Sulfur and carbon isotopic variations in Neoproterozoic sedimentary rocks from southern China*

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Abstract A new set of $\delta^{34}S_{sulfide}$, $\delta^{34}S_{sulfate}$ and $\delta^{13}C_{carbonate}$ values has been reported from Neoproterozoic sedimentary rocks in southern China. The interglacial black shales of the Datangpo Fm. display higher $\delta^{34}S_{sulfide}$ values with $> +20‰$ average, but the post-glacial black shales from the Doushantuo Fm. show negative $\delta^{34}S_{sulfide}$ values. However, the Jinjiadong Fm., the same post-glaciation as the Doushantuo Fm., has positive $\delta^{34}S_{sulfide}$ values, implying that the $\delta^{34}S$ value of sedimentary sulfides would be controlled by lithofacies and paleogeographic environments. The $\delta^{34}S_{sulfate}$ values relative to $\delta^{13}C_{carbonate}$ were obtained by extraction of trace sulfate from the successive carbonate sequences in the Yangtze Gorges sections. A preliminary interpretation suggests that the oceanic environment may fluctuate dramatically at the post-glacial Doushantuo stage and, then, recover its stability at the Dengying stage on the basis of the high resolution $\delta^{34}S$ and $\delta^{13}C$ curves of seawater.

Keywords: Neoproterozoic, southern China, sulfur isotopes, carbon isotopes, seawater, secular variations.

The Neoproterozoic (1000 ~ 545 Ma) has experienced dramatic geotectonic, environmental and biological changes[1~3]. At least two distinct global glaciations may have covered most, if not all, of the world's continents and oceans with ice[2,4]. Biogeochemical processes impose in part substantial and predictable isotopic fractionations on sulfur species as they are cycled between oxidized (i.e. sulfate) and reduced (i.e. sulfide) forms. Thus, the isotopic compositions of sedimentary sulfides and sulfates are sensitive indicators of environmental and biological changes. Respective secular variations of $\delta^{34}S$ values reflect changes in seawater chemistry, environmental conditions and life's evolution[5~7]. Similarly, stratigraphic variations in carbon isotopic values of marine carbonate and organic matter preserved with it also provide the above information and refine stratigraphic correlation[8].

In southern China, extraordinarily high $\delta^{34}S_{pyrite}$ values from the strata or Mn ore bodies of manganiferous carbonates, the Lower Sinian Datangpo Formation, have attracted attention of researchers[9~12]. Additional sulfur isotope data[13~15] for Sinian pyrite and sulfate extracted from phosphorite have been reported.

We systematically investigate the sulfur isotopic composition of sulfide and sulfate and carbon isotopic composition of carbonate in Neoproterozoic sedimentary rocks from the Yangtze Platform. The central objective is to assess the influence of glacial conditions on the biogeochemical cycling of sulfur and carbon. Preliminary result and brief discussion are reported here.

1 Geological setting

During the Neoproterozoic, the Yangtze Platform was separated from the Cathaysia Block by the South China Ocean (Fig. 1). The Yangtze Gorges section, established in 1924, has been the stratotype for Sinian stratigraphic correlation. It has also been the focus of both isotopic and paleontologic investigations[16]. In ascending stratigraphic order, the Lower Sinian succession comprises the Liantuo, Gucheng, Datangpo and Nantuo formations, while the Upper Sinian is composed of the Doushantuo and Dengying formations.

In order to correlate the Sinian succession with the international division scheme for the Neoproterozoic, it was split into two systems: Nanhua (Cryogenian) and Sinian (Neoproterozoic III)[17]. The

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stratigraphic sequences of Nanhua are mainly composed of pre-glacial (Liantuo stage), lower-glacial (Gucheng stage), interglacial (Datangpo stage), and upper-glacial (Nantuo stage) clastic rocks, such as sandstone, siltstone, black shale, and diamictite (tillite). At present, the Doushantuo and Dengying formations compose the Sinian system. Main lithologies include carbonate, phosphorite, siltstone, and shale[10]. Previously, Datangpo was called Xiangmeng or Minle in Hunan Province. In central Hunan, Hongjiang, Jinjiadong and Liuchapo formations correspond to Nantuo, Doushantuo and Dengying formations, respectively. The Hongjiang Fm. is composed of marine glacial mudstones, siltstones, and sandstones with rafted boulders and dolostone lenses. The Jinjiadong and Liuchapo formations comprise siliceous rocks. The lithological features indicate that the Hongjiang, Jinjiadong and Liuchapo formations might have been deposited on the continental slope, thus, deeper than on the carbonate platform.

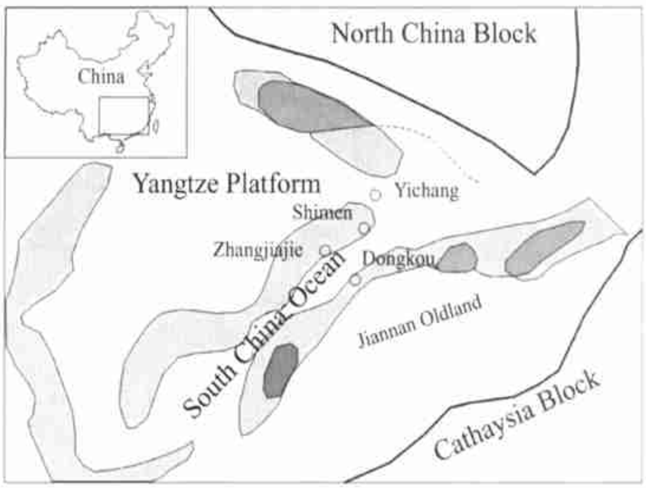

Fig. 1. Simplified tectonic map of southern China during the Neoproterozoic era and locations of sampled sections.

In southern China, the age of Neoproterozoic strata is poorly constrained. A reliable U-Pb zircon age of 748 ± 12 Ma was measured for tuffs in the underlying Liantuo[18]. Recently, the dating of Doushantuo phosphorites by Lu-Hf and Pb-Pb methods respectively yielded ages of 584 ± 26 Ma and 599.3 ± 4.2 Ma. This suggests that the Nantuo glaciation on the Yangtze Platform might predate other glacial rocks in other continents, which is commonly associated with the younger (Marinoan) of the two major Neoproterozoic glaciations[19].

2 Analytical methods

Sulfur isotope analyses on sulfides from black shales were performed by on-line measurements using a mass-spectrometer equipped with an elemental analyzer (EA-MS). The whole rock containing sulfides, such as pyrite, was crushed and pulverized into powder of < 200 mesh. The weighted ~1 mg sample was analyzed for S isotope ratio by EA-MS.

Trace sulfate was extracted from carbonate samples by a chemical method similar to Ref. [20]. About 50 g powder of each sample was dissolved in 6 mol/L HCl for 12 h. Insoluble residues were removed by filtration. 5 g of $(NH_4)_2(OH)Cl$ was added to the filtrate and its pH was adjusted to ~4 by using NH_4OH. $BaSO_4$ precipitate was obtained by adding saturated $BaCl_2$ solution into the boiling filtrate. SO_2 was prepared by thermal decomposition of $BaSO_4$[21].

Analytical errors for $\delta^{34}S$ errors were within ±0.3‰ for sulfide and ±0.2‰ for sulfate, respectively.

For carbon isotope analysis, carbonate sample was ground below 200 mesh size and treated with anhydrous H_3PO_4 for 24 h at 50 ℃ or 25 ℃ to librate CO_2, respectively for dolomite or limestone. The $\delta^{13}C$ is presented relative to the PDB standard and the analytical error was within ±0.2‰.

3 Result and discussion

35 black shale and mudstone samples rich in pyrite were collected for sulfur isotope analyses from the Yangjiaping Section in Shimen, the Tianping Section in Zhangjiajie, and the Jiangkou Section in Dongkou (Fig. 2). Sulfide from the interglacial black

shales of the Datangpo Fm. displays $\delta^{34}S$ values between +5.6 and +37.5‰ (avg. +21.6‰) for the Yangjiaping Section, and between +21.1 and +35.7‰ (avg. +27.0‰) for the Tianping Section. In contrast, black shales from the Doushantuo Fm. show negative $\delta^{34}S_{sulfide}$ values, ranging from −13.0 to +1.5‰ (avg. −6.9‰) for the Yangjiaping Section and from −13.7 to +4.6‰ (avg. −2.3‰) for the Tianping Section. Cap carbonates in the Yangjiaping and Tianping sections yielded negative $\delta^{13}C$ values, generally below −5‰ for the Datangpo Fm. and above −5‰ for the Doushantuo Fm.

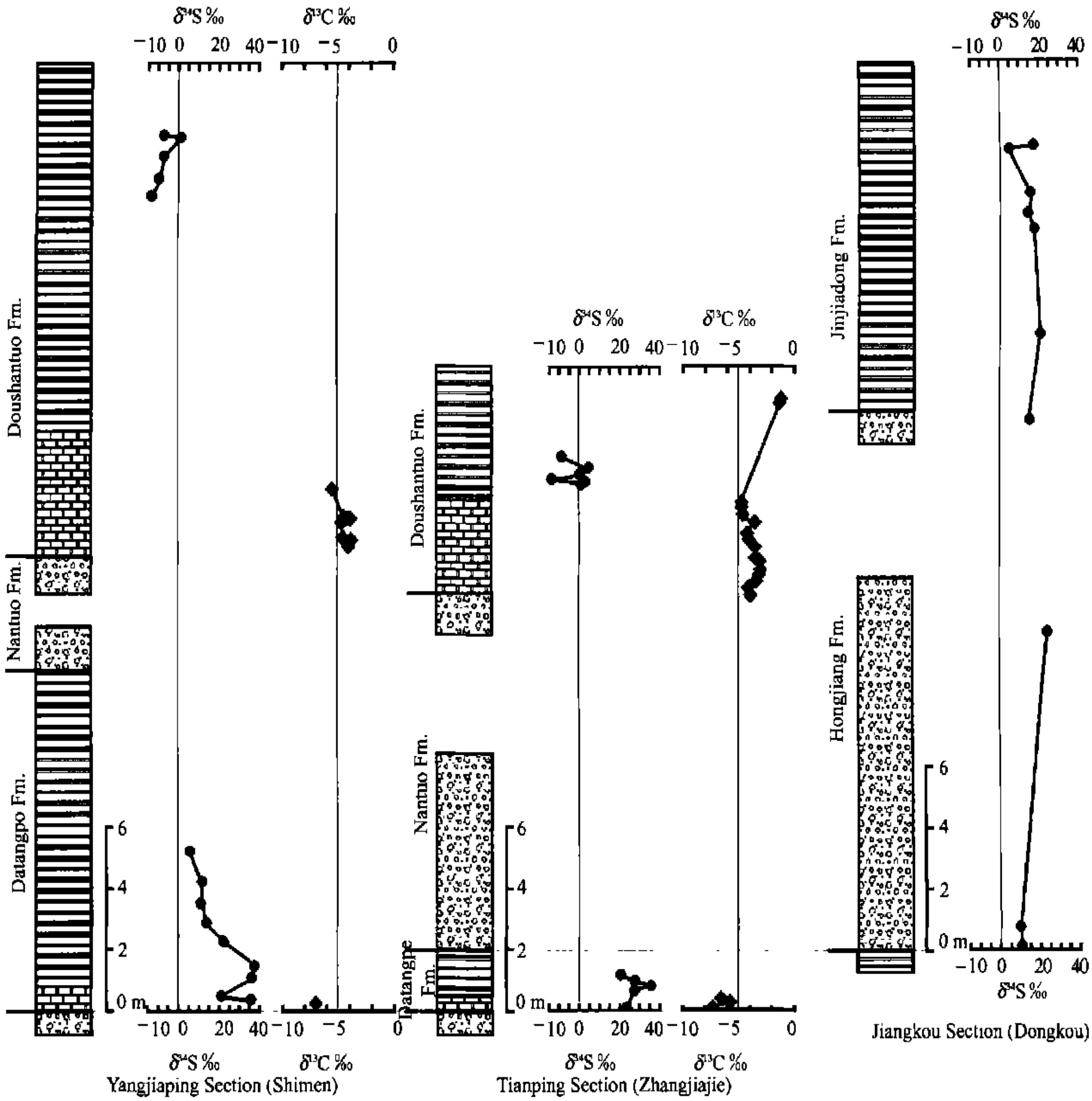

Fig. 2. Sulfur isotopic compositions of sulfides and carbon isotopic compositions of carbonates in three Neoproterozoic sections on the Yangtze Platform, southern China.

Highly positive $\delta^{34}S$ values for pyrite from the Early Sinian strata in the Yangtze Platform were reported to be ranging from +16.1 to +63.8‰. Obviously, this is consistent with the above data from sulfides in the Yangjiaping and Tianping sections, even though the $\delta^{34}S_{sulfide}$ values are not higher than +40‰ for both sections. Extraordinary $\delta^{34}S_{sulfide}$ value, in fact, has been found mostly in places where rhodochrosite mineralization occurred[9,10,12]. High $\delta^{34}S_{sulfide}$ values measured from the Datangpo Fm. suggest that the seawater might have once attained very high $\delta^{34}S$ values, prior to the Datangpo Fm. The occurrence of black shale suggests that biomass should be large during the interglacial stage. These imply that some basins on the Yangtze Platform might have limited or no access to the open ocean, or a sulfate-minimum zone (SMZ)[10] might be produced in the water column due to high organic productivity after the Jiangkou Ice-age[22].

In the upper glacial sedimentary rocks of the Hongjiang Fm., sulfide has significant positive $\delta^{34}S$ values, between +9.6 and +23.7‰ with an average of +14.8‰. Similar $\delta^{34}S$ values were measured for black shales from the Jinjiadong Fm. (+4.0 to +20.6‰, avg. +15.1‰), although it is stratigraphically equivalent to the Doushantuo Fm. The Jinjiadong Fm. has significantly different $\delta^{34}S_{sulfide}$ range from the Doushantuo Fm. as shown in Fig. 2. It suggests that the regional change in lithofacies possibly controls change in $\delta^{34}S$ for sulfides precipitated in the different paleogeographic environments.

Successive $\delta^{34}S_{sulfate}$ and $\delta^{13}C_{carbonate}$ data were obtained and shown in Fig. 3 through successful extractions of trace sulfate from the late Neoproterozoic carbonate sequences in the Yangtze Gorges section. The sequences are composed of two whole formations, Doushantuo Fm. and Dengying Fm. in ascending order. In Member I of the Doushantuo Fm., the $\delta^{13}C$ values of carbonate are mostly negative, while the $\delta^{34}S$ of sulfate are +30.4‰ on average. The $\delta^{34}S$ and $\delta^{13}C$ values all attain their highest values in Member II or lower Member III, on average +47.3‰ and +4.6‰ for S and C in Member II, respectively. Thereafter, values decline with oscillations. The $\delta^{34}S_{sulfate}$ from Member IV is +24.5‰ on average, and the $\delta^{13}C_{carbonate}$ becomes negative when entering Member V of the Doushantuo Fm. Large negative excursions of S and C isotopes characterize the boundary between the Doushantuo and Dengying formations with their lowest values at −11.3‰ and −5.7‰, respectively.

While the average $\delta^{13}C_{carbonate}$ value changes to +1.6‰ again, the average $\delta^{34}S_{sulfate}$ remains at 0.5‰ in the Hamajing Mbr., early Dengying stage. Stable or slightly decreasing values of $\delta^{34}S$ and $\delta^{13}C$ have been measured for the Shibantan and Baimatuo members. The $\delta^{34}S$ and $\delta^{13}C$ averages are at +34.5‰ and +3.3‰ for Shibantan and +28.4‰ and +2.1‰ for Baimatuo, respectively. Other negative excursions of $\delta^{34}S$ and $\delta^{13}C$ exist at the boundary between the Baimatuo and Aijiahe members. The values of $\delta^{34}S_{sulfate}$ decrease to <+20‰ and increase again up to +30‰ in the lowermost Tianzhushan Fm., but $\delta^{13}C_{carbonate}$ changes to negative values. This unit might already be Cambrian in age.

High-resolution isotope curves for S and C in seawater for the Neoproterozoic III have been determined from sedimentary rocks on the Yangtze Platform. Following the glacial Nantuo Fm., $\delta^{34}S_{seawater}$ exceeds +30‰, and $\delta^{13}C_{carbonate}$ changes from negative values in glacial sediments and cap carbonates to positive values higher up in stratigraphy. This suggests increasing biological activity (including bacterial sulfate reduction) and burial of reduced sulfur and organic carbon. Strong photosynthesis may result in increased oxygenation of surface waters. However, this may have occurred at a later Doushantuo stage, because the $\Delta_{sulfate\text{-}sulfide}$ changes from ~45‰ in early Doushantuo Fm. to >45‰ in the later Doushantuo Fm. (new data and Ref. [10]). Following Ref. [23], a sulfur isotope fractionation above 45‰ suggests the increased oxygenation of the environment.

Stronger oscillations in $\delta^{34}S_{sulfate}$ and $\delta^{13}C_{carbonate}$ in the Doushantuo Fm. suggest still variable environmental conditions, such as climate, sea-level, hydrothermal activity in oceanic ridge, etc., shortly after the global glaciation. The fluctuation of climate and/or sea-level would impact survival and propagation on organism and lead to variations in biomass and bacterial sulfate reduction with the oscillations in $\delta^{34}S_{sulfate}$ and $\delta^{13}C_{carbonate}$. The oceanic environment may recover its stability when entering the Dengying stage. Lithologically, thus, the Doushantuo Fm. comprising dolomite intercalated with black shale is significantly distinguished from the Dengying Fm. composed of thick dolomite and limestone.

Further synchronous declines in $\delta^{34}S$ and $\delta^{13}C$ values of seawater occurs at the boundaries between the Doushantuo and Dengying formations and between the Baimatuo and Aijiahe members, Dengying Fm., since bacterial sulfate reduction and biomass decrease, for examples, synchronous declines of $\delta^{34}S_{sulfate}$ and $\delta^{13}C_{carbonate}$ happening. The strongly negative $\delta^{34}S_{sulfate}$ value of −11.3‰ with possibly negative value of $\delta^{13}C_{carbonate}$ suggests that the increased oxygenation in water column resulted in the oxidation of H_2S and organic matter. The negative excursions in $\delta^{34}S$ and $\delta^{13}C$ values occurring at the end of the Doushantuo stage may represent a global event, which might be related to oxidation of deep seawater[24].

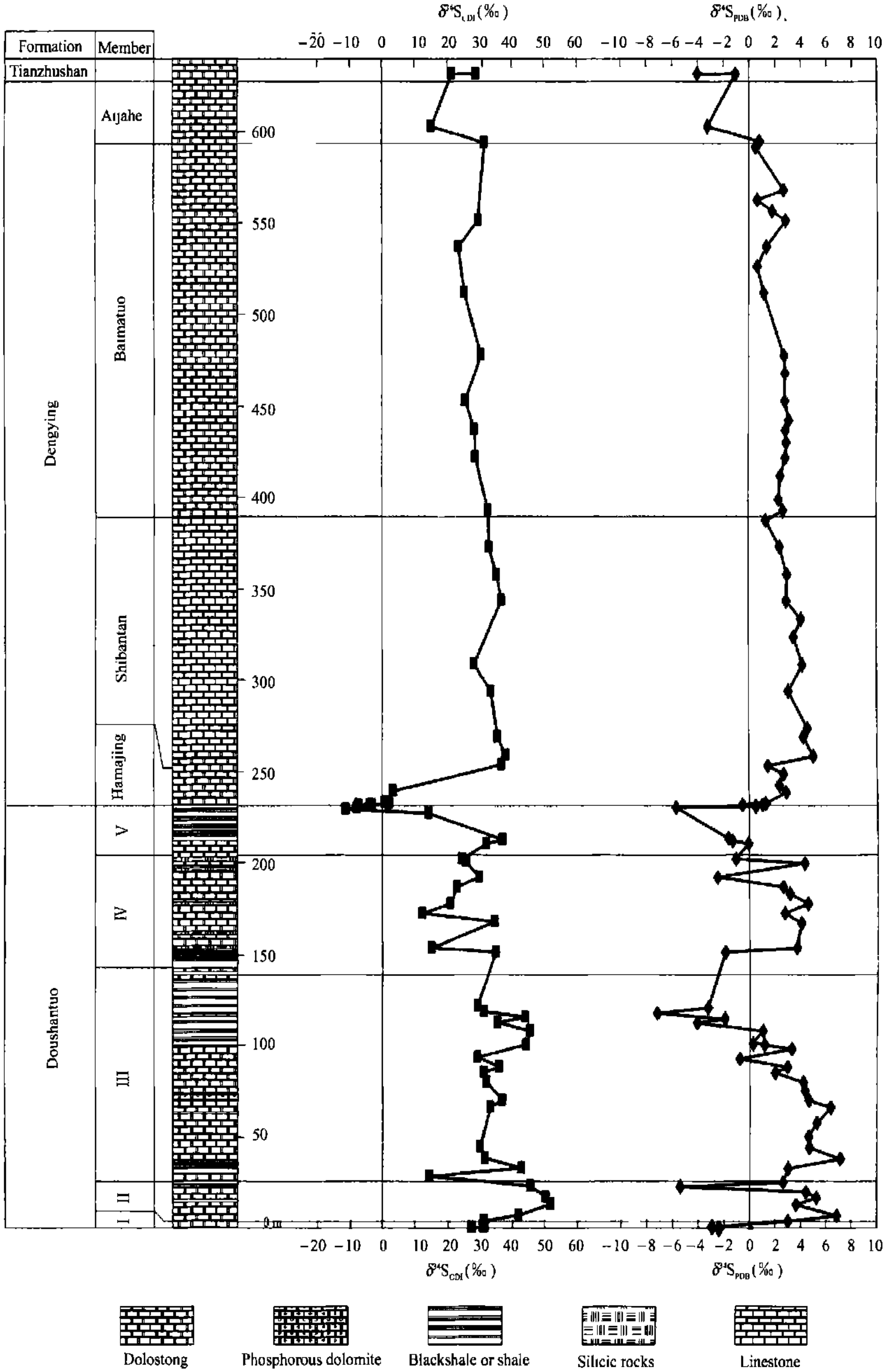

Fig. 3. Sulfur and carbon isotopic variations in successive carbonate sequences in the Yangtze Gorges sections near Yichang.

The large positive excursion in sulfur and carbon isotopes, as well as the very high $\delta^{34}S$ and $\delta^{13}C$ values in the marine sulfate and carbonate during the early Doushantuo stage, however, imply that the conditions of oceanic environment were beneficial for organism to survive and propagate after the Nantuo glaciation in the Yangtze Platform[24].

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References

1 Knoll, A. H. Neoproterozoic evolution and environmental change. In: Early Life on Earth (Nobel Symposium 84) (ed. Bengtson, S.), New York: Columbia University Press, 1994, 439.

2 Hoffman, P. F. et al. A Neoproterozoic snowball Earth. Science, 1998, 281: 1342.

3 Knoll, A. H. Learning to tell Neoproterozoic time. Precambrian Research, 2000, 100: 3.

4 Kennedy, M. J. et al. Two or four Neoproterozoic glaciations? Geology, 1998, 26: 1059.

5 Claypool, G. E. et al. The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation. Chemical Geology, 1980, 28: 199.

6 Canfield, D. E. et al. Late Proterozoic rise in atmospheric oxygen concentration inferred from phylogenetic and sulphur-isotope studies. Nature, 1996, 382: 127.

7 Strauss, H. The isotopic composition of Precambrian sulphides—seawater chemistry and biological evolution. Spec. Publs Int. Ass. Sediment., 2002, 33: 67.

8 Ripperdan, R. L. Stratigraphic variation in marine carbonate carbon isotope ratios. In: Stable Isotope Geochemistry (eds. Valley, J. W. et al.), Reviews in Mineralogy & Geochemistry, 2001, 43: 637.

9 Chu, X. et al. Sulfur isotope geochemistry of the late Proterozoic in southern China. Chinese Science Bulletin, 1998, 43(supp.): 27.

10 Li, R. et al. Spatial and temporal variation in carbon and sulfur isotopic compositions of Sinian sedimentary rocks in the Yangtze platform, South China. Precambrian Research, 1999, 97: 59.

11 Walter, M. R. et al. Dating the 840~544 Ma Neoproterozoic interval by isotopes of strontium, carbon, and sulfur in seawater, and some interpretive models. Precambrian Research, 2000, 100: 371.

12 Chu, X. et al. Implication of ultra-high $\delta^{34}S$ values of pyrite in manganese mineralization beds of Datangpo stage. Bulletin of the Mineralogy, Petrology and Geochemistry (in Chinese), 2001, 20: 320.

13 Hayes, J. M. et al. The sulfur-isotopic record. In: The Proterozoic Biosphere—A Multidisciplinary Study (eds. Schopf, J. W. et al.). London: Cambridge Press, 1992, 129.

14 Chu, X. et al. The sulfur isotopic composition and its implacation of phosphorite of later Sinian Epoch in Kaiyan, Guizhou Province. Chinese Science Bulletin, 1995, 40: 148.

15 Shen, Y. et al. Biogeochemical approach to understanding phosphogenic events of the terminal Proterozoic to Cambrian. Palaeogeography, Palaeoclimatology, Palaeoecology, 2000, 158: 99.

16 Lambert, I. B. et al. Paleoenvironment and carbon isotope stratigraphy of Upper Proterozoic carbonates of the Yangtze Platform. Nature, 1987, 325: 140.

17 Lu, S. A review of major problems of Precambrian research (in Chinese). Progress in Precambrian Research, 2002, 25: 65.

18 Ma, G. et al. An investigation of the age limits of the Sinian System in South China. Bulletin of Yichang Institute of Geology & Mineral Resources (in Chinese), Chinese Academy of Geological Sciences, 1984, 8: 1.

19 Barfod, G. H. et al. New Lu-Hf and Pb-Pb age constraints on the earliest animal fossils. Earth and Planetary Science Letters, 2002, 201: 203.

20 Hurtgen, M. T. et al. The sulfur isotopic composition of Neoproterozoic seawater sulfate; implications for a snowball Earth? Earth and Planetary Science Letters, 2002, 203: 413.

21 Coleman, M. L. et al. Direct reduction of sulfates to sulfur dioxide for isotopic analysis. Anal. Chem., 1978, 50: 1594.

22 Zhang, Q. R. et al. The stratigraphic architecture of the Neoproterozoic glacial rocks in the "Xiang-Qian-Gui" region of the central Yangtze Block, South China. Progress in Natural Science, 2003, 13(10): 783.

23 Anbar, A. D. et al. Proterozoic ocean chemistry and evolution: a bioinorganic bridge. Science, 2002, 297: 1137.

24 Zhang, T. et al. Variations of sulfur and carbon isotopes in seawater during the Doushantuo stage in late Neoproterozoic. Chinese Science Bulletin (in Chinese), 2003, 48: 850.