399 Wallrich et al., 2020). The UCC-normalized REE+Y pattern similarity between acid  
400 leachate water and sediment indicates that REE+Y in AMD were derived from  
401 sediments directly (Fig. 5). The HREE enrichment in the rock samples suggested that  
402 the parent rock acted as the original REE+Y source for the clay-rich sediment layers  
403 leached by the acidic waters. Therefore, origin of REE+Y in the AMD highly  
404 depended on the REE+Y-bearing mineral phases in the bedrocks, and weathering of  
405 bedrocks and desorption from the weathering product minerals were a main pathway  
406 mobilizing REE+Y into mine water. The REE+Y would be initially mobilized  
407 naturally, when rainwater infiltrated underground (Nesbitt, 1979). The acidic water in  
408 contact with the host rock led to a preferential dissolution of weathered minerals like  
409 feldspars (Nordstrom et al., 2015). Upon REE+Y being mobilized from the rocks, the  
410 majority of them were scavenged via ion exchange by clay-rich sediments/soils. A  
411 zone of soils/sediments was formed after weathering of rock crust in the study area,  
412 where igneous rocks, mainly composed of acidic granites, were exposed in a large  
413 area (Yang et al., 2013; Chi and Liu, 2019). The ion-exchanged REE+Y were readily  
414 desorbed from the sediments by acid leaching, where the acid extractant (ammonium  
415 sulfate) was injected into the soil/sediment layer. The coherent HREE-enriched  
416 patterns in all water samples indicated that the desorbed REE+Y were ultimately

---

417 discharged into streams/creeks, and were transported in form of sulfate complexes and  
418 free ions until solution conditions became neutral or weakly alkaline as discussed  
419 below. Consequently, REE+Y compositions were originally derived from the parent  
420 rocks and were immobilized by sediments via sorption, and ion exchange might  
421 mobilize REE+Y into the aquifer and surface waters.

#### 422 4.3 Control on REE+Y concentrations

423 Concentrations of REE+Y in the investigated acidic waters were controlled by  
424 the bulk solution chemistry and co-precipitation of secondary minerals. A negative  
425 correlation ( $r^2 = -0.72$ ,  $p < 0.01$ ) was observed between pH values and  $\Sigma\text{REE+Y}$   
426 concentrations. The lowest pH occurring in MW favored leaching of  
427 REE+Y-containing minerals in sediment (Dia et al., 2000; Worrall and Pearson, 2001;  
428 Janssen and Verweij, 2003). This controlled REE+Y concentrations in the source  
429 areas, as reflected by high  $\Sigma\text{REE+Y}$  concentrations in MW and NDT samples where  
430  $\text{pH} < 4.9$  occurred (Fig. 3a). A decrease in  $\Sigma\text{REE+Y}$  concentrations in CPT samples  
431 was due to REE+Y scavenging via ion-exchange and/or adsorption by secondary  
432 minerals resulting from increased pH values ( $> 7.4$ ). Similar decreasing trends of Fe,  
433 Mn, Al, and  $\text{SO}_4^{2-}$  concentrations with MW water moving CPT indicated that Fe-,  
434 Mn- and Al-bearing minerals were possible secondary phases to scavenge REE+Y in  
435 CPT samples (Fig. 3a). Results of XRD supported that clay minerals (i.e. kaolinite),  
436 iron oxide (i.e. ferrihydrite), and schwertmannite were the potentially scavenging  
437 secondary minerals (Fig. S3). The dominant Fe species shifted from Fe(II) in MW and  
438 NDT samples to Fe(III) in CPT (Fig. 3a), suggesting that the formation of ferrihydrite

439 and schwertmannite might occur following Eqs. (2) and (3):



440 These minerals have been suggested to be most commonly precipitated from AMD  
441 during neutralization processes (Lozano et al., 2020a).

442 The positive Y/Ho anomaly was a good indicator for the impact of sorption by  
443 solids on  $\Sigma\text{REE}+\text{Y}$  concentrations (Tweed et al., 2006), as Y behaves differently from  
444 Ho during sorption, with Ho having greater affinities than Y for surface complex  
445 formation (Bau, 1999), and thus leads to fractionation between them (Nozaki et al.,  
446 1997; Möller et al., 1998). The prevailing positive Y/Ho anomaly observed in water  
447 samples implied that sorption of REE+Y readily occurred during the neutralization  
448 processes (Table S3). Higher Y/Ho values found in CPT samples (1.70 to 1.81) as  
449 compared to MW (1.14 to 1.53) and NDT (1.21 to 1.36) samples was attributed to  
450 intensive sorption or/and co-precipitation of REE+Y in CPT samples. Indeed,  
451  $\Sigma\text{REE}+\text{Y}$  concentrations were negatively correlated with Y/Ho values ( $r^2 = 0.66$ ,  $p <$   
452  $0.05$ ), showing that low-pH conditions disfavored REE+Y sorption (De Carlo et al.,  
453 1998; Liu et al., 2017b). Scavenging of REE+Y by schwertmannite (Lozano et al.,  
454 2020a, b) and Al oxyhydroxides (Ogawa et al., 2019) was recently investigated with  
455 different pH ranges. Additionally, changes of REE+Y concentrations might also be  
456 coupled to scavenging by Mn oxyhydroxides, with a sorption edge low to pH 4 and a  
457 complete REE+Y sorption at pH around 8 (Pourret and Davranche, 2013). However,

---

458 Mn oxyhydroxides were not detected by XRD in the sludge samples of this study.  
459 Therefore, REE+Y concentrations were mainly determined by acidification-enhanced  
460 dissolution/desorption/ion exchange from the sedimentary mine body by the acidic  
461 ammonium sulfate solution injected, and scavenging by secondary mineral  
462 precipitates upon neutralization treatment.

#### 463 4.4 Control on REE+Y patterns

464 All water samples showed enrichments in HREE over LREE when normalized to  
465 UCC (Figs. 4a, c, e and g). This pattern has been reported also for AMD and  
466 AMD-impacted waters in solution mining for in-situ ion-exchange extraction of  
467 REE+Y (Luo et al., 2016). As shown in Fig. 6b, REE+Y patterns of this study and  
468 other deposits (Hao et al., 2016; Luo et al., 2016) exploited by the acidic  
469 ion-exchange process in southern China were characterized by  $(La/Sm)_{UCC}$  and  
470  $(Gd/Yb)_{UCC}$ . Results showed that all investigated samples were in the quadrant with  
471  $(La/Sm)_{UCC} < 1$  and  $(Gd/Yb)_{UCC} < 1$ , suggesting HREE-enriched patterns (Fig. 6b).  
472 These distribution patterns were thought to be mainly controlled by source sediment  
473 in this study. The possible mechanisms were addressed as follow.

474 The relatively flat UCC-normalized REE+Y pattern of rocks suggested that the  
475 host rock was not a direct cause for HREE enrichment in the acid mine waters. The  
476 clear resemblance between REE+Y patterns in sediment and those in the acid mine  
477 water indicated that the aqueous REE+Y patterns were probably controlled by the  
478 characteristics of the REE+Y sources. The pattern remained relatively constant  
479 irrespective of precipitation of secondary minerals with water processing. A model



---

480 could be developed as to the formation of HREE enrichment pattern in the acid mine  
481 waters, which was that (i) thick zones of clay rich sediment/soil developed above the  
482 granites via weathering; (ii) the REE+Y originally mobilized by weathering were  
483 sorbed by the sediment layers, whereby a preferential accumulation of HREE by the  
484 sediments led to HREE enrichment (Aström, 2001); and (iii) the desorption of  
485 previously sorbed REE+Y into the mining solutions, giving rise to enrichments of  
486 HREE relative to LREEs in the acidic mine waters (Leybourne et al., 2000;  
487 Migaszewski et al., 2016). The desorption process was not expected to significantly  
488 fractionate REE+Y in the acid mine waters. This was because: (i) sulfate complex and  
489 free ion were the main solution species as indicated by speciation calculations (Fig.  
490 5b), whereby the association of REE+Y with sulfate would not modify REE+Y  
491 patterns in aqueous solutions owing to the relatively constant REE+Y-sulfate  
492 formation constants (Wilkin et al., 2021); and (ii) REE+Y re-adsorption onto mineral  
493 phases was quite limited. This was due to the generally low pH values (<4) in the MW  
494 samples, where REE+Y behaved conservatively in spite of Fe and/or Mn  
495 oxyhydroxides present (Verplanck et al., 2004; Pourret and Davranche, 2013).

496       The impact of Fe and Al oxyhydroxide scavenging on HREE enrichment might  
497 only be found for the CPT. The low pH values in MW and NDT samples (<4; except  
498 for NDT1) disfavor formation of Fe and Al oxyhydroxides (Ogawa et al., 2019). This  
499 was why coefficients of distribution of the REE+Y between Al/Fe oxyhydroxide  
500 solids and water showed a very weak increase across lanthanide series at pH of 6.3 to  
501 6.8 (Lozano et al., 2020a). This suggested also that HREE fractionation during

---

502 enrichment by adsorption or/and co-precipitation with Fe/Al oxyhydroxides was  
503 insignificant for this study.

504 Influence of solution complexation on HREE enrichment in CPT and GW  
505 samples was insufficient to significantly fractionate REE+Y in the MW and NDT  
506 samples. The most plausible ligand responsible for enrichment of HREE in CPT and  
507 GW samples would be  $\text{CO}_3^{2-}$ , due to preferential stabilization of HREE relative to  
508 LREE during REE+Y- $\text{CO}_3^{2-}$  complexation (Guo et al., 2010; Liu et al., 2016).  
509 Although  $\text{SO}_4^{2-}$  complexes and free ions were the dominating lanthanide species in  
510 MW and NDT samples (Fig. 4),  $\text{SO}_4^{2-}$  was an almost equally strong complexant for  
511 all REE+Y (Wood, 1990). The possibility of HREE enrichment caused by other  
512 ligands including  $\text{OH}^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{F}^-$  and  $\text{Cl}^-$  could be excluded either by their low  
513 speciation predicted by the model (Fig. 4) or by the preferential complexation of  
514 LREE.

515 Effect of organic matter on HREE enrichment in waters could be ruled out due to  
516 preferential complexation of MREE relative to LREE and HREE (Wood, 1993;  
517 Pourret et al., 2007) and the low DOC concentrations (generally  $< 3.2$  mg/L). The  
518 REE+Y were mostly truly dissolved in the acidic mine waters, and the particulates  
519 were less important to control the REE+Y fractionation patterns under  $\text{pH}<4$   
520 conditions (Olías et al., 2018).

#### 521 4.5 Cerium anomaly

522 A narrow range in Ce anomaly values ( $\text{Ce}/\text{Ce}^*$ : 0.21 to 0.29) was observed for  
523 all water samples (Fig. 6d). The negative Ce anomaly was controlled by sedimentary

---

524 REE+Y patterns, where negative Ce anomaly was evident (0.61 to 0.79). Oxidation of  
525 soluble Ce(III) to insoluble Ce(IV) that is precipitated as CeO<sub>2</sub> and/or Ce(OH)<sub>4</sub> has  
526 been recognized as a mechanism immobilizing Ce and resulting in negative Ce  
527 anomaly in aqueous solution. This process might have occurred when REE+Y either  
528 were initially weathered from host rock or were secondarily mobilized from  
529 sediments. The lower Ce/Ce\* values in sediments than rocks supported the former to  
530 be a more plausible cause for negative Ce anomaly in the acid mine waters. It was  
531 unlikely that redox processes played a dominant role in the development of negative  
532 Ce anomalies over acid mine water flow, since Ce anomaly was relatively constant in  
533 all acid mine water samples despite variable redox conditions. Indeed, Eh-pH diagram  
534 regarding the Ce-H<sub>2</sub>O system showed that MW and NDT samples mostly were  
535 located in stability field of Ce(III), while CPT and GW sample in the stability field of  
536 CeO<sub>2</sub> (Fig. 6c). This indicated that Ce initially occurred as free cation when mobilized  
537 from sediments, and it tended to be precipitated in form of CeO<sub>2</sub> as pH increased and  
538 Eh decreased. In this respect, oxidative scavenging of Ce by Fe oxyhydroxides and/or  
539 Mn oxides due to co-precipitation of these secondary minerals might occur in CPT  
540 samples (Ohta and Kawabe, 2001; Takahashi et al., 2007). However, this process  
541 could not be a dominant control on negative Ce anomaly formation, because the  
542 Ce/Ce\* values in CPT samples were comparable to those of MW and NDT samples  
543 (Table S3), despite that Fe and Mn concentrations decreased substantially with acid  
544 mine waters downstream the processing line (Fig. 4a). Therefore, the negative Ce  
545 anomaly was suggested to be largely controlled by REE+Y sources in the sedimentary

---

546 strata. A similar case was reported by Smedley (1991), showing that Ce anomaly in  
547 slightly acidic groundwaters (pH 5.0 - 6.8) was related to rock aquifer as source.

#### 548 4.6 Implication for REE+Y recovery from AMD

549 Although AMD has been considered as an environmental concern globally due to  
550 its great hazard to ecosystems, it is a potential secondary source of REE+Y as well as  
551 coexisting metal elements, which are of economic interest, if appropriate control and  
552 treatment processes are implemented. Neutralization of mine water acidity constitutes  
553 a simple but promising option for recovering REE+Y from the acid waters. As shown  
554 in this study, REE+Y were efficiently sequestered in CPT samples, where pH values  
555 were increased to > 7.4. Correspondingly, high levels of REE+Y were found in  
556 precipitate sludge samples, and their concentrations on the g/kg levels were higher  
557 than those of source sediments. The yield of REE+Y that were potentially recoverable  
558 from acid mine waters were calculated by the difference between loads of REE+Y in  
559 original acid mine waters and effluents of the treated mine waters. The loads of  
560 REE+Y were obtained by multiplying plant treatment capacity by the REE+Y  
561 concentrations in studied waters. Results showed that the recoverable  $\sum$ LREE and  
562  $\sum$ HREE ranged between 1.11 and 3.37 kg/day, and between 1.29 and 3.76 kg/day,  
563 contributing nearly equally between 34% and 38%, and between 38% and 42% of the  
564 total  $\sum$ REE+Y, respectively. The recoverable Y ranged between 0.79 and 2.35 kg/day  
565 (20% to 28%) (Fig. S4). The highest total recoverable value occurred at the location  
566 of MW5, which was nearest the inlet of the WTP (Fig. 1).

567 It must be noted that the profitability of REE+Y recovery from AMD depends on

---

568 the amounts in AMD, the cost of separation and extraction, and the proportion of  
569 HREE over LREE in the AMD (Léon et al., 2021). The high proportions of HREE  
570 found in AMD of this area renders recovery of REE+Y from the acid mine waters  
571 attractive, considering that HREE are more precious compared to LREE, and that they  
572 are largely restricted to South China. The availability of recovering REE+Y as well as  
573 other critical metals like Cu, Zn, and Ni from acid mine leachate and their  
574 neutralization precipitates were documented by Zhang and Honaker (2020). Ayora et  
575 al. (2016) studied the recovery of REE+Y from passive remediation systems of AMD  
576 system with two mineral substrate -(schwertmannite and basaluminite) based  
577 treatments, showing that AMD remediation process serves as a suitable REE+Y  
578 source. Biochar may server as a potential sorbent as well to immobilize these metals  
579 in aqueous solution where pH value is acidic (Pourret and Houben, 2018). To sum up,  
580 the practical examples of REE+Y recovery from AMD render an environmental  
581 problem worthwhile as a source of raw materials, considering that alternative sources  
582 of REE+Y is warranted due to an ever increasing demand for these critical metals,  
583 particularly for the countries without primary deposits.

## 584 **5. Conclusions**

585 This study investigated the geochemistry of rare earth element (REE) and  
586 yttrium (REE+Y) in acid mine drainage from solution mining. Elevated  
587 concentrations of REE+Y were observed in the mine water with low pH. A  
588 progressive decrease in REE+Y concentrations occurred with MW flowing through  
589 nitrification-denitrification (NDT) and coagulating-precipitation treatment procedures

---

590 (CPT). Negative correlation between REE+Y concentrations and pH values ( $r^2 = 0.72$ )  
591 indicated that REE+Y were primarily derived from an enhanced acidic desorption and  
592 ion exchange from minerals in the source area. The similarity of HREE-enriched  
593 patterns exhibited by AMD to those of source sediment indicated a major role of  
594 sediments in controlling REE+Y signatures of AMD. A preferential precipitation of  
595 LREE over HREE during the plant treatment process provided for a limited  
596 contribution to HREE enrichment in AMD, because the degree of HREE enrichment  
597 changed slightly and Ce remained relatively constant in MW, NDT, and CPT samples.  
598 Results of XRD and SEM examination indicate that clay minerals (i.e. kaolinite), iron  
599 oxides (i.e. ferrihydrite), muscovite, and secondary schwertmannite minerals were the  
600 main hosts of REE+Y. Therefore, HREE-enrichment patterns in AMD resulted from  
601 preferential desorption of HREE from sediment under the conditions of the in-situ  
602 leaching process at the mine site. Free ions and sulfate complexes, which dominated  
603 REE+Y species in MW and NTD samples, facilitated the transport of REE+Y and  
604 preserved REE+Y patterns during AMD flow. Carbonate complexation accounted for  
605 HREE enrichment as well in CPT and GW samples. Results of this study  
606 demonstrated significant potential for REE+Y recovery from AMD.

## 607 **Acknowledgments**

608 This investigation has been funded by National Natural Science Foundation of  
609 China (No. 41902243), Natural Science Foundation of Jiangxi province, China  
610 (20202BABL211018), and East China University of Technology Research Foundation  
611 for Advanced Talents (Nos. DHBK2019094 and SHT201901). We gratefully

612 acknowledge Dr. Michael Kersten for editing the manuscript in English and  
613 comments. Dr Wei Xiu is thanked for his suggestions and comments. Anonymous  
614 reviewers and Associate Editor Mae Sexauer Gustin are also acknowledged for their  
615 helpful comments.

616

---

**617 References**

- 618 Akcil, A., Koldas, S. 2006. Acid Mine Drainage (AMD): causes, treatment and case  
619 studies. *J. Clean. Prod.* 14 (12- 13), 1139-1145.
- 620 Alonso, E., Sherman, A. M., Wallington, T. J., Everson, M. P., Field, F. R., Roth, R.,  
621 Kirchain, R. E. 2012. Evaluating rare earth element availability: a case with  
622 revolutionary demand from clean technologies. *Environ. Sci. Technol.* 46(6),  
623 3406-3414
- 624 Åström, M., Corin, N. 2003. Distribution of rare earth elements in anionic, cationic  
625 and particulate fractions in boreal humus-rich streams affected by acid sulphate  
626 soils. *Wat. Res.* 37, 273-280.
- 627 Åström, M. 2001. Abundance and fractionation patterns of rare earth elements in  
628 streams affected by acid sulphate soils. *Chem. Geol.* 175, 249-258.
- 629 Ayora, C., Macias, F., Torres, E., Lozano, A., Carrero, S., Nieto, J. M., Perez-Lopez,  
630 R., Fernandez-Martinez, A., Castillo-Michel, H., 2016. Recovery of rare earth  
631 elements and yttrium from passive-remediation systems of acid mine drainage.  
632 *Environ. Sci. Technol.* 50, 8255-8262.
- 633 Bau, M. 1999. Scavenging of dissolved yttrium and rare earths by precipitating iron  
634 oxyhydroxide: Experimental evidence for Ce oxidation, Y-Ho fractionation, and  
635 lanthanide tetrad effect. *Geochim. Cosmochim. Acta* 63, 67-77.
- 636 Binnemans, K., Jones, P. T., Blanpain, B., Van Gerven, T., Yang, Y., Walton, A.,  
637 Buchert, M. 2013. Recycling of rare earths: a critical review. *J. Clean. Prod.* 51,  
638 1-22.



- 
- 639 Bozau, E., Leblanc, M., Seidel, J. L., Strk, H. J. 2004. Light rare earth elements  
640 enrichment in an acidic mine lake (Lusatia, Germany). *Appl. Geochem.* 19(3),  
641 261-271.
- 642 Cánovas, C. R., Macías, F., Olías, M., Basallote, M. D, Pérez-López, R, Ayora, C,  
643 Nieto, J. M. 2020. Release of technology critical metals during sulfide oxidation  
644 processes: the case of the Poderosa sulfide mine (south-west Spain). *Environ.*  
645 *Chem.* 17, 93-104.
- 646 Chi, R. A., Liu, X. M. 2019. Prospect and development of weathered crust  
647 elution-deposited rare earth ore. *J. Chinese Rare Earth Soc.* 37(2), 129-140.
- 648 De Carlo, E. H.; Wen, X. Y.; Irving, M. 1998. The influence of redox reactions on the  
649 uptake of dissolved Ce by suspended Fe and Mn oxide particles. *Aquat.*  
650 *Geochem.* 3, 357-389.
- 651 Dia, A., Gruau G., Olivie-Lauquet G., Riou C., Molénat J. and Curmi P. 2000. The  
652 distribution of rare earth elements in groundwaters: Assessing the role of  
653 source-rock composition, redox changes and colloidal particles. *Geochim.*  
654 *Cosmochim. Acta* 64, 4131-4151.
- 655 Elderfield, J., Upstill-Goddard, R., Sholkovitz, E. R. 1990. The rare earth elements in  
656 rivers, estuaries and coastal seas and their significance to the composition of  
657 ocean waters. *Geochim. Cosmochim. Acta* 54, 971-991.
- 658 Gammons, C. H., Wood, S. A., Jonas, J. P., Madison, J. P. 2003. Geochemistry of rare  
659 earth elements and uranium in the acidic Berkeley Pit Lake, Butte, Montana.  
660 *Chem. Geol.* 198, 269-288.

- 
- 661 Gimeno, M. J., Auqué, L. F., Nordstrom, D. K. 2000. REE speciation in  
662 low-temperature acidic waters and the competitive effects of aluminium. *Chem.*  
663 *Geol.* 165, 167-180.
- 664 Guo, H. M., Zhang, B., Wang, G. C., Shen, Z. L. 2010. Geochemical controls on  
665 arsenic and rare earth elements approximately along a groundwater flow path in  
666 the shallow aquifer of the Hetao Basin, Inner Mongolia. *Chem. Geol.* 270,  
667 117-125.
- 668 Hao, X. Z., Wang, D. J., Wang, P. R., Wang, Y. X., Zhou D. M. 2016. Evaluation of  
669 water quality in surface water and shallow groundwater: a case study of a rare  
670 earth mining area in southern Jiangxi Province, China. *Environ. Monit. Assess.*  
671 188(1), 24.
- 672 Haxel, G. B., Hedrick, J. B., Orris, G. J. 2002. Rare earth elements critical resources  
673 for high technology. U.S. Geological Survey, Fact Sheet 087-02.
- 674 Hummel, W., Berner, U., Curti, E., Pearson, F. J., Thoenen, T. 2002. Nagra/PSI  
675 Chemical Thermodynamic Data Base 01/01. *Radiochim. Acta*, 90, 805-813.
- 676 Janssen, R. P. T., Verweij, W., 2003. Geochemistry of some rare earth elements in  
677 groundwater, Vierlingsbeek, The Netherlands. *Water Res.* 37, 1320-1350.
- 678 Johnson, D. B., Hallberg, K. B. 2005. Acid mine drainage remediation options: a  
679 review. *Sci. Total Environ.* 338 (1), 3-14.
- 680 León, R., Macías, F., Cánovas, C. R., Pérez-López, R., Ayora, C., Nieto, J. M., Olías,  
681 M. 2021. Mine waters as a secondary source of rare earth elements worldwide:  
682 the case of the Iberian Pyrite Belt. *J. Geochem. Explor.* 224, 106742.

- 
- 683 Leybourne, L., Goodfellow, W. D., Boyle, D. R., Hall, G. M. 2000. Rapid  
684 development of negative Ce anomalies in surface waters and contrasting ree  
685 patterns in groundwaters associated with Zn-Pb massive sulphide deposits. *Appl.*  
686 *Geochem.* 15(6), 695-723.
- 687 Liu, Y., Zhong, X., Huot, H., Liu, W. S., Liu, C., Guo, M. N., Li, Y. Y., Fei, Y. H., Chao,  
688 Y. Q., Wang, S. Z., Tang, Y. T., Qiu, R. L. 2020. Reclamation with organic  
689 amendments and plants remodels the diversity and structure of bacterial  
690 community in ion-adsorption rare earth element mine tailings. *J. Soils Sediments*  
691 20, 3669-3680.
- 692 Liu, W. S., Wu, L. L., Zheng, M. Y., Chao, Y. Q., Zhao, C. M., Zhong, X., Ding, K. B.,  
693 Huot, H., Zhang, M. Y., Tang, Y. T., Li, C., Qiu, R. L. 2019a. Controls on  
694 rare-earth element transport in a river impacted by ion-adsorption rare-earth  
695 mining. *Sci. Total Environ.* 660, 697-704.
- 696 Liu, W. S., Guo, M. N., Liu, C., Yuan, M., Chen, X. T., Huot, H., Zhao, C. M., Tang, Y.  
697 T., Morel, J. L. Qiu, R. L. 2019b. Water, sediment and agricultural soil  
698 contamination from an ion-adsorption rare earth mining area. *Chemosphere*, 216,  
699 75-83.
- 700 Liu, H. Y., Guo, H. M., Wu, L. H. 2017a. Rare earth elements as indicators of  
701 groundwater mixing in the North China Plain: A case study in the area of  
702 Hengshui city, China. *Pro. Earth Plant. Sci.* 17, 396-399.
- 703 Liu, H. Y., Pourret, O., Guo, H. M., Bonhoure, J. 2017b. Rare earth elements sorption  
704 to iron oxyhydroxide: Model development and application to groundwater. *Appl.*

- 
- 705 Geochem. 87, 158-166.
- 706 Liu, H. Y., Guo, H. M., Xing, L. N., Zhan, Y. H., Li, F. L., Shao, J. L., Niu, H., Liang,  
707 X., Li, C. C. 2016. Geochemical behaviors of rare earth elements in groundwater  
708 along a flow path in the North China Plain. *J. Asian Earth Sci.* 117, 33-51.
- 709 Lozano, A., Ayora, C., Macías, F., León, R., Gimeno, M. J., Auqué, L. 2020a.  
710 Geochemical behavior of rare earth elements in acid drainages: modeling  
711 achievements and limitations. *J. Geochem. Explor.* 216, 106577.
- 712 Lozano, A., Ayora, C., Fernández-Martínez, A. 2020b. Sorption of rare earth elements  
713 on schwertmannite and their mobility in acid mine drainage treatments. *Appl.*  
714 *Geochem.* 113, 104499.
- 715 Luo, J. M., Huo, Y. W., Shen, Y. J., Hu, J. W., Ji, H. B. 2016. Effects of colloidal  
716 particle size on the geochemical characteristics of REE in the water in southern  
717 Jiangxi province, China. *Environ. Earth Sci.* 75, 81.
- 718 Luo, Y. R., Byrne, R. H. 2004. Carbonate complexation of yttrium and the rare earth  
719 elements in natural waters. *Geochim. Cosmochim. Acta* 68, 691-699.
- 720 Marquez, J., Pourret, O., Faucon, M. P., Weber, S., Hoàng, T., Martinez, R. 2018.  
721 Effect of cadmium, copper and lead on the growth of rice in the coal mining  
722 region of Quang Ninh, Cam-Pha (Vietnam). *Sustainability*, 10, 1758
- 723 Medas, D., Cidu, R., Giudici, G. D., Podda, F. 2013. Geochemistry of rare earth  
724 elements in water and solid materials at abandoned mines in SW Sardinia (Italy).  
725 *J. Geochem. Explor.* 133, 149-159.
- 726 Migaszewski, Z. M., Gałuszka, A., Gowska, S. 2016. Rare earth and trace element

- 
- 727 signatures for assessing an impact of rock mining and processing on the  
728 environment: Wiśniówka case study, south-central Poland. *Environ. Sci. Pollut.*  
729 *Res.* 23, 24943-24959.
- 730 Migaszewski, Z., Gałuszka, A., Migaszewski, A. 2014. The study of rare earth  
731 elements in farmer's well waters of the Podwiśniówka acid mine drainage area  
732 (south-central Poland). *Environ. Monit. Assessm.* 186, 1609-1622.
- 733 Moraes, M. L., Ladeira, A. C. 2021. The role of iron in the rare earth elements and  
734 uranium scavenging by Fe-Al precipitates in acid mine drainage. *Chemosphere*,  
735 277, 130131.
- 736 Möller, P., Dulski, P., Gerstenberger, H., Morteani, G., Fuganti, A. 1998. Rare earth  
737 elements, yttrium and H, O, C, Sr, Nd and Pb isotope studies in mineral waters  
738 and corresponding rocks from NW-Bohemia, Czech Republic. *Appl. Geochem.*  
739 13 (8), 975-994.
- 740 Nesbitt, H. W. 1979. Mobility and fractionation of rare earth elements  
741 during weathering of a granodiorite. *Nature*, 279(19), 206.
- 742 Nordstrom, D. K., Blowes, D. W., Ptacek, C. J. 2015. Hydrogeochemistry and  
743 microbiology of mine drainage: an update. *Appl. Geochem.* 57, 3-16.
- 744 Nordstrom, D. K., Alpers, C. N. The geochemistry of acid mine waters. In *The*  
745 *Environmental Geochemistry of Mineral Deposits: Chapter 6: Processes,*  
746 *Methods and Health Issues*; Plumlee, G.S., Logsdon, M.J., Eds.; Society of  
747 Economic Geologists: Littleton, CO, USA, 1999; pp. 133-160.
- 748 Nozaki, Y., Zhang, J., Amakawa, H. 1997. The fractionation between Y and Ho in the

- 
- 749 marine environment. *Earth Planet. Sci. Lett.* 148, 329-340.
- 750 Ogawa, Y., Ishiyama, D., Shikazono, N., Iwane, K., Hoshino, T., Kajiwara, M.,  
751 Tsuchiya, N., Saini-Eidukat, B. Wood, S. A. 2019. Fractionation of rare earth  
752 elements (REEs) and actinides (U and Th) originating from acid thermal water  
753 during artificial and natural neutralization processes of surface waters. *Geochim.*  
754 *Cosmochim. Acta* 249, 247-262.
- 755 Ohta, A., Kawabe, I. 2001. REE(III) adsorption onto Mn dioxide and Fe  
756 oxyhydroxide: Ce(III) oxidation by Mn dioxide. *Geochim. Cosmochim. Acta* 65,  
757 695-703.
- 758 Olías, M., Cánovas, C. R., Basallote, D. B., Lozano, A. 2018. Geochemical behaviour  
759 of rare earth elements (REE) along a river reach receiving inputs of acid mine  
760 drainage. *Chem. Geol.* 493, 468-477.
- 761 Parkhurst, D.L., Appelo, C.A.J. 2013. Description of input and examples for  
762 PHREEQC version 3-a computer program for speciation, batch-reaction,  
763 one-dimensional transport, and inverse geochemical calculations. *US geological*  
764 *survey techniques and methods*, 6, 497.
- 765 Pérez-López, R., Delgado, J., Nieto J. M., Márquez-García, B. 2010. Rare earth  
766 element geochemistry of sulphide weathering in the São Domingos mine area  
767 (Iberian Pyrite Belt): a proxy for fluid-rock interaction and ancient mining  
768 pollution. *Chem. Geol.* 276: 29-4.
- 769 Pourret, O., Houben, D. 2018. Characterization of metal binding sites onto biochar  
770 using rare earth elements as a fingerprint. *Heliyon*, 4, e00543.

- 
- 771 Pourret, O., Davranche, M. 2013. Rare earth element sorption onto hydrous  
772 manganese oxide: A modeling study. *J. Colloid interface Sci.* 395, 18-23.
- 773 Pourret O., Davranche D., Gruau G., Dia A. 2007. Rare earth elements complexation  
774 with humic acid. *Chem. Geol.* 243, 128-141.
- 775 Rodushkin, I., Paulukat, C., Pontér, S., Engström, E., Baxter, D. C., Sörlin, D.,  
776 Pallavicini, N., Rodushkina, K. 2018. Application of double-focusing sector field  
777 icp-ms for determination of ultratrace constituents in samples characterized by  
778 complex composition of the matrix. *Sci. Total Environ.* 622-623, 203-213.
- 779 Schijf, J. Byrne R. H. 2004. Determination of  $\text{SO}_4\beta_1$  for yttrium and the rare earth  
780 elements at  $I = 0.66 \text{ m}$  and  $T = 25 \text{ }^\circ\text{C}$  - Implications for YREE solution  
781 speciation in sulfate-rich waters. *Geochim. Cosmochim. Acta* 68, 2825-2837.
- 782 Sharifi, R., Moore, F., Keshavarzi, B. 2013. Geochemical behavior and speciation  
783 modeling of rare earth elements in acid drainages at sarcheshmeh porphyry  
784 copper deposit, Kerman province, Iran. *Chem. Erde - Geochem.* 73(4), 509-517.
- 785 Smedley, P. L. 1991. The geochemistry of rare earth elements in groundwater from the  
786 Carnmenellis area, southwest England. *Geochim. Cosmochim. Acta* 55,  
787 2767-2779.
- 788 SMM. 2020. Shanghai Metals Market. <https://www.metal.com/> (accessed April 2021).
- 789 Stewart, B. W., Capo, R. C., Hedin, B. C., Hedin, R. S. 2017. Rare earth element  
790 resources in coal mine drainage and treatment precipitates in the Appalachian  
791 Basin, USA. *Int. J. Coal Geol.* 169, 28-39.
- 792 Sun, H. F., Zhao, F. H., Zhang, M., Z., Li, J. Q. 2012. Behavior of rare earth elements

- 
- 793 in acid coal mine drainage in Shanxi province, China. *Environ. Earth Sci.* 67(1),  
794 205-213.
- 795 Takahashi, Y., Manceau, A., Geoffroy, N., Marcus, M. A., Usui, A. 2007. Chemical  
796 and structural control of the partitioning of Co, Ce, and Pb in marine  
797 ferromanganese oxides. *Geochim. Cosmochim. Acta* 71(4), 984-1008.
- 798 Taylor, S. R. McClennan, S. M. 1988. The significance of the rare earths in  
799 geochemistry and cosmochemistry. In *Handbook on the Physics and Chemistry*  
800 *of the Rare Earths* (eds. K. A. Gschneidner Jr and L. Eyring), Vol. 11, pp.  
801 465-479, Elsevier, Amsterdam.
- 802 Tweed, S. O., Weaver, T. R., Cartwright, I., Schaefer, B. 2006. Behavior of rare earth  
803 elements in groundwater during flow and mixing in fractured rock aquifers: An  
804 example from the Dandenong Ranges, southeast Australia. *Chem. Geol.* 234,  
805 291-307.
- 806 U.S. Geological Survey. Rare Earth Statistics, in Kelly, T.D., and Matos, G.R., comps.,  
807 *Historical Statistics for Mineral and Material Commodities in the United States:*  
808 *U.S. Geological Survey Data Series 140*; US Geological Survey: Reston,  
809 Virginia, USA, 2014. Available online:  
810 <http://minerals.usgs.gov/minerals/pubs/historicalstatistics/> (accessed on 14  
811 August 2021).
- 812 Van Gosen, B. S., Verplanck, P. L., Long, K. R., Gambogi, J., Robert, R., Seal, I. I.  
813 *The Rare-Earth Elements: Vital to Modern Technologies and Lifestyles* (No.  
814 2014-3078). Available online:



- 
- 815 <https://pubs.usgs.gov/fs/2014/3078/pdf/fs2014-3078.pdf> (accessed on 5 April  
816 2021).
- 817 Vass, C. R., Noble, A., Ziemkiewicz, P. F. 2019. The occurrence and concentration of  
818 rare earth elements in acid mine drainage and treatment by-products: part  
819 1-initial survey of the northern Appalachian coal basin. *Mining, Metall. Explor.*  
820 36(5), 903-916.
- 821 Vaziri Hassas, B., Rezaee, M., Pisupati, S.V. 2021. Effect of various ligands on the  
822 selective precipitation of critical and rare earth elements from acid mine drainage.  
823 *Chemosphere* 280, 130684
- 824 Verplanck, P. L., Nordstrom, D. K., Taylor, H. E., Kimball, B. A. 2004. Rare earth  
825 element partitioning between hydrous ferric oxides and acid mine water during  
826 iron oxidation. *Appl. Geochem.* 19, 1339-1354.
- 827 Wall, F. 2014. Rare earth elements. In: Gunn G. (Ed.) *Critical Metals Handbook*. John  
828 Wiley & Sons, Ltd., 312-339.
- 829 Wallrich, I. L., Stewart, B. W., Capo, R. C., Hedin, B. C., Phan, T. T. 2020.  
830 Neodymium isotopes track sources of rare earth elements in acidic mine waters.  
831 *Geochim. Cosmochim. Acta* 269, 465-483.
- 832 Wilkin, R. T., Lee, T. R., Ludwig, R. D., Wadler, C., Brandon, W., Mueller, B., Davis,  
833 E., Luce, D., Edwards, T. 2021. Rare-earth elements as natural tracers for in situ  
834 remediation of groundwater. *Environ. Sci. Technol.* 55 (2), 1251-1259.
- 835 Wood, S. A. 1993. The aqueous geochemistry of the rare-earth elements: critical  
836 stability constants for complexes with simple carboxylic acids at 25°C and 1 bar

- 
- 837 and their application to nuclear waste management. *Eng. Geol.* 34, 229-259
- 838 Wood, S. A. 1990. The aqueous geochemistry of the rare-earth elements and yttrium:  
839 2. Theoretical predictions of speciation in hydrothermal solutions to 350°C at  
840 saturation water vapor pressure. *Chem. Geol.* 88, 99-125
- 841 Worrall, F., Pearson, D. G. 2001. Water-rock interaction in an acidic mine discharge as  
842 indicated by rare earth element patterns. *Geochim. Cosmochim. Acta* 65(18),  
843 3027-3040.
- 844 Yang, X. J., Li, A. J., Li, X. L., Wu, Y. D., Zhou, W. B., Chen, Z. H. 2013. China's  
845 ion-adsorption rare earth resources, mining consequences and preservation.  
846 *Environ. Dev.* 8 (1), 131-136.
- 847 Zhang, W., Honaker, R., 2020. Process development for the recovery of rare earth  
848 elements and critical metals from an acid mine leachate. *Miner. Eng.* 153,  
849 106382
- 850 Zhang, J., Liu, C. Q. 2004. Major and rare earth elements in rainwaters from Japan  
851 and East China Sea: natural and anthropogenic sources. *Chem. Geol.* 209(3-4),  
852 315-326.
- 853 Zhou, H. Y., Greig, A., Tang, J., You, C. F., Yuan D. X., Tong, X. N., Huang, Y. 2012.  
854 Rare earth element patterns in a Chinese stalagmite controlled by sources and  
855 scavenging from karst groundwater. *Geochim. Cosmochim. Acta* 83, 1-18.
- 856 Zhu, Z. Z., Liu, C. Q, Wang, Z. L., Liu, X. L., Li, J. 2016. Rare earth elements  
857 concentrations and speciation in rainwater from Guiyang, an acid rain impacted  
858 zone of southwest China. *Chem. Geol.* 442, 23-34.
- 859

---

860 **Figure captions**

861 **Figure 1** Study area and sampling locations (MW: mine water samples; NDT:  
862 samples from nitrification-denitrification treatment process in a treatment plant;  
863 CPT: samples from coagulating-precipitation treatment process in a treatment  
864 plant; GW: groundwater sample; R: rock samples; SS: sediment samples; SG:  
865 sludge samples)

866 **Figure 2** Piper plot of water sample compositions

867 **Figure 3** Changes of REE and Y with individual water samples ((a): pH, total REE  
868 and Y ( $\sum\text{REE}+\text{Y}$ ), total Fe ( $\text{Fe}_T$ ), Fe(II), Al and Mn concentrations; (b):  $\text{SO}_4^{2-}$ , Sr,  
869 Rb, Zn, U, and Pb concentrations)

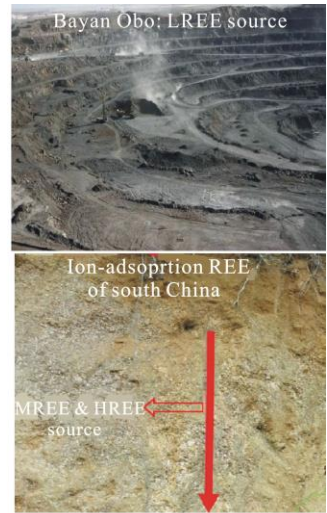
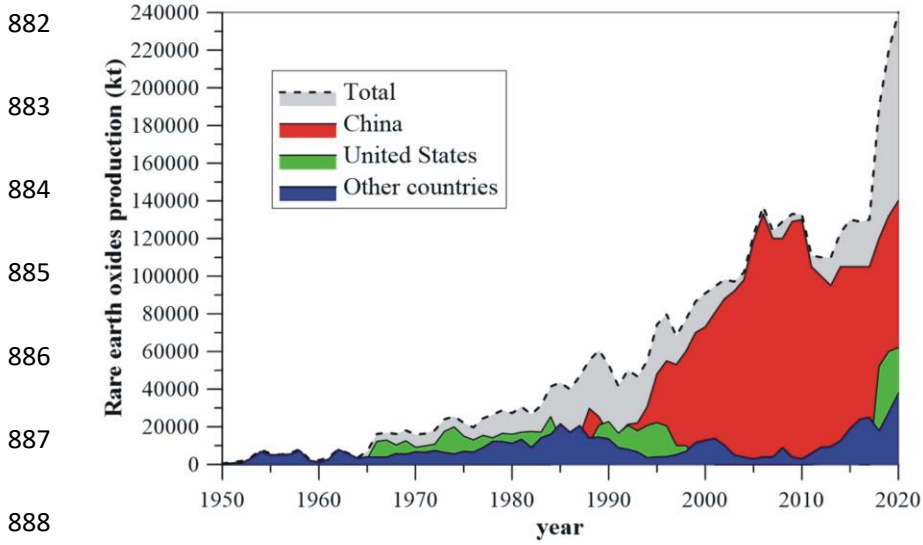
870 **Figure 4** Upper continental crust (UCC) normalized REE+Y patterns for water  
871 samples and speciation modeling results ((a) and (b): MW sample; (c) and (d):  
872 NDT sample; (e) and (f): CPT sample; (g) and (h): GW sample)

873 **Figure 5** Upper continental crust (UCC) normalized REE+Y patterns for rock,  
874 sediment and sludge samples from mine water treatment (R: rock; SS: sediment;  
875 SG: sludge)

876 **Figure 6** (a): a relationship between total REE+Y ( $\sum\text{REE}+\text{Y}$ ) and  $\text{SO}_4^{2-}$ , Al, Fe, and  
877 Mn concentrations; (b): distinct fractionations of REE+Y; (c): Eh-pH diagram for  
878 Ce-H<sub>2</sub>O system (modified from Wilkin et al. (2021)); (d) a relationship between  
879 pH and Ce/Ce\*.

880

881



888

### graphical abstract

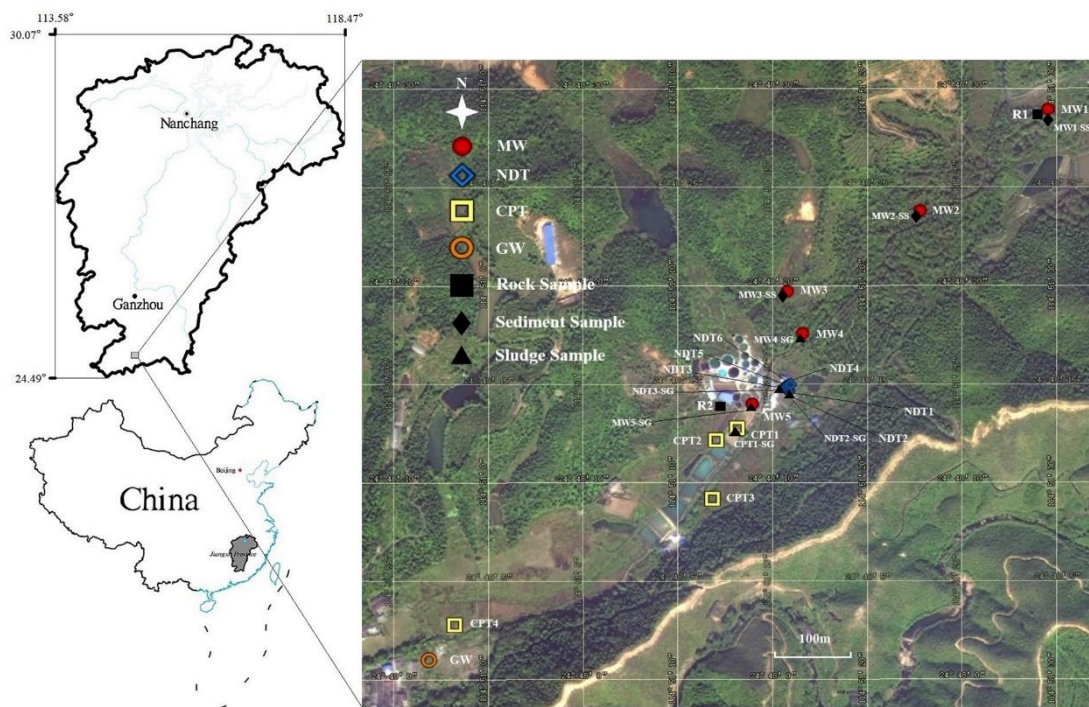
889

890

891

892

893



894

895

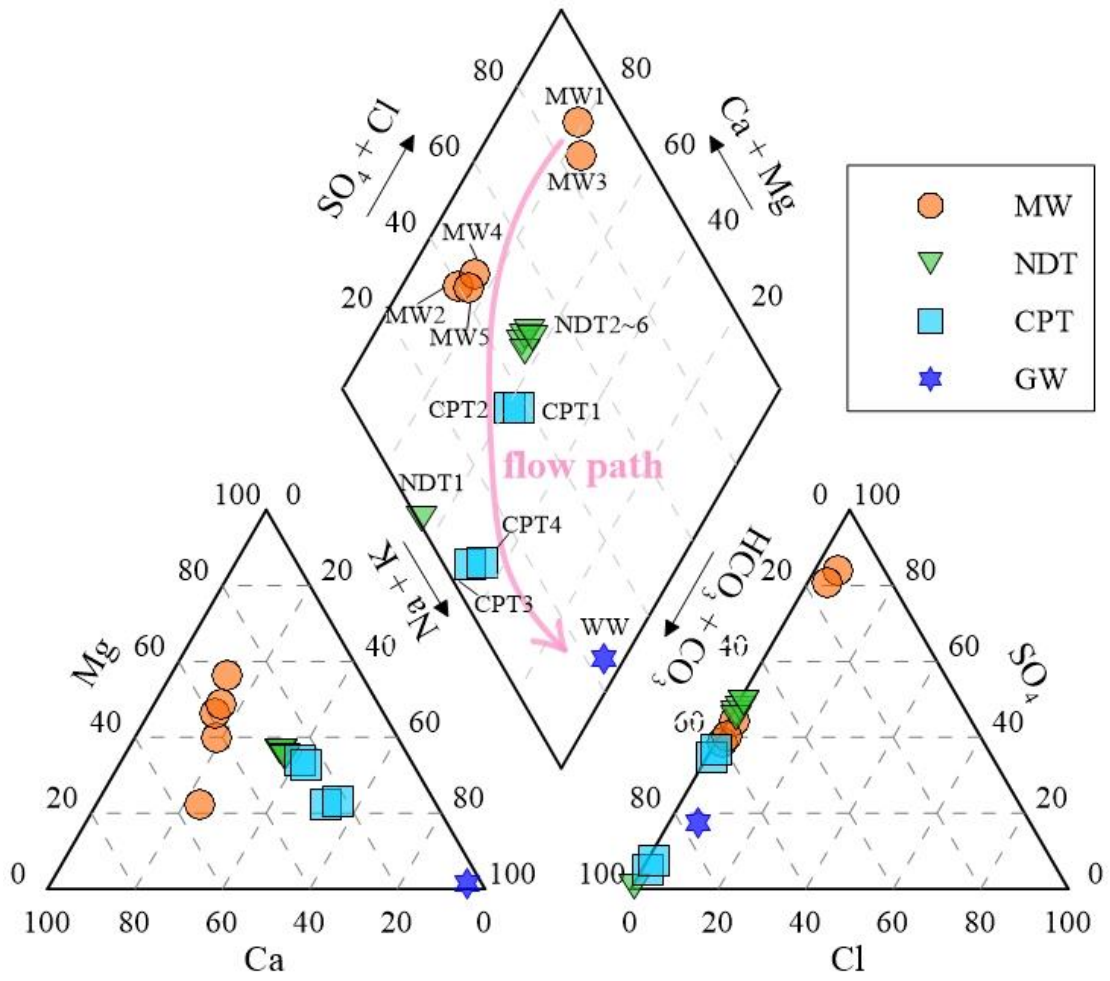
896

897

Fig. 1

898

899



900

901

Fig. 2

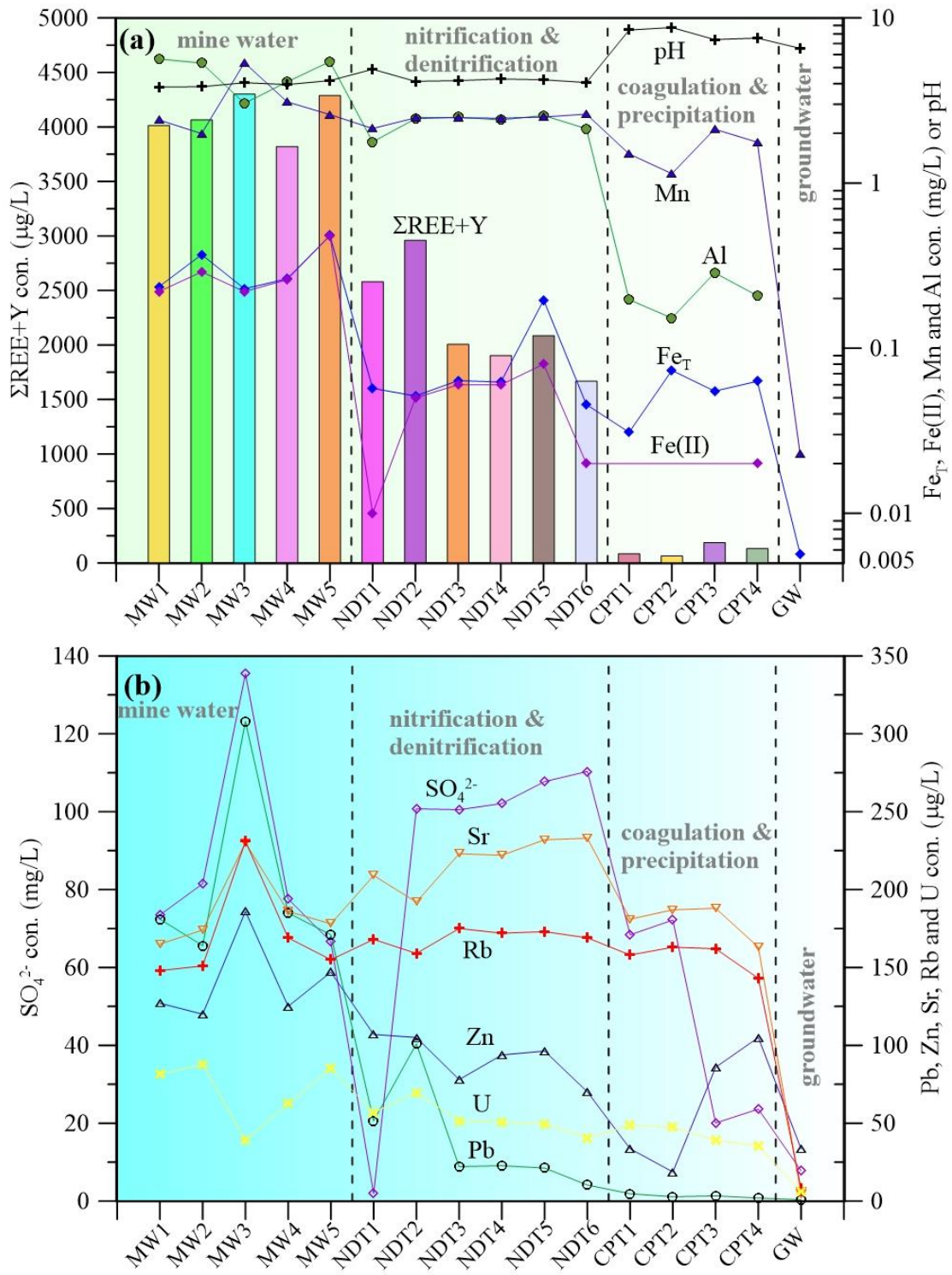


Fig. 3

902

903

904

905

906



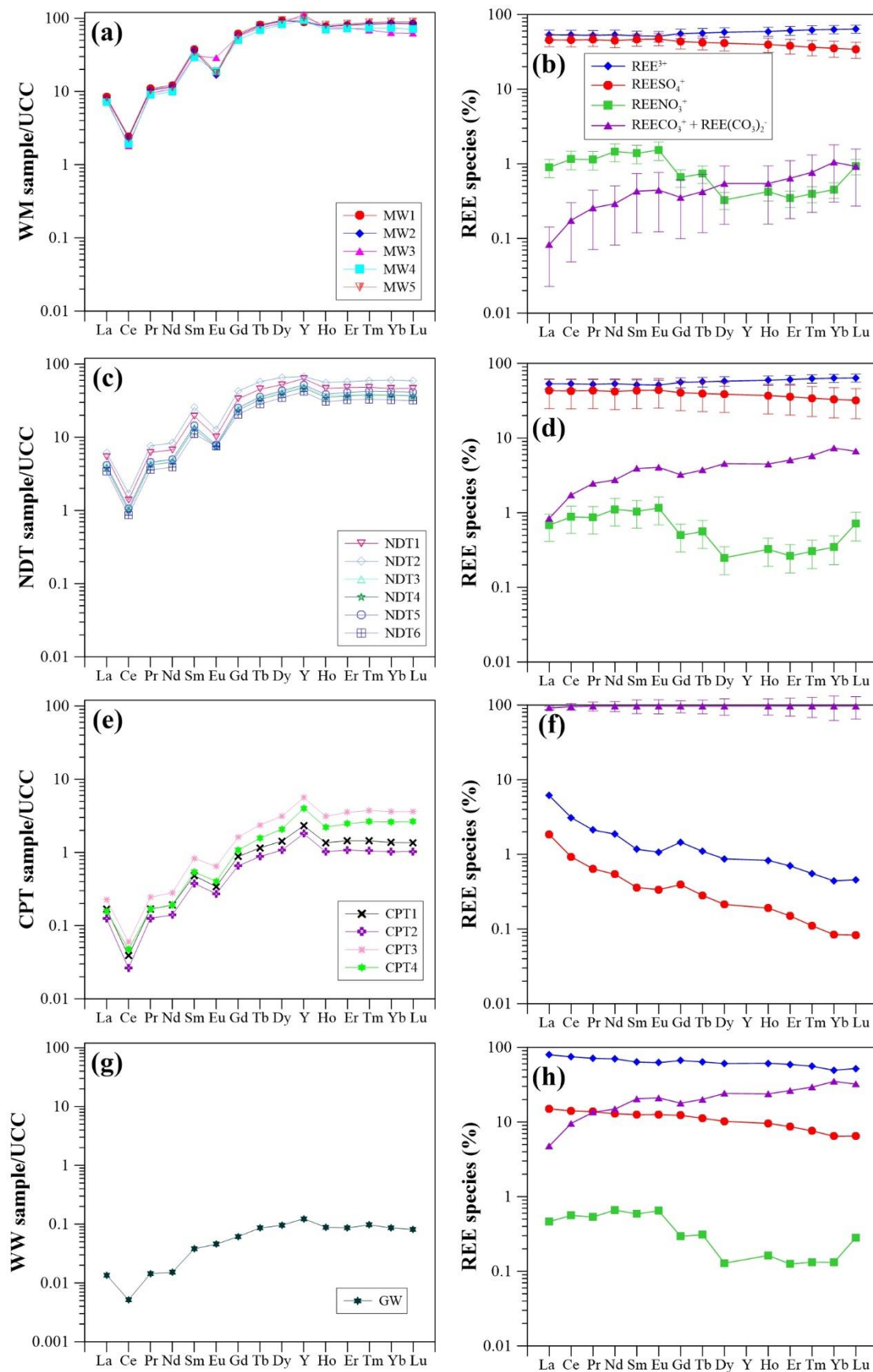


Fig. 4

907

908



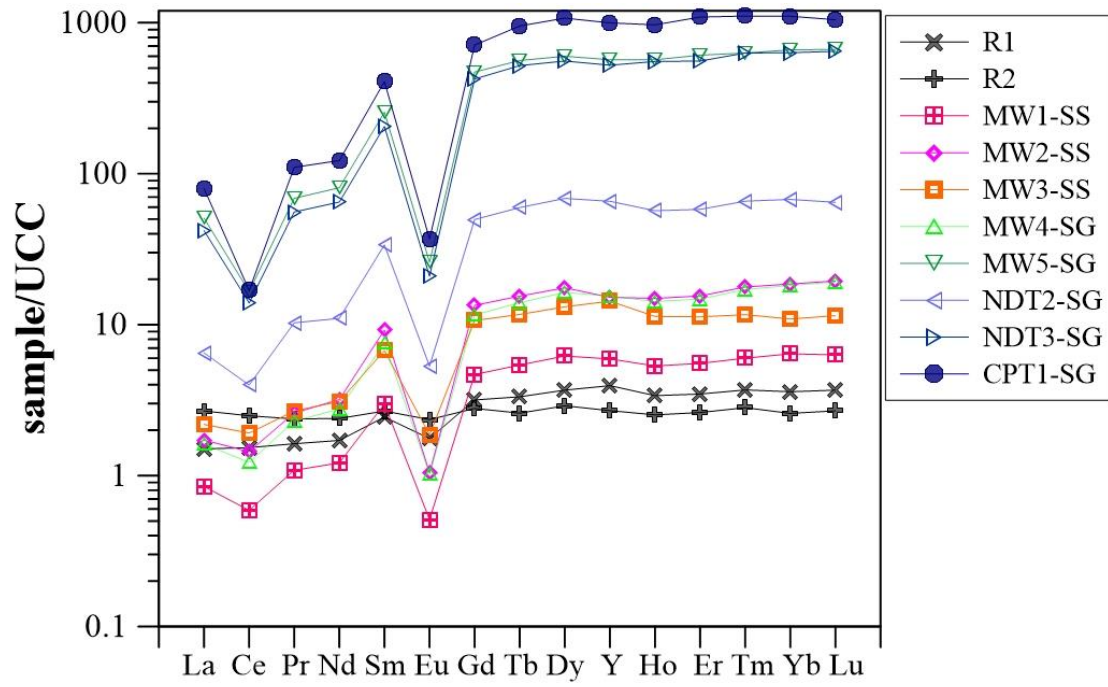


Fig. 5

909

910

911

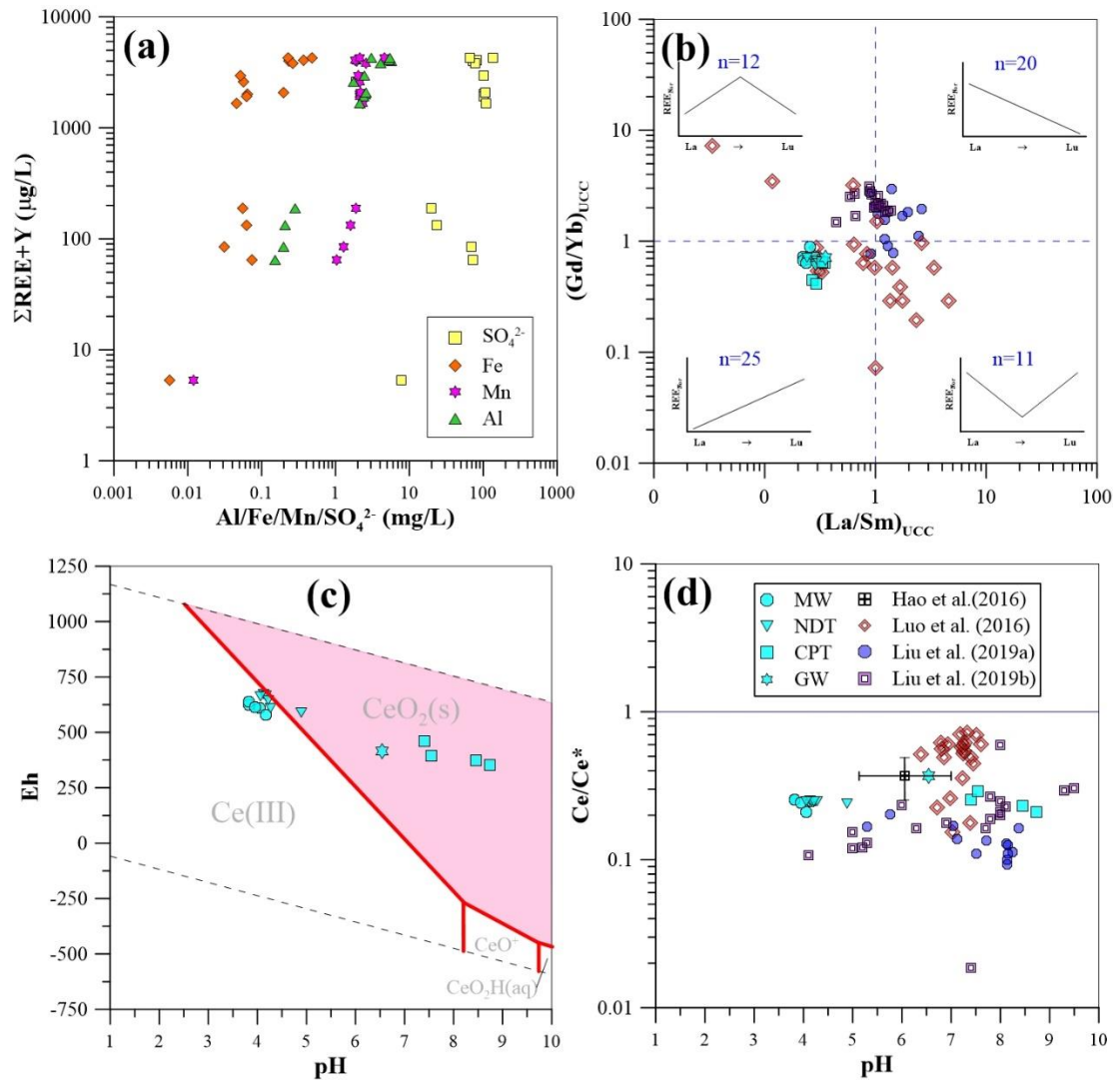


Fig. 6

912

913

914

915