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Evaluating episodic hydrothermal activity in South China during the early Cambrian: Implications for biotic evolution

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ABSTRACT

The early Cambrian (541–514 Ma) was a crucial interval for the evolution of life on Earth, popularly known as the "Cambrian Explosion". Here, we report the timing of changes in hydrothermal and depositional inputs, as well as paleo-redox state, which may have influenced biogeochemical changes. According to high-resolution petrology, fossil distributions, isotopic records, and inorganic geochemistry, the lower Cambrian 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); the lower part of the Cambrian Stage 3 Yu'anshan Formation (CAM-III); and the mid–upper Cambrian Stage 3 and the middle–upper part of the Yu'anshan Formation, continuing into the Canglangpu Formation (Cam-IV). Hydrothermal events are detected during the early Cam-I, Cam-II, and Cam-III intervals. During the early Cam-I and Cam-II intervals, these events coincided with extensive bottom water euxinia, which in turn may have restricted the spread or proliferation of Ediacaran fauna and small shelly fauna. Through the whole Cam-III interval, further hydrothermal events occurred concurrently with euxinic and ferruginous conditions, probably within a single spatially stratified water column, again plausibly restricting the spread of aerobic 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 into relatively deep-water regions, concurrent with the emergence of the Chengjiang and Qingjiang faunas. These data suggest that periodic hydrothermal events may have had a significant impact on the spread, radiation and extinction of macroscopic fauna

during the early Cambrian in South China.

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

1. Introduction

The late Ediacaran to early Cambrian (551–514 Ma) was one of the most bio-geochemically important periods in Earth history and included a number of significant geological events including the break-up of the supercontinent Rodinia, extinction of the Ediacaran biota, appearance and extinction of small shelly fossil assemblages (SSF1–4), establishment of anoxic and/or sulfidic water conditions, appearances of the Chengjiang and Qingjiang biotas, and the stepwise oxygenation of global oceans (Zhuravlev and Wood, 1996; Johnson et al., 2005; Marshall, 2006; Laflamme et al., 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 during the past two decades. Biological evolution during the early Cambrian plausibly exhibited a close relationship with oceanic and atmospheric oxygen levels (Lenton et al., 2014). Although redox conditions of the early Cambrian oceans in South China have 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 mechanistically connect such data to biological evolution; with some studies questioning the importance of any link between redox conditions and biological evolution (Jin et al., 2016; Xiang et al., 2017). A range of possible causal mechanisms exist for the extinction of small shelly faunas (Darroch et al., 2018), but which of these is likely the most significant is presently unclear.

More broadly within the geological record, there is a strong correlation between mass extinction events and the occurrence of Large Igneous Provinces (LIPs) (Wignall, 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 (66 Ma) mass extinctions were related to the Siberian LIP, Central Atlantic LIP, and Deccan LIP, respectively (Blackburn et al., 2013; Burgess and Bowring, 2015; Schoene 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 to temperature extremes and associated climatic cycles, with a knock-on effect on biological growth and diversification (Benton, 2018).

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

Few investigations of the paleo-environmental impacts of hydrothermal events on 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 and dolomite at the bottom of the Ediacaran Doushantuo Formation in South China. This hydrothermal event released a large amount of CH_4, leading to highly ^{13}C-depleted carbonate cements ($\delta^{13}C_{PDB}$ down to −48‰), and global warming (Bristow et al., 2011; Sahoo et al., 2012). Extinctions may be the result of a sequence of feedbacks triggered by such greenhouse input, or similar biogeochemical perturbations, including global 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; Clarkson et al., 2015). As the timing and duration of hydrothermal events during the early Cambrian also remains unclear, investigations on submarine hydrothermal events during the Cambrian may therefore provide new insights into understanding the driving forces for changes in the composition, distribution and diversity of Cambrian biota.

In this study, we established a systematic stratigraphic correlation of 18 lower Cambrian sections across South China, by means of high-resolution petrology, 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.

2. Geological setting and stratigraphy

2.1. Geological setting

During the Ediacaran–Cambrian transition, South China consisted of the Yangtze and Cathaysia blocks. Sedimentary environments from the northwest to southeast were comprised of platform, inner shelf, outer shelf, slope, and marine basin settings (Fig. 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 beds have also been discovered near the ECB in some sections across South China (Fig. 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 ± 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 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 Supercontinent, the Yangtze Block entered into a rifting phase, and a major 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 their stratigraphic equivalents, with formations gradually thickening from the northwest to southeast. Super continental break-up and seafloor expansion promoted widespread hydrothermal and volcanic events, as evidenced by extensive trace metal deposition (Steiner et al., 2001; Xu et al., 2011; Han et al., 2017). During the late Cambrian Stage 3 (518–514 Ma), the small shelly fossil assemblages subsequently disappeared and the Chengjiang and Qingjiang biotas then flourished.

Volcanic ash beds near the ECB suggest that volcanic events may have been extensive and widespread during this time interval (Fig. 2). Obvious unconformities 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 of the Cambrian in the Songlin section, Guizhou Province has a U–Pb age of 532.3 ± 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). The ECB may be located in these chert successions. Carbon isotope anomalies of the Longbizui and Three Gorges sections also confirm that the Liuchapo and Yanjiahe formations are diachronous. The lower boundaries of the Niutitang, Guojiaba, and Jiumenchong formations are also diachronous and should be older than 522 Ma. There is also an unconformity between the Yanjiahe and Shuijingtuo formations in Hubei Province.

2.2. Stratigraphic correlation

Stratigraphic correlation of Ediacaran to lower Cambrian successions in the Yangtze Block can be constrained by fossil assemblages, isotope dating and carbon isotope data ($\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$□ Fig. 9). Several lower Cambrian sections distributed across inner shelf to basin depositional facies have been studied previously for volcanic and biostratigraphic analyses, including the Xiaotan section in Yunnan Province (Jenkins et al., 2002; Yang et al., 2003; Compston et al., 2008; Och et al., 2013), the Maidiping section in Sichuan Province (Compston et al., 2008; Zi et al., 2017), the Songlin and Bahuang sections in Guizhou Province (Jiang et al., 2009; Pi et al., 2013), the Three Gorges section in Hubei Province (Okada et al., 2014), and the Ganziping and Longbizui sections in Hunan Province (Chen et al., 2009) (Fig. 2). In carbonate 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 China occurs in the siliceous interval between dolomite of the Dengying Formation and 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 ECB is 542.6 ± 3.7 Ma in Guizhou Province and 542.1 ± 5.0 Ma in Hunan Province (Fig. 2).

Integrating lithological and fossil data with isotope dating and inorganic geochemistry, the lower Cambrian strata from the ECB to the Yu'anshan Formation, (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 trisulcatus–Protohertzina unguliformis* (SSF1) and *Watsonella crosbyi* (SSF3) shelly fossil assemblages in shallow platform regions, with only occasional fossil preservation in deep-water areas. In the early Cambrian Stage 2, the upper Zhujiaqing Formation is characterized by an obvious positive carbon isotope excursion (Zhujiaqing Carbon Isotope Excursion, ZHUCE) (Zhu et al., 2007). The U–Pb age of tuff deposits in the Meishucun section (Yunnan Province) is 538.2 ± 1.5 Ma (Jenkins et al., 2002), close to that of tuff deposits in the Ganziping Section of Hunan Province (Chen et al., 2009). In addition, the zircon U–Pb age of the tuff deposited at the bottom of the Shiyantou Formation in the Xiaotan section is 526.5 ± 1.1 Ma, broadly consistent with base of the

Jiulaodong Formation in the Maidiping section (526.2 ± 1.9 Ma) and the Shuijingtuo Formation in the Three Gorges section (526.4 + 5.4 Ma) (Fig. 2).

Interval Cam-II consists of the Shiyantou sandstone and calcareous shale (Fig. 2) in which the *Sinosachites flabelliformis–Tannuolina zhangwentanggi* shelly fossil assemblage (SSF4) occupied shallow-water areas (Steiner et al., 2007), whereas *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 transgression, resulting in obvious marker of Ni–Mo layers (Zhu et al., 2003; Och et al., 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 isotopic excursion (the Shiyantou Carbon Isotope Excursion, SHICE) occurs in inner 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 to 521 ± 5 Ma (Xu et al., 2011).

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 changes from black shale to gray–green shale, carbonate, and calcareous shale, 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-sensitive trace elements (Jin et al., 2016). Trilobites occur in the upper part of the Niutitang Formation: *Hunnanocephalus* in Hunan Province and *Tusnyidicus* in Guizhou Province (Steiner et al., 2005). Above the Ni–Mo layer, the Cambrian Arthropod

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.

3. Materials and methods

The Xa1 well, located in Anhua County, Hunan Province, South China, was recently drilled. Recovered cores consist of the lower Cambrian Liuchapo, Niutitang, and Wunitang formations, in ascending order. The Liuchapo Formation primarily comprises of gray–black chert. The Niutitang Formation can be divided into three parts on the basis of lithological features. The lower part is mainly composed of dark gray calcareous shale with carbonate nodules, and the top is dolomite. The middle part consists of organic-rich siliceous shale interbedded with gray shale. The upper part principally comprises gray–black shale. In contrast, the overlying Wunitang Formation consists of dark gray muddy limestone intercalated with shale.

This investigation is based on 36 samples collected from the Xa1 well. Samples were ground to 200 mesh for total organic carbon, trace and major elements, rare earth elements, 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 ±0.2%.

For elemental analysis, sample powder was dried for 2 h at 105 °C in an oven under vacuum. To measure major elements, 500 mg of the dried sample was oxidized with 7000 mg of lithium borate (mixture of 67% $Li_2B_4O_7$ and 33% anhydrous $LiBO_2$) for 2 h at 200 °C, then melted to make a fusion glass disk. Measurements were conducted using an Axiosmax pw4400/40 X spectrometer. Major elements were represented by oxides. To determine trace elements, 50 mg of dried sample was weighed and treated using boric acid with a residence time of 30 s. Trace elements were then determined on a Quadrupole Inductively Coupled Plasma Mass Spectroscope (ICP-MS). Analytical precision was better than 5% for major and trace elements.

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, sodium hydroxide (0.5 mol/L) was added into the samples. Distilled water was added 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 (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 ±0.06‰.

For metal mineral observations, samples were cut into one cubic centimeter blocks. The surface was polished and then carbon sprayed. SEM microscopy including EDS elemental spectra were undertaken using an FEI Quanta 200 scanning electronic microscope (SEM), in China University of Geosciences, Wuhan.

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.

4. Results and discussion

4.1. Identification and intensity of hydrothermal activity

To obtain a comprehensive interpretation of hydrothermal events from shallow to 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 samples in the Xa1 well (this study) alongside data reported from wells drilled or 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 was also associated with celsian (Fig. 3A, C and F) and they constitute the main Ba-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. Hyalophane can be an important proxy for hydrothermal events. In addition, we also found several hydrothermal minerals at different depths of the Xa1 well including spehalerite and monazite. The hydrothermal minerals are present in the Niutitang shales, which indicate the potential occurrence of multi-stage hydrothermal activity in South China during the early Cambrian.

Al/(Al+Mn+Fe) ratios can be applied to determine the origin of siliceous materials (Adachi et al., 1986; Yamamoto, 1987). Silica originating from a pure hydrothermal event has a ratio of 0.01, whereas silica with a pure biogenic origin has a ratio > 0.60 (Yamamoto, 1987; Harris et al., 2011). In addition, biogenic shales are characterized by high SiO_2 and P_2O_5 and low Al_2O_3, TiO_2, and MgO values, whereas enrichment of Fe and Mn is mainly related to hydrothermal events (Wang et al., 2016; Liao et al., 2018). Similarly, (Fe+Mn)/Ti ratios can also be applied to determine conditions of hydrothermal deposition. The Al/(Al+Mn+Fe) ratio of hydrothermal sediments decreases with increasing hydrothermal input. Typical hydrothermal deposits are characterized by Al/(Al+Mn+Fe) < 0.4 and (Fe+Mn)/Ti > 15. The Fe/Ti vs. Al/(Al + Fe

+ Mn) diagram is helpful for testing the possible hydrothermal input into the hydrogenous sediments and their dilution with clastic or volcanic material (Sylvestre et al., 2017). The samples from five wells and sections are located in different zones of the diagram, indicating the range of hydrothermal input (Fig. 5). The samples close to East Pacific Rise Hydrothermal deposits (EPC) have more hydrothermal input during deposition, while the samples close to Pelagic Continental sediments (PC) and Upper Continental Crust (UC) are more related to hydrogenous origin. Here, we define Al/(Al+Mn+Fe) ratio <0.4 or (Fe+Mn)/Ti ratio > 15 as intense hydrothermal conditions, Al/(Al+Mn+Fe) ratio 0.4–0.6 or (Fe+Mn)/Ti > 10–15 as weak hydrothermal conditions, and Al/(Al+Mn+Fe) ratio > 0.6 or (Fe+Mn)/Ti < 10 as hydrothermal conditions absent.

Xa1 well. Interval I samples exhibit low Al/(Al+Mn+Fe) (0.12–0.65, mean 0.31) and high (Fe+Mn)/Ti (13.18–29.95, mean 22.72) values, reflecting intense hydrothermal conditions. In Interval II, samples show low Al/(Al+Mn+Fe) (0.43–0.56, mean 0.52) and high (Fe+Mn)/Ti (11.73–15.96, mean 13.49), reflecting dominantly weak with intermittently intense hydrothermal conditions (Figs. 3F and 6). Interval III can be also subdivided into several distinct units. Samples from 859–824.3 and 820.1–790.6 m exhibit low Al/(Al+Mn+Fe) (0.30–0.59, mean 0.50) and high (Fe+Mn)/Ti (7.78–32.40, mean 15.74) that imply intense to weak hydrothermal conditions (Figs. 3A-E 4, and 6). By contrast, samples from 857–851, 848.2–840.2 and 824.3–820.1 m exhibit high Al/(Al+Mn+Fe) (0.63–0.66 mean 0.64) and moderate (Fe+Mn)/Ti (8.90–12.92, mean 10.47) that imply no hydrothermal conditions. For Interval IV, all samples 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. Samples from Intervals I, II and III were significantly affected by hydrothermal input, 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 hydrothermal events during the early Cam-I, followed by a qualitative decline in the 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 during I Cam-II. A global transgression event occurred in the early Cam-III, which was followed by a major regression during the late Cam-III that continued through Cam-IV (Fig. 2).

From the geochemical data, there was obvious variability in the frequency and 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 events (Fig. 7). This is consistent with the U–Pb ages of tuffs near the ECB in South China, which both indicate volcanic events during the early Cambrian (Fig. 2). The volcanic events (especially LIPs) have affected conditions for biological diversification several times in Earth history. Early in Cam-I, sea level was likely falling based on inferences from lithofacies analysis. Concurrently, there were hydrothermal events in deep basins but not shallow-water regions (Fig. 7), suggesting that overall hydrothermal input gradually weakened or even ceased in Guizhou Province. In the late Cam-I, the ocean gradually regressed, consistent with discoveries of unconformities in Hubei and Guizhou provinces. In the middle Cam-II, hydrothermal events were not obvious 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).

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 conditions of sedimentary environments and migrate little during diagenesis, they are 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 studies of modern oceans have shown that Mo levels < 25 ppm, 25–100 ppm, and > 100 ppm indicate non-euxinic, intermittently euxinic, and euxinic environments respectively (Scott and Lyons, 2012). Uranium is not adsorbed by Fe(Mn)-oxides in oxic environments, and the U content fluctuates in the range 1–10 ppm in sediments (Algeo and Maynard, 2004; Tribovillard et al., 2006). In modern oxygen-depleted or even sulfidic deposits, the V content fluctuates within the range 10–300 ppm (Brumsack, 2006; Scholz et al., 2011). Studies have shown that "hyper enrichment" of the element V (> 500 ppm) in the Bakken organic-rich shale (TOC > 10 wt.%) indicated that the dissolved H_2S 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 Maynard, 2004). When H_2S exists, Zn is deposited rapidly. When dissolved H_2S was abundant in the bottom water, the "hyper-enrichment" of Zn (> 500 ppm) indicates photic zone euxinia (Scott et al., 2017). Sedimentary iron speciation data have been widely used as an indicator of paleoceanic redox conditions in several outcrops (i.e., Xiaotan, Shatan, Three George, Xy1 well, Jinsha, Songtao, Longbizui, and Yuanjia sections).

In this study, we applied iron speciation, redox-sensitive trace element (RSTE) 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 paleoredox proxies. Redox interpretations for the Longbizui and Yuanjia sections, and 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 wells in the region and compare the findings with previously published results (Tables S1-11).

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

(4–20 ppm, mean 15 ppm) and Mo content (3–33 ppm, mean 16 ppm). However, V content was as high as 1250 ppm (mean 1204 ppm). This "hyper-enrichment" of V content in shale is close to values from the Bakken shale, suggesting that the bottom water may have been extremely euxinic. Samples from Interval I show low levels of U (3–7 ppm, mean 4 ppm), V (14–71 ppm, mean 47 ppm) and Mo (2–4 ppm, mean 3 ppm), also reflecting oxic environments. Redox conditions could not be determined for Intervals II and IV due to an absence of RSTE data. Interval III can be subdivided into two units. Samples from the lower units (41.6–53.5 m) show high U (22–105 ppm, mean 43 ppm), V (109–1660 ppm, mean 1029 ppm) and Mo (44–400 ppm, 130 ppm), implying intermittently to permanently euxinic environments, consistent with high Mo_{EF} (63–403, mean 154) and U_{EF} (15–57, mean 27). Samples from the upper unit (53.5–60 m) show low U (3–13 ppm, mean 8 ppm), V (64–130 ppm, mean 97 ppm) and Mo (7–31 ppm, 21 ppm), suggesting oxic with intermittent dysoxic conditions.

Yd2 well. Redox conditions could not be determined for Interval I due to an absence of RSTE data. In Interval II, four samples exhibit high U (40–77 ppm, mean 53 ppm), V (144–624 ppm, mean 344 ppm) and Mo content (57–126 ppm, mean 82 ppm) that indicate intermittently euxinic environments, consistent with high Mo_{EF} (43–90, mean 62) and U_{EF} (16–30, mean 22). Interval III can be subdivided into three units. Samples from the lower unit (1723.2–1717.6 m) have high U (25–64 ppm, mean 35 ppm), V (547–1500 ppm, mean 973 ppm) and Mo content (88–179 ppm, mean 118 ppm), suggesting permanently euxinic environments. Samples from the middle unit (1717.6–1702.4 m) exhibit moderate U (6–18 ppm, mean 12 ppm), V (137–420 ppm, mean 258 ppm) and Mo content (13–65 ppm, mean 42 ppm), suggesting ferruginous environments. Samples from the upper unit (1702.4–1692.4 m) exhibit low U (5–8 ppm, mean 7 ppm), V (150–311 ppm, mean 198 ppm) and Mo content (11–26 ppm, mean 18 ppm), suggesting dysoxic with intermittent oxic conditions. All Interval IV samples show low U (4–5 ppm, mean 4 ppm), V (101–196 ppm) and Mo (4–10 ppm, mean 9 ppm). The Yd2 well is close to the Qingjiang fauna in the Changyang section (Fig. 1). The REST contents and lithology of two sections both indicate oxic environments.

4.2.2. Redox conditions in basin region

Xa1 well. One sample at bottom of Interval I exhibits high U (56 ppm), V (1206 ppm) and Mo content (69 ppm), which indicates an intermittently euxinic environment consistent with high Mo_{EF} (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 (1–2 ppm, mean 1 ppm), suggesting oxic environments. Samples from Interval II exhibit low U (4–38 ppm, mean 10 ppm), V (49–210 ppm, mean 76 ppm) and Mo content (1–24 ppm, mean 8 ppm), reflecting oxic to ferruginous environments (Fig. 7). For Interval III, almost all samples exhibit high U (30–726 ppm, mean 120 ppm), V (151–4075 ppm, mean 1568 ppm) and Mo content (22–506 ppm, mean 113 ppm), which indicates intermittently euxinic to permanently euxinic environments, consistent with high Mo_{EF} (116–3739, mean 485) and U_{EF} (28–2874, mean 341). Interval IV can be subdivided into two distinct units. Samples from 783.4–740.6 m exhibit moderate U (12–46 ppm, mean 19 ppm), V (145–348 ppm, mean 245 ppm), Mo content (31–76 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.

4.3. Links between fluctuating redox conditions and hydrothermal activity

As discussed above, hydrothermal events primarily occurred during the early Cam-I, Cam-II, and Cam-III (Figs. 6, 7). Through Cam-I, the depositional environment was mainly oxic in the Yangtze Block, consistent with low RSTE contents 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 ppm, mean 1204 ppm). The V levels in the basal Cambrian of the Longbizui section and the Xa1 well also exceed 500 ppm, and can be up to 7470 ppm. These measurements imply a brief, rapid period of water euxinia during the early Cam-I period (Ediacaran–Cambrian transition, Table 1). The H_2S content of the water column was more than 10 mM, which would have been extremely harmful to survival of organisms (Wignall and Twitchett, 1996). The lithology of the 11 sections is consistent near the ECB, and is dominated by dolomite/chert, and has not changed during this 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 around the time of the ECB. Hydrothermal events may be the main causes of euxinic depositional environments in South China. Nutrients (including Fe and Zn) and CO_2 generated by hydrothermal activity were conducive to phytoplankton reproduction, which increased OM supply (Uematsu et al., 2004; Duggen et al., 2010). At the same time, toxic elements including Hg, Pb and Cr, as well as volatile gasses including HCl and SO_2, emitted from hydrothermal events inhibited zooplankton growth (Jones and Gislason, 2008; Chambers et al., 2013), while decomposition of OM during the deposition process likely consumed large amounts of oxygen in the water column, 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.

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

U (3–38 ppm mean 16 ppm), and high V (113–936 ppm, mean 420 ppm) contents, consistent with the RSTE contents of samples from the Yk1 well (mean U content 15 ppm, mean V content 802 ppm), the Longbizui section (mean Mo content 7 ppm, mean U content 9 ppm, mean V content 491 ppm), and the Yuanjia section (mean Mo content 25 ppm, mean U content 22 ppm, mean V content 3442 ppm). This pattern is similar to the RSTE contents of samples from near the ECB, indicating that the shallow part of the water column was strongly affected by the euxinia caused by hydrothermal events. Zn contents of samples in the Xa1 well (27–666 ppm), Yuanjia (150–716 ppm) and Longbizui (165–593 ppm) sections are abnormally enriched. The "hyper enrichment" of trace elements and high TOC content of black shale may indicate that dissolved H_2S was intermittently present in the photic zone in the early Cambrian. During the Cam-III, as a result of the final break-up of the Rodinia Supercontinent, a major transgression occurred in South China. Hydrothermal events occurred periodically. In the early Cam-III, the depositional environments of the Yangtze region were mainly euxinic. Hydrothermal events enhanced the reduction potential of the water column, which was conducive to the burial and preservation of organic matter. Consistent with this interpretation, TOC content of the shale at the bottom of Interval III was the highest of the four intervals. The depositional environment began to change, and hydrothermal events became rarer. In the middle Cam-III, the water column near the Xiaotan section became oxic, the areas near the Shatan section and Yd2 well were mainly ferruginous, and the deeper water areas remained euxinic. In the late Cam-III, oxic conditions spread 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 hydrothermal events still occurred in deep waters during this period, their influence on 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 high. This suggests that H_2S was also intermittently present in the photic zone from slope to basin environments. Hydrothermal vents released huge amounts of greenhouse gases (methane) and volcanic-originated H_2S into the ocean and/or atmosphere during the early Cambrian (Chen et al., 2009; Gao et al., 2018).

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 mainly experienced ferruginous conditions. Intermittently euxinic conditions partly 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, and basin areas experienced ferruginous condition (Table 1). Depositional environments were dominated by an oxic water column over the whole Yangtze Block during the late Cam-IV.

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 phase is represented by the Chengjiang and Qingjiang faunas in South China (Fig. 10). Whether fluctuations in the oxygen content of the atmosphere–ocean system were the key factor controlling biological evolution during the Cambrian still remains controversial (Mills and Canfield, 2014).

The carbon isotope composition of marine sediments is mainly controlled by the burial of ^{12}C-rich organic matter and the addition of exotic carbon sources (Holser, 1997; Hayes et al., 1999; Kump and Arthur, 1999). Many major events in Earth history are associated with obvious fluctuations of carbon isotope ratios, reflecting perturbation to 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 ratios ($\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$) of sediments can be applied to clarify the evolution of early 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 the carbon negative excursions correspond to extinctions of the Ediacaran fauna (BACE) and SSFs (SHICE), whereas the two positive carbon excursions (ZHUCE, CARE) mark peaks in early Cambrian organisms event and abundance (Zhu et al., 2007). The carbon isotope ratios of samples from the Xa1 well show an obvious negative carbon isotope excursion (−33.69‰) at the boundary between Intervals II and III. This carbon isotope anomaly is located near the metal layer and corresponds to CARE (Fig. 9).

4.5. Implications for the "Cambrian Explosion"

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

Earth history were related to large igneous province volcanism (Wignall, 2001; Bond and Wignall, 2014). Volcanism (especially LIPs) could potentially heat OM in sediments and release large amounts of ^{12}C-rich CO_2 and CH_4 (Renne et al., 1995; Retallack and Jahren, 2008; Chen et al., 2009), driving negative carbon isotope excursions. Obvious signatures of hydrothermal events have been found in dolomites at the bottom of the Ediacaran Doushantuo Formation (Condon, 2005), with the hydrothermal activity producing highly ^{13}C-depleted carbonate cements ($\delta^{13}C_{PDB}$ down to −48‰), and resulting in global warming (Bristow et al., 2011; Sahoo et al., 2012). Volcanic/hydrothermal activity can be regarded, in conjunction with connected factors such as euxinic events, temperature extremes, and seawater acidification, as triggers for biological mass extinctions (Ganino and Arndt, 2009; Bond and Wignall, 2014).

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, the U–Pb dating of tuffs suggests that volcanic events were frequent (Fig. 2). This may have been related to the BACE. Sudden formation of euxinic environments could have restricted the spread of aerobic species and disrupted the original ecological balance, perhaps contributing to extinctions (Fig.10). In the middle of Cam-I, depositional environments in South China were shallow, dominated by oxic conditions and unaffected by hydrothermal events. This coincides with the first positive carbon excursion (ZHUCE).

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

Recent research has shown that the Chengjiang fauna assemblage began at 518 Ma (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 regression, the water column in the Xiaotan section (inner shelf) became oxic, with oxic 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 intermittently euxinic environments were limited to the basin areas (Table. 1). The Chengjiang and Qingjiang faunas were preserved during this period. Basin areas were mainly occupied by ferruginous environments in the late Cam-IV, which were replaced by dominantly oxic conditions following the end of Cam-IV.

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 of benthic trilobites and a large number of planktonic trilobites also appear to have thrived in ferruginous environments (e.g., Three Gorges and Songtao sections). The photic zone does not appear to have contained dissolved H_2S in shallow-water areas. There was no record of biological disturbance in these relatively deep-water areas. The Jinsha section in Guizhou Province, dominated by ferruginous conditions, also recorded a complex benthic assemblage mainly consisting of sponges and arthropods. Depositional environments in the slope to basin areas were mainly euxinic, with dissolved H_2S intermittently present in the photic zone.

Depositional environments in South China during Cam-III were affected by hydrothermal events, but an equivalent impact is not obvious in Cam-IV (Figs. 6, 7). 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 column was euxinic, and deeper parts of the water column were ferruginous. This stratified redox model describes Cam-III, but not Cam-IV, in which the surface water was oxic, whereas mid- and deep parts of the water column were ferruginous condition. Although the water column in Cam-IV was shallower than that in Cam-III, the formation of a stratified redox model in Cam-III was more influenced by hydrothermal events. In the middle and late Cam-III, depositional environments in Yunnan and Hubei provinces already appear to have been experiencing widespread oxic conditions. It is plausible that these limited regions of habitability may not have been sufficient for the large-scale rapid radiation of organisms (Table 1). The mid- and deep-water environments were still affected by hydrothermal events and intermittent euxinic conditions, which may have restricted the spread of aerobic species. These are obvious similarities between biological radiations during the two stages, with the SSFs and Chengjiang (Qingjiang) faunas both occurring in a persistently oxic environment. We tentatively suggest that the Chengjiang (Qingjiang) fauna radiated gradually whilst progressively colonizing inner shelf to the basin environments, as oxic conditions became more widespread. Above all, our data provides an exploratory record that may help to understand connections between hydrothermal events, variability in ocean redox state and the evolution of Early Cambrian life.

5. Conclusions

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 through the Cam- III intervals. During early Cam-I, and Cam-II, the water column was strongly affected by the euxinic conditions resulting from hydrothermal events, which were potentially connected to concurrent extinctions of the Ediacaran fauna and SSFs respectively. During the middle Cam-III interval, although inner shelf areas were oxygenated after the global transgression at 521 Ma, the persistence of extensive deep-water euxinic environments appears to have been not conducive to biological diversification. During the early Cam-IV interval, depositional environments in South China were mainly eutrophic and oxic, which was probably favorable for the rapid radiation of the Chengjiang/Qingjiang fauna. There are obvious similarities between the two episodes of biological radiation. The SSF and Chengjiang /Qingjiang faunas lived in oxic environments that were unaffected by hydrothermal fluids. However, intermittent hydrothermal events resulted in euxinic condition, which may have disrupted the ecological balance and restricted the spread of certain species. The fossil evidence of these evolutionary radiations has a complex but likely important connection 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 mechanistic understanding of the causes of the early "Cambrian Explosion and concurrent extinction of the Ediacaran-Cambrian Shelly fossil faunas in South China.

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Figure

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.

Fig. 2. Stratigraphic correlation with biostratigraphic and tuff/ore dating of lower Cambrian (ca. 541–514 Ma) sections across South China. Data sources: 1 – Xiaotan section, Yunnan Province (Jenkins et al., 2002; Yang et al., 2003; Compston et al., 2008; Och et al., 2013); 2 – Maidiping section, Sichuan Province (Compston et al., 2008; Zi 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, Hubei Province (Okada et al., 2014); 6 – Ganziping section, Hunan Province (Chen et al., 2009); 7 – Longbizui section, Hunan Province (Wang et al., 2012; Yeasmin et al., 2017); 8 – Xa1 well, Hunan Province (this study).

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).

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.

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.

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.

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.

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.

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.

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

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

Supplementary Data Table

Major element, trace element, iron speciation, and TOC contents of the Xiaotan section (inner shelf, Yunnan province, S1), Shatan section (inner shelf, Yunnan province, S2), 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 are shown in Fig. 1.