

Widespread iron-rich conditions in the mid-Proterozoic ocean

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The chemical composition of the ocean changed markedly with the oxidation of the Earth's surface¹, and this process has profoundly influenced the evolutionary and ecological history of life^{2,3}. The early Earth was characterized by a reducing ocean-atmosphere system, whereas the Phanerozoic eon (less than 542 million years ago) is known for a stable and oxygenated biosphere conducive to the radiation of animals. The redox characteristics of surface environments during Earth's middle age (1.8–1 billion years ago) are less well known, but it is generally assumed that the mid-Proterozoic was home to a globally sulphidic (euxinic) deep ocean^{2,3}. Here we present iron data from a suite of mid-Proterozoic marine mudstones. Contrary to the popular model, our results indicate that ferruginous (anoxic and Fe²⁺-rich) conditions were both spatially and temporally extensive across diverse palaeogeographic settings in the mid-Proterozoic ocean, inviting new models for the temporal distribution of iron formations and the availability of bioessential trace elements during a critical window for eukaryotic evolution.

It is well established that Earth evolved from having an early anoxic ocean devoid of eukaryotes to one that is fully oxygenated and teeming with complex life. However, the timing and mechanisms of Earth's redox evolution are still debated. Foremost, marine redox conditions and atmospheric oxygen levels remain poorly constrained during the period between the Earth's oxygen-deficient early history (more than ~2.4 billion years (Gyr) ago) and the dominantly oxygenated realm of the Phanerozoic (the last ~0.542 Gyr). Traditional arguments held that ocean oxygenation was responsible for the disappearance of large iron formations at 1.8 Gyr ago (ref. 1). More recently, the majority opinion among Precambrian workers has instead favoured a deep mid-Proterozoic ocean with a vast or perhaps even global reservoir of hydrogen sulphide^{4–6}, and H₂S, much like oxygen, would have titrated the dissolved iron needed for the deposition of iron formations. It is further proposed that these euxinic (anoxic and sulphidic) conditions would have hindered the expansion and diversification of eukaryotes, because of the insolubility of bioessential trace elements, such as molybdenum, in sulphidic waters⁷. Consistent with a shift to euxinia, well-preserved sedimentary rocks from the Animikie basin on the Superior craton were suggested to capture the transition to a global sulphidic ocean⁶ at ~1.8 Gyr ago. It is now apparent, however, that large iron formations were deposited tens of millions of years after the deposition of this sedimentary succession^{8,9} and that iron-rich conditions persisted in deep waters in the Animikie basin even after the deposition of the largest Animikie iron formations^{8,10}, demanding that we rethink the spatiotemporal details of Proterozoic ocean redox and specifically the character of the mid-Proterozoic ocean (1.8–1.0 Gyr ago)¹⁰.

In contrast with endmember euxinic or oxic Proterozoic deep-ocean models, a third possibility has recently been proposed: that anoxic and iron-rich deepwater conditions may have been common throughout the Precambrian, including the mid-Proterozoic^{3,8,10,11}. This surprising

view of ocean evolution finds its origins in part with recent evidence that the ocean was ferruginous in the terminal Proterozoic^{12–14}, suggesting continuity with the iron-formation-favouring conditions present before 1.8 Gyr ago. Alternatively, researchers have also asserted that the Neoproterozoic was instead a special case—marked by a return to the iron-rich state of the early Precambrian as a consequence of supercontinent break-up¹³, extensive glaciations¹⁵, and drawdown of marine sulphate caused by a billion years of deepwater euxinia and pyrite burial¹². Although tantalizing, the ferruginous mid-Proterozoic model is currently hindered by a billion-year gap in direct evidence from the geological record for this marine redox state. Our study fills that data gap with results from four diverse mid-Proterozoic depositional settings that all point to iron-rich marine waters. Included are samples from the McArthur basin in north-central Australia—the only basin so far that has yielded direct evidence for mid-Proterozoic euxinia^{16,17}.

To evaluate ancient redox chemistry, we have applied a well-established sequential iron extraction scheme to fine-grained sedimentary rocks¹⁸. The accumulation of biogeochemically reactive iron, termed 'highly reactive iron' (Fe_{HR}), is linked to the redox conditions in the water column overlying the site of sedimentary deposition. In modern oxic marine sediments, Fe_{HR} comprises less than 38% of the total sedimentary iron pool (that is, Fe_{HR}/Fe_T < 0.38), reflecting the detrital sediment flux in the absence of dissolved iron in the O₂-containing water column. Enrichments beyond this limit (Fe_{HR}/Fe_T > 0.38) are a clear signature of transport, scavenging and deposition of additional iron from an anoxic water column^{3,12}. Because mineralogical changes associated with even moderate burial alteration (such as iron uptake into secondary silicate minerals) can decrease the pool of Fe_{HR}, the upper limit is possibly lower than 0.38 in older rocks¹⁹, suggesting that essentially all of our samples could have formed under anoxic conditions (Fig. 1). Where anoxia is indicated, we can further distinguish between ferruginous (Fe²⁺ > H₂S) and euxinic (H₂S > Fe²⁺) environments by measuring the extent to which Fe_{HR} has reacted with H₂S to form pyrite (Fe_{PY}/Fe_{HR}). Accordingly, anoxic shales with Fe_{PY}/Fe_{HR} > 0.8 are considered to have been deposited under euxinic conditions^{11,12}.

Because the McArthur basin has had a defining role in previous arguments for mid-Proterozoic euxinia^{16,17,20,21}, we began our search for ferruginous conditions with an additional analysis of fresh drill cores of shale from deep-water settings in this region. We specifically investigated the iron chemistry of the ~1.64-Gyr-old Barney Creek and Lady Loretta formations in the McArthur and Mount Isa basins, respectively. Our samples are from geographically widespread marine sequences that extend over more than 2,000 km across northern Australia. We included locations with palaeogeographic positions closer to the open ocean compared with past studies in the region that also focused on marine palaeoredox. In addition, we targeted the deepest-water facies as delineated in previous detailed basin analysis (see, for example, ref. 22).

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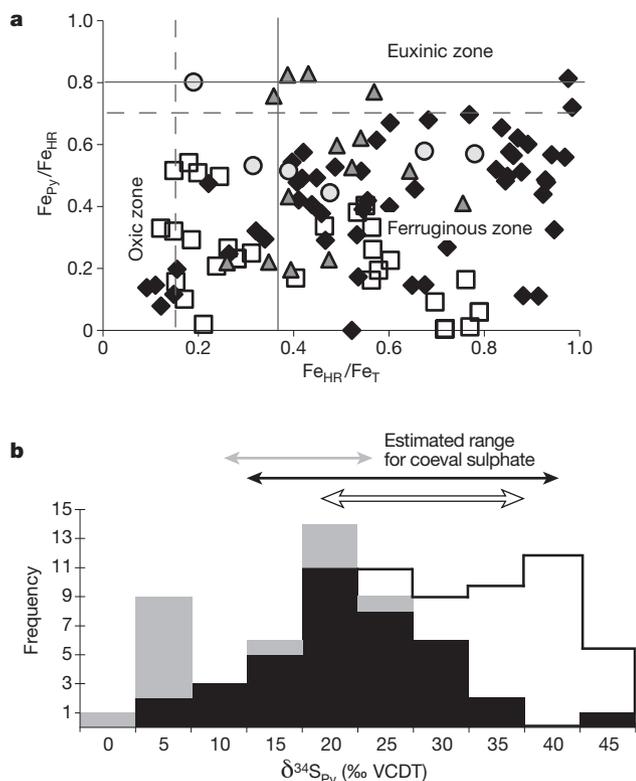


Figure 1 | Iron speciation and sulphur isotope data for mid-Proterozoic shales. Data from the 1.64-Gyr-old Mt Isa Superbasin (black diamonds and bars), the 1.7-Gyr-old Chuanlinggou Formation (white squares and bars), the 1.45-Gyr-old Newland Formation (grey triangles and bars) and the 1.2-Gyr-old Borden basin (grey circles). **a**, The vast majority of our samples have ratios of highly reactive to total iron (Fe_{HR}/Fe_T) and of pyrite to highly reactive iron (Fe_{Py}/Fe_{HR}) falling above 0.15–0.38 and below 0.7–0.8, respectively, which is diagnostic of sediment accumulation beneath an anoxic and iron-rich (non-sulphidic) water column. **b**, Pyrite $\delta^{34}S$ isotope values ($\delta^{34}S_{Py}$) relative to Vienna Canyon Diablo Troilite (VCDT). Estimates for sulphate $\delta^{34}S$ values are from refs 32, 33.

Fe_{HR}/Fe_T values in both the Barney Creek and Lady Loretta formations are generally above 0.38, conservatively indicating deposition under anoxic conditions (Fig. 1a). The vast majority of these samples have Fe_{Py}/Fe_{HR} ratios well below 0.8, which is consistent with a persistently sulphide-free water column. Together, these ratios point to widespread ferruginous conditions over thick (hundreds of metres) stratigraphic intervals, indicating prolonged periods of ferruginous deep waters, with the likelihood of laterally contemporaneous occurrences of euxinia^{16,17} in certain small or isolated sub-basins and/or on the shallower margins. Previous regional studies have argued for a relatively strong marine connection during deposition at our specific sample locations (see Supplementary Information), suggesting that deep ocean waters enriched in dissolved Fe^{2+} may have exchanged with the McArthur and Mt Isa basins.

Given these exciting results, we were obliged to look beyond this region for records of mid-Proterozoic ferruginous waters. With this goal, we analysed additional suites of carbonaceous shales from other, widely distributed mid-Proterozoic basins, emphasizing well-preserved (sub-greenschist) shales from diverse palaeogeographic settings spanning the mid-Proterozoic. Each of these additional units yielded abundant samples with $Fe_{HR}/Fe_T > 0.38$ and $Fe_{Py}/Fe_{HR} < 0.8$ (Fig. 1a), signifying widespread ferruginous depositional conditions. Our data include samples from the 1.7-Gyr-old Chuanlinggou Formation in northern China, the 1.45-Gyr-old Belt Supergroup in the north-central USA and the 1.2-Gyr-old Borden basin in Arctic Canada. The Chuanlinggou Formation is interpreted as being a passive-margin sequence, suggesting a strong connection to the open ocean, and the Borden basin was a

passive margin that evolved into a foredeep setting. In contrast, the Belt basin probably represents an extensional marine setting with transiently more restricted depositional conditions (see Supplementary Information).

A small subset of samples from the Mt Isa superbasin, the Belt Supergroup and the Borden basin have significant iron enrichments and Fe_{Py}/Fe_{HR} near 0.8 (Fig. 1a), suggesting that sulphidic conditions may have developed episodically in the water column. The lack of persistently euxinic conditions in the Belt Supergroup is surprising. As a semi-isolated, probably marginal marine system with evidence for high rates of primary productivity²³, the Belt basin would seem ideally suited to developing euxinia—as we see in the modern, restricted Black Sea. Clear fingerprints of ferruginous conditions in the Chuanlinggou Formation are also revealing: as a passive-margin sequence lacking indications of appreciable basin restriction, this setting provides one of our best windows on conditions in the open Proterozoic ocean.

Our finding of iron-rich conditions in several mid-Proterozoic marine settings contrasts with the widely accepted view of globally persistent and pervasive deep euxinia. However, this discovery is entirely consistent with an emerging view of Precambrian ocean chemistry brought to light by the most recent trace-metal and iron speciation studies from younger and older portions of the Precambrian ocean. Specifically, there is evidence for coexisting iron-rich and H_2S -rich conditions in several Neoproterozoic^{24–27}, early and middle Palaeoproterozoic^{10,28} and early and late Neoproterozoic settings^{13,14} (Fig. 2). Ferruginous conditions were apparently widespread in the deeper portions of the ocean, whereas sulphide was probably limited to highly productive regions along the continental margins^{10,13,25,26}, which is analogous to the more reducing conditions in modern oxygen minimum zones. Our data fill a billion-year gap in the evidence for this marine redox state, indicating a hitherto undocumented continuity of iron-rich conditions throughout the Precambrian.

Our finding of extensive ferruginous conditions is also consistent with a recent study of marine molybdenum inventories²⁷, which argued that the extent of euxinic depositional environments during the mid-Proterozoic could have been severalfold that of the modern ocean ($\ll 1\%$) but far from whole-ocean euxinia. Similarly, mid-Proterozoic Mo isotope data are easily explained through greatly expanded (relative to today) but still largely local euxinia, with deep

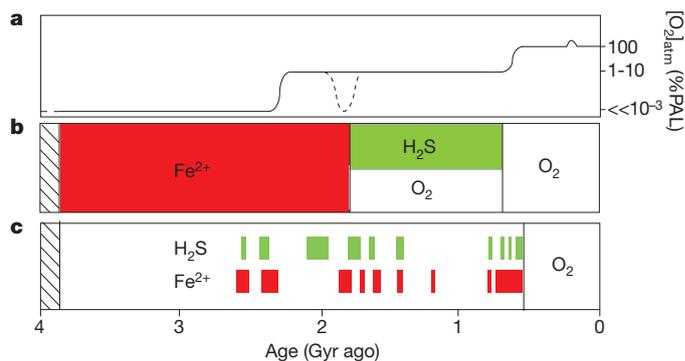


Figure 2 | Summary of marine chemical conditions in the Precambrian. **a**, Estimates of atmospheric oxygen compared with present atmospheric level (PAL). **b**, Classical models of the chemical composition of the deep ocean. **c**, Distribution of Precambrian euxinic and ferruginous deep waters, based on the shale record. Our study provides evidence for extensively developed and likely persistent ferruginous conditions in the deep ocean during the mid-Proterozoic, which was previously thought to have been characterized by either oxygenated or sulphide-rich conditions. The emerging view based on redox studies of marine shales is that during the mid-Proterozoic, when there were relatively low levels of atmospheric oxygen, both euxinic and ferruginous waters were common, and often stratified, below the oxygenated surface-mixing zone. In the Phanerozoic, with higher levels of atmospheric oxygen, the deep oceans were anoxic for only short periods (see the text for details).

waters that were dominantly ferruginous and thus less efficient at burying Mo (see, for example, ref. 20).

We argue that the flux of organic matter was central to controlling the redox landscape of the mid-Proterozoic ocean, as has been suggested for other—both older and younger—instances of Precambrian euxinia^{10,13,25}. Estimates for dissolved sulphate levels in the mid-Proterozoic ocean range from 500 to 3,000 μM (see Supplementary Information). Even the lower estimate for sulphate is well above the upper limit for dissolved iron, which is fixed at roughly 100 μM by the solubilities of iron carbonates and silicates². Therefore, ferruginous marine conditions must instead mirror limited sulphide production¹³. Sulphide is produced anaerobically by bacteria at the expense of organic matter. It follows that spatial gradients in the organic flux and, ultimately, organic productivity may have limited the extent of euxinia.

Consistent with an organic matter delivery control on the distribution of sulphidic marine conditions, the analysed samples contain substantially less organic carbon than do typical euxinic Precambrian and Phanerozoic shales. Samples in our study contain on average less than 1% organic carbon, which is severalfold lower than concentrations common in euxinic shales (see, for example, ref. 27). Low levels of organic matter in ferruginous shales suggest relatively low productivity in the overlying water column. In addition, there is a sulphur isotope signal consistent with bacterial sulphate reduction occurring predominantly in the porewaters. Pyrite in our samples has $\delta^{34}\text{S}$ values that are slightly lower than or equivalent to coeval sulphate (Fig. 1b). A simple explanation for these results is that bacterial sulphate reduction is occurring largely in sediments where potentially high isotopic fractionations are muted by limited sulphate availability. Sulphate supplies in the sediments would be controlled by rates of diffusional replenishment, and associated deficiencies would be exacerbated by the comparatively small amount of sulphate in mid-Proterozoic seawater. In other words, limited availability of organic matter probably caused the onset of appreciable bacterial sulphate reduction to be restricted to the sediments. However, these sulphur isotope results do not completely exclude water column sulphur cycling.

For ferruginous conditions to have been extensive in the mid-Proterozoic ocean, dissolved oxygen acquired in surface waters through photosynthesis and gas exchange with the overlying atmosphere must have been consumed as deep water masses aged. Oxygen will be consumed through the degradation of sinking organic matter and, if oxygen remains available at depth, by hydrothermally sourced reductants (see, for example, ref. 29). Our results indicate that the flux of Fe^{2+} into deep waters typically exceeded rates of sulphide generation in all but nearshore or restricted regions with relatively high rates of primary productivity that fuelled localized sulphate reduction in the water column.

Our results also call for a reconsideration of the factors controlling the temporal distribution of large iron formations. In contrast with the canonical view, in which iron formations disappeared as the deep ocean evolved from iron to oxygen or sulphide domination^{1,4}, the long persistence of ferruginous conditions in our model argues that iron formations are anomalous sedimentary deposits linked in most cases to an enhanced iron supply by means of strong hydrothermal inputs⁸. Consistent with our ocean model, the amount of hydrothermal iron released to the oceans has varied greatly with marine sulphate concentrations³⁰ and mantle plume activity as reflected by dyke swarms and large igneous provinces⁸.

Our findings cast a new perspective on mid-Proterozoic environmental conditions, ecology and evolution. For example, evidence for extensive ferruginous conditions throughout the Proterozoic ocean provides a simple answer to the apparent conundrum of increasing enzymatic use of iron, molybdenum and cobalt during the mid-Proterozoic as inferred by a recent study of the evolution of almost 4,000 gene families³¹. It is possible for these bioessential metals to have been readily available in an ocean with pervasively ferruginous deep

waters, in contrast with the certainty of biolimitation if deep waters were globally sulphidic⁷. Free sulphide in the water column greatly decreases the solubility of these elements. It remains to be tested, however, whether broad, but far from global, extents of euxinia in a stratified ocean were still able to pull down trace metal inventories at least locally to biologically critical levels, as suggested in previous work²⁷. More generally, our data now provide the foundation for a unified model for the chemical evolution of the Precambrian ocean consistent with diverse redox tracers and bridging past work bracketing the mid-Proterozoic. Recognizing the spatial and temporal heterogeneity expected in a dynamic early ocean, we propose the almost continuous coexistence of sulphide-rich and iron-rich conditions for billions of years beneath oxic surface waters as the backdrop for Precambrian biological evolution, and specifically the protracted radiation of eukaryotes and the ultimate rise of animals.

METHODS SUMMARY

Iron speciations were performed at the University of California, Riverside (UCR), using a well-calibrated sequential extraction protocol designed to quantify the different pools of Fe_{HR} (ref. 18). A small portion of sample powder (~ 100 mg) was used for the extractions, and iron concentrations were determined with an Agilent 7500ce inductively coupled plasma mass spectrometry (ICP-MS) at UCR. Fe_{Py} was calculated on the basis of the weight percentage of sulphur extracted during a 2-h hot chromous chloride distillation followed by iodometric titration. Total iron concentrations were determined by one of two methods: X-ray fluorescence at the CODES Research Centre at the University of Tasmania, or a three-acid digest and ICP-MS analysis at UCR. Sulphur isotope measurements were made at UCR with a ThermoFinnigan Delta V continuous-flow stable-isotope-ratio mass spectrometer after a chromous chloride distillation, where the pyrite-S was reprecipitated as Ag_2S .

Full Methods and any associated references are available in the online version of the paper at www.nature.com/nature.

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Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

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METHODS

The extraction method used in this study to speciate between the reactive iron pools in fine-grained siliciclastic rocks and sediments has been described in detail elsewhere, and we therefore provide only an overview here. In short, our iron speciations were performed at UCR, using a well-calibrated sequential extraction protocol designed to quantify the different pools of Fe_{HR} (refs 6, 18). Fe_{HR} is subdivided into three subpools, each with the potential to react with hydrogen sulphide on diagenetic timescales: carbonate-associated iron extracted with a sodium acetate solution (Fe_{carb}), ferric oxides extracted with a dithionite solution (Fe_{ox}), and mixed-valence iron oxides, principally magnetite, extracted with ammonium oxalate (Fe_{mag}). We used ~ 100 mg of sample powder, and the sequential extracts were analysed with an Agilent 7500ce ICP-MS. Pyrite (Fe_{py}) is also included in the Fe_{HR} pool. Fe_{py} was calculated (assuming a stoichiometry of FeS_2) on the basis of the weight percentage of sulphur extracted during a 2-h hot chromous chloride distillation followed by iodometric titration. The assumption of a FeS_2 stoichiometry in the sulphide pool was tested through extensive extractions for acid-volatile sulphide with hot SnCl_2 -HCl (15% SnCl_2 , 6 M HCl) for 1 h.

The samples included here all contain less than 0.1% sulphur extractable by HCl. Total iron concentrations were determined by one of two methods: X-ray fluorescence at the CODES Research Centre at the University of Tasmania, or a three-acid digestion followed by ICP-MS analysis at UCR. On the basis of duplicate analyses and Geostandard monitoring, reproducibility of iron measurements was better than 5%. However, samples with less than 0.1% iron were found to be reproducible to two decimal places, but the error can exceed 5%. At such low levels of iron, these errors have no impact on our conclusions.

We determined concentrations of total organic carbon by taking the difference between carbonate carbon liberated by 4 M HCl and total carbon released by combustion at 1,450 °C, both of which were measured with an ELTRA C/S determinator at UCR. Last, also at UCR, pyrite-S was extracted for isotope measurements by using the same chromous chloride distillation but, in this case, reprecipitating the pyrite-S as Ag_2S . Sulphur isotope measurements were made with a ThermoFinnigan Delta V continuous-flow stable-isotope-ratio mass spectrometer. Reproducibility was better than 0.2‰ on the basis of single-run and long-term standard monitoring.