Data Repository

Revisiting Ediacaran sulfur isotope chemostratigraphy with *in situ* NanoSIMS analysis of sedimentary pyrite

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Geological Background

In general, the Lantian drill-core consists of, in ascending order, members I, II, III, and IV of the Ediacaran Lantian Formation (Wang et al., 2017). It spans from the lower-to-middle Ediacaran strata, corresponding to the time between 635 Ma and 551 Ma (Condon et al., 2005; Wang et al., 2017). The Lantian Biota, a diverse assemblage of macroscopic fossils preserved as carbonaceous compressions, occurs in black shales more or less continually in the upper subunit of Member II and the lower subunit of Member III (Yuan et al., 2011). Twelve sampling intervals were selected for detailed petrographic observation and *in situ* NanoSIMS $\delta^{34}\text{S}_{\text{py}}$ analysis. One sampling interval in Member I represents cap dolostone overlying the Cryogenian diamictite in the area. Eight sampling intervals of Member II are shales, and three intervals from Member III are carbonate rocks. The detailed depth and lithologies of sampled intervals are provided in Table S1.

Condon, D., Zhu, M.Y., Bowring, S., Wang, W., Yang, A., and Jin, Y., 2005, U-Pb ages from the Neoproterozoic Doushantuo Formation, China: *Science*, v. 308, p. 95–98, <https://doi.org/10.1126/science.1107765>.

Yuan, X.L., Chen, Z., Xiao, S.H., Zhou, C.M., and Hua, H., 2011, An early Ediacaran assemblage of macroscopic and morphologically differentiated eukaryotes: *Nature*, v. 470, p. 390–393, <https://doi.org/10.1038/nature09810>.

Analysis Methods

Thin sections were cut and polished for petrographic observation with light and electron microscopy as well as *in situ* $\delta^{34}\text{S}$ analysis with nanoscale secondary ion mass spectroscopy (NanoSIMS). A reflected-light microscope (ZEISS scope A1) and scanning electron microscope (SEM, LEO 1530 VP) equipped with an energy dispersive spectrometer (EDS) were used for pyrite morphological observation and mineral detection at the Nanjing Institute of Geology and Paleontology, Chinese Academy of Sciences. SEM images were acquired using an accelerating voltage of 15 or 20 keV at a working distance of 10 mm. All the SIMS pits were imaged by SEM and are shown with corresponding $\delta^{34}\text{S}_{\text{py}}$ values in Figure S2.

After morphological observation, *in situ* sulfur isotopes (^{34}S , ^{32}S) of pyrite in 12 thin section samples were analyzed by CAMECA NanoSIMS 50L system at the Institute of Geology and Geophysics, Chinese Academy of Sciences. Polished thin sections were cut to fit the size of the sample holder holes (10 mm in diameter). Before putting samples into the instrument, all round samples were coated with black carbon. The *in situ* sulfur isotopes were measured using two analysis modes, according to the pyrite size and thickness to avoid puncturing through the pyrite: FC (^{32}S) – EM (^{34}S) mode and FC (^{32}S) – FC (^{34}S) mode. In the FC – EM mode, ~ 7-10 pA of Cs^+ primary beam was used to raster an area of $2\text{ }\mu\text{m} \times 2\text{ }\mu\text{m}$. $^{32}\text{S}^-$ and $^{34}\text{S}^-$ were detected with the Faraday cup (FC) and with the Electron multiplier (EM), respectively. This type of mode can meet the demands of a high lateral resolution and a shallow crater but with less intensity and larger precision. On the contrary, in the

FC-FC mode, ~80-100 PA of Cs^+ primary beam was used to raster an area of $2\ \mu\text{m} \times 2\ \mu\text{m}$ to achieve a better precision, but with a larger and deeper spot crater. And both of $^{32}\text{S}^-$ and $^{34}\text{S}^-$ were detected with FC. Certified international standards (Pyrite of Balmat, CAR-123 pyrite, with $\delta^{34}\text{S} = 16.04 \pm 0.2\text{‰}$) and working reference samples (pyrite PY-1117 with $\delta^{34}\text{S} = 0.3 \pm 0.1\text{‰}$, and CS01 with $\delta^{34}\text{S} = 4.6 \pm 0.2\text{‰}$) were used in this analysis. PY-1117 was obtained from pyrite veins (2–4 mm wide) at a depth of 62 m in Qulong, Tibet, China. CS01 was separated from a massive pyrite–pyrrhotite gold-bearing ore from the Chaoshan gold deposit, Eastern Yangtze Craton, Eastern China. Both pyrite reference samples have homogeneous sulfur isotopic compositions. Sulfur isotope ratios are reported in standard per mil (‰) notation relative to V-CDT, calculated as $\delta^{34}\text{S}_{\text{sample}} = [({}^{34}\text{S}/{}^{32}\text{S})_{\text{sample}} / ({}^{34}\text{S}/{}^{32}\text{S})_{\text{VCDT}} - 1] \times 1000$. The analytical precision (1SD) was better than 0.9‰ for $\delta^{34}\text{S}$ measurement. The detailed description of SIMS analysis method is provided in Yang et al. (2015).

Yang, W., Hu, S., Zhang, J., Hao, J. and Lin, Y., 2015, NanoSIMS analytical technique and its applications in earth sciences: *Science China Earth Sciences*, v. 58, p. 1758–1767, [https://doi: 10.1007/s11430-015-5106-6](https://doi.org/10.1007/s11430-015-5106-6).

Table S1. Sampling information of 12 thin sections from the Lantian drill-core

Sample Number	Field Sample Label	Depth (m)	Location	Lithology	TOC (%)	FeS ₂ (%)
LTD01	89 3/12	1.9	Member I	Siliceous dolostone	0.0	0.0
LTD02	77 7/7~7/7-1 dark	32.6	Member II	Black shale	4.1	0.3
LTD03	72 9/9	46.8	Member II	Black shale	6.6	0.1
LTD04	70 5/7-2	52.4	Member II	Black shale	2.4	1.2
LTD05	65 10/10	63.0	Member II	Shale/mudstone	0.2	0.2
LTD06	65 2/10	65.7	Member II	Shale/mudstone	0.1	0.2
LTD07	55 2/12	80.5	Member II	Black shale	7.8	1.5
LTD08	54 1/11~2/11	83.5	Member II	Black shale	3.5	1.2
LTD09	50 5/5 up	91.6	Member II	Shale/mudstone	1.0	9.1
LTD10	49 2/11	95.7	Member III	Argillaceous dolostone	1.2	0.2
LTD11	33 9/10	139.5	Member III	Limestone	0.0	0.1
LTD12	26 9/10-2	155.2	Member III	Limestone	2.4	2.0

Table S2. Statistics of NanoSIMS $\delta^{34}\text{S}_{\text{py}}$ values from 12 thin sections in the Lantian drill-core

Sample Number	Bulk $\delta^{34}\text{S}_{\text{py}}$ (‰)	NanoSIMS $\delta^{34}\text{S}_{\text{py}}$ range (‰)		Mean NanoSIMS $\delta^{34}\text{S}_{\text{py}}$ value (‰)			
		Framboidal	Euhedral and Subhedral	Framboidal	Standard Deviation (σ)	Euhedral and Subhedral	Standard Deviation (σ)
LTD01	30.7	—	19.6 ~ 32.4	—	—	28.1	4.1
LTD02	-29.6	-37.9 ~ -17.3	-37.6 ~ -19.2	-28.1	6.0	-30.6	5.3
LTD03	-8.7	-23.8 ~ -8.8	-8.9 ~ 15.3	-14.9	5.6	3.0	4.6
LTD04	3.8	-21.5 ~ -13.9	1.2 ~ 16.9	-17.1	2.5	6.6	3.6
LTD05	24.0	—	1.8 ~ 32.2	—	—	18.9	11.8
LTD06	36.5	—	7.1 ~ 14.8	—	—	10.0	2.8
LTD07	-13.6	-38.5 ~ -23.4	10.6 ~ 15.2	-31.4	4.3	12.2	1.3
LTD08	14.0	-31.7 ~ -21.7	5.9 ~ 18.3	-26.2	2.3	15.3	4.1
LTD09	-23.9	-30.4 ~ -12.5	15.2 ~ 20.3	-25.3	4.9	18.1	1.4
LTD10	-7.8	-12.4 ~ -6.3	7.8 ~ 37.6	-9.1	1.9	13.8	5.6
LTD11	9.9	—	-6.5 ~ 30.0	—	—	12.3	13.1
LTD12	17.9	-21.7 ~ -2.9	8.7 ~ 33.8	-11.5	5.2	25.8	7.7

97 Note: ‘—’ indicates no detection. Bulk $\delta^{34}\text{S}_{\text{py}}$ values are from Wang et al. (2017). Euhedral and subhedral crystals are sometimes difficult to be

98 distinguished from each other, thus they are classified to the same morphological pyrite type. Not all pyrite crystals included in samples were
99 analyzed by NanoSIMS due to limited machine time.

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Figure S1

Figure S1. Compilations of bulk sulfur isotopes measured in sedimentary pyrite ($\delta^{34}\text{S}_{\text{py}}$) and carbonate associated sulfate ($\delta^{34}\text{S}_{\text{CAS}}$) in early-middle

Ediacaran Period (635 Ma – 551 Ma). A) Data are compiled from Fike et al.

(2006), McFadden et al. (2008), Shen et al. (2008), Li et al. (2010), Sahoo et al.

(2016), Shi et al. (2018), and Wang et al. (2017, 2020). B) Histograms show

$\delta^{34}\text{S}_{\text{CAS}}$ values ($27.7 \pm 10.8\text{‰}$, N=298) and bulk $\delta^{34}\text{S}_{\text{py}}$ values ($5.9 \pm 15.5\text{‰}$,

N=749) in the Doushantuo Formation, South China. $\delta^{34}\text{S}_{\text{CAS}}$ data are compiled

from McFadden et al. (2008), Li et al. (2010), and Shi et al. (2018); bulk-rock

$\delta^{34}\text{S}_{\text{py}}$ data from McFadden et al. (2008), Shen et al. (2008), Li et al. (2010),

Sahoo et al. (2016), and Wang et al. (2017, 2020).

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Figure S2. Data of NanoSIMS $\delta^{34}\text{S}_{\text{py}}$ values for each thin-section sample. A, LTD01: euhedral-subhedral (A1, A2); B, LTD02: framboids (B1 – B3), euhedral-subhedral (B4, B5); C, LTD03: later diagenetic framboids (C1); euhedral-subhedral (C2 – C7); D, LTD04: later diagenetic framboids with indistinct framboidal figuration (D1, D2); euhedral-subhedral (D3, D4); E, LTD05: euhedral-subhedral (E1 – E6); F, LTD06: euhedral-subhedral (F1 – F2); G, LTD07: framboids (G1 – G12); framboidal pyrite cluster with pyrite cements or possible recrystallization of framboidal aggregate (G13, G14); adjacent framboid and the euhedral-subhedral grain (G15); euhedral-subhedral (G16 – G18); H, LTD08: framboids (H1 – H5); euhedral-subhedral (H6); I, LTD09: framboids (I1); euhedral-subhedral (I2); framboid with pyrite cements (I3, I4); J, LTD10: framboids (J1); euhedral-subhedral (J2 – J8); K, LTD11: euhedral-subhedral (K1 – K5); L, LTD12: later diagenetic framboidal clusters after initial formation (L1, L2), possibly experiencing recrystallization but remaining inside indistinct framboidal figuration; euhedral-subhedral (L3 – L5).

‘Rate-based method’ Description

Algeo et al. (2015) proposed a ‘rate-based method’ to model paleo-seawater sulfate concentrations according to two parameters of ancient marine systems: MSR-associated sulfur isotopic fractionation between cogenetic sedimentary sulfate and sulfide ($\Delta^{34}\text{S}$), and the maximum rate of change in seawater sulfate sulfur isotopes ($(\partial\delta^{34}\text{S}_{\text{CAS}}/\partial t (\text{max}))$). Quantitative calculation of the maximum $[\text{SO}_4^{2-}]_{\text{sw}}$ from measured values through geological time is given as:

$$[\text{SO}_4^{2-}]_{\text{sw}}(\text{max}) = k_1 \cdot k_2 \cdot F_{\text{PY}} \cdot \Delta^{34}\text{S} / \frac{\partial\delta^{34}\text{S}_{\text{CAS}}}{\partial t} (\text{max}) \quad (1)$$

Considering a remarkable difference in $\delta^{34}\text{S}_{\text{py}}$ values between bulk-rock pyrite ($\delta^{34}\text{S}_{\text{bulk}}$) and framboidal pyrite ($\delta^{34}\text{S}_{\text{framboid}}$), $\Delta[\text{SO}_4^{2-}]_{\text{sw}}$, referring to the difference of calculated maximum $[\text{SO}_4^{2-}]_{\text{sw}}$ caused by application of $\delta^{34}\text{S}_{\text{bulk}}$ and $\delta^{34}\text{S}_{\text{framboid}}$ can be defined as:

$$\Delta[\text{SO}_4^{2-}]_{\text{sw}} = k_1 \cdot k_2 \cdot F_{\text{PY}} / \frac{\partial\delta^{34}\text{S}_{\text{CAS}}}{\partial t} (\text{max}) \cdot (\delta^{34}\text{S}_{\text{bulk}} - \delta^{34}\text{S}_{\text{framboid}}) \quad (2)$$

Where k_1 represents a unit-conversion constant and is equal to 10^6 , and k_2 is equal to 2.22×10^{-20} mM/g, representing a constant relating to the mass of seawater sulfate to its molar concentration. The total sulfate sink flux F_{PY} is assumed to be 4×10^{13} g/yr in a widespread euxinia ocean (Algeo et al., 2015). Apparently, if $\frac{\partial\delta^{34}\text{S}_{\text{CAS}}}{\partial t} (\text{max})$ is a definite value, the formula (2) will express a linear function, with the $\Delta[\text{SO}_4^{2-}]_{\text{sw}}$ values linearly dependent on the changes of $(\delta^{34}\text{S}_{\text{bulk}} - \delta^{34}\text{S}_{\text{framboid}})$.

Figure S3

Figure S3. Quantitative model on the underestimated extent of seawater sulfate concentration ($\Delta[\text{SO}_4^{2-}]_{\text{sw}}$) based on the difference between framboidal $\delta^{34}\text{S}_{\text{py}}$ and bulk $\delta^{34}\text{S}_{\text{py}}$ values. The model is revised from Algeo et al. (2015). The four lines in blue, red, green and yellow colors represent assumed maximum change rates of sulfate $\delta^{34}\text{S}$ in seawater. Bulk $\delta^{34}\text{S}_{\text{py}}$ values ($\delta^{34}\text{S}_{\text{bulk}}$) from Wang et al. (2017). Framboidal $\delta^{34}\text{S}_{\text{py}}$ values ($\delta^{34}\text{S}_{\text{framboid}}$) are the mean values of *in situ* NanoSIMS spot values of each sample. Black solid, blue hollow, and red hollow points indicate the average, lower limit and upper limit values of ($\delta^{34}\text{S}_{\text{bulk}} - \delta^{34}\text{S}_{\text{framboid}}$) for each sample, respectively. The data of ($\delta^{34}\text{S}_{\text{bulk}} - \delta^{34}\text{S}_{\text{framboid}}$) are relatively concentrated in gray shaded area. Higher theoretical possible maximum rate of sulfate $\delta^{34}\text{S}$ relative to measured data ($\sim 1\text{‰}/\text{Myr}$) may produce the estimated value exceeds actual modern seawater $[\text{SO}_4^{2-}]_{\text{sw}}$ (Algeo et al., 2015).