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1 **Geochemical characteristics of rare earth elements in sediments of**
2 **the North China Plain: implication for sedimentation process**

3
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20

21 **Abstract:** Rare earth elements (REE) are powerful tracers for our understanding of
22 sedimentary provenance and depositional processes. The present study investigated
23 geochemical characteristics of REE in 226 sediment samples collected from piedmont,
24 central and littoral plains of the North China Plain. Results showed that average total
25 REE concentrations exhibited a decreasing trend as piedmont > central > littoral, and
26 82%, 70% and 67% samples had total REE concentrations higher than the value of
27 Upper Continental Crust (UCC). The variation in REE concentrations was associated
28 with sedimentary provenance and sediment physicochemical properties. Ternary
29 diagrams of sandstone classification and $Al_2O_3-CaO+Na_2O-K_2O$ reflected that
30 sediments originated from greywackes and they have been experienced an incipient to
31 intermediate chemical weathering with piedmont sediments to a higher degree.
32 Average Chemical Index of Alteration values are 68, 51 and 55 in piedmont, central
33 and littoral sediments, respectively. Sediment North American Shale Composite
34 (NASC)-normalized patterns were characterized by light REE (LREE) enrichment
35 over heavy REE (HREE) and coherent negative Eu anomalies (Eu/Eu^* ranging
36 between 0.57 and 1.00). Value of $(La/Yb)_{NASC}$ ranged from 0.86 to 1.15 (average
37 1.23), and from 1.03 to 1.49, and from 0.91 to 1.49 in three zones, indicating REE
38 fractionation from piedmont to littoral occurred over sedimentation processes. A
39 positive correlation between $(La/Yb)_{NASC}$ and total REE concentrations was observed
40 in piedmont and central sediment samples, implying that LREE were preferentially
41 enriched over HREE with an accumulation of REE. While this correlation was not
42 found in littoral sediment samples, where a general decreasing trend along depth for

43 REE concentrations existed. Results of present study shows implications for using

44 REE as a tracer of sedimentary provenance from a basin scale.

45

46 Keywords: Lanthanides; Geochemistry; Sedimentation; Fractionation; Critical Zone

47

48 **1. Introduction**

49 Rare earth elements are the lanthanides with atomic numbers ranging from 57 (La,
50 lanthanum) to 71 (Lu, lutetium) (Henderson, 1984) as well as yttrium (Y, atomic
51 number 39) and scandium (Sc, atomic number 21; Tyler, 2004). The geochemical
52 signatures of rare earth elements and yttrium (thereafter denoted REE) in sediments
53 and sedimentary rocks are powerful tracers in delineating the processes that govern
54 them. These include magmatism, chemical weathering, diagenesis, erosion and
55 water-rock interactions (McLennan, 1989). As a result, the concentrations and
56 fractionations of REE in sediments and soils have received considerable attention in
57 the past few decades.

58 Numerous investigations have been devoted to studying geochemical behaviors
59 and mobility of REE in different sediments and soils, including lake, river and marine
60 sediments (Pourret and Tuduri, 2017; Xu et al., 2018, Wang et al., 2018; Consani et al.,
61 2020), mining surroundings (Hu et al., 2004; Wang and Liang, 2015), wetlands
62 (Davranche et al., 2011; Cheng et al., 2012), agricultural areas (Silva et al., 2015; Han
63 et al., 2017), alluvial deposits (Pédrot et al., 2015; Xie et al., 2014), unconsolidated
64 clay sediments (Guo et al., 2010; Sá Paye et al., 2016) and sedimentary rocks
65 (McLennan, 2001; Šmuc et al., 2012). It's recognized that REE concentrations and
66 distributions in sediments depend on sedimentary provenance and sediment's
67 physicochemical properties. Significant correlations between REE concentrations and
68 contents of clay and metals (i.e., Fe, Mn, Al) were observed by Mihajlovic and
69 Rinklebe (2018); while pH value and cation exchange capacity were shown not

70 important factors in their study. Grain size impacted REE concentrations in sediment
71 as well. This is indicated by the results of Kimoto et al. (2006), showing that
72 decreasing grain size generally increased REE concentrations due to that clay
73 minerals could host REE (Laveuf and Cornu, 2009). More specific, the impact of clay,
74 silty and sand fractions on solid REE was recently investigated in different soil
75 profiles (Mihajlovic and Rinklebe, 2018). Presence of Fe/Mn oxides was another
76 factor influencing REE in sediments/soils, and more REE can be accumulated by
77 amorphous Fe/Mn oxides as compared to crystalline ones (Yan et al., 1999; Compton
78 et al., 2003).

79 Constituents of REE in sediments and soils for a large part result from natural
80 processes. A global distribution pattern of REE in the soils/sediments was recently
81 evaluated by Adeel et al. (2019), which was achieved by spatially visualized the
82 distribution of the REE concentrations in soils/sediments derived from all over the
83 world. Results obtained from the study showed that total REE concentrations of
84 agriculture soils/sediments ranged from 83 to 9840 mg/kg and concentrations of light
85 REE (LREE) were higher than heavy REE (HREE). This indicates that, in addition to
86 the natural processes, anthropogenic inputs contribute to the REE concentrations in
87 sediments/soils in some individual regions. Indeed, fertilization with REE-bearing
88 fertilizers and infiltration of residuals was suggested to be the main mechanism of
89 agriculture-sourced REE entering into soils and sediments (Hu et al., 2004). However,
90 mechanisms for REE mobilization in different soils/sediments and the potential risks
91 of long-term exposure to REE-abundant environment are not adequately understood.

92 Average REE concentration in China's soil was established to be 177 mg/kg
93 (Liang et al., 2005), being comparable to the value (189 mg/kg) in the earth's crust
94 (Wei et al. 1991). China is one of the countries that early widely applied REE in
95 various sectors (Pang et al., 2002; Hu et al., 2006), such as agriculture, the REE have
96 been used as a promoter for crops since 1990s. This has led to high REE pollution
97 levels (i.e. La >80; Nd >85; Sm >45) (Adeel et al., 2019; and references therein).
98 Indeed, sediment and soil contaminations caused by elevated REE have been reported
99 in various regions across China, including in Poyang lake (Wang et al., 2018), Baotou
100 city (Li et al., 2010), Tibet plateau (Wu et al., 2018), Jiaozuo Bay (Zhang and Gao,
101 2015), Sanjiang Plain (Cheng et al., 2012) and Liaodong Bay (Lin et al., 2013). The
102 North China Plain (NCP) is one of the largest sedimentary basin in Asia (Xing et al.,
103 2013), and is provincial politics, economy and culture center of China. The plain is
104 characterized by large population (> 0.35 billion) and highly-developed agricultural
105 industry, which plays an important role in the nation's grain manufacture (Chen and
106 Ni, 1987; Kendy et al., 2004). The densely-populated and industrialized areas were
107 shown to be accompanied by increased discharge of REE into environment (i.e., Gd
108 and Sm) (Kulaksız and Bau, 2013; Hatje et al., 2016), due to REE applications in
109 industry, medicine as well as agriculture. Studies concerning REE concentrations in
110 sediments of the NCP have been performed (Wei et al., 2010; Liu et al., 2016; Zhang
111 and Gao, 2015; Liu et al., 2019a, b), but a full of investigation of mobility,
112 distributions and behaviors of REE in sediments is still lacking. This would hinder a
113 systematical evaluation of REE levels as well as the possible anthropogenic impact,

114 which is vital for establishing a baseline of distribution and background of REE
115 concentration in the contaminated sediments and for administrating regulation
116 guidelines (Alfaro et al., 2018; Consani et al., 2020). Therefore, the objectives of this
117 study are to: (i) investigate REE concentration and fractionation characteristics in
118 sediments collected from three zones; (ii) characterize the relationships between REE
119 distribution and sediment properties; (iii) provide dataset concerning REE
120 geochemistry for future comparative studies in the region.

121 **2. Material and methods**

122 2.1 Study area

123 The North China Plain (NCP) is located in the eastern China with longitude of
124 112°30'~119°30'E, and latitude of 34°46'~40°25'N. The terrains are mostly plains with
125 two mountainous regions (Yanshan and Tanghang mountains) bounding to the north
126 and south, and an oceanic region (Bohai Bay) to the east (Chen et al., 1999),
127 respectively. The plain has a total area of approximately 31×10^4 km² and population
128 of about 0.35 billion inhabitants. The NCP has a semi-arid humid climate with a
129 temperature range of -23 °C~42.7 °C (in history). Average annual rainfall ranges from
130 500 mm to 600 mm, mostly (>74%) dominating in summer. Average annual
131 evaporation is 1.5 to 3 times of annual rainfall.

132 The NCP is one of largest sedimentary basins in Asia (Xing et al., 2013).
133 According to Chen et al. (1999), the NCP's geological strata are comprised of four
134 stratigraphic areas: Yinshan-Nuruerhu, Yanshan, Taihangshan and Hebei, with ages

135 ranging from the oldest Archaeozoic to the newest Holocene. Formations in study
136 area have been declining since the Cenozoic due to neotectonics. Geographically, the
137 plain generally decreases from the north to the east with a slope of 0.3‰~0.6‰, and
138 thus it's divided into three zones: piedmont alluvial-proluvial plain, central
139 alluvial-lacustrine plain and littoral plain.

140 Surface sediments in the NCP mainly are Cenozoic deposits with ages from
141 Paleogene to Holocene. Lower Tertiary stratum is composed of red mudstone with red
142 and gray sandstone being interbedded. Upper Tertiary strata are characterized by
143 consolidated to semi-consolidated alluvial-diluvial deposits, including siltstone,
144 mudstone, sandstone and pebbly sandstone. Quaternary sediments are divided into
145 four groups from top to bottom: Holocene (Q₄), Upper (Q_{3m}), Middle (Q_{2c}) and
146 Lower (Q_{1n}) Pleistocene (Chen, 1999). The Holocene sediments group has a
147 thickness of 5 m to 40 m, and mainly consists of yellow and gray sandy loam, fine
148 sand and clay being interbedded with sandy gravel. The Upper Pleistocene is alluvial,
149 diluvial and eolian losses and yellow loam. The Middle Pleistocene stratum is
150 widely distributed in intermountain basin and foothills, and consist of red and brown
151 clay, loam and sandy loam, and red mud pebble layers. The Lower Pleistocene
152 sediments group has a buried depth of 350 m to 500 m with a thickness of 80 m to
153 100m, and it's mainly loam, sand loam and lenticular sand layers.

154 Piedmont alluvial-proluvial sediments are suggested to derive from Taihang and
155 Yanshan mountains by weathering, transport and sedimentation process. Central
156 alluvial-lacustrine sediments are deposited from materials carried by Yellow River

157 and Zhangweinan River running from SW to NE since middle Pleistocene (Shao et al.,
158 1989). The littoral plain forms with interactions between terrene and ocean, and
159 sedimentary deposits come from terrestrial rivers draining into Bohai Bay eventually.

160 2.2 Sediment sampling

161 Sediment samples were taken from three boreholes (Y09, S30 and H02) drilled
162 in three different zones (Fig. 1) of the NCP in the July of 2013. The core sediments
163 were sampled with an interval generally ranging between 1 m and 2 m. Slurries and
164 muds attached on the surface of the core sediments were scrapped off to avoid
165 possible cross contaminations. The samples were parceled with silver paper and were
166 stored in clean plastic bags which were immediately filled with pure N₂ gas for further
167 preservation. All the sealed core sediments were placed in a shading environment with
168 temperature below 4 °C during sampling. Finally, the samples were transported to
169 laboratory and preserved in a freezer before analysis.

170 2.3 Sediment analysis

171 All samples used for major and minor constituents analyses were dried under
172 room temperature in the lab, and were ground to grain size <74 μm with an agate
173 mortar for analysis. The X-ray fluorescence (XRF) (ARL Advant X) technique was
174 used for measurement of various oxides (SiO₂, Fe₂O₃, Al₂O₃, MgO, CaO, Na₂O, K₂O,
175 MnO, P₂O₅ and TiO₂) following the national standard method (GB/T 14506).
176 Sediment samples were prepared with a glass flux sheet method. Specifically, 0.7 g
177 (±0.001) sample was firstly placed in a 25 mL porcelain crucible; followed by

178 addition of 5.2 g (± 0.001) anhydrous lithium tetraborate, 0.4 g (± 0.001) lithium
179 fluoride and 0.3 g (± 0.01) ammonium nitrate, the mixture was evenly stirred. Then
180 the mixture was transferred to a platinum (95%)-gold (5%) alloyed crucible for fusing
181 10 to 15 mins under temperature 1150 to 1250 °C. Finally, fusant was made into glass
182 beads using a fusion machine. All glass beads were preserved in a clean and dry
183 environment before analysis. Reference materials GSS (shown below) were prepared
184 with the same method for subsequent calibration of XRF. The sample intensity (I_s)
185 was calculated by the difference between peak (I_p) and background (I_b) values, as
186 shown with equation (2-1).

$$187 \quad I_s = I_p - I_b \quad (2-1)$$

188 Trace elements including REE were quantified by employing ICP-MS (AG 7500)
189 in the digested samples. The samples were digested following the method previously
190 described in Liu et al. (2016). Briefly, 9 mL concentrated HCl (37% v/v), 2 mL HNO₃
191 (65% v/v) and 9 mL HF (40% v/v) were used for digesting 0.5 g dried samples for 24
192 h under 108 °C condition. Then the mixture was dried and dissolved again with
193 purified HNO₃ (2% v/v). The obtained solutions were used for trace element analysis.
194 To check the stability of the equipment system and the analytical accuracy, reference
195 sample including GSS1, GSS2, GSS3 and GSS5, obtained from the Center of China
196 National Standard Reference Material, were ran simultaneously. The recommended
197 and test values of REE and metal oxides in standard references were shown in
198 supplementary materials (Table S1). Furthermore, the parallel sample was performed
199 every ten samples for further monitoring of the analytical precisions. The results show

200 that elements mostly had accuracies (RSD, $\delta 1$) ranging between 2% and 5%. The
201 standard materials had accuracy generally better than 3%, except for P₂O₅, which had
202 an accuracy better than 8% in some samples. The analytical precisions of REE in all
203 samples were generally better than 5%.

204 2.4 REE normalization

205 Rare earth element concentrations in all sediment samples were normalized with
206 average REE concentrations of the North American Shale Composite (NASC). The
207 corresponding normalization REE values were taken from Taylor and McLennan
208 (1985). Fractionation between LREE and HREE was quantified using fractionation
209 measures [(La/Lu)_{NASC} and (Nd/Yb)_{NASC}]. Anomalies including Ce (Ce/Ce*) and Eu
210 (Eu/Eu*) were calculated by extrapolation using normalized values of neighboring
211 REE. The corresponding formulas were shown with equations (2-2) to (2-4).

$$\text{Ce/Ce}^* = \text{Ce}_{\text{NASC}} / (\text{La}_{\text{NASC}} \times \text{Pr}_{\text{NASC}})^{0.5} \quad (2-2)$$

$$\text{Eu/Eu}^* = \text{Eu}_{\text{NASC}} / (\text{Sm}_{\text{NASC}} \times \text{Gd}_{\text{NASC}})^{0.5} \quad (2-3)$$

$$\text{Gd/Gd}^* = \text{Gd}_{\text{NASC}} / (\text{Eu}_{\text{NASC}} \times \text{Tb}_{\text{NASC}})^{0.5} \quad (2-4)$$

212 where the superscript * indicates the geogenic background.

213

214 **3. Results and discussion**

215 3.1 Sediment geochemistry and provenance

216 Sediment lithology in three boreholes are mainly clay, silt and silty clay (Fig. 2).

217 Fine and course sands were generally interbedded with silt and silty clay at different

218 sampling depths. This is better observed in the central (S30) and littoral (H02)
219 borehole bar graphs (Figs. 2b and c). In piedmont borehole, a gravel layer occurred at
220 depth between 38 m and 61 m (Fig. 2a). Gravel was not found in boreholes S30 and
221 HH02. Overall, fine grains prevailed in central and littoral sediment samples. Colors
222 of the fine grains changed in three zones as well. Pale yellow and pale
223 brownish-yellow clay and silty were mainly distributed in piedmont sediments. For
224 central borehole sediments, the color changed from pale brownish-yellow to brown
225 and tan vertically. For littoral sediments, taupe and tawny silty and silty clay were
226 mainly in upper and middle parts, and pale brownish-yellow and pale brown in lower
227 part (Fig. 2c).

228 The component of sediment samples was dominated by SiO_2 (Table 1). For
229 piedmont sediments (borehole Y09), contents (wt%) of SiO_2 ranged from 55.55 to
230 78.36 with an average value of 66.77. Central (borehole S30) and littoral (borehole
231 HH02) sediments had SiO_2 contents (wt%) lower than those of piedmont, being in the
232 ranges of 35.71 to 71.56 (average 56.62) and 32.04 to 77.03 (average 59.51),
233 respectively. Aluminum oxide (Al_2O_3) had the highest contents among the determined
234 metal oxides, with ranges of 6.37 wt% to 14.14 wt%, 7.42 wt% to 13.82 wt% and
235 7.32 wt% to 15.95 wt% and average values of 10.47 wt%, 10.95 wt% and 12.18 wt%
236 in piedmont, central and littoral sediments, respectively. Iron oxide (Fe_2O_3) was the
237 second abundant metal oxides, with a range from 1.86 wt% to 9.86 wt% and an
238 average of 5.46 wt% in piedmont sediments. The average content (wt%) of Fe_2O_3 in
239 central and littoral sediments was 4.45 wt% and 4.06 wt%, respectively, exhibiting

240 slightly lower than that of piedmont sediments. Other metal oxides including Na_2O ,
241 K_2O , CaO , MgO , P_2O_5 and TiO_2 showed relatively lower content in most of the
242 measured sediment samples as compared to SiO_2 and Al_2O_3 (Table 1). Average value
243 (wt%) of loss on ignition (LOI) was 3.88, 8.56 and 8.02 in piedmont, central and
244 littoral zones with ranges of 1.13 to 7.36, 3.12 to 19.91 and 2.5 to 17.56, respectively.

245 Changes of sediment lithology were related to the sedimentary provenances and
246 processes (McLennan, 2001). Piedmont sediments were thought to be derived from
247 piedmont regions (Taihang and Yanshan Mountains), where coarse-grained clastic
248 rocks were widely distributed (Zhang et al., 2018). Occurrences of central sediments
249 were attributed to fluviation of Yellow river and rivers springing in Taihang Mountain
250 (Zhang et al., 2018). This would account for sediments being deposited alternately
251 with clay, silty clay and fine sand (Fig. 2). Terrigenous clastics deposition and the
252 impact of ocean led to the formation of littoral sedimentation. Weathering and erosion
253 of the bedrocks around the piedmont plain and subsequent transport and
254 sedimentation contributed to the NCP sediments. Ternary diagram of sandstone
255 classification (Blatt et al., 1980) showed that the majority of sediment samples were
256 located in the left area, and three central samples in the right area, indicating that
257 sediments originally mostly were greywacke (Fig. 3a). The dominant SiO_2 contents
258 and fine-grained components reflected that the sedimentary materials had been
259 undergone intensive denudations and a long-distance transport before sink. Indeed,
260 the ternary diagram of Al_2O_3 - $\text{CaO}+\text{Na}_2\text{O}$ - K_2O (A-CN-K) showed that the weathering
261 trend of the sediment samples were mostly along the axis of $(\text{CaO}+\text{Na}_2\text{O})$ (Fig. 3b).

262 This probably indicates that sediment samples from the NCP were in an early
263 weathering stage where minerals such as plagioclase was incongruently decomposed
264 in association with leaching of Na and Ca generating products of illite, kaolinite and
265 smectite (Nesbitt et al., 1980). The offset to the uppermost of K₂O axis was attributed
266 to the addition of terrigenous detrital in the later sedimentary stage (Cox et al., 1995).

267 To quantify the weathering intensity in different samples, the chemical index of
268 alteration (CIA) values (initially was valid for granitic rocks) were calculated
269 following the method proposed by Nesbitt and Young (1982) [CIA = (Al₂O₃/(Al₂O₃ +
270 K₂O + Na₂O + CaO*))×100; CaO* = [CaO – (10/3×P₂O₅) (Panahi et al., 2000)].

271 Chemical index of alteration can be an index reflecting sample in a weathering trend
272 from fresh status to intensely-altered status. Granites and granodiorites usually have
273 CIA values ranging from 45 to 50, and fresh basalts have values between 30 and 45.
274 Muscovite has a value of 75, and illite, montmorillonites and beidellites give values
275 from 75 to 85 (Nesbitt and Young, 1982). Results showed that CIA value of piedmont
276 sediment samples ranged from 55 to 78 with an average value of 68, and central and
277 littoral samples ranged from 37 to 70 (average 51), and from 43 to 70 (average 55),
278 respectively. This indicates that sediment samples were incipiently (CIA: 50 to 60) to
279 intermediately (CIA: 60 to 80) chemically weathered, according to the classification
280 standards suggested by Fedo et al. (1995). It's also observed that piedmont sediment
281 samples generally had higher CIA values as compared to those of central and littoral
282 sediments, which means a stronger weathering may have occurred in the piedmont
283 sediment samples. These differences probably were associated with the

284 hydrogeological conditions (i.e. groundwater residence time, outcrop lithology and
285 aquifer replenishment condition). The results were consistent with piedmont samples
286 being located in the upper part of the A-CN-K diagram, while central and littoral
287 sediment samples below the piedmont samples (Fig. 3b). Similar studies have been
288 performed to investigate the impact of chemical weathering on sedimentary processes
289 based on sediment geochemical compositions (LaMaskin et al., 2008; Dostal and
290 Keppie, 2009; Xie et al., 2014). Conclusions have been made that sediment
291 geochemistry could serve as a good proxy for understanding the origins and processes
292 of sedimentation, as shown in the investigation.

293 3.2 REE distribution characteristics

294 3.2.1 REE concentrations

295 Total REE (Σ REE) concentrations were shown in Table 1. Piedmont sediment
296 (borehole Y09) Σ REE ranged from 190 mg/kg to 354 mg/kg with an average value of
297 227 mg/kg. Sediments from central (borehole S30) and littoral (borehole H02) zones
298 had Σ REE concentrations ranging from 89 mg/kg to 291 mg/kg (average 183mg/kg)
299 and from 87.90 mg/kg to 238 mg/kg (average 177 mg/kg), respectively. Generally,
300 sediment Σ REE concentrations showed a decreasing trend (piedmont > central >
301 littoral) along groundwater flow direction. The average Σ REE concentrations in
302 littoral sediment samples from study area were comparable to the values of Upper
303 Continental Crust (UCC) (169 mg/kg) (McLennan, 2001) and Chinese soil (177
304 mg/kg) (Wei et al., 1991). While average Σ REE concentrations of littoral and central

305 sediments were higher than the values of UCC and soil in China. All measured
306 average REE concentrations were within in the levels (166 mg/kg to 222 mg/kg)
307 reported in similar researches performed in the same study area (Lan et al., 2016).
308 Others showed that core sediments' Σ REE concentrations were slightly higher than
309 the value of surface sediment (Liu et al., 2019b).

310 Sediment Σ REE concentrations varied along depth. In piedmont borehole, Σ REE
311 were relatively constant within 11 m below sea level. A small decrease was observed
312 at depth from 11 m to 16 m, before Σ REE concentrations increased to >300 mg/kg at
313 25 m. After a new decrease until about 63 m, Σ REE concentrations fluctuated for the
314 remaining sampling depths (Fig. 2a). Σ REE concentrations in central sediments were
315 highly variable along borehole, although a decreasing trend occurred from land
316 surface to 30 m. Vertical changes of Σ REE concentrations were mainly related to
317 sediment physicochemical properties. Sediment with different grain sizes, such as clay,
318 silt and silty clay, had different capacities in hosting REE. The major minerals in the
319 aquifer sediments of study area included quartz, K-feldspar, hornblende and calcite
320 accounting for 5%-14% in the piedmont (Chen and Ni, 1987). Clay minerals (i.e.
321 kaolinite, illite and montmorillonite) were more commonly distributed in the central
322 and littoral plains as compared to the piedmont plain (Chen et al., 2005). In piedmont
323 where fine sand prevailed (i.e. from 38 m to 62 m), Σ REE concentrations
324 progressively decreased (Fig. 2a). Low Σ REE concentrations of central sediments
325 were found at depth of approximately 30 m, 65 m to 68 m, 107 m, 151 m to 154 m,
326 where fine sands were sandwiched with silt and silty clay (Fig. 2b). Silt sand and fine

327 sand more commonly occurred at deeper depth, leading to a decreasing trend of Σ REE
328 concentrations (Fig. 2c). This demonstrates that presence of clay was one of factors
329 controlling Σ REE concentrations. REE were thought to be hosted by clay component
330 containing in the sediments (Yang et al., 2002). The disparities of clay content along
331 depth for a large part could account for REE variations. This was further supported by
332 the vertical variations of Si/Al and Ti/Al values, which were proxies for grain size
333 classification (i.e. clay, silt, and silty clay) (Fig. S2). Statistical analyses showed that
334 Σ REE concentrations were negatively correlated to SiO_2 and were significantly
335 positively correlated to Fe_2O_3 and Al_2O_3 (except for littoral sediment samples) (Table
336 2), reflecting that REE mainly adsorbed onto/incorporated into Fe and Al -containing
337 oxides/clay minerals while repelled SiO_2 . Moreover, trends of $\text{SiO}_2/\text{Al}_2\text{O}_3$ values were
338 generally consistent with those of CIA, suggesting that silicate weathering like
339 feldspar played a role in this process (Fig. 2). In other words, in addition to clay
340 content, Fe and Al-bearing oxides could be another factor influencing REE
341 concentrations in investigated sediment samples. Metal oxides containing Fe, Mn and
342 Al provides important binding sites for sorption of REE (Ohta and Kawabe, 2000;
343 Pourret and Davranche, 2013; Liu et al., 2017; Mihajlovic et al., 2019). These
344 findings are in line with the results documented by Wang et al. (2014), showing that
345 fine fractions with abundant clay minerals and Fe/Al/Mn-containing oxides tended to
346 accumulate REE, while coarse fractions with less clay minerals and more quartz led to
347 a dilution of REE. However, further information on mineralogical compositions of
348 sediment samples is needed for better constraining the impact of mineralogy on REE

349 concentrations from a quantitative perspective. In all, sediment REE concentrations
350 were essentially regulated by their genetic properties and were revealed by their
351 vertical variations.

352 3.2.2 REE fractionation patterns

353 All sediment samples had relatively flat NASC-normalized REE patterns with a
354 gentle enrichment of LREE over HREE (Fig. 4). The degree of LREE enrichment was
355 quantified by $(La/Yb)_{NASC}$ values, which ranged between 0.86 and 1.15 with an
356 average of 1.23 in piedmont sediments. Central and littoral sediment samples had
357 $(La/Yb)_{NASC}$ ranges of 1.03 to 1.14 (average 1.21) and 0.91 to 1.49 (average 1.09),
358 respectively (Table 1). Sediments mostly showed negative Ce anomalies with Ce/Ce^*
359 ranging between 0.69 and 1.17 (average 0.91), and between 0.85 and 0.98 (average
360 0.90), and between 0.80 and 0.98 (average 0.89) in piedmont, central and littoral
361 plains, respectively. Negative Eu anomalies commonly occurred in investigated
362 sediments with Eu/Eu^* ranges of 0.82 to 1.07 (average 0.91), 0.83 to 1.31 (average
363 0.95), and 0.86 to 1.34 (average 0.95) in three zones, respectively. Correlation
364 analysis indicated that ΣREE concentrations generally increased with an increase of
365 $(La/Yb)_{NASC}$ in piedmont and central sediments, while this trend was not observed in
366 littoral sediment samples (Fig. 5a). These results reflected REE fractionation occurred
367 with the accumulation processes. The correlation between $(La/Yb)_{NASC}$ and CIA
368 values showed that the larger $(La/Yb)_{NASC}$ values occurred in samples containing
369 higher REE concentrations and generally having higher CIA values (Fig. 5b). Thus,
370 LREE enrichment could result from the chemical weathering of silicate in crustal

371 materials leading to an increase in LREE concentrations in sediments (Oliveira et al.,
372 2003; Lin et al., 2013). Larger CIA values were obtained in piedmont and central
373 zones as compared to the values in littoral zones (discussed above). The different
374 domain of littoral sediment samples from their piedmont and central counterparts may
375 be related to impact of ocean and/or human activities as well. However, more studies
376 are needed to verify this speculation.

377 Sediment samples mostly had negative Eu anomalies (Fig. 5d). Average Eu/Eu*
378 anomalies were quite similar in three different zones. This indicated that sedimentary
379 processes, which evolved weathering of bedrocks around plains and migration and
380 deposition in the flat plains, did not fractionate Eu to a larger extent with respect to
381 its neighboring Sm and Gd. Early investigations demonstrated that Eu compositions
382 and distributions in continental crust were fundamentally controlled by shallow,
383 intracrustal differentiation involving Eu-bearing minerals (i.e. plagioclase) (McLennan,
384 2001), which was shown to possess 4% to 23% (wt) in piedmont sediments (Liu et al.,
385 2016). However, Eu/Eu* values were negatively correlated to Σ REE concentrations
386 (Fig. 5d), which suggested that evolution of Eu anomalies was related to changes of
387 redox conditions as well during sedimentation. Preferential mobilization of Eu(II)
388 over other trivalent REE leads to a segregation of Eu from lanthanide series under
389 reducing conditions (Lee et al., 2003), and hence higher Σ REE concentrations occur
390 in lower-Eu/Eu* samples, as shown in Figure 5d. This mechanism has been proposed
391 for using Eu anomalies as an indicator for investigating REE origins as well as
392 mobility of redox-sensitive metal(oid) (Guo et al., 2010; Davranche et al., 2011).

393 Another possibility resulting in negative correlation between Eu anomalies and Σ REE
394 concentrations would be related to minerals contained in sediments. Such as
395 plagioclase, which tends to preferentially accumulate Eu(II) over trivalent REE by
396 means of isomorphism with Ca^{2+} , Na^+ and K^+ (Banks et al., 1999).

397 Cerium anomalies (Ce/Ce^*) were relatively constant in central and littoral
398 sediments despite the variable Σ REE concentrations, while they were distributed
399 scattered as a function of Σ REE concentrations in piedmont sediment samples (Fig.
400 5c). The fluctuation of redox conditions could account for this phenomenon due to
401 fact that Ce is readily to be precipitated as insoluble Ce(IV) via oxidative scavenging,
402 and when conditions evolve into reducing, the precipitated Ce will be released into
403 solution by reductive dissolutions (Bau and Koschinsky, 2009; Steinmann and Stille,
404 2008). Cerium cycle was believed to be biologically mediated (Moffett, 1990; Tanaka
405 et al., 2010) and evolved metal (i.e. Fe, Mn) oxides (Yu et al., 2017). Results of our
406 recent study showed that Ce precipitation from oxic aqueous solution was more likely
407 to occur in the piedmont aquifers where low-Fe/Mn-concentration groundwater
408 prevailed (Liu et al., 2019a), while no pronounced positive Ce anomalies were
409 commonly observed in the piedmont aquifer sediments. Thus, both positive and
410 negative Ce anomalies, and no Ce anomalies can be found in solid phases in nature, as
411 the results shown in present study.

412 3.3 Implication for REE signatures

413 Statistical analyses showed that individual REE concentrations were significantly
414 correlated with correlation coefficient (R^2) all better than 0.8. These results, together

415 with the findings that all investigated sediment samples had coherent normalized
416 patterns, indicated that sediments had similar sources/inputs of REE as well as
417 common geochemistry. The remarkable uniformity of sedimentary REE patterns, with
418 absolute concentration ranging from La to Lu, slight LREE enrichment and common
419 negative Eu anomalies, implied that REE were migrated and transported as an integral
420 whole during chemical weathering and sedimentation processes including erosion,
421 sedimentary sorting and diagenesis. The sediment paralleled NASC-normalized REE
422 patterns suggested that REE information recorded in sediments could serve as an ideal
423 tool for studying crustal evolution and sedimentary provenance. The higher REE
424 abundances in sediment than the values of UCC reflected that an enrichment of REE
425 occurred during the process of sedimentation. Since sedimentary REE uniformity was
426 thought to result from effective mixing of various provenance components from the
427 upper crust (McLennan, 2001) and they were transported primarily in particulates, the
428 sedimentary origins and secondary mobilization would be the plausible cause for
429 higher REE abundance. It should be noted that, in addition to natural processes, REE
430 can be accumulated in sediments and soils by various ways including sewage
431 discharges (Verplanck et al., 2005; Hatje et al., 2016), agricultural activities (Alfaro et
432 al., 2018) and atmospheric depositions (Tyler, 2004). Positive REE anomalies will
433 show up in REE normalized patterns when individual elemental concentration is
434 greater than its background value, as for Gd anomalies that have been reported
435 worldwide (Ebrahimi and Barbieri, 2019). However, the sediments cannot suffer from
436 anthropogenic pollutions in this study since no pronounced positive REE anomalies

437 were observed in their normalized patterns. In summary, sedimentary REE patterns
438 conveys important information regarding the composition of the continental crust and
439 anthropogenic impact.

440 **4. Conclusions**

441 226 sediment samples were collected from three different zones (i.e. piedmont,
442 central and littoral) of the north China plain (NCP) to investigate the concentrations
443 and fractionations of rare earth element (REE). Sediment geochemistry indicated that
444 sediments mostly were derived from greywacke, as suggested by triangular diagram
445 of sandstone classification. All sediment samples had been undergone incipient to
446 intermediate weathering with average CIA of 68, 51 and 55 in three zones,
447 respectively. Total REE concentrations ranged from 190.24 to 353.87 mg/kg (average
448 228.62 mg/kg), and from 88.85 to 290.80 mg/kg (average 182.88 mg/kg), and from
449 87.90 to 237.61 mg/kg (average 176.69 mg/kg) in piedmont, central and littoral plains,
450 exhibiting a decreasing trend as piedmont > central > littoral. Sediment
451 physicochemical properties such as mineral composites and metal oxide abundance
452 controlled REE concentrations, as observed along depth in three sediment sampling
453 profiles. All sediment samples had coherent NASC-normalized REE patterns that
454 were characterized by light REE (LREE) enrichment over heavy REE (HREE) with
455 $(La/Yb)_{NASC}$ ranging between 0.86 and 1.49. Negative Ce and Eu anomalies generally
456 occurred in the investigated sediments with Ce/Ce* and Eu/Eu* ranges of 0.69 to 1.17
457 and 0.82 to 1.34, respectively. The present study provides important dataset for future
458 studies in this region.

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684

685 **Figure and Table captions**

686 **Table 1** Concentrations of REE and major oxides and REE fractionation indices in the
687 sediment samples from three zones

688 **Table 2** Pearson's correlations between REE concentrations and major oxides, CIA
689 and LOI in the sediment samples from three zones (Y09 (118 m): piedmont, n = 50;
690 S30 (184 m): central, n=163; H02 (110 m): littoral, n = 63; "***" indicates $p < 0.01$,
691 "*" $p < 0.05$)

692 **Figure 1** Study area and sediments sampling locations (boreholes)

693 **Figure 2** Changes of sediment lithology and REE parameters along depth: (a)
694 piedmont borehole Y09, (b) central borehole S30, (c) littoral borehole H02.

695 **Figure 3** Ternary diagram of sandstone classification and Al_2O_3 -CaO+Na₂O-K₂O
696 (A-CN-K)

697 **Figure 4** NASC normalized REE patterns and absolute REE concentrations all
698 sediment samples (The line indicates a trend of normalized REE concentrations. The
699 box-whisker shows distributions of absolute REE concentrations)

700 **Figure 5** Total REE concentrations as a function of $(La/Yb)_{NASC}$ (a), Ce/Ce* (c) and
701 Eu/Eu* (d); a relationship between CIA and $(La/Yb)_{NASC}$ (b).

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Table 1

Component	Unit	piedmont			central			littoral		
		Min.	Avg.	Max.	Min.	Avg.	Max.	Min.	Avg.	Max.
		Y09			S30			H02		
La	mg/kg	19.54	40.93	63.81	16.59	33.16	54.53	16.80	32.05	43.99
Ce	mg/kg	39.75	82.99	135.94	31.99	66.34	108.59	31.81	63.09	87.26
Pr	mg/kg	4.60	9.71	14.98	3.87	7.72	12.38	3.87	7.39	10.01
Nd	mg/kg	16.50	35.71	55.46	13.96	28.41	45.28	13.70	27.28	36.75
Sm	mg/kg	3.12	6.81	10.43	2.66	5.56	8.73	2.58	5.40	7.30
Eu	mg/kg	0.70	1.31	1.91	0.72	1.12	1.60	0.72	1.09	1.50
Gd	mg/kg	2.73	6.09	9.67	2.32	4.99	7.72	2.22	4.87	6.97
Tb	mg/kg	0.45	0.97	1.52	0.34	0.78	1.24	0.34	0.78	1.10
Dy	mg/kg	2.49	5.41	8.35	1.97	4.34	6.75	1.97	4.32	6.03
Ho	mg/kg	0.55	1.11	1.70	0.40	0.88	1.35	0.41	0.88	1.22
Er	mg/kg	1.53	3.10	4.42	1.11	2.46	3.72	1.08	2.47	3.40
Tm	mg/kg	0.26	0.53	0.75	0.19	0.42	0.64	0.20	0.43	0.59
Yb	mg/kg	1.59	3.20	4.47	1.24	2.64	3.93	1.18	2.62	3.50
Lu	mg/kg	0.27	0.53	0.73	0.20	0.44	0.66	0.21	0.44	0.60
Y	mg/kg	14.60	30.20	44.94	10.53	23.61	36.11	10.80	23.59	34.05
SiO ₂	wt%	55.55	66.77	78.36	35.71	56.62	71.56	32.04	59.51	77.03
Fe ₂ O ₃	wt%	1.86	5.46	9.86	2.00	4.45	6.51	1.83	4.06	6.61
Al ₂ O ₃	wt%	6.37	10.47	14.14	7.42	10.95	13.82	7.32	12.18	15.96
MgO	wt%	0.27	1.38	2.41	1.01	2.34	3.70	0.61	2.14	5.27
CaO	wt%	0.40	1.25	5.45	0.97	7.01	19.23	1.30	6.12	18.63
Na ₂ O	wt%	0.15	1.15	2.28	0.66	1.65	3.31	0.52	3.38	46.29
K ₂ O	wt%	1.89	2.58	3.37	1.55	2.20	2.82	1.57	2.26	2.89
MnO	wt%	0.02	0.07	0.30	0.03	0.07	0.15	0.04	0.07	0.16
P ₂ O ₅	wt%	0.06	0.1	0.69	0.13	0.25	0.36	0.04	0.12	0.17
TiO ₂	wt%	0.26	0.69	0.99	0.44	0.93	1.54	0.51	0.96	1.22
LOI	wt%	1.13	3.88	7.36	3.12	8.56	19.91	2.5	8.02	17.56
∑REE	mg/kg	109	229	354	89	183	291	88	177	238
LREE	mg/kg	84	178	279	70	142	231	7	136	183
HREE	mg/kg	9.93	20.94	31.59	7.77	16.96	26.00	7.61	16.81	23.39
LREE/HREE	-	6.93	8.43	10.83	7.51	8.36	9.69	7.33	8.15	9.80
Ce/Ce*	-	0.69	0.91	1.17	0.85	0.90	0.98	0.80	0.89	0.98
Eu/Eu*	-	0.82	0.91	1.07	0.83	0.95	1.31	0.86	0.95	1.34
Gd/Gd*	-	0.95	1.06	1.15	0.93	1.05	1.12	0.87	1.04	1.10
(Y/Ho) _{NASC}	-	1.09	1.13	1.22	1.04	1.11	1.17	1.06	1.11	1.19
(La/Yb) _{NASC}	-	0.86	1.23	1.15	1.03	1.21	1.49	0.91	1.09	1.49

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Table 2

	borehole	REE	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	LOI	CIA
REE	Y09	1									
	S30	1									
	H02	1									
SiO ₂	Y09	-0.79**	1								
	S30	-0.58**	1								
	H02	-0.67**	1								
Fe ₂ O ₃	Y09	0.72**	-0.92**	1							
	S30	0.90**	-0.56**	1							
	H02	0.89**	-0.67**	1							
Al ₂ O ₃	Y09	0.67**	-0.77**	0.85**	1						
	S30	0.51**	0.249**	0.60**	1						
	H02	0.19	0.430**	0.30*	1						
MgO	Y09	0.55**	-0.77**	0.79**	0.55**	1					
	S30	0.66**	-0.61**	0.79**	0.31**	1					
	H02	0.71**	-0.84**	0.71**	-0.32**	1					
CaO	Y09	-0.06	-0.11	0.05	-0.342*	0.44**	1				
	S30	0.12	-0.82**	0.04	-0.72**	0.21*	1				
	H02	0.15	-0.58**	0.06	-0.40**	0.12	1				
Na ₂ O	Y09	-0.74**	0.78**	-0.70**	-0.79**	-0.31*	0.31*	1			

	S30	-0.81**	0.79**	-0.75**	-0.24*	-0.57**	-0.44**	1			
	H02	0.19	-0.51**	0.13	-0.76**	0.68**	-0.07	1			
K ₂ O	Y09	0.13	-0.09	0.001	-0.125	-0.19	-0.40**	-0.18	1		
	S30	0.17	0.26**	0.36**	0.58**	0.17	-0.61**	0.09	1		
	H02	0.17	-0.003	0.46**	0.49**	0.08	-0.39**	-0.19	1		
LOI	Y09	0.50**	-0.84**	0.60**	0.46**	0.44**	0.03	-0.52**	-0.003	1	
	S30	0.21*	0.91**	0.16	0.64**	0.23*	0.83**	0.52**	1.74	1	
	H02	0.27*	0.85**	0.25*	0.47**	0.42**	0.62**	-0.04	-0.03	1	
CIA	Y09	0.51**	-0.75**	0.82**	0.54**	0.44**	-0.003	-0.66**	-0.04**	0.56**	1
	S30	0.26	0.06	0.36**	0.02	0.09	-0.52**	-0.06	0.34**	0.002	1
	H02	0.35**	0.03	0.48**	0.25*	0.26*	-0.29*	-0.01	0.21*	-0.01	1

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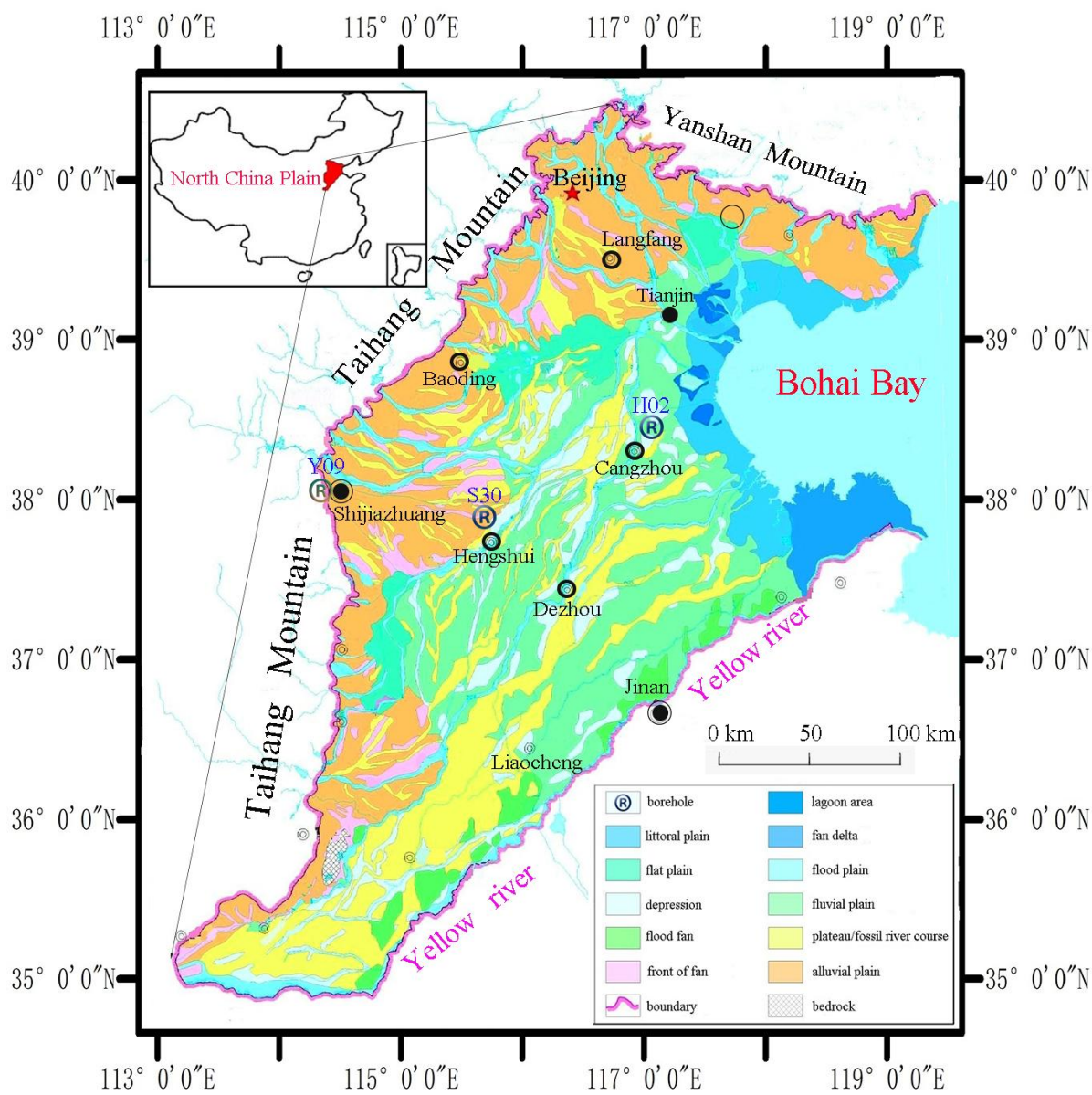


Fig. 1

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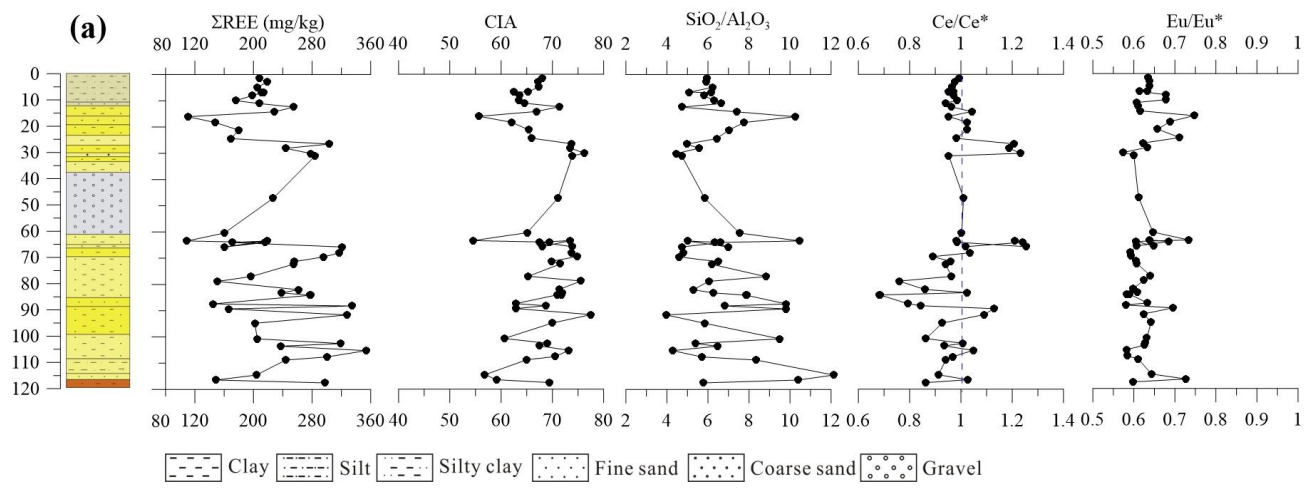
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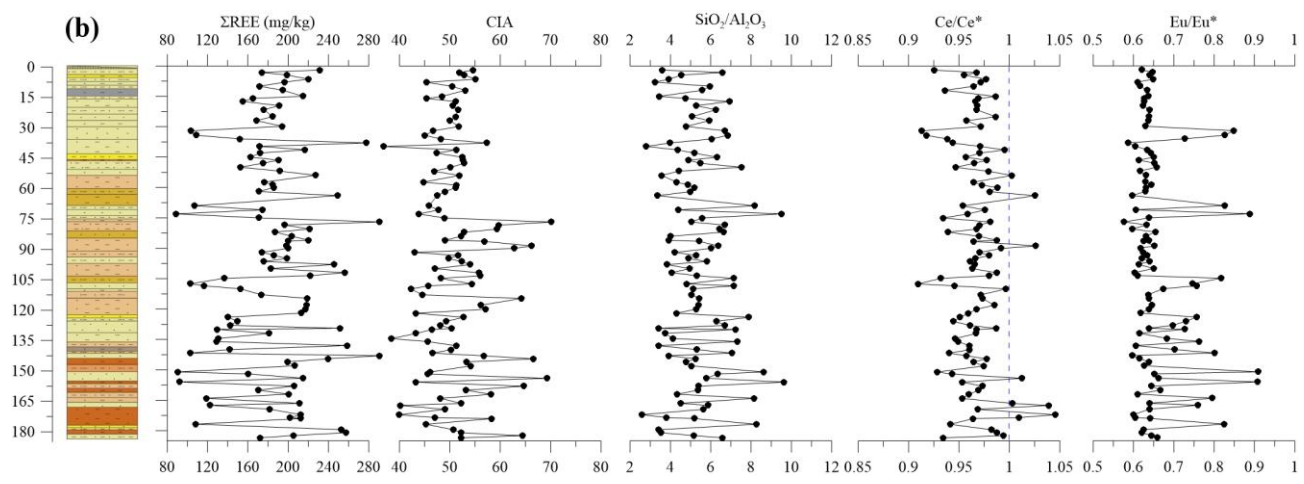
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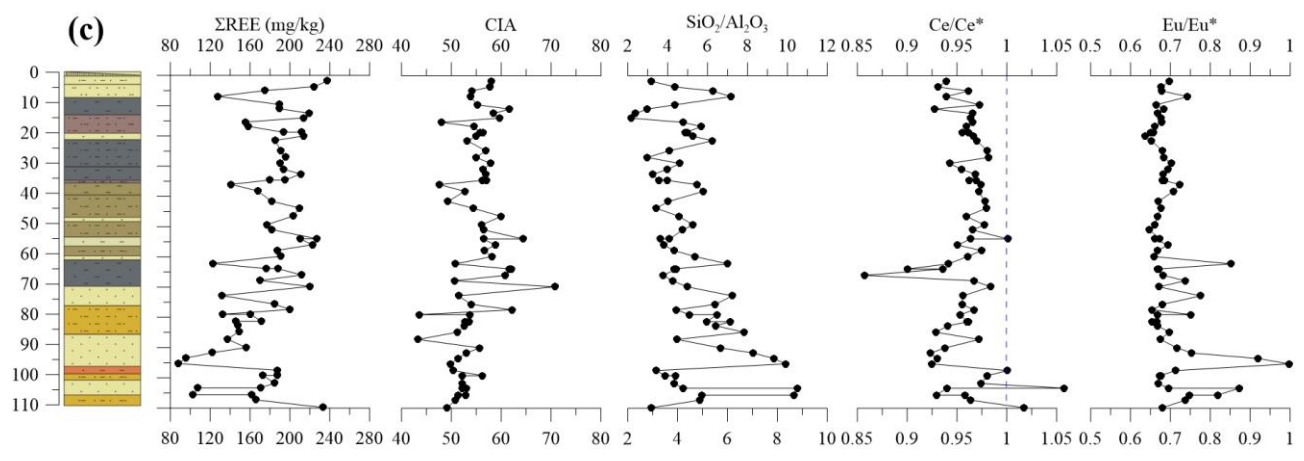
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Fig. 2

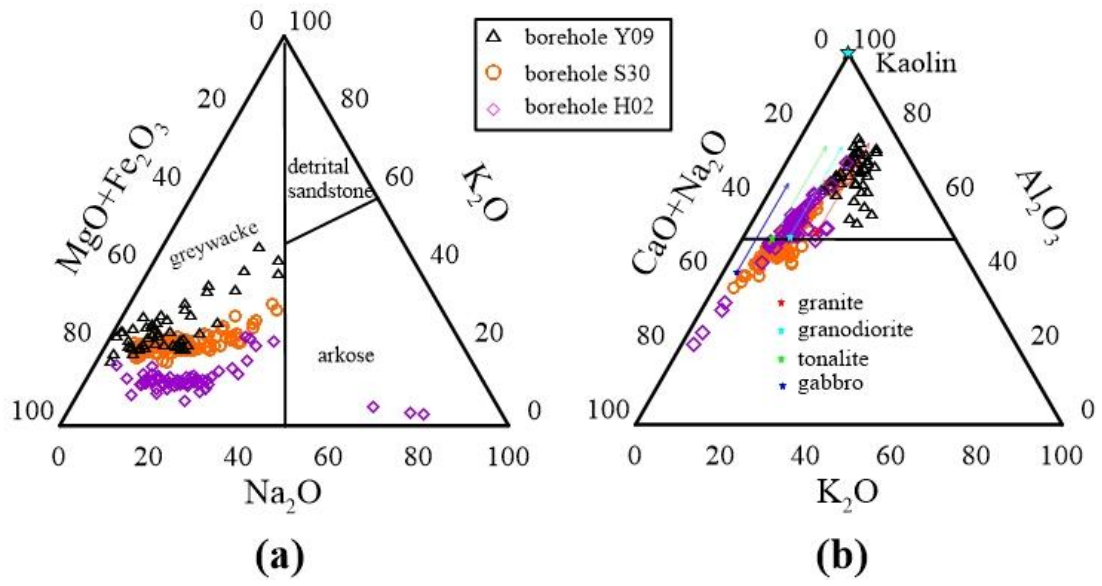


Fig. 3

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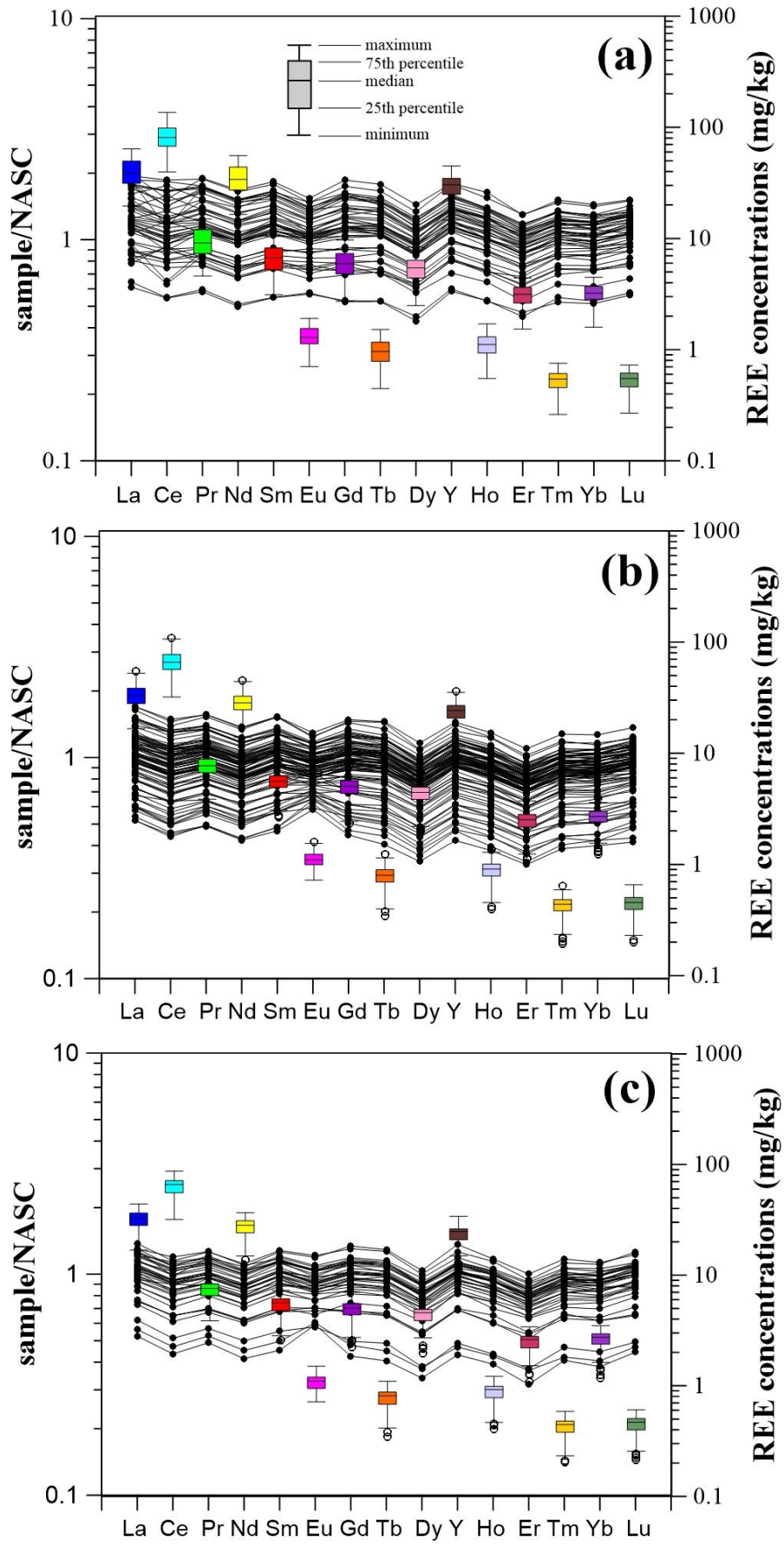
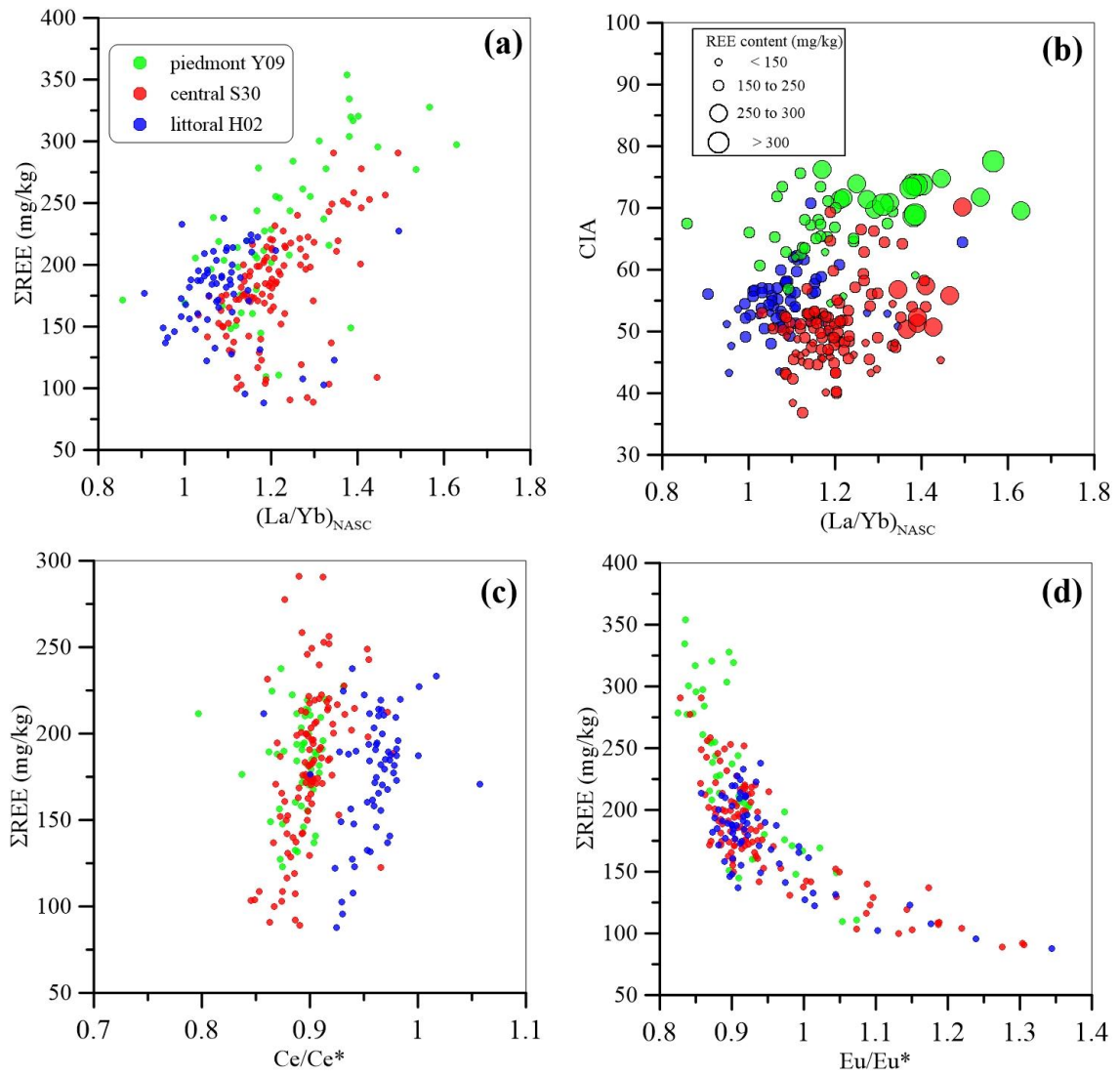


Fig. 4

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Fig. 5