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# Lacustrine microbiome characteristics and sedimentary environment of Qingshuihe Formation in the southern margin of Junggar Basin

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## Abstract

Lacustrine microbiome deposits were discovered for the first time at the bottom of the Cretaceous Qingshuihe Formation in Honggou Section in the middle part of the southern margin of Junggar Basin, Xinjiang, and the lithology is gray-white microbial limestone. The lacustrine microbiome deposits is about 10~50cm thick and it occurred as thin layers in the conglomerate at the bottom of the Cretaceous Qingshuihe Formation with unstable thickness and great lateral variation (Figure 1). Thin sections of the samples show that the microbiome structure is a single columnar cross section sub-round or irregular cone, where the columnar stromatolite column size is 0.2~0.5 cm. In addition, there are a lot of interlayer (connecting bridge) between the columns, the interlayer gradually thickened and transited to crust or layer column, and the stromatolite has obvious alternating growth layers (Figure 2). The overall size of pyramidal microstromatolites is smaller than that of columnar stromatolites, and most of them consist of three to six small vertebral bodies arranged around columnar stromatolites. The size of the bottom of the vertebral body ranges from 0.1-0.3mm, and alternated laminae can be observed, but its scale is much smaller than that of columnar stromatolites.

According to its microscopic characteristics and previous studies, the sedimentary environment of microbiome can be inferred:

1. Under plane-polarized light microscope, obvious dark-bright superimposed growth layer

characteristics can be observed . The dark layer is composed of organic-rich carbonates, reflecting microorganisms playing an important role in carbonate deposition. However, the bright layer is composed of sparry calcite, reflecting carbonate deposition during intermittent microbial development.

2. The stromatolites in the samples are mostly columnar and cone-shaped with large scale variations, which are often filled with sparry algal sand-clastic limestone and associated with nucleoliths, with calcite and other minerals visible, and few micrite. This suggest that the water column is relatively volatile, indicating a relatively high-energy shallow lake environment.

3. Under the microscope, there is an obvious wavy extinction phenomenon produced by radiating axial fiber calcite, so it is inferred that the salinity of the water body of Qingshuihe Formation changes and is higher than that of the water body of the underlying Jurassic Kalaza Formation.

The composition of the lamentosomes is composed of ferric, siliceous, argillaceous carbonate microcrystals and relatively pure carbonate microstriations, which reflects the main role of microorganisms in carbonate deposition. The stable isotopic results of carbon and oxygen in microbial rock are as follows:  $\delta^{13}\text{C}_{\text{PDB}}(\text{‰})=-4.01$ ,  $\delta^{13}\text{O}_{\text{PDB}}(\text{‰})=-10.52$ , and the paleosalinity was calculated  $S=24.23$ . According to the Z-value criterion proposed by Keith, lacustrine microbiome of Cretaceous Qingshuihe Formation in Honggou Section is calculated  $Z=113.849$ . It shows that the lacustrine sedimentary environment was characterized by high salinity. The discovery of Qingshuihe Formation microbiome in the southern margin of Junggar Basin provides a new basis for reshaping the sedimentary system and lithofacies paleogeographic pattern of the southern margin of Junggar Basin during the early Cretaceous period, and provides a new reference for oil and gas exploration in the southern margin of Junggar Basin.



Figure 1 Feild map of lacustrine microbiome in Qingshuihe Formation, southern margin of Junggar Basin.

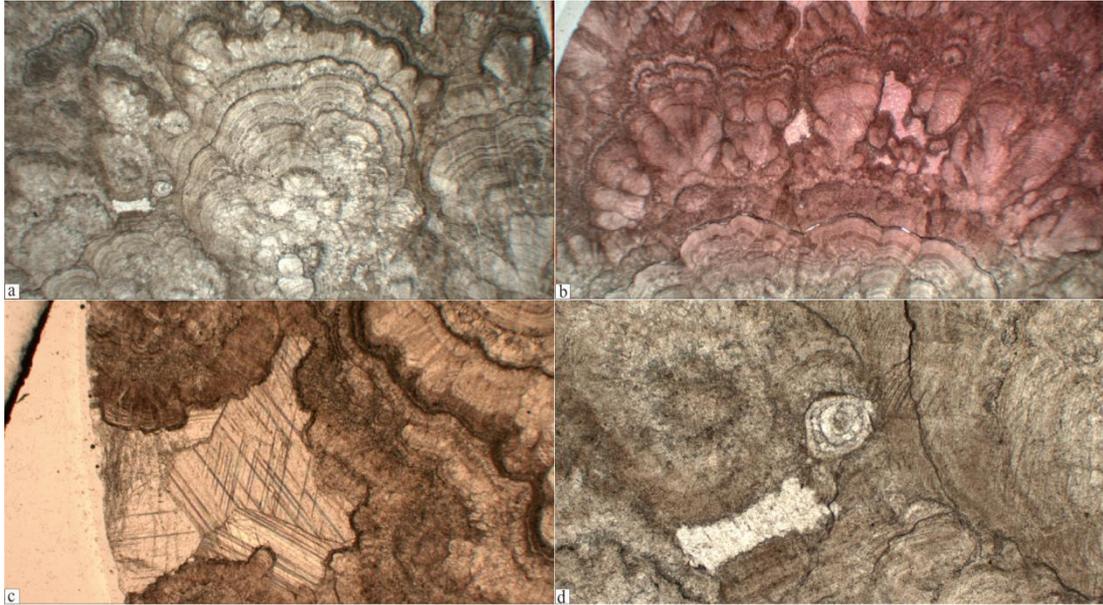


Figure 2 Microphotographs of thin slice sampling of Qingshuihe Formation, Honggou, southern margin of Junggar Basin.

# The impact of multi-stage metamorphism on preservation of traces of life in ~2.5 Ga banded iron formations, North China

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## Abstract

Biological organic molecules preserved within Precambrian banded iron formations (BIFs) can provide valuable information about the origin and evolution of life [1]. It is widely acknowledged that metamorphic alterations of biological organics result in an obstacle in identifying early life traces [2]. Nevertheless, the physiochemical mechanisms responsible for these alterations remain insufficiently comprehended. In this study, we present petrographic observations and nano-

geochemical investigations on the carbonaceous matter (CM) in ~2.5 Ga BIFs from North China, which have undergone significant alteration during lower amphibolite-facies prograde metamorphism, and subsequent retrograde alteration. The CM is in paragenetic equilibrium with prograde mineral phases, and is often associated with apatite that occurs in Fe-rich bands parallel to layering. This implies that the CM is most likely inherited from syn-depositional biomass, as confirmed by the nanoscale infrared spectroscopy, which shows the presence of C=C, C-H, and C-N/N-H bonds. Raman spectroscopy reveals that the maximum metamorphic crystallization temperature is consistent with the metamorphic peak conditions of the host BIFs. The BIFs possess average bulk  $\delta^{13}\text{C}_{\text{organic}}$  values of  $-20.0\text{‰}$  and  $\delta^{13}\text{C}_{\text{carbonate}}$  values of  $-12.9\text{‰}$ , further indicating syngenetic biomass remineralization during prograde metamorphism. This thermal cracking process may have released gaseous hydrocarbons, as shown by secondary  $\text{CH}_4$  fluid inclusions in quartz. We further use quantum mechanical simulations to assess the stability of organic chemical bonds during prograde metamorphism (0-600°C, 0-15 kbar). The relatively high thermal durability of C-H and the armoring effects of primary organic-phyllsilicate complexes may account for C-H preservation in BIFs. Furthermore, the electron microscopy reveals widespread nano-chlorite infiltration into CM during retrograde metamorphism, which is likely responsible for the absence of C-O bonds via nanopore-scale reactions. Our findings highlight the importance of evaluating metamorphic effects on the preservation of primordial microorganisms, particularly those found in ancient iron-rich sediments.

## References

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# The deposition of Ediacaran non-glacial iron formations and its implications for marine phosphorus cycle

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## Abstract

Most Neoproterozoic iron formations (NIF) are closely associated with global or near-global “Snowball Earth” glaciations. Increasingly however, some studies indicate that some NIFs show no robust evidence of glacial association. Many aspects of non-glacial NIF genesis, including the paleo-environmental setting, Fe(II) source, and oxidation mechanisms are poorly understood. Here, we present a major non-glacial NIF within a Neoproterozoic volcano-sedimentary sequence in North Qilian, northwestern China. New U–Pb geochronological data place the depositional age of these NIF in North Qilian at ~600 Ma. Petrographic and geochemical evidence supports its identification as a primary chemical sediment with significant detrital input. Major and trace element concentrations, REE+Y systematics and  $\epsilon\text{Nd}(t)$  values indicate that iron was sourced from mixed seawater and hydrothermal fluids. Iron isotopic values are indicative of partial oxidation of an Fe(II) reservoir. We infer that these NIF was deposited in a redox stratified water column, where hydrothermally-sourced Fe(II)-rich fluids underwent oxidation under suboxic conditions.

Phosphorus (P) is the key nutrient thought to limit primary productivity on geological timescales, and hence P bioavailability exerted a major influence on Earth surface oxygenation dynamics through the Precambrian, with ensuing implications for biological evolution. Here, we document highly elevated P contents in the non-glacial

Ediacaran (635-541 Ma) iron formations from Northwestern China, with P dominantly occurring as carbonate fluorapatite formed during early diagenesis. These analyses, in combination with marine sediment P contents and phosphorite abundance data, point to a state change in oceanic P concentrations during the Ediacaran, which we attribute to enhanced recycling from marine sediments under redox stratified conditions. Subsequent elevated rates of primary productivity and organic carbon production may have sustained the contemporaneous first appearance of complex deep marine habitats, and would have increased the extent and stability of surface water oxygen concentrations, leading to conditions conducive to the subsequent evolution of more complex animals.

# Direct and indirect anaerobic oxidation of methane by Mn oxides in sulfate-poor environments

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## Abstract

Strongly  $^{13}\text{C}$ -depleted authigenic carbonates (e.g.,  $\delta^{13}\text{C}_{\text{VPDB}} < -30\text{‰}$ ) in nature are generally believed to form by sulfate-dependent anaerobic oxidation of methane (AOM). Here, however, we demonstrate that such calcites with  $\delta^{13}\text{C}_{\text{VPDB}}$  as low as  $-60\text{‰}$  can be derived from direct or indirect biogenic oxidation of methane by Mn oxides in sulfate-poor, non-marine environments during the early Triassic in the Junggar Basin, NW China and in early Ediacaran sulfate-poor marine environments ( $\sim 635$  Ma) in the Nanhua Basin, respectively. For case of the Junggar basin, higher-Mn, less  $^{13}\text{C}$ -depleted and more  $^{18}\text{O}$ -depleted calcites are associated with more  $^{13}\text{C}$ -enriched methane gas in the Lower Triassic conglomerate reservoirs, resulting from the preferential oxidation of  $^{13}\text{C}$ -depleted methane and more incorporation of  $^{18}\text{O}$ -depleted oxygen from  $\text{MnO}_2$ . For the case of the Nanhua Basin, we demonstrate that the strongly  $^{13}\text{C}$ -depleted calcite in the association with superheavy pyrites in the Doushantuo cap dolostones was formed via biological oxidation of methane by  $\text{MnO}_2$  via microbial sulfate reduction in an environment with sulfate concentrations of  $\sim 1$  to  $3$  mM. Such low sulfate concentrations were initially consumed by sulfate reducing microorganisms to extremely low levels ( $< \sim 0.2$  mM), and thus Mn-driven anaerobic oxidation of methane (AOM) by sulfate occurred in pore water to produce  $\text{H}_2\text{S}$ , which was in turn oxidized by Mn oxides back to sulfate. Consequently, with increasing Mn reduction and

decreasing sulfate concentrations in pore waters, the produced pyrite shows an increase of *in situ*  $\delta^{34}\text{S}$  values, and is in association with calcite with more negative  $\delta^{13}\text{C}$  values. Finally, the pyrite with the highest  $\delta^{34}\text{S}$  value may have co-precipitated with the  $^{13}\text{C}$ -depleted calcite, and thus show similarly high Mn concentrations. Thus, Mn-rich and  $^{13}\text{C}$ -depleted carbonates can be used to reflect methane oxidation by Mn oxides, and such a process may have served as a main sink of methane in the Precambrian Earth with low sulfate concentrations.

# Postdepositional behavior of molybdenum in deep sediments and implications for paleoredox reconstruction

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## Abstract

Molybdenum (Mo) serves as a proxy for marine paleoredox reconstruction, offering valuable insights into how the oceanic oxygen level evolves with Earth's climate. The reliability of the Mo proxy depends on how much Mo is transferred in and out of the sediments after deposition. In this study, we investigate the Mo content and Mo-isotope composition of sediments, along with porewater geochemistry, from the International Ocean Discovery Program (IODP) Site C0023 down to 1,200 metres below seafloor. We find that post-depositional remobilization of Mo leads to Mo enrichments in sulfidic intervals of the sediment pore-water. By contrast, at the underthrust hydrothermal zone, we suggest that Mo from hydrothermal fluids is mainly adsorbed onto oxides resulting in the Mo-isotope value to as low as  $-1.59\%$ . These Mo signals deviate from their primary values during deposition, but share some similarities with those derived from a range of marine redox conditions. As such, future studies need to evaluate the Mo behavior after burial before using this proxy for paleoredox reconstruction.

# Extremely variable sulfur isotopic compositions of pyrites in carbonate pipes trace a non-steady microenvironment in the northern South China Sea

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## Abstract

To further constrain the microenvironment during the growth of carbonate pipes at cold seeps, we report on the whole-rock carbon and oxygen, and *in situ* pyrite sulfur isotopic compositions along the cross-sections in pyrite-bearing carbonate pipes from the northern South China Sea. The whole-rock geochemical data suggest that these carbonate pipes were formed in an anoxic and methane-rich environment. Furthermore, *in situ*  $\delta^{34}\text{S}$  values in pyrites across the carbonate pipe display an extremely wide range on a centimetre scale. The majority of pyrites have  $\delta^{34}\text{S}$  values ranging from 19.4‰ to 45.8‰, reflecting the dominance of sulfate-driven anaerobic oxidation of methane (AOM) at below the sulfate methane transition zone (SMTZ). Two abnormal areas show heavier or lighter  $\delta^{34}\text{S}$  values than the majority of pyrites, respectively. Pyrites in the abnormal area I have  $\delta^{34}\text{S}$  values ranging from 62.2‰ to 130.3‰, suggesting an extremely  $^{34}\text{S}$ -enriched microenvironment produced via Rayleigh fractionation of limited sulfate in a closed system. The model calculation indicates that the maximum positive  $\delta^{34}\text{S}$  value (130.3‰) could be produced when ~93% sulfate is consumed. Pyrites in the abnormal area II have  $\delta^{34}\text{S}$  values ranging from -

32.7‰ to -18.0‰, and are interpreted as a result of early organoclastic sulfate reduction with a low proportion of later sulfate-driven AOM above the SMTZ. Collectively, the extreme variations in  $\delta^{34}\text{S}$  values point to local migration of the SMTZ in a non-steady microenvironment during the growth of carbonate pipes. This study reveals that the *in situ* pyrite  $\delta^{34}\text{S}$  value is a diagnostic tool for tracing the change in the local microenvironment, and opens new avenues for a more comprehensive picture of biogeochemical cycles at continental margins.

**Keywords:** Sulfur isotopic compositions; Pyrites; Microenvironment; Carbonate pipes; South China Sea

# Marine euxinia during the melting of the Sturtian glaciation

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## Abstract

The Neoproterozoic snowball Earth events include the Sturtian (717-660Ma) and the Marinoan glaciation (~650-635 Ma). The snowball Earth hypothesis suggested that the global ocean was completely frozen during these glaciations. It is possible that global melting of ice sheets can cause significant marine stratification. In the aftermath of the Marinoan glaciation, this change has been tested. The Sturtian glaciation is the longest Snowball Earth event, but the marine redox during the termination of the Sturtian glaciation remain unclear. Here we report massive pyrite from the top of the Sturtian Tiesiao diamictite from 4 drill cores in the South China. Three types of pyrite are observed from the Tiesiao Formation: nodule, laminae and disseminated pyrite. Disseminated pyrite, including framboids, euhedral pyrite, are generally < 100  $\mu\text{m}$  in size and are pervasively distributed in the matrix or within intergranular pores of diamictites and pebbly sandstones. The mean diameter of framboids ranges from 3.53 to 7.46  $\mu\text{m}$ , and 59.20% of these framboid are < 5  $\mu\text{m}$ . The proportion of framboids in all disseminated pyrites varies between 1.01–62.75%, with a mean value of 17.94%. Geochemical analysis of these pyrite shows a low Co contents (mean=104.25ppm), low Co/Ni ratios (mean=0.79), but large sulfur isotope enrichments (27.2–75.8‰). Iron chemistry shows  $\text{FeHR}/\text{FeT} > 0.38$  in all samples and  $\text{Fepy}/\text{FeHR} > 0.8$  in most samples. Meanwhile, there is a strong correlation between Fepy and FeHR. These results suggest that the ocean was stratified and  $\text{H}_2\text{S}$ -enriched during the melting of the Sturtian glaciation. Since maintaining a marine euxinic condition requires enough seawater sulfate and organic matter, our results show that continental weathering increased and the marine biosphere recovered quickly after the Sturtian glaciation.

# Low marine sulfate levels during the initiation of the Cryogenian Marinoan glaciation

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## Abstract

Microbial sulfate reduction plays a significant role in regulating marine organic matter degradation and thus the variation of ancient marine sulfate levels is closely coupled with the changes in global organic carbon burials as well as Earth's surface redox evolution in geological time. It is widely assumed that seawater sulfate concentration was extremely low during the Cryogenian Marinoan glaciation (ca.650–635 Ma) which represents the most extreme icehouse condition in Earth's history. However, such a low seawater sulfate level has not been explicitly confirmed to date. To address this, here we carried out pyrite content and sulfur isotope ( $\delta^{34}\text{S}_{\text{py}}$ ) analysis of the Cryogenian non-glacial (the top Datangpo Formation) and the Marinoan glacial successions (the basal Nantuo Formation) in South China. Both the Datangpo and Nantuo Formation show relatively high values of  $\delta^{34}\text{S}_{\text{py}}$ , ranging from +19.9 ‰ to +32.9 ‰, and low values of pyrite content (mean value=0.72 wt.%). Mineralogical analysis suggests these pyrites are dominated by euhedral crystals with a rare occurrence of framboids, indicating an early diagenetic origin, i.e. pyrite formed in sediments with sulfate supplied from seawater. By using a one-dimensional diffusion-advection-reaction (DAR) model, we calculate marine sulfate levels during the transition from the non-glacial to glacial period. The modeling results show that the seawater sulfate concentration is < 1 mM during the transition from the top Datangpo to the basal Nantuo Formation, suggesting a shrink of the marine sulfate reservoir at the onset of Marinoan glaciation. We propose the low marine sulfate concentration

resulted from a decrease in chemical weathering prior to the initiation of the global Marinoan glaciation. This study provides a quantitative constraint on marine sulfate levels during the snowball Earth event and may shed new light on our understanding of the marine biogeochemical changes during the Neoproterozoic global glaciation.

Keywords: the top Datangpo Formation, the basal Nantuo Formation, pyrite sulfur isotope, marine sulfate concentration, snowball Earth