

clays, considered diagnostic of oceanic depositional environments on Earth¹² — is needed to settle the debate. And, of course, the geomorphic examination of deltas and valley networks provides no information on the composition of the aqueous deposits that formed the deltas (Fig. 1). But the new vision of deltas and river networks conducting water from the highlands to the lowlands of Mars provides strong support for the hypothesis that the lowlands once harboured a vast ocean. □

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BIOGEOCHEMISTRY

Earth's redox evolution

The timing and nature of changes in the chemistry of the early oceans are intensely debated. Geochemical analyses show that a prominent transition to sulphidic marine conditions 1.8 billion years ago may have been restricted to near-shore environments.

David Fike

The balance of chemical oxidizing and reducing agents in fluids, known as the redox state, plays an important role in regulating biological activity on Earth today. In particular, redox conditions determine whether and where specific metabolic pathways are, thermodynamically, the most favourable. Biological activity, in turn, can have profound consequences on redox conditions, both locally and globally: in the most dramatic example, the evolution of oxygenic photosynthesis by cyanobacteria inexorably brought the world into a more oxidized state. But the transition to oxygen-rich oceans was interrupted by the appearance of anoxic and sulphide-rich (sulphidic) conditions about 1.8 billion years ago^{1–3}. Writing in *Nature Geoscience*, Poulton and colleagues⁴ show that rather than reflecting a global shift in ocean chemistry, the sulphidic waters were confined between the oxygenated ocean surface and anoxic, iron-rich waters below.

Before the dawn of oxygenic photosynthesis, the oceans were anoxic and rich in dissolved iron (ferruginous). Oxygen was first produced by cyanobacteria at least 2.5 billion years ago, and for the past 542 million years, the oceans have been dominantly oxygenated. The sulphidic conditions 1.8 billion years ago² were postulated to have arisen after an initial accumulation of atmospheric oxygen spurred oxidative weathering of the continents¹. This led to the enhanced delivery of sulphate to the oceans and

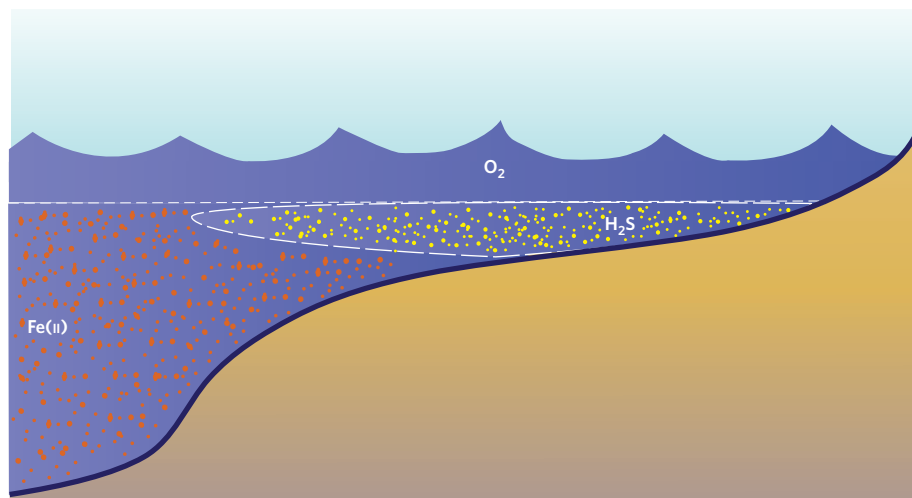


Figure 1 | Schematic of ocean redox conditions 1.8 billion years ago. In this scenario, the shallow waters are oxic (purple), reflecting contact with an, at least minimally, oxygenated atmosphere, whereas the deeper oceans are anoxic and ferruginous (red spots), reflecting the influx of dissolved iron into the deep oceans. Poulton and colleagues⁴ present data that suggest the presence of a thin wedge of sulphidic conditions between these layers (yellow spots), maintained in part by the delivery of organic matter from shallow waters and the microbial reduction of sulphate.

an increase in the bacterial reduction of sulphate to hydrogen sulphide¹. The widespread presence of sulphidic conditions is also supported by the discovery of organic biomarkers that reflect the presence of photosynthetic bacteria that utilize sulphide³.

However, as the record of oceanic conditions becomes better resolved, reports of coeval but conflicting redox conditions

have been published. For example, it has long been thought that the transition from anoxic to oxic conditions occurred during the Ediacaran period (~635–542 Myr)⁵, a time that also marks the first-known appearance of multicellular life. However, recent geochemical evidence indicates that, at least locally, ferruginous⁶ or even sulphidic⁷ conditions persisted throughout this period. Such different assessments

can arise in part from the interpretation of different geochemical proxies used to reconstruct redox conditions, from genuine physiographic separations between different ocean basins around the globe, or as the result of secondary alteration of the original geochemical signals⁸.

One way to wring order from this chaos is to use several adjacent locations to reconstruct a three-dimensional framework of redox variability over time. Recently, this approach was applied to the Ediacaran-aged Nanhua Basin in China, which led to suggestions that Ediacaran oceans may have been doubly redox-stratified, with a wedge of sulphidic waters separating deep ferruginous waters from oxic surface waters⁷.

Poulton and colleagues⁴ have used a similar approach to investigate redox conditions more than one billion years earlier, examining several stratigraphic sections in the 1.8 billion-year-old Animikie basin of North America to look for spatial variation associated with the transition to sulphidic conditions. The distribution of redox-sensitive phases of iron clearly indicates a stratified redox structure, with a near-shore wedge of sulphidic waters intruding between overlying oxic surface waters and deeper ferruginous waters. These results imply the coexistence of ferruginous and sulphidic conditions in spatially distinct zones, similar to those found in the Ediacaran oceans (Fig. 1).

In both cases, it remains unclear exactly what physical (and biological) conditions are necessary to support these redox gradients in the water column, and how long such stratified conditions are likely to remain stable. For this we can look to modern ocean settings such as the Cariaco Basin⁹ off the

coast of Venezuela, where circulation with the open ocean is restricted by physical barriers, resulting in localized reducing conditions at depth. Spatial redox variability can also arise in the open ocean in the form of oxygen minimum zones¹⁰. There, bursts of biological productivity in the upper ocean lead to localized depletion of oxygen at intermediate depths, as the sinking biomass is eventually degraded and respired. Oxygen minimum zones often occur where nutrient-rich waters from the deep ocean upwell to the surface, such as off the western coast of Chile.

Thus there are modern physical mechanisms that could plausibly be invoked to generate spatial gradients in redox conditions in the ancient ocean, in addition to any conditions perhaps unique to such ancient biogeochemical cycling^{4,8}. However, the expected duration of these oceanic redox gradients remains an open question. Presumably the conditions would have needed to persist for millions of years to be preserved in the Animikie sediments, but transient conditions lasting for short periods cannot necessarily be ruled out.

The apparent spatial variability found in redox signals at such critical biogeochemical junctures in Earth history may put many ill at ease. It is difficult to tell whether these reports reflect spatially varying conditions in the ancient ocean itself or from some other means, such as chemical alteration of the signal during or after deposition⁷. A note of caution comes from the analysis of many of our most trusted redox proxies (iron speciation, sulphur isotopes and carbon/sulphur ratios) in samples from the mobile mud belts of the Amazon River delta¹¹. Taken at face value, the geochemical redox indicators of these sediments suggest

deposition under an anoxic, sulphate-poor system¹¹, but we know they were deposited in well-oxygenated, sulphate-rich marine waters. In this instance, the proxies instead reflect the continued reworking of these sediments as they migrate along the coast of South America. As this example demonstrates, a detailed understanding of the depositional context is essential for building robust interpretations of geochemical data.

Poulton and colleagues⁴ have provided intriguing evidence for early spatial variability in redox structure, which will undoubtedly spur renewed efforts to model early ocean chemistry. However, much work integrating geochemical and stratigraphic data sets remains ahead of us before we can have a true sense of the three-dimensional redox structure in the oceans, and how this has varied through time. □

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STRUCTURAL GEOLOGY

To fault or not to fault

Most of the oceanic crust has a simple layered structure. The discovery that slow-spreading ridges exhibit a comparatively complex crustal structure and some of the largest extensional faults on Earth is leading to the recognition of a new mode of seafloor spreading.

Michael Cheadle and Craig Grimes

Mid-ocean ridges are the locations where the Earth's crust is renewed. Here, the tectonic plates that form the sea floor spread apart and new oceanic crust is generated from upwelling magma. Studies of ancient oceanic crust have led to the idea that it forms in simple layers¹.

However, in 1983, large faults that expose rocks from deep below the mid-ocean ridge were discovered at the Mid-Atlantic Ridge². These structures have since been identified in most ocean basins. At the American Geophysical Union Chapman Conference³ on 'Detachments in oceanic lithosphere'

in May 2010, geoscientists and biologists concluded these oceanic fault systems should be recognized as a fundamentally distinct mode of seafloor spreading.

Conventionally, oceanic crust is thought to have a relatively constant thickness of 6–7 km and a simple layered structure. The