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**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**

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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

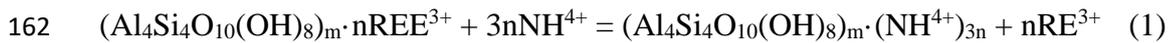
128 The mining site (longitude: 114°47'28", latitude: 24°54'25") is located in the
129 Jiangxi province, southern China (Fig. 1), and has a subtropical monsoon climate. The
130 temperature ranges from 39°C to -3.1°C (recorded historically), with an annual

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 m³/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 km². 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-SO₄, Ca-SO₄-HCO₃, Ca-Cl, and Ca-HCO₃-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 (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 μm 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 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) H_2SO_4 . Samples for REE+Y analysis were sampled in 500 mL
182 HDPE bottles following an acidification with 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), NH₃-N, NO₂-N, and S²⁻ 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 HNO₃ 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 HNO₃ (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 ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵¹Eu, ¹⁶³Dy,
230 ¹⁶⁵Ho, and ¹⁷²Yb, and a high resolution mode (HR, m/Δm approximately 12000) was
231 used for monitoring the isotopes ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶⁶Er, ¹⁶⁹Tm, and
232 ¹⁷⁵Lu, 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⁺ on the ¹⁵¹Eu and
235 ¹⁵³Eu 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 2θ of
245 20° to 70° and a step size of 0.02° . 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 CO_3^{2-} , SO_4^{2-} , OH^- , Cl^- , F^- , and 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 REECO_3^+ were taken from Luo and Byrne (2004), and those for
257 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 Ca^{2+} and Mg^{2+} , and NO_3^- and SO_4^{2-} were the dominant anions,
274 while Cl^- concentrations were < 5 mg/L. Water types thus determined for MW 1 to 5
275 were Ca/Mg- SO_4 and Ca/Mg- HCO_3/SO_4 . Over the CPT pathway (CPT 1 to 4), the
276 major cation composition shifted towards Na^+ predominance (52 to 104 mg/L),
277 followed by Mg^{2+} (23 to 26 mg/L) and Ca^{2+} (31 to 48 mg/L), while the dominant
278 anion was HCO_3^- (>156 mg/L), hydrochemical type for these samples being
279 Na-Ca/Mg- 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- HCO_3 - SO_4 . The GW collected from the village was of
282 Na- HCO_3 water type.

283 Total dissolved Fe (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 SiO₂ (66 to 68 wt.-%), while Al₂O₃ was the
333 second most abundant component (9 to 18 wt.-%), followed by Fe₂O₃ (4 to 7 wt. %)
334 (Table S4). Composition of surface sediment samples ranged from 61 to 76 wt. % for
335 SiO₂, 10 to 3 wt. % for Al₂O₃, and 2 to 5 wt. % for Fe₂O₃. Other metal oxides were
336 generally < 6 wt. %. For the sludge samples, SiO₂ contents ranged from 60 to 67
337 wt. %, Al₂O₃ from 15 to 18 wt. %, and Fe₂O₃ 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)_{UCC} 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 μm . 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 (KAlSi_3O_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 (ΣREE) 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 SO_4^{2-} and NO_3^- concentrations (Table S2 and S3). Although a poor positive
385 correlation was observed between SO_4^{2-} and $\Sigma\text{REE}+\text{Y}$ concentrations ($r^2 = 0.18$, $p =$
386 0.1) (Fig. 6a), the predominance of 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 NO_3^- concentrations, and the relatively
390 constant 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 SO_4^{2-} and 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 Σ 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 Σ REE+Y concentrations in MW and NDT samples where
430 $\text{pH} < 4.9$ occurred (Fig. 3a). A decrease in Σ 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 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 CO_3^{2-} , due to preferential stabilization of HREE relative to
508 LREE during REE+Y- CO_3^{2-} complexation (Guo et al., 2010; Liu et al., 2016).
509 Although SO_4^{2-} complexes and free ions were the dominating lanthanide species in
510 MW and NDT samples (Fig. 4), 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 OH^- , NO_3^- , PO_4^{3-} , F^- and 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 (Ce/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_2 and/or $\text{Ce}(\text{OH})_4$ 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_2O 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_2 (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_2 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.

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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 (Fe_T), Fe(II), Al and Mn concentrations; (b): SO_4^{2-} , Sr,
869 Rb, Zn, U, and Pb concentrations)

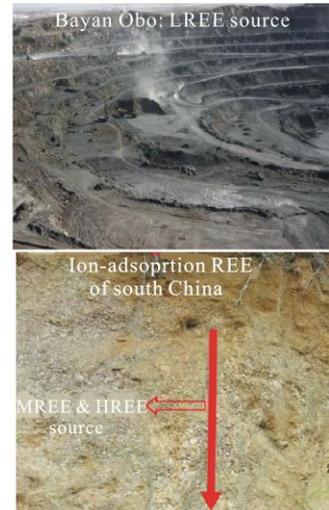
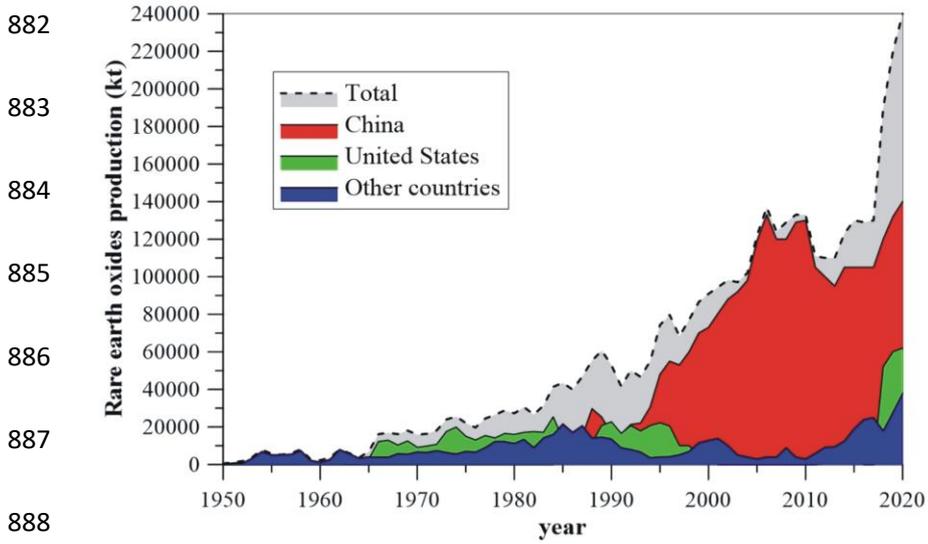
870 **Figure 4** Upper continental crust (UCC) normalized REE+Y patterns for water
871 samples and speciation modeling results ((a) and (b): MW sample; (c) and (d):
872 NDT sample; (e) and (f): CPT sample; (g) and (h): GW sample)

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 SO_4^{2-} , Al, Fe, and
877 Mn concentrations; (b): distinct fractionations of REE+Y; (c): Eh-pH diagram for
878 Ce-H₂O system (modified from Wilkin et al. (2021)); (d) a relationship between
879 pH and Ce/Ce*.

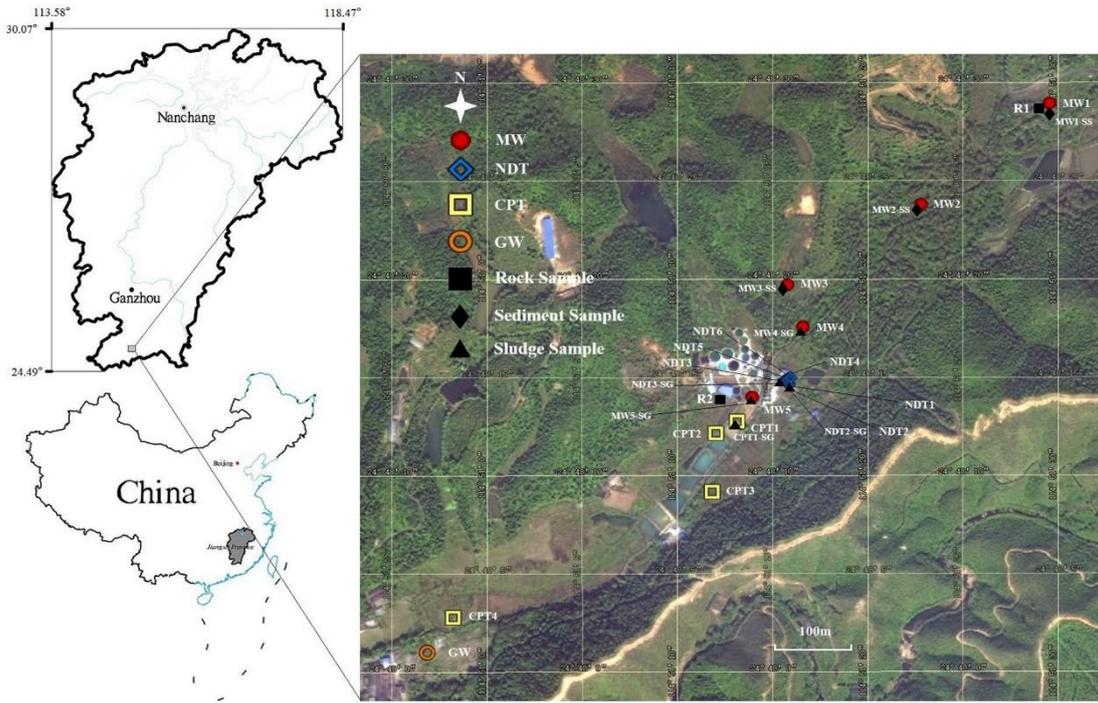
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graphical abstract

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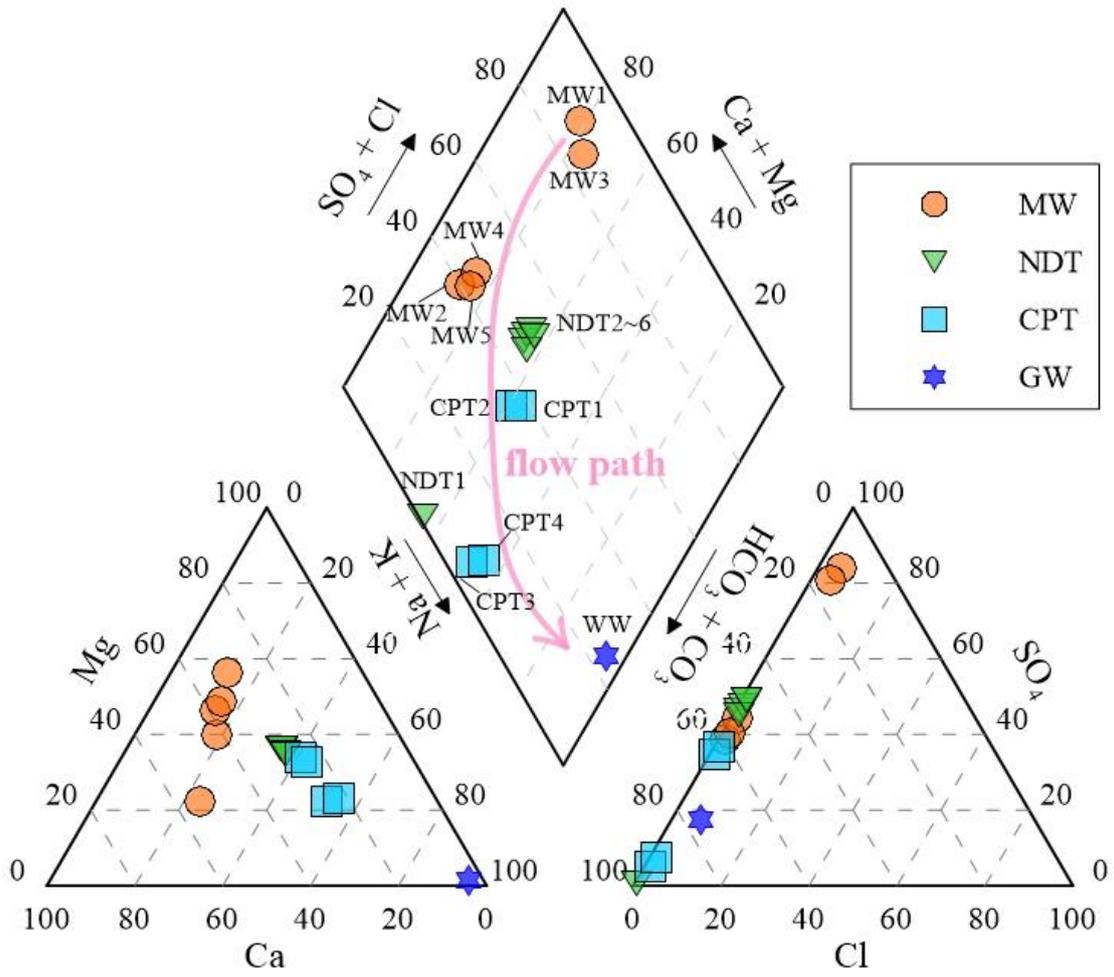
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Fig. 1

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Fig. 2

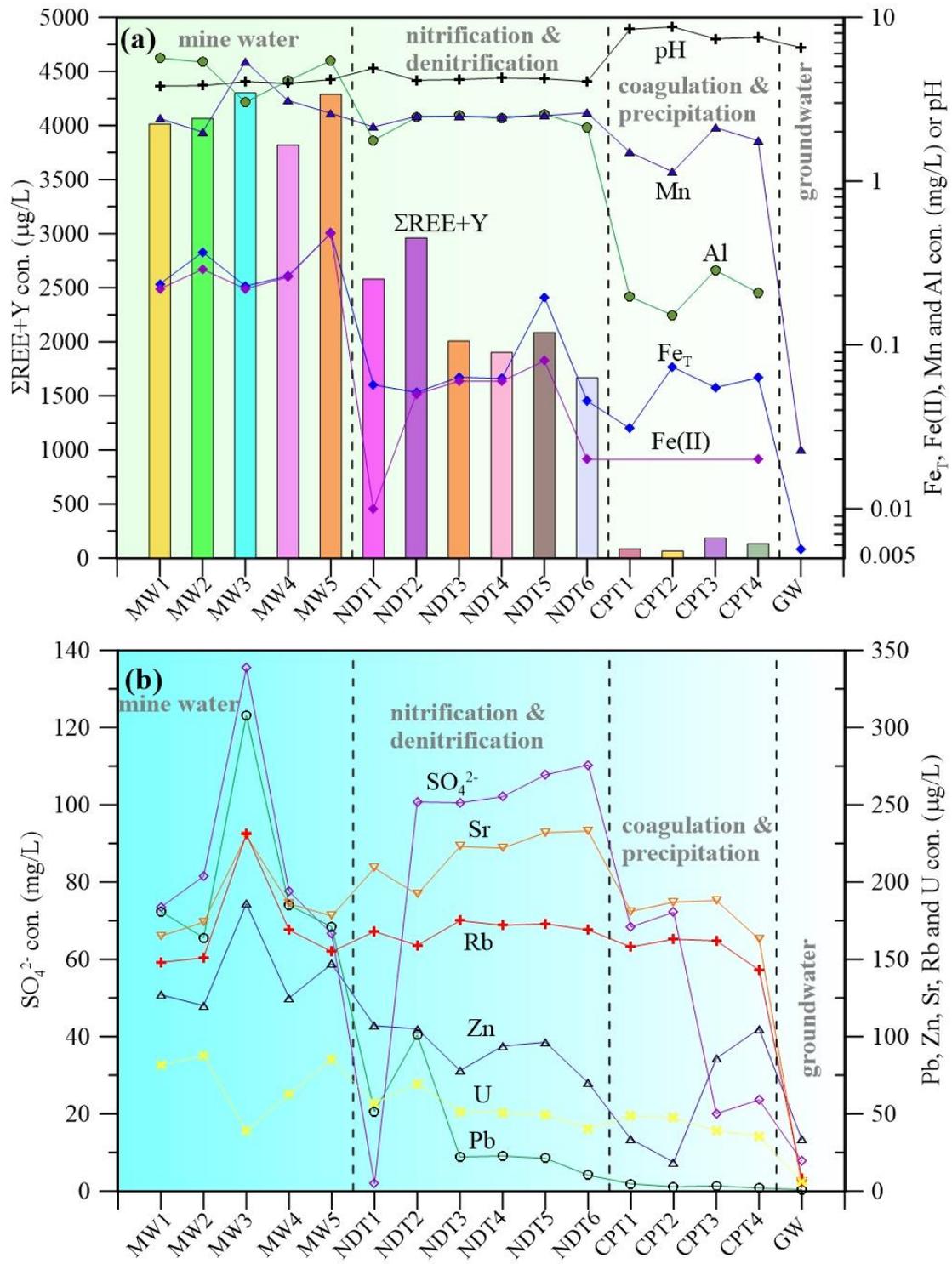


Fig. 3

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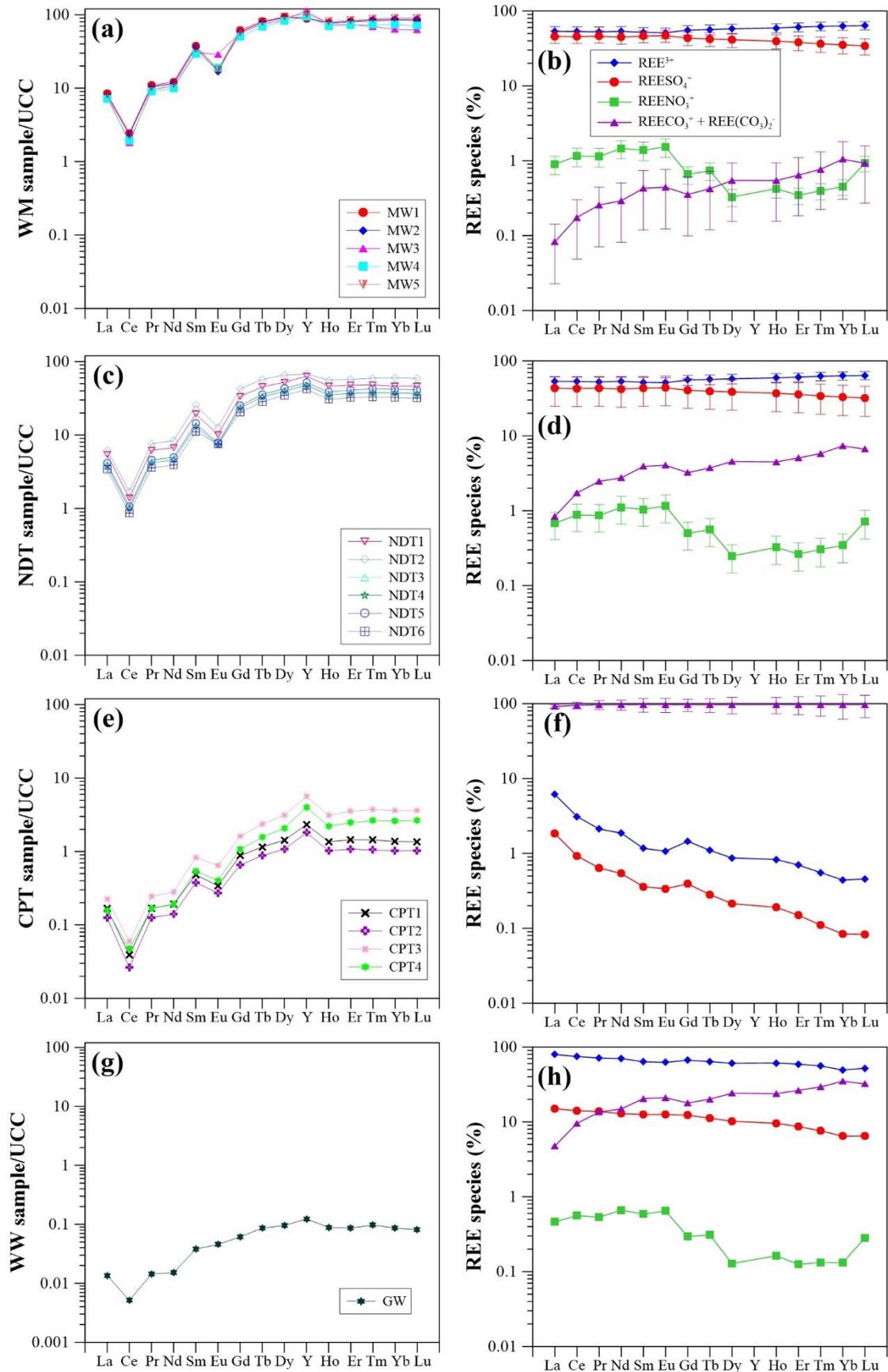


Fig. 4

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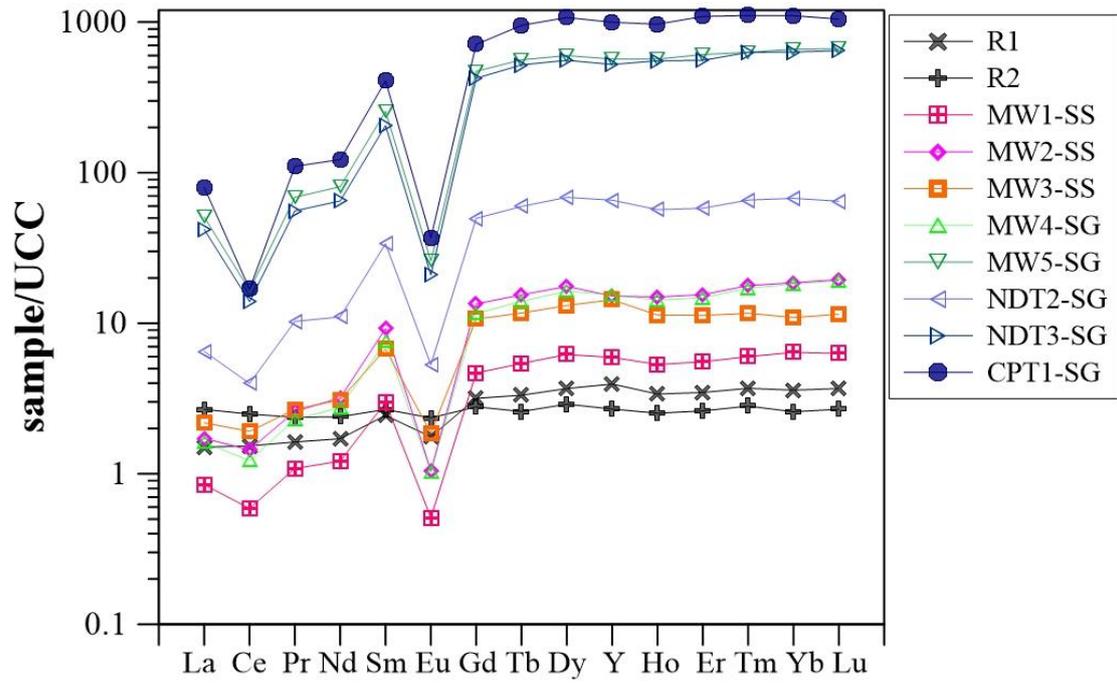


Fig. 5

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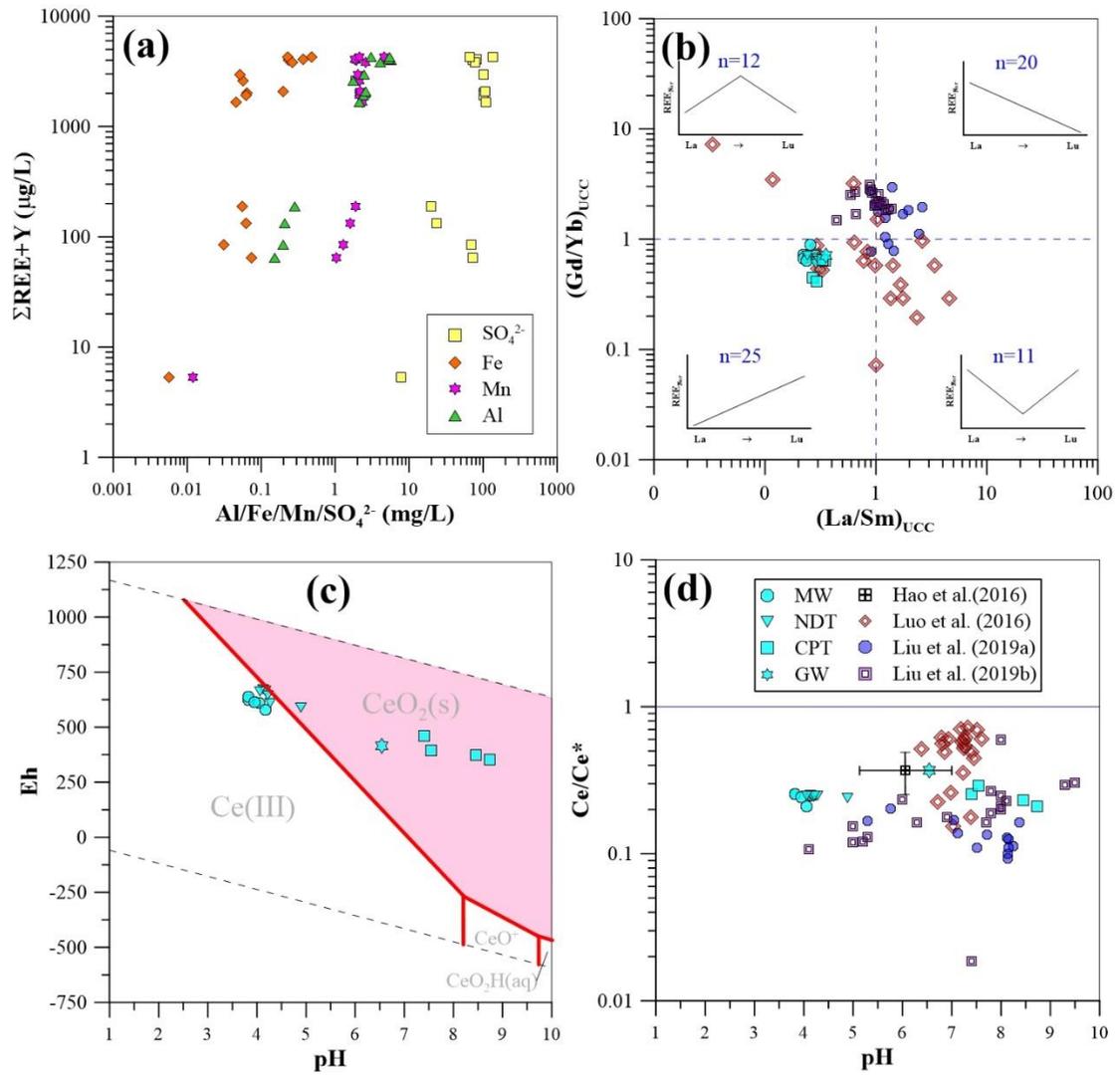


Fig. 6

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