Vanadium isotope evidence for widespread marine oxygenation from the late Ediacaran to early Cambrian

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Abstract

Early animals experienced multiple-phase radiations and extinctions from the late Ediacaran to the Early Cambrian. Oxygen likely played an important role in these evolutionary events, but detailed marine redox evolution during this period remains highly debated. The emerging vanadium (V) isotope system can better capture short-term perturbations to global ocean redox conditions. In this study, we analyzed V isotope compositions ($\delta^{51}V$) of organic-rich cherts and black shales deposited from the late Ediacaran to the Early Cambrian (ca. 560–518 Ma) in the Yangtze Block, South China. The robust positive correlation between the $\delta^{51}V$ values and previously reported $\delta^{98}Mo$ values validates V isotope system as a paleo-oxybarometer. The continuously temporal open-ocean seawater $\delta^{51}V$ variation reconstructed from the sedimentary $\delta^{51}V$ records, suggest that the ocean experienced a rapid transition from expansive euxinia at ca. 560–553 Ma to widespread oxygenation likely reaching the modern level at ca. 552–551 Ma, kept extensively oxygenated afterwards (ca. 551–521 Ma), and possibly reached the modern oxygenation level again at ca. 521–518 Ma. The prolonged and widespread oceanic oxygenation may have been beneficial to the ecological radiation of early animals from the late Ediacaran to Early Cambrian, ultimately leading up to the “Cambrian Explosion”.

Keywords: Paleo-oxybarometer; Metazoan diversity; Yangtze Block; Black shale

1. Introduction

The late Ediacaran to Early Cambrian is a crucial period in evolutionary history, witnessing multiple-phase radiations and extinctions of early animals (e.g., Shu et al., 2014; Zhu et al., 2019). The Ediacaran soft-body bilaterian clades characterized the late Ediacaran (e.g., Chen et al., 2019), which died out across the Ediacaran-Cambrian transition (Narbonne, 2005). Instead, hard skeletal metazoans appeared and rapidly diverged, leading to widespread occurrences of small shelly fossils in the earliest Cambrian strata (Knoll and Carroll, 1999; Butterfield, 2011). During the Cambrian Stage 3 (521–514 Ma), most extant animal phyla appeared, accompanied by increase in complexity of morphologies and behaviors, establishment of metazoan-dominated marine ecosystems, and major diversification in eukaryotic organisms, namely "Cambrian Explosion" (e.g., Butterfield, 2011; Erwin et al., 2011).

Marine redox evolution during this period was proposed to be one of the main drivers for these evolutionary events, but the reconstruction results based on various redox proxies are highly debated. They include progressive increase (e.g., Chen et al., 2015) or large fluctuation (e.g., Wei et al., 2021) in global oceanic oxygenation extent, dynamic shelf oxygenation (e.g., Li et al., 2020), and persistent marine anoxia (e.g., Sperling et al., 2015). This distinction likely results from different responses of various elemental and isotopic tracers to different threshold levels of oxygen (e.g., Algeo and Li, 2020; Kendall, 2021). Some can only trace local redox conditions, such as Fe speciation, Ce anomaly, and Cr isotope system (e.g., Poulton and Canfield, 2011; Ling et al., 2013; Wei et al., 2020); while some can reconstruct global marine redox state, but are insensitive to short-term change due to their long oceanic residence times, such as Mo and U isotope systems (e.g., Chen et al., 2015; Wei et al., 2021). Early animals evolved via multiple phases of radiations and extinctions from the late Ediacaran to Early Cambrian, necessitating a proxy to reconstruct short-term evolution in global marine oxygenation extent.

Vanadium isotope system is an emerging redox proxy with such an ability sensitively enough to trace short-term change in global marine redox state (see Section

2; e.g., Wu et al., 2020; Nielson, 2021). The Yangtze Block preserves widespread distributed Ediacaran-Cambrian organic-rich sedimentary rocks, which may document contemporary marine redox information. In this study, we analyzed V isotope compositions of organic-rich cherts and black shales deposited from the late Ediacaran to Early Cambrian (ca. 560–518 Ma) in the Yangtze Block, which have been investigated for their element enrichments, Fe speciation, and Mo isotope compositions before (Chen et al., 2015). The aims of this study include, (1) to validate the V isotope composition in black shale as a paleo-oxybarometer, (2) to reconstruct the evolution in global marine oxygenation extent from the late Ediacaran to Early Cambrian, and (3) to explore the relationship between marine redox change and early animal evolution.

2. V isotope system as an oceanic paleo-oxybarometer

Vanadium has two isotopes, ^{50}V and ^{51}V, with abundances of 0.24% and 99.76%, respectively. Its isotope composition is usually reported in the δ notation (in per mil) relative to an Alfa Aesar (AA) standard solution first employed at Oxford University (Nielsen et al., 2011):

$$\delta^{51}V_{sample} = [(^{51}V/^{50}V)_{sample}/(^{51}V/^{50}V)_{AA} - 1] \times 1000\ (‰) \quad (1)$$

As a redox-sensitive transition metal, V has multiple oxidation states, V(III), V(IV), or V(V) in the Earth's surface environment, controlled by environmental Eh and pH conditions (Taylor and van Staden, 1994). During continental chemical weathering, V(III) or V(IV) in silicate rocks could be oxidized to V(V) and be mobilized into rivers (Gustafsson, 2019), which is the dominant source of the modern oceanic V (Shiller and Mao, 2000). The average $\delta^{51}V$ value of the run-off (including both dissolved and particulate V pools; $\delta^{51}V_{river}$) of the Yangtze River Basin is −0.6 ± 0.4‰ (Schuth et al., 2019), matching the estimated total riverine input value of −0.6‰ required by mass balance (Wu et al., 2019a). It should be noted that the $\delta^{51}V$ values of the particulate V pool of the Yangtze River Basin are much lower from −2.1‰ to −0.1‰, possibly due to the preferential adsorption of lighter V isotopes onto particulate Fe (oxyhydr)oxides (Schuth et al., 2019). The $\delta^{51}V$ value of the upper continental crust (UCC) is estimated to range from −0.8‰ to −0.6‰, based on the reported values of the andesite and quartz latite standards (Wu et al., 2016). Therefore, the riverine $\delta^{51}V$ signatures inherit those of silicate rocks, indicating no significant V isotope fractionation occurs during weathering, which has been corroborated by the latosol V isotope profile (Qi et al., 2022).

In the modern open ocean, V is a conservative element with a residence time of ca. 92 kyr (Nielsen, 2021), longer than the oceanic mixing time (~1600 yr; Broecker and Peng, 1982). This leads to the global homogeneity of the modern open-ocean seawater $\delta^{51}V$ values ($\delta^{51}V_{OSW} = +0.20 \pm 0.15‰$; Wu et al., 2019a). Depositional manners of oceanic V into various sediments are completely different, as well as associated V isotope fractionations (Wu et al., 2019b, 2020). In the oxic seawater ($[O_2] > 10$ μM), the dominant V species is soluble vanadate (VO_4^{3-}) or its protonated states (HVO_4^{2-} and $H_2VO_4^{-}$), which can be readily adsorbed onto Fe-Mn (oxyhydr)oxides and clay minerals (e.g., Morford and Emerson, 1999; Gustafsson, 2019). The expressed V isotope fractionation between oxic sediment and open-ocean seawater ($\Delta^{51}V_{OX-OSW}$) is ~−1.1‰ (Wu et al., 2020). Under oxygen-deficient conditions ($[O_2] < 10$ μM), dissolved V(V) is reduced to vanadyl ions (VO^{2+}) or its hydrolyzed species, $VO(OH)^+$ or $VO(OH)_2$, and these V(IV) species tends to be deposited by adsorption or formation of organic complexes (e.g., Tribovillard et al., 2006; Gustafsson, 2019). The expressed V isotope fractionation between anoxic sediment and open-ocean seawater ($\Delta^{51}V_{ANOX-OSW}$) is ~−0.7‰ (Wu et al., 2020). Under euxinic conditions, although V(IV) can be reduced to insoluble V(III) by H_2S, this process is kinetically slow (Wanty and Goldhaber, 1992) and does not induce V enrichment even in Framvaren Fjord having the highest H_2S concentration (8 mM) in the modern marine euxinic settings (Scott et al., 2017). Hence, V(IV) species likely dominate in euxinic settings and the expressed V isotope fractionation between euxinic sediment and open-ocean seawater ($\Delta^{51}V_{EUX-OSW}$) should be similar to $\Delta^{51}V_{ANOX-OSW}$. However, the observed $\Delta^{51}V_{EUX-OSW}$ in the Cariaco Basin is only ~−0.4‰, which may be due to the reservoir effect (Wu et al., 2020). Hydrothermal sediments are an additionally important sink for oceanic V, due to the adsorption of Fe oxides, and the associated V isotope offset

($\Delta^{51}V_{HT-OSW}$) is ~−0.4‰ (Wu et al., 2022).

The modern oceanic mass balance model of V isotopes has been summarized by Nielsen (2021), and shown in Fig. 1A. The $\delta^{51}V_{OSW}$ value is controlled by the proportions of major V sinks (oxic, anoxic, euxinic, and hydrothermal sediments) and consequently by global marine redox states. The redox potential of the V(V)−V(IV) pair is higher than those of U(VI)−U(IV) and Mo(VI)−Mo(IV) pairs (Algeo and Li, 2020), and the oceanic residence time of V (ca. 92 kyr in the open ocean and probably shorter in locally anoxic/euxinic environments due to the reduction of organic matter) is much shorter than those of U (ca. 400 kyr; Ku et al., 1977) and Mo (ca. 440–700 kyr; Miller et al., 2011). Therefore, relative to $\delta^{238}U_{OSW}$ and $\delta^{98}Mo_{OSW}$ values, temporary $\delta^{51}V_{OSW}$ values reconstructed from sedimentary $\delta^{51}V$ records should be more sensitive to short-term global marine redox evolution, especially subtler marine deoxygenation.

3. Geological background and samples

All the samples studied herein were collected from the Yangtze Block, South China. They include black shales from the Upper Ediacaran Miaohe Member of the Doushantuo Formation at the Jiulongwan section in the Yangtze Gorges area (Hubei Province), organic-rich cherts and black shales from the Ediacaran−Cambrian Liuchapo and Niutitang Formations at the Longbizui section in Hunan Province, and black shales from the Lower Cambrian Shuijingtuo Formation at the Yanjiahe section in the Yangtze Gorge area (Fig. 2).

3.1. Upper Ediacaran Miaohe Member at the Jiulongwan section

The Doushantuo Formation in the Yangtze Gorges area was deposited in shallow water below or near wave base in an intrashelf basin or in a shelf lagoon (Jiang et al., 2011). It can be litho-stratigraphically subdivided into four members. The first member comprises ~5-m-thick cap dolostones overlying the diamictites of the Nantuo Formation, which are equivalent to Marinoan glacial sediments (Condon et al., 2005). The second member (~70-m-thick) consists of interbedded organic-rich shales and dolostones with abundant pea-sized cherty nodules, preserving complex microfossils such as acanthomorphic acritarchs, probable animal eggs and embryos, multicellular algae, and filamentous and coccoidal cyanobacteria (Yin et al., 2007). The third member (~50-m-thick) comprises dolostones intercalated with cherty layers in the lower part and interbedded with limestones in the upper part. The fourth member, Miaohe Member, is ~10-m-thick black shales, usually used as a marker bed for stratigraphic correlation. The Miaohe Member at the Jiulongwan section is devoid of fossils. At an adjacent section, however, this member contains more than 20 species of carbonaceous compressions macrofossils, which are likely colonial prokaryotes or macroalgae (Xiao et al., 2002). The top of the Miaohe Member was constrained by the U-Pb age of ca. 551 Ma (Condon et al., 2005).

3.2. Ediacaran-Cambrian Liuchapo and Niutitang Formations at the Longbizui section

At the Longbizui section, the Liuchapo Formation is conformably overlying the Doushantuo Formation and conformably overlain by the Niutitang Formation. It consists of dark grey to black cherts intercalated with thin layers of black shales, deposited in the deep-water slope to basin setting (Wang et al., 2012). It could be generally correlated with the Piyuancun Formation in South Anhui Province, and shallow-water Dengying Formation in the Yangtze Gorges area, East Yunnan Province, and North Guizhou Province (Fig. 2C). In the upper Liuchapo Formation, the Cambrian small shelly fossils first appear (Qian and Yin, 1984). A zircon U-Pb age of 545.76 ± 0.66 Ma was reported for the lower Liuchapo Formation at the Longbizui section (Yang et al., 2017), and a zircon U-Pb age of 536.3 ± 5.5 Ma was reported for the top of the Liuchapo Formation at an adjacent section (Chen et al., 2009). Therefore, the Ediacaran-Cambrian boundary could be placed in the upper Liuchapo Formation.

The overlying Niutitang Formation consists of a lower unit of siliceous and phosphorous shales (~10 m thick) with thin phosphorite intercalations, and an upper thicker succession of black shales and mudstones. Its lower part generally lacks fossils, but the upper part and its equivalents contain fossils of Qiongzhusian age, such as the assemblage of hexactinellid sponges and demosponges, some organic tissues, and mineralised spicules in Hunan Province, and trilobites in Guizhou Province, representing the peak of the "Cambrian Explosion". Therefore, the upper Niutitang Formation is correlated approximately with Cambrian Stage 3 (Fig. 2C).

3.3. Lower Cambrian Shuijingtuo Formation at the Yanjiahe section

In the Yangtze Gorges area, the Shuijingtuo Formation consists of black shales uncomfortably overlying the Ediacaran-Cambrian Yanjiahe Formation, and could be generally correlated with the Shiyantou and Yu'anshan Formations in East Yunnan Province, Niutitang Formation in West Hunan Province, and Hetang Formation in South Anhui Province (Fig. 2C). The Lower Cambrian black shales in the Yangtze Block are characterized by the Ni-Mo sulphide layer, which is typically 1–30 cm in thickness and has varying Ni-Mo enrichments from several times higher than average UCC contents to ore-level in different areas. A relatively precise Re–Os isochron age of 521 ± 5 Ma has been obtained from three mine sites in Guizhou and Hunan Provinces (Xu et al., 2011).

4. Methods

4.1. Major and trace elements, Fe speciation, and Mo isotope analyses

The geochemical data of major and trace elements, Fe speciation, and Mo isotope composition (δ^{98}Mo) of the studied samples were reported by Chen et al. (2015), except those of some samples from the Miaohe Member at the Jiulongwan section (marked in Table S1). In this study, Al, V, Mo, and U contents, Fe_{HR}/Fe_T and Fe_{py}/Fe_{HR} ratios, and δ^{98}Mo values of all samples are listed in Table S1.

4.2. V isotope analyses

For V isotope analyses, sample digestion, V purification via ion chromatographic procedures, and high-precision spectrometry measurements, were carried out at the CAS Key Laboratory of Crust-Mantle Materials and Environments at the University of Science and Technology of China. Labwares were acid-cleaned prior to use and samples were treated using ultra-pure reagents.

4.2.1. Sample digestion

Sample powders containing at least 6 μg of V were ashed overnight at 550 °C to remove organic phases. The ashed samples were completely digested using a mixture of 3 mL of concentrated HCl, 1 mL of concentrated HNO_3, and 2 mL of concentrated HF. After dry-down, the samples were re-dissolved in 1 mL of 1 M HNO_3 for the following chromatographic procedures, which were identical with those developed by Wu et al. (2016).

4.2.2. V purification

The first column was charged with 2 mL of Bio-Rad AG 50W-X12 cation resin (200–400 mesh). The sample dissolved in 1 mL of 1 M HNO_3 together with 4 mL of 1 M HNO_3 + 0.1 M HF was loaded onto the column to elute Ti and Al. Vanadium was collected with 19 mL of 1.2 M HNO_3 and thus separated from most matrix elements (e.g., Fe, Ca, Mn, and Cr). This cation exchange procedure described above was run twice in order to completely remove Fe and Ti.

Afterwards, the dried sample was dissolved in 1 mL of dilute HCl ($2 < pH < 3$) added with 33 μL of H_2O_2, in preparation for the following anion exchange procedure modified after Nielsen et al. (2011). In such a weakly acidic condition, V can react with H_2O_2 to form oxyanions which can be strongly adsorbed onto the anion exchange resin (Kiriyama and Kuroda, 1983). The sample solution was loaded onto the column charged with 1.4 mL of Bio-Rad AG 1-X8 anion resin (200–400 mesh), together with 15 mL of dilute HCl (2 < pH < 3) + 1% H_2O_2 to elute residual matrix elements. Vanadium was collected with 17 mL of 1 M HCl and 3 mL of 6 M HCl, and was then dried down. The sample was subsequently processed with a similar anion chromatographic separation to completely remove the residual matrix elements, especially Cr. The solution containing purified V was dried down, and was re-dissolved in 2% HNO_3 for MC-ICP-MS measurements.

The overall chemical procedure yields of V were >99%, and the total procedural blank was <2 ng, which was negligible compared to V in the digested sample.

4.2.3. MC-ICP-MS measurements

Vanadium isotope compositions were analyzed using a Thermo-Fisher Scientific Neptune-Plus MC-ICP-MS. An Aridus II desolvator (CETAC Technologies) system connected to a 50 μL/min PFA MicroFlow Teflon nebulizer (Elemental Scientific Inc) was used to introduce sample and standard solutions. The MC-ICP-MS is equipped with nine Faraday cups that allow the simultaneous collection of two V isotopes ($^{50}V^+$ and $^{51}V^+$) and the potentially interfering beams ($^{49}Ti^+$, $^{52}Cr^+$, and $^{53}Cr^+$). The center cup was equipped with a 10^{10} Ω resistor to accommodate the large beam of ^{51}V which has a natural abundance of 99.76%. Measurements were run in the medium-resolution mode (resolution >5500) with Ni sampler and Ni X-skimmer cones (Thermo Fisher), to resolve target isotopes from polyatomic interferences. The data were collected for 40 cycles with an integration time of 4.194 s, and each analysis was repeated three times for the same sample/standard solution. The typical sensitivity of ^{51}V was ~150 V/ppm, and we thus kept V concentrations of the sample and standard solutions around 0.8 ppm, which were sufficient for high-precision analyses. Between each measurement, the sample introduction system was cleaned with 5% HNO_3 (60 s) and then 2% HNO_3 (60 s). After the wash-out procedure, the background ^{51}V signal was lower than 30 mV that can be negligible.

To correct isobaric interferences of ^{50}Ti and ^{50}Cr on ^{50}V, the $^{50}Ti/^{49}Ti$ ratio of 100 ppb GSB Ti and $^{50}Cr/^{53}Cr$ ratios of 100 ppb GSB Cr standard solutions were measured before each sequence analysis. The instrumental mass-bias factors for Ti (β^{Ti}) and Cr (β^{Cr}) were estimated from the differences between the measured and true (0.972537; Leya et al., 2007) ^{50}Ti/^{49}Ti ratios and between the measured and true (0.45737; Shields et al., 1966) ^{50}Cr/^{53}Cr ratios, respectively. During the measurements of samples, the ion beam intensities of ^{50}Ti and ^{50}Cr were subtracted from mass 50 intensity, based on the measured ^{49}Ti and ^{53}Cr ion beams and calculated β^{Ti} and β^{Cr}, respectively. Every sample was bracketed by the USTC-V before and after each single measurement. The USTC-V is an ultrapure single V solution from GuoBiao Testing & Certification (Beijing), whose δ^{51}V value relative to the AA from Oxford University ($\delta^{51}V_{USTC\text{-}V}$) has been calibrated to be +0.06 ± 0.08‰ (2SD, *n* = 186; Fig. S1A). The good long-term reproducibility demonstrates that the USTC-V is a reliable bracketing standard to address the instrumental mass-bias effect on V isotopes. Thus, the final V isotope compositions were reported after being converted into δ^{51}V value relative the AA from Oxford University by Eq. (2):

$$\delta^{51}V_{sample} = 1000 \times [(^{51}V/^{50}V)_{sample}/(^{51}V/^{50}V)_{USTC\text{-}V} - 1] + \delta^{51}V_{USTC\text{-}V}\ (‰) \qquad (2)$$

The data quality was monitored based on the measurements of another in-house V isotope standard (BDH), rock reference materials, and duplicated sample. The short-term average δ^{51}V value of the BDH during the measurements of the V isotope data in this study is –1.23 ± 0.06‰ (2SD, *n* = 30; Fig. S2), well consistent with the long-term (over five years) value of –1.24 ± 0.08‰ (2SD, *n* = 367; Fig. S3) in our lab and values reported by other labs (e.g., Nielsen et al., 2011; Schuth et al., 2019). The δ^{51}V values of the rock reference materials, SGR-1 (shale, –0.18 ± 0.03‰) and BCR-2 (basalt, –0.71 ± 0.03‰), are consistent with the previously reported values, –0.21 ± 0.11‰ (Wu et al., 2020) and –0.78 ± 0.08‰ (Wu et al., 2016), respectively (Table S1). The δ^{51}V value of a selected sample (08LBZ-19; –0.75 ± 0.06‰) is consistent with that of the replicate (–0.75 ± 0.07‰; including digestion, purification, and MC-ICP-MS measurement). The reported δ^{51}V values have 2SD smaller than 0.08‰ (Table S1), within the long-term external reproducibility of the δ^{51}V measurements (±0.08‰). All these above demonstrate the reliability of our δ^{51}V analyses.

4.3. $\delta^{51}V$ correction for detrital V

Detrital materials may contribute significant amount of V to the digested solutions, considering high V content of the UCC (107 ppm; McLennan, 2001). We thus infer that variable proportions of detrital contributions, as indicated by the large range of Al contents (0.2–8.4 wt.%; Table S1), may cause significant shifts on measured V contents and δ^{51}V values. We use following equations to obtain the content (V_{auth}), proportion (f_{auth}), and isotope composition ($\delta^{51}V_{auth}$) of authigenic (non-detrital) V:

$$V_{auth} = V_{sample} - (V/Al)_{det} \times Al_{sample} \qquad (3)$$

$$f_{auth} = 1 - (V/Al)_{det} \times (Al/V)_{sample} \qquad (4)$$

$$\delta^{51}V_{auth} = [\delta^{51}V_{sample} - \delta^{51}V_{det} \times (1 - f_{auth})]/f_{auth} \qquad (5)$$

in which the V/Al ratio and δ^{51}V value of detrital components are assumed to be close to those of the UCC, 13.3 ppm/wt.% (McLennan, 2001) and from –0.8‰ to –0.6‰ (Wu et al., 2016), respectively. All the samples contain significant authigenic V components, with f_{auth} values from 0.67 to nearly 1.00 (Table S1). Therefore, the potential effect of the $\delta^{51}V_{UCC}$ uncertainty on the corrected $\delta^{51}V_{auth}$ results could be negligible (Table S1). The corrected results based on the $\delta^{51}V_{UCC}$ of –0.6‰ were used in the following discussions. In addition, the differences between measured and corrected δ^{51}V values are within the uncertainties of our δ^{51}V analyses for the most of the samples (Table S1), implying negligible corrections to our analyzed results. The exceptions are 08LBZ-22 and 08LBZ-21, whose $\delta^{51}V_{auth}$ values have differences of 0.13‰ and 0.14‰ greater than the measured values, respectively.

5. Results

The V_{auth} and $\delta^{51}V_{auth}$ values of the organic-rich cherts and black shales from the Miaohe Member at the Jiulongwan section, Liuchapo and lower Niutitang Formations at the Longbizui section, and lower Shuijingtuo Formation at the Yanjiahe section are listed in Table S1, and are plotted in Fig. 3 together with the δ^{98}Mo, Fe_{HR}/Fe_T, and

Fe_{py}/Fe_{HR} profiles.

The V_{auth} contents vary within a large range, from 112 ppm to 2348 ppm in the Miaohe Member, from 96 ppm to 541 ppm in the Liuchapo Formation and from 124 ppm to 1928 ppm in the lower Niutitang Formation, and from 16 ppm to 153 ppm in the lower Shuijingtuo Formation. The $\delta^{51}V_{auth}$ values of the majority part of the Miaohe Member (with depth from 82 m to 72.65 m) show an increasing trend from –1.06‰ to –0.52‰, generally consistent with the previously published data from the same section (Fan et al., 2021). The elevated $\delta^{51}V_{auth}$ values (–0.28‰ and –0.25‰) at the top of the Miaohe Member, however, were not reported by Fan et al. (2021) possibly due to low sampling resolution. At the Longbizui section, the $\delta^{51}V_{auth}$ values keep relatively low between –0.78‰ and –0.47‰ in the Liuchapo Formation and increase from –0.75‰ to –0.05‰ in the lower Niutitang Formation. At the Yanjiahe section, the $\delta^{51}V_{auth}$ values of the lower Shuijingtuo Formation stay within a narrow range between –0.53‰ and –0.36‰.

6. Discussion

6.1. Validation of V isotope system as a paleo-oxybarometer

The V isotope system has been advocated as a paleo-oxybarometer (Wu et al., 2020; Nielson, 2021), but its application is in infancy yet (Fan et al., 2021). In this study, we find a robust positive correlation between the $\delta^{51}V_{auth}$ and $\delta^{98}Mo$ values of the studied samples ($R^2 = 0.66$, $n = 28$), as well as a roughly positive correlation between the V_{auth} and Mo contents ($R^2 = 0.41$, $n = 28$) (Fig. 4).

Molybdenum is also a redox-sensitive metal element, and its isotope system has been widely applied to trace the evolution in global marine oxygenation extents throughout the Earth history (e.g., Arnold et al., 2004; Kendall et al., 2015; Chen et al., 2015; Wei et al., 2021). As shown in Fig. 1B, the rivers are the dominant input of the modern oceanic Mo, with an average $\delta^{98}Mo$ value ($\delta^{98}Mo_{river}$) of +0.7‰ (Archer and

Vance, 2008). In the modern open ocean, Mo is present as the conservative oxyanion (molybdate) with long residence time of ca. 440–700 kyr (Miller et al., 2011). The modern open-ocean seawater δ^{98}Mo value (δ^{98}Mo$_{\mathrm{OSW}}$) is globally homogeneous (+2.34‰; e.g., Barling et al., 2001; Siebert et al., 2003), and significantly higher than the modern δ^{98}Mo$_{\mathrm{river}}$. This is because that in well-oxygenated settings, dissolved molybdate is adsorbed by precipitating Fe or Mn oxyhydroxides, with a significantly negative isotope fractionation (Δ^{98}Mo$_{\mathrm{OX-OSW}}$) of ~–3‰ (Barling et al., 2001). Whereas, in strongly euxinic basins, molybdate from the open ocean is converted into thiomolybdate species and nearly quantitatively removed into the sediment, so that the Mo isotope fractionation between the sediment and open-ocean seawater (Δ^{98}Mo$_{\mathrm{EUX-OSW}}$) is muted (mean = –0.5‰; Arnold et al., 2004; Neubert et al. 2008); in suboxic, ferruginous, and weakly euxinic settings, the average isotope fractionation associated with Mo precipitation (Δ^{98}Mo$_{\mathrm{RED-OSW}}$) is –0.7‰ (Poulson Brucker et al., 2009; Goldberg et al., 2012).

The positive correlation between the V$_{\mathrm{auth}}$ and Mo contents of the studied samples (Fig. 4A) indicates a same source of authigenic V and Mo, likely from riverine input and/or open ocean. Hydrothermal source is not considered especially for V, since its V contribution is negligible based on the consistent V contents of fresh and hydrothermally-altered basalts (Humphris and Thompson, 1978). The investigated areas were intrashelf basin (Yangtze Gorges area) and slope/basin (Longbizui section) facies of the Yangtze Block from the late Ediacaran to Early Cambrian, far away from the continent (Fig. 2A), and the co-variation trend of the Mo and U enrichment factors (Mo$_{\mathrm{EF}}$ and U$_{\mathrm{EF}}$; Fig. 5A and Table S1) additionally suggests that they were well-connected to the open ocean or weakly restricted, rather than strongly restricted. Therefore, we think the authigenic V and Mo in the studied samples were sourced from the open ocean, rather than directly from riverine input.

Relative to the reductive burials in reducing sediments, lighter isotopes of both V and Mo tend to be more preferentially enriched in oxic sediments by the adsorption onto Fe or Mn oxyhydroxides (Fig. 1), so that the open-ocean seawater is more enriched in heavier isotopes (i.e. both δ^{51}V$_{\mathrm{OSW}}$ and δ^{98}Mo$_{\mathrm{OSW}}$ increase) when the global ocean is more oxygenated. Therefore, the positive correlation between the $\delta^{51}V_{auth}$ and $\delta^{98}Mo$ values of the studied samples (Fig. 4B) may reflect similar co-variation between the $\delta^{51}V_{OSW}$ and $\delta^{98}Mo_{OSW}$ values in response to *global* marine redox variation from the late Ediacaran to Early Cambrian. Moreover, similar trends of both V and Mo isotope fractionations in response to *local* redox variation and the extent of basin restriction would have further strengthened the $\delta^{51}V_{auth}$ and $\delta^{98}Mo$ co-variation of the studied samples.

As mentioned above, the $\delta^{51}V_{OSW}$ value is more sensitive to short-term marine redox changes due to higher redox potential and shorter oceanic residence time of V. Our V isotope data however show variability similar to the Mo isotope data. This may be because: (1) V isotope system is more sensitive to marine deoxygenation, but our data likely indicate an increase in marine oxygenation extent from the late Ediacaran to Early Cambrian (see Section 6.3); and (2) our sampling resolution (Table S1) are generally longer than the residence time of both oceanic Mo and V. Therefore, paired high-resolution V and Mo isotope studies for other sections documenting marine deoxygenation events, are needed to test the proposed higher sensitivity of V isotopes compared to Mo isotopes.

6.2. $\delta^{51}V_{OSW}$ variation from the late Ediacaran to Early Cambrian

Uptake of oceanic V into various redox types of sediments is accompanied by distinct isotope fractionations (Fig. 1A; Wu et al., 2019b, 2020). Based on the $\delta^{51}V_{auth}$ values recorded in black shales and their local depositional redox conditions, we can reconstruct contemporary $\delta^{51}V_{OSW}$ variation that should be globally homogeneous from the late Ediacaran to Early Cambrian. The Mo_{EF} and U_{EF} co-variation trend and Fe speciation data (Fig. 5 and Table S1) indicate that the samples of the Miaohe Member at the Jiulongwan section were deposited in euxinic settings, except the two topmost samples (09JLW-41 and -42) that were deposited in anoxic (ferruginous and non-sulfidic) settings; the ones of the Liuchapo Formation at the Longbizui section were deposited in anoxic settings, while those of the lower Niutitang Formation were generally deposited in euxinic settings, except the basal one (08LBZ-19); and the ones of the lower Shuijingtuo Formation at the Yanjiahe section were deposited in anoxic settings.

For anoxic samples, the $\Delta^{51}V_{ANOX\text{-}OSW}$ of –0.7‰ can be used to reconstruct contemporary $\delta^{51}V_{OSW}$ values ($\delta^{51}V_{OSW} = \delta^{51}V_{auth} - \Delta^{51}V_{ANOX\text{-}OSW}$; Wu et al., 2020). For euxinic samples, the $\Delta^{51}V_{EUX\text{–}OSW}$ is between –0.7‰ and 0.0‰ controlled by the V drawdown efficiency (Wu et al., 2020; Fan et al., 2021). A simple Rayleigh fractionation model suggested that the $\Delta^{51}V_{EUX\text{–}OSW}$ should increase with the V depletion extent (Wu et al., 2020). In other word, if the $\delta^{51}V_{OSW}$ was constant, samples with higher V_{auth} contents should possess higher $\delta^{51}V_{auth}$ values ($\delta^{51}V_{auth} = \delta^{51}V_{OSW} + \Delta^{51}V_{EUX\text{-}OSW}$). In fact, however, there is a negative correlation between the V_{auth} contents and $\delta^{51}V_{auth}$ values, especially for the euxinic samples ($R^2 = 0.48$, $n = 17$; Fig. 6). This negative correlation doesn't support the effect related to V drawdown efficiency on the V_{auth} and $\delta^{51}V_{auth}$ variations, and also not support larger oceanic V reservoir with higher $\delta^{51}V_{OSW}$ values under greater extent of global marine oxygenation. Instead, we think this should result from both V drawdown efficiency (related to *local* redox state and basin restriction extent) and $\delta^{51}V_{OSW}$ variation (related to *global* marine oxygenation extent). The samples of the Miaohe Member (with higher V_{auth} contents and lower $\delta^{51}V_{auth}$ values; Fig. 6) should have been deposited under less globally oxygenated condition with locally more enhanced drawdown efficiency, relative to those of the Niutitang Formation (with lower V_{auth} contents and higher $\delta^{51}V_{auth}$ values; Fig. 6).

As said before, the investigated areas were well-connected to the open ocean or weakly restricted from the late Ediacaran to Early Cambrian (Fig. 5A). Therefore, we reconstructed continuously temporal $\delta^{51}V_{OSW}$ variation from the sedimentary $\delta^{51}V_{auth}$ records of this study (Fig. 7A), by using $\Delta^{51}V_{ANOX\text{-}OSW}$ of –0.7‰ and $\Delta^{51}V_{EUX\text{–}OSW}$ of –0.4‰ (Wu et al., 2020). It should be noted that the reconstructed $\delta^{51}V_{OSW}$ results from the euxinic samples of the Niutitang Formation may be lower than the reality, due to potentially low V drawdown efficiency (see above). The $\delta^{51}V_{OSW}$ values are listed in Table S1, and plotted against the depositional ages estimated by Chen et al. (2015) in

Fig. 7B. During the deposition of the Miaohe Member, the $\delta^{51}V_{OSW}$ values increase progressively from –0.66‰ to –0.12‰ from ca. 560 Ma to 553 Ma, and sharply to +0.45‰ slightly higher than the modern $\delta^{51}V_{OSW}$ value at ca. 552–551 Ma. Afterwards, the $\delta^{51}V_{OSW}$ values are generally slightly lower than the modern $\delta^{51}V_{OSW}$ value, between –0.08‰ and +0.23‰ from ca. 549 Ma to 527 Ma. At the onset of the Cambrian Stage 3 (ca. 521–518 Ma), the $\delta^{51}V_{OSW}$ values reconstructed from the $\delta^{51}V_{auth}$ values of the anoxic samples at the Yanjiahe section are from +0.17‰ to +0.34‰, which are well consistent with the potential lower limits of the $\delta^{51}V_{OSW}$ values (from +0.10‰ to +0.35‰) reconstructed from the $\delta^{51}V_{auth}$ values of the euxinic samples at the Longbizui section. This indicates that the difference in the effect related to V drawdown efficiency in the investigated areas is actually minimal, but also suggests that the $\delta^{51}V_{OSW}$ values at ca. 521–518 Ma are robust within the modern $\delta^{51}V_{OSW}$ range.

6.3. Evolution in global marine redox oxygenation extent from the late Ediacaran to Early Cambrian

The increasing $\delta^{51}V_{OSW}$ trend from ca. 560 Ma to 551 Ma indicates a rapid transition in the global marine redox condition from expansive euxinia (Fan et al., 2021) to widespread oxygenation likely reaching the modern level, which was also supported by the higher $\delta^{98}Mo$ values from the top of the Miaohe Member (+2.1‰; Kendall et al., 2015). This marine oxygenation event was thought to be episodic (Kendall et al., 2015), and to happen again at ca. 521 Ma (Chen et al., 2015), since strongly euxinic samples that can faithfully record contemporary $\delta^{98}Mo_{OSW}$ values were lacking between the two oxygenation events. However, the elevated $\delta^{51}V_{OSW}$ values reconstructed from the sedimentary $\delta^{51}V_{auth}$ records of the Liuchapo, lower Niutitang, and lower Shuijingtuo Formations suggest that the ocean kept extensively oxygenated since ca. 551 Ma, and possibly reached the modern oxygenation level at ca. 521 Ma, in good agreement with the Mo and U isotope evidence (e.g., Wen et al., 2015; Chen et al., 2015; Wei et al., 2021).

A V isotope mass balance model could be used to constrain the evolution in the proportion of oxic V output flux and oxic seafloor area from the late Ediacaran to Early Cambrian. Assuming the oceanic V cycle is at a steady state, the V input flux to the ocean is balanced in mass and isotope by output fluxes. The main V input to the ocean is riverine transport (Shiller and Mao, 2000), while the V outputs could be subdivided into four types, oxic, anoxic, euxinic, and hydrothermal sediments (represented by subscriptions of OX, ANOX, EUX, and HT, respectively) (Fig. 1A; Wu et al., 2020; Nielsen, 2021). Accordingly, we can get following equations:

$$\mathrm{F_{river} = F_{OX} + F_{ANOX} + F_{EUX} + F_{HT}} \tag{6}$$

$$f_{\mathrm{river}} = f_{\mathrm{OX}} + f_{\mathrm{ANOX}} + f_{\mathrm{EUX}} + f_{\mathrm{HT}} = 1 \tag{7}$$

$$\delta^{51}\mathrm{V_{river}} = \delta^{51}\mathrm{V_{OX}} \times f_{\mathrm{OX}} + \delta^{51}\mathrm{V_{ANOX}} \times f_{\mathrm{ANOX}} + \delta^{51}\mathrm{V_{EUX}} \times f_{\mathrm{EUX}} + \delta^{51}\mathrm{V_{HT}} \times f_{\mathrm{HT}} \tag{8}$$

where $\mathrm{F_{river}}$, $\mathrm{F_{OX}}$, $\mathrm{F_{ANOX}}$, $\mathrm{F_{EUX}}$, and $\mathrm{F_{HT}}$ are fluxes of riverine V input to the ocean and various outputs from the ocean, f_{OX}, f_{ANOX}, f_{EUX}, and f_{HT} are the fractions of various V output fluxes relative to the input flux, and $\delta^{51}\mathrm{V_{river}}$, $\delta^{51}\mathrm{V_{OX}}$, $\delta^{51}\mathrm{V_{ANOX}}$, $\delta^{51}\mathrm{V_{EUX}}$, and $\delta^{51}\mathrm{V_{HT}}$ are the δ^{51}V values of riverine input and respective outputs.

Enhanced V enrichments (several thousand ppm) in the Ediacaran and Phanerozoic black shales suggests extensive oxidative weathering of continental V after the Marinoan glaciation (Sahoo et al., 2012). Therefore, it is reasonable to infer that the post-Marinoan $\delta^{51}\mathrm{V_{river}}$ value was invariably close to the modern one (–0.6 ± 0.4‰; Schuth et al., 2019), considering that oxidative weathering process has been demonstrated to be accompanied with insignificant V isotope fractionation (Qi et al., 2022). The $\Delta^{51}\mathrm{V_{OX-OSW}}$, $\Delta^{51}\mathrm{V_{ANOX-OSW}}$, $\Delta^{51}\mathrm{V_{EUX-OSW}}$, and $\Delta^{51}\mathrm{V_{HT-OSW}}$ are –1.1‰, –0.7‰, –0.7‰ to 0.0‰, and –0.4‰, respectively (Wu et al., 2020, 2022; Nielsen, 2021). Among them, the average $\Delta^{51}\mathrm{V_{EUX-OSW}}$ controlled by V drawdown efficiency, is inferred to be smaller in the Ediacaran-Cambrian ocean, relative to the modern ocean (Fan et al., 2021). We tentatively set $\Delta^{51}\mathrm{V_{EUX-OSW}}$ to be –0.4‰, –0.2‰, and 0.0‰ in the model. Hydrothermal V output should be strongly controlled by seafloor oxygenation extent. According to the modern oxic (~377 Mmol/yr) and hydrothermal (~60 Mmol/yr) V output fluxes (Nilsen, 2021), we set f_{H} to be $0.16f_{\mathrm{O}}$. The $\delta^{51}\mathrm{V_{OSW}}$ value thus can be expressed through the following equation:

$$\delta^{51}\mathrm{V_{OSW}} = \delta^{51}\mathrm{V_{river}} - (\Delta^{51}\mathrm{V_{OX-OSW}} \times f_{\mathrm{OX}} + \Delta^{51}\mathrm{V_{ANOX-OSW}} \times f_{\mathrm{ANOX}} + \Delta^{51}\mathrm{V_{EUX-OSW}} \times f_{\mathrm{EUX}}$$

$$+ \Delta^{51}V_{HT-OSW} \times f_{HT}) \quad (9)$$

In addition, the V output flux is determined by V output rate (F'_{output}) and seafloor areas of various sediments (A_{output}). Among them, the V output rates are assumed to be controlled by first-order kinetics with respect to the coeval V reservoir in the ocean (R). That is, each $F'_{output} = F'_{output0} \times R/R_0$ (subscript 0 represents the modern values). Then we replace each f_{output} in the mass balance equations (Eqs. 7 and 8) with:

$$f_{output} = [(F'_{output0} \times R/R_0) \times A_{output}]/F_{river} = (F'_{output0} \times A_{output})/F_{river0} \quad (10)$$

The parameters used in the mass balance model are listed in Table S2. We can drive $\delta^{51}V_{OSW}$ value as a function of the proportions of V output fluxes into oxic, anoxic, and euxinic sediments relative to the input flux, f_{OX} and $f_{EUX}/(f_{ANOX} + f_{EUX})$, and as a function of the proportions of oxic, anoxic, and euxinic seafloor areas relative to the total seafloor area, A_{OX}/A_{Total} and $A_{EUX}/(A_{ANOX} + A_{EUX})$ (Fig. 8). Our modelling sensitivity analyses show that (1) $\delta^{51}V_{OSW}$ values lower than –0.2‰, characterized by the period between ca. 560 Ma and 553 Ma (Table S1 and Fig. 7B), cannot be modeled when $\Delta^{51}V_{EUX-OSW} = -0.4‰$ (Figs. 8A and D), demonstrating that the average $\Delta^{51}V_{EUX-OSW}$ was smaller relative to that of the modern ocean, when the ocean was expansively euxinic; (2) the oxic V output flux accounts for <34% of the global seawater V removal (Fig. 8C) and consequently the oxic sediments may have covered <41% of the seafloor (Fig. 8F) at ca. 560–553Ma ($\delta^{51}V_{OSW}$ values generally lower than –0.2‰); and (3) the oxic V output flux accounts for >57% of the global seawater V removal (Fig. 8A) and consequently the oxic sediments may have covered >68% (Fig. 8D) of the seafloor at ca. 551 Ma and 521–518 Ma ($\delta^{51}V_{OSW} = +0.3‰$).

6.4. Prolonged and widespread oxygenation and early animal evolution

The Ediacaran metazoans are characterized by three successive assemblages, the Avalon, White Sea, and Nama biotas (Darroch et al., 2018). Notably, both the diversity and taxonomic disparity of macroscopic soft-bodied organisms increase significantly after ca. 560 Ma (Droser et al., 2017), together with key evolutionary innovations including the appearance of bilaterians, shallow burrow, biomineralization, and predation (Fig. 7C; Wood et al., 2019). The low $\delta^{51}V_{OSW}$ values at ca. 560–553 Ma suggests the ocean may have been expansively euxinic, but the increasing trend indicates the global oxygenation extent should have increased, especially in shallow shelf settings (Fig. 7B). Afterwards, the phyla, classes, and genera of early animals increased, and reached their first peaks (Cambrian Explosion) at the onset of the Cambrian Stage 3 (Fig. 7C; Erwin et al., 2011; Fan et al., 2020), coincident with that the ocean kept widespread oxygenation from ca. 551 Ma to 521 Ma, and possibly reached the modern oxygenation level at ca. 521–518 Ma.

Based on this coincidence, we propose that prolonged and widespread marine oxygenation from the late Ediacaran to Early Cambrian should have played an essential role in the ecological radiation of marine eukaryotes and early animals. It not only could supply life-essential O_2 for early animals, but also could permit large size and ecological dominance of the characteristic Ediacaran-Cambrian fauna. Meanwhile, the establishment of the complex ecosystem may have in turn contributed to marine oxygenation, due to (1) the consumption of the large dissolved organic carbon reservoir by sponges, (2) enhanced biological pump by planktonic animals and algae, and (3) shallow burrow of benthic motile animals (Butterfield, 2011; Lenton et al., 2014).

The focused interval between ca. 560 Ma and 518 Ma also witnessed the extinctions of the Ediacaran-type soft-body animals across the Ediacaran-Cambrian transition and the small shelly animals during the Cambrian Stage 2 (529–521 Ma) (e.g., Narbonne, 2005; Shu et al., 2014; Zhu et al., 2019). These extinctions were thought to be caused by extensive marine anoxia (e.g. Zhang et al., 2018; Wei et al., 2018; Wang et al., 2018), but not supported by our reconstructed $\delta^{51}V_{OSW}$ data (Fig. 7B). We think this is possibly because that the marine anoxia was not the dominant driver for the Ediacaran-Cambrian animal extinctions, or because the relatively low sampling resolution in this study led to the missing documents of marine anoxia events across the Ediacaran-Cambrian transition and Cambrian Stage 2 (Fig. 7B).

7. Conclusions and outlook

In this study, we analyzed $\delta^{51}V$ values of organic-rich cherts and black shales deposited from the late Ediacaran to Early Cambrian in the Yangtze Block. Based on these sedimentary $\delta^{51}V$ records, we reconstructed the temporary $\delta^{51}V_{OSW}$ variation from ca. 560 Ma to 518 Ma. It suggests a rapid transition in the global marine redox condition from expansive euxinia at ca. 560–553 Ma to widespread oxygenation likely reaching the modern level at ca. 552–551 Ma. Afterwards (ca. 551–521 Ma), the ocean kept extensively oxygenated and possibly reached the modern oxygenation level again at ca. 521–518 Ma. The prolonged and widespread oceanic oxygenation may have been beneficial to the ecological radiation of marine eukaryotes and early animals from the late Ediacaran to Early Cambrian, which may have in turn contributed to marine oxygenation. The application of V isotope system as a paleo-oxybarometer is still in infancy. Further V isotope investigation is needed to trace high-resolution evolution in global marine redox condition throughout the Earth history, especially for oceanic deoxygenation event, and to explore the relationship between marine redox change and radiation and/or extinction of early animals.

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References

Algeo, T.J., Li, C., 2020. Redox classification and calibration of redox thresholds in sedimentary systems. *Geochim. Cosmochim. Acta* 287, 8-26.

Algeo, T.J., Tribovillard, N., 2009. Environmental analysis of paleoceanographic systems based on molybdenum–uranium covariation. *Chem. Geol.* 268, 211-225.

Archer, C., Vance, D., 2008. The isotopic signature of the global riverine molybdenum flux and anoxia in the ancient oceans. *Nat. Geosci.* 1, 597–600.

Arnold, G.L., Anbar, A.D., Barling, J., Lyons, T.W., 2004. Molybdenum isotope evidence for widespread anoxia in mid-Proterozoic oceans. *Science* 304, 87-90.

Barling, J., Arnold, G.L., Anbar, A.D., 2001. Natural mass-dependent variations in the isotopic composition of molybdenum. *Earth Planet. Sci. Lett.* 193, 447-457.

Broecker, W.S., Peng, T.H., 1982. Tracers in the Sea. Eldigio Press, Palisades, New York.

Butterfield, N.J., 2011. Animals and the invention of the Phanerozoic Earth system. *Trends Ecol. Evol.* 26, 81-87.

Chen, D., Wang, J., Qing, H., Yan, D., Li, R., 2009. Hydrothermal venting activities in the Early Cambrian, South China: Petrological, geochronological and stable isotopic constraints. *Chem. Geol.* 258, 168-181.

Chen, X., Ling, H.-F., Vance, D., Shields-Zhou, G.A., Zhu, M., Poulton, S.W., Och, L.M., Jiang, S.-Y., Li, D., Cremonese, L., Archer, C., 2015. Rise to modern levels of ocean oxygenation coincided with the Cambrian radiation of animals. *Nat. Commun.* 6, 7142.

Chen, Z., Zhou, C., Yuan, X., Xiao, S., 2019. Death march of a segmented and trilobate bilaterian elucidates early animal evolution. *Nature* 573, 412-415.

Condon, D., Zhu, M., Bowring, S., Wang, W., Yang, A., Jin, Y., 2005. U-Pb Ages from the Neoproterozoic Doushantuo Formation, China. *Science* 308, 95-98.

Darroch, S.A.F., Smith, E.F., Laflamme, M., Erwin, D.H., 2018. Ediacaran extinction and Cambrian explosion. *Trends Ecol. Evol.* 33, 653–663.

Droser, M.L., Tarhan, L.G., Gehling, J.G., 2017. The rise of animals in a changing environment: global ecological innovation in the late Ediacaran. *Annu. Rev. Earth Planet. Sci.* 45, 593–617.

Erwin, D.H., Laflamme, M., Tweedt, S.M., Sperling, E.A., Pisani, D., Peterson, K.J., 2011. The Cambrian conundrum: Early divergence and later ecological success in the early history of animals. *Science* 334, 1091-1097.

Fan, H., Ostrander, C.M., Auro, M., Wen, H., Nielsen, S.G., 2021. Vanadium isotope evidence for expansive ocean euxinia during the appearance of early Ediacara biota. *Earth Planet. Sci. Lett.* 567, 117007.

Fan, J.-X., Shen, S.-Z., Erwin, D.H., Sadler, P.M., MacLeod, N., Cheng, Q.-M., Hou, X.-D., Yang, J., Wang, X.-D., Wang, Y., Zhang, H., Chen, X., Li, G.-X., Zhang, Y.-C., Shi, Y.-K., Yuan, D.-X., Chen, Q., Zhang, L.-N., Li, C., Zhao, Y.-Y., 2020. A high-resolution summary of Cambrian to Early Triassic marine invertebrate biodiversity. *Science* 367, 272–277.

Goldberg, T., Archer, C., Vance, D., Thamdrup, B., McAnena, A., Poulton, S.W., 2012. Controls on Mo isotope fractionations in a Mn-rich anoxic marine sediment, Gullmar Fjord, Sweden. *Chem. Geol.* 296-297, 73-82.

Gustafsson J.P., 2019. Vanadium geochemistry in the biogeosphere-speciation, solid-solution interactions, and ecotoxicity. *Appl. Geochem.* 102, 1–25.

Humphris, S.E., Thompson, G., 1978. Trace element mobility during hydrothermal alteration of oceanic basalts. *Geochim. Cosmochim. Acta* 42, 127–136.

Jiang, G., Shi, X., Zhang, S., Wang, Y., Xiao, S., 2011. Stratigraphy and paleogeography of the Ediacaran Doushantuo Formation (ca. 635–551 Ma) in South China. *Gondwana Res.* 19, 831-849.

Kendall, B., 2021. Recent advances in geochemical paleo-oxybarometers. *Annu. Rev. Earth Planet. Sci.* 49, 399-433.

Kendall, B., Komiya, T., Lyons, T.W., Bates, S.M., Gordon, G.W., Romaniello, S.J., Jiang, G., Creaser, R.A., Xiao, S., McFadden, K., Sawaki, Y., Tahata, M., Shu, D., Han, J., Li, Y., Chu, X., Anbar, A.D., 2015. Uranium and molybdenum isotope evidence for an episode of widespread ocean oxygenation during the late Ediacaran Period. *Geochim. Cosmochim. Acta* 156, 173-193.

Kiriyama, T., Kuroda, R., 1983. Anion-exchange separation and spectrophotometric determination of vanadium in silicate rocks. *Talanta* 30, 261-264.

Knoll, A.H., Carroll, S.B., 1999. Early animal evolution: Emerging views from comparative biology and geology. *Science* 284, 2129-2137.

Ku, T.-L., Mathieu, G.G., Knauss, K.G., 1977. Uranium in open ocean: concentration and isotopic composition. *Deep Sea Res.* 24, 1005-1017.

Lenton, T.M., Boyle, R.A., Poulton, S.W., Shields-Zhou, G.A., Butterfield, N.J., 2014. Co-evolution of eukaryotes and ocean oxygenation in the Neoproterozoic era. *Nat. Geosci.* 7, 257–265.

Leya, I., Schönbächler, M., Wiechert, U., Krähenbühl, U., Halliday, A.N., 2007. High precision titanium isotope measurements on geological samples by high resolution MC-ICP-MS. *Int. J. Mass Spectrom*. 262, 247–255.

Li, C., Shi, W., Cheng, M., Jin, C., Algeo, T.J., 2020. The redox structure of Ediacaran and early Cambrian oceans and its controls. *Sci. Bull.* 65, 2141-2149.

Ling, H., Chen, X., Li, D., Wang, D., Shields-Zhou, G.A., Zhu, M., 2013. Cerium anomaly variations in Ediacaran–earliest Cambrian carbonates from the Yangtze Gorges area, South China: Implications for oxygenation of coeval shallow seawater. *Precambrian Res.* 225, 110–127.

McLennan, S.M., 2001. Relationships between the trace element composition of sedimentary rocks and upper continental crust. *Geochem. Geophy. Geosy.* 2, 2000GC000109.

Miller, C.A., Peucker-Ehrenbrink, B., Walker, B.D., Marcantonio, F., 2011. Re-assessing the surface cycling of molybdenum and rhenium. *Geochim. Cosmochim. Acta* 75, 7146-7179.

Morford, J.L., Emerson, S., 1999. The geochemistry of redox sensitive trace metals in sediments. *Geochim. Cosmochim. Acta* 63, 1735-1750.

Narbonne, G.M., 2005. The Ediacara biota: Neoproterozoic origin of animals and their ecosystems. *Annu. Rev. Earth Planet. Sci.* 33, 421-442.

Neubert, N., Nägler, T.F., Böttcher, M.E., 2008. Sulfidity controls molybdenum isotope fractionation into euxinic sediments: Evidence from the modern Black Sea. *Geology* 36, 775-778.

Nielsen, S.G., 2021. Vanadium isotopes: A proxy for ocean oxygen variations. Cambridge University Press, Cambridge.

Nielsen, S.G., Prytulak, J., Halliday, A.N., 2011. Determination of precise and accurate $^{51}V/^{50}V$ isotope ratios by MC-ICP-MS, part 1: Chemical separation of vanadium and mass spectrometric protocols. *Geostand. Geoanal. Res.* 35, 293-306.

Poulson Brucker, R.L., McManus, J., Severmann, S., Berelson, W.M., 2009. Molybdenum behavior during early diagenesis: Insights from Mo isotopes. *Geochem. Geophy. Geosy.* 10, Q06010.

Poulton, S.W., Canfield, D.E., 2011. Ferruginous conditions: A dominant feature of the ocean through Earth's history. *Elements* 7, 107-112.

Qi, Y.-H., Gong, Y.-Z., Wu, F., Lu, Y., Cheng, W., Huang, F., Yu, H.-M., 2022. Coupled variations in V-Fe abundances and isotope compositions in latosols: Implications for V mobilization during chemical weathering. *Geochim. Cosmochim. Acta* 320, 26-40.

Qian, Y., Yin, G., 1984. Small shelly fossils from the lowerest Cambrian in Guizhou. *Prof. Pap. Stratigr. Palaeontol.* 13, 91-123.

Reinhard, C.T., Planavsky, N.J., Robbins, L.J., Partin, C.A., Gill, B.C., Lalonde, S.V., Bekker, A., Konhauser, K.O., Lyons, T.W., 2013. Proterozoic ocean redox and biogeochemical stasis. *Proc. Natl. Acad. Sci.* 110, 5357–5362.

Sahoo, S.K., Planavsky, N.J., Kendall, B., Wang, X., Shi, X., Scott, C., Anbar, A.D., Lyons, T.W., Jiang, G., 2012. Ocean oxygenation in the wake of the Marinoan glaciation. *Nature* 489, 546–549.

Schuth, S., Brüske, A., Hohl, S.V., Jiang, S.-Y., Meinhardt, A.-K., Gregory, D.D., Viehmann, S., Weyer, S., 2019. Vanadium and its isotope composition of river water and seawater: Analytical improvement and implications for vanadium isotope fractionation. *Chem. Geol.* 528, 119261.

Scott, C., Slack, J.F., Kelley, K.D., 2017. The hyper-enrichment of V and Zn in black shales of the Late Devonian-Early Mississippian Bakken Formation (USA). *Chem. Geol.* 452, 24-33.

Shields, W.R., Murphy, T.J., Catanzaro, E.J., Garner, E.L., 1966. Absolute isotopic abundance ratios and the atomic weight of a reference sample of chromium. *J. Res. Natl. Bur. Stand.* 70, 193–197.

Shiller, A.M., Mao, L., 1999. Dissolved vanadium on the Louisiana Shelf: effect of oxygen depletion. *Cont. Shelf Res.* 19, 1007-1020.

Shu, D., Isozaki, Y., Zhang, X., Han, J., Maruyama, S., 2014. Birth and early evolution of metazoans. *Gondwana Res.* 25, 884-895.

Siebert, C., Nägler, T.F., von Blanckenburg, F., Kramers, J.D., 2003. Molybdenum isotope records as a potential new proxy for paleoceanography. *Earth Planet. Sci. Lett.* 211, 159–171.

Sperling, E.A., Wolock, C.J., Morgan, A.S., Gill, B.C., Kunzmann, M., Halverson, G.P., Macdonald, F.A., Knoll, A.H., Johnston, D.T., 2015. Statistical analysis of iron geochemical data suggests limited late Proterozoic oxygenation. *Nature* 523, 451-454.

Taylor, M.J.C., van Staden, J.F., 1994. Spectrophotometric determination of vanadium(IV) and vanadium(V) in each other's presence. Review. *Analyst* 119, 1263-1276.

Tribovillard, N., Algeo, T.J., Lyons, T., Riboulleau, A., 2006. Trace metals as paleoredox and paleoproductivity proxies: An update. *Chem. Geol.* 232, 12-32.

Wang, D., Ling, H.-F., Struck, U., Zhu, X.-K., Zhu, M., He, T., Yang, B., Gamper, A., Shields, G.A., 2018. Coupling of ocean redox and animal evolution during the Ediacaran-Cambrian transition. *Nat. Commun.* 9, 2575.

Wang, J., Chen, D., Yan, D., Wei, H., Xiang, L., 2012. Evolution from an anoxic to oxic deep ocean during the Ediacaran–Cambrian transition and implications for bioradiation. *Chem. Geol.* 306, 129-138.

Wanty, R.B., Goldhaber, M.B., 1992. Thermodynamics and kinetics of reactions involving vanadium in natural systems: Accumulation of vanadium in sedimentary rocks. *Geochim. Cosmochim. Acta* 56, 1471-1483.

Wei, G.-Y., Planavsky, N.J., He, T., Zhang, F., Stockey, R.G., Cole, D.B., Lin, Y.-B., Ling, H.-F., 2021. Global marine redox evolution from the late Neoproterozoic to the early Paleozoic constrained by the integration of Mo and U isotope records. *Earth-Sci. Rev.* 214, 103506.

Wei, G.-Y., Planavsky, N.J., Tarhan, L.G., Chen, X., Wei, W., Li, D., Ling, H.-F., 2018. Marine redox fluctuation as a potential trigger for the Cambrian explosion. *Geology* 46, 587–590.

Wei, W., Klaebe, R., Ling, H.-F., Huang, F., Frei, R., 2020. Biogeochemical cycle of chromium isotopes at the modern Earth's surface and its applications as a paleo-environment proxy. *Chem. Geol.* 541, 119570.

Wen, H., Fan, H., Zhang, Y., Cloquet, C., Carignan, J., 2015. Reconstruction of early Cambrian ocean chemistry from Mo isotopes. *Geochim. Cosmochim. Acta* 164, 1-16.

Wood, R., Liu, A.G., Bowyer, F., Wilby, P.R., Dunn, F.S., Kenchington, C.G., Cuthill, J.F.H., Mitchell, E.G., Penny, A., 2019. Integrated records of environmental change and evolution challenge the Cambrian Explosion. *Nat. Ecol. Evol.* 3, 528–538.

Wu F., Owens J.D., German C.R., Mills R.A., Nielsen S.G., 2022. Vanadium isotope fractionation during hydrothermal sedimentation: Implications for the vanadium cycle in the oceans. *Geochim. Cosmochim. Acta* 328, 168-184.

Wu, F., Owens, J.D., Huang, T., Sarafian, A., Huang, K.-F., Sen, I.S., Horner, T.J., Blusztajn, J., Morton, P., Nielsen, S.G., 2019a. Vanadium isotope composition of seawater. *Geochim. Cosmochim. Acta* 244, 403-415.

Wu, F., Owens, J.D., Scholz, F., Huang, L., Li, S., Riedinger, N., Peterson, L.C., German, C.R., Nielsen, S.G., 2020. Sedimentary vanadium isotope signatures in low oxygen marine conditions. *Geochim. Cosmochim. Acta* 284, 134-155.

Wu, F., Owens, J.D., Tang, L., Dong, Y., Huang, F., 2019b. Vanadium isotopic fractionation during the formation of marine ferromanganese crusts and nodules. *Geochim. Cosmochim. Acta* 265, 371-385.

Wu, F., Qi, Y., Yu, H., Tian, S., Hou, Z., Huang, F., 2016. Vanadium isotope measurement by MC-ICP-MS. *Chem. Geol.* 421, 17-25.

Xiao, S., Yuan, X., Steiner, M., Knoll, A.H., 2002. Macroscopic carbonaceous compressions in a terminal Proterozoic shale: a systematic reassessment of the Miaohe biota, South China. *J. Paleontol.* 76, 347-376.

Xu, L., Lehmann, B., Mao, J., Qu, W., Du, A., 2011. Re-Os Age of Polymetallic Ni-Mo-PGE-Au Mineralization in Early Cambrian Black Shales of South China—A Reassessment. *Econ. Geol.* 106, 511-522.

Yang, C., Zhu, M., Condon, D.J., Li, X.H., 2017. Geochronological constraints on stratigraphic correlation and oceanic oxygenation in Ediacaran-Cambrian transition in South China. *J. Asian Earth Sci.* 140, 75-81.

Yin, L., Zhu, M., Knoll, A.H., Yuan, X., Zhang, J., Hu, J., 2007. Doushantuo embryos preserved inside diapause egg cysts. *Nature* 446, 661–663.

Zhang, F., Xiao, S., Kendall, B., Romaniello, S.J., Cui, H., Meyer, M., Gilleaudeau, G.J., Kaufman, A.J., Anbar, A.D., 2018. Extensive marine anoxia during the terminal Ediacaran Period. *Sci. Adv.* 4, eaan8983.

Zhu M, Zhao F, Yin Z, Zeng H, Li G. 2019. The Cambrian explosion: Advances and perspectives from China. *Sci. China Earth Sci.* 49, 1455-1490.

Figure caption

Fig. 1. Schematic diagrams showing the modern oceanic (A) V and (B) Mo isotope mass balance models. In (A), the data are sourced from Wu et al. (2019a), (2020), Schuth et al. (2019), and Nielsen (2021). In (B), the data are sourced from Reinhard et al. (2013), Wei et al. (2021), and Kendall (2021).

Fig. 2. (A) Simplified paleogeographic map of the Yangtze Block during the Ediacaran-Cambrian transition modified after Jiang et al. (2011), showing the sampling locations of the Yangtze Gorges area and Longbizui section. (B) Geological map of the Yangtze Gorges area modified after Ling et al. (2013), showing the sampling locations of the Jiulongwan and Yanjiahe sections. (C) late Ediacaran to Early Cambrian (560–510 Ma) chrono-stratigraphy as well as stratigraphic correlation in the relevant sections in the Yangtze Block modified after Chen et al. (2015).

Fig. 3. Various profiles of V_{auth}, $\delta^{51}V_{auth}$, $\delta^{98}Mo$, Fe_{HR}/Fe_T, and Fe_{py}/Fe_{HR} of the organic-rich cherts and black shales from the Miaohe Member at the Jiulongwan section, Liuchapo and lower Niutitang Formations at the Longbizui section, and lower Shuijingtuo Formation at the Yanjiahe section. The data of $\delta^{98}Mo$, Fe_{HR}/Fe_T, and Fe_{py}/Fe_{HR} are sourced from Chen et al. (2015). NTT and LCP stand for Niutitang and Liuchapo, respectively. In the $\delta^{51}V_{auth}$ profiles, the error bar shows external reproducibility of ±0.08‰. In the Fe speciation profiles, the divisions between oxic and anoxic conditions ($Fe_{HR}/Fe_T = 0.22$–0.38; red dashed lines) and between ferruginous and euxinic conditions ($Fe_{py}/Fe_{HR} = 0.7$–0.8; green dashed lines) are derived from Poulton and Canfield (2011).

Fig. 4. Cross-plots of (A) V_{auth} versus Mo contents and (B) $\delta^{51}V_{auth}$ versus $\delta^{98}Mo$ values of the organic-rich cherts and black shales from the Miaohe Member at the Jiulongwan section, Liuchapo and lower Niutitang Formations at the Longbizui

section, and lower Shuijingtuo Formation at the Yanjiahe section. The data of Mo contents and δ^{98}Mo values are sourced from Chen et al. (2015).

Fig. 5. Cross-plots of (A) U_{EF} versus Mo_{EF} and (B) Fe_{HR}/Fe_T versus Fe_{py}/Fe_{HR} of the organic-rich cherts and black shales from the Miaohe Member at the Jiulongwan section, Liuchapo and lower Niutitang Formations at the Longbizui section, and lower Shuijingtuo Formation at the Yanjiahe section. The data of U_{EF}, Mo_{EF}, Fe_{HR}/Fe_T, and Fe_{py}/Fe_{HR} are sourced from Chen et al. (2015). In (A), the trend lines for different reducing depositional systems in the modern ocean are modified after Algeo and Tribovillard (2009), including open marine system, weakly restricted basin (i.e., Cariaco Basin), and strongly restricted basin (i.e., Black Sea). The dashed line represents the average weight Mo/U ratio of 3.1 for the modern seawater. In (B), the divisions between oxic and anoxic conditions (Fe_{HR}/Fe_T = 0.22–0.38) and between ferruginous and euxinic conditions (Fe_{py}/Fe_{HR} = 0.7–0.8) are derived from Poulton and Canfield (2011).

Fig. 6. Cross-plot of (A) V_{auth} contents versus $\delta^{51}V_{auth}$ values of the organic-rich cherts and black shales from the Miaohe Member at the Jiulongwan section, Liuchapo and lower Niutitang Formations at the Longbizui section, and lower Shuijingtuo Formation at the Yanjiahe section. The green and blue labels indicate that samples were deposited in anoxic and euxinic environments (no studied samples were deposited in oxic environments). The trend line ($R^2 = 0.48$, $n = 17$) is defined by the data of the euxinic samples.

Fig. 7. Temporal evolutions in (A) $\delta^{51}V_{auth}$ values of the organic-rich cherts and black shales in the Yangtze Block, (B) reconstructed $\delta^{51}V_{OSW}$ values, and (C) known fossil record of animals at the phylum, class, and genus levels as well as key evolutional innovations from ca. 560 Ma to 518 Ma. In (A), YJH, NTT, LCP, and JLW stand for Yanjiahe, Niutitang, Liuchapo, and Jiulongwan, respectively. The green and blue labels indicate that samples were deposited in anoxic and euxinic

environments (no studied samples were deposited in oxic environments). The green vertical bar represents the average $\delta^{51}V_{auth}$ value (–0.52 ± 0.17‰) of the modern anoxic sediments (represented by the Peruvian margin and Santa Barbara Basin sediments with $[O_2] < 10$ µM), and the blue vertical bar represents the average $\delta^{51}V_{auth}$ value (–0.22 ± 0.13‰) of the modern euxinic sediments (represented by the euxinic Cariaco Basin sediments) (Wu et al., 2020). In (B), the gray vertical bar represents the estimated $\delta^{51}V_{UCC}$ value from −0.8‰ to −0.6‰ (Wu et al., 2016), and the blue vertical bar represents the modern $\delta^{51}V_{OSW}$ value (+0.20 ± 0.15‰; Wu et al., 2019a). In (C), the numbers of the Ediacaran genera, marine animal phyla and classes are sourced from Erwin et al. (2011), the marine animal genus diversity is sourced from a recent analysis of the Geobiodiversity Database, which is largely based on data from China (Fan et al., 2020), and the key evolutional innovations are sourced from Wood et al. (2019).

Fig. 8. Results of sensitivity analyses showing how $\delta^{51}V_{OSW}$ value would vary as a function of the proportions of V output fluxes into oxic (f_{OX}), anoxic (f_{ANOX}), and euxinic (f_{EUX}) sediments relative to the input flux, and as a function of the proportions of oxic (A_{OX}), anoxic (A_{ANOX}), and euxinic (A_{EUX}) seafloor areas relative to the total seafloor area (A_{total}), assuming that the V input and output in the ocean are at a steady state. Calculations are operated for (A, D) $\Delta^{51}V_{EUX-OSW}$ = –0.4‰, (B, E) $\Delta^{51}V_{EUX-OSW}$ = –0.2‰, and (C, F) $\Delta^{51}V_{EUX-OSW}$ = 0.0‰.