

# Sulfur isotope evidence for transient marine-shelf oxidation during the Ediacaran Shuram Excursion

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## ABSTRACT

The Ediacaran Shuram Excursion (SE) was a major negative  $\delta^{13}\text{C}_{\text{carb}}$  excursion (to  $-12\text{‰}$ ) thought to reflect significant atmospheric-oceanic oxidation, although direct evidence is limited. Here, we model changes in seawater sulfate concentrations ( $[\text{SO}_4^{2-}]_{\text{sw}}$ ) during the SE by using paired S-isotope data of cogenetic sedimentary pyrite and carbonate-associated sulfate from the Ediacaran Doushantuo Formation (South China), making independent calculations for inner-shelf and upper-slope sections. Our results show a significant increase of  $[\text{SO}_4^{2-}]_{\text{sw}}$  toward the peak of the SE and a large proximal-to-distal gradient across the Yangtze Platform. Our findings provide direct evidence for transient oxidation of marine-shelf water masses during the SE, providing insights into Ediacaran oceanic oxygenation, the origin of the SE, and contemporaneous bioevolutionary events.

## INTRODUCTION

The Ediacaran Period (ca. 635–541 Ma) was a critical time in Earth history, characterized by a significant rise of atmospheric and oceanic oxygen levels and rapid biological evolution culminating in the advent of metazoans (Och and Shields-Zhou, 2012). It also witnessed large perturbations of the global carbon cycle, among which the late Ediacaran Shuram Excursion (SE) of carbonate carbon isotopes ( $\delta^{13}\text{C}_{\text{carb}}$ ) was the largest (minimum to  $-12\text{‰}$ ) and possibly most important (e.g., coinciding with an increase in metazoan size) (Grotzinger et al., 2011). The SE is unusual also in that organic carbon isotopes ( $\delta^{13}\text{C}_{\text{org}}$ ) are decoupled from  $\delta^{13}\text{C}_{\text{carb}}$ , which does not conform to the prevailing carbon-cycle paradigm in which organic and inorganic carbon in marine sediments are derived from the same dissolved inorganic carbon source.

The origin of the SE has long been debated, with two types of hypotheses being advanced to account for its highly negative  $\delta^{13}\text{C}_{\text{carb}}$  values. The first is a non-seawater origin of the  $\delta^{13}\text{C}_{\text{carb}}$  signatures through diagenetic alteration of primary  $\delta^{13}\text{C}_{\text{carb}}$  signatures (e.g., Derry, 2010) or precipitation of  $^{13}\text{C}$ -depleted authigenic carbonates (e.g., Cui et al., 2017). The second is a primary seawater origin of the  $\delta^{13}\text{C}_{\text{carb}}$  signatures mainly involving oxidation of dissolved organic carbon, other reduced carbon species in the ocean (e.g., subsurface hydrocarbon seeps) (Rothman et al., 2003; Fike et al., 2006; McFadden et al., 2008; Lee et al., 2015; Li et al., 2017), or sedimentary organic carbon through subaerial weathering (e.g., Kaufman et al., 2007). These hypotheses invoke significant atmospheric-oceanic oxidation, although direct evidence is limited.

In this study, we generated S-isotopic data for cogenetic carbonate-associated sulfate (CAS) ( $\delta^{34}\text{S}_{\text{CAS}}$ ) and sedimentary pyrite ( $\delta^{34}\text{S}_{\text{py}}$ ) through the SE interval in the upper Ediacaran Doushantuo Formation at two South China locales: the inner-shelf Jiulongwan (JLW;  $30^{\circ}47'51''\text{N}$ ,  $110^{\circ}59'32''\text{E}$ ) and upper-slope Siduping (SDP;  $28^{\circ}55'01''\text{N}$ ,  $110^{\circ}27'00''\text{E}$ )

sections. These data provide the basis for a quantitative analysis of spatiotemporal changes in seawater sulfate concentrations ( $[\text{SO}_4^{2-}]_{\text{sw}}$ ) during the SE, which provides insights into Ediacaran oceanic oxygenation, the origin of the SE, and contemporaneous bioevolutionary events.

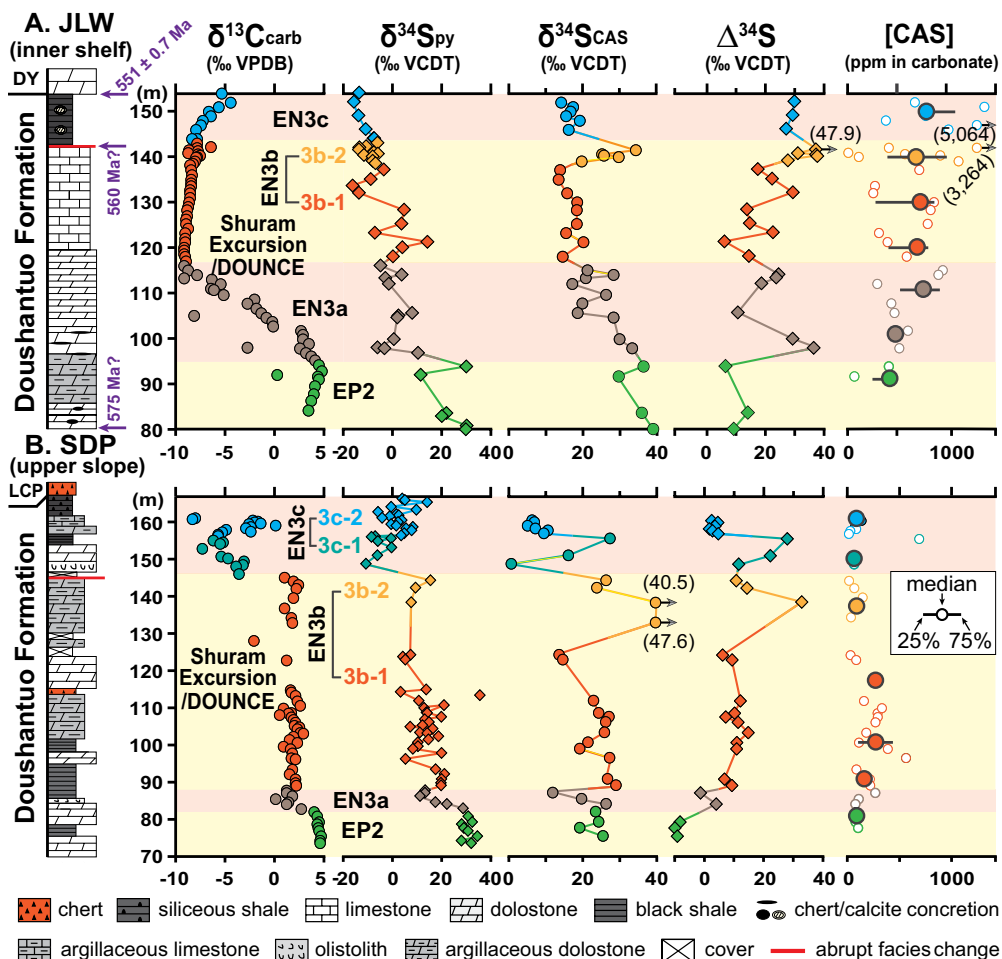
## STRATIGRAPHIC FRAMEWORK

The Doushantuo Formation is a succession of carbonate, shale, and phosphatic shale in its type area of the Yangtze Gorges, with inner-shelf facies to the northwest and basinal facies to the southeast of the Yangtze Platform, and no evidence for basinal isolation from the open ocean (Jiang et al., 2011; Fig. DR1 in the GSA Data Repository<sup>1</sup>). The SE is considered equivalent to Ediacaran negative excursion 3 (EN3, or Doushantuo negative carbon isotope excursion [DOUNCE]), which is located in the upper part of this formation and can be correlated regionally on the basis of lithostratigraphy, sequence stratigraphy, and chemostratigraphy (Jiang et al., 2011). The SE shows three distinct intervals of  $\delta^{13}\text{C}_{\text{carb}}$  variation at JLW (from base to top): (1) a negative shift from  $+5\text{‰}$  during Ediacaran positive excursion 2 (EP2) to  $-9\text{‰}$  over an interval of  $\sim 20$  m (EN3a), (2) stable values of  $\sim -9\text{‰}$  over an interval of  $\sim 33$  m (EN3b), and (3) a positive shift from  $-9\text{‰}$  to  $-2\text{‰}$  over an interval of  $>10$  m (EN3c) (Li et al., 2017; Fig. 1A). The deeper SDP section shows some differences in detail: (1) a negative shift from  $+5\text{‰}$  during EP2 to  $+1.5\text{‰}$  over an interval of  $\sim 5$  m (EN3a), (2) stable values of  $\sim +1.5\text{‰}$  over an interval of  $\sim 60$  m (EN3b), and (3) a pronounced decline to a minimum of  $-8.3\text{‰}$  followed by a positive shift to  $+0.1\text{‰}$  (EN3c) (Li et al., 2017; Fig. 1B).

The age of the SE is constrained by a zircon U-Pb date of  $551.1 \pm 0.7$  Ma from the uppermost Doushantuo black shale, which is close to the termination of the SE (Condon et al., 2005), and by a stratigraphically estimated date of ca. 560 Ma for the base of the black shale, which marks the peak of the SE (Kendall et al., 2015) and is related to the globally correlatable Miaohu Biota (Zhu et al., 2008). The age of onset of the SE is comparatively poorly constrained, but stratigraphic analyses and Sr isotope data suggest that the SE is younger than the ca. 580 Ma Gaskiers glaciation (Sawaki et al., 2010), which has been correlated to a stratigraphic hiatus located immediately below EP2 in the Doushantuo Formation (Condon et al., 2005). Linear interpolation based on available Doushantuo U-Pb dates suggests an age range of ca. 595–587 Ma for the stratigraphic hiatus and an age range of ca. 575–551 Ma for the SE-EN3-DOUNCE (Jiang et al., 2007), which is consistent with the SE being younger than the Gaskiers glaciation. A detailed description of the geological setting, age constraints, and stratigraphic correlation framework is provided in the Data Repository.

<sup>1</sup>GSA Data Repository item 2018075, detailed geological settings, analytical methods, modeling, data evaluation, and supplemental figures and data tables, is available online at <http://www.geosociety.org/datarepository/2018/> or on request from [editing@geosociety.org](mailto:editing@geosociety.org).

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**Figure 1.** Integrated carbon-sulfur (C-S) chemostratigraphy of upper Doushantuo Formation at Jiulongwan (JLW) (A) and Siduping (SDP) (B), South China. Sources for JLW: carbonate  $\delta^{13}\text{C}_{\text{carb}}$ , carbonate-associated sulfate concentration [CAS], and CAS  $\delta^{34}\text{S}$  ( $\delta^{34}\text{S}_{\text{CAS}}$ ) data for Ediacaran negative excursions EN3a and EN3b are from Li et al. (2017); pyrite  $\delta^{34}\text{S}$  ( $\delta^{34}\text{S}_{\text{py}}$ ) and  $\Delta^{34}\text{S}$  ( $\delta^{34}\text{S}_{\text{CAS}} - \delta^{34}\text{S}_{\text{py}}$ ) data for EN3a and EN3b are original to present study; and S-isotope data for Ediacaran positive excursion 2 (EP2) and EN3c are from McFadden et al. (2008) and Li et al. (2010), respectively. Sources for SDP:  $\delta^{13}\text{C}_{\text{carb}}$  data are from Li et al. (2017), and all S-system data are original to present study. Height values marked for each section are relative to the base of the Doushantuo Formation at the section. DY—Dengying Formation; LCP—Liuchapo Formation; DOUNCE—Doushantuo negative carbon isotope excursion.

## SAMPLES AND METHODS

Fresh rock samples were collected for petrographic and geochemical analyses ( $n = 7$  and  $57$  at JLW;  $n = 8$  and  $97$  at SDP, respectively). Pyrite framboid size distributions were analyzed with an FEI Quanta 200 scanning electron microscope, and pyrite sulfur was extracted from whole-rock samples using the chromium reduction method. CAS analyses, which were undertaken only on samples with total inorganic carbon content  $>3\%$  to limit the influence of porewater-derived CAS, followed the methods described by Li et al. (2017). Isotopic determinations were performed on a Thermo Fisher Scientific Delta V Plus isotope ratio mass spectrometer coupled with a Flash elemental analyzer. Results are reported in  $\delta$  notation as per mil (‰) variation relative to the Vienna Canyon Diablo Troilite (VCDT) standard, and  $\Delta^{34}\text{S}$  is the difference between paired  $\delta^{34}\text{S}_{\text{CAS}}$  and  $\delta^{34}\text{S}_{\text{py}}$ . A detailed description of all analytical methods and data quality evaluation can be found in the Data Repository.

## RESULTS AND DISCUSSION

### Pyrite Morphology

Pyrite framboids formed in the water column are generally smaller and less variable in size than early diagenetic framboids because of their rapid formation and sinking in anoxic waters (Wilkin and Barnes, 1996). In backscattered electron images, pyrite in both sections is well preserved and randomly distributed, mostly as framboids although with smaller numbers of euhedral or semi-euhedral crystals (Fig. DR7). A majority of the framboids ( $>93\%$ ) are  $<10\ \mu\text{m}$  in diameter with a standard deviation of  $2.2\ \mu\text{m}$  in most samples (Fig. DR8), which is consistent with their formation in the water column.

### Sulfur Chemostratigraphy at JLW and SDP

The S-isotope profiles of the JLW and SDP sections show broad similarities through the SE (Tables DR1 and DR2 in the Data Repository; Fig. 1). At JLW,  $\delta^{34}\text{S}_{\text{py}}$  exhibits a decrease from  $>+30\text{‰}$  in EP2 to  $<-10\text{‰}$  in excursion EN3c, and  $\delta^{34}\text{S}_{\text{CAS}}$  exhibits a decrease from  $>+35\text{‰}$  in EP2 to  $<+20\text{‰}$  in EN3c (except for a minor increase in EN3b-2; Fig. 1A). In contrast,  $\Delta^{34}\text{S}$  and [CAS] show a generally increasing trend, although with large variability, from EP2 to EN3c. At SDP (Fig. 1B),  $\delta^{34}\text{S}_{\text{py}}$  exhibits a decrease from  $>+30\text{‰}$  to  $<-10\text{‰}$  from EP2 to EN3c-1, although this is followed by a return to  $>0\text{‰}$  in EN3c-2.  $\delta^{34}\text{S}_{\text{CAS}}$  exhibits a decrease from  $>+25\text{‰}$  in EP2 to  $<+10\text{‰}$  in EN3c, although this trend is interrupted by an excursion to  $>+40\text{‰}$  in EN3b-2. The  $\Delta^{34}\text{S}$  and [CAS] profiles at SDP exhibit positive trends from EP2 to mid-EN3b-1, but large variations for  $\Delta^{34}\text{S}$  and a general decrease for [CAS] thereafter.

Patterns similar to those in the study sections, i.e., declining  $\delta^{34}\text{S}_{\text{py}}$  and  $\delta^{34}\text{S}_{\text{CAS}}$  and rising  $\Delta^{34}\text{S}$  during the SE, have been interpreted in earlier studies to reflect secular increases in  $[\text{SO}_4^{2-}]_{\text{sw}}$  and oceanic oxidation based on their empirical relationship to greater isotopic fractionation (i.e.,  $\Delta^{34}\text{S}$ ) during microbial sulfate reduction (MSR) (e.g., Fike et al., 2006; McFadden et al., 2008). This interpretation is consistent with a general increase in [CAS] through the lower SE at SDP and the full SE at JLW (Fig. 1). At the scale of individual stratigraphic units, the JLW and SDP sections show significant differences (Table DR2): (1) mean  $\delta^{34}\text{S}_{\text{py}}$  values at SDP are  $6.2\text{‰}$ – $20.3\text{‰}$  higher than at JLW; (2) mean  $\delta^{34}\text{S}_{\text{CAS}}$  values at SDP are  $1.8\text{‰}$ – $12.1\text{‰}$  lower than at JLW, except within EN3b-1 and EN3b-2, which are  $6.7\text{‰}$  and  $7.6\text{‰}$  higher, respectively; (3) mean  $\Delta^{34}\text{S}$  values at SDP are  $7.7\text{‰}$ – $25.5\text{‰}$  lower than at JLW; and (4) median [CAS] values at SDP are  $154$ – $708$  ppm lower than at JLW. These substantial differences

suggest that S cycling in the Yangtze cratonic sea was laterally heterogeneous during the SE. In order to quantify these differences, we modeled  $[\text{SO}_4^{2-}]_{\text{sw}}$  for each stratigraphic unit at JLW and SDP.

### Quantitative Modeling of Late Ediacaran Seawater Sulfate Concentrations

CAS and pyrite S-isotope compositions can provide constraints on ancient  $[\text{SO}_4^{2-}]_{\text{sw}}$  (e.g., Kah et al., 2004). We quantified secular variation in  $[\text{SO}_4^{2-}]_{\text{sw}}$  based on the “rate method” of Algeo et al. (2015), which makes use of paired  $\delta^{34}\text{S}_{\text{CAS}}$  and  $\delta^{34}\text{S}_{\text{py}}$  data (Fig. DR2; Table DR3). The conceptual underpinning of this method is that the S-isotope composition of seawater ( $\delta^{34}\text{S}_{\text{sw}}$ ) changes in response to imbalances in isotopic fluxes into and out of a non-steady-state system.  $[\text{SO}_4^{2-}]_{\text{sw}}$  can be estimated from observed rates of  $\delta^{34}\text{S}_{\text{CAS}}$  variation ( $\partial\delta^{34}\text{S}_{\text{CAS}}/\partial t$ , where  $t$  is time) in combination with observed S-isotope fractionations (i.e.,  $\Delta^{34}\text{S}$ ) (for a detailed description, see the Data Repository).

Modeled  $[\text{SO}_4^{2-}]_{\text{sw}}$  values are systematically higher at JLW relative to SDP throughout the SE (Fig. 2; Table DR3). This relationship is consistent with observations of lighter  $\delta^{34}\text{S}_{\text{py}}$  and larger  $\Delta^{34}\text{S}$  and [CAS] values at JLW (Fig. 1). Despite these differences, the two sections show similar secular trends: at JLW, mean  $[\text{SO}_4^{2-}]_{\text{sw}}$  increases from 3.5 mM in EP2 to 8.7 mM in EN3b-1 and then declines to 4.1 mM in EN3b-2, and at SDP, mean  $[\text{SO}_4^{2-}]_{\text{sw}}$  increases from ~0 mM in EP2 to 3.1–4.0 mM in EN3b–EN3c-1 and then declines to 1.0 mM in EN3c-2. These estimates are subject to some uncertainties in that the rate method (1) overestimates  $[\text{SO}_4^{2-}]_{\text{sw}}$  if observed rates of  $\delta^{34}\text{S}_{\text{CAS}}$  change are lower than actual maximum rates, but

(2) underestimates  $[\text{SO}_4^{2-}]_{\text{sw}}$  if pyrite forms in the sediment rather than the water column, which reduces  $\Delta^{34}\text{S}$  owing to limited fractionation in a semi-closed porewater system (Algeo et al., 2015). However, we infer that our  $[\text{SO}_4^{2-}]_{\text{sw}}$  estimates are robust because (1)  $\delta^{34}\text{S}_{\text{CAS}}$  variation is large, suggesting that observed rates approach actual maxima, and (2) framboid-size evidence suggests that most pyrite formed in the water column. A sensitivity test indicates that age uncertainties (e.g.,  $\pm 5$  m.y.) may modestly alter the absolute values of modeled  $[\text{SO}_4^{2-}]_{\text{sw}}$  but will not change secular patterns of  $[\text{SO}_4^{2-}]_{\text{sw}}$  variation or the relative differences in  $[\text{SO}_4^{2-}]_{\text{sw}}$  between the two study sections (see Fig. 2; see the Data Repository for details). A transient increase in  $[\text{SO}_4^{2-}]_{\text{sw}}$  during the SE is also supported by data from Oman (Halverson and Hurtgen, 2007; see the Data Repository for details).

### A Marine Sulfate Gradient during the Shuram Excursion?

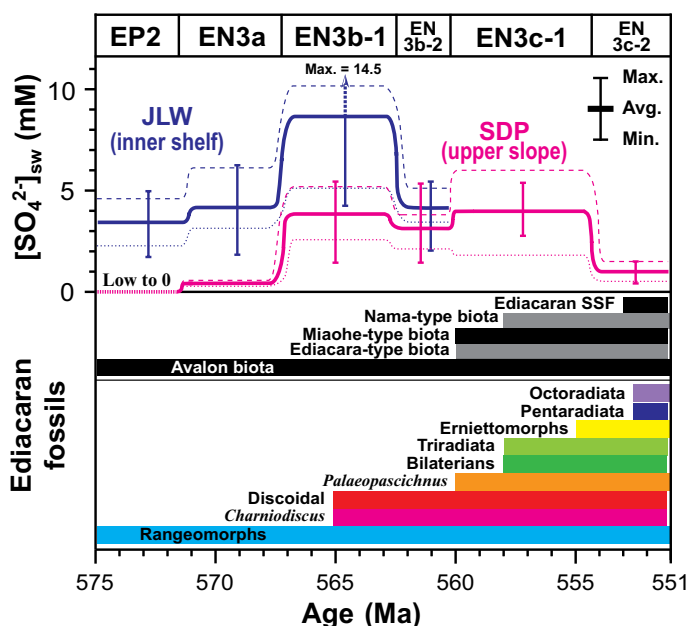
Our modeling results imply the existence of a large shelf-to-basin gradient in  $[\text{SO}_4^{2-}]_{\text{sw}}$ . This sulfate gradient cannot be attributed to restriction of Yangtze inner-shelf waters, as suggested for the middle Doushantuo Formation (Jiang et al., 2011), because persistent sulfate consumption via MSR in a restricted-marine setting would have yielded lower sulfate concentrations for JLW than for SDP, which is opposite to the observed  $[\text{SO}_4^{2-}]_{\text{sw}}$  gradient.

Development of a lateral sulfate gradient in the late Ediacaran ocean would have been possible only if the seawater sulfate residence time was similar to or shorter than the oceanic mixing time. The mixing time of the Ediacaran ocean is unknown but was likely longer than the modern mixing time of ~1–2 k.y. given evidence for widespread oceanic redox stratification and spatial heterogeneity (see the review by Bowyer et al., 2017). The residence time of Ediacaran seawater sulfate can be quantitatively estimated based on sulfate reservoir size and riverine sulfate fluxes, with shorter residence times yielded by smaller marine sulfate reservoir sizes and larger riverine fluxes. A simple linear response system model (Figs. DR3 and DR4; see the Data Repository for model details) shows that a seawater sulfate residence time of <2 k.y. is possible given average global  $[\text{SO}_4^{2-}]_{\text{sw}}$  of <0.1 to <0.3 mM and a riverine sulfate flux >20× to >60× the modern flux.

The conditions for a short seawater sulfate residence time may have been met during the SE. Earlier studies have inferred  $[\text{SO}_4^{2-}]_{\text{sw}}$  of <2 mM for shallow carbonate platforms prior to the SE (e.g., Loyd et al., 2012; but cf. Halverson and Hurtgen, 2007), and our  $[\text{SO}_4^{2-}]_{\text{sw}}$  estimate for the SE is <3 mM in distal areas beyond the slope SDP section (Fig. 2). Further, riverine sulfate weathering fluxes may have been greatly elevated during the SE, as suggested by a transient increase in modeled  $[\text{SO}_4^{2-}]_{\text{sw}}$  (Fig. 2) and increases in marine carbonate  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios from <0.708 to >0.709 (Sawaki et al., 2010; Li et al., 2017). Although accurate estimates of  $[\text{SO}_4^{2-}]_{\text{sw}}$  and sulfate weathering fluxes are lacking, the considerations above support a residence time for seawater sulfate during the SE that was potentially shorter than the contemporaneous oceanic mixing time.

### Implications for Ediacaran Oceanic Oxygenation, Shuram Excursion, and Ediacaran Biota

Our results demonstrate a transient increase in  $[\text{SO}_4^{2-}]_{\text{sw}}$  and development of a seawater sulfate gradient across the Yangtze Platform, which suggest transient oxidation of shelf seas during the SE. This inference mirrors the multiple, transient oceanic oxygenation events suggested recently for Ediacaran–early Cambrian oceans (Sahoo et al., 2016). Coupled variation of modeled  $[\text{SO}_4^{2-}]_{\text{sw}}$  with  $\delta^{13}\text{C}_{\text{carb}}$  in the two study sections supports the link between rising oxygen levels, enhanced sulfate weathering fluxes, transient increases of  $[\text{SO}_4^{2-}]_{\text{sw}}$ , and concurrent oxidation of a reduced carbon reservoir through MSR, making the last-named process the mostly likely cause of the SE. Given spatial variability in marine sulfate concentrations, we predict a corresponding pattern of  $\delta^{13}\text{C}_{\text{carb}}$  heterogeneity during the SE. This prediction is consistent with  $\delta^{13}\text{C}_{\text{carb}}$  variability in South China and with heterogeneous oxidation of oceanic reduced carbon as recently proposed by Li et al. (2017). However, our findings are also consistent with weathering hypotheses for the SE, in which enhanced



**Figure 2.** Variation in seawater sulfate concentrations ( $[\text{SO}_4^{2-}]_{\text{sw}}$ ) during the late Ediacaran Shuram Excursion at Jiulongwan (JLW) and Siduping (SDP) sections in South China and coeval global fossil records. C-isotope intervals (Ediacaran positive excursion 2 [EP2] to Ediacaran negative excursion 3 [EN3c-2]) are as in Figure 1.  $[\text{SO}_4^{2-}]_{\text{sw}}$  (solid lines) was calculated per “rate method” of Algeo et al. (2015), using average  $\Delta^{34}\text{S}$  for time bins based on C-isotope intervals (top). EP2 at SDP yielded  $[\text{SO}_4^{2-}]_{\text{sw}}$  of ~0 mM owing to  $\Delta^{34}\text{S} < 0\text{‰}$ , and  $[\text{SO}_4^{2-}]_{\text{sw}}$  is not shown for EN3c at JLW due to low sample total inorganic carbon content (<3%). Results of sensitivity test for age model uncertainties are shown by dashed lines: shifting age anchor points at 575 and 560 Ma by  $-5$  m.y. and  $+5$  m.y. leads to higher and lower  $[\text{SO}_4^{2-}]_{\text{sw}}$  estimates, respectively, relative to baseline values (solid lines); note that these estimates are plotted strictly against carbon-isotope intervals at top instead of time scale at bottom. Fossil data are from Xiao and Laflamme (2009) and Grazhdankin (2004). Max., Avg., Min.—maximum, average, minimum; SSF—small shelly fauna.

oxidation of sedimentary organic carbon and sulfides on land led to more  $^{13}\text{C}$ -depleted marine carbonates and higher  $[\text{SO}_4^{2-}]_{\text{sw}}$  in proximal than in distal shelf areas (e.g., Kaufman et al., 2007). Thus, more work will be needed to test these different oxidation models.

The transient shelf oxidation event during the SE may have contributed to the evolution and diversification of larger, more complex, and more active animals during the late Ediacaran (Fig. 2). The interval ca. 565 Ma was marked by modest increases in biodiversity, including the appearance of *Charniodiscus*, discoidal forms, and *Palaeopascichnus*, as well as the first evidence of animal motility (Liu et al., 2010). The interval ca. 558–555 Ma witnessed a large increase in biodiversity, including the appearance of late rangeomorphs (e.g., *Rangia*) and early members of the erniettomorph, triradial, and bilaterian clades, as well as forms of uncertain affinity such as *Dickinsonia*. These transitions were global, occurring simultaneously in geographically separated late Ediacaran assemblages, e.g., the Ediacara (South Australia), Nama (southwestern Africa), and Miaohu faunas (South China) (Grazhdankin, 2004; Xiao and Laflamme, 2009). Potential linkage of these biotic events to concurrent marine-shelf oxidation implies that a tight biosphere-environment co-evolutionary coupling existed in shallow-marine habitats during the Ediacaran.

## CONCLUSIONS

Modeling of the late Ediacaran Shuram Excursion (SE) based on paired  $\delta^{34}\text{S}_{\text{CAS}}-\delta^{34}\text{S}_{\text{py}}$  data from the inner-shelf Jiulongwan and upper-slope Siduping sections (South China) demonstrates a significant increase in  $[\text{SO}_4^{2-}]_{\text{sw}}$  toward the peak of the SE and the existence of a lateral sulfate gradient across the Yangtze Platform. These developments likely reflect a seawater sulfate residence time shorter than the contemporaneous oceanic mixing time in the stratified and sulfate-poor late Ediacaran ocean. These findings are consistent with a transient marine-shelf oxidation event during the SE, placing mechanistic constraints on possible drivers of extreme isotopic perturbations and early metazoan diversification during a critical period in Earth history.

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