BIOGEOCHEMISTRY

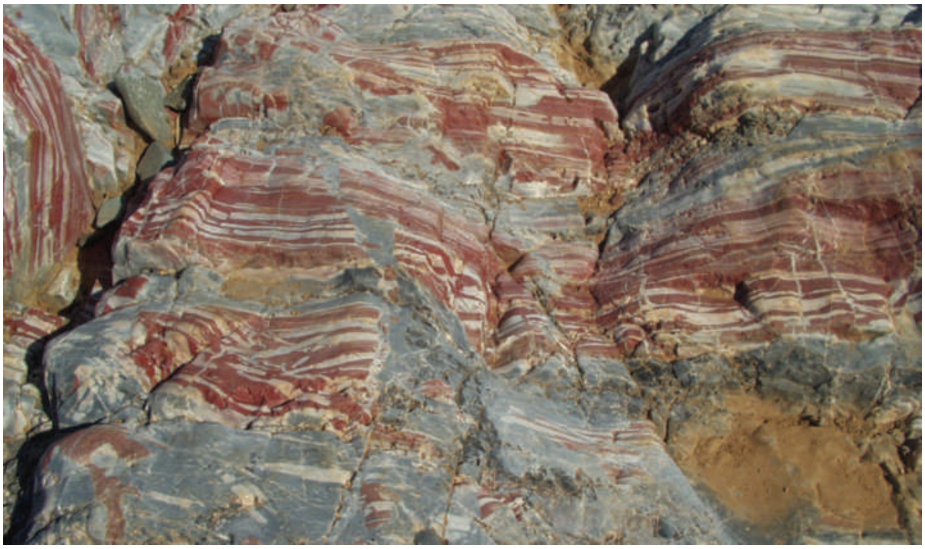
# Deepening the early oxygen debate

The timing of the earliest production of oxygen by photosynthesis is hotly debated. Haematite crystals from Pilbara, Australia, may provide evidence for a deep ocean that was at least occasionally oxygenated by photosynthetic microbes 3.46 billion years ago.

Kurt Konhauser

Primitive bacteria, most probably the forerunners of modern cyanobacteria, developed the ability to strip electrons from water through oxygenic photosynthesis, simultaneously generating an important by-product: oxygen gas. This evolutionary feat arguably represents the most important biological innovation in the history of life on Earth, and it set the stage for profound changes in the redox state of the oceans and atmosphere, ultimately enabling more complex, oxygen-dependent organisms, such as ourselves, to emerge[1]. At present, the oldest evidence for oxygenic photosynthesis comes from 2.7-Gyr-old molecular fossils in shales[2]; however, the interpretation of these relict biomolecules is not straightforward[3]. On page 301 of this issue, Hoashi and colleagues[4] radically propose that the mineralogy of 3.46-Gyr-old iron-rich cherts (jasper) in Western Australia provides evidence for the availability of free oxygen more than 700 Myr earlier.

These sedimentary rocks, similar to banded iron formations from the Archaean eon (about 3.8–2.5 Gyr ago), contain alternating layers of chert and the fully oxidized ferric iron mineral haematite. Previous explanations for the oxidation of dissolved ferrous (reduced) iron have centred on photochemical reactions driven by ultraviolet radiation or anoxygenic bacterial photosynthesis[5]. These processes require the ferrous iron entering the oceans from hydrothermal vents to be transported to the shallow, well-lit ocean surface. Many workers have therefore taken the view that bulk ocean waters must have been anoxic, to allow the long-distance transport of reduced iron from the deep oceans to the shallow depositional environments where it was oxidized. In turn, the termination of banded iron formation about 1.8 Gyr ago has been linked to either deep-ocean oxygenation[6] or sulphidation[7] brought on by increased atmospheric oxygen at that time. However, several highly controversial lines of evidence, including the sulphur isotopic compositions of pyrites[8] and the elemental compositions of ancient soil horizons[9], have been put forth to support instead the presence of appreciable amounts of oceanic and atmospheric oxygen hundreds of millions of years before the Great Oxidation event, about 2.4 Gyr ago[10].



HIROSHI OHMOTO

**Figure 1 |** Hoashi and colleagues[4] suggest that the haematite contained within the complex layers of the Marble Bar Chert provides evidence of oxygenated deep water 3.46 Gyr ago.

In further support for early oxygen, Hoashi and colleagues[4] posit that the haematite that occurs in jasper units of the 3.46-Gyr-old Marble Bar Chert Member in the Pilbara Craton, Western Australia (Fig. 1) was formed in a submarine volcanic depression at depths between 200 and 1,000 m. As this depth is well below that which sunlight can penetrate, the team argues that the mineral must have precipitated directly when hot hydrothermal fluids (above 60 °C), rich in reduced iron, mixed rapidly with sea water containing the only remaining plausible oxidant in this setting — oxygen. They thus call for the availability of free oxygen in the last place you would expect to find it in an anoxic world.

Hoashi and colleagues report that the haematite occurs in thin bands — 10 μm to 1 mm in thickness — that formed parallel to the bedding. The haematite is composed of clusters of sub-micrometre-sized crystals that are chemically and mineralogically homogeneous. Many crystals are also observed as inclusions within ferrous iron-containing minerals, such as siderite and magnetite, which the authors provide as evidence that the haematite crystals are primary, or at the very least a dehydration product of an initial amorphous ferric oxyhydroxide precursor. Furthermore, on the basis of stratigraphic, textural and mineralogical relationships between the haematite-bearing layers and those immediately below and above, the authors discount the possibility that the haematite was produced by more recent circulation of hydrothermal fluids or oxygenated groundwater.

Considering the lightning rod of controversy that surrounds this subject, I predict that a flurry of papers will try to rebut this study. Certainly there is no shortage of published work showing the complete opposite: that the oceans remained largely anoxic until about 2.4 Gyr ago[10].

Indeed, so firmly entrenched are the views on the advent of cyanobacterial evolution around, or slightly earlier than, 2.7 Gyr ago and the progressive rise of atmospheric oxygen at 2.4 Gyr ago that current research is more focused on explaining the 300-Myr time lag[11] than on pushing back the timing for the evolution of oxygenic photosynthesis.

Future studies exploring whether this haematite is really a reflection of oxygenated deep water will most probably focus on the mechanisms by which haematite nucleates directly from sea water, the syndepositional nature of the haematite and whether the haematite is a localized feature. It is also critical to determine the exact depth at which the iron oxidation and mineral precipitation reactions occurred, considering its influence on our understanding of the chemo-stratigraphy of the Archaean oceans.

Although it is possible to envisage localized oxygen oases in shallow water settings if cyanobacteria had already evolved at that time[12], explaining the presence of oxygen in deep water is a completely different matter. In my opinion, the authors make a strong case for sediment accumulation in a deep-water setting. And if the haematite is truly primary and penecontemporaneous with the chert, it most probably formed from a hot fluid, close to the hydrothermal source. However, the alternative possibility that amorphous ferric oxyhydroxides precipitated in the photic zone and sank about 200 m to the sea floor, only to transform later into haematite, is not, in my mind, completely ruled out.

Hoashi and colleagues[4] question current thinking of anoxia throughout the early and middle Archaean by bringing their views on early ocean oxygenation to deeper waters. The scrutiny of the wider scientific community will show whether this idea will stand the test of time. ❐

*Kurt Konhauser is at the Department of Earth and Atmospheric Sciences University of Alberta, Edmonton, Alberta T6G 2E3, Canada.*
*e-mail: kurtk@ualberta.ca*

References

1. Knoll, A. H. *Geobiology* **1,** 3–14 (2003).
2. Brocks, J. J., Logan, G. A., Buick, R. & Summons, R. E. *Science* **285,** 1033–1036 (1999).
3. Rasmussen, B., Fletcher, I. R., Brocks, J. J. & Kilburn, M. R. *Nature* **455,** 1101–1104 (2008).
4. Hoashi, M. *et al. Nature Geosci.* **2,** 301–306 (2009).
5. Konhauser, K. O. *et al. Earth Planet. Sci. Lett.* **258,** 87–100 (2007).
6. Holland, H. D. *The Chemical Evolution of the Atmosphere and Oceans* (Princeton Univ. Press, 1984).
7. Poulton, S. W., Fralick, P. W. & Canfield, D. E. *Nature* **431,** 173–177 (2004).
8. Ohmoto, H., Kakegawa, T. & Lowe, D. R. *Science* **262,** 555–557 (1993).
9. Ohmoto, H. *Geology* **24,** 1135–1138 (1996).
10. Kaufman, A. J. *et al. Science* **317,** 1900–1903 (2007).
11. Barley, M. E., Bekker, A. & Krapež, B. *Earth Planet. Sci. Lett.* **238,** 156–171 (2005).
12. Rosing, M. T. & Frei, R. *Earth Planet. Sci. Lett.* **217,** 237–244 (2004).

PALAEOCLIMATE

# Tales of collapse

Deep beneath the ice shelves of Antarctica, sediments have been slowly accumulating on the sea floor, marking the passage of time for millions of years. These sediments should record changes in the overlying ice-sheet conditions, potentially providing an archive of variations in the West Antarctic ice sheet. However, the thick layer of ice that seals the sediments has rendered these archives unreachable.

In 2006, the scientists of the Antarctic Geological Drilling (ANDRILL) project took on the technological challenge of drilling through 85 m of the Ross Ice Shelf to reach the sediments below. Not only did they reach the sea floor, but they recovered over 1,200 m of sediments, spanning up to 13 million years of Earth's history. Now the team, led by Tim Naish of the University of Wellington, New Zealand, have reconstructed the behaviour of the West Antarctic ice sheet during the early to middle Pliocene epoch, 3–5 million years ago. At the time, climate was about 3 °C warmer than at present, and atmospheric carbon dioxide levels probably hovered around 400 ppmv, similar to today's levels (*Nature* **458,** 319–325; 2009).

Their sediment analyses reveal a long history of alternations between grounded ice sheets, floating ice shelves (like those found today) and open waters.

GAVIN DUNBAR

These cycles occurred with a periodicity of 40,000 years, consistent with the cyclic variations of the tilt of the Earth's axis. From 3.6 to 3.4 million years ago, the microfossil assemblage suggests largely sea-ice free conditions, implying that winter temperatures were generally above freezing. During this period the West Antarctic ice sheet probably disintegrated.

Meanwhile, David Pollard of Pennsylvania State University and Robert DeConto of the University of Massachusetts at Amherst faced technical challenges of their own as they created a numerical model capable of simulating variations in the ice sheets of Antarctica over the same time frame (*Nature* **458,** 325–329; 2009). According to their simulations, multiple collapses of the West Antarctic ice sheet have occurred throughout the Pliocene epoch; one period of prolonged and frequent collapses occurred about 3.4 million years ago, coinciding with the interval described from the ANDRILL core. Indeed, most of the main ice-sheet collapses simulated by the model closely correspond to open-water conditions reported from the sediment records.

By running simulations at a higher resolution to examine the mechanisms of ice-shelf collapse, Pollard and DeConto found that melting along the interface between the ice and the underlying sea water is the dominant regional control on the stability of the Ross Ice Shelf, which serves as an accurate indicator of West Antarctic ice volume. In their model, it takes about 5 °C of warming in nearby ocean waters to trigger a collapse of the West Antarctic ice sheet, starting from modern conditions. With a projected surface air temperature change of up to 3 °C near Antarctica by 2100 — as suggested by the 2007 report of the Intergovernmental Panel on Climate Change — such a time may not be as far off as we would like.

ALICIA NEWTON