Sulfur and mercury isotopic evidence for a causal link between LIP emissions and trilobite extinction

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Abstract

The first major mass extinction of trilobites occurred at the transition from Cambrian Series 2 (CS2) to Miaolingian (M) and coincided with a large marine transgression and volcanic eruptions of a large igneous province (LIP). Understanding the causal links between these events is important in deciphering environmental changes and the evolution of life at that time.

This paper presents S-Hg-C isotopic and Fe speciation data for calcareous shales from the CS2-M Yangliugang Formation in the Dongjin section, South China. In the lower part of this section (Interval I), sulfate (δ34SCAS) and pyrite (δ34SPy) in calcareous shales vary little, with Δ34S values from -4.2 to +8.3‰; they also have high FeHR/FeT ratios from 0.5 to 0.66, that are indicative of a low SO42- content in anoxic seawater. Calcareous shales from Interval I display at least two Hg/TOC peaks (up to 207 ppb/wt%), coincident with volcanic eruptions associated with the ca. 510 Ma Kalkarindji LIP in Australia. In the middle part of the Dongjin section (Interval II), calcareous shales display negative excursions of Δ199Hg values, δ34SPy values and FeHR/FeT ratios, which were likely led by a large terrestrial input into a marginal basin from where Interval II deposited. Calcareous shales in the upper part of the section (Interval III)contain pyrite framboids with a mean diameter of <4 μm and high ratios of FeHR/FeT (>0.82) and FePy/FeHR (>0.78), indicating an euxinic depositional environment. They also record negative excursions of δ13C and δ202Hg values (as low as -3.05‰ and -1.68‰, respectively), providing evidence for the influence of ocean upwelling. The negative shift of δ13C values in the Dongjin section was temporally comparable to the C isotope excursions that coincided with the Redlichiid-Olenellid Extinction (ROECE) event. We conclude that volcanic gas emissions of the ca. 510 Ma Kalkarindji LIP greatly enhanced the continental erosion rate, leading to high...

terrestrial \( \text{SO}_4^{2-} \) input and accumulation of \( \text{H}_2\text{S} \) in deep marginal basins at the end of CS\(_2\). The subsequent marine upwelling (>506 Ma) brought anoxic/euxinic seawaters into the continental shelf, contributing to the mass extinction of Redlichiid and Olenellid.

**Keywords:** Hg-S-C isotopes, Pyrite, Cambrian Series 2, Miaolingian, Calcareous shales, Nanhua Basin

1 **Introduction**

The Cambrian was an important period in Earth's history marked by a sudden appearance of most major animal phyla (Paterson et al., 2019). Trilobites, one of the earliest known groups of arthropods, appeared at the beginning of Cambrian Series 2 (CS\(_2\); 521–506 Ma) and diversified rapidly with oceanic oxidation (Karlstrom et al., 2020; Paterson et al., 2019). The Redlichiid and Olebellid, two of three major trilobite taxa in CS\(_2\) (Paradoxidids being the other taxon), suddenly disappeared at the CS\(_2\)-Miaolingian (CS\(_2\)-M) transition, roughly coeval with a globally recognizable negative carbon isotope excursion (ROECE) (Lin et al., 2019; Sundberg et al., 2020). Eruptions of flood basalts in the ca. 510 Ma Kalkarindji large igneous province (LIP) (Australia) (Fig. 1a) have long been regarded as an important trigger for this biotic crisis, because they were coincident with the trilobite extinction and might have induced ocean anoxia at the CS\(_2\)-M transition (Faggetter et al., 2019; Hough et al., 2006; Jourdan et al., 2014; Zhang et al., 2015). Recent chronostratigraphic research, however, has advanced the time of extinction from ca. 509 Ma to ca. 506 Ma (Karlstrom et al., 2020), placing doubt on a direct link between the mass extinction and the ca. 510 Ma Kalkarindji LIP.

The sulfur isotopic composition of marine sediments is a sensitive indicator of ocean sulfate concentration and redox state (Canfield and Farquhar, 2009; Fike et al., 2015; Gomes...
Cambrian Series 2 and Miaolingian sediments generally have variable $\delta^{34}$S$_{\text{sulfate}}$ values (0 to $>+$45‰) recorded in gypsum, calcite, dolomite, and apatite (Hough et al., 2006; Kampschulte and Strauss, 2004; Wotte et al., 2012b), and positive $\delta^{34}$S$_{\text{Py}}$ values (0 to $>+$30‰) (Guo et al., 2014; Loyd et al., 2012; Wotte et al., 2012b). The low $\Delta^{34}$S values ($\delta^{34}$S$_{\text{sulfate}}$ – $\delta^{34}$S$_{\text{Py}}$) of CS$_2$-M sediments suggest that the coeval seawater sulfate concentration was low (<2.0 mM; Loyd et al., 2012). A negative shift in $\delta^{34}$S$_{\text{Py}}$ values (about -10‰) occurred before the $\delta^{13}$C excursion (ROECE) (Guo et al., 2010; Guo et al., 2014) and is recognized globally, e.g., in the Wuliu-Zengjiayan and Jianshan sections, South China, the Genestosa and Cre´menes sections, Spain, and the Carro Rajon section, Mexico (Guo et al., 2014; Loyd et al., 2012; Wotte et al., 2012b). However, owing to the low abundance of pyrite in these sections, systematic S isotopic studies, based on the mode of occurrence of pyrite, have not been carried out, leading to a poor understanding of the reason for this negative shift of $\delta^{34}$S$_{\text{Py}}$ values prior to the mass extinction.

Mercury (Hg) concentrations, the ratios of Hg to total organic carbon (Hg/TOC ratios), and Hg isotopes have recently been developed as new proxies for investigating mass extinction, large-scale volcanism, and anoxic oceanic events in Earth’s history (e.g., Grasby et al., 2019). Anomalously high Hg concentrations and Hg/TOC ratios have been observed in marine sediments associated with all of the ‘big five’ Phanerozoic mass extinctions, implying that LIP events may contribute to mass extinctions (Grasby et al., 2019). Extensive Hg emission during LIP events increases the input of Hg to the ocean through (1) directly increasing atmospheric Hg deposition (Grasby et al., 2017; Thibodeau et al., 2016) and (2) inducing large-scale surface weathering that causes enhanced watershed runoff of soil Hg (Grasby et al., 2017; Shen et al.,...
Mercury isotopes, especially their mass-independent fractionation (MIF) signature, provide constraints on causes of Hg anomalies from atmospheric deposition or soil erosion (Blum et al., 2014; Grasby et al., 2019; Them et al., 2019). Recently, Hg anomalies have been detected in sediments deposited at or before the CS2-M boundary in the Great Basin (Western USA) (Faggetter et al., 2019). Owing to the lack of systematic Hg isotopic data, however, it is unclear whether these Hg anomalies resulted from volcanic emissions or were due to other causes.

The Nanhua Basin in South China was one of the main depositional sites of marine sediments during the Cambrian (Fig. 1b) (Wang and Li, 2003; Yao and Li, 2016). The Yangliugang Formation in the eastern part of the Nanhua Basin is a time-equivalent of the Kaili Formation in the Wuliu-Zengjiayan section, a Global Boundary Stratotype Section and Point (GSSP) for the boundary between the Cambrian Series 2 and the Miaolingian Series (Chang et al., 2019; Zhao et al., 2019). Calcareous shales from the CS2-M Yangliugang Formation in the Dongjin section (N 29°01′09.9″; E 114°18′13.7″), Jiangxi Province, were deposited in a slope-basin environment (Fig. 1) (Zhang et al., 2008). They are characterized by relatively high abundances of pyrite, calcite, and organic matter (Fig. 2). In this study, calcareous shales from the Dongjin section were systematically analyzed for their S-Hg-C isotopic compositions and Fe speciation. Using these data and previous S-C data from the Wuliu-Zengjiayan section and Hg-S-C from sections in other parts of the world, this paper aims to shed light on the linkages between marine redox state, mass extinction, and the volcanic eruption of LIPs during the later stages of the ‘Cambrian explosion’.

2 Geological setting
The Nanhua Basin in the South China Craton was opened after the amalgamation of the Yangtze and Cathaysia Blocks at ca. 820 Ma and closed during the Ordovician-Silurian orogeny (Wang and Li, 2003; Yao and Li, 2016). It is widely accepted that the Nanhua Basin was well-connected to the open ocean from the Cambrian Terreneuvian to the Miaolingian Epoch, based on the similarity of the carbonate carbon isotopic (δ^{13}C) signatures (Guo et al., 2014; Lin et al., 2019) and animal fauna (Hughes, 2016; Lin et al., 2019; Paterson et al., 2019) of South China to those of coeval marginal basins in other cratons. From the paleogeography and stratigraphy of the CS_{2}-M transition, the Nanhua Basin has been subdivided into clastic platform, carbonate platform, carbonate basin, and slope basin facies (Zhang et al., 2008). The Wuliu-Zengjiayan section (GSSP) was located in the shale facies of the slope basin in an overall oxic-suboxic depositional environment (Fig. 1b) (Guo et al., 2014). The boundary between the Cambrian Series 2 and the Miaolingian Series is marked by the first appearance of Oryctocephalus Indicus in the CS_{2}-M Kaili Formation at ca. 506 Ma (Karlstrom et al., 2020; Sundberg et al., 2020; Zhao et al., 2019), which was coincident with the last appearance datum of Redlichiids in South China (Lin et al., 2019; Sundberg et al., 2020).

A continuous Cambrian succession outcrops in Xiushui county, Jiangxi province, South China (see Supplementary Figure S1 for a regional geological map). The early Cambrian Wangyinpu Formation at the base of this succession, which consists of black shales with cherty interlayers and phosphoric nodules, is correlative to the lower Niutitang Formation in SW China (Liu et al., 2019). This formation is overlain by black shales of the Guanyintang Formation and, in turn, the CS_{2}-M Yangliugang Formation with thickness of 180-310 m. The Yangliugang Formation is dominated by argillaceous limestones, calcareous shales and
siliciclastic sedimentary rocks and is overlain by siltstones of the late Cambrian Huayansi and Xiyangshan Formations (Chang et al., 2019; Ju, 1989). Recently, a negative excursion of δ13C has been recognized in the lower part of the Yangliugang Formation in the Xuancheng section, comparable to the global ROECE excursion at the CS2-M transition (ca. 506 Ma) (Chang et al., 2019). Ptychagnostus gibbus first appeared in the middle part of the Yangliugang Formation (Ju, 1989; Peng et al., 2012), marking the transition from the Wuliu Stage to the Drumian Stage at 504.5 Ma (Zhu et al., 2019).

In the Dongjin section, Xiushui county, the lower part of the Yangliugang Formation (ca. 38 m) is well exposed, and the rocks are dominated by organic-rich (ca. 1 wt% TOC) argillaceous limestones and calcareous shales (the term calcareous shale is used hereafter to refer to argillaceous limestone and calcareous shale) (Figs. 2 and 3a) that conformably overlie the black shales of the early Cambrian Guanyintang Formation. The calcareous shale successions have been subdivided into three intervals based on the nature and distribution of pyrite in the rocks. Calcareous shales from the lower 11 m of the Dongjin section (Interval I) contain layers of pyrite about 2 cm apart and nodular pyrite aggregates (Figs. 2a, b and 3b). In the middle part of this section (Interval II), the abundance of nodular pyrite aggregates decreases rapidly (Figs. 2c and d), and the distance between adjacent pyrite layers increases to > 10 cm. The middle part of Interval II was covered by soil and plant (about 3.5 m in thickness), and was therefore not accessible for sampling. Calcareous shales from Interval III (top 8 m) are rich in pyrite, the content of which increases abruptly to > 5 vol% from field observations and hand specimen estimates (Figs. 2c and e).

3 Sampling and analyses
A total of 38 calcareous shale samples were collected from the Dongjin section with a resolution of one sample per meter for Hg-S-C-Fe-trace element geochemical/isotopic analyses. Fourteen of the samples are from the lower part of Interval II and five samples are from the upper part of Interval II. Detailed descriptions of the analytical methods are available in Supplementary Note 1. A brief description of these methods is provided here.

Morphological data for pyrite were collected from polished thin sections, using a Hitachi S-3400N variable pressure scanning electron microscope (SEM) at the Electron Microscope Unit, the University of Hong Kong. In-situ S isotope analyses of pyrite were performed on thin sections (>100 μm in thickness) using a Nu Plasma HR multi-collector inductively coupled plasma mass spectrometer and a Photon Machine Analyte G2 laser microprobe (MC-LA-ICPMS), both at the Geological Survey of Finland in Espoo. Nodular pyrite aggregates in samples from Interval I and II have δ\(^{34}\)S\(_{\text{Py}}\) values that are significantly higher than those of disseminated pyrite (Table S1), indicating that the nodular pyrite did not form during sediment deposition or early diagenesis. This pyrite was therefore removed before powdering for bulk rock analysis.

Approximately 500 g of the remaining rock was ground with an agate mortar and pestle for subsequent extraction of H\(_2\)S from the disseminated pyrite and extraction of sulfate from the carbonates. Disseminated pyrite was extracted using the chromium reduction method, in which the powders were reacted with 50 ml of 1 M CrCl\(_2\) and 20 ml of 10 M HCl in a N\(_2\) atmosphere (Canfield et al., 1986). To eliminate non-CAS compounds and conduct the final extraction of CAS, we used a HCl–BaCl\(_2\) procedure similar to that described in Wotte et al. (2012a). Approximately 100 μg BaSO\(_4\) (for CAS) or Ag\(_2\)S (for pyrite separates) was measured...
out for analysis of their sulfur isotopic composition using a Thermo Finnigan Delta Plus mass
spectrometer connected to an Elemental Analyzer. Carbon and oxygen isotope compositions
($\delta^{13}$C$_{carb}$ and $\delta^{18}$O$_{carb}$) of calcareous shales were determined using a Thermo Fisher Scientific
carbonate-preparation device and a Gas Bench II connected to a Delta Plus XL isotope ratio
mass spectrometer (IRMS) that was operated in continuous He flow mode, at the Institute of
Geochemistry, Chinese Academy of Sciences, Guiyang, China. The CO$_2$ was extracted from
carbonates with 100% phosphoric acid at 70 °C for calcite and 90 °C for dolomite. The stable
C and O isotope ratios are reported in delta (δ) notation as the per mil (‰) deviation relative to
the Vienna Pee Dee belemnite (V-PDB) standard. The analytical reproducibility estimated from
replicate analyses of the laboratory standards, Carrara marble, and Binn dolomite, is better than
±0.05‰ for $\delta^{13}$C and ±0.1‰ for $\delta^{18}$O.

We measured the concentration of Fe in four highly reactive iron phases (Fe$_{HR}$): pyrite
(Fe$_{Py}$), carbonate (Fe$_{carb}$), ferric oxide (Fe$_{ox}$) and magnetite (Fe$_{mag}$), and the total iron content
(Fe$_T$). The Fe$_{Py}$ contents were determined using the chromous chloride technique of Canfield
et al. (1986), in which the sequential extraction procedure of Poulton and Canfield (2005) was
used to analyze the other highly reactive iron phases, specifically Fe$_{carb}$, Fe$_{ox}$ and Fe$_{mag}$. All the
solutions were analyzed for their respective iron contents using an atomic absorption
spectrometer (AAS), with an RSD of <5% for all stages. The Fe$_T$ contents were determined
using an Olympus DP-6000 hand-held X-ray fluorescence spectrocope (HH-XRF) with a Rh
tube, as described in Lenniger et al. (2014). The analytical errors for Fe$_T$ are better than 2%
(Jin et al., 2016; Lenniger et al., 2014).

The TC-TOC-TS contents were measured using a Multi EA 4000 carbon/sulfur analyzer
with a high-temperature furnace and acidification module (Eltra, Germany) at the China University of Geoscience (Wuhan). Analytical errors for TC-TOC-TS were ± 0.1 wt%, based on analyses of carbonate standard, AR4007 (Alpha, USA). The TIC (total inorganic carbon) content was calculated by subtracting the TOC from the TC. Concentrations of Mn and Sr were analyzed using a Perkin-Elmer ELAN 6000 inductively-coupled plasma source mass spectrometer (ICP-MS) at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. The analytical precision for Mn and Sr was better than 3%.

Total Hg concentrations were determined in the Institute of Geochemistry, Chinese Academy of Sciences, using a LUMEX RA915F automatic mercury vapor analyzer, which has a detection limit of 0.5 ng g\(^{-1}\). Mercury isotope ratios were measured using the methods described in Geng et al. (2018). About 0.2-0.5 g of sample powder was digested using 5 mL of aqua regia in a water bath (95 °C for 6 hours). Certified reference materials (NIST SRM 2711, Montana soil) were prepared for analysis after every 13 samples, and digested in the same way as the samples. The samples were analyzed using a Neptune Plus multiple collector inductively coupled plasma mass spectrometer (Thermo Electron Corp, Bremen, Germany) at the University Research Facility in Chemical and Environmental Analysis (UCEA) at the Hong Kong Polytechnic University. Mercury isotopic compositions were expressed as \(\delta\) and \(\Delta\) values, in units of per mil (‰) following the convention recommended by Bergquist and Blum (2007).

**4 Analytical results**

**4.1 Morphology and *in-situ* \(\delta^{34}\)S values of pyrite**

Calcereous shales from the Dongjin section consist mainly of calcite with TIC from 2.1
to 10.7 wt%, organic matter with TOC from 0.2 to 3.3 wt%, pyrite with TS from 0.1 to 6.0 wt%, and silicate minerals dominated by quartz and clays (Fig. 3). In calcareous shales from Interval I and II, pyrite occurs as disseminations and nodular aggregates. Pyrite grains in nodular aggregates are large (50-100 μm in diameter) and have extremely large positive δ³⁴S<sub>Py</sub> values, ranging from +37.6 to +68.1‰, with an average of +60‰ (Fig. 3b; Table S1). In Interval I, disseminated pyrite comprises 6–12 vol% euhedral grains with diameters ranging from 3 μm to 25 μm and 88–94 vol% framboids with diameters ranging from 1 μm to 25.5 μm (5 μm on average) (Figs. 3c, e, f and 4; Table S2). The δ³⁴S<sub>Py</sub> values of the two pyrite varieties (not distinguished) range from +8.8 to +21.4‰ (ca. +15.9‰ on average) (Figs. 3c; Table S1). In Interval II, pyrite framboids represent 85–92 vol% of the pyrite and their diameters range from 1 to 18.6 μm with an average of 5.3 μm (Table S2). The δ³⁴S<sub>Py</sub> values vary from +3.2 to +25.7‰ (+10.2‰ on average).

Pyrite in Interval III accounts for >5 vol% of the rock (Fig. 2), and occurs mainly as large sub-euhedral to euhedral crystals (>50 μm in diameter) and small pyrite framboids (< 5 μm) (Figs. 3 and 4; Table S2). The δ³⁴S<sub>Py</sub> values of the large pyrite grains ranges from +13.8 to +31.0‰. Reliable in-situ δ³⁴S<sub>Py</sub> values of pyrite framboids could not be acquired by MC-LA-ICPMS due to their small grain-size.

4.2 Bulk rock elemental and isotopic compositions

Calcareous shales from Interval I have TS values from 0.4 to 1.7 wt%, and disseminated pyrite separates have δ³⁴S<sub>Py</sub> values ranging from +5.0 to +21.0‰ (+14.8‰ on average) (Fig. 5a; Table S3). These shales are rich in organic matter with TOC contents from 0.6 to 3.3 wt%,
averaging at 1.6 wt%, and TIC contents from 1.1 to 7.6 wt%, averaging at 4.1 wt% (Fig. 5a; Table S3). They have relatively constant $\delta^{13}C$ values ranging from -0.98 to -0.79‰, $\delta^{18}O$ values from -11.2 to -10.1‰ and Mn/Sr ratios from 0.38 to 2.54 (Fig. 4). Samples with TS <1 wt% and TIC >3.5 wt% have CAS contents from 66 to 155 ppm and $\delta^{34}S_{CAS}$ values from +11.9 to +24.6‰ (average +16.7‰). The $\Delta^{34}S$ ($\delta^{34}S_{CAS} - \delta^{34}S_{Py}$) values in these samples vary from -4.2 to +8.3‰ with an average of +0.8‰. The $Hg$ content of the bulk rock in Interval I ranges from 31.3 to 137 ppb, which is higher than those in the other two intervals (Table S3). The $\delta^{202}Hg$ values in this interval are relatively constant (-1.08 to -0.74‰), whereas the $\Delta^{199}Hg$ values increase upwards from -0.16 to 0.00‰. The samples have high Fe$_T$ contents, ranging from 1.6 to 3.0 wt%. Their Fe$_{HR}$/Fe$_T$ and Fe$_{py}$/Fe$_{HR}$ values range from 0.5 to 0.66 and from 0.28 to 0.90, respectively (Figs. 4 and 5b; Table S3).

The calcareous shales from Interval II have relatively low contents of disseminated pyrite with an average TS of 0.63 wt% and display a gradual $\delta^{34}S_{Py}$ shift upwards from +16.1 to -2‰. They have a TOC content of 0.2-1.6 wt%, a TIC content of 1.2-10.3 wt%, and $\delta^{13}C$ and $\delta^{18}O$ carbonate values of -0.95 to -0.53‰ and -11.2 to -9.8‰, respectively. The CAS contents are in the range 61 to 184 ppm and their $\delta^{34}S_{CAS}$ values are +11.7 to +21‰ with an average of +16.1‰ (Table S3). The $\Delta^{34}S$ ($\delta^{34}S_{CAS} - \delta^{34}S_{Py}$) values increase upwards from +3 to +10‰, with an average of +5.7‰ (Table S3). The bulk rock Mn/Sr ratio ranges from 0.2 to 1.55. The Hg content of these shales is relatively constant (ca. 30 ppb), the $\Delta^{199}Hg$ values vary from slightly negative to near zero (-0.11 to +0.02‰) and the $\delta^{202}Hg$ values (-1.0 to -0.5‰) are similar to those of Interval I. The Fe$_T$ contents ranges from 0.6 to 2.8 wt% (the average is 1.90 wt%) and the Fe$_{HR}$/Fe$_T$ and Fe$_{py}$/Fe$_{HR}$ ratios vary from 0.25 to 0.73 (the average is 0.53) and from 0.26 to
0.75 (the average is 0.49), respectively (Figs. 4 and 5b; Table S3).

In interval III, calcareous shales have high TS contents (3.0-6.0 wt%), relatively low TOC contents (0.7-1.3 wt%) and variable Hg contents (5.9-52 ppb). They have TIC contents from 2.8 to 4.8 wt%, Mn/Sr ratios from 0.3 to 1.4, and constant δ¹⁸O carbonate values (-11.6 to -10.1‰). In the basal part of this interval, the δ¹³C values of the shales decrease sharply from -0.80 to -3.05‰ (Fig. 4) and are coupled to a negative shift in δ²⁰²Hg from -1.05 to -1.68‰. The Δ₁⁹⁹Hg values range from -0.07 to +0.06‰, indicating the absence of mass-independent fractionation (Table S3). The Feₚ contents, Feₚ/Feₜ ratios, and Feₚ/Feₚ ratios are all high, ranging from 3.35 to 4.38 wt%, from 0.82 to 0.93, and from 0.78 to 0.85, respectively (Figs. 4 and 5b; Table S3).

5 Discussion

5.1 The redox state and sulfate content of the ocean at the CS₂-M transition

5.1.1 The anoxic state and low sulfate content of the Dongjin section during Interval I

The iron speciation method, which determines the nature of ‘highly-reactive’ iron (Feₚ) in fine-grained sediments, has been widely used to distinguish oxic, ferruginous, and euxinic conditions in siliciclastic rocks and in carbonate rocks with >0.5 wt% Feₚ (Clarkson et al., 2014; Poulton and Canfield, 2011). Anoxic sediments have Feₚ/Feₜ ratios of >0.38 through the incorporation/precipitation of Feₚ from the anoxic water column. Under anoxic and sulfidic (euxinic) conditions, Feₚ is converted to Feₚ through its reaction with H₂S to form pyrite, resulting in Feₚ/Feₚ ratios of >0.7–0.8 (Poulton and Canfield, 2011). All samples investigated in this study have Feₚ contents >0.5 wt% (Table S3). Calcareous shales from Interval I have an
average Fe_{HR}/Fe_T ratio of 0.6 and the same average Fe_{Py}/Fe_{HR} ratio (0.6), which are indicative of an overall anoxic depositional environment low in H_2S that contains excess Fe (Figs. 4 and 5b; Table S3). Inadequate H_2S production under anoxic conditions could be caused by a limited supply of organic matter (reducer) or sulfate (reactant), or both (Poulton and Canfield, 2011; Wilkin and Barnes, 1996). Given that the TOC values represent preserved organic matter, the high TOC contents (ca. 1.6 wt%) in these calcareous shales preclude the possibility of limited organic matter supply suggesting, instead, a low sulfate supply and anoxic conditions in the water column above the Dongjin section.

The moderately negative to moderately positive Δ^{34}S values (-4.2 to +8.3‰) of calcareous shales from Interval I place additional constraints on the end-CS_2 sulfur cycle (Table S3). Carbonate-associated sulfate (CAS) is the trace quantity of sulfate that replaces carbonate ions structurally in marine carbonate and can be used to represent the δ^{34}S value of sulfate in the water column (cf., Wotte et al., 2012a). The reduction of sulfate is promoted strongly by microbes (sulfate-reducing bacteria), which favor the lighter, more weakly bonded isotope of sulfur (^{32}S) (Kasten et al., 1998). The magnitude of Δ^{34}S (δ^{34}S_{CAS} - δ^{34}S_{Py}) values between sulfate in seawater and pyrite preserved in sedimentary rocks has been widely utilized to reconstruct ancient marine sulfate levels (e.g., Loyd et al., 2012; Gomes and Hurtgen, 2015).

It has been estimated that a ca. 20–70‰ fractionation between sulfate and sulfide can be achieved in an aqueous system with a sulfate content of >0.2 mM (Canfield, 2001; Habicht et al., 2002; Sim et al., 2011), and that Δ^{34}S would be larger if the recycling of sulfur species, e.g., re-oxidation and disproportionation, in the water column were considered (Fike et al., 2015). This fractionation, however, is suppressed at a low sulfate content, approaching 0‰ at sulfate...
levels below 0.2 mM (Bradley et al., 2016; Habicht et al., 2002), because that the size of the sulfate reservoir is sufficiently small that Rayleigh fractionation affects the S isotope equilibrium.

In Interval I, separates of disseminated pyrite grains from the calcareous shales have $\delta^{34}$S$_{py}$ values from +5 to +21.0‰ (+14.8‰ on average), consistent with in-situ analyses of individual disseminated pyrite grains, which yielded an average $\delta^{34}$S$_{py}$ value of +15.9‰ (Table S1). The proportion of CAS extracted from these calcareous shales is low and has $\delta^{34}$S$_{CAS}$ values varying from +11.9 to +24.6‰. Values of $\delta^{34}$S$_{CAS}$ can be modified by the oxidation of pyrite during sample preparation. In the present study, this contamination was minimized by avoiding the usage of oxidants, and rapidly dissolving the carbonate slurry without drying during the extraction (Wotte et al., 2012a). To further minimize the influence of this effect on the $\delta^{34}$S$_{CAS}$ values, only samples with >3.5 wt% TIC and <1 wt% TS were considered further (Li et al., 2017), and these returned a very low standard deviation (<1.4‰) for duplicate analyses (Table S3) (see Supplementary Note 2 for a more detailed discussion of the reliability of the $\delta^{34}$S$_{CAS}$ data). The $\Delta^{34}$S values in our samples from Interval I are in the range from -4.2 to +8.4‰, which is low and indicative of a sulfate-depleted end-CS$_2$ ocean (Fig. 4). Low $\Delta^{34}$S values are also preserved in marine sediments deposited in end-CS$_2$ marginal basins elsewhere, for example, from -22.9 to -0.2‰ in the Carro Rajon section, Mexico (Loyd et al., 2012) and from -0.7 to +15.2‰ in the Cre’menes section, Spain (Wotte et al., 2012b). The results of these studies support our interpretation that the SO$_4^{2-}$ concentration was very low in the end-CS$_2$ ocean (i.e., <2.0 mM; Loyd et al., 2012)).
5.1.2 A less anoxic depositional environment with increased seawater SO$_4^{2-}$ in Interval II

Calcareous shales from Interval II have Fe$_T$ contents varying from 0.6 to 2.8 wt%. There is an obvious upwards decrease in Fe$_{HR}$/Fe$_T$ ratios from 0.73 to 0.25 without obvious stratigraphic variation in the Fe$_{Py}$/Fe$_{HR}$ ratios of the calcareous shales from Interval II (Fig. 4). The Fe speciation and TS data, therefore, suggest a decline of Fe$_{HR}$ availability and a less anoxic depositional environment towards the late-Interval II in the Dongjin section.

The disseminated pyrite in calcareous shales from Interval II have $\delta^{34}$S$_{Py}$ values that decrease upwards stratigraphically from +16.1 to -2‰ (Fig. 4). This negative excursion of $\delta^{34}$S$_{Py}$ values at the end-CS$_2$ has been widely observed in the Wuliu-Zengjiayan and Jianshan sections, South China, in the Carro Rajon section, Mexico (Loyd et al., 2012), and in the Genestosa and Cre’menes sections, Spain (Wotte et al., 2012b) (Fig. 6). In concert with the stratigraphically upward decreasing trend of $\delta^{34}$S$_{Py}$ values, $\Delta^{34}$S values from Interval III of the Dongjin section increase upwards from +3 to +10‰ (Table S3), indicating an increase in seawater sulfate content (Loyd et al., 2012; Gomes and Hurtgen, 2015). As mentioned above, the elevated sulfate content in an aqueous system will increase the S isotopic fractionation between the pyrite precipitate and the dissolved sulfate, leading to a decrease of $\delta^{34}$S values in pyrite (Canfield, 2001; Habicht et al., 2002; Sim et al., 2011). The covariation of $\delta^{34}$S$_{Py}$ and $\Delta^{34}$S values in calcareous shales from the Dongjin section, therefore, indicate that this globally detectable negative excursion of $\delta^{34}$S$_{Py}$ values was most likely due to an increase in seawater sulfate content at the end-CS$_2$. 

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5.1.3 The sudden development of euxinic conditions during Interval III

Pyrite framboids can persist for a long time, and their size distributions have been widely used in determining whether the pyrite was deposited under euxinic or non-euxinic conditions (Wignall and Newton, 1998). It has been observed that framboids crystallized directly from H₂S-rich seawater (euxinic conditions) generally have a narrow size range with an average diameter <5 μm (Wignall and Newton, 1998). This is due to the rapid crystallization of pyrite above the sediment-water interface and limited access to H₂S and/or Fe²⁺ after burial (Wignall and Newton, 1998). In H₂S-poor seawater (oxic-anoxic), conditions favorable for the crystallization of pyrite framboids are restricted to those of pore water in sediments. Because of a variation in the time-integrated availability of Fe and S, pyrite framboids formed in pore water tend to be larger and more variable in size (Wignall and Newton, 1998; Wilkin and Barnes, 1996). In calcareous shales from Interval I and Interval II, the pyrite framboids display a large size-range, i.e., from 1 to 25.5 μm in diameter, indicating that these grains did not precipitate in euxinic seawater. The disseminated pyrite framboids in calcareous shales from Interval III have diameters from 0.5 to 7.1 μm and a mean-diameter of ca. 3.2 μm, i.e., they are similar in size to pyrite framboids forming from euxinic seawaters in the modern Black Sea (Wignall and Newton, 1998). The small grain-size and narrow size-range of pyrite framboids in shales from Interval III, therefore reflected a rapid change in the depositional environment from an anoxic to an euxinic state.

Calcareous shales from Interval III contain abundant large pyrite grains with a TS content exceeding 3.0 wt% (Fig. 4). Large pyrite grains are generally thought to precipitate and crystallize slowly from pore waters with or without frequent S-exchange with the bottom water.
In pore waters for which there is limited S exchange with seawater, continual removal of isotopically light $^{32}\text{S}$ generated by BSR would lead to an increase in $\delta^{34}\text{S}$ values during the downwards diffusion of sulfate, through Rayleigh fractionation distillation (Ries et al., 2009). Pyrite precipitated under such conditions usually has much higher $\delta^{34}\text{S}_{\text{Py}}$ values than disseminated pyrite (Jørgensen and Kasten, 2006). This is exemplified by the super-heavy (isotopically) nodular pyrite from Interval I and II, which has $\delta^{34}\text{S}_{\text{Py}}$ values of +37.6 to +68.1‰ (see further discussion in Supplementary Note 3). In contrast to the nodular pyrite in Interval I and II, the coarse-grained pyrite in Interval III has much lower $\delta^{34}\text{S}_{\text{Py}}$ values of +13.8 to +31.0‰, which are only slightly higher than those of the disseminated pyrite (-2.0 to +21.0‰; Table S3). We therefore infer that these large pyrite grains may have precipitated and grown from sulfidic pore water that was well-connected to the bottom seawater. The abundant large pyrite grains and the high TS content in calcareous shales from the Interval III are also suggestive of an euxinic depositional environment during Interval III.

The calcareous shales from the upper part of the Dongjin section also have a high Fe$_{\text{Py}}$/Fe$_{\text{HR}}$ ratio of 0.78-0.85 and a high Fe$_{\text{HR}}$/Fe$_{\text{T}}$ ratio of 0.82-0.93 (Figs. 4 and 5), features that are typical of sediments forming under euxinic conditions. To sum up, the high pyrite content, the small grain-size of pyrite framboids, and the high Fe$_{\text{Py}}$/Fe$_{\text{HR}}$ and Fe$_{\text{HR}}$/Fe$_{\text{T}}$ ratios of the calcareous shales from this interval are indicative of the sudden onset of euxinic conditions above the Dongjin section across the CS2-M transition.

5.2 Anomalous Hg due to volcanic eruptions and a marine transgression

The Hg content and Hg isotopic composition of calcareous shales from the Dongjin
section both vary stratigraphically (Fig. 4). These variations provide additional information about the changing conditions in the CS$_2$-M ocean that complement the C and S isotope data.

### 5.2.1 Volcanic eruptions revealed by Hg spikes and Hg-MIF signals

Mercury entering the ocean is readily scavenged by organic matter and transported to marine sediments (Shen et al., 2020). Anomalously high Hg concentrations and Hg/TOC ratios in marine sediments therefore provide a promising tool for identifying periods of enhanced volcanic activity (Grasby et al., 2019). Mercury concentrations in calcareous shales from Interval I in the Dongjin section are higher (70 ppb on average) than those from the other intervals in this section (34 ppb in Interval II and 27 ppb in Interval III on average). Two distinct Hg peaks are evident for the upper part of Interval I, with the highest Hg concentration reaching 136.9 ppb (Fig. 4). The Hg concentrations do not correlate with the TOC contents, and the peak Hg values are associated with high Hg/TOC ratios (as high as 207 ppb/wt%) (Figs. 5c). Therefore, organic matter drawdown was not a driver of these Hg peaks, and the enrichments of Hg were likely a result of external Hg-loading due to extensive volcanic activity (Grasby et al., 2019). It has been reported that Hg accumulation by pyrite may also lead to anomalously high Hg concentrations in sediments, e.g., in sediments deposited at the Ordovician/Silurian boundary (Shen et al., 2019). The Hg content, however, does not correlate with the TS content, and the peak Hg values are associated with high Hg/TS ratios (as high as 325 ppb/wt%) (Fig. 5d and Table S3), indicating that these enrichments of Hg were not from incorporation of Hg by sulfides (Shen et al., 2020).

Evidence of extensive volcanic activity in the upper part of Interval I is also provided by
the Hg-MIF signatures. Volcanic gas emissions are the primary source of Hg for the environment. These emissions and associated volcanic rocks display limited MIF with a mean $\Delta^{199}\text{Hg}$ value of +0.03‰, 1 SD = -0.07‰, n=14 (Moynier et al., 2020; Zambardi et al., 2009). Photochemical processes alter the MIF signals during global transportation of Hg, resulting in the negative $\Delta^{199}\text{Hg}$ of the atmospheric Hg (0) pool and the positive $\Delta^{199}\text{Hg}$ of the residual atmospheric Hg (II) pool (Blum et al., 2014). Oceans receive Hg mainly through atmospheric Hg (II) deposition, whereas soil and vegetation mainly receive Hg from atmospheric Hg (0) deposition. For this reason, seawater and marine sediments are characterized by positive $\Delta^{199}\text{Hg}$, and the terrestrial inputs by negative $\Delta^{199}\text{Hg}$ (Meng et al., 2019; Yin et al., 2015). Prior to the evolution of plants, the terrestrial Hg reservoir was probably smaller and characterized by a slightly negative $\Delta^{199}\text{Hg}$ value (Fan et al., 2020), although the actual $\Delta^{199}\text{Hg}$ value of this reservoir is not well constrained. Previous studies have shown that sediments near estuaries with a high portion of continental Hg have much lower $\Delta^{199}\text{Hg}$ values (-0.15 to +0.16‰) than those in the deep ocean (+0.21 to +0.45‰) (Yin et al., 2015). In our samples, the $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ ratio is close to unity (see Supplementary Figure S2) and is consistent with that observed during aqueous Hg (II) photoreduction. The negative $\Delta^{199}\text{Hg}$ values of calcareous shales from Interval I indicate that the Dongjin section had a terrestrial-dominant Hg source, which is consistent with a paleo-geographical reconstruction showing that the Dongjin section was located in a continental margin basin (Fig. 1). A gradual increase of $\Delta^{199}\text{Hg}$ values from -0.16‰ at the base of Interval I to 0‰ at the top of this interval suggests an increase of volcanic Hg input, given that volcanic Hg generally has a near-zero $\Delta^{199}\text{Hg}$ value (Zambardi et al., 2009). A decrease in terrestrial Hg-input might also explain the upwards increase of $\Delta^{199}\text{Hg}$ values in shales from
Interval I, but it cannot explain the Hg and Hg/TOC spikes in the upper part of this interval (Fig. 4).

Spikes in the concentration of Hg before the CS$_2$-M transition have been reported from the Emigrant Pass, Oak Springs Summit, and Ruin Wash sections, in the western Great Basin (USA) (Faggetter et al., 2019). These Hg anomalies in the USA and South China (this study) developed synchronously with the ca. 510 Ma flood basalt volcanism of the Kalkarindji province in Australia (Faggetter et al., 2019; Hough et al., 2006; Jourdan et al., 2014), indicating that there were large inputs of volcanic Hg into the regions of Laurentia and the South China Craton.

5.2.2 Enhanced SO$_4^{2-}$ flux into the end CS$_2$ ocean in the aftermath of a LIP

Throughout Earth’s history, volcanic eruptions of LIPs have led to an increase in atmospheric CO$_2$ and erosion of the continents, resulting in higher terrestrial input into the ocean that may have affected the ocean redox state and biogeochemical circulation (Grasby et al., 2017; Them et al., 2019). In calcareous shales from Interval II, there is a gradual decrease of $\Delta^{199}$Hg values from $+0.02\%$ at the base to $-0.11\%$ at the top. Volcanic emissions, as noted above, are characterized by a $\Delta^{199}$Hg value of ca. 0%, whereas terrestrial Hg is marked by negative $\Delta^{199}$Hg values. The negative shift of $\Delta^{199}$Hg values, therefore, indicates that terrestrial Hg flux into the ocean outperformed the volcanic Hg input from the atmosphere. A sharp decrease in sea-level with a larger area of the continental crust exposed and eroded might cause an enhanced terrestrial Hg input into the ocean. There are, however, no obvious lithological differences between Interval I and II in the Dongjin section and its equivalent strata in the

Wuliu-Zengjiayan section and the Jianshan section, South China (Guo et al., 2014), which argue against a major ocean regression before the ROECE event.

As mentioned earlier, lower $\delta^{34}$S<sub>Py</sub> values reflect an increased seawater SO<sub>4</sub><sup>2-</sup> content during Interval II, but the driving force for this variation is unclear. Enhanced terrestrial SO<sub>4</sub><sup>2-</sup> input from continental weathering and eruptions in the aftermath of the 510 Ma Kalkarindji LIP would be a reasonable explanation for the increased SO<sub>4</sub><sup>2-</sup> content of the oceans at the end-CS<sub>2</sub>. Moreover, the small increase in $\delta^{13}$C from -0.9 to -0.6‰ and the corresponding decrease of $\Delta^{199}$Hg values recorded in calcareous shales from Interval II are consistent with an increase of ocean productivity and net organic burial during enhanced terrestrial nutrient input.

5.2.3 Upwelling of deep H<sub>2</sub>S-rich seawater at the CS<sub>2</sub>-M transition

The abrupt increase in pyrite abundance across the boundary between Interval II and Interval III was accompanied by a negative excursion of $\delta^{13}$C and $\delta^{202}$Hg values and a slightly positive shift in $\Delta^{199}$Hg values (Fig. 4). Empirical research suggests that carbonates with Mn/Sr < 10 generally retain a primary marine C isotopic signature (Kaufman et al., 1993). In samples from Interval III, Mn/Sr ratios are < 1.5, and there is no obvious correlation among $\delta^{13}$C, $\delta^{18}$O, and Mn/Sr values (Figs. 5e, f), indicating that the temporal variation of $\delta^{13}$C might have been preserved and the negative $\delta^{13}$C values in the calcareous shales were not a result of diagenesis (Li et al., 2013). Moreover, negative excursions of $\delta^{13}$C also have been recorded in the CS<sub>2</sub>-M shales in the Wuliu-Zengjiayan, and Jianshan sections, Guizhou province, South China, where they are interpreted to reflect marine transgression and upwelling of $^{13}$C depleted seawater (Guo et al., 2010; Guo et al., 2014). The sharp sedimentological and geochemical contact
between Interval II and Interval III indicates that H$_2$S enrichment occurred rapidly. Thus, it is possible that the H$_2$S enrichment in Interval III also was caused by the upwelling of deep euxinic water during the transgression. The marine transgression would have caused the coastline to move towards the continent, resulting in less Hg input from terrestrial reservoirs, which is consistent with a small positive shift of the $\Delta^{199}$Hg values in calcareous shales from Interval III.

Mass-dependent fractionation of Hg isotopes is ubiquitous and has been used as a source tracer in many studies, particularly in cases of regular stratigraphic changes (Grasby et al., 2017). Samples from Interval I and II have a constant $\delta^{202}$Hg value of -0.76 ± 0.16‰, which is similar to that of volcanic ash and silicate rocks, which have a mean $\delta^{202}$Hg value of −0.68 ± 0.45‰ (Blum et al., 2014). In Interval III, the $\delta^{202}$Hg values decrease abruptly to -1.68‰. It has been proposed that the formation of the Hg-S bond would lead to a negative shift of -0.6‰ in the $\delta^{202}$Hg value (Foucher et al., 2013). The decrease of $\delta^{202}$Hg in calcareous shales from Interval III thus could be attributed to the increased abundance of pyrite. However, the $\delta^{202}$Hg value increases upwards to ca. -1‰, and is decoupled from the consistently high TS but, instead, is coupled with $\delta^{13}$C values in calcareous shales from Interval III (Fig. 4). This indicates that the negative excursion of $\delta^{202}$Hg might have been caused by a marine transgression rather than the precipitation of pyrite. Microbial methylation, forming monomethyl mercury (MMHg) with low $\delta^{202}$Hg values is one of the major processes leading to MDF of Hg in aqueous systems (Blum et al., 2014). Indeed, Yin et al. (2015) showed that marine sediments (in the deep ocean) have lower $\delta^{202}$Hg values than coastal sediments, which implies that upwelling deep waters can carry a substantial amount of Hg from marine to coastal regions.
Large pyrite grains from calcareous shale of Interval III have large positive $\delta^{34}$S values, i.e., from +13.8 to +31‰ (Table S1; Fig. 3d), which may reflect inheritance from deeper euxinic seawater. In modern ocean basins that receive sufficient $\text{SO}_4^{2-}$ input for pyrite formation, e.g., the modern Black Sea, the euxinic bottom waters generally have consistently high sulfate contents, negative $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ values, and stable $\Delta^{34}\text{S}$ values between $\delta^{34}\text{S}$ of sulfate from surface water and $\delta^{34}\text{S}$ of pyrite in sediments (Gomes and Hurtgen, 2015). By contrast, $\Delta^{34}\text{S}$ values in low-sulfate euxinic systems are positively correlated with sulfate concentration, leading to high $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ values in bottom euxinic water (Gomes and Hurtgen, 2015). The high $\delta^{34}\text{S}_{\text{Py}}$ values of coarse-grained pyrite in Interval III may, therefore, reflect intense sulfate reduction in basins with initially low sulfate concentration, which would have allowed a nearly quantitative reduction of sulfate and promoted high $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ values in the euxinic bottom water (Gomes and Hurtgen, 2015; Magnall et al., 2016). This is consistent with our interpretation, presented above, that terrestrial $\text{SO}_4^{2-}$ input fertilized the $\text{SO}_4^{2-}$-depleted Nanhua Basin of Interval II. The reduction of sulfate contributed to seawater $\text{H}_2\text{S}$ accumulation in the deep ocean.

### 5.3 An integrated model and implications for the trilobite crisis

Chemo-stratigraphic variations in organic-rich calcareous shales from the Dongjin section are comparable to those in the Wuliu-Zengjiayan and Jianshan sections (Guo et al., 2010; Guo et al., 2014). Pyrite in CS$_2$-M sediments from these sections has high $\delta^{34}\text{S}_{\text{Py}}$ values but displays a negative shift in $\delta^{34}\text{S}_{\text{Py}}$ values before the negative $\delta^{13}\text{C}$ excursion (Fig. 6) (Guo et al., 2010; Guo et al., 2014). In the Wuliu-Zengjiayan section, the negative $\delta^{13}\text{C}$ excursion at the base of Interval III coincided with the extinction of trilobites (Fig. 6) and defines the CS$_2$-M boundary.
These geochemical similarities of the three sections, taken in conjunction with our Hg isotopic data, allow us to propose a genetic model for the S-C-Hg biogeochemical cycle in the CS₂-M Nanhua Basin.

The early Cambrian Nanhua basin was characterized by high productivity and widespread deposition of organic-rich shales. With continuous crystallization and burial of pyrite and a limited terrestrial supply of sediment, the seawater in the Nanhua basin was depleted in SO₄²⁻ and had high δ³⁴S₀ values at the end of CS₂. Without sufficient SO₄²⁻ for oxidation of the organic matter (DOC and methane), the seawater in the Dongjin section became anoxic (Fig. 7a). The source of Hg in the calcareous shales deposited in the Dongjin section was mainly from continental erosion as shown by Δ¹⁹⁹Hg < 0‰. Eruptions of flood basalts in the Kalkarindji LIP at ca. 510 Ma interfered with the Hg cycle of the Earth’s surface system and caused an increase of Δ¹⁹⁹Hg to a near-zero value (Fig. 7a). The volcanic eruptions increased the erosion rate of the continental crust, resulting in higher terrestrial Hg and SO₄²⁻ input into the ocean. Consequently, the Δ¹⁹⁹Hg and δ³⁴S₀ values decreased in Interval II (Fig. 7b). This higher terrestrial SO₄²⁻ input led to a H₂S rich reservoir in the deeper ocean. Owing to the initially low sulfate content of the CS₂ Nanhua Basin, H₂S in the deep euxinic water had high δ³⁴S₀ values (Fig. 7b). This euxinic water upwelled into the shallow ocean during the earliest Miaolingian, leading to abundant deposition of pyrite in carbonate muds of Interval III and mass extinction of trilobites on the shelf (as in the Wuliu-Zengjianyan section) (Fig. 7c).

Geochemical changes in the Nanhua Basin were duplicated globally as discussed above. Thus, high δ³⁴S values have been reported for sulfate-bearing minerals and pyrite from CS₂-M sediments in Spain (Wotte et al., 2012b), Siberia (Kampschulte and Strauss, 2004) and
Australia (Hough et al., 2006), and inferred to record the depletion of sulfate in the CS$_2$-M ocean. Moreover, the ca. 510 Ma eruptions of the Kalkarindji LIP have been shown to be recorded by the CS$_2$-M strata in the USA (Faggetter et al., 2019). The subsequent negative excursion of $\delta^{34}$S$_{Py}$ values, likewise, has been widely documented (Fig. 6) and is coincident with a positive shift of seawater $^{87}$Sr/$^{86}$Sr ratios around the CS$_2$-M transition (Zhang et al., 2020), which also supports an increased terrestrial input after the Kalkarindji LIP. Finally, the $\delta^{13}$C negative excursion at ca. 506 Ma (Fig. 6) was globally detectable (the ROECE event), and is considered to have been caused by a marine transgression (Guo et al., 2014; Karlstrom et al., 2020; Lin et al., 2019; Sundberg et al., 2020).

Our analysis of ocean redox conditions and sulfate content provides strong evidence that changes in seawater chemistry may have been linked to a global bio-evolutionary change after the ca. 510 Ma Kalkarindji LIP that led to the extinction of Redlichiid and Olebellid. Moreover, our interpretation that upwelling of anoxic/euxinic deep seawater was the direct cause for the extinction could help explain the ~4 Ma time interval between the ca. 510 Ma Kalkarindji LIP and this event.

6 Conclusions

The CS$_2$-M ocean was characterized by low sulfate content, resulting in high $\delta^{34}$S$_{Py}$ values in the sediments. Spikes in Hg content and Hg isotopic anomalies in calcareous shales from Interval I of the Dongjin section were due to volcanic Hg loading from the flood basalt eruptions of the ca. 510 Ma Kalkarindji LIP. These extensive volcanic eruptions changed the Earth’s surface environment and led to higher rates of continental erosion and hence larger inputs of terrestrial material into the end-CS$_2$ ocean. With greater Hg and SO$_4^{2-}$ input, the
Δ¹⁹⁹Hg values of Interval II decreased, as did the δ³⁴S_{py} values of the disseminated pyrite. Hydrogen sulfide with high δ³⁴S values accumulated in the deep water and was upwelled into the shallow ocean during a marine transgression at the CS₂-M boundary. This upwelling of deep euxinic water drove the accumulation of pyrite and a negative excursion of δ¹³C values in calcareous shales from Interval III and was likely responsible for the extinction of Redlichiid and Oulebellid.

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Figure captions

Figure 1. (A) Geological setting of the Nanhua Basin, South China (A) Global paleogeography of the 550-510 Ma Gondwana, showing the location of South China and the 510 Ma Kalkarindji LIP (adapted from Faggetter et al. (2019)). (B) A simplified paleogeographic map of the Nanhua Basin during the CS2-M transition, showing the three major facies identified by Zhang et al. (2008) and the locations of the Wuliu-Zengjiayan (yellow triangle) and the Dongjin (red triangle) sections.

Figure 2. Stratigraphy and photographs of the Dongjin section, South China. (A) and (B) nodular pyrite aggregates in Interval I; (C) and (D) the boundary between Interval II and Interval III; (E) pyrite layers in calcareous shales from Interval III; (F) and (G) outcrops of the Dongjin section, showing Interval I, II and III.

Figure 3. Morphology and S isotopic composition of different forms of pyrite from the calcareous shales of the Dongjin section, South China. (A) Calcites from the calcareous shales; (B) nodular pyrite aggregates in calcareous shales from Interval I with extremely high δ34S values; (C) disseminated pyrite and corresponding δ34S values in Interval I; (D) pyrite from calcareous shale of Interval III; (E) pyrite frambooids; and (F) occurrences of finely disseminated euhedral pyrite.

Figure 4. A stratigraphic column showing the intervals in the Cambrian Series 2-Miaolingian calcareous shale succession of the Dongjin section, South China, and the variation in grain sizes of pyrite frambooids, bulk-rock Hg-S-C isotopic compositions and several other compositional parameters in the three intervals.

Figure 5. Plots of TS vs. TOC (A); FePy/FeHR vs. FeHR/FeT (B); Hg vs. TOC (C); Hg vs. TS (D);
Mn/Sr vs. δ¹³C (E) and, δ¹³C vs. δ¹⁸O (F) in CS₂-M strata of the Dongjin section, South China.

Figure 6. A stratigraphic column showing the δ¹³C and δ³⁴S_py values in the Cambrian Series 2 Miaolingian sedimentary successions of the Dongjin Section, South China (SC) (this study), Jianshan and Wuliu-Zengjiayan sections, SC (Guo et al., 2014), Genestosa and Cremenes sections, Spain (Sp) (Wotte et al., 2012b) and Carro Rajon section, Mexico (Mx) (Loyd et al., 2012).

Figure 7. A proposed model showing the evolution of the CS₂-M ocean in the Nanhua Basin, South China, and the locations of the Wuliu-Zengjiayan and Dongjin sections during this evolution. The unit for the Hg and S isotopic data in the figure is ‘‰’.
Figure 1 Liu et al., 2021


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Figure 2 Liu et al., 2021

Figure 3 Liu et al., 2021

Figure 4 Liu et al., 2021

Figure 5 Liu et al., 2021
Figure 6 Liu et al., 2021

Mercury and sulfur isotopic evidence for the linkages between the ca. 510 Ma Kalkarindji large igneous province and trilobite crisis: 
Sulfur and mercury isotopic evidence for a causal link between LIP emissions and trilobite extinction

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Supplementary Figures S1-S4

Figure S1. A simplified geological map of the study area, showing the distribution of CS₂-M strata near the Dongjin section, South China.

Figure S2. A plot of $\Delta^{199}$Hg vs. $\Delta^{201}$Hg (A) for CS₂-M strata in the Dongjin section, South China.
Figure S3. A plot of CAS vs. δ³⁴Scas for CS₂-M strata in the Dongjin section, South China.

Figure S4. (A) A vertical profile of δ¹³C_carb through a 14 cm thick sample of calcareous shales in Interval I; (B) a schematic illustration of a pore water chemistry showing the changes, with depth below the seawater/sediment interface in the Dongjin section of the Nanhua basin, in SO₄²⁻ content, δ³⁴S_{sulfate}, and δ³⁴S of the different types of pyrite, and the processes controlling these changes. SRZ = sulfate reduction zone.

Supplementary Note 1 Methods

1.1 Morphological observations and *in-situ* S isotopic analysis of pyrite

Morphological data for pyrite were collected from polished thin sections, using a Hitachi S-3400N variable pressure scanning electron microscope (SEM) at the Electron Microscope Unit, the University of Hong Kong. *In-situ* S isotope analyses of pyrite were performed on thin sections (>100 μm) using a Nu Plasma HR multi-collector ICPMS and a Photon Machine Analyte G2 laser microprobe, both at the Geological Survey of Finland in Espoo. Samples were ablated in He gas (gas flows = 0.4 and 0.1 L/min) within a HelEx ablation cell (Müller et al., 2009). All analyses were performed in spot mode using a laser beam of 30 μm with a fluence of 0.83 J/cm² at 5Hz. During the ablation, the data were collected in static mode (³²S, ³⁴S). The total S signal obtained for pyrite was typically 1.9-2.3 V. Under these conditions, after a 20 s baseline, 50-60 s of ablation was needed to attain an internal precision of ³⁴S/³²S ≤ ± 0.000005 (1 SE). Two pyrite standards were used for external standard bracketing (PPP-1) (Gilbert et al., 2014) and quality control (Py2) of analyses. The in-house standard, Py2, has been analyzed previously by gas source mass spectrometry yielding a δ³⁴Sᵥ-CDT (‰) value of -0.4 ± 0.5‰ (1s). We obtained an average value of -0.22 ± 0.35‰ (1s, n=35) for the measurements reported in this study (Table S4).

1.2 S isotopic analysis of pyrite separates and carbonate-associated sulfates (CAS)

Based on the *in-situ* δ³⁴S analyses, nodular pyrite aggregates in samples from Interval I and II have δ³⁴Sₚyw values (Table S1) that are significantly higher than those of the disseminated...
pyrite, indicating that the nodular pyrite did not form during sediment deposition or early
diagenesis. This pyrite was therefore removed before powdering for bulk rock analysis. In
addition, all potentially weathered surfaces and post-depositional veins were removed before
powdering. Pyrite in the pyritic layers of samples from the upper part of the Dongjin section
(Interval III) could not be completely eliminated due to its high abundance (Figs. 2 and 3).
These samples were thus not included in the S isotopic analyses.

Approximately 500 g of the remaining rock was ground with an agate mortar and pestle
for subsequent extraction of the H₂S from the disseminated pyrite and sulfate extraction from
carbonates. Disseminated pyrite was extracted using the chromium reduction method, in which
the powders were reacted with 50 ml of 1 M CrCl₂ and 20 ml of 10 M HCl in a N₂ atmosphere
(Canfield et al., 1986). Hydrogen sulfide released during decomposition of the pyrite was
bubbled through a 1M zinc acetate trap where it was precipitated as ZnS, which was then
converted to Ag₂S by ion exchange with AgNO₃. The Ag₂S was centrifuged, washed three times
using deionized water, and dried at 60 °C for analysis.

To eliminate non-CAS compounds and conduct the final extraction of CAS, we used a
HCl–BaCl₂ procedure similar to that described in Wotte et al. (2012). This was applied to
carbonate-rich mudstones containing < 1 wt% TS and > 3 wt% total inorganic carbon (TIC)
(Shi et al., 2018). The procedure involved first rinsing 100-300 g of sample powder (200 mesh)
with a 10% NaCl solution to remove later-stage sulfate. To ensure that as much as possible of
the non-CAS sulfate was removed from the powder before CAS extraction, the powders were
rinsed repeatedly with the NaCl solution until sulfate was not detectable in the solution. In the
next step, 4 N HCl was added in small aliquots to the samples to enable complete dissolution.
of the carbonates. Possible ferric iron-mediated pyrite oxidation during CAS extraction was inhibited by adding 15% SnCl\(_2\) to the HCl. After the HCl treatment, samples were processed immediately by vacuum filtration to remove the CAS-bearing solution and minimize potential pyrite oxidation after dissolution. Finally, the liberated CAS was crystallized as BaSO\(_4\) for isotopic measurements by adding a saturated BaCl\(_2\) solution.

Approximately 100 μg BaSO\(_4\) (for CAS) or Ag\(_2\)S (for pyrite separates) was measured out for analysis of their sulfur isotopic composition using a ThermoFinnigan Delta Plus mass spectrometer connected to an Elemental Analyzer. International standards for barite, IAEA-S-05 (\(\delta^{34}\)S = +0.49‰), IAEA-S-06 (\(\delta^{34}\)S = -34.05‰), and NBS 127 (\(\delta^{34}\)S = +21.10‰) were measured to correct the barite measurements, and IAEA-S-01 (\(\delta^{34}\)S = -1.34‰), IAEA-S-02 (\(\delta^{34}\)S = +21.18‰), and IAEA-S-03 (\(\delta^{34}\)S = -33.54‰) were used to correct the sulfide mineral measurements (Table S4). The results are reported in delta notation as per mil differences from the V-CDT standard. The analytical reproducibility was generally better than ±0.3‰.

Concentrations of CAS were calculated based on barium sulfate yields, following a correction for the insoluble residue.

### 1.3 Iron species analyses

We measured the concentration of Fe in four highly reactive iron phases (Fe\(_{HR}\)): pyrite (Fe\(_{Py}\)), carbonate (Fe\(_{carb}\)), ferric oxide (Fe\(_{ox}\)) and magnetite (Fe\(_{mag}\)), and the total iron content (Fe\(_T\)). The Fe\(_{Py}\) content was determined using the chromous chloride technique of Canfield et al. (1986), in which the sequential extraction procedure of Poulton and Canfield (2005) was used to analyze the other highly reactive iron phases, specifically Fe\(_{carb}\), Fe\(_{ox}\) and Fe\(_{mag}\).
determine FeT, about 100 mg of sample powder was dissolved using the method mentioned above for total dissolution, and then diluted 50 times. All solutions were analyzed for their respective iron contents using an atomic absorption spectrometer (AAS), with a RSD of <5% for all stages.

1.4 Mercury elemental and isotopic analyses

Total Hg concentrations were determined in the Institute of Geochemistry, Chinese Academy of Sciences, using a LUMEX RA915F automatic mercury vapor analyzer, which has a detection limit of 0.5 ng g⁻¹. The reproducibility monitored by repetitive measurements of a reference material (GSS-5, soil, 290 ppb Hg) was better than 10%.

Mercury isotope ratios were measured using the methods described by Geng et al. (2018). About 0.2-0.5 g of sample powder was digested using 5 mL of aqua regia in a water bath (95 °C for 6 hours). Certified reference materials (NIST SRM 2711, Montana soil) were prepared for analysis after every 13 samples and digested in the same way as the samples. After digestion, the solution was centrifuged (3000 rpm for 10 min) at room temperature and then decanted to obtain the supernatant liquid. The resulting solutions were diluted to 0.5-1 ng/mL with 10% HCl (v/v), based on THg values measured using the LUMEX RA915F instrument, and have acid concentrations of 10-20% (v/v). Bracketing NIST SRM 3133 standard solutions were also prepared, with Hg concentration and acid matrices matched to the neighboring samples. The analytical uncertainty was estimated from replication of the composition of the UM-Almadén secondary standard solution, and a full procedural analysis of NIST SRM 2711. Samples were analyzed using a Neptune Plus multiple collector inductively coupled plasma mass...
spectrometer (Thermo Electron Corp, Bremen, Germany) at the University Research Facility in Chemical and Environmental Analysis (UCEA) at the Hong Kong Polytechnic University, following the methods described by Geng et al. (2018). Mercury isotopic compositions were expressed as δ and Δ values, in units of per mil (‰) following the convention recommended by Bergquist and Blum (2007).

The average isotopic ratio and uncertainty of all the UM-Almadén measurements (δ²⁰²Hg:
-0.52 ± 0.04‰; Δ¹⁹⁹Hg: +0.00 ± 0.03‰; Δ²⁰⁰Hg: +0.02 ± 0.04‰; Δ²⁰¹Hg: -0.02 ± 0.05‰; 2SD, n=6) agree well with those reported previously (Bergquist and Blum, 2007). Measurements of replicate digests of NIST 2711 (δ²⁰²Hg: -0.18 ± 0.06‰; Δ¹⁹⁹Hg: -0.22 ± 0.04‰; Δ²⁰⁰Hg: 0 ± 0.05‰; Δ²⁰¹Hg: -0.19 ± 0.05‰, 2SD, n=3) were also comparable with those of previous studies (Table S5).

### 1.5 Carbon and oxygen isotopic analyses

Carbon and oxygen isotope compositions (δ¹³C_carb and δ¹⁸O_carb) of calcareous shales were determined using a Thermo Fisher Scientific carbonate-preparation device and a Gas Bench II connected to a Delta Plus XL isotope ratio mass spectrometer (IRMS) that was operated in continuous He flow mode, at the Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, China. The CO₂ was extracted from carbonates with 100% phosphoric acid at 70 °C for calcite and 90 °C for dolomite. The stable C and O isotope ratios are reported in delta (δ) notation as the per mil (‰) deviation relative to the Vienna Pee Dee belemnite (V-PDB) standard. The analytical reproducibility estimated from replicate analyses of the laboratory standards, Carrara marble, and Binn dolomite, was better than ±0.05‰ for δ¹³C and ±0.1‰ for
1.6 Total carbon (TC), total organic carbon (TOC) and total sulfur (TS) contents

The TC-TOC-TS contents were measured using a Multi EA 4000 carbon/sulfur analyzer with a high-temperature furnace and acidification module (Eltra, Germany). Approximately 20 to 300 mg of the powder was weighed into a ceramic boat and combusted in pure (99.95%) O\textsubscript{2} at 1350 °C for ~3 minutes to measure TC and TS. The TOC was analyzed in two steps. Firstly, inorganic carbon was removed by adding 4 mol/L HCl into about 2 g powder. Then, ~100 mg of the solid residue was weighed and combusted using the same methods as for TC-TS. Analytical errors for TC-TOC-TS were ± 0.1 wt%, based on analyses of carbonate standard, AR4007 (Alpha, USA). The TIC (total inorganic carbon) content was calculated by subtracting the TOC from the TC.

1.7 Bulk-rock Mn and Sr concentrations

Concentrations of Mn and Sr were analyzed using a Perkin-Elmer ELAN 6000 inductively-coupled plasma source mass spectrometer (ICP-MS) at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. Samples were heated to 700°C, and then submitted to a two-day closed-beaker digestion using a mixture of HF and HNO\textsubscript{3} acid in high-pressure autoclaves (Qi et al., 2000). Pure elemental standard solutions were used for external calibration, and BHVO-1 and SY-4 were used as reference materials. The analytical precision for most elements was better than 3%.
Supplementary Note 2: Possible modification of carbonate-associated sulfur (CAS)

Carbonate-associated sulfur is the trace quantity of sulfate that replaces carbonate ions structurally in marine carbonate. It is incorporated into the lattice of carbonate minerals and its $\delta^{34}S$ signature is thought to be unaffected by processes such as meteoric diagenesis (Gill et al., 2008) and remineralization of organic-bonded sulfur (Werne et al., 2008). Because carbonate sequences are deposited very rapidly, it is possible to estimate marine sulfate isotopic compositions with a very high temporal resolution using CAS (something that is generally a problem with other sulfate-bearing minerals). However, it has been argued recently that $\delta^{34}S$ values of CAS can be affected by diagenetic processes such as dolomitization (Shen et al., 2008), present-day atmospheric sulfate (Peng et al., 2014), as well as by the oxidation of pyrite during sample preparation (Loyd et al., 2012; Marenco et al., 2008; Wotte et al., 2012). Thus, before evaluating oceanic sulfur states using CAS data, it is essential to carefully evaluate the CAS $\delta^{34}S$ values to ensure that the recovered sulfate truly represents the original CAS.

Progressive diagenetic alteration of carbonates generally raises Mn and lowers Sr contents, as well as the $\delta^{13}C$ and $\delta^{18}O$ values of carbonate rocks (Kaufman et al., 1993; Li et al., 2013; Swart, 2015). In the absence of obvious correlations among $\delta^{13}C$, $\delta^{18}O$ and Mn/Sr values (Fig. 5e, f), we therefore conclude that diagenetic alteration had a negligible effect on isotopic variation in the samples from the Dongjin section, and their temporal variations of $\delta^{34}S_{\text{CAS}}$ has been preserved.

As discussed in the main text, sulfate contamination from oxidized pyrite prior to the final CAS extraction can modify the $\delta^{34}S$ values of CAS. In the present study, this contamination was minimized by avoiding the usage of oxidants, such as NaOCl and H$_2$O$_2$, during the pre-
leaching, and rapidly dissolving the carbonate slurry (4N HCl) without drying during the extraction (Wotte et al., 2012). The absence of contamination from this source is supported by duplicate analyses that returned results with a standard deviation less than 1.4‰ (Table S3). Further evidence that the $\delta^{34}$S$_{CAS}$ values were not contaminated by sulfate from the oxidation of pyrite is provided by the observation that in some of the samples the values are much lower than the $\delta^{34}$S$_{Py}$ values (Table S3). It is conceivable that, if the low $\delta^{34}$S values of CAS were generated by contamination from oxidized pyrite, $\delta^{34}$Scas values could be higher than or similar to the values of $\delta^{34}$S$_{Py}$.

Carbonate-associated sulfur may also be subject to natural contamination by recent secondary atmospheric sulfate (SAS). This may be especially the case, if the sampled carbonates are from outcrops in arid to semi-arid regions that have experienced limited leaching by meteoric water, or outcrops that have experienced strong atmospheric pollution (Peng et al., 2014). However, the present climate in the Dongjin section, South China is humid. The road-cut outcrop of the calcareous shales from the Dongjin section that was sampled has been recently blasted, and thus the samples escaped long-term exposure to the atmosphere. Moreover, as mentioned above, surfaces of the fresh samples were removed before powdering to minimize the contamination from SAS. As atmospheric sulfate invariably has a low $\delta^{34}$S value, contamination of this type might be expected to produce a negative correlation between CAS concentrations and $\delta^{34}$S$_{CAS}$ values. However, such a correlation is not evident in our data (see Supplementary Figure S3).

Methods used for $\delta^{34}$S$_{CAS}$ measurement are mostly applied to carbonate with low TOC and pyrite contents, whereas the calcareous shale samples in this study have relatively high
TOC (0.3-1.8 wt%) and TS contents (0.07-0.95 wt%). Any oxidation of organic-S and pyrite during diagenesis or post-diagenetic processes could decrease the $\delta^{34}$S_{CAS} (Borowski et al., 2013; Shen et al., 2008). Of all samples analyzed, sample DJV-15 has the lowest TOC (0.3 wt%) and TS (0.07 wt%) contents and the highest TIC content (9.6 wt%), which means that calcite occupied ~80% of the sediment (Table S3). The sample has a $\delta^{34}$S_{CAS} value of +19‰, which is only +2.6‰ greater than the average $\delta^{34}$S_{CAS} value of all the samples analyzed (Table S3). This suggests that contamination, resulting from oxidation of organic-S and pyrite during diagenesis or post-diagenetic processes, of CAS of calcareous shales from the Dongjin section was limited.

Finally, the calcareous shales in the Dongjin section are dominated by calcite, but it is difficult to determine whether the calcite crystallized mainly in an evaporitic environment or near the sediment-water interface influenced by pore water. If the calcite crystallized near the sediment-water interface, the $\delta^{34}$S values of CAS would be a signature of the pore water rather than the seawater, something that could not be resolved in this study.

To sum up, despite very careful sample screening (only samples with TIC >3.5 wt% and TS <1 wt% were analyzed), a rigorous analytical procedure, and a very low standard deviation (<1.4‰) returned by duplicate analyses, we cannot exclude the possibility that there was some contamination. Indeed, the latter is likely because of the high TOC and TS content of the samples and uncertainty about the environment of calcite precipitation.

**Supplementary Note 3: Super-heavy pyrite crystallized slowly from pore water during diagenesis**

In-situ analyses show that the nodular aggregates of pyrite have extremely high $\delta^{34}$S
values with an average of \(\sim +61.1\%\), which is inconsistent with reduction by organic matter (Canfield et al., 2010; Sim et al., 2011). Large pyrite grains with high \(\delta^{34}S\) values (+50 to +70\%) have been reported from the post-Sturtian Mn-rich dolomites and black shales of the Datangpo Formation, South China (c.f. Cui et al., 2018). This led Cui et al. (2018) to propose that unusually isotopically heavy pyrite can form via thermochemical sulfate reduction (TSR), and that the S is mainly from external sulfate-rich hydrothermal fluids with extremely high \(\delta^{34}S\) values (> +70\%). The TSR process is not mediated by microbes, and instead sulfate is thermochemically reduced (c.f. Cui et al., 2018). As the TSR process generally operates during late-diagenesis or post-diagenesis, late-stage pyrite would tend to be overgrown on the primary pyrite and significantly increase the \(\delta^{34}S\) values of the disseminated pyrite, as reported by Cui et al. (2018) for framboids with \(\delta^{34}S > +50\%\). However, disseminated pyrite in calcareous shales from Interval I of the Dongjin section has relatively low \(\delta^{34}S\) values (Fig. 4). In addition, similarly to the large pyrite grains from Interval III, the overgrowth texture and other features related to diagenesis and hydrothermal alteration (e.g., vein-like pyrite aggregates and sulfate-rich minerals) are not observed in the calcareous shales (Figs. 2 and 3), which is inconsistent with an explanation for the generation of isotopically ultra-heavy pyrite aggregates involving TSR.

It has been observed in carbonaceous sediments that methane forms by the decomposition of organic matter and thus would react with \(\text{SO}_4^{2-}\) in the pore water during its upwards diffusion. In addition, anaerobic oxidation of methane and sulfate reduction (AOM-SR) localize the production of \(^{34}S\)-enriched HS\(^-\) near the SMT, which may result in the occurrence of layers of authigenic sulfide minerals (Kasten et al., 1998). The sulfate-methane transition zone (SMT)
is a fundamental boundary between two microbial worlds, separating sulfate reducers above from the methanogens below (Borowski et al., 2013; Hensen et al., 2003). This boundary reflects the reaction:

\[ \text{CH}_4 + \text{SO}_4^{2-} \rightarrow \text{HCO}_3^- + \text{HS}^- + \text{H}_2\text{O} \]  

(Jørgensen and Kasten, 2006)

which proceeds rapidly through fluid advection and bubble ebullition at cold seeps, and also can take place more slowly by diffusion in pore water at sites away from active seepage (Hensen et al., 2003). The $\delta^{13}$C value of HCO$_3^-$ formed in the SMT zone is thought to be extremely low (-60‰) (Borowski et al., 2013; Jiang et al., 2003). However, the $\delta^{13}$C values of the carbonates in the Dongjin section are ~-0.5‰ (see Supplementary Figure S4 and Table S6) and do not change from this value in the pyrite-rich layers. This suggests that extremely high $\delta^{34}$S values in the nodular pyrite were not the result of AOM process near the SMT zone (Hao et al., 2015).

The nodular occurrence of pyrite aggregates indicates that the pyrite might have precipitated and crystallized slowly from pore water. In pore waters, which had limited S exchange with the seawater, continual burial of isotopically light $^{32}$S generated by BSR would have led to a sustainable growth of $\delta^{34}$S values during the downwards diffusion of sulfate, through Rayleigh distillation (Ries et al., 2009). This interpretation is supported by analyses of drill core of modern seafloor sediments, showing that pore water $\delta^{34}$S values increase from +20‰ at the sediment-seawater interface to >+60‰ at depth (Rennie and Turchyn, 2014).

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