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Continental records of organic carbon isotopic composition (13Corg), weathering, paleoclimate and wildfire linked to the End-Permian Mass Extinction

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1	Continental records of organic carbon isotopic composition ($\delta^{13}C_{org}$),
2	weathering, paleoclimate and wildfire linked to the End-Permian Mass
3	Extinction
4	
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20 ABSTRACT

The late Permian was the acme of Pangea assembly, with collision and subduction of global plates 21 accompanied by major changes in atmospheric composition, paleoclimates and paleoenvironments of 22 the Earth's surface system. These events are extensively recorded in marine successions from the 23 Tethys, but much less are known from continental successions that typically lack high-resolution 24 stratigraphic control. In order to reveal these fluctuations in terrestrial strata and their relationship 25 with the End-Permian Mass Extinction (EPME), we investigate continental $\delta^{13}C_{org}$, mercury and 26 nickel concentrations, wildfire, and climate change proxies from the late Permian Changhsingian 27 28 stage to Early Triassic Induan stage in the Yuzhou coalfield in the North China Plate (NCP). Results show two negative organic carbon isotope excursions (CIE) within the Changhsingian aged 29 Sunjiagou Formation, the first (CIE-I, 2.2‰) during mid-Changhsingian and a second, larger, 30 excursion (CIE-II, 2.7‰) near the end of the Changhsingian that coincides with the peaks in the 31 Chemical Index of Alteration (CIA) value and extinction of plant species. We infer CIE-II to be the 32 global negative excursion of $\delta^{13}C_{org}$ associated with the EPME. Arid climates prevailed in the study 33 area from the Changhsingian to the early Induan inferred from the low kaolinite contents and weak 34 continental weathering, except for two short-duration episodes with higher humidity that correspond 35 with CIE-I and CIE-II. Extremely high fusinite content ($\bar{x} = 63.1\%$) and its increasing abundance 36 through the Changhsingian indicates that frequent wildfires may have been a direct cause for both 37 the destruction of terrestrial vegetation ecosystems and the rapid decline of terrestrial biodiversity at 38 the EPME. We consider that terrestrial ecosystems may have played an important role in the 39 extinction of marine communities at the EPME. This represents the first time the EMPE has been 40 demonstrated in the NCP based on combined evidence from negative carbon isotope excursion, 41 42 concurrent weathering trends, Ni/Al ratio and biotic extinctions, representing an important step in accurately identifying and correlating the EPME in continental settings from the NCP. 43

Keywords: terrestrial strata, organic carbon isotope composition, weathering, palaeoclimate, wildfire,
End-Permian Mass Extinction, North China Plate

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48 **1. Introduction**

The End-Permian Mass Extinction (EPME) represents the largest mass extinction event in Earth 49 history, and resulted in substantial loss of 90% marine and 70% terrestrial species (Erwin, 1994). The 50 51 extinction was related to extreme fluctuations in atmospheric composition, paleoclimates and paleoenvironments on the Earth's surface system, that included rapid and sustained global warming 52 53 (Joachimski et al., 2012; Sun et al., 2012), ocean anoxia (Wignall and Twitchett, 1996) and widespread wildfires (Shen et al., 2011; Chu et al., 2020) amongst other kill mechanisms (Bond and 54 Grasby, 2017). Although the underlying triggers and extinction mechanisms for the EPME are 55 complex and difficult to disentangle from each other (Bond and Grasby, 2017; Wignall et al., 2020), 56 it is generally considered that the deterioration of global climate and environment is related to 57 58 intense volcanic activity from the Siberian Traps during the Permian-Triassic (P-T) transition (Shen et al., 2011; Burgess and Bowring, 2015; Ernst and Youbi, 2017). 59 Studies linking the EPME to changes in global climate and environment primarily focus on 60 marine strata (Wignall and Hallam, 1992; Wignall and Twitchett, 1996; Grasby and Beauchamp, 61 2009; Shen et al., 2011, 2013; Grasby et al., 2013, 2016; Liao et al., 2016, 2020) due to their often 62 continuous deposition and well-dated stratigraphic frameworks. By contrast, fewer studies have 63 focused on contemporaneous continental conditions despite their obvious link to the EPME as a 64

major source of nutrients flushed into marine settings (Algeo et al., 2013; Wignall et al., 2020). At
the same time ocean hypoxia thought to be triggered by algal and cyanobacterial proliferation in

68 2007). However, the reason for cyanobacterial proliferation is controversial. Some studies have

surface waters is a common phenomenon accompanied by the extinction of marine life (e.g., Xie,

69 attributed it to increased terrestrial input of nutrients caused by enhanced continental weathering (e.g.,

Algeo and Twitchett, 2010) with post-EPME oceans having high bioproductivity (e.g., Meyer, 2011;
Shen et al., 2015). In contrast, other studies consider it may result from the transformation of
nitrogen into ammonium in anoxic environments (Sun et al., 2019), with the role of land-sourced
nutrients limited and oceanic primary productivity low (Grasby et al., 2016a, 2019a; Sun et al., 2019).
Therefore, contemporaneous continental strata are important to understand the relationship of climate,
weathering and environmental changes between continents and marine settings.

76 From the P-T transition interval in the NCP, numerous past studies have focused on stratigraphy, sedimentology, palaeontology and tectonics (e.g., Wang and Wang, 1986; Hou and Ouyang, 2000; 77 78 Chu et al., 2015, 2017, 2019; Zhao et al., 2017), making these continental strata ideal for evaluating climate and environmental changes during this time period. These have identified major changes in 79 terrestrial diversity including extinctions in conchostracans and ostracoda (Chu et al., 2015), as well 80 81 as a dramatic reduction in plant species diversity near the boundary of the Changshingian aged Sunjiagou Formation and Induan aged Liujiagou Formation (Chu et al., 2015, 2019). In recent years, 82 elevated mercury and nickel levels as a signature for volcanism have been documented in marine and 83 terrestrial sediments associated with the EPME (Sanei et al., 2012; Grasby et al., 2013, 2015, 2016b; 84 2019b; Burgess and Bowring, 2015; Rampino et al., 2017; Fielding et al., 2019; Shen J et al., 2019; 85 Chu et al., 2020), but elevated mercury and nickel levels have not previously been recorded in the 86 continental environments of the NCP. 87

⁸⁸ Using the ZK21-1 borehole core in the Yuzhou Coalfield of the southern NCP, we consider ⁸⁹ fluctuations in $\delta^{13}C_{org}$, mercury and nickel concentrations, clay mineral components, Mineralogical ⁹⁰ Index of Alteration (MIA) for sandstones, the Chemical Index of Alteration (CIA) for mudstones, ⁹¹ and kerogen macerals to evaluate the changes of global carbon cycle, volcanism, climate, continental ⁹² weathering trend and wildfires in relation to the EPME. This represents an important step in the ⁹³ application of these proxies to evaluate the Permian-Triassic boundary interval in the continental ⁹⁴ successions of the NCP.

95 2. Geological background

During early Lopingian period, the NCP, surrounded by the Inner Mongolia uplift (IMU) to the 96 north and the North Qinling Belt (NQB, or Funiu paleo-land) to the south, was located in the 97 northeastern margin of the Paleo-Tethys Ocean (Fig. 1a), with a latitude of approximately 20° N 98 (Ziegler et al., 1997; Shang, 1997; Li, 2006; Muttoni et al., 2009). It was separated from the South 99 China Plate by the Paleo-Tethys Ocean, and from the Mongolian plate by the paleo-Asian ocean 100 101 (Zhao et al., 2017; Fig. 1a, e). During this period, sediments were mainly sourced from the northern IMU for the ongoing southward subduction of the paleo-Asian Ocean beneath the NCP (Zhang et al., 102 103 2014). In the Changhsingian stage, the NQB begin to uplift and became the secondary provenance of the NCP, but the main provenance for the study area in the Yuzhou coalfield located in the southern 104 NCP (Shang, 1997). The main part of the NQB is represented by the Qinling Group consisting 105 106 predominantly of Precambrian basement units including gneiss and amphibolite (Zhang et al., 1995; Dong and Santosh, 2016). 107

The stratigraphic succession, rock types and fossil plant assemblages from the late Permian to 108 Early Triassic in the study area are shown in Figure 2. The strata studied in this paper conformably 109 overlie the Upper Shihezi Formation and comprise the Sunjiagou Formation and the lower part of the 110 overlying Liujiagou Formation. The Sunjiagou Formation has been divided into three members 111 according to their lithological association (Yang and Lei, 1987; Wang, 1997). The lower and middle 112 members of the Sunjiagou Formation are composed of medium-coarse, feldspathic quartz sandstone 113 114 and thin layers of siltstone and mudstone, while the upper part of the Sunjiagou Formation is composed only of thin layers of mudstone and siltstone, all deposited in a shore-shallow lake 115 environment (Guo et al., 1991). Based on sporo-pollen and plant fossil assemblages, previous studies 116 117 have assigned the Sunjiagou Formation to the Changhsingian stage, and the conformably overlying Liujiagou Formation to the early Early Triassic Induan stage (Wang and Wang, 1986; Hou and 118 119 Ouyang, 2000; Wang and Chen, 2001; Chu et al., 2015). The Liujiagou Formation mainly

encompasses thickly layered medium to coarse sandstone, fine-grained sandstones and siltstones
with few trace fossils, mainly deposited in a braided river sedimentary system. The base of its
lowermost Jindoushan Sandstone member has been regarded as a regional marker for the
Permian-Triassic boundary (Guo et al., 1991; Fig. 2d). Within the Yuzhou Coalfield, we studied
borehole ZK21-1 that lies within the Putaosi exploration area that is a monoclinal structure inclined
toward the southwest (Fig. 1b, c, d).

126

127 **3. Materials and methods**

128 From the ZK21-1 borehole in the Yuzhou coalfield, fresh sandstone (27 samples) and mudstone (22 samples), were collected from the Sunjiagou Formation to the lower part of the Liujiagou 129 Formation. Sampling locations are shown in Figure 3. Every mudstone sample was first broken down 130 131 to less than 1 mm and then divided into two parts. One part was prepared for kerogen enrichment and identification according to the China national standard (SY/T5125-2014), with no less than 300 132 effective points per sample analyzed. The remaining part of each mudstone sample was further 133 crushed below 200 mesh and divided into six subparts for (1) $\delta^{13}C_{org}$ analysis, (2) clay mineral 134 135 analysis, (3) Total organic content (TOC) analysis, (4) major elements analysis, (5) trace elements analysis, and (6) mercury concentration analysis. Clay mineral and mercury concentration were 136 measured at the State Key Laboratory Coal Resources and Safe Mining (Beijing), and the other 137 analyses in Beijing Research Institute of Uranium Geology. 138

Organic carbon isotope analysis was performed using a stable isotope mass spectrometer (MAT253), and $\delta^{13}C_{org}$ values are expressed in per mil (‰) with respect to the Vienna Pee Dee Belemnite (VPDB) standard, with the absolute analysis error of ±0.1‰. Clay mineral was analyzed using an X-ray diffractometer (D/max 2500 PC), and the data were interpreted using Clayquan 2016 software with the relative analysis error of ±5%. Samples for TOC were first treated with phosphoric acid to remove inorganic carbon, and then the TOC values were measured using a carbon-sulfur 145 analyzer (CS580-A) with the lower detection limits of 100 μ g/g and the absolute analysis error of $\pm 0.2\%$. Major elements analysis was undertaken with an X-ray fluorescence spectrometer (PW2404) 146 147 with the relative analysis error of $\pm 5\%$. Trace elements analysis was undertaken using an inductively coupled plasma mass spectrometer (Finnigan MAT) with the relative analysis error better than $\pm 5\%$. 148 149 Mercury concentration was undertaken using a mercury analyzer (Lumex RA-915+) with lower detection limits of 2ng/g and the relative analysis error of $\pm 5\%$. More details of the analytical method 150 are described by Ma et al. (2015), Liao et al. (2016), Wu et al. (2017), Hu et al. (2020) and Chu et al. 151 (2020). Sandstone samples were cut into slices and identified by the point-counting method under a 152 microscope with more than 300 effective points of each sample. The classification of sandstone 153 components is in accordance with that of Dickinson (1985). 154

In this study, mercury and nickel concentrations have been used to indicate the presence of 155 volcanic activity due to their relationship with volcanic eruptions and magmatic intrusions (Sanei et 156 al., 2012; Burgess and Bowring, 2015; Rampino et al., 2017; Grasby et al., 2019b). The indexes of 157 MIA of sandstone and CIA of mudstone were used to restore the weathering trends of the parent rock 158 in provenance, their concepts and implications are outlined by Nesbitt and Young (1984), Fedo et al. 159 160 (1995), and Roy and Roser (2013). Paleoclimate inferences have been recovered by the kaolinite content of mudstone, with MIA and CIA values used for reference. As the abundance of kaolinite in 161 modern sediments is dependent on the intensity of chemical weathering controlled by climate 162 (Chamley, 1989), and because of its strong diagenesis resistance, changes in its content are 163 considered to be a reliable climatic proxy (Thiry, 2000). Fusinite (Charcoal) content has been used to 164 indicate paleowildfire (e.g., Scott, 2000; Glasspool and Scott, 2010). 165

166

167 **4. Results**

168 4.1. Total organic content (TOC) and distribution pattern of $\delta^{13}C_{\text{org}}$

169 Results for TOC and $\delta^{13}C_{org}$ are shown in Table 1 and Figure 3a, b. TOC values vary from 0.05–

170 0.12 % ($\bar{x} = 0.09\%$). These values are low 0.2% detection limit (see Grasby et al., 2019b) and will

171 not be used in the following discussion.

 $\delta^{13}C_{\text{org}}$ values vary from -26.5–23.0 ‰ ($\bar{x} = -24.7\%$), and show a vertical variation trend from 172 fast negative excursion with an offset of 2.2‰ (CIE-I) in the middle of the Sunjiagou Formation, 173 followed by slow positive excursion with an offset of 1.4‰. Near the top of the Sunjiagou Formation, 174 a second, larger excursion occurs with an offset of 2.7‰ (CIE-II). After CIE-II, $\delta^{13}C_{org}$ values 175 176 increase at the base of the Liujiagou Formation (Fig. 3b). Vertically, CIE-I and CIE-II corresponds approximately with the position of the two zones of high TOC values (Fig. 3a). High TOC values 177 occur elsewhere in the succession without corresponding $\delta^{13}C_{org}$ excursions (Fig. 3a, b). 178 179 4.2. Mercury and Nickel concentration 180

181 Results for mercury and nickel concentrations are shown in Table 1. Hg concentrations vary 182 from 2.21–27.04 ng/g ($\bar{x} = 22.5$ ng/g) (Table. 1) with an obvious peak in Hg concentration 183 corresponding to the position of CIE-II. Although the peak value in Hg concentration is 3 times the 184 average concentration, the value of Hg concentrations are within the average values of marine shale 185 in published papers (c.f. Grasby et al., 2019b). The nature of the Hg peak is not clear and we do not 186 regard it as definitive evidence for volcanism in the study area.

Nickel concentrations vary from 21.5–69.7 $\mu g/g$ ($\bar{x} = 34.45 \ \mu g/g$) with an obvious peak in concentration corresponding to the position of CIE-II. The value of the peak (69.7 $\mu g/g$) is within the range recorded during the P-T transition (12-800 $\mu g/g$; see Ramponi et al., 2017 and references therein).

Although Ni concentration may be related to volcanism, some researchers consider it to be influenced by aluminium content (e.g., Fielding et al., 2019). We corrected Ni concentrations by aluminium concentration and the values of the Ni/Al ratio (Fig. 3e) vary from 2.36–6.72 ×10⁻⁴ ($\bar{x} =$ 3.87×10⁻⁴). Two peaks in Ni/Al ratio occur of which the lower one is coincident with the position of CIE-II (Fig. 3b), indicating that the peak in Ni concentration and Ni/Al ratio corresponding to CIE-II
is reasonable to be inferred as evidence of volcanism affecting the study area.

197

198 *4.3. Kerogen macerals*

199 Identification results of kerogen macerals are shown in Table 1 and Figure 3f. Inertinite content varies from 49.3–70.1 % ($\bar{x} = 63.1\%$) and entirely comprises fusinite (charcoal) which is opaque, 200 201 pure black, does not fluoresce under fluorescence illumination (Fig. 4a-c) and is usually long and thin or fragmental shaped with sharp edges. Vertically through the succession, fusinite concentration 202 203 increases slowly at first, reaches a peak value of 70.1% near the top of the Sunjiagou Formation, and then decreases slowly after entering the Liujiagou Formation. The vitrinite group, with contents 204 varying from 24.4–45.0 % ($\bar{x} = 29.0\%$) mainly comprises normal vitrinite (Fig. 4d, e). Exinite 205 content varies from 3.6–11.9 % ($\bar{x} = 7.7\%$) of which suberinite is the main component (Fig. 4f, g). 206 Sapropelinite content is very low with an average value of 0.3% (Fig. 4h-k). 207

208

209 4.4. MIA, CIA, and Clay mineral component

The values of the Th/U ratio vary from 2.04 - 4.92 (Table 3), indicating that the parent rocks of 210 the sediments in the study area are not recycled. This is because recycled mudrocks exhibit high 211 Th/U ratios of around 6 due to oxidation of U^{4+} to U^{6+} and its removal as a soluble component (c.f. 212 Bhatia and Taylor, 1981). This conclusion is consistent with the provenance properties (stable land) 213 214 indicated by the Dickson diagram (Fig. 5a) and is in agreement with Shang (1997) and Dong and Santosh (2016) who determined sediments of the study area mainly originated from the North 215 Qinling Terrane (NQT) based on paleogeographic restoration and lithofacies analysis. 216 A reliability test of the CIA values in the study area was undertaken by the A-CN-K diagram 217 (Nesbitt and Young, 1984) that shows the CIA values deviate from the ideal weathering trend line 218 (Fig. 5b) and are affected by potassium metasomatism. Subsequently, these CIA values were 219

220	calibrated by the method of Fedo et al. (1995). MIA values vary from 70.9–91.8 (\bar{x} =78.8) (Table 2,
221	Fig. 3g), most of which are between 70–80 and show a relatively stable vertical distribution through
222	the succession, except for two intervals with MIA values > 80 near the middle of the Sunjiagou
223	Formation and at the boundary of the Sunjiagou and Liujiagou formations. The corrected values
224	(CIA _{corr}) vary from 78.1–86.5 (\bar{x} =83.7) (Table 3, Fig. 3h) and are similar to the MIA results,
225	reflecting moderate weathering of source area and showing a similar vertical change pattern. This
226	shows MIA and CIA are reliable indexes for indicating weathering trends in the study area. The two
227	periods of enhanced weathering approximately correspond with negative excursions CIE-I and
228	CIE-II (Fig. 3b, g, h).
229	The clay mineral components of the mudstone samples are mainly illite-smectite mixed layers,
230	followed by kaolinite and illite (Table 3, Fig. 3i, 6). The content of illite-smectite mixed layers varies
231	from 79–96 % ($\bar{x} = 90.5$ %). Kaolinite content changes from 2–18 % ($\bar{x} = 5.8$ %) and presents a
232	vertical trend of first decreasing and then increasing, but with two peaks in kaolinite content (about
233	10% and 18%, respectively) corresponding roughly with the position of CIE-I and CIE-II. The illite
234	content is very low with an average of 3.8%.
235	
236	5. Discussion
237	
238	5.1. Stratigraphic correlation and the position of the EPME
239	Previous studies of continental weathering in the Yima and Shichuanhe sections in the NCP
240	during the P-T transition shown that CIA values tends to increase first and then decrease, with the
241	maximum CIA values occurring at the top of the Sunjiagou Formation and approximately correspond

- to the End-Permian Plant Extinction (EPPE) (Cao et al., 2019). This provide a timeline for the
- 243 position of the EPPE in the NCP. We follow this conclusion, using the peak in CIA as a marker for
- the EPPE and place the EPPE at the horizon coincident with CIE-II in the study area.

Furthermore, chemostratigraphy can provide evidence for the correlation between the EPPE in 245 NCP and marine settings. Investigations on $\delta^{13}C$ distribution patterns from stratigraphically 246 well-constrained Lopingian to early Triassic profiles have been undertaken in marine (Meishan, 247 Niushan) (e.g., Shen et al., 2013; Liao et al., 2016, 2020) and terrestrial (Dalongkou, Lubei, 248 Guanbachong, Chahe, Longmendong, Bunnerong-1) strata (e.g., Zhang et al., 2016; Shen J et al., 249 2019; Fielding et al., 2019). These reveal δ^{13} C is relatively stable during the early Changhsingian, 250 followed by a gradual and slow decrease during the late Changhsingian prior to a globally significant 251 excursion with an average negative offset of 3-5 ‰ shortly before the P-T boundary (Shen S et al., 252 2019). The end-Changhsingian negative excursion of δ^{13} C represents a major reorganization of the 253 global carbon cycle associated with the EPME interval and is a global phenomenon (Shen S et al., 254 2011, 2013, 2019). 255

In the study area, the $\delta^{13}C_{org}$ trend is very similar to that in Meishan Changhsingian stratotype 256 section at Changxing, South China (Nan and Liu, 2004). CIE-I occurs in mudstones on top of the 257 Pingdingshan Sandstone (Fig. 3), it may be a regional negative excursion as while it is present in the 258 Meishan section in South China, it is absent in many other sections globally (e.g., Yin et al., 2007). 259 In our study, no changes in plant species composition occur at this level (Fig. 2h). CIE-II occurs near 260 the top of the Sunjiagou Formation, and coincident it is a significant floral extinction event just 261 below the P-T boundary (Fig. 2h) that occurs across the NCP (Wang and Wang, 1986; Chu et al., 262 2015). Moreover, peaks in nickel concentration and Ni/Al ratio during the P-T transition period also 263 are within the extinction interval of the EPME (Rampino et al., 2017 and references therein; Fielding 264 et al., 2019). As a result, we interpret CIE-II as correlating with the end-Changhsingian negative 265 excursion associated with the EPME in Meishan Changhsingian stratotype section. Our study 266 support the hypothesis that the extinction is synchronous in both terrestrial and marine successions 267 (Shen S et al., 2011, 2013, 2019; Zhang et al., 2016) although other recent research shows that the 268 extinction of terrestrial life earlier than that of marine life (Fielding et al., 2019; Gastaldo et al., 2020; 269

Chu et al., 2020). This might suggest that the terrestrial extinction was not synchronous, occurring
earlier at higher latitudes and closer or at the same time as the marine extinction at lower latitudes
(Feng et al., 2020).

273

274 5.2. Paleoclimate changes and continental weathering regimes

In the NCP during the Changhsingian, previous studies considered that arid paleoclimates 275 276 prevailed (Yang and Lei, 1987; Cope et al., 2005; Yang and Wang, 2012), related to the northward drift of the NCP through arid subtropical latitudes and/or rain-shadow effect from topography 277 278 resulting from collision with the Mongolia block (Cope et al., 2005). In study area, the wetland Cathaysian flora was rapidly succeeded by a Zechstein-type drier flora at the end of the 279 Wuchiapingian (Yang and Wang, 2012; Fig. 2g). In the NCP, the absence of coal deposition, 280 281 widespread distribution of red beds in the Sunjiagou and Liujiagou formations, and the occurrence of calcareous nodules in the upper part of Sunjiagou Formation collectively indicate high evaporation 282 and an arid paleoclimate (Yang and Lei, 1987; Wang, 1997). 283 In our study a generally arid paleoclimate is evidenced based on low kaolinite content in 284 mudstones and the moderate-weak continental weathering of the source area (Fig. 3g, h, i, 7a). 285 However, this was not continuous with two short duration periods of relative humidity appearing in 286 the mid-Changhsingian and near the P-T boundary (Fig. 7h). This is more pronounced in the latter 287 event that coincides with CIE-II where kaolinite content of mudstones reaches 18%, and the values 288 of MIA and CIA exceed 80 and 85, respectively. This conclusion is supported by records from the 289 Yima and Shichuanhe sections in the NCP near the P–T boundary (Cao et al., 2019), where peaks in 290 CIA values roughly correspond to the EPPE. At the same time, similar peaks in CIA values and 291 292 Kaolinite content also were recorded in southeast Australia, the reason of which has been attributed to the intensification of humidity/warmth around the EPME (Fielding et al., 2019). Short-term 293

294 climatic humidification and enhanced continental weathering in the P-T transition has also been

recorded in other areas of the world (e.g., Bachmann and Kozur, 2004; Sheldon, 2005; Retallack,
2005; Song, 2015).

There is no consensus on whether or why the climate became wet near the P-T boundary. Many 297 previous studies suggested that paleoclimate humification around the Tethys Ocean may be related to 298 the increased precipitation and surface runoff caused by the intensification of Monsoon activity 299 (Winguth and Winguth, 2013), or acceleration of the land water cycle caused by the rising global 300 301 temperature (Van Soelen et al., 2018). However, some studies suggest that the increase of kaolinite content and the enhancement of continental weathering from the late Changhsingian to early Induan 302 303 are related to the increase of atmospheric pCO_2 and acid rain caused by frequent volcanic activity (Algeo and Twitchett, 2010; Sun et al., 2018; Cao et al., 2019). This is because elevated acidity and 304 temperature conditions can accelerate rock weathering rates. As such volcanic activity may mislead 305 306 the paleoclimate and continental weathering trends based on kaolinite content as well as influencing MIA and CIA values. 307

In the study area, the increased kaolinite content and MIA and CIA values after the EPME occurred in a period of rapidly rising global sea level (Cao et al., 2009; Yin and Song, 2013). This significantly increased water vapor transportation to land (Winguth and Winguth, 2013), resulting in continental climatic humidification. This may explain the terrestrial climate wetting after the EPME but it cannot rule out the possibility that climate humidification and the prevalence of acid rain occurred simultaneously.

314

315 5.3. Continental Wild-fire linked to EPME and marine extinctions

Fusinite, or charcoal, is fire-derived and evidences wildfires in the rock record (Scott, 2000; Glasspool and Scott, 2010). In the Yuzhou coalfield, inertinite (fusinite) is the most abundant kerogen maceral group ($\bar{x} = 63.1\%$). The high fusinite content and its vertical variation pattern (see

4.3) indicate that the paleo-fires prevailed in the southern NCP during the middle

Changhsingian-early Induan and reach their peak near the P–T boundary. This increasing frequency of continental paleo-fires appears to be a global phenomenon, with similar records recorded in other parts of NCP as well as in South China, Australia, and Canada (e.g., Wang and Chen, 2001; Grasby et al., 2011; Shen et al., 2011; Chu et al., 2020).

Factors affecting wildfire include availability of combustible fuel, atmospheric oxygen 324 concentration to enable burning, a suitable climate lacking high moisture, and an ignition mechanism 325 326 (Scott, 2000). The Zechstein-type flora present across the NCP during the Changhsingian was adapted for dry climates and would have been an appropriate source of fuel. Atmospheric oxygen 327 328 concentration at the end-Permian has been estimated as 21-27 %, far in excess of the minimum oxygen requirement of 15% for plant combustion (Glasspool and Scott, 2010). Dry and hot climates 329 favor the prevalence of wildfires, and water limited conditions persisted during the Changhsingian in 330 the study area prior to the EMPE (Fig. 7h). However, at the beginning of the EPME interval, the 331 climate tended to be relatively humid reducing the likelihood of wildfire. Therefore, the prevalence 332 of wildfire in the late Changhsingian may have been controlled by ignition factors. Under natural 333 conditions, ignition is caused by lightning, volcanic eruption and less probably meteor impact 334 (Glasspool et al., 2015). Of these, there is no volcanic activity in proximity to the Yuzhou coalfield 335 suitable to ignite wildfires, nor is there any evidence for meteor impact as an ignition mechanism at 336 this time. Lightning would have been the main ignition source of wildfire in the run-up to the EPME, 337 the occurrence of which was related to the climate and atmospheric pCO_2 (Glasspool and Scott, 2010; 338 Glasspool et al., 2015). 339

In the NCP, wildfire may be the direct cause for both the destruction of terrestrial ecosystems and the rapid decline of plant biodiversity at the EPME, also playing an important role in the extinction of marine organisms (Shen et al., 2011; Zhang et al., 2016). Damage to the land surface vegetation system by frequent wildfire during the EPME interval would have led to increased soil erosion as well as exposing bedrock and increasing continental weathering leading to siltation (Shen

345 et al., 2011).

In the study area, many greyish-green and purplish red mudstone clastics occur in the lake 346 347 mudstone associated with the CIE-II and persist into the early Triassic in the drill core ZK21-1 (Fig. 8a). This is a common phenomenon in the NCP and similar mudstone clastics also was observed in 348 the uppermost Sunjiagou Formation in borehole core profile in the Liujiang area in Hebei province 349 (middle NCP) (Fig. 8b), and the Shuiyuguan section in Shaanxi Province (middle NCP) (Fig. 8c, d). 350 351 These mudstone clastics may indicate the increased soil erosion after the collapse of terrestrial vegetation systems. This increased soil erosion does not have a significant effect on the chemical 352 353 weathering, because it promoted erosion and transportation of the surface soil. However, the decline in CIA values following the EPPE may reflect loss of weathered soils through physical erosion (Cao 354 et al., 2019). 355

As a result of wildfire, large amounts of organic matter (including charcoal and un-charred 356 matter) and nutrients (including phosphorus and potassium) produced by plant combustion and 357 weathering of parent rock would enter the oceans through surface runoff (Algeo et al., 2013; 358 Glasspool et al., 2015). These inert organic particles would float in ocean for some time, increasing 359 oceanic turbidity through siltation, and affect the penetration of light and the photosynthesis of 360 marine organisms (Glasspool et al., 2015). Large nutrient inputs may be one of the main reasons for 361 prospering cyanobacteria and algae in oceanic surface waters (Meyer et al., 2011; Shen et al., 2015). 362 Eutrophication of seawater during the P-T transition was considered as a localized phenomenon 363 (Algeo et al., 2013) while Sun et al. (2019) considered the transformation of nitrogen to ammonium 364 the main reason for the cyanobacterial proliferation at this time. In this context, oxygen circulation 365 between seawater and atmosphere would have been inhibited by floating inert organic particles, 366 cyanobacteria and algae in surface waters, increasing the consumption of dissolved oxygen by the 367 decomposition of dead cyanobacteria and algae remains (e.g., Algeo et al., 2013; Glasspool et al., 368 2015; Sun et al., 2019). This would have further contributed to oceanic anoxia and the extinction of 369

aerobic marine organisms.

371 While siltation may be a causal mechanism for mass extinctions in the marine realm, Wignall et al. (2020) concluded this was not the case for the EPME in the western Guizhou and eastern Yunnan 372 region of the South China Plate (SCP). Plant material in that region was trapped in alluvial settings 373 during base-level rise and did not enter the ocean. However, siltation may have occurred in the 374 southeastern sea area of the NCP. Here fluvial depositional systems, represented by the Jindoushan 375 Sandstone developed through nearly the whole NCP during the P-T transition period following rapid uplift 376 of the IMU to the north (Shang, 1997; Zhang et al., 2014). Large amount of sediment including organic 377 378 matter may have entered the ocean from the southeast exit of the basin. Sedimentological evidence for this 379 likely siltation is not available because sedimentary strata to the west of the Tanlu Fault (Fig. 1b, c) that 380 would have recorded this were eroded post-deposition.

381

382 6. Conclusions

1) Values of $\delta^{13}C_{org}$ show negative excursions in the middle (CIE-I) and end (CIE-II) Changhsingian, the latter roughly corresponds to End-Permian plant extinction (EPPE) in NCP through the comparison of continental weathering trend. We infer CIE-II to be the global negative excursion associated with the EPME, because it occurs in the Meishan and other sections globally, and is synchronous with peaks in nickel concentration and Ni/Al ratio and with the EPPE.

2) Two short-duration episodes with greater humidity, corresponding to CIE-I and CIE-II 388 occurred in the context of the prevailing arid climate from the Changhsingian to the early Induan, 389 inferred from the low kaolinite content and weak continental weathering. The extremely high fusinite 390 content of kerogen macerals and their vertically increasing trend indicates that frequent wildfires 391 392 occurred in the run up the end Permian. Widespread and frequent wildfire is likely to have been a causal mechanism for the destruction of terrestrial vegetation and ecosystems at the EPME. The 393 appearance of the mudstone clastics coincident with the CIE-II may indicate the increased soil 394 erosion after the collapse of land vegetation systems. The mudstone color shift to green may 395

indicated the development of less drained alluvial landscapes (e.g., more persistently wet), this isconsistent with the change in CIA values.

398

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Figure 2. Stratigraphic framework for the Permian-Triassic boundary strata from the Yuzhou 664 coalfield. Note: Lithology from Yang and Lei (1987) and the colors filling in lithology are similar to 665 that of the rocks. a, Strata in the basin highlighting the study interval; b, Formation thicknesses from 666 Guo et al. (1991) and Pan et al. (2008); c, Stratigraphic division of the Sunjiagou Formation from 667 Yang and Lei (1987) and Wang (1997); d, Marker beds from Guo et al. (1991); e, Summary 668 sedimentary environments from Guo et al. (1991); f, Fossil plant assemblages from Yang and Wang 669 (2012); g, Floral provinces from Wang and Wang (1986), Pan et al. (2008) and Yang and Wang 670 (2012); h, Vertical distribution of plant fossils from Chu et al. (2015) showing the extinction near the 671 672 boundary of the Sunjiagou and Liujiugou formations; i, Basin type from Hao et al. (2014); j,

Tectonic events from Shang (1997) and Zhao et al. (2017). Abbreviations: Ol. = Olenekian; Forma. =
Formation; He. = Heshanggou; S.S.H. = Shangshihezi; C = Clay; S = Siltstone; Sa. = Sandstone; Thi.
= Thick; Mark. B. = Marker bed; 8[#] = 8[#] coal seams; P.D.S.st: Pingdingshan sandstone; La. m.:
Lamellibranchiate marl; Gyp. Li.: Gypsum lime-nodule; J.D.S.: Jindoushan Sandstone; Dep. En. =
Depositional environment; Sporo. = Sporo-pollen; *Ginkgo*.: Ginkgopsida; Sp.: Sphenopsida; Pl.:



Figure 3. Change in value of TOC, $\delta^{13}C_{org}$, Hg and nickel concentrations, kerogen macerals, MIA and CIA, and clay minerals component in the study area. Note: the colors filling in lithology are similar to that of rocks, the interpretation of the deposition environment is from Guo et al. (1991) and Pan et al. (2008), and pay attention to the scales in column f and i. Abbreviations: C = claystone; S = siltstone; Sa. = sandstone; Mark. Bed = marker bed; Dep. En. = depositional environment; J.D.S st = Jindoushan Sandstone; P.D.S. sandstone = Pingdingshan sandstone; PTB = Permian-Triassic boundary; EPME = End Permian mass extinction.



Figure 4. Photomicrographs showing microstructure characteristics of kerogen macerals in the study area. **a**, overview showing characteristics of kerogen macerals (transmitted light, sample #23); **b** and **c**, fusinite (transmitted light, #45); **d** and **e**, vitrinite (transmitted light, sample #16 and #49); **f** and **g**, suberinite (transmitted light and fluorescence, respectively, sample #42); **h**, sapropelinite (transmitted light, sample #22); **i** and **j**, sapropelinite (transmitted light and fluorescence, respectively,

sample #50)



Figure 5. Qm-F-Lt diagram of sandstone and A-CN-K diagram of mudstone in the study area. a,
 Qm-F-Lt diagram of sandstone samples from Changhsingian to early Induan showing the main

provenance area of continental block (modified from Dickinson, 1985). Abbreviations: Qm = 699 monocrystalline quartz; F = feldspar (plagioclase + K-feldspar); Lt = total lithics (lithics + 700 polycrystalline quartz); A = Continental block; B = Magmatic arc; C = Recycled orogen. b, A-CN-K 701 diagram of mudstone samples from Changhsingian to early Induan with the chemical index of 702 alteration (CIA) scale to the left, showing the possible influence of Potassium metasomatism. For 703 comparison, the average upper crust CIA value of southern and interior North China Craton are 704 705 shown (modified from Cao et al., 2019). Abbreviations: $A = Al_2O_3$; $CN = CaO^* + Na_2O$; $K = K_2O$; CIA= chemical index of alteration; Ka = kaolinite; Gi = gibbsite; Il = illite; PI = Plagioclase; Chl = 706 707 chlorite; Sm = smectite; Ksp = K-feldspar; INCC = Interior North China Craton; SNCC = Southern North China Craton. 708

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Figure 6. X-ray diffraction (XRD) patterns of clay fractions of typical samples in the study area. N, E 711 and T designate spectra of a naturally-oriented slide, ethylene-glycol saturated for oriented slide and 712 713 high-temperature treated at 450°C for oriented slide, respectively. a, XRD patterns showing high content of illite-smectite mix layer and kaolinite (Sunjiagou Formation, sample #23); b, XRD 714 patterns showing high content of illite-smectite mix layer and lowest kaolinite content (Sunjiagou 715 716 Formation, sample #34); c, XRD patterns showing high content of illite-smectite mix layer and less 717 kaolinite content (Sunjiagou Formation, sample #45). Abbreviations: I/S = illite-smectite mixed layer; K = kaolinite; I = illite. 718









Figure 8. Pictures showing a lot of mudstone clastics was observed in uppermost Sunjiagou 739 Formation in NCP. a: lots of greyish-green and purplish-red mudstone clastics occur in the lake 740 mudstone associated with the CIE-II and last into early Triassic in the drill core ZK21-1, Henan 741 province (southern NCP). Note: the colors filling in lithology are similar to that of rocks, and the 742 numbers (e.g.,(1)-(3)) represent the vertical order of lithology. **b**: lots of mudstone clastics was 743 observed in the uppermost Sunjiagou Formation in borehole core profile in Liujiang area, Hebei 744 745 province (middle NCP). c: Picture of Shuiyuguan section (Shaanxi province, middle NCP) showing the boundary of Sunjiagou and Liujiagou formations with highlighted box enlarged in d. d: 746 enlargement from c showing details of mudstone clastics in the uppermost Sunjiagou Formation. 747