

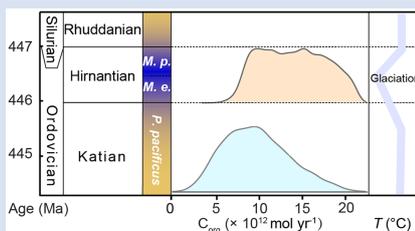
Enhanced organic carbon burial intensified the end-Ordovician glaciation

Y. Lv¹, S.-A. Liu^{1*}, H. Wu², Z. Sun³, C. Li⁴, J.X. Fan⁵



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Abstract



The end-Ordovician (Hirnantian) glaciation, causally linked with the first of five Phanerozoic mass extinction events, is the first major Phanerozoic-glaciation with short duration and paradoxically happened under a relative greenhouse-condition. Here, we present the first zinc isotope study on both carbonate and shale successions that span the Ordovician–Silurian boundary interval in South China. Two positive shifts in Zn isotope composition are observed during two main periods of glacial maxima, indicative of two pulses of extensive carbon burial. The enhanced organic carbon burial during glacial maxima intervals might be causatively linked to cooling-induced elevation in organic carbon burial efficiency. This implies that a large oceanic organic carbon reservoir played a vital role in regulating the atmospheric $p\text{CO}_2$, causing the Hirnantian glaciation and producing the pattern of glacial-to-deglacial change, sensitive to the temperature effect.

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Introduction

The end-Ordovician (Hirnantian) glaciation (~445 Ma) was the culmination of long-term climate cooling that had begun in the Early or Middle Ordovician, and was coeval and causally linked with the Late Ordovician mass extinction (LOME), the first of the ‘Big Five’ Phanerozoic catastrophic events (Finnegan *et al.*, 2011; Melchin *et al.*, 2013). This glaciation happened abruptly within a short duration of ~1 Myr at greenhouse conditions with a high atmospheric partial pressure of greenhouse gas ($p\text{CO}_2$), up to 3–16 times higher than present levels (Finnegan *et al.*, 2011; Pohl *et al.*, 2016). The causal mechanism has been connected to the drawdown of atmospheric $p\text{CO}_2$ caused by an increasing rate of silicate weathering, a mounting sink of organic matter burial, or a combination of both (Melchin *et al.*, 2013 and references therein). A global positive carbon isotopic excursion (Hirnantian Isotopic Curve Excursion, HICE; Fig. S-1) has been interpreted to indicate an enhanced burial of organic carbon and consequent drawdown of atmospheric $p\text{CO}_2$, even though it is at odds with stratigraphical observations of the disappearance of the black shales during the Hirnantian (Fig. S-2; Melchin *et al.*, 2013). The HICE may be alternatively explained by enhanced carbonate weathering during glacial regression, which would not draw down the atmospheric $p\text{CO}_2$, and the magnitude of HICE can also be influenced by local carbon cycling (*e.g.*, Kump *et al.*, 1999). These uncertainties call for additional geochemical tools to confirm the “missing” sink of carbon during the Hirnantian glaciation.

Zinc is a micronutrient in phytoplankton biomass (Morel and Price, 2003) and shows strong nutrient-like behaviour in the surface ocean (Bruland, 1980). Organic Zn dominates on shelves (92 %; Weber *et al.*, 2018) where about 80 % of global marine organic matter (Burdige, 2007) is accumulated and is characterised by lighter Zn isotopic compositions ($\delta^{66}\text{Zn}$) around -0.1‰ in comparison with the average seawater (0.5‰) and other oxic output flux, including Fe-Mn crusts and nodules (0.9‰ ; Little *et al.*, 2016). Therefore, Zn isotope record could be a promising tracer for change in organic carbon fluxes in past oceans (*e.g.*, Isson *et al.*, 2018; Sweere *et al.*, 2018), with increasing $\delta^{66}\text{Zn}$ values as more organic-rich sediments with isotopically light Zn are buried. Further, the shorter residence time (~11 kyr) of Zn than dissolved inorganic carbon (~83 kyr; De La Rocha, 2006) in the oceans makes Zn isotopes an appropriate proxy to identifying multiple pulses of enhanced organic carbon burial. Here, we decipher the $\delta^{66}\text{Zn}$ record and quantify organic carbon burial during the Hirnantian glaciation, relying on reproducible stratigraphic trends in $\delta^{66}\text{Zn}$ of two carbonate and shale successions at the Ordovician–Silurian transition.

Geological Settings and Samples

The Yangtze Block was attached to the margin of Gondwana located in a subtropical to tropical area during the Late Ordovician to Early Silurian (Chen *et al.*, 2010; see Supplementary Information). The Yangtze Platform was primarily covered by the broad epeiric sea connected to the open ocean in the Late

1. State Key Laboratory of Geological Processes and Mineral Resources, and School of Earth Science and Resources, China University of Geosciences, Beijing 100083, China
2. School of Marine Sciences, China University of Geosciences, Beijing 100083, China
3. Institute of Sedimentary Geology, State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Chengdu University of Technology, Chengdu 610059, China
4. Nanjing Institute of Geology and Palaeontology and Center for Excellence in Life and Palaeoenvironment, Chinese Academy of Sciences, Nanjing 210008, China
5. State Key Laboratory for Mineral Deposits Research, School of Earth Sciences and Engineering, Nanjing University, Nanjing 210023, China

* Corresponding author (email: lsa@cugb.edu.cn)



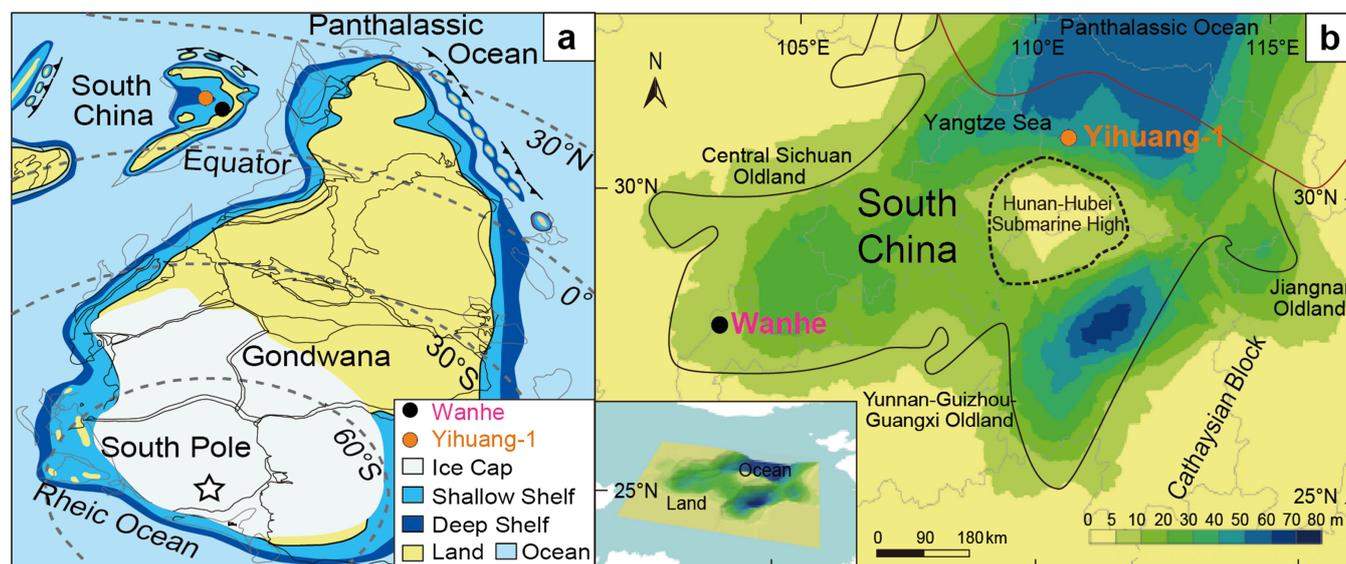


Figure 1 Palaeogeographic map for (a) South China and (b) the Yangtze Shelf Sea at ~445 Ma (Zhang *et al.*, 2016; Zou *et al.*, 2018). Orange circle and text represents the Yihuang-1 (YH-1) section located at outer shelf in the Upper Yangtze platform of South China and connected to open sea (Li *et al.*, 2020). Black circle and pink text represents the Wanhe (WH) carbonate section deposited on platform (Tang *et al.*, 2017).

Ordovician and then uplifted in the earliest Silurian (Fig. 1). Two well-preserved successions spanning the Ordovician–Silurian boundary were investigated in this study, including the Wanhe (WH) carbonate section and the Yihuang-1 (YH-1) shale drill core (Fig. 2; Zhang *et al.*, 2016; Tang *et al.*, 2017). Two glacial cycles of the Hirnantian glaciation in the YH-1 section have been identified by weathering intensities reflected by the chemical index of alteration (Li *et al.*, 2020). The Hirnantian glacial interval in the WH section was determined by the results of magnetic susceptibility (Zhong *et al.*, 2020), whereas within the Hirnantian ice age the multiple, shorter term periods of glaciation have not yet been identified in detail.

Results

In the shaly succession, two pulses of $\delta^{66}\text{Zn}$ (bulk rock digestion) increase were identified, ranging from 0.47 ‰ to 0.91 ‰ at the first glacial cycle and from 0.65 ‰ to 0.81 ‰ at the Kuanyinchiao (KYQ). The authigenic Zn component here is defined as the excess Zn in shales above the clastic level, a combination of the bio-authigenic fraction associated with particulate organic matter and authigenic sulfides. The normalisation of metal to aluminium was used to estimate and subtract the lithogenic component in order to calculate the fraction of authigenic Zn (X_{auth}). Only strongly Zn-enriched shales ($X_{\text{auth}} > 70\%$) were used to calculate the $\delta^{66}\text{Zn}$ of authigenic fractions ($\delta^{66}\text{Zn}_{\text{auth}}$) in order to reduce calculation error. For euxinic shales with $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}} > 0.38$ and $\text{Fe}_{\text{Py}}/\text{Fe}_{\text{HR}} > 0.7\text{--}0.8$, the calculated $\delta^{66}\text{Zn}_{\text{auth}}$ values mostly agree well within $\pm 0.1\%$ with the value obtained by the leaching extraction (a partial 2 M HNO_3 digestion) of sulfide and partial Zn bound to organic matter (see Supplementary Information for methods; Table S-2). The high $\delta^{66}\text{Zn}_{\text{auth}}$ value coincides with two intervals of glacial maximum (Fig. 2). In the carbonate succession, authigenic Zn in the carbonate phase was obtained by a weak (0.1 M) acetic acid leaching, and its $\delta^{66}\text{Zn}$ was relatively steady before the glaciation (0.80 ‰), followed by a positive excursion of $\sim 0.2\%$ reaching 0.99 ‰, and then drawing back to $\sim 0.8\%$. The second increase of $\delta^{66}\text{Zn}$, up to 1.11 ‰, occurs at the KYQ Bed supposed to be the peak of the Hirnantian glaciation.

Heavy Zinc Isotope Signature of the Glacial Maximum

Zinc isotopic ratios of the authigenic fractions (sulfides and organic matter) in euxinic sediments can record the coeval seawater $\delta^{66}\text{Zn}$ value due to the near quantitative removal of water column Zn to sediments (Little *et al.*, 2016; Vance *et al.*, 2016; Isson *et al.*, 2018). Thus, the Zn isotope data of euxinic shales that have been identified by Fe speciation data (Li *et al.*, 2020) could reflect the $\delta^{66}\text{Zn}$ variation of seawater during the Hirnantian glaciation (Fig. S-3). The $\delta^{66}\text{Zn}$ values do not vary with local changes in depositional setting, mineralogy, redox condition and primary productivity (Supplementary Information). Two positive $\delta^{66}\text{Zn}$ shifts also are observed in the carbonate WH section after inspecting possible diagenetic effects (Supplementary Information). Volcanic activities were identified in the Katian strata in South China (Melchin *et al.*, 2013), which may have resulted in a decline of seawater pH value. However, Zn isotope fractionation between carbonate and seawater ($\Delta^{66}\text{Zn}_{\text{carb-SW}}$) becomes larger as seawater pH decreases (Mavromatis *et al.*, 2019), which should result in elevated $\delta^{66}\text{Zn}$ in carbonates. This contrasts to the relatively low $\delta^{66}\text{Zn}_{\text{auth}}$ values during the Katian (Fig. 2). Thus, the high $\delta^{66}\text{Zn}$ values of two glacial maximum intervals most likely reflect global changes instead of local changes.

Flux Estimate of Increasing Organic Burial

Organic-rich shelf sediment is the major sink of isotopically light Zn in modern oceans (Weber *et al.*, 2018), although the mechanism is not well understood yet (probably ascribed to bio-uptake/scavenging of light Zn isotopes or the early diagenetic processes; Weber *et al.*, 2018; Köbberich and Vance, 2019; Horner *et al.*, 2021). The high $\delta^{66}\text{Zn}$ value of the Hirnantian ocean suggests an increasing removal flux of Zn into continental margin sediments compared to burial flux of Zn into oxic sediments. Burial of organic carbon in margin sediments is the major sink of the global organic carbon cycle (Burdige, 2007). Thus, the positive $\delta^{66}\text{Zn}_{\text{auth}}$ shifts might reflect two pulses of massive

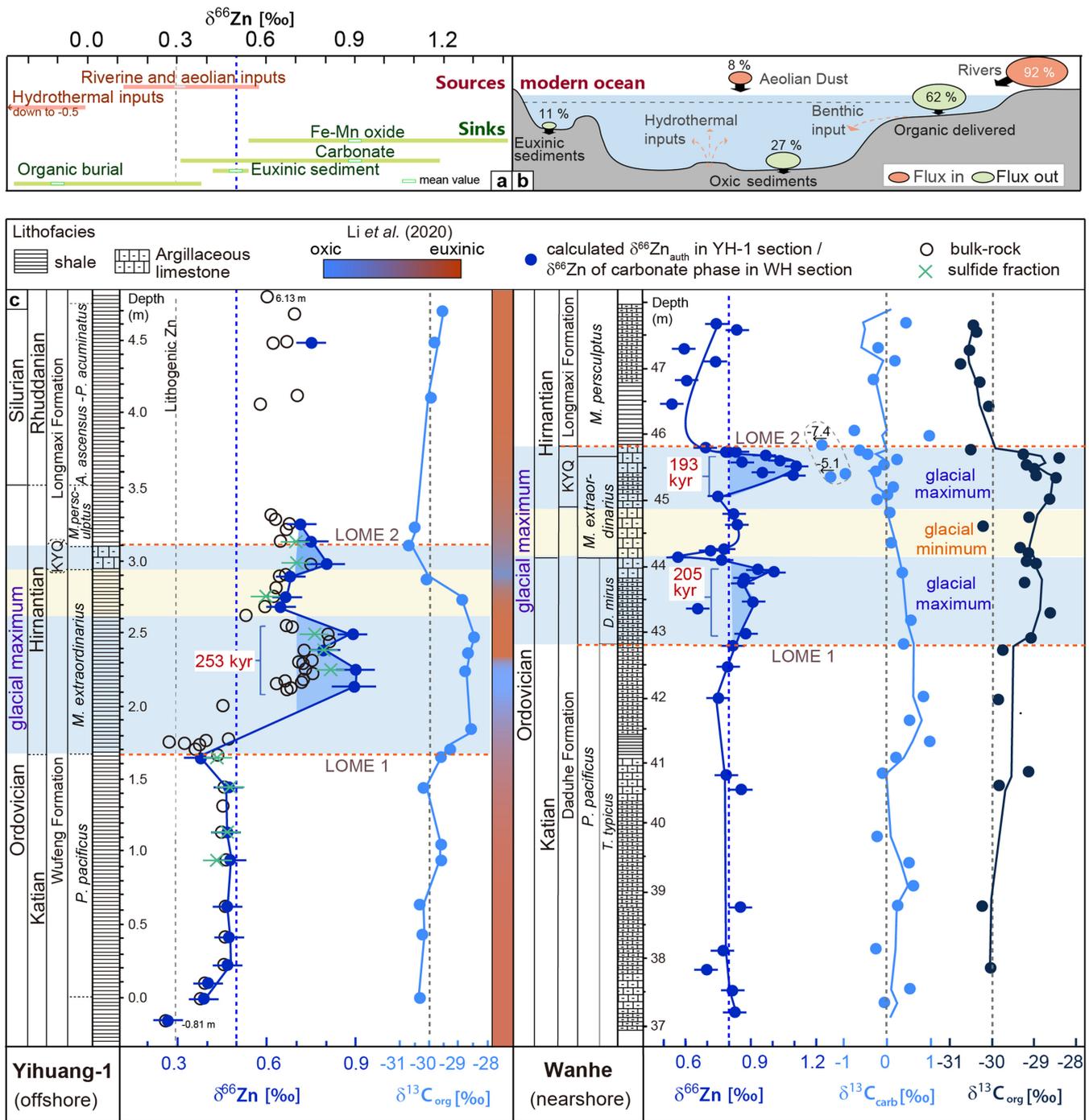


Figure 2 Zinc isotopic (a) mass balance and (b) major fluxes in modern oceans, modified from Little *et al.* (2016) and Isson *et al.* (2018), respectively. (c) Stratigraphy, $\delta^{66}\text{Zn}$ and $\delta^{13}\text{C}$ records from the YH-1 drill core and the WH section. The Late Ordovician mass extinction (LOME) includes two pulses. The durations (in kyr) of positive Zn isotope excursions during the glaciation were determined by astronomical time scale (Zhong *et al.*, 2020). Ocean redox condition in Yihuang-1 section was reported in Li *et al.* (2020) based on Fe-speciation and Mo concentration data. Low $\delta^{13}\text{C}_{\text{carb}}$ value at the KYQ Bed in the WH section is considered a result of diagenetic alteration. ‘Glacial maxima’ in the carbonate section is defined based on the positive $\delta^{13}\text{C}_{\text{carb}}$ excursions.

organic carbon burial during two main glacial cycles. More speculatively, the organic burial fluxes are quantitatively estimated from Zn isotopic mass balance and evaluated by means of Monte Carlo, using zinc isotopic data of the YH-1 shales deposited in euxinic environments (see the [Supplementary Information for methods](#)). The major Zn output fluxes in modern oceans include organic-rich sediments (F_{Org} mainly continental margin sediments in mildly reducing (suboxic-anoxic) conditions), oxic sediments (F_{Ox} mainly of Fe-Mn oxides), and euxinic

sinks (F_{Eux}) (Little *et al.*, 2016). When solving for F_{Org} the influx and other outfluxes, and their Zn isotopic ratios are forced by a uniformly distributed random number within their given ranges, considering their uncertainties in the oceanic zinc cycle (e.g., Li *et al.*, 2021; Table S-5). The results show that to produce the largest observed increase in seawater $\delta^{66}\text{Zn}$ from 0.47 ± 0.03 ‰ to 0.88 ± 0.06 ‰, a nearly double increase in organic Zn burial from $\sim 3.5 \times 10^8$ to 5.5×10^8 mol/yr is required, regardless of whether the euxinia expanded or shrank (Fig. 3). Considering

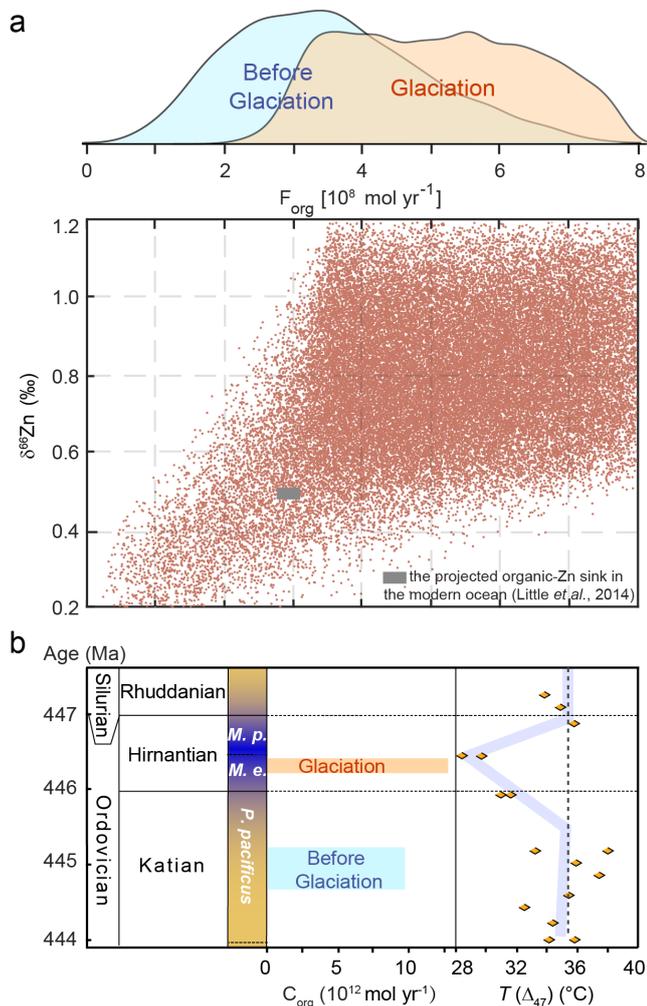


Figure 3 (a) Modelling results of organic Zn burial fluxes based on Zn isotopic mass balance. (b) The estimated organic carbon burial flux in this study and Δ_{47} temperatures of seawater recorded in brachiopods (Finnegan *et al.*, 2011). Modelling details are listed in Supplementary Information for methods.

a mean Zn/C ratio of 0.036 (mmol/mol) of plankton (Little *et al.*, 2015), our estimate suggests that the flux of organic carbon deposition has increased from 9.7×10^{12} mol/yr to 15.2×10^{12} mol/yr before and during the glaciation. LaPorte *et al.* (2009) reported a positive $\delta^{13}\text{C}_{\text{carb}}$ shift of 2.7 ‰ from the Nevada section during the Hirnantian glaciation and suggested a doubling organic carbon burial flux. The estimated flux of organic carbon burial based on carbon isotopic data is of the same order of magnitude as the independent estimate from zinc isotopes, supporting an enhanced organic carbon burial during the Hirnantian glaciation.

Temperature-Controlled Organic Carbon Burial

The sudden global climate cooling during the Hirnantian has been attributed to the enhanced silicate weathering and organic carbon burial (Melchin *et al.*, 2013 and references therein). In this study, we emphasise the important role of enhanced organic carbon burial on CO_2 sequestration during glacial intervals. The accumulation of organic matter in sediments is generally related to improved organic carbon preservation and enhanced primary production. In terms of organic carbon preservation, no more expanded dysoxia-anoxia that can increase the burial efficiency

of organic carbon has been globally observed within the Hirnantian glaciation, in comparison with the subsequent early Rhuddanian oceanic anoxic event (Stockey *et al.*, 2020). Furthermore, the glacial pulse is supposed to promote a more oxygenated ocean, at least a surface ocean, with a better ventilation (Pohl *et al.*, 2021). The input of additional nutrients from increased continental weathering is observed before the glaciation (Finlay *et al.*, 2010) which can promote primary productivity and organic carbon burial, although it is not significant during the glaciation in a recent study of osmium and lithium isotope record (Sproson *et al.*, 2022). Here, we speculate about a temperature-dependent control on the massive organic carbon burial since it significantly postdates the glacial onset, that is cooling-induced elevation in the burial efficiency of organic carbon. However, other factors of organic carbon burial, such as astronomical forcing, are not ruled out here (Sproson *et al.*, 2022). In the early Phanerozoic Ocean with relatively low dissolved oxygen, cooling, which could have been underestimated before, constitutes the dominant control on enhanced organic carbon burial through an elevation in organic carbon burial efficiency with rates of organic carbon degradation (Fakhræe *et al.*, 2020), compared with high eukaryotic export before the glacial maximum (Shen *et al.*, 2018). This scenario can also shed light on the several glacial cycles with short duration during the Hirnantian. The temperature-dependent, biological CO_2 fixation can be more fluctuant than other ways to consume atmosphere CO_2 , such as changes in chemical weathering of silicate rocks. Compared with two other major Phanerozoic glaciations (the Karoo and the Cenozoic glaciations) with high atmospheric O_2 condition, the biological carbon pumping efficiency in the Hirnantian glaciation is sensitive to a cooling climate, serving as positive feedback to encourage the organic carbon fixation after glacial onset and, consequently, the extreme icehouse climate.

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Additional Information

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2210>.



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