Cadmium isotope constraints on primary productivity and environmental perturbations across the Late Ordovician mass extinction

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ABSTRACT

The Late Ordovician mass extinction (LOME) constitutes the second largest of the "Big Five" extinctions of the Phanerozoic. The LOME comprised two extinction pulses associated with sea level changes linked to the Hirnantian glaciation. Although climate change has been implicated as a potential driver of the mass extinction, uncertainty remains as to its precise impact relative to the concurrent development of ocean anoxia. Here, we investigate the behaviour of the oceanic cadmium (Cd) cycle, as a key element involved in a number of biological processes, across the LOME and into the Early Silurian. Our focus is on the Wangjiawan section, South China, which is the Global Stratotype Section and Point (GSSP) marking the base of the Hirnantian Stage. We combine authigenic Cd isotope analyses ($\delta^{114}Cd_{auth}$) with total organic carbon (TOC) concentrations and isotopes, and major and trace element systematics, to determine the evolution of marine productivity across the LOME, and to provide insight into the mass extinction and relationships between climatic and environmental change. Our $\delta^{114}\mathrm{Cd}_{\mathrm{auth}}$ data display a gradually decreasing trend from the late Katian to the Katian–Hirnantian boundary, suggesting enhanced biological assimilation of isotopically light Cd followed by export to the sediments. This interpretation is supported by an increase in organic carbon isotope ($\delta^{13}\mathrm{C}_{\mathrm{org}}$) compositions, as well as a progressive decrease in P/Al ratios and increasing $\mathrm{C}_{\mathrm{org}}$/P ratios in the early part of the late Katian. A slight increase in Cd isotope values in the early Hirnantian was likely caused by drawdown of light Cd (as CdS) in euxinic shallower seawater settings. During glacial melting in the late Hirnantian, organic carbon burial declined, consistent with lower Cd/Al, Zn/Al and Ni/Al ratios. However, $\delta^{114}\mathrm{Cd}_{\mathrm{auth}}$ values remain low across this interval, possibly due to an increase in the supply of isotopically light Cd from enhanced weathering and rising sea level, as supported by elevated Al contents and Chemical Index of Alteration (CIA) values. Elevated $\delta^{114}\mathrm{Cd}_{\mathrm{auth}}$ values subsequently occurred in the Early Silurian (Rhuddanian), alongside a decline in CIA and Al values, suggesting that the Cd sink was gradually balanced by a decline in the weathering input of Cd and lower rates of primary productivity. Our data provide new insight into the Cd cycle through the Late Ordovician to Early Silurian, and suggest that elevated marine productivity drove enhanced burial of organic matter, which likely contributed to CO_2 drawdown and the initiation of the Hirnantian glaciation.

INTRODUCTION

The first of the “Big Five” mass extinctions occurred during the Hirnantian – the terminal stage of the Ordovician – which represents an interval of major climatic and environmental change (e.g., Yan et al., 2010; Melchin et al., 2013; Harper et al., 2014; Zhou et al., 2015; Luo et al., 2016; Smolarek et al., 2017). The late Ordovician mass extinction (LOME) occurred in two pulses associated with sea level change linked to the Hirnantian (Gondwanan) glaciation, and resulted in the loss of ~53% of marine species (Sheehan, 2001; Yan et al., 2010; Fan et al., 2020). The first pulse occurred at the beginning of the Hirnantian stage during climatic cooling, which occurred coincident with the onset of positive excursions in both inorganic carbon ($\delta^{13}\mathrm{C}_{\mathrm{carb}}$) and organic carbon ($\delta^{13}\mathrm{C}_{\mathrm{org}}$) isotope values (Fan et al., 2009; Yan et al., 2009; Jones et al., 2011; Finnegan et al., 2011), as well as widespread sulfidic (euxinic) anoxia (Hammarlund et al., 2012; Ahm et al., 2017; Zuo et al., 2018; Bond and Grasby, 2020; Kozik et al., 2022a; Liu et al., 2022). The second extinction pulse began with the onset of glacial melting, which occurred coincident with a rapid rise in eustatic sea-level and the re-development of widespread euxinia (Yan et al., 2010; Finnegan et al., 2011; Jones et al., 2011; Hammarlund et al., 2012; Melchin et al., 2013; Zhou et al., 2015; Luo et al., 2016; Smolarek et al., 2017; Zuo et al., 2018; Bond and Grasby, 2020; Sánchez-Roda et al., 2024).

Although climate change has been implicated as a driver of the late Ordovician mass extinction (LOME), the role of ocean anoxia has increasingly been stressed (Hammarlund et al., 2012; Ahm et al., 2017; Zuo et al., 2018; Bond and Grasby, 2020; Liu et al., 2022; Kozik et al., 2022a). As such, the causal relationships between climate change, marine redox changes and the biotic response are heavily debated. For instance, one model suggests the first pulse of the LOME was driven by cooling due to drawdown of atmospheric CO_2 caused by global silicate weathering and/or organic carbon burial (Kump et al., 1999; Melchin and Holmden, 2006; Yan et al., 2010; Finnegan et al., 2012; Lenton et al., 2012; Lv et al., 2022). By contrast, other studies suggest that the initial decline in biodiversity was caused by warming and anoxia, rather than cooling itself (Hammarlund et al., 2012; Zuo et al., 2018; Bond and Grasby, 2020; Kozik et al., 2022a; Liu et al., 2022; Sánchez-Roda et al., 2024), with global cooling playing a secondary role in the second extinction pulse (Zuo et al., 2018). Nevertheless, enhanced nutrient supply from intense volcanism, weathering and/or upwelling is thought to have stimulated marine primary productivity and contributed to the Hirnantian positive carbon isotopic excursion and the cooling event itself (Longman et al., 2021; Qiu et al., 2022). In this case, changes in marine primary productivity could have played a significant role in both climate change and marine redox conditions. However, the evolution of marine productivity across the Ordovician–Silurian boundary (LOME) is poorly understood (Brenchley et al., 2003; Saltzman and Young, 2005; Zhou et al., 2015; Bond and Grasby, 2020; Chen et al., 2021; Wang et al., 2022), which has hampered understanding of the mass extinction, as well as the mechanisms that drove the carbon cycle dynamics that are a hallmark of the Hirnantian.

As a biologically active trace element, cadmium (Cd) is involved in a number of biological processes in marine micro-organisms (e.g., assimilation by some phytoplankton species), and it has been demonstrated that biological uptake of Cd is associated with a significant isotopic fractionation (Ripperger et al., 2007; Abouchami et al., 2011, 2014; Conway and John, 2015). Biological assimilation in surface waters results in uptake of the lighter Cd isotopes, and these lighter isotopes are regenerated in the deep sea or preserved in the sediments along with organic matter, which overall leads to a monotonic transition to lighter values in the deep ocean (Abouchami et al., 2014;

Conway and John, 2015).

Modern seawater dissolved δ^{114}Cd measurements show that the isotopic signature of the deep ocean has low values of +0.2‰ to +0.5‰, whereas the surface ocean may exceed +2.0‰ (Ripperger et al., 2007; Xue et al., 2013; Conway et al., 2013; Abouchami et al., 2011, 2014; Conway and John, 2015). Cadmium isotope compositions in carbonates from various settings in the late Permian also display lower values in deeper water sections relative to shallow waters, demonstrating that this isotopic gradient may be preserved in ancient marine sediments (Zhang et al., 2023). In contrast to the Cd isotopic signature of seawater, potential inputs (upper continental crust) exhibit lighter isotopic compositions (~ –0.04‰; Schmitt et al., 2009), and in addition to the burial of isotopically-light Cd in association with organic matter, CdS precipitation under anoxic conditions has been proposed as an isotopically-light sink from ambient seawater (Janssen et al., 2014; Guinoiseau et al., 2018). In addition to biological uptake and CdS precipitation, experiments have shown that Cd can readily substitute for Ca in $CaCO_3$, resulting in an isotopic fractionation factor ($\alpha_{CaCO3–Cd(aq)}$) of ~0.99955 during calcite precipitation in seawater, although such an effect is unlikely to play a significant role when considered relative to Cd utilization by phytoplankton (Horner et al., 2011). These investigations of Cd isotope compositions in modern oceans provide critical insight into marine Cd cycling and the mechanisms controlling Cd uptake in the oceans, thus enabling the application of Cd isotopes as an effective paleo-proxy for past primary production (e.g., Georgiev et al., 2015; Zhang et al., 2018, 2023; Frederiksen et al., 2022; Dickson et al., 2022; Liu et al., 2024).

In order to investigate oceanic Cd cycling and the evolution of marine productivity across the LOME, we present new Cd isotope data alongside organic carbon isotopes and elemental compositions, for the Wangjiawan section in South China. This section is the Global Stratotype Section and Point (GSSP) for the basal Hirnantian Stage (Chen et al., 2006), and is well-studied in terms of its bio- and chemo-stratigraphy. These data enable an assessment of possible controls on measured δ^{114}Cd values, and in addition to providing a perspective on marine productivity, our approach provides insight into the relationships between climatic and environmental change in the Late Ordovician, as well as their role in the first mass extinction of the Phanerozoic.

GEOLOGICAL SETTING

During the Late Ordovician to Early Silurian, the South China craton was a microcontinent on the northwestern margin of Gondwana, situated approximately at the paleoequator (Fig. 1A). The Wangjiawan section lies to the north of Yichang City, Hubei Province, and was located on the Upper Yangtze Platform in an unrestricted, deep outer-shelf setting (Chen et al., 2006; Fig. 1B). The section comprises the Wufeng, Kuanyinchiao and Lungmachi formations in ascending order. The Wufeng Formation is composed mainly of black shale with abundant graptolites (Chen et al., 2006), whereas the Kuanyinchiao Formation, which is characterized by the Hirnantian Fauna, is dominated by carbonaceous mudstone containing many brachiopod shells, and sporadic argillaceous limestone turbidites that record lowstand conditions during the Hirnantian glaciation (Rong et al., 2002; Chen et al., 2006; Yan et al., 2010; Zhou et al., 2015; Luo et al., 2016). The overlying Lungmachi Formation represents an interval of rising and subsequently stable sea level, following Hirnantian glacial melting, and is similar lithologically to the Wufeng Formation, except for higher contents of siliceous minerals (Zhou et al., 2015; Luo et al., 2016). The complete biozones established for this section provide the international reference for the identification and correlation of strata across the LOME (Chen et al., 2006). The base and termination of the Hirnantian glaciation occur in the uppermost Wufeng and Kuanyinchiao formations, and are constrained by the basal boundary of *Metabolograptus* (*M.*) *extraordinarius* and the upper boundary of *Normalograptu* (*N.*) *ojsuensis* graptolite biozones, respectively (Fig. 2).

METHODS AND ANALYTICAL TECHNIQUES

Major and Trace Element Analyses

Whole-rock major element analyses were performed at the State Key Laboratory of Geological Processes and Mineral Resources (SKLGPMR), China University of Geosciences (CUG-Wuhan). Chemical dissolution and separation methods for each element followed the national standard procedure (GB/T 14506-2010) that includes alkali fusion, extraction, titration, weight loss and colorimetry. In brief, weight loss and titration were used for determining Al contents, and a Hitachi atomic absorption spectrophotometer (180-70) was utilized for Ca, K and Na analysis, with an ultraviolet-visible spectrophotometer (UV-754) used for P analysis. Uncertainties of less than 5% were achieved for all reported elements, as monitored by national standard samples, GBW07114 and GBW07122. Trace elements were analyzed at SKLGPMR via ICP–MS (Agilent 7500a). The dissolution procedure follows that described by Liu et al. (2008). The sample powder was weighed into Teflon bombs and 1 mL of HNO_3 and 1 mL of HF were added. The sealed bombs were heated at 190°C for 48 h, and then the solution was evaporated on a hot plate, followed by the addition of 1 ml of HNO_3 and evaporation to dryness. The resultant salt was re-dissolved by adding ~3 ml of 30% HNO_3, and the bomb was resealed and heated at 190°C for 12–24 h. The final solution was diluted to 100 mL with 2% HNO_3 for ICP-MS analysis. Blanks and national standards AGV-2, BHVO-2, BCR-2 and RGM-2 were used for calibrating elemental concentrations, with an analytical uncertainty of <2% for all elements of interest.

Organic Carbon Isotopes

Before analysis, sample powders were digested in 2 N HCl at 50°C for 12 h to dissolve carbonate phases. Then ~0.5–0.8 mg of powder was analyzed using a MAT 253 IR-MS interfaced with a Flash EA 2000 auto-sampler. $\delta^{13}C_{org}$ results are reported relative to the Vienna Pee Dee belemnite (V-PDB) standard, with a precision better than ± 0.1‰, based on repeat analyses (n = 2) of national standard GBW04407 ($\delta^{13}C = -22.4‰$).

Chemical Separation and Cd Isotope Measurements

Sample digestions, chemical separation and Cd isotope measurements were conducted at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences (Guiyang). The detailed procedure follows that described by Wen et al. (2015) and Zhang et al. (2018, 2023). In brief, powdered sample containing approximately 0.15 µg of Cd was placed in a centrifuge tube, then enough aqua regia (a 3:1 volume mixture of HCl and HNO_3) was added to dissolve Cd. After 48 h, the mixture was centrifuged to separate the supernatant from the residue. A $^{110}Cd/^{111}Cd$ double-spike solution, with $^{110}Cd/^{111}Cd \approx 0.5$ and a Cd concentration of 200 µg/mL, was then added to the supernatant to achieve a Cd spike–sample ratio of approximately 2, followed by shaking to ensure isotopic equilibrium (Zhang et al., 2018). Finally, the supernatant was dried in a 30 mL beaker, then 5 mL of 2 M HCl was added and the solution was evaporated to dryness. After this, 5 mL of 2 M HCl was added to prepare the sample for chemical anion-exchange separation. A blank sample was prepared by this method to monitor the sample digestion and chemical separation procedure.

Strong anion resin AG-MP-1M was used in ion-exchange chromatography to purify Cd from the matrix, to remove elements that could potentially interfere with the determination of Cd isotopes, including Sn, In, Zn and Pb (the detailed procedure is reported in Wen et al., 2015). This step was repeated twice in order to thoroughly purify the Cd. Cadmium isotope analysis was conducted using a Neptune Plus multi-collector inductively coupled plasma mass-spectrometer (MC-ICP-MS). A 0.15 mol/L HNO_3 solution was used as a carrier for isotopic analysis, with Cd concentrations of approximately 1 ppm. High-sensitivity (X) Ni cones were used for increasing transmission to ensure that signal intensity was at a level of ~65 V/1 ppm. After each analysis, the nebulizer and spray chamber were rinsed using 0.6 mol/L HNO_3, in order to prevent cross contamination between samples. Reference standards, Spex and JMC, were analyzed during the course of the study and yielded δ^{114}Cd values of –0.08 ± 0.04‰ (n=2) and –1.74 ± 0.09‰ (n=2), respectively, which agree with values reported by Zhang et al. (2018) (–0.10 ± 0.07‰ and –1.71 ± 0.06‰), indicating that Cd was completely purified by the column chromatography and no Cd isotope fractionation occurred during the measurements. Double-spike data reduction was calculated according to a MATLAB-based script described by Ripperger and Rehkämper (2007). The reported $\delta^{114}Cd/^{110}Cd$ values are the mean of replicate measurements of the same samples. Cd isotopic compositions were calculated relative to the NIST SRM 3108 Cd solution using the following delta notation:

$$\delta^{x}/^{110}Cd\ (‰) = [(^{x}Cd/^{110}Cd)_{sample}/(^{x}Cd/^{110}Cd)_{standard} - 1] \times 1000 \qquad (1)$$

where x = 114, 112 or 111.

RESULTS

Organic Carbon Isotopes

Values of $\delta^{13}C_{org}$ vary from -30.3 to -27.8‰ through the section, with a gradually elevated trend through the late Katian (Fig. 2; Table S1). This is followed by a positive shift that marks the global Hirnantian $\delta^{13}C_{org}$ excursion (HICE) (Underwood et al., 1997; LaPorte et al., 2009). High values then persist until the end of the Hirnantian glaciation, when $\delta^{13}C_{org}$ returns to pre-extinction levels through the latest Ordovician and Early Silurian (Fig. 2).

U/Th Ratios, TOC Contents and C_{org}/P Ratios

Uranium (U) is a redox-sensitive element and occurs in solution as U^{6+} under oxic conditions. In anoxic environments, however, U^{6+} is generally reduced to U^{4+}, and may be enriched in sediments

(Tribovillard et al., 2006). By contrast, the behaviour of thorium (Th) is not affected by redox conditions and usually occurs in the form of insoluble Th^{4+} (Wignall and Myers, 1988). Thus, U/Th ratios can be used to evaluate redox-driven changes in U drawdown to the sediments (Wignall and Myers, 1988; Sun et al., 2015). U/Th ratios vary from 0.94 to 4.92 through the Wangjiawan section, with a declining trend from the late Katian to minimum values in the early Hirnantian, after which ratios rise in a fluctuating manner to relatively high values (~3.0) in the late Hirnantian, with maximum values in the Rhuddanian (Fig. 2; Table S1).

The same samples from the Wangjiawan section have previously been measured for TOC contents (Gong et al., 2017). Relatively high values (generally >1 wt. %) occur throughout the section, with a similar trend to U/Th ratios, notably with minimum values in the early Hirnantian (Fig. 2; Table S1). However, in contrast to U/Th ratios, TOC contents yield maximum values in the Late Hirnantian. A plot of TOC versus U/Th displays a positive correlation (Fig. 3a), indicating that TOC preservation and/or production rates were likely controlled by redox conditions.

The molar C_{org}/P ratio is another paleoredox proxy that may be applied to shale and mudstone formations (Algeo and Ingall, 2007). Values of C_{org}/P vary from 16 to 826 through the Wangjiawan section, with a generally similar profile to TOC, displaying a declining trend from relatively high values (mostly more than 100) in the late Katian, to lower values (less than 50) at the Katian-Hirnantian boundary (Fig. 2). The ratios rise again to high values (~100 to 800) in the late Hirnantian and through most of the early Rhuddanian.

Chemical Index of Alteration (CIA) and Aluminum

The Chemical Index of Alteration (CIA) may be used to evaluate the degree of chemical weathering in siliciclastic sediments, and is widely used to evaluate climatic controls on chemical weathering in the sediment source region (Nesbitt and Young, 1982). High CIA values (85–100) generally reflect intense chemical weathering under warm and humid conditions. Conversely, lower values (less than 65) commonly indicate low chemical weathering rates under cool and dry conditions (Nesbitt and Young, 1982; Yan et al., 2010). The CIA was calculated as (Nesbitt and Young, 1982):

$$CIA = Al_2O_3/(Al_2O_3 + CaO^* + K_2O + Na_2O) \qquad (2)$$

where all values represent molar concentrations and CaO^* represents CaO in silicate minerals only.

To correct measured CaO contents for the presence of carbonates and apatite, CaO^* was calculated by determining the CaO/Na_2O molar ratio of the bulk sediment followed by comparison with an assumed CaO/Na_2O molar ratio of 1.0 for the detrital silicate fraction (McLennan, 1993). If the measured CaO/Na_2O molar ratio was <1.0, the measured CaO concentration was adopted as CaO^*. If the measured CaO/Na_2O molar ratio was >1.0, the concentration of Na_2O replaced CaO^*:

$$\mathrm{CIA} = Al_2O_3/(Al_2O_3 + K_2O + 2\times Na_2O) \qquad (3)$$

Calculated CIA values vary from 0.69 to 0.80 through the Wangjiawan section (Fig. 2; Table S1). During the Katian stage, CIA values gradually increase to relatively high values (~0.79) in the late Katian, followed by a sharp decline to minimum values (~0.69) at the base of the Hirnantian stage. The CIA values then rapidly return to higher levels (maximum of ~0.80) through the rest of the Hirnantian, followed by a progressive decline to relatively low values through the Rhuddanian stage (Fig. 2).

Aluminium (Al) is commonly considered a proxy for the terrigenous flux due to its incorporation into aluminosilicate minerals such as clays and its stability during transfer and diagenesis (Shi et al., 2016). The Al_2O_3 contents range from 2.97 to 25.37 wt. % in the Wangjiawan section, with a similar trend to the CIA values, showing minimum values at the bottom of the Hirnantian stage and maximum values in the late Hirnantian (Fig. 2; Table S1).

Nutrient Elements

Phosphorus (P) is an essential macronutrient that is commonly considered to limit primary productivity on geological timescales (Tyrell, 1999), while cadmium (Cd), zinc (Zn) and nickel (Ni) are micronutrients that can be used as proxies for relative changes in oceanic primary productivity (Tribovillard et al., 2006; Grasby et al., 2016). P/Al, Cd/Al, Zn/Al and Ni/Al ratios vary widely through the section, from 2×10^{-3} to 104×10^{-3} (wt. %/wt. %), from 4.6 to 855 (ppb/wt. %), from 2.7 to 409 (ppm/wt. %), and from 3.7 to 152 (ppm/wt. %), respectively (Fig. 4; Table S1). All four ratios have similar profiles, with relatively low values in the late Katian (although P/Al ratios show a gradual decrease), followed by a rapid rise at the end of the Katian to maximum values in the early Hirnantian. Ratios then decrease in the mid-Hirnantian, remaining relatively constant through the Rhuddanian (Fig. 4).

Cadmium Isotopes

Bulk Cd isotope ($\delta^{114}Cd/^{110}Cd_{bulk}$) values range from -0.22 ± 0.11‰ to 1.0 ± 0.1‰ through the section, with an overall progressive decrease from the late Katian to the Hirnantian, followed by a slight increase in the early Hirnantian and then a sharp decrease at the end of the Hirnantian glaciation (Fig. 4; Table S1). Low values (~ -0.2‰) are then maintained until the early Rhuddanian, followed by a progressive increase to higher values (~0.6‰).

DISCUSSION

Carbon Cycling and Redox Conditions Across the Late Ordovician to Early Silurian

The Hirnantian glaciation is characterized by a global positive excursion in both inorganic and organic carbon isotopes (e.g., Kump et al., 1999; Chen et al., 2006; Yan et al., 2009; Zou et al., 2018; Lv et al., 2022). This excursion begins near the Katian-Hirnantian boundary and peaks during the Hirnantian *M. extraordinarius–M. persculptus* graptolite zone (Chen et al., 2006; Liu et al., 2022), consistent with the $^{13}C_{org}$ profile at the Wangjiawan section (Fig. 2). A global increase in organic matter burial has been invoked as a mechanism to explain the positive excursion, which is supported by a positive shift in Zn isotopes (as a tracer for changing organic carbon fluxes in ancient oceans) during the Hirnantian in South China (Lv et al., 2022). Both marine anoxia and high marine primary productivity aid in the burial of organic matter. Hence, reconstructing marine redox conditions across the Late Ordovician to Early Silurian is pivotal to understand the cause of elevated organic matter burial during the Hirnantian.

Ratios of U/Th can be used to assess bottom water redox conditions, with U/Th ratios <0.75, 0.75–1.25 and >1.25 being indicative of oxic, dysoxic (2.0-0.2 mL/L O_2) and suboxic–anoxic (0.2-0.0 mL/L O_2) environments, respectively (Tyson and Pearson, 1991; Jones and Manning, 1994). Ratios of C_{org}/P can provide further insight into benthic redox conditions as oxygen depletion simultaneously enhances the preservation of organic C and may cause a diffusive loss of remineralized organic P, with values of <50, ~50–100 and >100 being indicative of oxic, suboxic and anoxic environments, respectively (Algeo and Ingall, 2007). Values of U/Th and C_{org}/P range from 1.96 to 2.46 and from 16 to 459 (mostly more than 100), respectively, throughout most of the late Katian (through the *Dicellograptus complexus* and all but the uppermost *Paraorthograptus pacificus* graptolite zones; Fig. 2) at the Wangjiawan section, suggesting a suboxic/anoxic environment. This suggestion is consistent with δ^{98}Mo records at the Wangjiawan and Nanbazi sections, South China (Zhou et al., 2015), and a $\delta^{238}U_{carb}$ record for the Wuhe section in South China (Liu et al., 2022). In addition, a detailed study of iron speciation and Mo data from inner-shelf to outer-shelf settings in South China also shows persistent anoxia during the late Katian (Zou et al., 2018), indicating widespread anoxia during this time in South China.

Both U/Th and C_{org}/P show a declining trend in the latest Katian, with relatively low values (0.94–1.83 for U/Th; mostly less than 100 for C_{org}/P) persisting through the Hirnantian glaciation, indicative of fluctuations between oxic to suboxic bottom waters (Fig. 2). This result is in agreement with a positive shift in δ^{98}Mo values during the latest Katian to early Hirnantian in South China (Zhou et al., 2015), as well as iron speciation data reported for the Wangjiawan section, that reveal a shift from anoxic bottom waters in the Katian to a more oxygenated deep outer-shelf in the early Hirnantian (Yan et al., 2012). By contrast, Fe speciation systematics alongside elevated Mo concentrations on the Shuanghe inner shelf section in South China indicate persistent euxinia during the early Hirnantian (*Metabolograptus extraordinarius* graptolite zone), while less reducing (ferruginous) conditions were prevalent in mid-shelf and outer-shelf sections (Zou et al., 2018). This suggests a redox gradient, with shallow water euxinia during the latest Katian to early Hirnantian, giving way to better ventilated deeper waters.

In the upper part of the Hirnantian glacial interval, where an increase in CIA values documents the deglaciation phase, initially elevated U/Th and C_{org}/P ratios suggest a return to water column anoxia (Fig. 2). While U/Th ratios remain slightly elevated in the upper part of the Hirnantian glacial interval, indicating persistent water column anoxia, C_{org}/P ratios fall to low values. Low C_{org}/P ratios at this time are also observed in the Yangtze shelf sea, where a detailed study of the phase partitioning of P demonstrated that these low ratios occur as a result of limited chemical weathering (hence retaining high concentrations of detrital P phases) of source sediments produced during the glacial phase (Qiu et al., 2022). A subsequent return to elevated C_{org}/P ratios, alongside a transition to particularly high U/Th ratios, support continued water column anoxia as chemical weathering intensity increased across the base of the *Metabolograptus persculptus* graptolite zone (corresponding to the LOME-2 horizon; Fig. 2). Anoxia was also widespread in South China across this interval, and spanned from shallow to deep water settings, as recorded by multiple independent proxies (Yan et al., 2012; Zhou et al., 2015; Zou et al., 2018; Liu et al., 2022). Anoxic oceanic conditions persisted through the Rhuddanian stage of the Early Silurian, as shown by continually high U/Th and C_{org}/P values in the Wangjiawan section (Fig. 2), and multiple proxies from other global localities (e.g., Hammarlund et al., 2012; Melchin et al., 2013; Zhou et al., 2018; Stockey et al., 2020; Qiu et al., 2022; Sánchez-Roda et al., 2024).

Evaluation of Authigenic Cd Concentrations and Isotopes

Evaluation of the Cd flux from seawater to the sediments requires correction for the lithogenic (terrigenous) component of the sediment. The samples generally have high Cd concentrations (up to 2700 ppb), which are significantly elevated above the average value for upper continental crust (~90 ppb), although there are three samples (WS-10, WS-4 and WOO3L-13) that have low Cd concentrations (less than 90 ppb) (Fig. 4; Table S1). Furthermore, a plot of Cd versus Al reveals no correlation (Fig. 3b), indicating that lithogenic Cd played an insignificant role in controlling Cd concentrations, and the sedimentary Cd budget is instead largely controlled by authigenic Cd enrichments. Nevertheless, we correct Cd concentrations for the lithogenic component by assuming an homogenous Cd/Al ratio ($(Cd/Al)_{lith}$) and Cd isotopic composition for the lithogenic component. Thus, authigenic Cd contents (Cd_{auth}) are expressed as:

$$Cd_{auth} = Cd_{sample} - Al_{sample} \times (Cd/Al)_{lith} \quad (4)$$

where Cd_{sample} and Al_{sample} are the sample concentrations of each element, and $(Cd/Al)_{lith}$ is the global average for upper continental crust (11.3 ppb/wt. %; Rudnick and Gao, 2003). The fraction of authigenic Cd (f_{auth}) and lithogenic Cd (f_{lith}) can then be calculated using the formulae:

$$f_{auth} = Cd_{auth}/Cd_{sample} \quad (5)$$

$$f_{auth} + f_{lith} = 1 \quad (6)$$

Finally, the isotopic composition of authigenic Cd ($\delta^{114}Cd_{auth}$) is calculated from the equation:

$$\delta^{114}Cd_{bulk} = \delta^{114}Cd_{auth} \times f_{auth} + \delta^{114}Cd_{lith} \times f_{lith} \quad (7)$$

where $\delta^{114}Cd_{lith}$ (-0.04‰; Schmitt et al., 2009) and $\delta^{114}Cd_{bulk}$ are the isotopic compositions of the lithogenic component and the measured sample values, respectively.

The results from these calculations show that authigenic contributions to the sedimentary Cd budget dominate in the Wufeng and Kuanyinchiao Formations, with only one sample having an f_{auth} value of less than 0.8 (0.6) (Table S1). By contrast, the Lungmachi Formation generally has lower proportions of authigenic Cd, with most f_{auth} values being less than 0.5 (Table S1). This indicates an increased lithogenic Cd contribution to the sediments during the transition period from the Kuanyinchiao Formation to the Lungmachi Formation, which corresponds to the melting phase of the Hirnantian glaciation (as documented by the return to higher CIA and Al values), as well as the second mass extinction pulse (Fig. 2; Table S1). Authigenic $\delta^{114}Cd_{auth}$ values show a similar trend to the $\delta^{114}Cd_{bulk}$ values, but slightly offset by the lithogenic correction (Fig. 4).

The Cd Cycle Across the LOME

Studies of the modern oceanic Cd cycle show that biological uptake of isotopically-light Cd in surface waters plays an important role in the distribution of Cd and its isotopes (Ripperger et al., 2007; Abouchami et al., 2011; 2014; Conway and John, 2015), and this results in lower Cd concentrations and heavier Cd isotope signatures in the mixed surface layer, compared to deeper waters. In addition, CdS precipitation under anoxic conditions can also have a significant local impact on Cd cycling, resulting in removal of isotopically-light Cd to the sediments (Janssen et al., 2014; Guinoiseau et al., 2018). Both of these output mechanisms have been invoked to explain higher $\delta^{114}Cd/^{110}Cd$ seawater values (~0.38‰; Schmitt et al., 2009) relative to the terrestrial influx (-0.04‰; Schmitt et al., 2009). Here, we utilize this understanding of Cd isotope systematics to interpret our $\delta^{114}Cd_{auth}$ data in terms of the major local and global perturbations that occurred during the Late Ordovician and into the Early Silurian.

We first evaluate the potential effects of biological organic matter and CdS precipitation on $\delta^{114}Cd/^{110}Cd$ compositions. TOC shows a weak negative correlation with Cd concentrations ($R^2 = 0.16$, $p=0.04$; Fig. 5a) and no correlation with $\delta^{114}Cd/^{110}Cd$ ($R^2 = 0.01$, $p>0.1$; Fig. 5b), indicating that Cd derived from organic matter likely had little effect on the Cd isotopic composition of the studied samples. As mentioned above, TOC preservation and/or production rates at the Wangjiawan section were mainly controlled by bottom water redox conditions, as indicated by a strong positive correlation between TOC and U/Th (Fig. 3a). The lack of correlation between TOC contents and $\delta^{114}Cd/^{110}Cd$ values thus also implies that CdS precipitation likely had a minor effect on the Cd isotopic composition of the studied samples. Thus, our $\delta^{114}Cd/^{110}Cd$ values appear to provide a robust approximation of seawater Cd isotopic compositions.

The gradual decrease in $\delta^{114}Cd_{auth}$ compositions at the Wangjiawan section, from 1.1‰ in the late Katian to 0.3‰ at the Katian-Hirnantian boundary (Fig. 4), is consistent with sinking of isotopically-light organic-bound Cd to deeper water depths. As mentioned above, the late Katian ocean was characterized by widespread anoxia, which can draw down isotopically light Cd, leaving the water column enriched in heavier Cd isotopes, rather than resulting in the observed decline in $\delta^{114}Cd_{auth}$ values. Therefore, the Cd isotope cycle during the late Katian was likely dominated by preferential assimilation of isotopically-light Cd by phytoplankton in surface waters, which is consistent with Cd isotope cycling in the modern ocean (Ripperger et al., 2007; Abouchami et al., 2011, 2014; Conway and John, 2015). The negative $\delta^{114}Cd_{auth}$ shift during the late Katian thus likely indicates a progressive increase in marine primary productivity. This is consistent with the progressive decrease in P/Al ratios (Fig. 4) and increasing C_{org}/P ratios (Fig. 2) observed throughout the early part of the late Katian. This suggests progressively enhanced redox-promoted recycling of P from the sediments back to the water column, which would be expected to promote a positive productivity feedback (e.g., Ingall et al., 1993; Ingall and Jahnke, 1994; Van Cappellen and Ingall, 1994)

The Wangjiawan section shows a slight increase in Cd isotopes in the early Hirnantian (from 0.3‰ to 0.6‰; Fig. 4), although the values are lower than those of the late Katian. Previous studies have shown the development of more widespread euxinia in shallow water settings at this time (e.g., Zou et al., 2018). In this case, drawdown of light Cd (as CdS) in shallower water settings likely contributed to the observed enrichment in heavier Cd isotopes in the oxygenated, deep outer-shelf Wangjiawan setting. The global positive shift in $\delta^{13}C_{org}$ at this time (Kump et al., 1999; Chen et al., 2006; Yan et al., 2009; Zou et al., 2018; Lv et al., 2022; Fig. 2), indicates increased burial of organic ^{12}C due to high primary marine productivity, which is consistent with elevated Cd/Al, Zn/Al and Ni/Al ratios in the early Hirnantian (Fig. 4). These high ratios occur despite only a modest increase in preserved TOC in the early Hirnantian (Fig. 2), which is likely due to relatively decreased preservation of TOC as the regional water column (and shallow porewaters) became oxygenated (e.g., Canfield, 1994). High rates of primary productivity were likely enhanced by preferential recycling of P back to the water column from sediments deposited under euxinic conditions elsewhere (Qiu et al., 2022), although as expected, low C_{org}/P ratios and high P/Al ratios occur at Wangjiawan (less than the Redfield ratio of 106:1; Fig. 2), due to the local oxic depositional setting (e.g., Ingall et al., 1993). Overall, our data suggest that global marine primary productivity increased from the latest Katian to early Hirnantian, thereby resulting in the progressive decrease in $\delta^{114}Cd_{auth}$

values observed through the late Katian, with the slight increase in $\delta^{114}Cd_{auth}$ values during the early Hirnantian being due to globally-enhanced CdS precipitation. This increased CdS precipitation masked the expression of isotopically-light $\delta^{114}Cd_{auth}$ values originating from particularly enhanced primary productivity during the early Hirnantian.

In the mid to late Hirnantian (during and following glacial retreat), global rates of primary productivity progressively declined, as indicated by a decrease in both organic ^{12}C burial (Fig. 2), and Cd/Al, Zn/Al and Ni/Al ratios (Fig. 4). Thus, the increase in TOC contents and C_{org}/P ratios across the LOME-2 interval (Fig. 2) likely reflects a local response to the re-establishment of water column anoxia on the deep outer-shelf. This water column anoxia persisted throughout most of the overlying succession, with the exception of a temporally-restricted return to better oxygenated conditions during the earliest Silurian (indicated by low U/Th, decreased TOC contents, and low C_{org}/P ratios in the *Akidograptus ascensus* graptolite zone; Fig. 2). However, given that the ocean was characterized by particularly widespread (commonly euxinic) anoxia at this time (e.g., Hammarlund et al., 2012; Melchin et al., 2013; Zhou et al., 2018; Stockey et al., 2020; Qiu et al., 2022; Sánchez-Roda et al., 2024), it is likely that global rates of primary productivity remained relatively high. Nevertheless, the particularly low $\delta^{114}Cd_{auth}$ values (as low as -0.6‰) require further consideration.

Elevated precipitation of CdS under widespread anoxic/euxinic conditions would be expected to sequester isotopically-light Cd. As such, similar to the increase observed in the early Hirnantian (Fig. 4), $\delta^{114}Cd_{auth}$ values would be expected to display heavier values, rather than the observed low values that characterize the lower two thirds of the Lungmachi Formation (Fig. 4). This suggests that redox conditions had a limited effect on Cd isotope compositions across this interval. The Cd isotope composition of the oceans can be expressed as (John et al., 2017):

$$\delta^{114}Cd_{ocean} = \delta^{114}Cd_{input} - \Delta^{114}Cd_{output} \qquad (8)$$

where $\delta^{114}Cd_{ocean}$ and $\delta^{114}Cd_{input}$ are the mean values for seawater and the input flux, respectively, while $\Delta^{114}Cd_{output}$ represents the isotopic offset between $\delta^{114}Cd_{ocean}$ and the combined sinks of $\delta^{114}Cd$. Thus, if an increased weathering influx of Cd is not balanced by a similar increase in the sinks, $\delta^{114}Cd_{ocean}$ and $\delta^{114}Cd_{auth}$ values would both change. Thus, although speculative, one possibility is that isotopically-light Cd from enhanced chemical weathering (as indicated by high CIA and Al values; Fig. 2), which may have been exacerbated by rising sea level (Fig. 5), was imported to the ocean. However, without a similar increase in the magnitude of the sinks, this would have lowered seawater δ^{114}Cd in the late Hirnantian to early Silurian ocean, ultimately resulting in the particularly low sediment $\delta^{114}Cd_{auth}$ compositions observed in the Wangjiawan section.

A rise in $\delta^{114}Cd_{auth}$ values then occurs in the upper part of the Rhuddanian, where values approach pre-extinction levels towards the top of the sampled interval (Fig. 4). Correspondingly, CIA values and Al contents show a declining trend across this interval, suggesting that the Cd sinks were gradually balanced by a declining weathering input, in addition to biological assimilation of isotopically-light Cd.

Implications for Environmental Perturbations Across the LOME

The integration of our Cd isotope and elemental data with previously published Late Ordovician paleotemperature records, and local and global paleo-redox proxy (δ^{98}Mo and δ^{238}U) data (Fig. 5), enable a holistic assessment of marine environmental conditions across the LOME. The negative trend in $\delta^{114}Cd_{auth}$ values through the late Katian occurs coincident with an overall decrease in sea surface temperatures (Fig. 6; Finnegan et al., 2011; Kozik et al., 2022a). Cooling during the Late Ordovician has commonly been considered to be due to drawdown of atmospheric CO_2 through silicate weathering and/or organic carbon burial (Kump et al., 1999; Melchin and Holmden, 2006; Lenton et al., 2012; Swanson-Hysell and Macdonald, 2017; Longman et al., 2021; Qiu et al., 2022), which may have been enhanced through orogenesis (Swanson-Hysell and Macdonald, 2017), the expansion of early land plants (Lenton et al., 2012), and/or enhanced volcanism (Gong et al., 2017; Hu et al., 2020; Longman et al., 2021). These processes are thought to have increased the delivery of P to the oceans, thereby stimulating increased primary productivity and organic carbon burial, and hence CO_2 drawdown (Longman et al., 2021; Qiu et al., 2022).

The declining trend in $\delta^{114}Cd_{auth}$ and increasing trend in $\delta^{13}C_{org}$ through the late Katian (Fig. 6) therefore likely reflect elevated marine primary productivity and organic carbon burial driven by increased nutrient supply (Fig. 7), which is consistent with the observation of eukaryotic blooms during this period (Shen et al., 2018). Indeed, the increasing CIA trend at the Wangjiawan section supports increased chemical weathering on land (Fig. 6), and hence an enhanced terrestrial nutrient input into the ocean system (Fig. 7). Since this increase in chemical weathering occurs during an interval of cooling (rather than the general link to warming), this highlights the significant roles that the expansion of early land plants (Lenton et al., 2012) and/or enhanced volcanism (Gong et al., 2017; Hu et al., 2020; Longman et al., 2021) played in enhancing the weathering influx of P. The potential influence of land plants and volcanism could have led to an increase in the extent of global anoxia, as indicated by a negative shift in δ^{238}U values at the onset of the Hirnantian glaciation (Fig. 6; Bond and Grasby, 2020; Kozik et al., 2022a), although better oxygenated bottom waters are indicated by decreased U/Th ratios and elevated δ^{98}Mo values for the deeper outer-shelf setting of the Wangjiawan section (Fig. 6).

Following the declining trend in $\delta^{114}\mathrm{Cd}_{\mathrm{auth}}$ in the late Katian, a slight increase in $\delta^{114}\mathrm{Cd}_{\mathrm{auth}}$ values occurs in the early Hirnantian at the Wangjiawang section, likely due to drawdown of light Cd (as CdS) due to widespread euxinia in shallow water settings at this time (Fig. 7; e.g., Zou et al., 2018). The increases in Cd/Al, Zn/Al and Ni/Al ratios, along with the positive excursion in organic carbon isotopes (Fig. 4), are indicative of high primary productivity and enhanced organic matter burial (Fig. 7), coincident with the development of glacial deposits from Gondwana and records of sea level regression (Caputo and Crowell, 1985; Holmden et al., 2013). This glacial event is thought to have played an important role in organism losses because of climate cooling and habitat loss (Yan et al., 2010; Finnegan et al., 2012), although widespread euxinia appears increasingly likely to have played a major role in the first pulse of the LOME (LOME-1; e.g., Zou et al., 2018; Bond and Grasby, 2020). Climate cooling could also have helped promote a redox gradient from euxinic shallow waters to better ventilated deeper waters (Zou et al., 2018), as indicated by iron speciation, U/Th and δ^{98}Mo data presented in this study and previous work (Yan et al., 2012; Zhou et al., 2015; Zou et al., 2018; Fig. 6).

The $\delta^{114}\mathrm{Cd}_{\mathrm{auth}}$ values show the onset of a second negative shift in the middle Hirnantian where elevated CIA values occur, likely indicating a global sea level rise associated with climatic warming (Fig. 6). This climatic warming and sea level rise could have led to widespread oceanic anoxia in the Early Silurian (Zhou et al., 2015; Stockey et al., 2020; Kozik et al., 2022a), as reflected by elevated U/Th ratios and negative shifts in both δ^{98}Mo and δ^{238}U across the LOME-2 horizon (Fig. 6). Indeed, the expansion of anoxic/euxinic conditions associated with deglaciation has been implicated as the most likely kill mechanism for the LOME-2 interval (Bond and Grasby, 2020; Liu et al., 2022; Kozik et al., 2022a). Meanwhile, terrestrial chemical weathering was enhanced in response to climate warming during the mid-Hirnantian to early Rhuddanian (Figs. 6, 7), which may explain the low $\delta^{114}Cd_{auth}$ values due to input of isotopically-light continental Cd (Fig. 7). The Cd/Al, Zn/Al and Ni/Al profiles, along with $d^{13}C_{org}$, gradually returned to lower values relative to those of the early Hirnantian (Fig. 4), suggesting decreased productivity, which is similar to the record from Dob's Linn, UK (Bond and Grasby, 2020).

Elevated $\delta^{114}Cd_{auth}$ values occurred in the Rhuddanian *Cystograptus vesiculosus* graptolite zone (Fig. 6), corresponding to subdued terrestrial chemical weathering as indicated by decreased CIA and Al values (Figs. 2, 6). Hence, a decreased isotopically-light Cd input to the oceans could have contributed to the elevated $\delta^{114}Cd_{auth}$ values (Fig. 7). High U/Th ratios and invariable $\delta^{98}Mo$ values imply that the oceans were still starved of oxygen at this time (Fig. 6), which may explain the protracted and turbulent recovery of marine groups after the LOME (Rasmussen et al., 2019; Stockey et al., 2020).

CONCLUSIONS

Cadmium and organic carbon isotopes, in combination with TOC and elemental paleoenvironmental proxies, from the deep outer-shelf setting of the Wangjiawan section, South China, provide a unique dataset for evaluating controls on marine primary productivity and environmental perturbations across the LOME. A declining trend in $\delta^{114}Cd_{auth}$, coupled with a slight positive shift in organic carbon isotopes, from the late Katian to the Katian-Hirnantian boundary, suggest that elevated marine productivity resulted in enhanced sedimentation of isotopically-light organic-bound Cd. Climate cooling in the early Hirnantian then appears to have promoted a redox gradient from euxinic shallow waters to better ventilated deeper waters, as supported by a positive shift in $\delta^{114}Cd_{auth}$ that was likely caused by drawdown of isotopically-light Cd (as CdS) in shallower water settings.

The early Hirnantian was associated with high marine productivity, as indicated by elevated Cd/Al, Zn/Al and Ni/Al ratios, which accounts for the global positive shift in $\delta^{13}C_{org}$ at this time. Following this, deeper water anoxia was re-established (indicated by elevated U/Th ratios) during the Hirnantian deglacial phase (indicated by increased CIA values), and enhanced terrestrial chemical weathering likely contributed to low $\delta^{114}Cd_{auth}$ values. A subsequent increase in $\delta^{114}Cd_{auth}$ then occurred in the Rhuddanian, which can be explained by a decreased input of isotopically-light Cd input to the oceans, as supported by low CIA and Al values indicative of low rates of chemical weathering. Overall, our data provide new insight into the Late Ordovician to Early Silurian Cd cycle, and support the hypothesis that an increase in marine productivity drove enhanced burial of organic matter, potentially contributing to CO_2 drawdown and the initiation of the Hirnantian glaciation.

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Figure Captions

Fig. 1 Palaeogeographic setting. (A) Late Ordovician global palaeogeography (modified from Zhou et al., 2015) showing the location of South China; (B) Late Ordovician map of the Yangtze block area (modified from Gong et al., 2017) showing the locating of the Wangjiawan (WJW) section.

Fig. 2 Lithology and chemostratigraphic profiles for $^{13}C_{org}$, TOC, U/Th, molar C_{org}/P, CIA and Al_2O_3 at the Wangjiawan section. Se = Series, St = Stage, F = Formation, Lith = Lithology, GZ = graptolite Zones, *D.c = Dicellograptus complexus*, P. *pacificus = Paraorthograptus pacificus*, *M. e = Metabolograptus extraordinarius*, *N. o = Normalograptus ojsuensis*, *M. p = Metabolograptus persculptus*, *A. a = Akidograptus ascensus*, *P. a = Parakidograptus acuminatus*, *C. v = Cystograptus vesiculosus*, KYC = Kuanyinchiao. Biostratigraphy based on Chen et al. (2000; 2006).

Fig. 3 Scatter plots of TOC versus U/Th (a) and Cd versus Al (b).

Fig. 4 Lithology and chemostratigraphic profiles for $\delta^{114}Cd/^{110}Cd_{bulk}$, $\delta^{114}Cd/^{110}Cd_{auth}$, Cd concentrations, Cd/Al, Zn/Al, Ni/Al and P/Al at the Wangjiawan section. Se = Series, St = Stage, F = Formation, Lith = Lithology, GZ = graptolite Zones, *D.c = Dicellograptus complexus*, P. *pacificus = Paraorthograptus pacificus*, *M. e = Metabolograptus extraordinarius*, *N. o = Normalograptus ojsuensis*, *M. p = Metabolograptus persculptus*, *A. a = Akidograptus ascensus*, *P. a = Parakidograptus acuminatus*, *C. v = Cystograptus vesiculosus*, KYC = Kuanyinchiao, UCC = upper continental crust. Biostratigraphy based on Chen et al. (2000; 2006).

Fig. 5 Scatter plots of Cd versus TOC (a) and $\delta^{114}Cd/^{110}Cd$ versus TOC (b).

Fig. 6 Summary profiles of $\delta^{114}Cd/^{110}Cd_{auth}$, $\delta^{13}C_{org}$, U/Th, $\delta^{98}Mo$, $\delta^{238}U$ and average sea surface temperature (SST) across the LOME. $\delta^{114}Cd/^{110}Cd_{auth}$, $d^{13}C_{org}$ and U/Th data are from this study, $\delta^{98}Mo$ values for the Wangjiawan section are from Zhou et al. (2015), $\delta^{238}U$ data are from Kozik et al. (2022b), and average sea surface temperatures are from Finnegan et al. (2011).

Fig. 7 Summary of the Cd cycle and environment change across the LOME.