A Stratified Redox Model for the Ediacaran Ocean

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The Ediacaran Period (635-542 million years ago) was a time of fundamental environmental and evolutionary change, culminating in the first appearance of macroscopic animals. Here we present a detailed spatial and temporal record of Ediacaran ocean chemistry for the Doushantuo Formation in the Nanhua Basin, South China. We find evidence for a metastable zone of euxinic (anoxic and sulfidic) waters impinging on the continental shelf and sandwiched within ferruginous [Fe(II)-enriched] deep waters. A stratified ocean with coeval oxic, sulfidic and ferruginous zones, favored by overall low oceanic sulfate concentrations, was maintained dynamically throughout the Ediacaran Period. Our model reconciles seemingly conflicting geochemical redox conditions proposed previously for Ediacaran deep oceans and helps explain the patchy temporal record of early metazoan fossils.

Numerous lines of geochemical and stable isotopic evidence indicate that the Ediacaran (635-542 million years ago) ocean underwent a stepwise and protracted oxidation (e.g., 1-4). Some geochemical studies suggest that ocean basins were fully oxygenated by the late Ediacaran (1, 2, 4), yet others provide seemingly conflicting evidence for anoxic deep waters (5, 6), with ferruginous conditions [Fe(II)-enriched] persisting into the Cambrian (5). Although a stratified ocean maintained through the Ediacaran Period (7) may help reconcile these seemingly conflicting views, the details remain unclear.

The Doushantuo Formation in the Nanhua Basin, South China, presents a unique opportunity to study Ediacaran ocean chemistry across spatial and temporal scales (e.g., 8). It is comprised of a succession of both shallow- and deep-water siliciclastic, carbonate and phosphatic sedimentary rocks deposited immediately after the last globally extensive Neoproterozoic glacial episode (9), widely known as the Marinoan glaciation. Zircon U-Pb ages indicate that deposition of the Doushantuo Formation lasted from ~635 to ~551 million years ago (10), spanning most of the Ediacaran Period.

To investigate the marine redox structure, we characterized the composition of sedimentary Fe mineral species and measured S-isotope signatures for sulfides and sulfates (11) at four sections of the Doushantuo Formation, which encompass the full range of sedimentary facies from continental shelf to slope to deep basin (fig. S1). We focused on quantifying the fractional abundance of Fe in several highly reactive mineral species (FeHR): pyrite (FePy), Fe(III) oxides, magnetite and carbonate minerals relative to total Fe (FeT) contents. High FeHR/FeT ratios indicate anoxic conditions (12). If anoxic, low associated FePy/FeHR ratios indicate ferruginous bottom waters, whereas high FePy/FeHR points to euxinic conditions defined as having an anoxic and H2S-containing water column (5, 12). In most modern and ancient sediments deposited beneath anoxic bottom waters, FeHR/FeT exceeds 0.38, but this threshold value can be reduced to 0.15 (±0.10) for thermally altered ancient sedimentary rocks (13) such as the Doushantuo Formation, due to conversion of FeHR to non-reactive iron during burial. For a euxinic water column, FePy/FeHR in the underlying sediments usually exceeds 0.8 (12). Previous Fe-speciation data obtained from Paleo- and Mesoproterozoic sedimentary rocks (14, 15) reveal two distinct redox end members in marine basins characterized by either euxinic or ferruginous deep waters (fig. S2). In contrast, the iron speciation data from the Doushantuo Formation are not confined to a single end member (Fig. 1A), suggesting non-uniform redox conditions for deep waters of the Nanhua Basin.

The inner shelf JiuLongwan section records sedimentary deposition in the shallowest water facies but well below wave base (3) and far from shore along a broad continental shelf. The associated Fe data from this section plot in both the euxinic and ferruginous fields (Fig. 1A); late Ediacaran black shales from this section all plot in the euxinic zone (table S1). In contrast, samples from the Zhongling section, a deeper shelf margin setting, plot mainly in the ferruginous region, with only three samples having FePy/FeHR ratios >0.8 (Fig. 1A). The deepest water samples from the slope Minle and basinal Longe sections, which are all early Ediacaran black
shales, contain very low levels of pyrite (thus low Fe<sub>py</sub>/Fe<sub>HR</sub>) and yield Fe mineral parameters suggesting ferruginous bottom waters. Considering all the data, the paleoenvironmental trends suggest a co-occurrence of euxinic waters on the shelf with ferruginous deep water toward the center of the basin.

Carbonate lithologies dominate the shallow platform of the Nanhua Basin, grading into shales in basinal settings (16, 17), reflecting preferential precipitation of carbonates in shallower waters and enhanced hydrodynamic sorting of fine aluminosilicates into deeper waters. Accordingly, a stratigraphic decrease in carbonate content or, inversely, increasing Al content in samples (fig S3) from the same site broadly reflects increasing water depth with rising sea level. Doushantuo samples exhibit two dominant trends when Fe<sub>py</sub>/Fe<sub>HR</sub> ratios are viewed in light of Al concentration (Fig. 1B). Almost all inner shelf samples show an increase in Fe<sub>py</sub>/Fe<sub>HR</sub> with increasing Al (Path A in Fig. 1B), suggesting generally more sulfidic conditions with higher sea levels. In contrast, most samples from the distal sections show a reverse pattern (Path B in Fig. 1B), with low Fe<sub>py</sub>/Fe<sub>HR</sub> values found for samples with moderate-to-high Al content (>1 wt%) regardless of organic content, suggesting a dominantly ferruginous and thus sulfate-limited deep-water setting. Taken together, these opposing trends can only be explained by a metastable mid-water-column sulfidic zone located between the inner shelf and shelf margin nested within a ferruginous water mass (Fig. 2). The location and dimensions of this sulfidic zone would have fluctuated temporally. In most cases, euxinia is suggested independently by diagnostic Mo enrichments (fig S4) above typical crustal values (14).

We did not observe direct evidence for oxic shallow waters in the sections we sampled, although such conditions are expected in shallow settings given appreciable atmospheric O<sub>2</sub> in the Ediacaran atmosphere (18) and early benthic animal fossils at shallow sites (19 - 22). Therefore, it is likely that the sulfidic and ferruginous zones in the deep anoxic waters persisted beneath shallower oxic and ferruginous layers (Fig. 2).

It is difficult to envisage that a metastable sulfidic water mass could have co-existed with ferruginous deep water for 84 million years without mixing if seawater [SO<sub>4</sub>²⁻] in the Nanhua Basin was high. Net reduction in the surface S inventory may have limited the resupply of sulfate during the Neoproterozoic (23), particularly if reduced weathering during the Neoproterozoic glaciations suppressed the riverine flux (24). In combination with efficient sulfate removal from seawater through bacterial sulfate reduction and pyrite formation (24-26), enhanced by hydrothermal release of dissolved iron (27) during the glaciations and thereafter, this reduced delivery of sulfate reset Ediacaran ocean chemistry back to the ferruginous conditions (3) with extremely low [SO<sub>4</sub>²⁻] that have been prevalent in the Archean (28). Under such conditions, the continental sulfate supply was exhausted before reaching the deep basinal areas, resulting in a dynamically maintained lateral sulfate concentration gradient from shore to basin (Fig. 2 insert) and, in turn, a metastable euxinic zone. Lack of sufficient sulfate to support extensive organic matter remineralization in distal marine settings is consistent with the large and long-stable pool of organic matter suggested for the deep Ediacaran ocean by the unusual carbon isotope systematics expressed in carbonate rocks and sedimentary organic matter of this age (1,3,29).

Several lines of evidence support the existence of a persistent sulfate concentration gradient in the Nanhua basin. First, larger ratios of organic C to pyrite S (C<sub>org</sub>/S<sub>py</sub>) in the distal sections (34, n=49) compared to the inner shelf site (4; n=42), similar to those found under modern low sulfate conditions (30), suggest lower sulfate concentrations in the distal regions (fig. S5). Second, an average offset of 30‰ in the S isotope composition of pyrite (δ<sup>34</sup>S<sub>py</sub>) was observed between most of the inner shelf and shelf margin sections (Fig. 3A), with δ<sup>34</sup>S-enriched pyrites formed in the deeper water settings. Furthermore, differences in S isotope ratios (Δδ<sup>34</sup>S) between coeval carbonate associated sulfate (δ<sup>34</sup>S<sub>CAS</sub>) and δ<sup>34</sup>S<sub>py</sub> were on average ~10‰ lower for the shelf margin (~20‰) compared to the inner shelf section (~30‰), suggesting lower [SO<sub>4</sub>²⁻] availability along the shelf margin (Fig. 3B). Finally, concentrations of carbonate associated sulfate were consistently much lower for the shelf margin rocks compared with those from the inner shelf, with concentrations in the deeper sections frequently too low to permit isotopic analysis (table S1).

Modern seawater [SO<sub>4</sub>²⁻] is ca. 28 mM, and the isotopic fractionation associated with bacterial sulfate reduction under such high sulfate availability is often large (up to 46‰). In contrast, limited fractionation occurs when sulfate concentration is low, particularly when it falls below a biological threshold of ~200 μM (28). These observations provide upper and lower limits for our estimates of [SO<sub>4</sub>²⁻] in the Ediacaran Nanhua Basin, albeit within a broad range. The Δδ<sup>34</sup>S in the inner shelf Jiulongwan section increases abruptly from 1.5‰ in the basal cap carbonate to ~30‰ in the overlying ~40 m and thereafter, with a few samples having Δδ<sup>34</sup>S >30‰ in the upper section (Fig. 3B). These trends are consistent with an increase of [SO<sub>4</sub>²⁻] from <200 μM during post-Marinoan deglaciation to >200 μM thereafter and extending into the late Ediacaran. Although Δδ<sup>34</sup>S values from the shelf margin section are no more than 24‰, such fractionations are large enough to point to local sulfate levels >200 μM during the late Ediacaran. Δδ<sup>34</sup>S data do not provide a clear upper limit for late Ediacaran sulfate concentrations,
but the isotopic and concentration gradients inferred from our study demand a sulfate level that was only a small fraction of the modern 28 mM.

Because the sulfidic zone could expand into previously oxygenated areas of the shelf during transgression and during pulses of high productivity, the generally patchy record of metazoa observed through the Ediacaran (3, 19-22) might be explained by fluctuating oceanic redox conditions in and around the continental shelf. The finding of Ediacaran metazoan resting cysts — in the form of large ornamented acritarch fossils or animal embryos and intervals with the lowest pyrite contents (fig. S6), suggesting a correlation between sedimentary horizons containing the most diverse assemblage of acritarch fossils or animal embryos and the absence of oxygen, hindered colonization of the shelf seafloor by early animals.

References and Notes

11. Supporting material is available on Science Online.
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Supporting Online Material

www.sciencemag.org/cgi/content/full/science.1182369/DC1

Materials and Methods
Figs. S1 to S7
Table S1
References

Fig. 1. (A) A crossplot of Fe2/FeH versus FeH/FeT shows a co-occurrence of euxinic with ferruginous conditions for deep waters of the Nanhua Basin. Horizontal and vertical (solid for thermally immature and dashed for thermally mature rocks, respectively) lines indicate the boundaries for distinguishing euxinic from ferruginous and anoxic from oxic water columns. Dashed lines indicate the most appropriate
boundary values for Doushantuo Formation. (B) FePy/FeHR versus Al content shows two distinct redox profiles (Path A and Path B) that constrain the spatial location of the metastable sulfidic water mass to a region between the inner shelf and shelf margin. Samples in the shaded area were deposited in a stratigraphic interval during an early Ediacaran transgressive period and are outliers for Path B.

**Fig. 2.** Schematic representation of a stratified redox model for the Ediacaran Nanhua Basin. Most prevalent is a sulfidic water wedge, located at intermediate water depths within a ferruginous deep water mass and maintained by low riverine sulfate input and consumption of sulfate by bacterial sulfate reduction on the continental shelf. A lateral shore-to-basin sulfate concentration gradient (lower insert) is assumed to be metastable.

**Fig. 3.** Chemostratigraphic comparisons of (A) $\delta^{34}$S$_{py}$ and (B) $\Delta\delta^{34}$S for the inner shelf (Jiulongwan) and shelf margin (Zhongling) sections. The sections are correlated based on alignment with published sequence stratigraphic data and three similar transgressive-regressive sedimentary cycles can be identified (3, 16). The lateral S-isotope gradient is also apparent when the sections are aligned using carbonate C isotope stratigraphy (fig. S7).
Oxidative weathering

Fe(II) → Jiujiangwan

SO$_4^{2-}$ → [CH$_2$O]$_x$

H$_2$S → Zhongling

34$^S$-enriched pyrite

34$^S$-depleted pyrite

Minle

Proposed [SO$_4^{2-}$] Gradient in Ediacaran Nanhua Basin

Shore

μM

>200

Jiujiangwan

Zhongling

Minle

Longe

Basinal