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1	Evaluating episodic hydrothermal activity in South China
2	during the early Cambrian: Implications for biotic evolution
3	
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24 ABSTRACT

The early Cambrian (541–514 Ma) was a crucial interval for the evolution of life on 25 Earth, popularly known as the "Cambrian Explosion". Here, we report the timing of 26 changes in hydrothermal and depositional inputs, as well as paleo-redox state, which 27 may have influenced biogeochemical changes. According to high-resolution petrology, 28 fossil distributions, isotopic records, and inorganic geochemistry, the lower Cambrian 29 30 of the South China can be subdivided into four intervals: the lowermost Cambrian Zhujiaqing Formation (Cam-I); the Cambrian Stage 2 Shiyantou Formation (Cam-II); 31 the lower part of the Cambrian Stage 3 Yu'anshan Formation (CAM-III); and the mid-32 upper Cambrian Stage 3 and the middle-upper part of the Yu'anshan Formation, 33 continuing into the Canglangpu Formation (Cam-IV). Hydrothermal events are 34 detected during the early Cam-I, Cam-II, and Cam-III intervals. During the early Cam-35 I and Cam-II intervals, these events coincided with extensive bottom water euxinia, 36 37 which in turn may have restricted the spread or proliferation of Ediacaran fauna and 38 small shelly fauna. Through the whole Cam-III interval, further hydrothermal events occurred concurrently with euxinic and ferruginous conditions, probably within a single 39 spatially stratified water column, again plausibly restricting the spread of aerobic 40 41 organisms. In conjunction with the cessation of hydrothermal events and the gradual lowering of sea level during the late Cam-III, oxic water environments gradually spread 42 into relatively deep-water regions, concurrent with the emergence of the Chengjiang 43 and Qingjiang faunas. These data suggest that periodic hydrothermal events may have 44 had a significant impact on the spread, radiation and extinction of macroscopic fauna 45

46 during the early Cambrian in South China.

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Keywords: Yangtze Block, Niutitang Formation, Cambrian Radiation, extinction,
hydrothermal event

50

51 **1. Introduction**

The late Ediacaran to early Cambrian (551-514 Ma) was one of the most bio-52 geochemically important periods in Earth history and included a number of significant 53 geological events including the break-up of the supercontinent Rodinia, extinction of 54 the Ediacaran biota, appearance and extinction of small shelly fossil assemblages 55 (SSF1-4), establishment of anoxic and/or sulfidic water conditions, appearances of the 56 Chengjiang and Qingjiang biotas, and the stepwise oxygenation of global oceans 57 58 (Zhuravlev and Wood, 1996; Johnson et al., 2005; Marshall, 2006; Laflamme et al., 59 2013; Jin et al., 2016; Li et al., 2017; Fu et al., 2019). Attempts to explain the biological radiation and extinction by co-occurring environmental events have been conducted 60 61 during the past two decades. Biological evolution during the early Cambrian plausibly exhibited a close relationship with oceanic and atmospheric oxygen levels (Lenton et 62 al., 2014). Although redox conditions of the early Cambrian oceans in South China have 63 64 been widely studied from inner-shelf to basin settings (Goldberg et al., 2007; Guo et al., 2013; Och et al., 2013; Feng et al., 2014), uncertainties remain as to how to 65 mechanistically connect such data to biological evolution; with some studies 66 questioning the importance of any link between redox conditions and biological 67 evolution (Jin et al., 2016; Xiang et al., 2017). A range of possible causal mechanisms 68 3

exist for the extinction of small shelly faunas (Darroch et al., 2018), but which of theseis likely the most significant is presently unclear.

71 More broadly within the geological record, there is a strong correlation between mass extinction events and the occurrence of Large Igneous Provinces (LIPs) (Wignall, 72 73 2001; Courtillot and Renne, 2003; Bond and Wignall, 2014; Ernst, 2014). For example, the Permian-Triassic (252 Ma), Triassic-Jurassic (201 Ma), and Cretaceous-Paleogene 74 (66 Ma) mass extinctions were related to the Siberian LIP, Central Atlantic LIP, and 75 Deccan LIP, respectively (Blackburn et al., 2013; Burgess and Bowring, 2015; Schoene 76 77 et al., 2015; Font et al., 2016; Thibodeau et al., 2016). The general mechanism for this connection is thought to be the large scale input of associated greenhouse gases, leading 78 79 to temperature extremes and associated climatic cycles, with a knock-on effect on 80 biological growth and diversification (Benton, 2018).

In South China, a major marine transgression occurred during the early Cambrian, 81 followed by widespread deposition of organic matter- (OM-) rich shale across the 82 83 Yangtze Block, which was accompanied by chert, phosphorite, barite, and Ni-Mo polymetallic ores (Coveney and Chen, 1991). Studies from outcrop sections in South 84 China have also demonstrated the presence of frequent hydrothermal (submarine 85 volcanic) deposits (Steiner et al., 2001; Chen et al., 2009; Liu et al., 2015; Guo et al., 86 2016; Han et al., 2017; Gao et al., 2018), typically represented by ore bodies. For 87 example, early Cambrian hydrothermal vent communities were found in Guizhou 88 Province (Yang et al., 2008). However, the effects of hydrothermal events on 89 depositional environments and biological patterns have, by comparison, been largely 90

91 overlooked.

Few investigations of the paleo-environmental impacts of hydrothermal events on 92 93 Cambrian biotas in a more general sense have been conducted as summarized by Yang et al. (2008). Condon (2005) found obvious signatures of hydrothermal events in shale 94 95 and dolomite at the bottom of the Ediacaran Doushantuo Formation in South China. This hydrothermal event released a large amount of CH₄, leading to highly ¹³C-depleted 96 carbonate cements ($\delta^{13}C_{PDB}$ down to -48‰), and global warming (Bristow et al., 2011; 97 Sahoo et al., 2012). Extinctions may be the result of a sequence of feedbacks triggered 98 99 by such greenhouse input, or similar biogeochemical perturbations, including global 100 temperature extremes, oceanic anoxia, ocean acidification, and toxicity resulting from input of metals and gases into oceans (Chen et al., 2009; Wegener and Boetius, 2009; 101 102 Clarkson et al., 2015). As the timing and duration of hydrothermal events during the early Cambrian also remains unclear, investigations on submarine hydrothermal events 103 during the Cambrian may therefore provide new insights into understanding the driving 104 105 forces for changes in the composition, distribution and diversity of Cambrian biota. In this study, we established a systematic stratigraphic correlation of 18 lower 106 Cambrian sections across South China, by means of high-resolution petrology, 107

biostratigraphy, isotope dating, and inorganic geochemistry. Our objective was to examine the occurrence, magnitude and extent of the influence of hydrothermal and volcanic events, with particular focus on their likely impact on oceanic environments

and biological patterns in South China during the early Cambrian.

112

113 **2.** Geological setting and stratigraphy

114 2.1. Geological setting

115 During the Ediacaran–Cambrian transition, South China consisted of the Yangtze 116 and Cathavsia blocks. Sedimentary environments from the northwest to southeast were 117 comprised of platform, inner shelf, outer shelf, slope, and marine basin settings (Fig. 118 1A). The Ediacaran–Cambrian boundary (ECB) is recognized on the basis of small shelly fauna and trace fossils (Goldberg et al., 2007; Wang et al., 2012). Volcanic ash 119 beds have also been discovered near the ECB in some sections across South China (Fig. 120 2, U-Pb dating: 538.2±1.5 Ma, 539.6±1.4 Ma, 542.1±5.0 Ma, 542.6±3.7 Ma, and 545.8 121 122 ± 0.7 Ma). Shallow-water areas to the northwest are mainly associated with the deposition of dolomite and limestone, whereas deep-water areas to the southeast mainly 123 124 are dominated by chert and siliceous rocks (Fig. 2).

During the late Cambrian Stage 2, as a result of the final break-up of the Rodinia 125 Supercontinent, the Yangtze Block entered into a rifting phase, and a major 126 127 transgression occurred (Fig. 1B). Black shale was widely deposited across South China, which was developed in the lower Cambrian Yu'anshan and Guojiaba formations and 128 129 their stratigraphic equivalents, with formations gradually thickening from the northwest to southeast. Super continental break-up and seafloor expansion promoted widespread 130 hydrothermal and volcanic events, as evidenced by extensive trace metal deposition 131 (Steiner et al., 2001; Xu et al., 2011; Han et al., 2017). During the late Cambrian Stage 132 3 (518–514 Ma), the small shelly fossil assemblages subsequently disappeared and the 133 Chengjiang and Qingjiang biotas then flourished. 134

Volcanic ash beds near the ECB suggest that volcanic events may have been 135 extensive and widespread during this time interval (Fig. 2). Obvious unconformities 136 137 occur in shallow-water carbonate platform settings (mainly in Yunnan and Guizhou provinces), suggesting rapid tectonic uplift near the ECB. The tuff layer at the bottom 138 139 of the Cambrian in the Songlin section, Guizhou Province has a U–Pb age of $532.3 \pm$ 140 0.7 Ma (Fig. 2). However, unconformity surfaces are absent in chert formations developed in deeper-water basin facies (i.e., the Liuchapo and Yanjiahe formations). 141 The ECB may be located in these chert successions. Carbon isotope anomalies of the 142 143 Longbizui and Three Gorges sections also confirm that the Liuchapo and Yanjiahe formations are diachronous. The lower boundaries of the Niutitang, Guojiaba, and 144 Jiumenchong formations are also diachronous and should be older than 522 Ma. There 145 146 is also an unconformity between the Yanjiahe and Shuijingtuo formations in Hubei Province. 147

148 2.2. Stratigraphic correlation

Stratigraphic correlation of Ediacaran to lower Cambrian successions in the 149 Yangtze Block can be constrained by fossil assemblages, isotope dating and carbon 150 isotope data ($\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ Fig. 9). Several lower Cambrian sections distributed 151 across inner shelf to basin depositional facies have been studied previously for volcanic 152 and biostratigraphic analyses, including the Xiaotan section in Yunnan Province 153 (Jenkins et al., 2002; Yang et al., 2003; Compston et al., 2008; Och et al., 2013), the 154 Maidiping section in Sichuan Province (Compston et al., 2008; Zi et al., 2017), the 155 Songlin and Bahuang sections in Guizhou Province (Jiang et al., 2009; Pi et al., 2013), 156

the Three Gorges section in Hubei Province (Okada et al., 2014), and the Ganziping 157 and Longbizui sections in Hunan Province (Chen et al., 2009) (Fig. 2). In carbonate 158 159 platform and shelf facies, the ECB is located in the siliceous dolomite overlying the Dengying Formation. The earliest small shelly fossil assemblage zone (SSF1) in South 160 161 China occurs in the siliceous interval between dolomite of the Dengying Formation and 162 Cambrian phosphorus-rich strata, and is near a significant carbon negative excursion (Steiner et al., 2007; Zhu et al., 2007). The U-Pb geological age of volcanic tuff at the 163 164 ECB is 542.6 ± 3.7 Ma in Guizhou Province and 542.1 ± 5.0 Ma in Hunan Province 165 (Fig. 2).

Integrating lithological and fossil data with isotope dating and inorganic 166 geochemistry, the lower Cambrian strata from the ECB to the Yu'anshan Formation, 167 168 (Niutitang Formation) including the Xa1 well, can be divided into four distinct intervals (Fig. 2). Interval I consists of the Zhujiaqing limestone and contains the Anabarites 169 trisulcatus–Protohertzina unguliformis (SSF1) and Watsonella crosbyi (SSF3) shelly 170 fossil assemblages in shallow platform regions, with only occasional fossil preservation 171 in deep-water areas. In the early Cambrian Stage 2, the upper Zhujiaging Formation is 172 characterized by an obvious positive carbon isotope excursion (Zhujiaqing Carbon 173 Isotope Excursion, ZHUCE) (Zhu et al., 2007). The U-Pb age of tuff deposits in the 174 Meishucun section (Yunnan Province) is 538.2 ± 1.5 Ma (Jenkins et al., 2002), close to 175 that of tuff deposits in the Ganziping Section of Hunan Province (Chen et al., 2009). In 176 addition, the zircon U-Pb age of the tuff deposited at the bottom of the Shiyantou 177 Formation in the Xiaotan section is 526.5 ± 1.1 Ma, broadly consistent with base of the 178

179

Jiulaodong Formation in the Maidiping section (526.2 \pm 1.9 Ma) and the Shuijingtuo

180 Formation in the Three Gorges section (526.4 + 5.4 Ma) (Fig. 2).

181 Interval Cam-II consists of the Shiyantou sandstone and calcareous shale (Fig. 2) in which the Sinosachites flabelliformis-Tannuolina zhangwentanggi shelly fossil 182 183 assemblage (SSF4) occupied shallow-water areas (Steiner et al., 2007), whereas 184 Sunella and Sphenothallus occurred in slope regions (Steiner et al., 2001; Yang et al., 2003). The boundary between Intervals II and III was characterized by a global 185 transgression, resulting in obvious marker of Ni-Mo layers (Zhu et al., 2003; Och et al., 186 187 2013). Total organic carbon (TOC) contents of the lower Cambrian shale near the boundary are generally high (ranging from 8–30 wt.%). In addition, a negative carbon 188 189 isotopic excursion (the Shiyantou Carbon Isotope Excursion, SHICE) occurs in inner 190 shelf to marine basin facies below a Ni-Mo layer (Jiang et al., 2012). The Ni-Mo layer was deposited in the transition period between Cambrian Stages 2 and 3, and is dated 191 to 521 ± 5 Ma (Xu et al., 2011). 192

193 Interval III consists of the lower Niutitang black shale (Fig. 2). Towards the end of Interval III, the lithology from outer shelf to carbonate platform facies gradually 194 changes from black shale to gray-green shale, carbonate, and calcareous shale, 195 196 indicating a gradual regression. Lithological changes in basin to slope facies are not obvious, but can be categorized based on silica contents and enrichments of redox-197 sensitive trace elements (Jin et al., 2016). Trilobites occur in the upper part of the 198 Niutitang Formation: Hunnanocephalus in Hunan Province and Tusnvidicus in Guizhou 199 Province (Steiner et al., 2005). Above the Ni-Mo layer, the Cambrian Arthropod 200

Radiation isotope Excursion (CARE) occurs from inner shelf to marine basin facies (Zhu et al., 2007). In addition, formation of barite deposits near the Ni–Mo layer are dated at 520.6 ± 6.1 Ma in Guizhou Province (Wang, 2017). The top of Interval III in the marine basin can be identified by the first appearance of trilobites.

Interval IV consists of Yu'anshan yellow shale and includes the Chengjiang biota in Yunnan Province, and the Qingjiang fauna in Hubei Province. The earliest date at which these fauna appear is 518.03 ± 0.69 Ma (Yang et al., 2017). The top of Interval IV is characterized by sandstone in shallow-water areas (Yunnan Province) and muddy limestone in deep-water areas (Guizhou, Sichuan, Hunan, and Hubei provinces). The water depth was shallower in South China than in Interval III.

211

212 **3. Materials and methods**

The Xal well, located in Anhua County, Hunan Province, South China, was 213 recently drilled. Recovered cores consist of the lower Cambrian Liuchapo, Niutitang, 214 and Wunitang formations, in ascending order. The Liuchapo Formation primarily 215 comprises of gray-black chert. The Niutitang Formation can be divided into three parts 216 on the basis of lithological features. The lower part is mainly composed of dark gray 217 calcareous shale with carbonate nodules, and the top is dolomite. The middle part 218 consists of organic-rich siliceous shale interbedded with gray shale. The upper part 219 principally comprises gray-black shale. In contrast, the overlying Wunitang Formation 220 221 consists of dark gray muddy limestone intercalated with shale.

222 This investigation is based on 36 samples collected from the Xa1 well. Samples

10

were ground to 200 mesh for total organic carbon, trace and major elements, rare earthelements, and carbon isotope of kerogen.

To determine TOC levels, excess hydrochloric acid (volume ratio 1:7) was added to 200 mg of sample to remove inorganic carbon in a combustion crucible. The crucible was then dried for 1 h at 105 °C in an oven under vacuum. TOC content was analyzed using a Germany Multi N/C 3100 Analyzer at Chongqing Institute of Geology and Mineral Resources, Chongqing, China. Analytical errors were better than $\pm 0.2\%$.

For elemental analysis, sample powder was dried for 2 h at 105 °C in an oven 230 231 under vacuum. To measure major elements, 500 mg of the dried sample was oxidized with 7000 mg of lithium borate (mixture of 67% Li₂B₄O₇ and 33% anhydrous LiBO₂) 232 233 for 2 h at 200 °C, then melted to make a fusion glass disk. Measurements were 234 conducted using an Axiosmax pw4400/40 X spectrometer. Major elements were represented by oxides. To determine trace elements, 50 mg of dried sample was 235 weighed and treated using boric acid with a residence time of 30 s. Trace elements were 236 237 then determined on a Quadrupole Inductively Coupled Plasma Mass Spectroscope (ICP-MS). Analytical precision was better than 5% for major and trace elements. 238

For kerogen separation, hydrochloric acid (6 mol/L) was slowly added into 100g of sample in an acid reaction vessel to remove carbonate minerals. Distilled water was added to remove the acid. Secondly, hydrochloric acid (6 mol/L) and hydrofluoric acid (40 %) (ratio: sample 1 g: HCl 2.4 mL: HF 3.6 mL) were slowly added in the acid reaction vessel to remove the other inorganic minerals. Then, hydrochloric acid (1 mol/L) was added to remove the other acids. The above stages were then repeated.

Subsequently, distilled water was added to remove the hydrochloric acid. Thirdly, 245 sodium hydroxide (0.5 mol/L) was added into the samples. Distilled water was added 246 247 to remove the alkalinity. For each sample, 30-60 mg of dried kerogen was measured using a Thermo Fisher Liquid Chromatography-Isotope Ratio Mass Spectrometer 248 249 (LC-IRMS) at the Guangzhou Institute of Geochemistry, Guangzhou, China. Each sample was tested three times. Analytical precision for $\delta^{13}C_{org}$ was better than $\pm 0.06\%$. 250 For metal mineral observations, samples were cut into one cubic centimeter blocks. 251 The surface was polished and then carbon sprayed. SEM microscopy including EDS 252 253 elemental spectra were undertaken using an FEI Quanta 200 scanning electronic microscope (SEM), in China University of Geosciences, Wuhan. 254

Enrichment factors (EF) were calculated based on the ratio between trace element concentration and aluminum (Al) of the sample and the same ratio in upper continental crust (McLennan, 2001; Tribovillard et al., 2006). The following formula was used for this calculation: $X_{EF} = (X_{sample}/Al_{sample})/(X_{ucc}/Al_{ucc})$. X_{sample} and Al_{sample} are concentrations of trace element X and Al samples, respectively; X_{ucc} and Al_{ucc} are concentrations of trace element X and Al in the upper continental crust. $X_{EF} > 1.0$ and $X_{EF} < 1.0$ indicate enrichment and depletion of X element, respectively.

262

263 4. Results and discussion

264 *4.1. Identification and intensity of hydrothermal activity*

265 To obtain a comprehensive interpretation of hydrothermal events from shallow to 266 deep marine environments in the Yangtze region during the early Cambrian, in Tables

S1-11 we summarize the analytical results of metal minerals and major elements from 267 samples in the Xa1 well (this study) alongside data reported from wells drilled or 268 269 sections located in the shelf zone. There are four Ba-bearing minerals in the shales of the Xa1 well, hyalophane, celsian, witherite and barite (Fig. 3). Of these hyalophane 270 was also associated with celsian (Fig. 3A, C and F) and they constitute the main Ba-271 272 bearing minerals, while barite and witherite are relatively rare. Celsian is an uncommon feldspar, which may be formed by the disintegration of barite in euxinic conditions. 273 Hyalophane can be an important proxy for hydrothermal events. In addition, we also 274 275 found several hydrothermal minerals at different depths of the Xa1 well including spehalerite and monazite. The hydrothermal minerals are present in the Niutitang shales, 276 which indicate the potential occurrence of multi-stage hydrothermal activity in South 277 278 China during the early Cambrian.

Al/(Al+Mn+Fe) ratios can be applied to determine the origin of siliceous materials 279 (Adachi et al., 1986; Yamamoto, 1987). Silica originating from a pure hydrothermal 280 event has a ratio of 0.01, whereas silica with a pure biogenic origin has a ratio > 0.60281 (Yamamoto, 1987; Harris et al., 2011). In addition, biogenic shales are characterized by 282 high SiO₂ and P₂O₅ and low Al₂O₃, TiO₂, and MgO values, whereas enrichment of Fe 283 and Mn is mainly related to hydrothermal events (Wang et al., 2016; Liao et al., 2018). 284 Similarly, (Fe+Mn)/Ti ratios can also be applied to determine conditions of 285 hydrothermal deposition. The Al/(Al+Mn+Fe) ratio of hydrothermal sediments 286 decreases with increasing hydrothermal input. Typical hydrothermal deposits are 287 characterized by Al/(Al+Mn+Fe) < 0.4 and (Fe+Mn)/Ti > 15. The Fe/Ti vs. Al/(Al + Fe 288

289	+ Mn) diagram is helpful for testing the possible hydrothermal input into the
290	hydrogenous sediments and their dilution with clastic or volcanic material (Sylvestre et
291	al., 2017). The samples from five wells and sections are located in different zones of
292	the diagram, indicating the range of hydrothermal input (Fig. 5). The samples close to
293	East Pacific Rise Hydrothermal deposits (EPC) have more hydrothermal input during
294	deposition, while the samples close to Pelagic Continental sediments (PC) and Upper
295	Continental Crust (UC) are more related to hydrogenous origin. Here, we define
296	Al/(Al+Mn+Fe) ratio <0.4 or (Fe+Mn)/Ti ratio > 15 as intense hydrothermal conditions,
297	Al/(Al+Mn+Fe) ratio 0.4–0.6 or (Fe+Mn)/Ti $>$ 10–15 as weak hydrothermal conditions,
298	and Al/(Al+Mn+Fe) ratio > 0.6 or (Fe+Mn)/Ti < 10 as hydrothermal conditions absent.
299	Xa1 well. Interval I samples exhibit low Al/(Al+Mn+Fe) (0.12–0.65, mean 0.31)
300	and high (Fe+Mn)/Ti (13.18-29.95, mean 22.72) values, reflecting intense
301	hydrothermal conditions. In Interval II, samples show low Al/(Al+Mn+Fe) (0.43–0.56,
302	mean 0.52) and high (Fe+Mn)/Ti (11.73-15.96, mean 13.49), reflecting dominantly
303	weak with intermittently intense hydrothermal conditions (Figs. 3F and 6). Interval III
304	can be also subdivided into several distinct units. Samples from 859-824.3 and 820.1-
305	790.6 m exhibit low Al/(Al+Mn+Fe) (0.30-0.59, mean 0.50) and high (Fe+Mn)/Ti
306	(7.78–32.40, mean 15.74) that imply intense to weak hydrothermal conditions (Figs.
307	3A-E 4, and 6). By contrast, samples from 857–851, 848.2–840.2 and 824.3–820.1 m
308	exhibit high Al/(Al+Mn+Fe) (0.63–0.66 mean 0.64) and moderate (Fe+Mn)/Ti (8.90–
309	12.92, mean 10.47) that imply no hydrothermal conditions. For Interval IV, all samples
310	exhibit high Al/(Al+Mn+Fe) (0.62–0.73, mean 0.68) and moderate (Fe+Mn)/Ti (7.41–

11.48, mean 9.81) values, suggesting a continued absence of hydrothermal conditions. 311 Samples from Intervals I, II and III were significantly affected by hydrothermal input, 312 313 but those from Interval IV appear to show no hydrothermal influence (Figs. 3, 4 and 6). The broad trend illustrated by our results is the occurrence of high intensity 314 hydrothermal events during the early Cam-I, followed by a qualitative decline in the 315 316 intensity of such events and ultimately their cessation by Cam-IV. From lithofacies analysis, a major transgression occurred during Interval I and a regression occurred 317 during I Cam-II. A global transgression event occurred in the early Cam-III, which was 318 319 followed by a major regression during the late Cam-III that continued through Cam-IV (Fig. 2). 320

From the geochemical data, there was obvious variability in the frequency and 321 322 intensity of hydrothermal events across the four intervals (Fig. 6). Samples near the ECB from inner shelf to basin facies were obviously affected by intense hydrothermal 323 events (Fig. 7). This is consistent with the U-Pb ages of tuffs near the ECB in South 324 325 China, which both indicate volcanic events during the early Cambrian (Fig. 2). The volcanic events (especially LIPs) have affected conditions for biological diversification 326 several times in Earth history. Early in Cam-I, sea level was likely falling based on 327 inferences from lithofacies analysis. Concurrently, there were hydrothermal events in 328 deep basins but not shallow-water regions (Fig. 7), suggesting that overall hydrothermal 329 input gradually weakened or even ceased in Guizhou Province. In the late Cam-I, the 330 ocean gradually regressed, consistent with discoveries of unconformities in Hubei and 331 Guizhou provinces. In the middle Cam-II, hydrothermal events were not obvious 332

throughout South China, which may have been conducive to biological productivity and reproduction. During the late Cam-II, hydrothermal events occurred again from inner shelf to basin areas (Fig. 7).

During the whole Cam-III, there were at least three episodes of hydrothermal activity. The first occurred in the early Cam-III and was the most intense, resulting in enrichment of organic matter and metal ores (Fig. 1B). During the next two stages, hydrothermal events were intense in some regions, but were not obvious, including the Xy1 and Yk1 wells. During the Cam-IV, hydrothermal events were not obvious across the entire Yangtze region, with normal marine environments and deposition resuming (Fig. 7).

343

344 4.2. Oceanic redox conditions from carbonate platform to basin environments

As some redox-sensitive trace elements (e.g., Mo, U and V) are sensitive to redox 345 conditions of sedimentary environments and migrate little during diagenesis, they are 346 347 excellent proxies for reconstructing redox conditions (Algeo and Maynard, 2008; Algeo and Tribovillard, 2009; Algeo and Rowe, 2012; Wu et al., 2016). For instance, previous 348 studies of modern oceans have shown that Mo levels < 25 ppm, 25-100 ppm, and > 349 100 ppm indicate non-euxinic, intermittently euxinic, and euxinic environments 350 respectively (Scott and Lyons, 2012). Uranium is not adsorbed by Fe(Mn)-oxides in 351 oxic environments, and the U content fluctuates in the range 1-10 ppm in sediments 352 (Algeo and Maynard, 2004; Tribovillard et al., 2006). In modern oxygen-depleted or 353 even sulfidic deposits, the V content fluctuates within the range 10–300 ppm (Brumsack, 354

2006; Scholz et al., 2011). Studies have shown that "hyper enrichment" of the element 355 V (> 500 ppm) in the Bakken organic-rich shale (TOC > 10 wt.%) indicated that the 356 357 dissolved H₂S content in the paleo-environment may exceed 10 mM (Scott et al., 2017). In the reduced environment, Zn occurs in pyrite in the form of zinc sulfide (Algeo and 358 Maynard, 2004). When H₂S exists, Zn is deposited rapidly. When dissolved H₂S was 359 abundant in the bottom water, the "hyper-enrichment" of Zn (> 500 ppm) indicates 360 photic zone euxinia (Scott et al., 2017). Sedimentary iron speciation data have been 361 widely used as an indicator of paleoceanic redox conditions in several outcrops (i.e., 362 Xiaotan, Shatan, Three George, Xy1 well, Jinsha, Songtao, Longbizui, and Yuanjia 363 sections). 364

In this study, we applied iron speciation, redox-sensitive trace element (RSTE) 365 366 geochemistry (Scott and Lyons, 2012; Scott et al., 2017) and assessment of Mo-U enrichment (Mo_{EF} and U_{EF}) (Tribovillard et al., 2006; Algeo and Tribovillard, 2009) as 367 paleoredox proxies. Redox interpretations for the Longbizui and Yuanjia sections, and 368 369 the Xy1 and Yk1 wells have been discussed in detail elsewhere (Li et al., 2015; Wang et al., 2015; Han et al., 2018), so we concentrate on analyses of the other sections and 370 wells in the region and compare the findings with previously published results (Tables 371 S1-11). 372

373 *4.2.1. Redox conditions in outer shelf regions*

Zigui section. Almost all samples of the Dengying Formation exhibit low U (1–
33 ppm, mean 19 ppm), V (11–118 ppm, mean 90 ppm) and Mo levels (1–11 ppm,
mean 3 ppm) indicative of oxic environments. Four samples at the ECB display low U

377	(4-20 ppm, mean 15 ppm) and Mo content (3-33 ppm, mean 16 ppm). However, V
378	content was as high as 1250 ppm (mean 1204 ppm). This "hyper-enrichment" of V
379	content in shale is close to values from the Bakken shale, suggesting that the bottom
380	water may have been extremely euxinic. Samples from Interval I show low levels of U
381	(3–7 ppm, mean 4 ppm), V (14–71 ppm, mean 47 ppm) and Mo (2–4 ppm, mean 3
382	ppm), also reflecting oxic environments. Redox conditions could not be determined for
383	Intervals II and IV due to an absence of RSTE data. Interval III can be subdivided into
384	two units. Samples from the lower units (41.6–53.5 m) show high U (22–105 ppm,
385	mean 43 ppm), V (109–1660 ppm, mean 1029 ppm) and Mo (44–400 ppm, 130 ppm),
386	implying intermittently to permanently euxinic environments, consistent with high
387	Mo _{EF} (63–403, mean 154) and U _{EF} (15–57, mean 27). Samples from the upper unit
388	(53.5–60 m) show low U (3–13 ppm, mean 8 ppm), V (64–130 ppm, mean 97 ppm) and
389	Mo (7–31 ppm, 21 ppm), suggesting oxic with intermittent dysoxic conditions.
390	Yd2 well. Redox conditions could not be determined for Interval I due to an
391	absence of RSTE data. In Interval II, four samples exhibit high U (40-77 ppm, mean
392	53 ppm), V (144-624 ppm, mean 344 ppm) and Mo content (57-126 ppm, mean 82
393	ppm) that indicate intermittently euxinic environments, consistent with high Mo_{EF} (43–
394	90, mean 62) and U_{EF} (16–30, mean 22). Interval III can be subdivided into three units.
395	Samples from the lower unit (1723.2–1717.6 m) have high U (25–64 ppm, mean 35
396	ppm), V (547–1500 ppm, mean 973 ppm) and Mo content (88–179 ppm, mean 118
397	ppm), suggesting permanently euxinic environments. Samples from the middle unit

398 (1717.6–1702.4 m) exhibit moderate U (6–18 ppm, mean 12 ppm), V (137–420 ppm,

399	mean 258 ppm) and Mo content (13–65 ppm, mean 42 ppm), suggesting ferruginous
400	environments. Samples from the upper unit (1702.4–1692.4 m) exhibit low U (5–8 ppm,
401	mean 7 ppm), V (150–311 ppm, mean 198 ppm) and Mo content (11–26 ppm, mean 18
402	ppm), suggesting dysoxic with intermittent oxic conditions. All Interval IV samples
403	show low U (4-5 ppm, mean 4 ppm), V (101-196 ppm) and Mo (4-10 ppm, mean 9
404	ppm). The Yd2 well is close to the Qingjiang fauna in the Changyang section (Fig. 1).
405	The REST contents and lithology of two sections both indicate oxic environments.

406

407 *4.2.2. Redox conditions in basin region*

Xal well. One sample at bottom of Interval I exhibits high U (56 ppm), V (1206 408 ppm) and Mo content (69 ppm), which indicates an intermittently euxinic environment 409 410 consistent with high M_{OEF} (182) and U_{EF} (80) (Table S8). The other samples of Interval I have low U (1–2 ppm, mean 1 ppm), V (16–230 ppm, mean 76 ppm) and Mo content 411 (1-2 ppm, mean 1 ppm), suggesting oxic environments. Samples from Interval II 412 exhibit low U (4-38 ppm, mean 10 ppm), V (49-210 ppm, mean 76 ppm) and Mo 413 content (1–24 ppm, mean 8 ppm), reflecting oxic to ferruginous environments (Fig. 7). 414 For Interval III, almost all samples exhibit high U (30-726 ppm, mean 120 ppm), V 415 (151-4075 ppm, mean 1568 ppm) and Mo content (22-506 ppm, mean 113 ppm), 416 which indicates intermittently euxinic to permanently euxinic environments, consistent 417 with high Mo_{EF} (116–3739, mean 485) and U_{EF} (28–2874, mean 341). Interval IV can 418 be subdivided into two distinct units. Samples from 783.4-740.6 m exhibit moderate U 419 (12-46 ppm, mean 19 ppm), V (145-348 ppm, mean 245 ppm), Mo content (31-76 420

ppm, mean 47 ppm) and Mo_{EF} (31–81, mean 52) > U_{EF} (5–28, mean 12); these values indicate intermittently euxinic environments. Samples from 740.6–730 m exhibit low U (8–14 ppm, mean 11 ppm), V (103–190 ppm, mean 140 ppm) and Mo (24–31 ppm, mean 28 ppm), reflecting ferruginous to oxic environments. In addition, five samples from above Interval IV have low U (1–17 ppm, mean 6 ppm), V (7–183 ppm, mean 73 ppm) and Mo (1–48 ppm, mean 15 ppm), reflecting oxic with intermittent suboxic environments.

428 *4.3. Links between fluctuating redox conditions and hydrothermal activity*

429 As discussed above, hydrothermal events primarily occurred during the early Cam-III (Figs. 6, 7). Through Cam-I, the depositional 430 Cam-I. Cam-II, and environment was mainly oxic in the Yangtze Block, consistent with low RSTE contents 431 432 in samples. However, samples from the Zigui section exhibit low Mo (3–33 ppm, mean 16 ppm) and low U levels (3-20 ppm, mean 15 ppm), but high V contents (66-2540 433 ppm, mean 1204 ppm). The V levels in the basal Cambrian of the Longbizui section 434 and the Xa1 well also exceed 500 ppm, and can be up to 7470 ppm. These 435 measurements imply a brief, rapid period of water euxinia during the early Cam-I 436 period (Ediacaran–Cambrian transition, Table 1). The H₂S content of the water column 437 was more than 10 mM, which would have been extremely harmful to survival of 438 organisms (Wignall and Twitchett, 1996). The lithology of the 11 sections is consistent 439 near the ECB, and is dominated by dolomite/chert, and has not changed during this 440 441 transition. Therefore, sea-level fluctuations could not have been the cause of the euxinic water-column. Intense hydrothermal events occurred from the inner shelf to the basin 442

around the time of the ECB. Hydrothermal events may be the main causes of euxinic 443 depositional environments in South China. Nutrients (including Fe and Zn) and CO₂ 444 445 generated by hydrothermal activity were conducive to phytoplankton reproduction, which increased OM supply (Uematsu et al., 2004; Duggen et al., 2010). At the same 446 time, toxic elements including Hg, Pb and Cr, as well as volatile gasses including HCl 447 and SO₂, emitted from hydrothermal events inhibited zooplankton growth (Jones and 448 Gislason, 2008; Chambers et al., 2013), while decomposition of OM during the 449 deposition process likely consumed large amounts of oxygen in the water column, 450 451 contributing to the spread of euxinic conditions. The effect of hydrothermal events was weak in the late Cam-I, where oxic depositional environments were dominant. 452

During the early Cam-II, depositional environments were dominated by 453 454 ferruginous conditions in Yunnan and Sichuan provinces, oxic conditions in Hunan Province, and intermittently euxinic to permanently euxinic conditions in Guizhou 455 Province (Table 1). Of the selected wells/sections, the Xy1 and Xa1 wells exhibit 456 evidence for weak hydrothermal events. In the late Cam-II interval, the water column 457 was affected by weak to intense hydrothermal events. Lithology transitioned from 458 gray-black shale, sandy shale, and calcareous shale to limestone, dolomite and 459 sandstone as a result of sea-level change. The entire Yangtze Block experienced a 460 regression at this time, the oxygen content of the water column decreased rapidly. 461 Depositional environments exhibited mainly intermittently euxinic conditions, with the 462 exception of oxic conditions in the area of the Xiaotan section. The samples of this 463 interval in the Xa1 well are characterized by low Mo (2–24 ppm, mean 15 ppm), low 464

465	U (3-38 ppm mean 16 ppm), and high V (113-936 ppm, mean 420 ppm) contents,
466	consistent with the RSTE contents of samples from the Yk1 well (mean U content 15
467	ppm, mean V content 802 ppm), the Longbizui section (mean Mo content 7 ppm, mean
468	U content 9 ppm, mean V content 491 ppm), and the Yuanjia section (mean Mo content
469	25 ppm, mean U content 22 ppm, mean V content 3442 ppm). This pattern is similar to
470	the RSTE contents of samples from near the ECB, indicating that the shallow part of
471	the water column was strongly affected by the euxinia caused by hydrothermal events.
472	Zn contents of samples in the Xa1 well (27-666 ppm), Yuanjia (150-716 ppm) and
473	Longbizui (165–593 ppm) sections are abnormally enriched. The "hyper enrichment"
474	of trace elements and high TOC content of black shale may indicate that dissolved H_2S
475	was intermittently present in the photic zone in the early Cambrian. During the Cam-
476	III, as a result of the final break-up of the Rodinia Supercontinent, a major transgression
477	occurred in South China. Hydrothermal events occurred periodically. In the early Cam-
478	III, the depositional environments of the Yangtze region were mainly euxinic.
479	Hydrothermal events enhanced the reduction potential of the water column, which was
480	conducive to the burial and preservation of organic matter. Consistent with this
481	interpretation, TOC content of the shale at the bottom of Interval III was the highest of
482	the four intervals. The depositional environment began to change, and hydrothermal
483	events became rarer. In the middle Cam-III, the water column near the Xiaotan section
484	became oxic, the areas near the Shatan section and Yd2 well were mainly ferruginous,
485	and the deeper water areas remained euxinic. In the late Cam-III, oxic conditions spread
486	to the Shatan section, the Xy1 and Yd2 wells and the Zigui section, whereas the deep-

water areas were still dominated by intermittent euxinic conditions. Although 487 hydrothermal events still occurred in deep waters during this period, their influence on 488 489 shallow-water areas were insignificant. Throughout Interval III, Zn and V contents of samples from the Yk1, Xa1 well, the Yuanjia, and Longbizui sections are relatively 490 high. This suggests that H₂S was also intermittently present in the photic zone from 491 492 slope to basin environments. Hydrothermal vents released huge amounts of greenhouse gases (methane) and volcanic-originated H₂S into the ocean and/or atmosphere during 493 the early Cambrian (Chen et al., 2009; Gao et al., 2018). 494

495 Hydrothermal events were not obvious in South China during the Cam-IV. In the early Cam-IV, oxic environments spread to the outer shelf areas, whereas the slope areas 496 497 mainly experienced ferruginous conditions. Intermittently euxinic conditions partly 498 existed in slope and basin regions. At this stage, the Chengjiang and Qingjiang faunas thrived in South China. In the late Cam-IV, oxic environments spread to the slope areas, 499 and basin areas experienced ferruginous condition (Table 1). Depositional 500 501 environments were dominated by an oxic water column over the whole Yangtze Block during the late Cam-IV. 502

503 4.4. Biotic evolution in the early Cambrian

The "Cambrian Explosion" represents a significant biological radiation within a short time interval, during which diversity and abundance of macroscopic heterotrophs and other forms of life increased dramatically (Knoll and Carroll, 1999; Vannier and Chen, 2005; Zhu et al., 2006). Within Chinese sections, the first phase of the Cambrian explosion is represented by the Meishucun and Tommotian SSFs, whereas the second 509 phase is represented by the Chengjiang and Qingjiang faunas in South China (Fig. 10).
510 Whether fluctuations in the oxygen content of the atmosphere–ocean system were the
511 key factor controlling biological evolution during the Cambrian still remains
512 controversial (Mills and Canfield, 2014).

The carbon isotope composition of marine sediments is mainly controlled by the 513 burial of ¹²C-rich organic matter and the addition of exotic carbon sources (Holser, 1997; 514 Hayes et al., 1999; Kump and Arthur, 1999). Many major events in Earth history are 515 associated with obvious fluctuations of carbon isotope ratios, reflecting perturbation to 516 517 the carbon mass balance, often in connection with ecological changes in the marine environment (Saltzman et al., 2000; Wignall et al., 2009). Therefore, carbon isotopic 518 ratios ($\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$) of sediments can be applied to clarify the evolution of early 519 520 Cambrian oceanic environments and organisms. In the early Cambrian, four obvious carbon isotope anomalies occurred in South China (Fig. 9) (Zhu et al., 2019). Two of 521 the carbon negative excursions correspond to extinctions of the Ediacaran fauna 522 523 (BACE) and SSFs (SHICE), whereas the two positive carbon excursions (ZHUCE, CARE) mark peaks in early Cambrian organisms event and abundance (Zhu et al., 524 2007). The carbon isotope ratios of samples from the Xa1 well show an obvious 525 negative carbon isotope excursion (-33.69‰) at the boundary between Intervals II and 526 III. This carbon isotope anomaly is located near the metal layer and corresponds to 527 CARE (Fig. 9). 528

529 4.5. Implications for the "Cambrian Explosion"

530 Previous studies have shown that several of the major mass extinction events in

531 Earth history were related to large igneous province volcanism (Wignall, 2001; Bond and Wignall, 2014). Volcanism (especially LIPs) could potentially heat OM in 532 sediments and release large amounts of ¹²C-rich CO₂ and CH₄ (Renne et al., 1995; 533 Retallack and Jahren, 2008; Chen et al., 2009), driving negative carbon isotope 534 excursions. Obvious signatures of hydrothermal events have been found in dolomites 535 at the bottom of the Ediacaran Doushantuo Formation (Condon, 2005), with the 536 hydrothermal activity producing highly ¹³C-depleted carbonate cements ($\delta^{13}C_{PDB}$ down 537 to -48‰), and resulting in global warming (Bristow et al., 2011; Sahoo et al., 2012). 538 539 Volcanic/hydrothermal activity can be regarded, in conjunction with connected factors such as euxinic events, temperature extremes, and seawater acidification, as triggers for 540 biological mass extinctions (Ganino and Arndt, 2009; Bond and Wignall, 2014). 541 542 In the early Cam-I, geochemical data suggest that the oxic water column experienced a large-scale, rapid euxinic event due to hydrothermal activity. In addition, 543 the U–Pb dating of tuffs suggests that volcanic events were frequent (Fig. 2). This may 544 have been related to the BACE. Sudden formation of euxinic environments could have 545 restricted the spread of aerobic species and disrupted the original ecological balance, 546 perhaps contributing to extinctions (Fig.10). In the middle of Cam-I, depositional 547 environments in South China were shallow, dominated by oxic conditions and 548 unaffected by hydrothermal events. This coincides with the first positive carbon 549

551 In the early Cam-II, an euxinic event, likely caused by episodic hydrothermal 552 activity emerged in South China again. The redox proxies, hydrothermal proxies, and

excursion (ZHUCE).

550

volcanic tuff dating all correspond to the SHICE. The conditions during this period were likely similar to those recorded during the early Cam-I interval. Two episodes of water-column euxinia with hydrothermal/ volcanic activity occurred in conjunction with the extinction of the Ediacaran fauna and the SSFs in South China (Fig. 10). This fluctuation and regional heterogeneity suggests that at least some environments contained sufficient oxygen to support the needs of animal life well before the "Cambrian Explosion" itself.

560 Recent research has shown that the Chengjiang fauna assemblage began at 518 Ma 561 (Yang et al., 2017). In the early Cam-III, South China experienced euxinic conditions and episodic hydrothermal activity. Then during Cam-III, with gradual marine 562 regression, the water column in the Xiaotan section (inner shelf) became oxic, with oxic 563 564 water column conditions gradually expanding to Hubei Province in the late Cam-III. In the early Cam-IV, oxic conditions expanded from inner-shelf to outer-shelf areas, whilst 565 intermittently euxinic environments were limited to the basin areas (Table. 1). The 566 Chengjiang and Qingjiang faunas were preserved during this period. Basin areas were 567 mainly occupied by ferruginous environments in the late Cam-IV, which were replaced 568 by dominantly oxic conditions following the end of Cam-IV. 569

The Lantian fauna, dominated by macroscopic algae, thrived in euxinic environments (Yuan et al., 2011), while the Miaohe fauna containing benthic algae thrived in suboxic environments, indicating that phytoplankton can live in different oxygenated conditions and environments. During Cambrian Stage 3, our data suggest that stable and persistent oxic environments (e.g., Xiaotan section) occurred

concurrently with a large number of planktonic and benthic trilobites. A small number 575 of benthic trilobites and a large number of planktonic trilobites also appear to have 576 577 thrived in ferruginous environments (e.g., Three Gorges and Songtao sections). The photic zone does not appear to have contained dissolved H₂S in shallow-water areas. 578 579 There was no record of biological disturbance in these relatively deep-water areas. The 580 Jinsha section in Guizhou Province, dominated by ferruginous conditions, also recorded a complex benthic assemblage mainly consisting of sponges and arthropods. 581 Depositional environments in the slope to basin areas were mainly euxinic, with 582 583 dissolved H₂S intermittently present in the photic zone.

Depositional environments in South China during Cam-III were affected by 584 hydrothermal events, but an equivalent impact is not obvious in Cam-IV (Figs. 6, 7). 585 586 Past research has suggested strong stratification of the early Cambrian seawater, as recorded the Yangtze Block (Feng et al., 2014). Surface waters were oxic, the mid-water 587 column was euxinic, and deeper parts of the water column were ferruginous. This 588 stratified redox model describes Cam-III, but not Cam-IV, in which the surface water 589 was oxic, whereas mid- and deep parts of the water column were ferruginous condition. 590 Although the water column in Cam-IV was shallower than that in Cam-III, the 591 formation of a stratified redox model in Cam-III was more influenced by hydrothermal 592 events. In the middle and late Cam-III, depositional environments in Yunnan and Hubei 593 provinces already appear to have been experiencing widespread oxic conditions. It is 594 plausible that these limited regions of habitability may not have been sufficient for the 595 large-scale rapid radiation of organisms (Table 1). The mid- and deep-water 596

597 environments were still affected by hydrothermal events and intermittent euxinic conditions, which may have restricted the spread of aerobic species. These are obvious 598 599 similarities between biological radiations during the two stages, with the SSFs and Chengijang (Oingijang) faunas both occurring in a persistently oxic environment. We 600 601 tentatively suggest that the Chengjiang (Qingjiang) fauna radiated gradually whilst progressively colonizing inner shelf to the basin environments, as oxic conditions 602 became more widespread. Above all, our data provides an exploratory record that may 603 help to understand connections between hydrothermal events, variability in ocean redox 604 605 state and the evolution of Early Cambrian life.

606

607 **5. Conclusions**

608 Hydrothermal events were frequent but episodic in the Yangtze Block during the Early Cambrian of South China, and mainly occurred during the early Cam-I, Cam-II, and 609 through the Cam- III intervals. During early Cam-I, and Cam-II, the water column was 610 strongly affected by the euxinic conditions resulting from hydrothermal events, which 611 were potentially connected to concurrent extinctions of the Ediacaran fauna and SSFs 612 respectively. During the middle Cam-III interval, although inner shelf areas were 613 oxygenated after the global transgression at 521 Ma, the persistence of extensive deep-614 water euxinic environments appears to have been not conducive to biological 615 diversification. During the early Cam-IV interval, depositional environments in South 616 China were mainly eutrophic and oxic, which was probably favorable for the rapid 617 radiation of the Chengjiang/Qingjiang fauna. There are obvious similarities between 618

the two episodes of biological radiation. The SSF and Chengjiang /Qingjiang faunas 619 lived in oxic environments that were unaffected by hydrothermal fluids. However, 620 621 intermittent hydrothermal events resulted in euxinic condition, which may have disrupted the ecological balance and restricted the spread of certain species. The fossil 622 evidence of these evolutionary radiations has a complex but likely important connection 623 624 to the redox changes and hydrothermal conditions recorded by the sedimentary geochemical data. Consequently, the data we present here help us move towards a more 625 mechanistic understanding of the causes of the early "Cambrian Explosion and 626 627 concurrent extinction of the Ediacaran-Cambrian Shelly fossil faunas in South China.

628

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- 917

918 Figure

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Fig. 1. Paleogeographic maps of the Yangtze Block during the late Ediacaran and early
Cambrian. A, latest Ediacaran to earliest Cambrian Fortunian (modified after Jiang et
al., 2012); B, early Cambrian Stage 3, the ore sites are (modified from Han et al., 2017).
Note that the studied sections are approximately aligned along two shelf-to-basin
transects (A–C and B–C). Red squares indicate sections and wells previously published,
yellow squares indicates our study area, and green stars indicate occurrences of the
Chengjiang and Qingjiang faunas.

927

Fig. 2. Stratigraphic correlation with biostratigraphic and tuff/ore dating of lower 928 Cambrian (ca. 541-514 Ma) sections across South China. Data sources: 1 - Xiaotan 929 section, Yunnan Province (Jenkins et al., 2002; Yang et al., 2003; Compston et al., 2008; 930 931 Och et al., 2013); 2 – Maidiping section, Sichuan Province (Compston et al., 2008; Zi 932 et al., 2017); 3 – Songlin section, Guizhou Province (Jiang et al., 2009; Pi et al., 2013); 4 -Bahuang section, Guizhou Province (Chen et al., 2015); 5 - Three Gorges section, 933 Hubei Province (Okada et al., 2014); 6 - Ganziping section, Hunan Province (Chen et 934 935 al., 2009); 7 - Longbizui section, Hunan Province (Wang et al., 2012; Yeasmin et al., 2017); 8 – Xa1 well, Hunan Province (this study). 936

937

Fig. 3. Petrographic observations of studied samples in Xa1 well by scanning electronic
microscopy. A, celsian and hyalophane in shale (depth 809.3 m); B, sphalerite in shale
(depth 818.2 m); C, celsian and hyalophane in siliceous shale (depth 843.3 m); D,
monazite, celsian, and V-bearing mineral in shale (depth 849.8 m); E, c hyalophane in
siliceous shale (depth 855.2 m); F, celsian, hyalophane, and sphalerite in calcareous
shale (depth 863.5 m).

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Fig. 4. Al–Fe–Mn ternary diagrams from Intervals I to IV. The positions of cherts with hydrothermal and non-hydrothermal origins are from Adachi et al. (1986) and

- Yamamoto (1987). These include data from the Xy1 (Li, 2018) and Yk1 wells (Li et al.,
 2015) in Guizhou Province, the Yd2 well (Chen et al., 2018) and Zigui section (Hu and
 Chen, 2017) in Hubei Province.
- 950

Fig. 5. Fe/Ti vs. Al/(Al + Fe + Mn) diagram of the Xy1 well, Yk1 well, Yd2 well, Zuigui
section and Xa1 well, modified after Sylvestre et al. (2017). The curve presents mixing
of East Pacific Rise (EPR) deposits with pelagic sediments (PC) whereas the numbers
indicate the approximate percentage of EPR in the mixture.

955

Fig. 6. Stratigraphic distribution of hydrothermal proxies (Al/(Al+Fe+Mn) and
(Fe+Mn)/Ti) in the Xy1, Yk1, Xa1 and Yd2 wells and the Zigui section.

958

Fig. 7. Spatiotemporal variations of hydrothermal and redox conditions. Data from the
Xy1 (Li, 2018) and Yk1 wells (Li et al., 2015) in Guizhou Province, the Yd2 well (Chen
et al., 2018) and Zigui section (Hu and Chen, 2017) in Hubei province, the Longbizui
section (Wang et al., 2012; Han et al., 2018) and Yuanjia section (Guo et al., 2013;
Wang et al., 2015) in Hunan Province. Redox conditions are analyzed by iron speciation
and redox-sensitive trace elements.

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Fig. 8. Spatiotemporal variations of redox conditions. Data from the Xiaotan section (Och et al., 2013; Feng et al., 2014) in Yunnan Province, the Shatan section (Goldberg et al., 2007; Guo et al., 2007) in Sichuan Province, and the Jinsha (Jin et al., 2016) and Songtao sections (Goldberg et al., 2007; Guo et al., 2007) in Guizhou Province. The redox conditions are analyzed by iron speciation and redox-sensitive trace elements.

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Fig. 9. Carbon isotope stratigraphic correlation from inner shelf (Xiaotan and Shatan sections), outer shelf (Xy1 well, Changyang section), slope (Ganziping and Longbizui sections), and basin (Xa1 well, Yuanjia section) environments. The red, green, blue and yellow arrows correspond to BACE, ZHUCE, SHICE, and CARE events respectively.

976

Fig. 10. Summary of $\delta^{13}C_{carb}$, $\delta^{13}C_{org}$, redox-sensitive trace elements, and episodic 977 hydrothermal events with evolutionary events during the late Ediacaran to early 978 Cambrian (551–514Ma). A, Key bio-events during the late Ediacaran–early Cambrian 979 (Zhu et al., 2007). B, Temporal trends in $\delta^{13}C_{carb}$ of three sections and $\delta^{13}C_{org}$ of ten 980 sections. C, and D, Temporal trends in Mo and V contents in lower Cambrian rocks, 981 982 respectively. E, Spatiotemporal variations of hydrothermal conditions in various depositional facies on the Yangtze Block. The Mo and V records indicate that the ocean 983 experienced a rapid euxinic process during the ECB and late Interval II period, which 984 can be linked to hydrothermal events. E, episodic hydrothermal events with volcanic 985 tuff dating in lower Cambrian rocks. 986

987

- **Table 1.** Summary of redox conditions of 11 sections in various depositional facies on
- 989 the Yangtze Block. Fe = Ferruginous, Eu = Euxinic, O = Oxic, and / = no data.

990 Supplementary Data Table

991 Major element, trace element, iron speciation, and TOC contents of the Xiaotan section

992 (inner shelf, Yunnan province, S1), Shatan section (inner shelf, Yunnan province, S2),

993 Xy1 well (outer shelf, Guizhou province, S3), Jinsha section (outer shelf, Guizhou

- province, S4), Songtao (slope, Guizhou province, S5),Yk1(slope, Guizhou province,
- S6), Yuanjia section (basin, Hunan province, S7), Xa1well (basin, Hunan province, S8),
 Longbizui (slope, Hunan province, S9), Yd2 wells (outer shelf, Hubei province, S10)
- and Zigui sections(outer shelf, Hubei province, S11). The locations of wells/sections
- 998 are shown in Fig. 1.