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Ocean euxinia and climate change double whammy drove the Late Ordovician mass extinction

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ABSTRACT

The Late Ordovician mass extinction (LOME) was the first of the “Big Five” Phanerozoic extinction events and comprised two extinction pulses. Proposed kill mechanisms include glacially-induced global cooling and the expansion of water column anoxia and/or euxinia (sulfidic conditions), but no general consensus has been reached with regard to the precise role of these mechanisms. A more definitive understanding is hampered by poorly constrained temporal links between the extinction pulses and climate change, and by uncertainty over the spatial distribution and intensity of euxinia. Here, we utilize Fe speciation and Mo concentrations, in addition to the chemical index of alteration weathering proxy, to reconstruct ocean redox conditions and climate change across a Late Ordovician to Early Silurian shelf to slope transect on the Yangtze Shelf Sea. These data show two cycles of expanded euxinia corresponding to the two pulses of the LOME, suggesting a strong causal relationship. Significantly, we show that intermittent or weak euxinia developed during the first extinction pulse, which likely accounts for the loss of benthic fauna and some planktonic organisms and nektonic groups. By contrast, the development of more intense euxinia throughout the water column during the second pulse likely drove survival fauna extinct. Superimposed upon this, significant global cooling occurred across the first extinction phase, reflecting a secondary role in driving certain low-latitude taxa extinct.

INTRODUCTION

The Late Ordovician mass extinction resulted in the extinction of ~85% of marine animal species (Sheehan, 2001) across a relatively short time span (Brenchley et al., 1994; Finnegan et al., 2011). The LOME comprised two pulses: the first pulse (LOMEI-1) occurred at the Katian/Hirnantian transition and was the primary extinction phase during which benthic organisms, planktonic organisms and nektonic groups became extinct. The second pulse (LOMEI-2) occurred during the late Hirnantian, when survivors of the first pulse became extinct (Harper et al., 2014). Numerous lines of evidence have demonstrated that rapid global cooling occurred during the late Ordovician, broadly coincident with the LOME (e.g., Finnegan et al., 2012; Crampton et al., 2016). However, the timing of glaciation is controversial and does not precisely match the onset of the LOME (see the GSA Data Repository[1] for further details).

Conversely, ocean anoxia and widespread euxinia have been proposed as kill mechanisms (e.g., Zhang et al., 2009; Hammarlund et al., 2012; Ahm et al., 2017), but the spatial and temporal distribution, and intensity, of anoxia/euxinia, remain largely unknown.

Here, we reconstruct the evolution of Late Ordovician (Katian Stage) to Early Silurian (Rhudanian stage) water column redox conditions across a shelf to slope depth transect in the Yangtze Shelf Sea, South China (Fig. 1), based on Fe-speciation and Mo concentrations. In addition, we utilize the chemical index of alteration (CIA) weathering index (Nesbitt and Young, 1982) to evaluate contemporaneous climate change. Our multi-proxy approach allows a detailed evaluation of the temporal and spatial intensity of ocean redox conditions and coeval climate change, thus resolving the roles of these different mechanisms in driving the LOME.

GEOLOGIC SETTING

South China was located near the equator during the Late Ordovician (Torsvik and Cocks, 2013). From the Late Ordovician to Early Silurian, the Yangtze shallow carbonate platform in South China evolved into a siliciclastic-dominated deep shelf basin, called the Yangtze Shelf Sea, which deepened northwards to the Panthalassic Ocean (Figure 1 and Fig. DR1). Samples were collected from an inner shelf section (Shuanghe; SH) (Fig. DR2), a mid-shelf section (Qiliao; QL) (Fig. DR3) and an outer shelf to slope section (Tianba; TB) (Fig. DR4), primarily spanning the Late Ordovician (Katian Stage) through to the Early Silurian (Rhudanian stage). Full details of the geologic setting and methods are given in the GSA Data Repository[1].

RESULTS

Water Column Redox Conditions

Fe speciation and redox-sensitive trace metals (e.g., Mo) are well-established proxies for water column redox conditions (e.g., Poulton and Canfield, 2011; Scott and Lyons, 2012). Using these techniques (see the GSA Data Repository[1] for full details), we identify four distinct intervals of evolving redox conditions across the Yangtze shelf transect (Fig. 2). For Interval I, representing the early to Middle Katian stage (D. Complantus and D. Complexus graptolite zones), all sections have variable Fe_{HR}/Fe_{T} ratios and low Mo concentrations (<25 ppm), coupled with low Fe_{Py}/Fe_{HR} ratios (Fig. 2), suggesting fluctuations between oxic and anoxic ferruginous (Fe-rich) bottom waters.

During Interval II, representing the late Katian stage (P. pacificus graptolite zone) and the first Late Ordovician mass extinction interval (LOMEI-1), most samples across the bathymetric transect have elevated Fe_{HR}/Fe_{T} ratios, reflecting persistent anoxia (Fig. 2). Mo concentrations in the mid-shelf section are generally above 25 ppm but less than 100 ppm, likely reflecting the development of at least intermittent euxinia below the LOMEI-1 interval (Scott and Lyons, 2012), although such a signal might also develop under weakly euxinic conditions if sulfide concentrations fluctuated around the level (~11 µM) where dissolved molybdate becomes particle reactive (Erickson and Helz, 2000). Higher Mo contents (80–116 ppm) then occur at the LOMEI-1 horizon, suggesting persistent euxinia (Scott and Lyons, 2012). By contrast, Mo contents only increase just before the LOMEI-1 horizon on the inner shelf and the outer shelf/slope, but moderate Mo contents (>25 ppm) at these two sites, combined with high Fe_{Py}/Fe_{HR} ratios on the inner shelf, support the development of intermittent or weak euxinia in shallower and deeper settings across the first extinction horizon (Fig. 2).

For Interval III, during the early Hirnantion (N. extraordinarius graptolite zone), elevated Fe_{HR}/Fe_T, Fe_{Py}/Fe_{HR} and Mo on the inner shelf suggest persistent euxinia, before a return to anoxic ferruginous conditions at the top of this zone (Fig. 2). This interval is more condensed in the deeper water sections, but a clear transition from euxinic to ferruginous conditions in deeper waters is supported by low concentrations of Mo (<25 ppm) and low Fe_{Py}/Fe_{HR}.

The base of Interval IV during the late Hirnantian and Rhudanian stages (N. persculptus and A. ascensus graptolite zones) marks the second (LOMEI-2) extinction horizon. Water column redox dynamics across the LOMEI-2 horizon are very similar to the LOMEI-1 horizon, whereby euxinia develops on the mid-shelf prior to the extinction horizon (as indicated by elevated Mo concentrations) (Fig. 2). The extinction horizon itself shows evidence of persistent strong euxinia across all three sections, as indicated by uniformly high Mo concentrations (>100 ppm) across the basin transect, and by high Fe_{Py}/Fe_{HR} ratios in the inner-shelf section.

Chemical Index of Alteration and Palaeoclimatic Changes

Consistent trends are apparent in CIA values across the Yangtze shelf transect (Fig. 3). High values throughout the Katian stage suggest relatively intense chemical weathering, reflecting warm climatic conditions. However, a gradual decrease in CIA values through the Katian stage prior to the LOMEI-1 horizon implies progressive cooling. During the LOMEI-1 interval, CIA values show some scatter across the basin, but values tend to decrease before reaching a minimum between the two extinction horizons (Fig. 3). These very low CIA values have been observed elsewhere in the Yangtze basin (Yan et al., 2010), suggesting that chemical weathering intensity was significantly decreased under cold climatic conditions. The low CIA values correlate with a pronounced positive $\delta^{13}C_{org}$ excursion (Fig. 3), which represents the global Hirnantian $\delta^{13}C_{org}$ excursion (HICE) (Underwood et al., 1997; LaPorte et al., 2009) (Fig. 4). Following this minimum, CIA values increase above the LOMEI-2 horizon (Fig. 3), suggesting a gradual increase in chemical weathering, but values remain below those found lower in the section, implying the maintenance of relatively cool climatic conditions.

DISCUSSION

A Redox Control on the Extinction Pulses?

Our data can be considered in the context of previous studies to provide a more widespread evaluation of temporal changes in ocean redox conditions, and hence links to the two extinction pulses (Fig. 4). Yan et al. (2012) studied an inner shelf section of the Yangtze Sea (Nanbazi; NBZ), representing a shallower water setting in comparison to our sections. When combined, the four sections show the initial spread of anoxia from the mid-shelf and across the Yangtze Shelf Sea during the Katian stage (Fig. 4). These redox conditions then intensified, with euxinia originating on the mid-shelf prior to the LOMEI-1 horizon, followed by an expansion of intermittent or weak euxinia to the inner shelf and outer shelf/slope during the first extinction phase itself, although the shallowest waters do not show evidence of euxinia at this time (Fig. 4).

The three more distal sections all show clear increases in total organic carbon (TOC) during the development of euxinia across the LOMEI-1 horizon (Figs. DR2-DR4), reflecting an increase in regional burial rates of organic matter. This relationship between euxinia and TOC has also been observed at an inner shelf location off Baltica

(Hammarlund et al., 2012), and in the deep marine Vinini Creek section in Nevada (Ahm et al., 2017), suggesting that expanded euxinia may have been a widespread phenomenon across the first extinction pulse of the LOME.

During the early Hirnantian as sea level decreased (Brenchley et al., 2006; Yan et al., 2012) between the two extinction horizons, redox conditions varied across the Yangtze Shelf Sea (Fig. 4). Geochemical evidence suggests that the shallowest water NBZ section became oxic-suboxic, presumably due to the sea level regression (Yan et al., 2012), which is similar to records from the Baltica inner shelf at Bilegrav, Denmark (Hammarlund et al., 2012). In addition, the extent of euxinic waters gradually decreased across the shelf, giving way to anoxic ferruginous conditions at the point of maximum retreat (Fig. 4). Thus, during the early Hirnantian stage, the evolution of ocean redox chemistry across the Yangtze Shelf Sea, and probably elsewhere, was mainly driven by falling sea level. This sea-level fall was itself a consequence of global cooling, highlighting the close links between the evolution of water column redox and climate in the Late Ordovician.

As temperatures increased and sea level rose, a return to anoxia and widespread euxinia is evident across the Yangtze Shelf Sea, coincident with the LOMEI-2 horizon (Fig. 4). Water column redox dynamics across this second extinction pulse are very similar to those of the first pulse (Fig. 4), whereby euxinia originates on the mid-shelf and subsequently spreads to the inner shelf and outer shelf/slope at the extinction interval. One significant difference, however, is that Mo concentrations are much higher across the three euxinic sites during the second extinction pulse (Fig. 2), likely indicating persistent euxinia (Scott and Lyons, 2012) with relatively high concentrations of dissolved sulfide.

In addition, evidence from elsewhere suggests that euxinia was particularly widespread on continental shelves at this time (Hammarlund et al., 2012; Melchin et al., 2013; Zhou et al., 2015). The development of euxinia is initiated at the maximum extent of the $\delta^{13}C_{org}$ excursion observed at a variety of sites (Fig. 4). This is consistent with increased availability of nutrients to drive productivity during the maximum extent of glaciation, facilitated either by enhanced release of nutrients from organic matter degradation in the water column as sea level fell (Hammarlund et al., 2012) or by nutrient input from exposed continental shelves.

The Intensity of Euxinia as a Selective Kill Mechanism

Sulfide is highly toxic to almost all eukaryotes at micromolar concentrations (Knoll et al., 2007) and water column euxinia has been implicated as a major driver of several extinction events (e.g., Wignall and Twitchett, 1996). However, our observation of a difference in the relative intensity or persistence of euxinia across the two extinction horizons, combined with overall global cooling, allows a more nuanced evaluation of the precise roles of sulfide and climate change in driving the two pulses of the LOME across the Yangtze shelf transect.

The LOMEI-1 interval mainly eradicated benthic fauna, including sessile (brachiopods, rugose and tabulate corals) and mobile (trilobites) animals on the deep shelf, in addition to phytoplankton and zooplankton such as graptolites (Brenchley et al., 2001). It is difficult to invoke global cooling as a kill mechanism for many of the high-latitude, cool-water taxa, particularly deep-shelf benthic faunas (Harper et al., 2014). However, glacially-induced global cooling is more significant for lower-latitude taxa, particularly phytoplankton and zooplankton such as graptolites (Brenchley et al., 2001;

Crampton et al., 2016). Hence global cooling, rather than the spread of euxinia, was likely responsible for the loss of phytoplankton and zooplankton. By contrast, the development of intermittent or weak euxinia across the LOMEI-1 horizon implies that sulfide may have been largely restricted to bottom waters across the shelf to upper slope, and thus sulfide was likely a major kill mechanism for benthic fauna only.

During the LOMEI-2 interval, more persistent, intense and widespread euxinia is indicated, which is entirely consistent with an observed loss of survival fauna across a wide range of water depths (Harper et al., 2014). The implication of sulfide, rather than global cooling, as the main kill mechanism during the second extinction phase also reconciles our observation, based on the CIA weathering index, of a gradual return to warmer climatic conditions during this interval (Fig. 4).

CONCLUSIONS

The Yangtze shelf transect allows a particularly well-resolved dynamic-redox system to be reconstructed across a bathymetric shelf transect. The system shows two cycles of water column euxinia, with the first being an expansion of intermittent or weakly euxinic bottom waters at the end of the late Katian stage, and the second being a period of more intense persistent euxinia during the late Hirnantian stage. These two euxinic episodes correspond to the two pulses of the LOME, suggesting that the LOME was trigged by the expansion of euxinia. However, the intensity of euxinia throughout the water column apparently affected the nature of each extinction pulse, with the first euxinic episode affecting benthic fauna only, while the second episode affected survival fauna throughout the water column. Superimposed on this redox control, global cooling placed additional stress on marine fauna, and likely affected lower-latitude taxa, in particular phytoplankton and zooplankton such as graptolites.

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FIGURE CAPTIONS

Figure 1. Geological reconstruction. (A) Late Ordovician (445 Ma) palaeogeography showing South China (Torsvik and Cocks, 2013). Red circle represents the Shuanghe (SH) inner shelf section; green circle represents the Qiliao (QL) mid-shelf section; pink circle represents the Tianba (TB) outer shelf-slope section. Black circle represents the Nanbazi (NBZ) shallow inner shelf section (Yan et al., 2012). (B) Simplified palaeogeographic map of the Yangtze Shelf Sea during the Late Ordovician showing section localities (scale bar = 100 km). (C) Schematic cross-section of the Late Ordovician Yangtze Shelf Sea showing estimated relative palaeo-depths and study sections.

Figure 2. Fe speciation and Mo concentration data for the Yangtze Shelf Sea. Samples with Fe_T >0.5 wt% (closed circles) can be utilized for Fe speciation (Clarkson et al., 2014); Fe_{HR}/Fe_T ratios are not presented for samples with Fe_T <0.5 wt% (open circles). Dashed line at 0.22 shows the upper limit for identification of oxic conditions from Fe_{HR}/Fe_T ratios; dashed line at 0.38 indicates the lower limit for identification of anoxic conditions. Dashed lines at 0.7 and 0.8 for Fe_{Py}/Fe_{HR} ratios show the range above which euxinic conditions are indicated and below which ferruginous (FER) conditions are indicated. Yellow arrows in the LOMEI-2 horizon indicate samples with higher values than the range shown. Four time intervals of differing redox conditions are defined by I, II, III and IV. Extinction intervals shown in pink represent the first (LOMEI-1) and second (LOMEI-2) pulses of the late Ordovician mass extinction. Graptolite zones: D. cn. – Dicellograptus Complanatus; D. cx. – Dicellograptus Complexus; M. e. – Metabolograptus extraodinarius; M. p. –Metabolograptus persculptus; A. a. – Atavograptus ascensus. Approximate positions of graptolite zone boundaries are represented by dashed lines. Rhud. = Rhuddanian.

Figure 3. Chemical Index of Alteration (CIA) and C isotope systematics. Purple arrows indicate samples with values outside the range shown. Gray bold lines represent CIA trends for the three sections.

Figure 4. Summary of global records in relation to climate change and redox conditions across the Yangtze Shelf Sea. (A) Regional $\delta^{13}C_{org}$ excursions (the global Hirnantian C-

isotope excursion) from South China, Dob's Linn (DL), Scotland (Underwood et al., 1997), Blacktone River (BR), Canada (LaPorte et al., 2009) in Laurentia, and Bellegrav (BL), Denmark in Baltica (Hammarlund et al., 2012). (B) Summary of climate and redox changes across the Yangtze Shelf Sea. (C) Schematic illustrating redox dynamics across the Yangtze Shelf Sea. Changes in sea level (relative to sea level position during the Middle Katian stage) are shown by fine dashed lines in (C).

[1] GSA Data Repository item 2018xxx, more details of section description, analytical methods, geochemical data and cross plots, is available online at http://www.geosociety.org/datarepository/2018/ or on request from editing@geosociety.org.