Coupled oceanic oxygenation and metazoan diversification during the early–middle Cambrian?

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We conducted a high-resolution Fe-trace element geochemical study of lower-middle Cambrian (Fortunian to Age 4) sections of the South China Craton representing intermediate- to deep-marine settings, including outer shelf (Jiuqunao-Wangiapijing, JW; note: Jiuqunao data were compiled from Och et al. [2016]), slope (Wuhe-Geyi, WG), and basinal (Zhalagou, ZLG) sections of the Yangtze Block (Fig. DR1 in the GSA Data Repository1). Linking our redox proxy analysis with detailed paleontological data from the lower-middle Cambrian of South China affords the unique opportunity to investigate the association, if any, between ocean-redox evolution and metazoan diversification during the early to middle Cambrian in South China and possibly elsewhere.

**LITHOSTRATIGRAPHY AND STRATIGRAPHIC CORRELATION**

The lower-middle Cambrian succession at JW (30°53′0.93″N, 110°52′47.25″E for Jiuqunao, 30°48′41″N, 111°11′12″E for Wangjiaping) comprises, moving upsection, the Yanjiahe, Shuijingtuo, Shipai, and Tianheban Formations (Fig. 1A). The upper Yanjiahe, uppermost Shuijingtuo, and Tianheban Formations consist mainly of limestones, whereas the Shuijingtuo and Shipai Formations are mainly black shales, mudstones, and siltstones. The lower-middle Cambrian succession at WG (26°45′34″N, 108°24′33″E for Wuhe, 26°48′12″N, 108°14′10″E for Geyi) comprises the upper Liuchapo, Jiujianzhuang, Bianmachong, and Balang Formations (Fig. 1B). The section consists mainly of black shales, mudstones, and siltstones, although phosphatic chert is present in the upper Liuchapo Formation and muddy limestones are present in the upper Jiujianzhuang Formation. The lower-middle Cambrian succession at ZLG (25°59′6″N, 107°53′32″E) consists of the Laobao, Zhalagou, and Dulijiang Formations (Fig. 1C). The Zhalagou and Dulijiang Formations are black shales, and the upper Laobao Formation is phosphatic chert.

Correlations among the study sections are based on radiometric ages and extensive biostratigraphic work. The key tiepoints among sections are shown in Figure 1. The lowermost Cambrian black shale layer, which is a correlation marker across the Yangtze Platform, has been dated to early Cambrian Age 2 based on zircon U-Pb ages: 526.4 ± 5.4 Ma at Wuhe-Aijiage, ~20 km from the JW section (Okada et al., 2014), and 522.3 ± 3.7 Ma at Bahuang, ~80 km from the WG section (Chen et al., 2015a). The upper Shuijingtuo Formation at JW and the upper Jiujianzhuang Formation at WG are dated to early Cambrian Age 3 based on the trilobite Hupediscus orientalis (Yang et al., 2016). The basal Shipai Formation at JW and uppermost Jiujianzhuang Formation at WG are constrained to

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1GSA Data Repository item 2017245, detailed geological settings, analytical methods, and supplemental figures and data tables, is available online at http://www.geosociety.org/datarerepository/2017/, or on request from editing@geosociety.org.
early Age 4 of the middle Cambrian (ca. 514–509 Ma) based on the trilobites *Redlichia metanensis* and *Maiyella* (Yang et al., 2016). This age framework is confirmed by the trilobites *Breviredlichia liantuoensis* in the basal Tianheban Formation at JW and *Arthroicellus chauveauvi* in the middle Balang Formation at WG, which belong to the *Megapalaeolenus* Zone of middle Age 4 (Yuan and Zhao, 1999; Na and Kiessling, 2015). The trilobite *Kunmingaspis*, found in the basal Dulijujiang Formation at ZLG, belongs to the latest *Chittidilla plana*–*Paralaguruss lantenosis* Zone, demonstrating an age of late Age 4 for the lower part of that unit (Yuan and Zhao, 1999; Na and Kiessling, 2015).

GEOCHEMICAL PROXIES FOR MARINE REDOX CONDITIONS

Iron speciation is a widely used palaeoredox proxy that, based on analysis of reactive iron phases in siliciclastic rocks, can track local water-column redox conditions (cf. Poulton and Canfield, 2011). Iron speciation is an empirically calibrated proxy, and therefore care must be taken when interpreting data, enrichments of redox-sensitive trace elements (RSTEs) (expressed as EF) for ferruginous and euxinic units of Ediacaran age (e.g., Sperling et al., 2016). All Age 4 (Shipai and Tianheban Formations) samples are characterized by high Fe_T/Fe_T (>0.92–1.00) and moderate to high Fe_Py/Fe_T (0.56–0.75), indicating ferruginous to euxinic conditions. Reducing conditions are supported by enrichment factors of 45 (7–52) for Mo and 18 (7–23) for U (note that reported values are the median and 16th–84th percentile range). V exhibits lower enrichment factors (2.3; 1.3–3.7) similar to that reported for ferruginous and euxinic units of Ediacaran age (e.g., Sperling et al., 2016). All Age 4 (Shipai and Tianheban Formations) samples are characterized by low Fe_Py/Fe_T (0.08–0.44) and low Fe_Py/Fe_T (0.0–0.62), suggesting oxic depositional conditions. This inference is consistent with low Mo EF (0.3 ± 0.2; mean ± SD), U EF (0.8 ± 0.2), and V EF (0.7 ± 0.3) in the Age 4 formations.

In the slope WG section (Fig. 1B), available Age 2 to early Age 4 (Jiunenchang and Biammachong Formations) samples have variable Fe_Py/Fe_T (0.23–0.88) and variable Fe_Py/Fe_T (0.24–0.89), indicating dominantly ferruginous conditions punctuated by episodic euxinia. In contrast, all older Age 4 (Balang Formation) samples show low Fe_Py/Fe_T (0.08–0.35) and low Fe_Py/Fe_T (0.0–0.3), suggesting oxic depositional conditions, consistent with low Mo EF (0.5 ± 0.2), U EF (0.3 ± 0.1), and V EF (0.3 ± 0.1). This is also consistent with trace metal enrichment patterns: samples from the lower member (0–29 m) show greater enrichments [Mo EF = 18 (5–50), U EF = 8 (4–14), V EF = 7 (4–15)] than samples from the upper member (29–92 m) [Mo EF = 12 (7–18), U EF = 2.3 (1.0–6.8), V EF = 1.0 (0.7–1.6)]. These small enrichments are consistent with sulfide restricted to sediment pore waters (cf. Scott and Lyons, 2012).
In the basinal ZLG section (Fig. 1C), available Age 2 to middle Age 4 (Zhalagou Formation) samples have relatively high Fe_{HR}/Fe_{T} (0.70–1.00) and relatively low Fe_{HR}/Fe_{IR} (0.33–0.71), indicative of dominantly ferruginous conditions. This redox interpretation is in agreement with the moderate trace metal enrichments of the lower member (0–20 m) of the Zhalagou Formation (Mo_{EF} = 35 (16–42), U_{EF} = 7 (6–9), V_{EF} = 27 (19–54)), and with the reduced trace metal enrichments of the middle member (20–50 m; Mo_{EF} = 2.7 ± 1.2, U_{EF} = 1.2 ± 0.3, V_{EF} = 1.2 ± 0.2) and upper member (50–85 m; Mo_{EF} = 9.6 ± 5.5, U_{EF} = 1.7 ± 0.8, V_{EF} = 1.4 ± 1.0). Given Mo concentrations as high as hundreds of parts per million in some Cambrian black shales of South China (Jin et al., 2016), the small Mo enrichments in the middle and upper members may have resulted from low H_2S concentrations (<10 μm) that limited the formation of thiomolybdates (e.g., Erickson and Helz, 2000). In contrast, all late Age 4 (Duliujiang Formation) samples have low Fe_{HR}/Fe_{T} (0.30–0.46) and low Fe_{HR}/Fe_{IR} (0.0–0.44), suggesting dominantly oxic conditions, consistent with extremely low Mo_{EF} (0.5 ± 0.1), U_{EF} (0.4 ± 0.0), and V_{EF} (0.5 ± 0.0).

In summary, our results suggest that the outer shelf to basinal facies of the Yangtze Block, which were initially anoxic, transitioned to more oxygenated conditions during Cambrian Age 3–Age 4 (Fig. 2C). During the first increase, at the end of Age 3 or the beginning of Age 4 (ca. 514 Ma), anoxia yielded to oxic conditions at the outer shelf JW section. During the second increase, in middle Age 4, persistently oxic conditions expanded from outer shelf to slope areas (e.g., WG), although basinal settings (e.g., ZLG) remained dominantly anoxic at that time. In late Age 4, oxic waters expanded from slope to basinal environments (e.g., ZLG).

Our new results demonstrate that deeper waters on the Yangtze Block remained anoxic during Age 3, and that an additional stepwise rise of oxygen levels occurred from Age 3 to Age 4. There is no obvious sedimentological evidence to indicate that transitions were linked to changes in sedimentation rates or depositional facies that shut off a reactive iron or RSTE trap (e.g., the entire ZLG section is characterized by uniform mudstone deposition; Fig. 1C).

With the addition of our new data, increasing oceanic oxygenation during Cambrian Age 2–Age 4 becomes statistically evident in the full South China deep-water Fe speciation database (Table DR4), as shown by a progressive decline of mean Fe_{HR}/Fe_{T} from 0.73 in the Fortunian to 0.43 in Age 4 [see Fig. 2D; p < 0.05 for ANOVA (analysis of variance) and Kruskal-Wallis tests; Table DR1]. This is in marked contrast to the mostly unchanged average redox conditions for the same interval (mean Fe_{HR}/Fe_{T} < 0.38 but p > 0.05; Table DR2) suggested by available Fe speciation data from other continents (Fig. 2D; Table DR4). In addition, we conducted a single-point detection test (using the R package Changepoint: https://cran.r-project.org/web/packages/changepoint/changepoint.pdf) with published global deep-water iron speciation data from 635 to 497 Ma (Table DR4), in which each iron speciation value was assigned an age based on available age constraints in order to create a time series. Using this approach, the most significant change in Fe_{HR}/Fe_{T} ratios occurred at 514 Ma (see Fig. DR3). Despite these statistical results, we stress that a dearth of early-middle Cambrian units in the database renders uncertain whether the pattern that we observe for South China, i.e., stepwise oceanic oxygenation during Cambrian Age 2–Age 4, represents a global phenomenon. Our results should provide motivation for additional redox studies of other early-middle Cambrian continental margins with paleodepth constraints.

Our findings allow for a reevaluation of some of the current controversies surrounding atmospheric and oceanic oxygen levels during the early-middle Cambrian.

Figure 2. Marine redox and biodiversity patterns of the early-middle Cambrian. A: Number of phyla and classes globally (Erwin et al., 2011). B: Spatiotemporal distribution of key biotas in South China, including biotas dominated by small shelly faunas, sponges, and arthropods and echinoderms (Zhu et al., 2010). C: Spatiotemporal variation in ocean redox conditions in South China (this study; Jin et al., 2016, and references therein). D: Comparison of mean Fe_{HR}/Fe_{total} (highly reactive iron/total iron) ratios in four time bins between South China database and other continent databases. This statistical analysis includes only samples from outer shelf and basinal environments. The four time bins are divided by the major changing points of full Fe_{HR}/Fe_{T} data identified through a single-point detection test (see the Data Repository [see footnote 1]). The sample number and time range of each bin are shown in brackets. Each whisker represents the standard error. Abbreviations: SSF—small shelly fauna, SS—sponge spicule, AS—articulated sponge, SC—South China, SW—surface waters, MW—mid-depth waters, DW—deep waters.

Our finding of stepwise oceanic oxygenation in South China during Cambrian Age 2–Age 4 provides new insights into environmental controls on early metazoan evolution. For example, this stepwise oceanic oxygenation corresponds temporally to the regional replacement in South China of small shelly faunas and sponge-dominated communities (Fortunian and Age 2) by more complex arthropod- and echinoderm-rich biotas (Age 3 and Age 4) (Figs. 2B and 2C; Peng et al., 2005). Given the relatively high respiratory oxygen demands of echinoderms and mobile metazoans like arthropods, rising oceanic oxygen levels are likely to have facilitated the diversification of metazoans during Age 2–Age 3 (Sterling et al., 2013). Furthermore, a spatial expansion of marine invertebrates is recorded in South China during Cambrian Age 3–Age 4, as evidenced by (1) the stepwise expansion of complex arthropod-dominated biotas from shallow-shelf to deep-slope facies (Fig. 2B), and (2) the invasion of deepwater habitats by sponges, echinoderms, and trilobites (Fig. 2B; Peng et
Collectively, these observations suggest a pronounced redox control on early metazoan ecology.

Rising oceanic oxygen levels in South China during Age 2 and early Age 3 also coincided with regional increases in the diversity of basic metazoan body plans (i.e., numbers of classes and phyla) (Fig. 2A), providing evidence for causal links between these factors, as hypothesized by Knoll and Carroll (1999). However, the lack of major body plan diversification (in South China and globally; Erwin et al., 2011) during Age 3–Age 4, which was the key interval of oxygenation in South China (>12 m.y.; Fig. 2A), casts doubt on the Knoll and Carroll (1999) model. Alternatively, the initial appearance of morphologically (and functionally) complex, metabolically demanding metazoan body plans may not have been immediately followed by a radiation of representative taxa; there was likely a slow transition between morphological innovation and ecologically meaningful implementation (e.g., Erwin et al., 2011). In this case, environmental factors such as oceanic redox state may have played an important role in the widespread implementation of ecological innovations.

CONCLUSIONS

Our Fe-trace element geochemical study of Cambrian Age 2–Age 4 strata in the outer shelf (Jiuquiao-Wangjiaping), slope (Wuhe-Geyi), and basinal (Zhalagou) sections of the Yangtze Platform indicates a stepwise expansion of oxic waters from shallow- to deep-marine settings during the early–middle Cambrian. These findings differ from the results of earlier studies that inferred stable or decreasing oceanic oxygen levels at that time (Boyle et al., 2014; Sperling et al., 2015). Coupling our redox proxy work with detailed lower–middle Cambrian paleontological records from South China suggests that this stepwise oceanic oxygenation process may have facilitated metazoan diversification and ecological expansion during Cambrian Age 2–Age 4. More broadly, despite a surge in redox work over the past decade, our study highlights the need to continue to develop sedimentary geochemistry databases.

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