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## Distribution of rare earth elements in sediments of the North China Plain: A probe of sedimentation process

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1 **Distribution of rare earth elements in sediments of the North China**

2 **Plain: A probe of sedimentation process**

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23 **Abstract:** Rare earth elements (REE) are powerful tracers for our understanding of  
24 sedimentary provenance and depositional processes. This study investigated  
25 geochemical characteristics of REE in 226 sediment samples collected from piedmont,  
26 central and littoral plains of the North China Plain. Results showed that total REE  
27 concentrations exhibited a decreasing trend as piedmont > central > littoral, and 82%,  
28 70% and 67% samples had total REE concentrations higher than the value of Upper  
29 Continental Crust. The REE concentrations were controlled by sedimentary  
30 provenance and sediment physicochemical properties. Ternary diagrams of sandstone  
31 classification and  $Al_2O_3$ -CaO+Na<sub>2</sub>O-K<sub>2</sub>O reflected that sediments originated from  
32 greywackes and they experienced an incipient to intermediate chemical weathering.  
33 Average Chemical Index of Alteration values were 68, 51 and 55 for sediments from  
34 piedmont, central and littoral sediments, respectively. Sediment North American  
35 Shale Composite (NASC)-normalized patterns were characterized by light REE  
36 (LREE) enrichment over heavy REE (HREE) and coherent negative Eu anomalies  
37 (Eu/Eu\* ranging between 0.57 and 1.00). Value of (La/Yb)<sub>NASC</sub> ranged from 0.86 to  
38 1.15 (average 1.23), and from 1.03 to 1.49, and from 0.91 to 1.49 in three zones,  
39 indicating REE fractionation from piedmont to littoral occurred during sedimentation  
40 processes. A positive correlation between (La/Yb)<sub>NASC</sub> and total REE concentrations  
41 was observed in piedmont and central sediment samples, implying that LREE were  
42 preferentially enriched over HREE with an accumulation of REE. This positive  
43 correlation was not found in littoral sediment samples, where a general decreasing  
44 trend along depth for REE concentrations existed. Results of this study shows

45 implications for using REE as a tracer in provenance studies from a basin scale.

46

47 **Keywords: Lanthanides; Geochemistry; Sedimentation; Fractionation; Critical Zone**

48

## 49 **1. Introduction**

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

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

71 important factors in their study. Grain size impacted REE concentrations in sediment  
72 as well. This is indicated by the results of Kimoto et al. (2006), showing that  
73 decreasing grain size generally increased REE concentrations due to that clay  
74 minerals could host REE (Laveuf and Cornu, 2009). The impact of clay, silty and sand  
75 fractions on solid REE was recently investigated in different soil profiles (Mihajlovic  
76 and Rinklebe, 2018). Presence of Fe/Mn oxides was another factor influencing REE  
77 in sediments/soils, and more REE can be accumulated by amorphous Fe/Mn oxides as  
78 compared to crystalline ones (Yan et al., 1999; Compton 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 using spatial visualization of  
82 REE concentration distributions in soils/sediments derived from all over the world.  
83 Results obtained from the study showed that total REE concentrations of agriculture  
84 soils/sediments ranged from 83 to 9840 mg/kg and concentrations of light REE  
85 (LREE) were higher than heavy REE (HREE). This indicates that, in addition to the  
86 natural processes, anthropogenic inputs (i.e. fertilizer) contribute to the REE  
87 concentrations in sediments/soils in some individual regions. Indeed, fertilization with  
88 REE-bearing fertilizers and infiltration of residuals was suggested to be the main  
89 mechanism of agriculture-sourced REE entering into soils and sediments (Hu et al.,  
90 2004). However, mechanisms for REE mobilization in different soils/sediments and  
91 the potential risks of long-term exposure to REE-abundant environment are not  
92 adequately understood.

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

115 possible anthropogenic impact, which is vital for establishing a baseline of  
116 distribution and background of REE concentration in the contaminated sediments and  
117 for administrating regulation guidelines (Alfaro et al., 2018; Consani et al., 2020).  
118 Therefore, the objectives of this study are to: (i) investigate REE concentration and  
119 fractionation characteristics in sediments collected from three zones (The zonation  
120 was previously specified by Chen et al. (2005)), (ii) characterize the relationships  
121 between REE distribution and sediment properties, (iii) assess the feasibility of using  
122 REE as a probe of sedimentation process.

## 123 **2. Material and methods**

### 124 2.1 Study area

125 The North China Plain (NCP) is located in the eastern China with longitude of  
126 112°30'~119°30'E, and latitude of 34°46'~40°25'N. The terrains are mostly plains with  
127 two mountainous regions (Yanshan and Tanghang mountains) bounding to the north  
128 and south, and an oceanic region (Bohai Bay) to the east (Chen et al., 1999),  
129 respectively. The plain has a total area of approximately  $31 \times 10^4$  km<sup>2</sup> and population  
130 of about 0.35 billion inhabitants. The NCP has a semi-arid humid climate with a  
131 temperature range of -23 °C~42.7 °C (in history). Average annual rainfall ranges from  
132 500 mm to 600 mm, mostly (>74%) dominating in summer. Average annual  
133 evaporation is 1.5 to 3 times of annual rainfall.

134 The NCP is one of largest sedimentary basins in Asia (Xing et al., 2013).  
135 According to Chen et al. (1999), the NCP's geological strata are comprised of four



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

142 Surface sediments in the NCP mainly are Cenozoic deposits with ages from  
143 Paleogene to Holocene. Lower Tertiary stratum is composed of red mudstone which is  
144 interbedded by red and gray sandstones. Upper Tertiary strata are characterized by  
145 consolidated to semi-consolidated alluvial-diluvial deposits, including siltstone,  
146 mudstone, sandstone and pebbly sandstone. Quaternary sediments are divided into  
147 four groups from top to bottom: Holocene (Q<sub>4</sub>), Upper (Q<sub>3m</sub>), Middle (Q<sub>2c</sub>) and  
148 Lower (Q<sub>1n</sub>) Pleistocene (Chen, 1999). The Holocene sediments group has a  
149 thickness of 5 m to 40 m, and mainly consists of yellow and gray sandy loam, fine  
150 sand, clay and sandy gravel. The Upper Pleistocene is alluvial, diluvial and eolian  
151 losses and yellow loam. The Middle Pleistocene stratum is widely distributed in  
152 intermountain basin and foothills, and consist of red and brown clay, loam and sandy  
153 loam, and red mud pebble layers. The Lower Pleistocene sediments group has a  
154 buried depth of 350 m to 500 m with a thickness of 80 m to 100m, and it's mainly  
155 loam, sand loam and lenticular sand layers.

156 Piedmont alluvial-proluvial sediments are suggested to derive from Taihang and  
157 Yanshan mountains by weathering, transport and sedimentation process. Central

158 alluvial-lacustrine sediments are deposited from materials carried by Yellow River  
159 and Zhangweinan River running from SW to NE since middle Pleistocene (Shao et al.,  
160 1989). The littoral plain forms with interactions between terrene and ocean, and  
161 sedimentary deposits come from terrestrial rivers draining into Bohai Bay.

## 162 2.2 Sediment sampling

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

## 172 2.3 Sediment analysis

173 All samples used for major and minor constituents analyses were dried under  
174 room temperature in the lab, and were ground to grain size <74 μm with an agate  
175 mortar for analysis. The X-ray fluorescence (XRF) (ARL Advant X) technique was  
176 used for measurement of various oxides (SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, CaO, Na<sub>2</sub>O, K<sub>2</sub>O,  
177 MnO, P<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub>) following the national standard method (GB/T 14506).  
178 Sediment samples were prepared with a glass flux sheet method. Specifically, 0.7 g

179 ( $\pm 0.001$ ) sample was first placed in a 25 mL porcelain crucible; followed by addition  
180 of 5.2 g ( $\pm 0.001$ ) anhydrous lithium tetraborate, 0.4 g ( $\pm 0.001$ ) lithium fluoride and  
181 0.3 g ( $\pm 0.01$ ) ammonium nitrate, the mixture was evenly stirred. Then the mixture  
182 was transferred to a platinum (95%)-gold (5%) alloyed crucible for fusing 10 to 15  
183 mins under temperature 1150 to 1250 °C. Finally, fusant was made into glass beads  
184 using a fusion machine. All glass beads were preserved in a clean and dry  
185 environment before analysis. Reference materials GSS (shown below) were prepared  
186 with the same method for subsequent calibration of XRF. The sample intensity ( $I_s$ )  
187 was calculated by the difference between peak ( $I_p$ ) and background ( $I_b$ ) values, as  
188 shown with Eq. (2-1).

$$189 \quad I_s = I_p - I_b \quad (2-1)$$

190 Rare earth elements were quantified by employing ICP-MS (AG 7500) with the  
191 digested samples. The samples were digested following the method previously  
192 described in Liu et al. (2016). Briefly, 9 mL concentrated HCl (37% v/v), 2 mL HNO<sub>3</sub>  
193 (65% v/v) and 9 mL HF (40% v/v) were used for digesting 0.5 g dried samples for 24  
194 h under 108 °C condition. Then the mixture was dried and dissolved again with  
195 purified HNO<sub>3</sub> (2% v/v). The obtained solutions were used for REE analysis. To check  
196 the stability of the equipment system and the analytical accuracy, reference soil  
197 sample including GSS1, GSS2, GSS3 and GSS5, obtained from the Center of China  
198 National Standard Reference Material, were ran simultaneously. The recommended  
199 and test values of REE and metal oxides in standard references were shown in  
200 supplementary materials (Table S1). Furthermore, the parallel sample was performed

201 every ten samples for further monitoring of the analytical precisions. The results show  
202 that elements mostly had accuracies (RSD,  $\delta 1$ ) ranging between 2% and 5%. The  
203 standard materials had accuracy generally better than 3%, except for  $P_2O_5$ , which had  
204 an accuracy better than 8% in some samples. The analytical precisions of REE in all  
205 samples were generally better than 5%.

#### 206 2.4 REE normalization

207 Rare earth element concentrations in all sediment samples were normalized with  
208 average REE concentrations of the North American Shale Composite (NASC). The  
209 corresponding normalization REE values were taken from Taylor and McLennan  
210 (1985). Fractionation between LREE and HREE was quantified using fractionation  
211 measures  $[(La/Lu)_{NASC}$  and  $(Nd/Yb)_{NASC}]$ . Anomalies including Ce ( $Ce/Ce^*$ ) and Eu  
212 ( $Eu/Eu^*$ ) were calculated by extrapolation using normalized values of neighboring  
213 REE. The corresponding formulas were shown with Eq. (2-1) to (2-4).

$$(La/Lu)_{NASC} = (La_{sample}/La_{NASC})/(Lu_{sample}/Lu_{NASC}) \quad (2-1)$$

$$(Nd/Yb)_{NASC} = (Nd_{sample}/Nd_{NASC})/(Yb_{sample}/Yb_{NASC}) \quad (2-2)$$

$$Ce/Ce^* = Ce_{NASC}/(La_{NASC} \times Pr_{NASC})^{0.5} \quad (2-3)$$

$$Eu/Eu^* = Eu_{NASC}/(Sm_{NASC} \times Gd_{NASC})^{0.5} \quad (2-4)$$

214 where the superscript \* indicates the geogenic background.

#### 215 2.5 Calculation of mass transfer coefficient

216 To evaluate REE mobility, the mass transfer coefficient ( $\tau$ ) was calculated by the  
217 Eq. (2-5). The  $\tau_{i, REE}$  values are an indicator of depletion or enrichment of REE after

218 normalization against reference element  $i$  in standard materials (NASC for this study).  
219 Positive  $\tau_{i, \text{REE}}$  values mean enrichment of REE (total or individual) in the sediments  
220 (s) with respect to NASC; negative values indicate depletion and zero indicate REE  
221 are immobile. Elements include Fe, Al, Mn, Ti, and Ca can be used as reference  
222 element  $i$ . This study chooses Ti as the reference because it has been used previously  
223 (Wu et al., 2018).

$$\tau_{i, \text{REE}} = (C_{\text{REE}}/C_i)_{\text{sample}} / (C_{\text{REE}}/C_i)_{\text{NASC}} - 1 \quad (2-5)$$

### 224 **3. Results and discussion**

#### 225 3.1 Sediment geochemistry and provenance

226 Sediment lithology in three boreholes were mainly clay, silt and silty clay (Fig.  
227 2). Fine and course sands were generally interbedded with silt and silty clay at  
228 different sampling depths. This was well observed in the central (S30) and littoral  
229 (H02) borehole bar graphs (Figs. 2b and c). In piedmont borehole, a gravel layer  
230 occurred at depth between 38 m and 61 m (Fig. 2a). Gravel was not found in  
231 boreholes S30 and HH02. Overall, fine grains prevailed in central and littoral  
232 sediment samples. Colors of the fine grains changed in three zones as well. Pale  
233 yellow and pale brownish-yellow clay and silty were mainly distributed in piedmont  
234 sediments. For central borehole sediments, the color changed from pale  
235 brownish-yellow to brown and tan vertically. For littoral sediments, taupe and tawny  
236 silty and silty clay were mainly in upper and middle parts, and pale brownish-yellow  
237 and pale brown in lower part (Fig. 2c).

238 The component of sediment samples was dominated by  $\text{SiO}_2$  (Table 1). For

239 piedmont sediments (borehole Y09), contents (wt%) of SiO<sub>2</sub> ranged from 55.55 to  
240 78.36 with an average value of 66.77. Central (borehole S30) and littoral (borehole  
241 HH02) sediments had SiO<sub>2</sub> contents (wt%) lower than those of piedmont, being in the  
242 ranges of 35.71 to 71.56 (average 56.62) and 32.04 to 77.03 (average 59.51),  
243 respectively. Aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) had the highest contents among the determined  
244 metal oxides, with ranges of 6.37 to 14.14 wt%, 7.42 to 13.82 wt% and 7.32 to 15.95  
245 wt% and average values of 10.47 wt%, 10.95 wt% and 12.18 wt% in piedmont,  
246 central and littoral sediments, respectively. Iron oxide (Fe<sub>2</sub>O<sub>3</sub>) was the second  
247 abundant metal oxides, with a range from 1.86 wt% to 9.86 wt% and an average of  
248 5.46 wt% in piedmont sediments. The average content (wt%) of Fe<sub>2</sub>O<sub>3</sub> in central and  
249 littoral sediments was 4.45 wt% and 4.06 wt%, respectively, exhibiting slightly lower  
250 than that of piedmont sediments. Other metal oxides including Na<sub>2</sub>O, K<sub>2</sub>O, CaO,  
251 MgO, P<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub> showed relatively lower content in most of the measured  
252 sediment samples as compared to SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> (Table 1). Average value (wt%) of  
253 loss on ignition (LOI) was 3.88, 8.56 and 8.02 in piedmont, central and littoral zones  
254 with ranges of 1.13 to 7.36, 3.12 to 19.91 and 2.5 to 17.56, respectively.

255 Changes of sediment lithology were controlled by the sedimentary provenances  
256 and processes (Bhuiyan et al., 2011; Blake et al., 2017). This would account for that  
257 sediments were deposited alternately with clay, silty clay and fine sand (Fig. 2).  
258 Terrigenous clastic deposition and land-ocean interactions led to the formation of  
259 littoral sedimentation. Weathering and erosion of the bedrocks around the piedmont  
260 plain and subsequent transport and sedimentation contributed to the NCP sediments.

261 Ternary diagram of sandstone classification (Blatt et al., 1980) showed that the  
262 majority of sediment samples were located in the greywacke domain, and three  
263 central samples in the arkose domain indicating that sediments originally mostly were  
264 greywacke (Fig. 3a). The dominant SiO<sub>2</sub> contents and fine-grained components  
265 reflected that the sedimentary materials had been undergone intensive denudations  
266 and a long-distance transport before sink. Indeed, the ternary diagram of  
267 Al<sub>2</sub>O<sub>3</sub>-CaO+Na<sub>2</sub>O-K<sub>2</sub>O (A-CN-K) showed that the weathering trend of the sediment  
268 samples were mostly along the axis of (CaO+Na<sub>2</sub>O) (Fig. 3b). This probably indicated  
269 that sediment samples from the NCP were in an early weathering stage where  
270 minerals such as plagioclase was incongruently decomposed in association with  
271 leaching of Na and Ca generating products of illite, kaolinite and smectite (Nesbitt et  
272 al., 1980). The offset to the uppermost of K<sub>2</sub>O axis was attributed to the addition of  
273 terrigenous detrital in the later sedimentary stage (Cox et al., 1995).

274 To quantify the weathering intensity in different samples, the chemical index of  
275 alteration (CIA) values (initially was valid for granitic rocks) were calculated  
276 following the method proposed by Nesbitt and Young (1982) [CIA = (Al<sub>2</sub>O<sub>3</sub>/(Al<sub>2</sub>O<sub>3</sub> +  
277 K<sub>2</sub>O + Na<sub>2</sub>O + CaO\*))×100; CaO\* = [CaO - (10/3×P<sub>2</sub>O<sub>5</sub>) (Panahi et al., 2000)].  
278 Chemical index of alteration can be an index reflecting sample in a weathering trend  
279 from fresh status to intensely-altered status. Granites and granodiorites usually have  
280 CIA values ranging from 45 to 50, and fresh basalts have values between 30 and 45.  
281 Muscovite has a value of 75, and illite, montmorillonites and beidellites give values  
282 from 75 to 85 (Nesbitt and Young, 1982). Results showed that CIA value of piedmont

283 sediment samples ranged from 55 to 78 with an average value of 68, and central and  
284 littoral samples ranged from 37 to 70 (average 51), and from 43 to 70 (average 55),  
285 respectively. This indicates that sediment samples were incipiently (CIA: 50 to 60) to  
286 intermediately (CIA: 60 to 80) chemically weathered, according to the classification  
287 standards suggested by Fedo et al. (1995). It's also observed that piedmont sediment  
288 samples generally had higher CIA values as compared to those of central and littoral  
289 sediments, which means a stronger weathering may have occurred in the piedmont  
290 sediment samples. These differences probably were associated with the  
291 hydrogeological conditions such as REE residence time, outcrop lithology and aquifer  
292 replenishment conditions (Condie, 1991; Blake et al., 2017). The results were  
293 consistent with piedmont samples being located in the upper part of the A-CN-K  
294 diagram, while central and littoral sediment samples below the piedmont samples (Fig.  
295 3b). The role of chemical weathering on sedimentary processes was studied  
296 previously based on sediment geochemical compositions (LaMaskin et al., 2008;  
297 Dostal and Keppie, 2009; Xie et al., 2014). Combined to studies of the residence time  
298 of REE (Condie, 1991), it's accepted that REE fingerprinting in sediment could serve  
299 as a good proxy for understanding the origins and processes of sedimentation, as  
300 shown in this investigation.

## 301 3.2 REE distribution characteristics

### 302 3.2.1 REE concentrations

303 Total REE ( $\Sigma$ REE) concentrations were shown in Table 1. Piedmont sediment



304 (borehole Y09)  $\Sigma$ REE ranged from 190 mg/kg to 354 mg/kg with an average value of  
305 227 mg/kg. Sediments from central (borehole S30) and littoral (borehole H02) zones  
306 had  $\Sigma$ REE concentrations ranging from 89 mg/kg to 291 mg/kg (average 183mg/kg)  
307 and from 87.90 mg/kg to 238 mg/kg (average 177 mg/kg), respectively. Generally,  
308 sediment  $\Sigma$ REE concentrations showed a decreasing trend (piedmont > central >  
309 littoral) along a groundwater flow direction. The average  $\Sigma$ REE concentrations in  
310 littoral sediment samples from study area were comparable to the values of Upper  
311 Continental Crust (UCC) (169 mg/kg) (McLennan, 2001) and Chinese soil (177  
312 mg/kg) (Wei et al., 1991); while average  $\Sigma$ REE concentrations of piedmont and  
313 central sediments were higher than the values of UCC and soil in China, showing a  
314 spatial disparity. All measured average REE concentrations were within in the levels  
315 (166 mg/kg to 222 mg/kg) reported in similar researches performed in the same study  
316 area (Lan et al., 2016). Others showed that core sediment  $\Sigma$ REE concentrations were  
317 slightly higher than the value of surface sediment (Liu et al., 2019b).

318 Sediment  $\Sigma$ REE concentrations varied along depth. In the piedmont borehole,  
319  $\Sigma$ REE concentrations were relatively constant within 11 m below land surface. A  
320 small decrease in  $\Sigma$ REE concentrations was observed at depth from 11 m to 16 m  
321 before they increased to >300 mg/kg at 25 m. After a new decrease to about 63 m,  
322  $\Sigma$ REE concentrations fluctuated for the remaining sampling depths (Fig. 2a).  $\Sigma$ REE  
323 concentrations in central sediments were highly variable along borehole, although a  
324 decreasing trend occurred from land surface to 30 m. Vertical changes of  $\Sigma$ REE  
325 concentrations were mainly related to sediment physicochemical properties (Kimoto

326 et al., 2006; Mihajlovic and Rinklebe, 2018). Sediments with different grain sizes,  
327 such as clay, silt and silty clay, had different capacities in hosting REE. The major  
328 minerals in the aquifer sediments of study area were shown to be quartz, K-feldspar,  
329 hornblende and calcite accounting for 5%-14% in the piedmont (Chen and Ni, 1987).  
330 Clay minerals (i.e. kaolinite, illite and montmorillonite) were more commonly  
331 distributed in the central and littoral plains as compared to the piedmont plain (Chen  
332 et al., 2005). In the piedmont, where fine sand prevailed (i.e. from 38 m to 62 m),  
333  $\Sigma$ REE concentrations progressively decreased (Fig. 2a). Low  $\Sigma$ REE concentrations of  
334 central sediments were found at depth of approximately 30 m, 65 m to 68 m, 107 m,  
335 151 m to 154 m, where fine sands were sandwiched with silt and silty clay (Fig. 2b).  
336 Silt sand and fine sand more commonly occurred at deeper depth, leading to a  
337 decreasing trend of  $\Sigma$ REE concentrations (Fig. 2c). This demonstrated that presence  
338 of clay was one of factors controlling  $\Sigma$ REE concentrations. Lanthanides were  
339 thought to be hosted by clay component containing in the sediments (Yang et al.,  
340 2002). The disparities of clay content along depth for a large part accounted for REE  
341 variations along depth. This was supported by the vertical variations of Si/Al values,  
342 which were proxies for grain size classification (i.e. clay, silt, and silty clay) (Fig. S2).  
343 Statistical analyses showed that  $\Sigma$ REE concentrations were negatively correlated to  
344  $\text{SiO}_2$  and were significantly positively correlated to  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  (except for  
345 littoral sediment samples) (Table 2), reflecting that REE mainly adsorbed  
346 onto/incorporated into Fe and Al-containing clay minerals. Normalization of REE to  
347 Ti showed that  $\tau_{i, \text{REE}}$  values mostly changed slightly, and generally were positive for

348 piedmont sediments and negative for central and littoral sediment. This suggested that  
349 dilution of weathered residuals (i.e.  $\text{SiO}_2$ ) did not significantly modify REE  
350 concentrations in sediment samples. Moreover, trends of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  values were  
351 generally consistent with those of CIA, suggesting that weathering of silicates like  
352 feldspar played a role in this process (Fig. 2). In other words, in addition to clay  
353 content, Fe and Al-bearing oxides could be another factor influencing REE  
354 concentrations in investigated sediment samples. Therefore, mixture of clay minerals  
355 and Fe-Mn oxides accounted for normalized REE values. Metal oxides containing Fe,  
356 Mn and Al provide important binding sites for sorption of REE (Ohta and Kawabe,  
357 2000; Pourret and Davranche, 2013; Liu et al., 2017; Mihajlovic et al., 2019). These  
358 findings are in line with the results documented by Wang et al. (2014), showing that  
359 fine fractions with abundant clay minerals and Fe/Al/Mn-containing oxides tended to  
360 accumulate REE, while coarse fractions with less clay minerals and more quartz led to  
361 less REE contents. However, further information on mineralogical compositions of  
362 sediment samples is needed for better constraining the impact of mineralogy on REE  
363 concentrations from a quantitative perspective. In all, sediment REE concentrations  
364 were essentially regulated by their genetic properties and were revealed by their  
365 vertical variations.

### 366 3.2.2 REE fractionation patterns

367 All sediment samples had relatively flat NASC-normalized REE patterns with a  
368 gentle enrichment of LREE over HREE (Fig. 4). The degree of LREE enrichment was  
369 quantified by  $(\text{La}/\text{Yb})_{\text{NASC}}$  values, which ranged between 0.86 and 1.15 with an

370 average of 1.23 in piedmont sediments. Central and littoral sediment samples had  
371  $(La/Yb)_{NASC}$  ranges of 1.03 to 1.14 (average 1.21) and 0.91 to 1.49 (average 1.09),  
372 respectively (Table 1). Sediments mostly showed negative Ce anomalies with  $Ce/Ce^*$   
373 ranging between 0.69 and 1.17 (average 0.91), and between 0.85 and 0.98 (average  
374 0.90), and between 0.80 and 0.98 (average 0.89) in piedmont, central and littoral  
375 plains, respectively. Negative Eu anomalies commonly occurred in investigated  
376 sediments with  $Eu/Eu^*$  ranges of 0.82 to 1.07 (average 0.91), 0.83 to 1.31 (average  
377 0.95), and 0.86 to 1.34 (average 0.95) in three zones, respectively. Correlation  
378 analysis indicated that  $\Sigma REE$  concentrations generally increased with an increase of  
379  $(La/Yb)_{NASC}$  in piedmont and central sediments, while this trend was not observed in  
380 littoral sediment samples (Fig. 5a). These results reflected REE were nonuniformly  
381 accumulated by sediments during their transport. The correlation between  
382  $(La/Yb)_{NASC}$  and CIA values showed that the larger  $(La/Yb)_{NASC}$  values occurred in  
383 samples containing higher  $\Sigma REE$  concentrations and generally having higher CIA  
384 values (Fig. 5b). Thus, LREE enrichments could result from the chemical weathering  
385 of silicates in crustal materials, which led to higher levels of LREE in sediments  
386 (Oliveira et al., 2003; Lin et al., 2013). Larger CIA values were obtained from  
387 piedmont and central zones as compared to the values in littoral zones (shown above).  
388 The different domains of littoral sediment samples from their piedmont and central  
389 counterparts might be related to impact of ocean and/or human activities. However,  
390 more studies are needed to verify this speculation.

391 Sediment samples mostly had negative Eu anomalies (Fig. S2). Average  $Eu/Eu^*$

392 anomalies were quite similar in three different zones. This indicated that sedimentary  
393 processes, which evolved weathering of bedrocks around plains and migration and  
394 deposition in the flat plains, did not fractionate Eu to a larger extent with respect to  
395 its neighboring Sm and Gd. Early investigations demonstrated that Eu compositions  
396 and distributions in continental crust were fundamentally controlled by shallow,  
397 intracrustal differentiation involving Eu-bearing minerals (i.e. plagioclase)  
398 (McLennan, 2001), which was shown to possess 4% to 23% (wt) in piedmont  
399 sediments (Liu et al., 2016). However, Eu/Eu\* values were negatively correlated to  
400  $\Sigma$ REE concentrations (Fig. 5d), suggesting that evolution of Eu anomalies was related  
401 to changes of redox conditions as well during sedimentation. Preferential mobilization  
402 of Eu(II) over other trivalent REE leads to a segregation of Eu from lanthanide series  
403 under reducing conditions (Lee et al., 2003), and hence higher  $\Sigma$ REE concentrations  
404 occur in lower-Eu/Eu\* samples, as shown in Figure 5d. This mechanism has been  
405 proposed for using Eu anomalies as an indicator for investigating REE origins as well  
406 as mobility of redox-sensitive metal(oid) (Guo et al., 2010; Davranche et al., 2011).  
407 Another possibility resulting in negative correlation between Eu anomalies and  $\Sigma$ REE  
408 concentrations would be related to minerals contained in sediments. Such as  
409 plagioclase, which tends to preferentially accumulate Eu(II) over trivalent REE by  
410 means of isomorphism with  $\text{Ca}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$  (Banks et al., 1999).

411 Cerium anomalies ( $\text{Ce}/\text{Ce}^*$ ) were relatively constant in central and littoral  
412 sediments despite variable  $\Sigma$ REE concentrations, while they were distributed scattered  
413 as a function of  $\Sigma$ REE concentrations in piedmont sediment samples (Fig. S2). The

414 fluctuation of redox conditions could account for this phenomenon due to fact that Ce  
415 is readily to be precipitated as insoluble Ce(IV) via oxidative scavenging, and when  
416 conditions evolve into reducing, the precipitated Ce will be released into solution by  
417 reductive dissolutions (Bau and Koschinsky, 2009; Steinmann and Stille, 2008).  
418 Cerium cycle was believed to be biologically mediated (Moffett, 1990; Tanaka et al.,  
419 2010) and involved metal (i.e. Fe, Mn) oxides (Yu et al., 2017). Results of our recent  
420 study showed that Ce precipitation from oxic aqueous solution was more likely to  
421 occur in the piedmont aquifers where low-Fe/Mn-concentration groundwater  
422 prevailed (Liu et al., 2019a), though no pronounced positive Ce anomalies were  
423 commonly observed in the piedmont aquifer sediments. Thus, both positive and  
424 negative Ce anomalies, and no Ce anomalies can be found in solid phases in nature, as  
425 the results shown in present study.

### 426 3.3 Implication for REE signatures

427 Statistical analyses showed that individual REE concentrations were significantly  
428 correlated with correlation coefficient ( $R^2$ ) all better than 0.8. These results, together  
429 with the findings that all investigated sediment samples had coherent normalized  
430 patterns, indicated that sediments had similar sources/inputs of REE as well as  
431 common geochemistry. The remarkable uniformity of sedimentary REE patterns, with  
432 absolute concentration ranging from La to Lu, slight LREE enrichment and common  
433 negative Eu anomalies, implied that REE were migrated and transported as an integral  
434 whole during chemical weathering and sedimentation processes including erosion,  
435 sedimentary sorting and diagenesis. The sediment paralleled NASC-normalized REE

436 patterns suggested that REE information recorded in sediments could serve as an ideal  
437 tool for studying crustal evolution and sedimentary provenance. The higher REE  
438 abundances in sediment than the values of UCC reflected that an enrichment of REE  
439 occurred during the process of sedimentation. Since sedimentary REE uniformity was  
440 thought to result from effective mixing of various provenance components from the  
441 upper crust (McLennan, 2001) and they were transported primarily in particulates, the  
442 sedimentary origins and secondary mobilization would be the plausible cause for  
443 higher REE abundance. It should be noted that, in addition to natural processes, REE  
444 can be accumulated in sediments and soils by various ways including sewage  
445 discharges (Verplanck et al., 2005; Hatje et al., 2016), agricultural activities (Alfaro et  
446 al., 2018) and atmospheric depositions (Tyler, 2004), although the investigated  
447 sediments were unlikely to suffer from these anthropogenic pollutions due to that  
448 most of them were not formed nowadays. Positive REE anomalies will show up in  
449 REE normalized patterns when individual elemental concentration is greater than its  
450 background value, such as Gd anomalies, which have been reported worldwide  
451 (Ebrahimi and Barbieri, 2019; and references therein). In summary, sedimentary REE  
452 patterns conveys important information regarding the composition of the continental  
453 crust and anthropogenic impact.

#### 454 **4. Conclusions**

455 The 226 sediment samples were collected from three different zones (i.e.  
456 piedmont, central and littoral) of the north China plain to investigate the  
457 concentrations and fractionations of rare earth element (REE). Sediment geochemistry

458 indicated that sediments mostly were derived from greywacke, as suggested by  
459 triangular diagram of sandstone classification. All sediment samples had been  
460 undergone incipient to intermediate weathering with average CIA of 68, 51 and 55 in  
461 three zones, respectively. Total REE concentrations ranged from 190.24 to 353.87  
462 mg/kg (average 228.62 mg/kg), and from 88.85 to 290.80 mg/kg (average 182.88  
463 mg/kg), and from 87.90 to 237.61 mg/kg (average 176.69 mg/kg) in piedmont, central  
464 and littoral plains, exhibiting a decreasing trend as piedmont > central > littoral.  
465 Sediment physicochemical properties such as mineral composites and metal oxide  
466 abundance controlled REE concentrations, as observed along depth in three sediment  
467 sampling profiles. All sediment samples had coherent NASC-normalized REE  
468 patterns that were characterized by light REE (LREE) enrichment over heavy REE  
469 (HREE) with  $(La/Yb)_{NASC}$  ranging between 0.86 and 1.49. Negative Ce and Eu  
470 anomalies generally occurred in the investigated sediments with Ce/Ce\* and Eu/Eu\*  
471 ranges of 0.69 to 1.17 and 0.82 to 1.34, respectively. The present study provides  
472 important dataset for future comparative studies in this region.

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711 **Figure and Table captions**

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

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

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

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

721 **Figure 3** Ternary diagram of sandstone classification and  $Al_2O_3$ -CaO+Na<sub>2</sub>O-K<sub>2</sub>O  
722 (A-CN-K)

723 **Figure 4** NASC-normalized REE patterns and absolute REE concentrations in all  
724 sediment samples (The line indicates a trend of normalized REE concentrations. The  
725 box-whisker shows distributions of absolute REE concentrations; (a) piedmont  
726 borehole Y09, (b) central borehole S30, (c) littoral borehole H02)

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

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Table 1

| Component                      | Unit  | piedmont |       |        | central |       |        | littoral |       |       |
|--------------------------------|-------|----------|-------|--------|---------|-------|--------|----------|-------|-------|
|                                |       | Y09      |       |        | S30     |       |        | H02      |       |       |
|                                |       | Min.     | Avg.  | Max.   | Min.    | Avg.  | Max.   | Min.     | Avg.  | Max.  |
| 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 <sub>2</sub>               | wt%   | 55.55    | 66.77 | 78.36  | 35.71   | 56.62 | 71.56  | 32.04    | 59.51 | 77.03 |
| Fe <sub>2</sub> O <sub>3</sub> | wt%   | 1.86     | 5.46  | 9.86   | 2.00    | 4.45  | 6.51   | 1.83     | 4.06  | 6.61  |
| Al <sub>2</sub> O <sub>3</sub> | 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 <sub>2</sub> O              | wt%   | 0.15     | 1.15  | 2.28   | 0.66    | 1.65  | 3.31   | 0.52     | 3.38  | 46.29 |
| K <sub>2</sub> 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 <sub>2</sub> O <sub>5</sub>  | wt%   | 0.06     | 0.1   | 0.69   | 0.13    | 0.25  | 0.36   | 0.04     | 0.12  | 0.17  |
| TiO <sub>2</sub>               | 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) <sub>NASC</sub>         | -     | 1.09     | 1.13  | 1.22   | 1.04    | 1.11  | 1.17   | 1.06     | 1.11  | 1.19  |
| (La/Yb) <sub>NASC</sub>        | -     | 0.86     | 1.23  | 1.15   | 1.03    | 1.21  | 1.49   | 0.91     | 1.09  | 1.49  |

Table 2

|                                | borehole | REE     | SiO <sub>2</sub> | Fe <sub>2</sub> O <sub>3</sub> | Al <sub>2</sub> O <sub>3</sub> | MgO     | CaO     | Na <sub>2</sub> O | K <sub>2</sub> O | LOI | CIA |
|--------------------------------|----------|---------|------------------|--------------------------------|--------------------------------|---------|---------|-------------------|------------------|-----|-----|
| REE                            | Y09      | 1       |                  |                                |                                |         |         |                   |                  |     |     |
|                                | S30      | 1       |                  |                                |                                |         |         |                   |                  |     |     |
|                                | H02      | 1       |                  |                                |                                |         |         |                   |                  |     |     |
| SiO <sub>2</sub>               | Y09      | -0.79** | 1                |                                |                                |         |         |                   |                  |     |     |
|                                | S30      | -0.58** | 1                |                                |                                |         |         |                   |                  |     |     |
|                                | H02      | -0.67** | 1                |                                |                                |         |         |                   |                  |     |     |
| Fe <sub>2</sub> O <sub>3</sub> | Y09      | 0.72**  | -0.92**          | 1                              |                                |         |         |                   |                  |     |     |
|                                | S30      | 0.90**  | -0.56**          | 1                              |                                |         |         |                   |                  |     |     |
|                                | H02      | 0.89**  | -0.67**          | 1                              |                                |         |         |                   |                  |     |     |
| Al <sub>2</sub> O <sub>3</sub> | 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 <sub>2</sub> 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 <sub>2</sub> 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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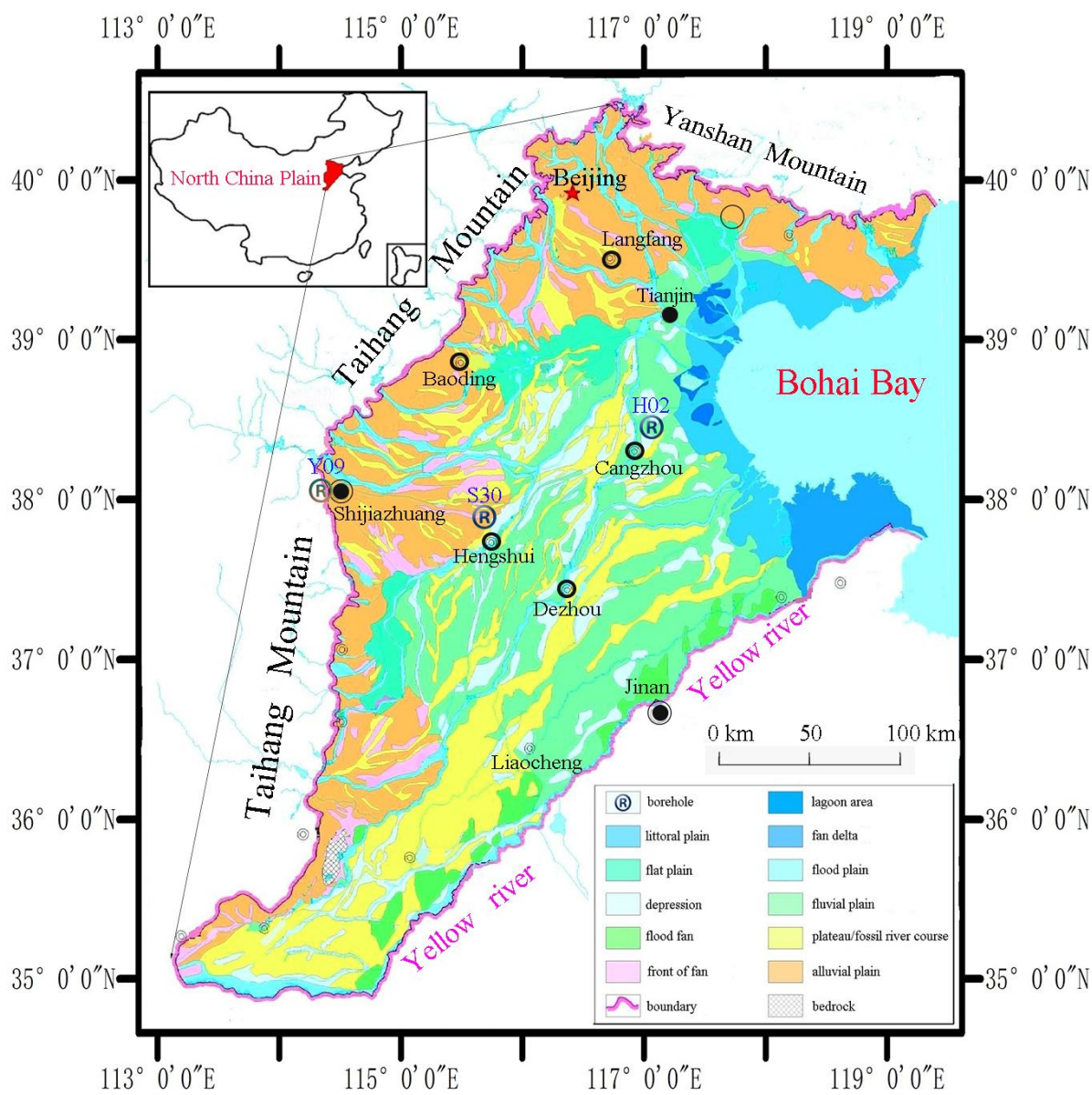


Fig. 1

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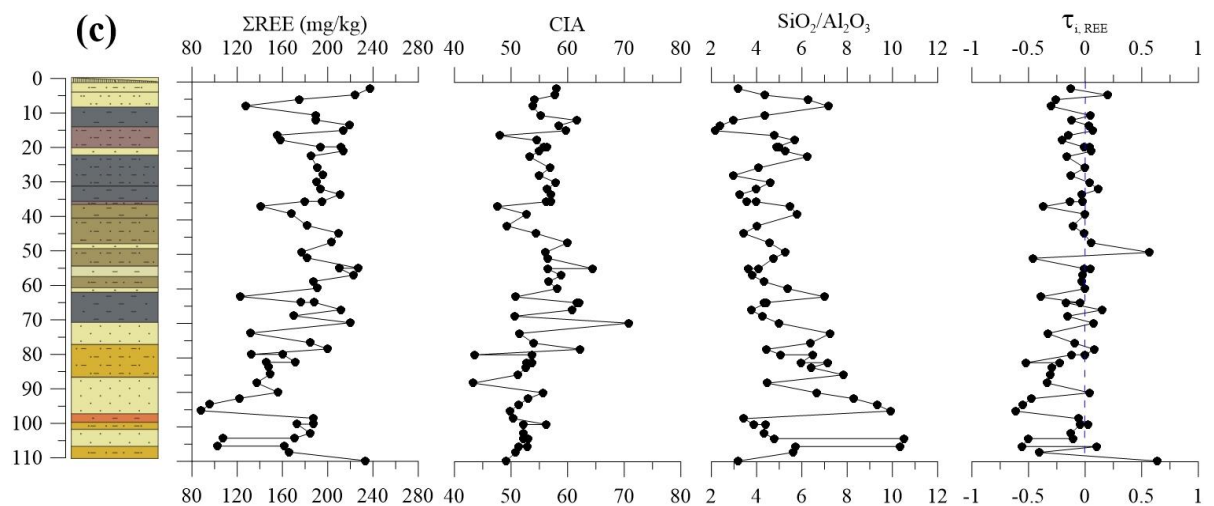
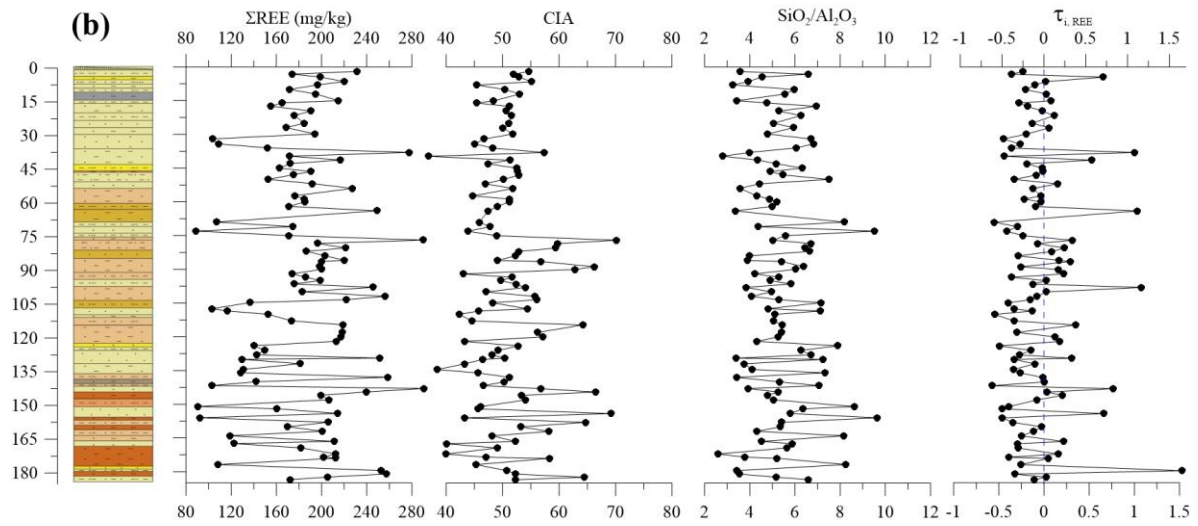
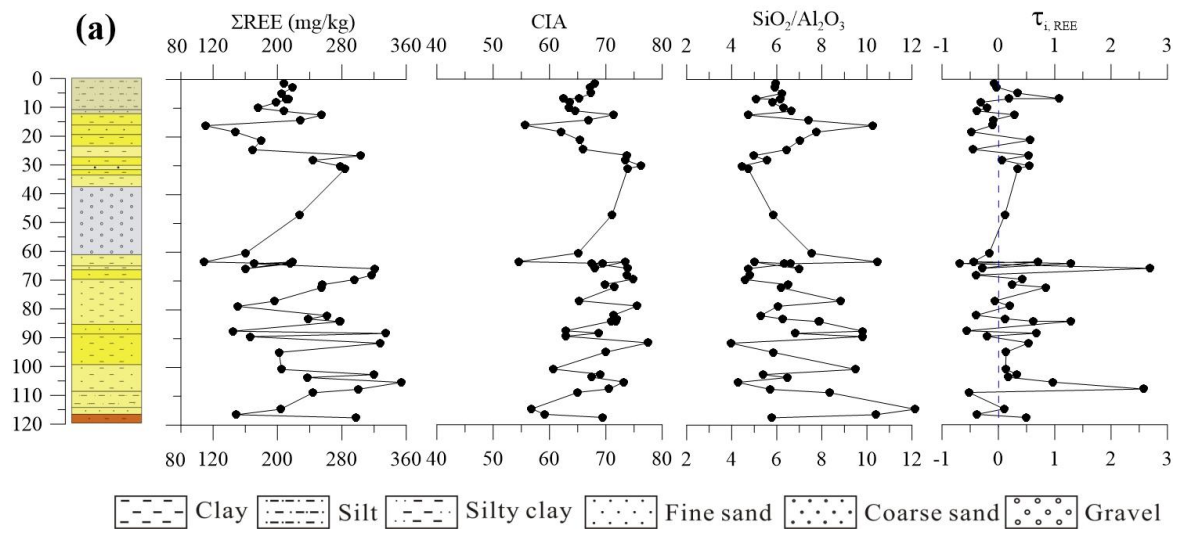


Fig. 2

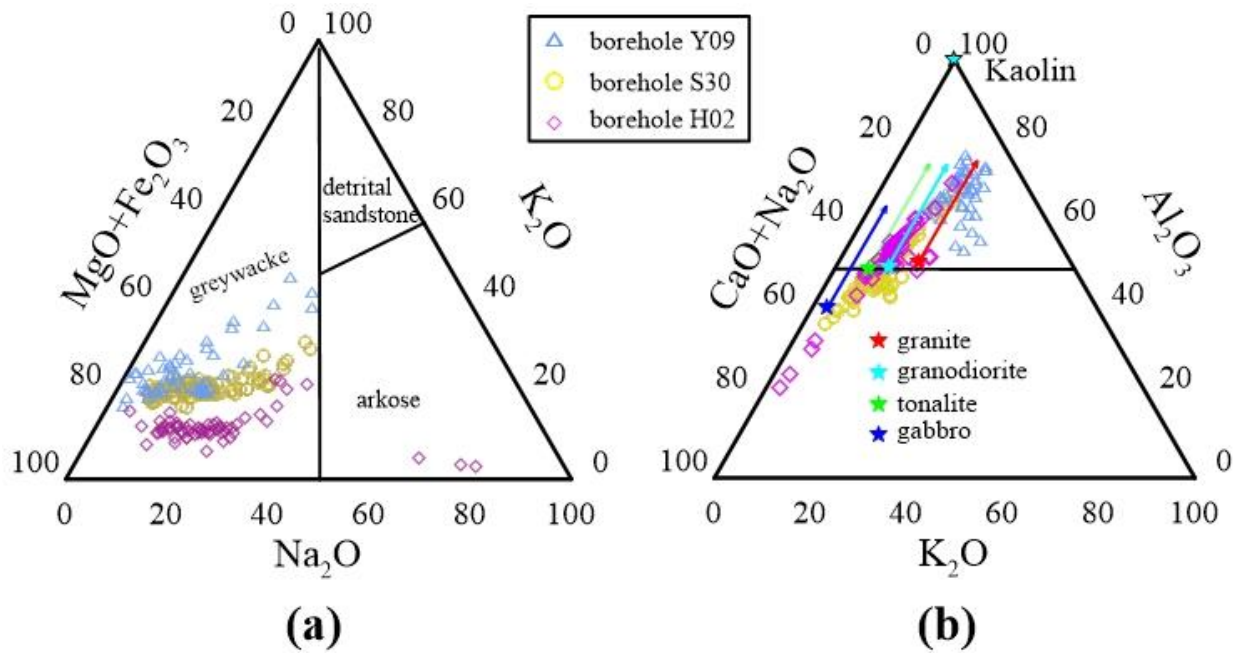


Fig. 3

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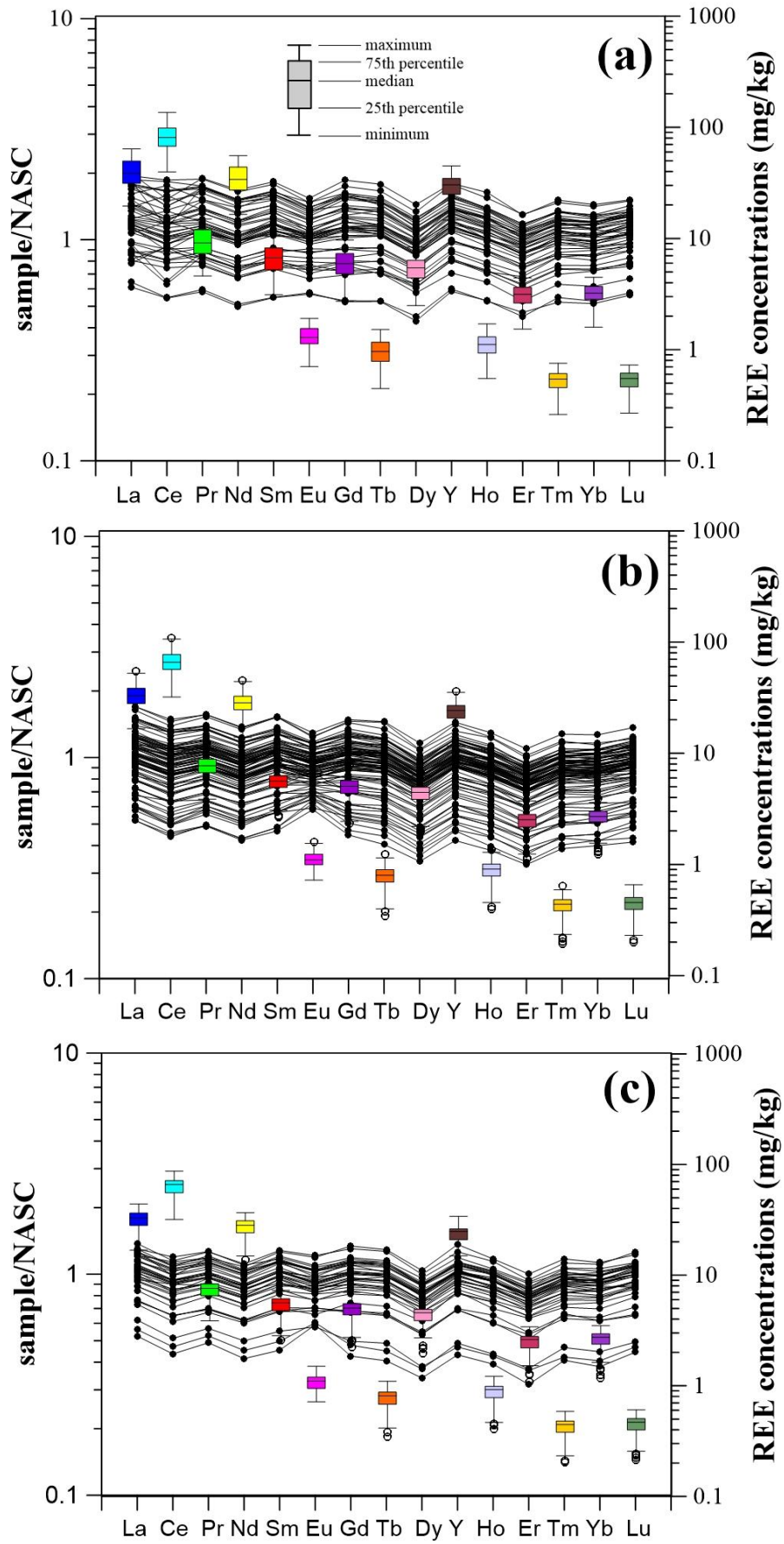
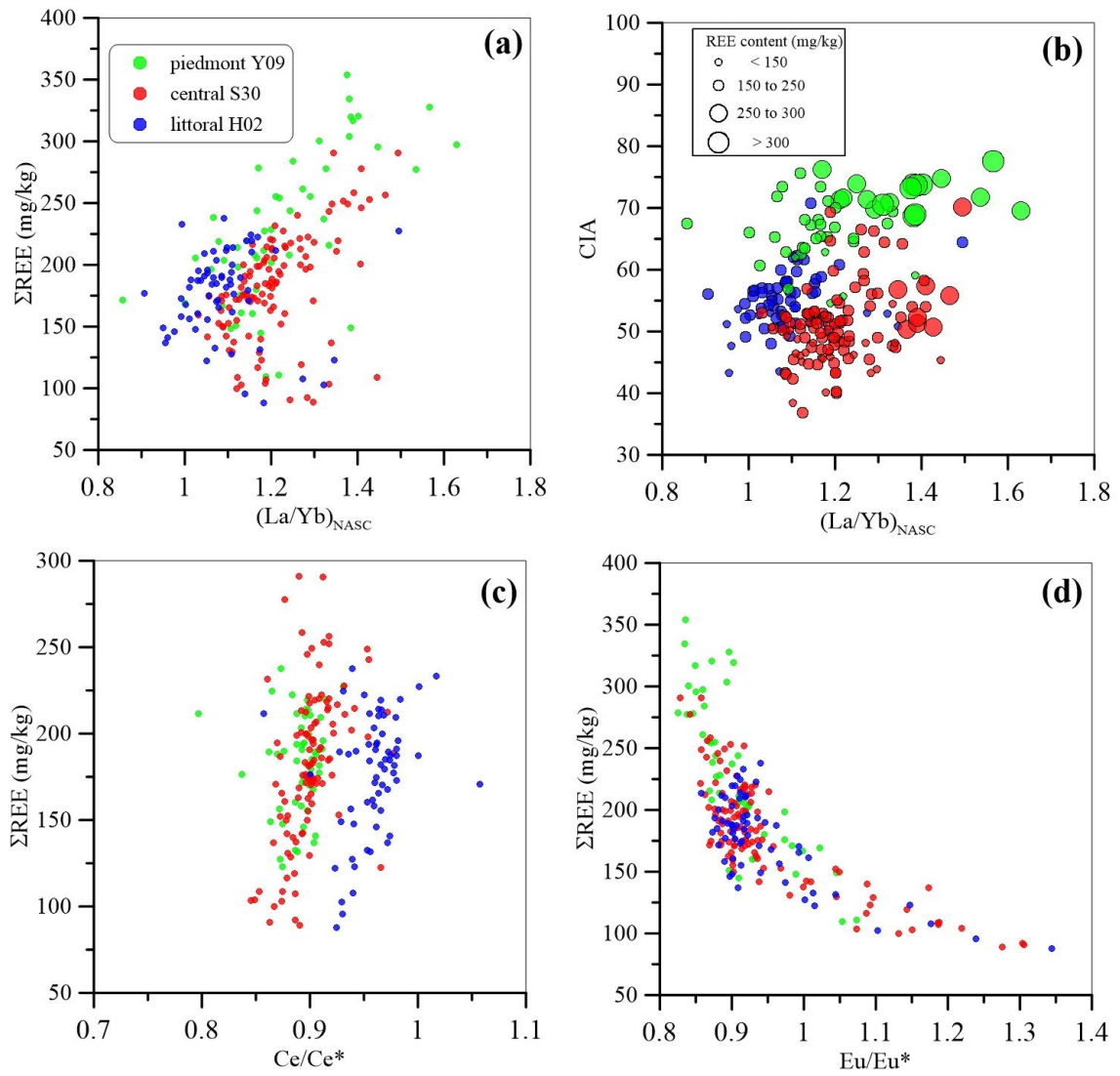


Fig. 4

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**Fig. 5**