1	Sulfur and mercury isotopic evidence for a causal link between LIP emissions and
2	trilobite extinction
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21 Abstract

22	The first major mass extinction of trilobites occurred at the transition from Cambrian
23	Series 2 (CS ₂) to Miaolingian (M) and coincided with a large marine transgression and volcanic
24	eruptions of a large igneous province (LIP). Understanding the causal links between these
25	events is important in deciphering environmental changes and the evolution of life at that time.
26	This paper presents S-Hg-C isotopic and Fe speciation data for calcareous shales from the CS ₂ -
27	M Yangliugang Formation in the Dongjin section, South China. In the lower part of this section
28	(Interval I), sulfate ($\delta^{34}S_{CAS}$) and pyrite ($\delta^{34}S_{Py}$) in calcareous shales vary little, with $\Delta^{34}S$
29	values from -4.2 to +8.3‰; they also have high Fe _{HR} /Fe _T ratios from 0.5 to 0.66, that are
30	indicative of a low SO42- content in anoxic seawater. Calcareous shales from Interval I display
31	at least two Hg/TOC peaks (up to 207 ppb/wt%), coincident with volcanic eruptions associated
32	with the ca. 510 Ma Kalkarindji LIP in Australia. In the middle part of the Dongjin section
33	(Interval II), calcareous shales display negative excursions of Δ^{199} Hg values, $\delta^{34}S_{Py}$ values and
34	Fe _{HR} /Fe _T ratios, which were likely led by a large terrestrial input into a marginal basin from
35	where Interval II deposited. Calcareous shales in the upper part of the section (Interval III)
36	contain pyrite framboids with a mean diameter of <4 μ m and high ratios of Fe _{HR} /Fe _T (>0.82)
37	and Fe _{Py} /Fe _{HR} (>0.78), indicating an euxinic depositional environment. They also record
38	negative excursions of δ^{13} C and δ^{202} Hg values (as low as -3.05‰ and -1.68‰, respectively),
39	providing evidence for the influence of ocean upwelling. The negative shift of $\delta^{13}C$ values in
40	the Dongjin section was temporally comparable to the C isotope excursions that coincided with
41	the Redlichiid-Olenellid Extinction (ROECE) event. We conclude that volcanic gas emissions
42	of the ca. 510 Ma Kalkarindji LIP greatly enhanced the continental erosion rate, leading to high

43 terrestrial SO4²⁻ input and accumulation of H₂S in deep marginal basins at the end of CS₂. The
44 subsequent marine upwelling (>506 Ma) brought anoxic/euxinic seawaters into the continental
45 shelf, contributing to the mass extinction of Redlichiid and Olenellid.

46 Keywords: Hg-S-C isotopes, Pyrite, Cambrian Series 2, Miaolingian, Calcareous shales,

47 Nanhua Basin

48 **1 Introduction**

The Cambrian was an important period in Earth's history marked by a sudden appearance 49 50 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 (CS₂; 521-506 Ma) and 51 diversified rapidly with oceanic oxidation (Karlstrom et al., 2020; Paterson et al., 2019). The 52 Redlichiid and Olebellid, two of three major trilobite taxa in CS₂ (Paradoxidids being the other 53 54 taxon), suddenly disappeared at the CS₂-Miaolingian (CS₂-M) transition, roughly coeval with a globally recognizable negative carbon isotope excursion (ROECE) (Lin et al., 2019; 55 Sundberg et al., 2020). Eruptions of flood basalts in the ca. 510 Ma Kalkarindji large igneous 56 57 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 58 ocean anoxia at the CS₂-M transition (Faggetter et al., 2019; Hough et al., 2006; Jourdan et al., 59 60 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 61 link between the mass extinction and the ca. 510 Ma Kalkarindji LIP. 62

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

65	and Hurtgen, 2015; Loyd et al., 2012). Cambrian Series 2 and Miaolingian sediments generally
66	have variable $\delta^{34}S_{sulfate}$ values (0 to >+45‰) recorded in gypsum, calcite, dolomite, and apatite
67	(Hough et al., 2006; Kampschulte and Strauss, 2004; Wotte et al., 2012b), and positive $\delta^{34}S_{Py}$
68	values (0 to >+30‰) (Guo et al., 2014; Loyd et al., 2012; Wotte et al., 2012b). The low Δ^{34} S
69	values ($\delta^{34}S_{sulfate} - \delta^{34}S_{Py}$) of CS2-M sediments suggest that the coeval seawater sulfate
70	concentration was low (<2.0 mM; Loyd et al., 2012). A negative shift in $\delta^{34}S_{Py}$ values (about -
71	10‰) occurred before the δ^{13} C excursion (ROECE) (Guo et al., 2010; Guo et al., 2014) and is
72	recognized globally, e.g., in the Wuliu-Zengjiayan and Jianshan sections, South China, the
73	Genestosa and Cre'menes sections, Spain, and the Carro Rajon section, Mexico (Guo et al.,
74	2014; Loyd et al., 2012; Wotte et al., 2012b). However, owing to the low abundance of pyrite
75	in these sections, systematic S isotopic studies, based on the mode of occurrence of pyrite, have
76	not been carried out, leading to a poor understanding of the reason for this negative shift of
77	δ^{34} S _{Py} values prior to the mass extinction.
78	Mercury (Hg) concentrations, the ratios of Hg to total organic carbon (Hg/TOC ratios),
79	and Hg isotopes have recently been developed as new proxies for investigating mass extinction,
80	large-scale volcanism, and anoxic oceanic events in Earth's history (e.g., Grasby et al., 2019).
81	Anomalously high Hg concentrations and Hg/TOC ratios have been observed in marine

events may contribute to mass extinctions (Grasby et al., 2019). Extensive Hg emission during

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sediments associated with all of the 'big five' Phanerozoic mass extinctions, implying that LIP

84 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

86 weathering that causes enhanced watershed runoff of soil Hg (Grasby et al., 2017; Shen et al.,

2019; Shen et al., 2020; Them et al., 2019). Mercury isotopes, especially their massindependent 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 94 95 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 96 Formation in the Wuliu-Zengjiayan section, a Global Boundary Stratotype Section and Point 97 98 (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 99 Dongjin section (N 29°01'09.9"; E 114°18'13.7"), Jiangxi Province, were deposited in a slope-100 101 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 102 103 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 104 Hg-S-C from sections in other parts of the world, this paper aims to shed light on the linkages 105 between marine redox state, mass extinction, and the volcanic eruption of LIPs during the later 106 107 stages of the 'Cambrian explosion'.

108 2 Geological setting

The Nanhua Basin in the South China Craton was opened after the amalgamation of the 109 Yangtze and Cathaysia Blocks at ca. 820 Ma and closed during the Ordovician-Silurian 110 111 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 112 Epoch, based on the similarity of the carbonate carbon isotopic (δ^{13} C) signatures (Guo et al., 113 114 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 115 and stratigraphy of the CS₂-M transition, the Nanhua Basin has been subdivided into clastic 116 117 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 118 oxic-suboxic depositional environment (Fig. 1b) (Guo et al., 2014). The boundary between the 119 120 Cambrian Series 2 and the Miaolingian Series is marked by the first appearance of Oryctocephalus Indicus in the CS₂-M Kaili Formation at ca. 506 Ma (Karlstrom et al., 2020; 121 Sundberg et al., 2020; Zhao et al., 2019), which was coincident with the last appearance datum 122 123 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 CS₂-M Yangliugang Formation with thickness of 180-310 m. The Yangliugang Formation is dominated by argillaceous limestones, calcareous shales and

137 Stage at 504.5 Ma (Zhu et al., 2019).

In the Dongjin section, Xiushui county, the lower part of the Yangliugang Formation (ca. 138 139 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 140 refer to argillaceous limestone and calcareous shale) (Figs. 2 and 3a) that conformably overlie 141 142 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 143 pyrite in the rocks. Calcareous shales from the lower 11 m of the Dongjin section (Interval I) 144 145 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 146 decreases rapidly (Figs. 2c and d), and the distance between adjacent pyrite layers increases 147 to > 10 cm. The middle part of Interval II was covered by soil and plant (about 3.5 m in 148 thickness), and was therefore not accessible for sampling. Calcareous shales from Interval III 149 (top 8 m) are rich in pyrite, the content of which increases abruptly to > 5 vol% from field 150 151 observations and hand specimen estimates (Figs. 2c and e).

152 **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 158 S-3400N variable pressure scanning electron microscope (SEM) at the Electron Microscope 159 Unit, the University of Hong Kong. In-situ S isotope analyses of pyrite were performed on thin 160 161 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-162 ICPMS), both at the Geological Survey of Finland in Espoo. Nodular pyrite aggregates in 163 samples from Interval I and II have $\delta^{34}S_{Py}$ values that are significantly higher than those of 164 disseminated pyrite (Table S1), indicating that the nodular pyrite did not form during sediment 165 deposition or early diagenesis. This pyrite was therefore removed before powdering for bulk 166 167 rock analysis.

Approximately 500 g of the remaining rock was ground with an agate mortar and pestle for subsequent extraction of H₂S 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 CrCl₂ and 20 ml of 10 M HCl in a N₂ atmosphere (Canfield et al., 1986). 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. (2012a). Approximately 100 µg BaSO₄ (for CAS) or Ag₂S (for pyrite separates) was measured

175	out for analysis of their sulfur isotopic composition using a Thermo Finnigan Delta Plus mass
176	spectrometer connected to an Elemental Analyzer. Carbon and oxygen isotope compositions
177	$(\delta^{13}C_{carb}$ and $\delta^{18}O_{carb})$ of calcareous shales were determined using a Thermo Fisher Scientific
178	carbonate-preparation device and a Gas Bench II connected to a Delta Plus XL isotope ratio
179	mass spectrometer (IRMS) that was operated in continuous He flow mode, at the Institute of
180	Geochemistry, Chinese Academy of Sciences, Guiyang, China. The CO ₂ was extracted from
181	carbonates with 100% phosphoric acid at 70 °C for calcite and 90 °C for dolomite. The stable
182	C and O isotope ratios are reported in delta (δ) notation as the per mil (∞) deviation relative to
183	the Vienna Pee Dee belemnite (V-PDB) standard. The analytical reproducibility estimated from
184	replicate analyses of the laboratory standards, Carrara marble, and Binn dolomite, is better than
185	$\pm 0.05\%$ for δ^{13} C and $\pm 0.1\%$ for δ^{18} O.

186 We measured the concentration of Fe in four highly reactive iron phases (FeHR): pyrite (Fe_{Py}), carbonate (Fe_{carb}), ferric oxide (Fe_{ox}) and magnetite (Fe_{mag}), and the total iron content 187 (Fe_T). The Fe_{Py} contents were determined using the chromous chloride technique of Canfield 188 189 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 Fecarb, Feox and Femag. All the 190 191 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 192 using an Olympus DP-6000 hand-held X-ray fluorescence spectroscope (HH-XRF) with a Rh 193 tube, as described in Lenniger et al. (2014). The analytical errors for FeT are better than 2% 194 195 (Jin et al., 2016; Lenniger et al., 2014).

196 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 204 205 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 206 described in Geng et al. (2018). About 0.2-0.5 g of sample powder was digested using 5 mL of 207 208 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 209 as the samples. The samples were analyzed using a Neptune Plus multiple collector inductively 210 211 coupled plasma mass spectrometer (Thermo Electron Corp, Bremen, Germany) at the University Research Facility in Chemical and Environmental Analysis (UCEA) at the Hong 212 213 Kong Polytechnic University. Mercury isotopic compositions were expressed as δ and Δ values, in units of per mil (‰) following the convention recommended by Bergquist and Blum (2007). 214

215 4 Analytical results

216 **4.1 Morphology and** *in-situ* δ^{34} S values of pyrite

217 Calcareous shales from the Dongjin section consist mainly of calcite with TIC from 2.1

218	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%,
219	and silicate minerals dominated by quartz and clays (Fig. 3). In calcareous shales from Interval
220	I and II, pyrite occurs as disseminations and nodular aggregates. Pyrite grains in nodular
221	aggregates are large (50-100 μ m in diameter) and have extremely large positive $\delta^{34}S_{Py}$ values,
222	ranging from +37.6 to +68.1‰, with an average of +60‰ (Fig. 3b; Table S1). In Interval I,
223	disseminated pyrite comprises 6–12 vol% euhedral grains with diameters ranging from 3 μ m
224	to 25 μm and 88–94 vol% framboids with diameters ranging from 1 μm to 25.5 μm (5 μm on
225	average) (Figs. 3c, e, f and 4; Table S2). The $\delta^{34}S_{Py}$ values of the two pyrite varieties (not
226	distinguished) range from +8.8 to +21.4‰ (ca. +15.9‰ on average) (Figs. 3c; Table S1). In
227	Interval II, pyrite framboids represent 85-92 vol% of the pyrite and their diameters range from
228	1 to 18.6 μ m with an average of 5.3 μ m (Table S2). The δ^{34} S _{Py} values vary from +3.2 to +25.7‰
229	(+10.2‰ on average).

230 Pyrite in Interval III accounts for >5 vol% of the rock (Fig. 2), and occurs mainly as large 231 sub-euhedral to euhedral crystals (>50 μ m in diameter) and small pyrite framboids (< 5 μ m) 232 (Figs. 3 and 4; Table S2). The $\delta^{34}S_{Py}$ values of the large pyrite grains ranges from +13.8 to 233 +31.0‰. Reliable in-situ $\delta^{34}S_{Py}$ values of pyrite framboids could not be acquired by MC-LA-234 ICPMS due to their small grain-size.

235 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 $\delta^{34}S_{Py}$ 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%,

239	averaging at 1.6 wt%, and TIC contents from 1.1 to 7.6 wt%, averaging at 4.1 wt% (Fig. 5a;
240	Table S3). They have relatively constant δ^{13} C values ranging from -0.98 to -0.79‰, δ^{18} O values
241	from -11.2 to -10.1‰ and Mn/Sr ratios from 0.38 to 2.54 (Fig. 4). Samples with TS <1 wt%
242	and TIC >3.5 wt% have CAS contents from 66 to 155 ppm and $\delta^{34}S_{CAS}$ values from +11.9 to
243	+24.6‰ (average +16.7‰). The Δ^{34} S (δ^{34} S _{CAS} - δ^{34} S _{Py}) values in these samples vary from -4.2
244	to $+8.3\%$ with an average of $+0.8\%$. The Hg content of the bulk rock in Interval I ranges from
245	31.3 to 137 ppb, which is higher than those in the other two intervals (Table S3). The δ^{202} Hg
246	values in this interval are relatively constant (-1.08 to -0.74‰), whereas the Δ^{199} Hg values
247	increase upwards from -0.16 to 0.00‰. The samples have high FeT contents, ranging from 1.6
248	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,
249	respectively (Figs. 4 and 5b; Table S3).

250 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 δ^{34} S_{Py} shift upwards from +16.1 to -2‰. 251 They have a TOC content of 0.2-1.6 wt%, a TIC content of 1.2-10.3 wt%, and δ^{13} C and δ^{18} O 252 253 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 δ^{34} S_{CAS} values are +11.7 to +21‰ with an average of +16.1‰ 254 (Table S3). The Δ^{34} S (δ^{34} S_{CAS} - δ^{34} S_{Py}) values increase upwards from +3 to +10‰, with an 255 average of +5.7‰ (Table S3). The bulk rock Mn/Sr ratio ranges from 0.2 to 1.55. The Hg 256 content of these shales is relatively constant (ca. 30 ppb), the Δ^{199} Hg values vary from slightly 257 negative to near zero (-0.11 to +0.02‰) and the δ^{202} Hg values (-1.0 to -0.5‰) are similar to 258 those of Interval I. The FeT contents ranges from 0.6 to 2.8 wt% (the average is 1.90 wt%) and 259 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 260

261 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 262 contents (0.7-1.3 wt%) and variable Hg contents (5.9-52 ppb). They have TIC contents from 263 2.8 to 4.8 wt%, Mn/Sr ratios from 0.3 to 1.4, and constant δ^{18} O carbonate values (-11.6 to -264 10.1%). In the basal part of this interval, the δ^{13} C values of the shales decrease sharply from -265 0.80 to -3.05% (Fig. 4) and are coupled to a negative shift in δ^{202} Hg from -1.05 to -1.68%. The 266 Δ^{199} Hg values range from -0.07 to +0.06‰, indicating the absence of mass-independent 267 fractionation (Table S3). The FeT contents, FeHR/FeT ratios, and Fepy/FeHR ratios are all high, 268 ranging from 3.35 to 4.38 wt%, from 0.82 to 0.93, and from 0.78 to 0.85, respectively (Figs. 4 269 and 5b; Table S3). 270

271 **5 Discussion**

272 5.1 The redox state and sulfate content of the ocean at the CS₂-M transition

273 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 (Fe_{HR}) 274 in fine-grained sediments, has been widely used to distinguish oxic, ferruginous, and euxinic 275 conditions in siliciclastic rocks and in carbonate rocks with >0.5 wt% Fe_T (Clarkson et al., 2014; 276 Poulton and Canfield, 2011). Anoxic sediments have FeHR/FeT ratios of >0.38 through the 277 incorporation/precipitation of Fe_{HR} from the anoxic water column. Under anoxic and sulfidic 278 (euxinic) conditions, Fehr is converted to Fepy through its reaction with H₂S to form pyrite, 279 resulting in Fe_{Py}/Fe_{HR} ratios of >0.7–0.8 (Poulton and Canfield, 2011). All samples investigated 280 in this study have Fe_T contents >0.5 wt% (Table S3). Calcareous shales from Interval I have an 281

average Fe_{HR}/Fe_T ratio of 0.6 and the same average Fe_{Py}/Fe_{HR} ratio (0.6), which are indicative 282 of an overall anoxic depositional environment low in H₂S that contains excess Fe (Figs. 4 and 283 284 5b; Table S3). Inadequate H₂S production under anoxic conditions could be caused by a limited supply of organic matter (reducer) or sulfate (reactant), or both (Poulton and Canfield, 2011; 285 Wilkin and Barnes, 1996). Given that the TOC values represent preserved organic matter, the 286 high TOC contents (ca. 1.6 wt%) in these calcareous shales preclude the possibility of limited 287 organic matter supply suggesting, instead, a low sulfate supply and anoxic conditions in the 288 water column above the Dongjin section. 289

The moderately negative to moderately positive Δ^{34} S values (-4.2 to +8.3‰) of calcareous 290 shales from Interval I place additional constraints on the end-CS₂ sulfur cycle (Table S3). 291 Carbonate-associated sulfate (CAS) is the trace quantity of sulfate that replaces carbonate ions 292 structurally in marine carbonate and can be used to represent the δ^{34} S value of sulfate in the 293 water column (cf., Wotte et al., 2012a). The reduction of sulfate is promoted strongly by 294 microbes (sulfate-reducing bacteria), which favor the lighter, more weakly bonded isotope of 295 sulfur (³²S) (Kasten et al., 1998). The magnitude of $\Delta^{34}S$ ($\delta^{34}S_{CAS}$ - $\delta^{34}S_{Py}$) values between 296 sulfate in seawater and pyrite preserved in sedimentary rocks has been widely utilized to 297 reconstruct ancient marine sulfate levels (e.g., Loyd et al., 2012; Gomes and Hurtgen, 2015). 298 It has been estimated that a ca. 20-70‰ fractionation between sulfate and sulfide can be 299 achieved in an aqueous system with a sulfate content of >0.2 mM (Canfield, 2001; Habicht et 300 al., 2002; Sim et al., 2011), and that Δ^{34} S would be larger if the recycling of sulfur species, e.g., 301 re-oxidation and disproportionation, in the water column were considered (Fike et al., 2015). 302 This fractionation, however, is suppressed at a low sulfate content, approaching 0‰ at sulfate 303

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 $\delta^{34}S_{py}$ 307 308 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 309 proportion of CAS extracted from these calcareous shales is low and has δ^{34} S_{CAS} values varying 310 from +11.9 to +24.6‰. Values of δ^{34} S_{CAS} can be modified by the oxidation of pyrite during 311 sample preparation. In the present study, this contamination was minimized by avoiding the 312 usage of oxidants, and rapidly dissolving the carbonate slurry without drying during the 313 extraction (Wotte et al., 2012a). To further minimize the influence of this effect on the δ^{34} Scas 314 values, only samples with >3.5 wt% TIC and <1 wt% TS were considered further (Li et al., 315 2017), and these returned a very low standard deviation (<1.4‰) for duplicate analyses (Table 316 S3) (see Supplementary Note 2 for a more detailed discussion of the reliability of the $\delta^{34}S_{CAS}$ 317 data). The Δ^{34} S values in our samples from Interval I are in the range from -4.2 to +8.4‰, 318 which is low and indicative of a sulfate-depleted end-CS₂ ocean (Fig. 4). Low Δ^{34} S values are 319 also preserved in marine sediments deposited in end-CS2 marginal basins elsewhere, for 320 example, from -22.9 to -0.2‰ in the Carro Rajon section, Mexico (Loyd et al., 2012) and from 321 -0.7 to +15.2‰ in the Cre'menes section, Spain (Wotte et al., 2012b). The results of these 322 studies support our interpretation that the SO4²⁻ concentration was very low in the end-CS₂ 323 ocean (i.e., <2.0 mM; Loyd et al., 2012)). 324

325 **5.1.2** A less anoxic depositional environment with increased seawater SO₄²⁻ in Interval II

Calcareous shales from Interval II have FeT contents varying from 0.6 to 2.8 wt%. There is an obvious upwards decrease in Fe_{HR}/FeT 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 331 decrease upwards stratigraphically from +16.1 to -2‰ (Fig. 4). This negative excursion of 332 δ^{34} S_{Py} values at the end-CS₂ has been widely observed in the Wuliu-Zengjiayan and Jianshan 333 sections, South China, in the Carro Rajon section, Mexico (Loyd et al., 2012), and in the 334 335 Genestosa and Cre'menes sections, Spain (Wotte et al., 2012b) (Fig. 6). In concert with the stratigraphically upward decreasing trend of δ^{34} SPv values, Δ^{34} S values from Interval III of the 336 Dongjin section increase upwards from +3 to +10% (Table S3), indicating an increase in 337 seawater sulfate content (Loyd et al., 2012; Gomes and Hurtgen, 2015). As mentioned above, 338 the elevated sulfate content in an aqueous system will increase the S isotopic fractionation 339 between the pyrite precipitate and the dissolved sulfate, leading to a decrease of δ^{34} S values in 340 pyrite (Canfield, 2001; Habicht et al., 2002; Sim et al., 2011). The covariation of δ^{34} SPy and 341 Δ^{34} S values in calcareous shales from the Dongjin section, therefore, indicate that this globally 342 detectable negative excursion of $\delta^{34}S_{Py}$ values was most likely due to an increase in seawater 343 344 sulfate content at the end-CS₂.

345 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 346 used in determining whether the pyrite was deposited under euxinic or non-euxinic conditions 347 (Wignall and Newton, 1998). It has been observed that framboids crystallized directly from 348 H₂S-rich seawater (euxinic conditions) generally have a narrow size range with an average 349 diameter <5 µm (Wignall and Newton, 1998). This is due to the rapid crystallization of pyrite 350 above the sediment-water interface and limited access to H₂S and/or Fe²⁺ after burial (Wignall 351 and Newton, 1998). In H₂S-poor seawater (oxic-anoxic), conditions favorable for the 352 crystallization of pyrite framboids are restricted to those of pore water in sediments. Because 353 of a variation in the time-integrated availability of Fe and S, pyrite framboids formed in pore 354 water tend to be larger and more variable in size (Wignall and Newton, 1998; Wilkin and 355 Barnes, 1996). In calcareous shales from Interval I and Interval II, the pyrite framboids display 356 a large size-range, i.e., from 1 to 25.5 µm in diameter, indicating that these grains did not 357 precipitate in euxinic seawater. The disseminated pyrite framboids in calcareous shales from 358 Interval III have diameters from 0.5 to 7.1 µm and a mean-diameter of ca. 3.2 µm, i.e., they are 359 similar in size to pyrite framboids forming from euxinic seawaters in the modern Black Sea 360 (Wignall and Newton, 1998). The small grain-size and narrow size-range of pyrite framboids 361 in shales from Interval III, therefore reflected a rapid change in the depositional environment 362 from an anoxic to an euxinic state. 363

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

367	(e.g., Cui et al., 2018). In pore waters for which there is limited S exchange with seawater,
368	continual removal of isotopically light ^{32}S generated by BSR would lead to an increase in $\delta^{34}S$
369	values during the downwards diffusion of sulfate, through Rayleigh fractionation distillation
370	(Ries et al., 2009). Pyrite precipitated under such conditions usually has much higher $\delta^{34}S_{Py}$
371	values than disseminated pyrite (Jørgensen and Kasten, 2006). This is exemplified by the super-
372	heavy (isotopically) nodular pyrite from Interval I and II, which has $\delta^{34}S_{Py}$ values of +37.6 to
373	+68.1‰ (see further discussion in Supplementary Note 3). In contrast to the nodular pyrite in
374	Interval I and II, the coarse-grained pyrite in Interval III has much lower $\delta^{34}S_{Py}$ values of +13.8
375	to $+31.0\%$, which are only slightly higher than those of the disseminated pyrite (-2.0 to $+21.0\%$;
376	Table S3). We therefore infer that these large pyrite grains may have precipitated and grown
377	from sulfidic pore water that was well-connected to the bottom seawater. The abundant large
378	pyrite grains and the high TS content in calcareous shales from the Interval III are also
379	suggestive of an euxinic depositional environment during Interval III.
380	The calcareous shales from the upper part of the Dongjin section also have a high
381	Fe _{Py} /Fe _{HR} ratio of 0.78-0.85 and a high Fe _{HR} /Fe _T ratio of 0.82-0.93 (Figs. 4 and 5), features that
382	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_{Py}/Fe_{HR} and Fe_{HR}/Fe_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

387 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 CS₂-M ocean that complement the C and S isotope data.

390 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 391 marine sediments (Shen et al., 2020). Anomalously high Hg concentrations and Hg/TOC ratios 392 in marine sediments therefore provide a promising tool for identifying periods of enhanced 393 volcanic activity (Grasby et al., 2019). Mercury concentrations in calcareous shales from 394 Interval I in the Dongjin section are higher (70 ppb on average) than those from the other 395 intervals in this section (34 ppb in Interval II and 27 ppb in Interval III on average). Two distinct 396 Hg peaks are evident for the upper part of Interval I, with the highest Hg concentration reaching 397 136.9 ppb (Fig. 4). The Hg concentrations do not correlate with the TOC contents, and the peak 398 Hg values are associated with high Hg/TOC ratios (as high as 207 ppb/wt%) (Figs. 5c). 399 Therefore, organic matter drawdown was not a driver of these Hg peaks, and the enrichments 400 of Hg were likely a result of external Hg-loading due to extensive volcanic activity (Grasby et 401 402 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 403 boundary (Shen et al., 2019). The Hg content, however, does not correlate with the TS content, 404 and the peak Hg values are associated with high Hg/TS ratios (as high as 325 ppb/wt%) (Fig. 405 5d and Table S3), indicating that these enrichments of Hg were not from incorporation of Hg 406 by sulfides (Shen et al., 2020). 407

408

Evidence of extensive volcanic activity in the upper part of Interval I is also provided by

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

431 Interval I, but it cannot explain the Hg and Hg/TOC spikes in the upper part of this interval432 (Fig. 4).

Spikes in the concentration of Hg before the CS₂-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.

440 **5.2.2** Enhanced SO₄²⁻ flux into the end CS₂ ocean in the aftermath of a LIP

Throughout Earth's history, volcanic eruptions of LIPs have led to an increase in 441 atmospheric CO₂ and erosion of the continents, resulting in higher terrestrial input into the 442 ocean that may have affected the ocean redox state and biogeochemical circulation (Grasby et 443 al., 2017; Them et al., 2019). In calcareous shales from Interval II, there is a gradual decrease 444 of Δ^{199} Hg values from +0.02‰ at the base to -0.11‰ at the top. Volcanic emissions, as noted 445 above, are characterized by a Δ^{199} Hg value of ca. 0‰, whereas terrestrial Hg is marked by 446 negative Δ^{199} Hg values. The negative shift of Δ^{199} Hg values, therefore, indicates that terrestrial 447 Hg flux into the ocean outperformed the volcanic Hg input from the atmosphere. A sharp 448 decrease in sea-level with a larger area of the continental crust exposed and eroded might cause 449 an enhanced terrestrial Hg input into the ocean. There are, however, no obvious lithological 450 differences between Interval I and II in the Dongjin section and its equivalent strata in the 451

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 $\delta^{34}S_{Py}$ values reflect an increased seawater SO4²⁻ content during Interval II, but the driving force for this variation is unclear. Enhanced terrestrial SO4²⁻ input from continental weathering and eruptions in the aftermath of the 510 Ma Kalkarindji LIP would be a reasonable explanation for the increased SO4²⁻ content of the oceans at the end-CS₂. Moreover, the small increase in δ^{13} C from -0.9 to -0.6‰ and the corresponding decrease of Δ^{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.

461 **5.2.3 Upwelling of deep H₂S-rich seawater at the CS₂-M transition**

The abrupt increase in pyrite abundance across the boundary between Interval II and 462 Interval III was accompanied by a negative excursion of δ^{13} C and δ^{202} Hg values and a slightly 463 positive shift in Δ^{199} Hg values (Fig. 4). Empirical research suggests that carbonates with Mn/Sr 464 < 10 generally retain a primary marine C isotopic signature (Kaufman et al., 1993). In samples 465 from Interval III, Mn/Sr ratios are < 1.5, and there is no obvious correlation among δ^{13} C. δ^{18} O. 466 and Mn/Sr values (Figs. 5e, f), indicating that the temporal variation of δ^{13} C might have been 467 preserved and the negative δ^{13} C values in the calcareous shales were not a result of diagenesis 468 (Li et al., 2013). Moreover, negative excursions of δ^{13} C also have been recorded in the CS₂-M 469 shales in the Wuliu-Zengjiayan, and Jianshan sections, Guizhou province, South China, where 470 they are interpreted to reflect marine transgression and upwelling of ¹³C depleted seawater 471 (Guo et al., 2010; Guo et al., 2014). The sharp sedimentological and geochemical contact 472

between Interval II and Interval III indicates that H₂S enrichment occurred rapidly. Thus, it is possible that the H₂S 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 Δ^{199} Hg values in calcareous shales from Interval III.

Mass-dependent fractionation of Hg isotopes is ubiquitous and has been used as a source 479 tracer in many studies, particularly in cases of regular stratigraphic changes (Grasby et al., 480 2017). Samples from Interval I and II have a constant δ^{202} Hg value of -0.76 ± 0.16‰, which is 481 similar to that of volcanic ash and silicate rocks, which have a mean δ^{202} Hg value of $-0.68 \pm$ 482 0.45% (Blum et al., 2014). In Interval III, the δ^{202} Hg values decrease abruptly to -1.68%. It 483 484 has been proposed that the formation of the Hg-S bond would lead to a negative shift of -0.6‰ in the δ^{202} Hg value (Foucher et al., 2013). The decrease of δ^{202} Hg in calcareous shales from 485 Interval III thus could be attributed to the increased abundance of pyrite. However, the δ^{202} Hg 486 487 value increases upwards to ca. -1‰, and is decoupled from the consistently high TS but, instead, is coupled with δ^{13} C values in calcareous shales from Interval III (Fig. 4). This indicates that 488 the negative excursion of δ^{202} Hg might have been caused by a marine transgression rather than 489 the precipitation of pyrite. Microbial methylation, forming monomethyl mercury (MMHg) with 490 low δ^{202} Hg values is one of the major processes leading to MDF of Hg in aqueous systems 491 (Blum et al., 2014). Indeed, Yin et al. (2015) showed that marine sediments (in the deep ocean) 492 have lower δ^{202} Hg values than coastal sediments, which implies that upwelling deep waters can 493 carry a substantial amount of Hg from marine to coastal regions. 494

Large pyrite grains from calcareous shale of Interval III have large positive δ^{34} S values, 495 i.e., from +13.8 to +31‰ (Table S1; Fig. 3d), which may reflect inheritance from deeper 496 euxinic seawater. In modern ocean basins that receive sufficient SO₄²⁻ input for pyrite formation, 497 e.g., the modern Black Sea, the euxinic bottom waters generally have consistently high sulfate 498 contents, negative δ^{34} S_{H2S} values, and stable Δ^{34} S values between δ^{34} S of sulfate from surface 499 water and δ^{34} S of pyrite in sediments (Gomes and Hurtgen, 2015). By contrast, Δ^{34} S values in 500 low-sulfate euxinic systems are positively correlated with sulfate concentration, leading to high 501 δ^{34} SH2S values in bottom euxinic water (Gomes and Hurtgen, 2015). The high δ^{34} SPy values of 502 coarse-grained pyrite in Interval III may, therefore, reflect intense sulfate reduction in basins 503 with initially low sulfate concentration, which would have allowed a nearly quantitative 504 reduction of sulfate and promoted high δ^{34} S_{H2S} values in the euxinic bottom water (Gomes and 505 506 Hurtgen, 2015; Magnall et al., 2016). This is consistent with our interpretation, presented above, that terrestrial SO4²⁻ input fertilized the SO4²⁻-depleted Nanhua Basin of Interval II. The 507 reduction of sulfate contributed to seawater H₂S accumulation in the deep ocean. 508

509 5.3 An integrated model and implications for the trilobite crisis

510 Chemo-stratigraphic variations in organic-rich calcareous shales from the Dongjin section 511 are comparable to those in the Wuliu-Zengjiayan and Jianshan sections (Guo et al., 2010; Guo 512 et al., 2014). Pyrite in CS₂-M sediments from these sections has high δ^{34} S_{Py} values but displays 513 a negative shift in δ^{34} S_{Py} values before the negative δ^{13} C excursion (Fig. 6) (Guo et al., 2010; 514 Guo et al., 2014). In the Wuliu-Zengjiayan section, the negative δ^{13} C excursion at the base of 515 Interval III coincided with the extinction of trilobites (Fig. 6) and defines the CS₂-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 519 deposition of organic-rich shales. With continuous crystallization and burial of pyrite and a 520 limited terrestrial supply of sediment, the seawater in the Nanhua basin was depleted in SO₄²⁻ 521 and had high $\delta^{34}S_{Py}$ values at the end of CS₂. Without sufficient SO₄²⁻ for oxidation of the 522 organic matter (DOC and methane), the seawater in the Dongjin section became anoxic (Fig. 523 7a). The source of Hg in the calcareous shales deposited in the Dongjin section was mainly 524 from continental erosion as shown by Δ^{199} Hg < 0‰. Eruptions of flood basalts in the 525 Kalkarindji LIP at ca. 510 Ma interfered with the Hg cycle of the Earth's surface system and 526 caused an increase of Δ^{199} Hg to a near-zero value (Fig. 7a). The volcanic eruptions increased 527 the erosion rate of the continental crust, resulting in higher terrestrial Hg and SO₄²⁻ input into 528 the ocean. Consequently, the Δ^{199} Hg and δ^{34} S_{Py} values decreased in Interval II (Fig. 7b). This 529 higher terrestrial SO4²⁻ input led to a H₂S rich reservoir in the deeper ocean. Owing to the 530 initially low sulfate content of the CS₂ Nanhua Basin, H₂S in the deep euxinic water had high 531 δ^{34} S_{Py} values (Fig. 7b). This euxinic water upwelled into the shallow ocean during the earliest 532 Miaolingian, leading to abundant deposition of pyrite in carbonate muds of Interval III and 533 mass extinction of trilobites on the shelf (as in the Wuliu-Zengjianyan section) (Fig. 7c). 534

535 Geochemical changes in the Nanhua Basin were duplicated globally as discussed above. 536 Thus, high δ^{34} S values have been reported for sulfate-bearing minerals and pyrite from CS₂-M 537 sediments in Spain (Wotte et al., 2012b), Siberia (Kampschulte and Strauss, 2004) and

538	Australia (Hough et al., 2006), and inferred to record the depletion of sulfate in the CS ₂ -M
539	ocean. Moreover, the ca. 510 Ma eruptions of the Kalkarindji LIP have been shown to be
540	recorded by the CS ₂ -M strata in the USA (Faggetter et al., 2019). The subsequent negative
541	excursion of $\delta^{34}S_{Py}$ values, likewise, has been widely documented (Fig. 6) and is coincident
542	with a positive shift of seawater ⁸⁷ Sr/ ⁸⁶ Sr ratios around the CS ₂ -M transition (Zhang et al.,
543	2020), which also supports an increased terrestrial input after the Kalkarindji LIP. Finally, the
544	δ^{13} C negative excursion at ca. 506 Ma (Fig. 6) was globally detectable (the ROECE event), and
545	is considered to have been caused by a marine transgression (Guo et al., 2014; Karlstrom et al.,
546	2020; Lin et al., 2019; Sundberg et al., 2020).

547 Our analysis of ocean redox conditions and sulfate content provides strong evidence that 548 changes in seawater chemistry may have been linked to a global bio-evolutionary change after 549 the ca. 510 Ma Kalkarindji LIP that led to the extinction of Redlichiid and Olebellid. Moreover, 550 our interpretation that upwelling of anoxic/euxinic deep seawater was the direct cause for the 551 extinction could help explain the ~4 Ma time interval between the ca. 510 Ma Kalkarindji LIP 552 and this event.

553 6 Conclusions

The CS₂-M ocean was characterized by low sulfate content, resulting in high δ^{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-CS₂ ocean. With greater Hg and SO₄²⁻ input, the

 Δ^{199} Hg values of Interval II decreased, as did the δ^{34} S_{Py} values of the disseminated pyrite. Hydrogen sulfide with high δ^{34} S 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 δ^{13} C values in calcareous shales from Interval III and was likely responsible for the extinction of Redlichiid and Olebellid.

566 Acknowledgements

This research was financially supported by the National Natural Science Foundation of 567 China (41772087). We thank Dr. Wen Zhao for his assistance in the field, Dr. Zihu Zhang for 568 the S isotope analysis, Prof. Xinbin Feng, Dr. Wenjun Hu and Dr. Hongyan Geng for the Hg 569 analysis, and Prof. Chao Li for his discussion and suggestions during the revision. We 570 571 gratefully acknowledge the support of the University Research Facility in Chemical and Environmental Analysis (UCEA), the Hong Kong Polytechnic University. Prof. Frédéric 572 Moynier is thanked for efficient editorial handling. The constructive comments from Dr. Geoff 573 574 Gilleaudeau and Dr. Ganqing Jiang that helped improve the paper significantly are much appreciated. 575

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752

753 Figure captions

754	Figure 1. (A) Geological setting of the Nanhua Basin, South China (A) Global paleogeography
755	of the 550-510 Ma Gondwana, showing the location of South China and the 510 Ma
756	Kalkarindji LIP (adapted from Faggetter et al. (2019)). (B) A simplified paleogeographic
757	map of the Nanhua Basin during the CS2-M transition, showing the three major facies
758	identified by Zhang et al. (2008) and the locations of the Wuliu-Zengjiayan (yellow
759	triangle) and the Dongjin (red triangle) sections.
760	Figure 2. Stratigraphy and photographs of the Dongjin section, South China. (A) and (B)
761	nodular pyrite aggregates in Interval I; (C) and (D) the boundary between Interval II and
762	Interval III; (E) pyrite layers in calcareous shales from Interval III; (F) and (G) outcrops
763	of the Dongjin section, showing Interval I, II and III.
764	Figure 3. Morphology and S isotopic composition of different forms of pyrite from the
765	calcareous shales of the Dongjin section, South China. (A) Calcites from the calcareous
766	shales; (B) nodular pyrite aggregates in calcareous shales from Interval I with extremely
767	high δ^{34} S values; (C) disseminated pyrite and corresponding δ^{34} S values in Interval I; (D)
768	pyrite from calcareous shale of Interval III; (E) pyrite framboids; and (F) occurrences of
769	finely disseminated euhedral pyrite.
770	Figure 4. A stratigraphic column showing the intervals in the Cambrian Series 2-Miaolingian
771	calcareous shale succession of the Dongjin section, South China, and the variation in grain
772	sizes of pyrite framboids, bulk-rock Hg-S-C isotopic compositions and several other
773	compositional parameters in the three intervals.

Figure 5. Plots of TS vs. TOC (A); Fe_{Py}/Fe_{HR} vs. Fe_{HR}/Fe_T (B); Hg vs. TOC (C); Hg vs. TS (D);

775	Mn/Sr vs. δ^{13} C (E) and, δ^{13} C vs. δ^{18} O (F) in CS ₂ -M strata of the Dongjin section, South
776	China.

- Figure 6. A stratigraphic column showing the δ^{13} C and δ^{34} S_{Py} values in the Cambrian Series 2
- 778 Miaolingian sedimentary successions of the Dongjin Section, South China (SC) (this
- study), Jianshan and Wuliu-Zengjiayan sections, SC (Guo et al., 2014), Genestosa and
- 780 Cre'menes sections, Spain (Sp) (Wotte et al., 2012b) and Carro Rajon section, Mexico
- 781 (Mx) (Loyd et al., 2012).
- Figure 7. A proposed model showing the evolution of the CS₂-M ocean in the Nanhua Basin,
- 783 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 '%.'

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Figure 2 Liu et al., 2021



Figure 3 Liu et al., 2021



Figure 4 Liu et al., 2021







Figure 6 Liu et al., 2021

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Figure 7 Liu et al., 2021

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

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19 Supplementary Figures S1-S4





21 Figure S1. A simplified geological map of the study area, showing the distribution of CS₂-M

22 strata near the Dongjin section, South China.



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Figure S2. A plot of Δ^{199} Hg vs. Δ^{201} Hg (A) for CS₂-M strata in the Dongjin section, South

25 China.



26

Figure S3. A plot of CAS vs. δ^{34} Scas for CS₂-M strata in the Dongjin section, South China.



28

Figure S4. (A) A vertical profile of $\delta^{13}C_{carb}$ 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, $\delta^{34}S_{sulfate}$, and $\delta^{34}S$ of the different types of pyrite, and the processes controlling these changes. *SRZ= sulfate reduction zone*

35 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 37 S-3400N variable pressure scanning electron microscope (SEM) at the Electron Microscope 38 Unit, the University of Hong Kong. In-situ S isotope analyses of pyrite were performed on thin 39 40 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 41 ablated in He gas (gas flows = 0.4 and 0.1 L/min) within a HelEx ablation cell (Müller et al., 42 2009). All analyses were performed in spot mode using a laser beam of 30 µm with a fluence 43 of 0.83 J/cm² at 5Hz. During the ablation, the data were collected in static mode (³²S, ³⁴S). The 44 total S signal obtained for pyrite was typically 1.9-2.3 V. Under these conditions, after a 20 s 45 baseline, 50-60 s of ablation was needed to attain an internal precision of ${}^{34}S/{}^{32}S \le \pm 0.000005$ 46 (1 SE). Two pyrite standards were used for external standard bracketing (PPP-1) (Gilbert et al., 47 2014) and quality control (Py₂) of analyses. The in-house standard, Py₂, has been analyzed 48 previously by gas source mass spectrometry yielding a δ^{34} Sv-CDT (‰) value of -0.4 ± 0.5‰ (1s). 49 We obtained an average value of $-0.22 \pm 0.35\%$ (1s, n=35) for the measurements reported in 50 this study (Table S4). 51

52 1.2 S isotopic analysis of pyrite separates and carbonate-associated sulfates (CAS)

Based on the *in-situ* δ^{34} S analyses, nodular pyrite aggregates in samples from Interval I and II have δ^{34} S_{Py} 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 61 for subsequent extraction of the H₂S from the disseminated pyrite and sulfate extraction from 62 carbonates. Disseminated pyrite was extracted using the chromium reduction method, in which 63 the powders were reacted with 50 ml of 1 M CrCl₂ and 20 ml of 10 M HCl in a N₂ atmosphere 64 (Canfield et al., 1986). Hydrogen sulfide released during decomposition of the pyrite was 65 bubbled through a 1M zinc acetate trap where it was precipitated as ZnS, which was then 66 converted to Ag₂S by ion exchange with AgNO₃. The Ag₂S was centrifuged, washed three times 67 using deionized water, and dried at 60 °C for analysis. 68

69 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 70 carbonate-rich mudstones containing < 1 wt% TS and > 3 wt% total inorganic carbon (TIC) 71 (Shi et al., 2018). The procedure involved first rinsing 100-300 g of sample powder (200 mesh) 72 with a 10% NaCl solution to remove later-stage sulfate. To ensure that as much as possible of 73 the non-CAS sulfate was removed from the powder before CAS extraction, the powders were 74 rinsed repeatedly with the NaCl solution until sulfate was not detectable in the solution. In the 75 next step, 4 N HCl was added in small aliquots to the samples to enable complete dissolution 76

of the carbonates. Possible ferric iron-mediated pyrite oxidation during CAS extraction was
inhibited by adding 15% SnCl₂ 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 BaSO₄ for
isotopic measurements by adding a saturated BaCl₂ solution.

Approximately 100 µg BaSO₄ (for CAS) or Ag₂S (for pyrite separates) was measured out 82 for analysis of their sulfur isotopic composition using a ThermoFinnigan Delta Plus mass 83 spectrometer connected to an Elemental Analyzer. International standards for barite, IAEA-S-84 05 ($\delta^{34}S = +0.49\%$), IAEA-S-06 ($\delta^{34}S = -34.05\%$), and NBS 127 ($\delta^{34}S = +21.10\%$) were 85 measured to correct the barite measurements, and IAEA-S-01 ($\delta^{34}S = -1.34\%$), IAEA-S-02 86 $(\delta^{34}S = +21.18\%)$, and IAEA-S-03 $(\delta^{34}S = -33.54\%)$ were used to correct the sulfide mineral 87 measurements (Table S4). The results are reported in delta notation as per mil differences from 88 the V-CDT standard. The analytical reproducibility was generally better than $\pm 0.3\%$. 89 Concentrations of CAS were calculated based on barium sulfate yields, following a correction 90 for the insoluble residue. 91

92 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}. To determine Fe_T, 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.

102 **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). 107 About 0.2-0.5 g of sample powder was digested using 5 mL of aqua regia in a water bath (95 °C 108 for 6 hours). Certified reference materials (NIST SRM 2711, Montana soil) were prepared for 109 analysis after every 13 samples and digested in the same way as the samples. After digestion, 110 the solution was centrifuged (3000 rpm for 10 min) at room temperature and then decanted to 111 112 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 113 acid concentrations of 10-20% (v/v). Bracketing NIST SRM 3133 standard solutions were also 114 prepared, with Hg concentration and acid matrices matched to the neighboring samples. The 115 analytical uncertainty was estimated from replication of the composition of the UM-Almadén 116 secondary standard solution, and a full procedural analysis of NIST SRM 2711. Samples were 117 analyzed using a Neptune Plus multiple collector inductively coupled plasma mass 118

spectrometer (Thermo Electron Corp, Bremen, Germany) at the University Research Facility 119 in Chemical and Environmental Analysis (UCEA) at the Hong Kong Polytechnic University, 120 following the methods described by Geng et al. (2018). Mercury isotopic compositions were 121 expressed as δ and Δ values, in units of per mil (‰) following the convention recommended 122 by Bergquist and Blum (2007). 123 The average isotopic ratio and uncertainty of all the UM-Almadén measurements (δ^{202} Hg: 124 $-0.52 \pm 0.04\%$; Δ^{199} Hg: $+0.00 \pm 0.03\%$; Δ^{200} Hg: $+0.02 \pm 0.04\%$; Δ^{201} Hg: $-0.02 \pm 0.05\%$; 2SD, 125 n=6) agree well with those reported previously (Bergquist and Blum, 2007). Measurements of 126 replicate digests of NIST 2711 (δ^{202} Hg: -0.18 ± 0.06‰; Δ^{199} Hg: -0.22 ± 0.04‰; Δ^{200} Hg: 0 ± 127 0.05%; Δ^{201} Hg: -0.19 ± 0.05‰, 2SD, n=3) were also comparable with those of previous studies 128 (Table S5). 129

130 **1.5 Carbon and oxygen isotopic analyses**

Carbon and oxygen isotope compositions ($\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$) of calcareous shales were 131 determined using a Thermo Fisher Scientific carbonate-preparation device and a Gas Bench II 132 connected to a Delta Plus XL isotope ratio mass spectrometer (IRMS) that was operated in 133 continuous He flow mode, at the Institute of Geochemistry, Chinese Academy of Sciences, 134 Guiyang, China. The CO₂ was extracted from carbonates with 100% phosphoric acid at 70 °C 135 for calcite and 90 °C for dolomite. The stable C and O isotope ratios are reported in delta (δ) 136 notation as the per mil (‰) deviation relative to the Vienna Pee Dee belemnite (V-PDB) 137 standard. The analytical reproducibility estimated from replicate analyses of the laboratory 138 standards, Carrara marble, and Binn dolomite, was better than $\pm 0.05\%$ for δ^{13} C and $\pm 0.1\%$ for 139

140 $\delta^{18}O.$

141 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 142 with a high-temperature furnace and acidification module (Eltra, Germany). Approximately 20 143 to 300 mg of the powder was weighed into a ceramic boat and combusted in pure (99.95%) O₂ 144 at 1350 °C for ~3 minutes to measure TC and TS. The TOC was analyzed in two steps. Firstly, 145 inorganic carbon was removed by adding 4 mol/L HCl into about 2 g powder. Then, ~100 mg 146 of the solid residue was weighed and combusted using the same methods as for TC-TS. 147 Analytical errors for TC-TOC-TS were ± 0.1 wt%, based on analyses of carbonate standard, 148 AR4007 (Alpha, USA). The TIC (total inorganic carbon) content was calculated by subtracting 149 the TOC from the TC. 150

151 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 HNO₃ acid in highpressure 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%.

159

160 Supplementary Note 2: Possible modification of carbonate-associated sulfur (CAS)

Carbonate-associated sulfur is the trace quantity of sulfate that replaces carbonate ions 161 structurally in marine carbonate. It is incorporated into the lattice of carbonate minerals and its 162 δ^{34} S signature is thought to be unaffected by processes such as meteoric diagenesis (Gill et al., 163 2008) and remineralization of organic-bonded sulfur (Werne et al., 2008). Because carbonate 164 sequences are deposited very rapidly, it is possible to estimate marine sulfate isotopic 165 compositions with a very high temporal resolution using CAS (something that is generally a 166 problem with other sulfate-bearing minerals). However, it has been argued recently that $\delta^{34}S$ 167 values of CAS can be affected by diagenetic processes such as dolomitization (Shen et al., 168 2008), present-day atmospheric sulfate (Peng et al., 2014), as well as by the oxidation of pyrite 169 during sample preparation (Loyd et al., 2012; Marenco et al., 2008; Wotte et al., 2012). Thus, 170 before evaluating oceanic sulfur states using CAS data, it is essential to carefully evaluate the 171 CAS δ^{34} S values to ensure that the recovered sulfate truly represents the original CAS. 172 Progressive diagenetic alteration of carbonates generally raises Mn and lowers Sr contents, as 173 well as the δ^{13} C and δ^{18} O values of carbonate rocks (Kaufman et al., 1993; Li et al., 2013; 174 Swart, 2015). In the absence of obvious correlations among δ^{13} C, δ^{18} O and Mn/Sr values (Fig. 175 5e, f), we therefore conclude that diagenetic alteration had a negligible effect on isotopic 176 variation in the samples from the Dongjin section, and their temporal variations of $\delta^{34}S_{CAS}$ has 177 been preserved. 178

As discussed in the main text, sulfate contamination from oxidized pyrite prior to the final CAS extraction can modify the δ^{34} S values of CAS. In the present study, this contamination was minimized by avoiding the usage of oxidants, such as NaOCl and H₂O₂, during the pre-

leaching, and rapidly dissolving the carbonate slurry (4N HCl) without drying during the 182 extraction (Wotte et al., 2012). The absence of contamination from this source is supported by 183 duplicate analyses that returned results with a standard deviation less than 1.4% (Table S3). 184 Further evidence that the $\delta^{34}S_{CAS}$ values were not contaminated by sulfate from the oxidation 185 of pyrite is provided by the observation that in some of the samples the values are much lower 186 than the $\delta^{34}S_{Pv}$ values (Table S3). It is conceivable that, if the low $\delta^{34}S$ values of CAS were 187 generated by contamination from oxidized pyrite, δ^{34} Scas values could be higher than or similar 188 to the values of δ^{34} SPy. 189

Carbonate-associated sulfur may also be subject to natural contamination by recent 190 secondary atmospheric sulfate (SAS). This may be especially the case, if the sampled 191 carbonates are from outcrops in arid to semi-arid regions that have experienced limited leaching 192 193 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-194 cut outcrop of the calcareous shales from the Dongjin section that was sampled has been 195 196 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 197 the contamination from SAS. As atmospheric sulfate invariably has a low δ^{34} S value, 198 contamination of this type might be expected to produce a negative correlation between CAS 199 concentrations and $\delta^{34}S_{CAS}$ values. However, such a correlation is not evident in our data (see 200 Supplementary Figure S3). 201

202 Methods used for δ^{34} S_{CAS} measurement are mostly applied to carbonate with low TOC 203 and pyrite contents, whereas the calcareous shale samples in this study have relatively high

204	TOC (0.3-1.8 wt%) and TS contents (0.07-0.95 wt%). Any oxidation of organic-S and pyrite
205	during diagenesis or post-diagenetic processes could decrease the $\delta^{34}S_{CAS}$ (Borowski et al.,
206	2013; Shen et al., 2008). Of all samples analyzed, sample DJV-15 has the lowest TOC (0.3
207	wt%) and TS (0.07 wt%) contents and the highest TIC content (9.6 wt%), which means that
208	calcite occupied ~80% of the sediment (Table S3). The sample has a $\delta^{34}S_{CAS}$ value of +19‰,
209	which is only +2.6‰ greater than the average $\delta^{34}S_{CAS}$ value of all the samples analyzed (Table
210	S3). This suggests that contamination, resulting from oxidation of organic-S and pyrite during
211	diagenesis or post-diagenetic processes, of CAS of calcareous shales from the Dongjin section
212	was limited.
213	Finally, the calcareous shales in the Dongjin section are dominated by calcite, but it is
214	difficult to determine whether the calcite crystallized mainly in an evaporitic environment or
215	near the sediment-water interface influenced by pore water. If the calcite crystallized near the
216	sediment-water interface, the $\delta^{34}S$ values of CAS would be a signature of the pore water rather
217	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.

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

224 diagenesis

In-situ analyses show that the nodular aggregates of pyrite have extremely high δ^{34} S

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

It has been observed in carbonaceous sediments that methane forms by the decomposition of organic matter and thus would react with 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 ³⁴S-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:

251
$$CH_4 + SO_4^{2-} \rightarrow HCO_3^{-} + HS^{-} + H_2O$$
 (Jørgensen and Kasten, 2006)

which proceeds rapidly through fluid advection and bubble ebullition at cold seeps, and also 252 can take place more slowly by diffusion in pore water at sites away from active seepage 253 (Hensen et al., 2003). The δ^{13} C value of HCO₃⁻ formed in the SMT zone is thought to be 254 extremely low (-60‰) (Borowski et al., 2013; Jiang et al., 2003). However, the δ^{13} C values of 255 the carbonates in the Dongjin section are $\sim -0.5\%$ (see Supplementary Figure S4 and Table S6) 256 and do not change from this value in the pyrite-rich layers. This suggests that extremely high 257 δ^{34} S values in the nodular pyrite were not the result of AOM process near the SMT zone (Hao 258 259 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 ³²S generated by BSR would have led to a sustainable growth of δ^{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 δ^{34} S values increase from +20‰ at the sediment-seawater interface to >+60‰ at depth (Rennie and Turchyn, 2014).

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