The rise of atmospheric oxygen

Lee R. Kump

Clues from ancient rocks are helping to produce a coherent picture of how Earth's atmosphere changed from one that was almost devoid of oxygen to one that is one-fifth oxygen.

Imagine a *Star Trek* episode in which the Starship Enterprise stumbles into a time warp and is transported to Earth 3 billion years ago. The crew are eager to disembark but, before they do, they need to discover more about the pink methane haze[1] that surrounds the planet. The Starship Enterprise analyses a sample and, to the crew's surprise, it finds that Earth's atmosphere is as inhospitable as those of most of the celestial bodies they have encountered. Although the crew's hopes of exploring the surface of the early Earth are dashed, they did manage something that no one has done before. They determined the oxygen content of the early atmosphere.

Timing is everything

Although it is probable that the history of atmospheric oxygen will be unravelled before the twenty-third century, which is when the television series *Star Trek* is set, more than 40 years of analysis of ancient rocks and of theoretical development have yet to produce a definitive picture of the planet's early history[2]. Two facts are known with certainty: Earth's earliest atmosphere was essentially devoid of oxygen; and today's atmosphere is composed of 21% oxygen. Most of the events that took place between these two time points are highly uncertain. By the end of the twentieth century, a battery of geological indicators suggested a shift from an anoxic to an oxic atmosphere some time between 2.5 and 2.0 billion years ago. This shift is known as the great oxidation event[3]. The most compelling evidence was the absence in older stratigraphic units of 'red beds', sedimentary rocks stained red by iron oxide. Instead, an abundance of lithified ancient soils that had lost their iron during weathering were found, reflecting the absence of oxygen in the weathering environment.

The 'smoking gun' for the rise of atmospheric oxygen was discovered and reported in 2000 (ref. 4). Rocks older than about 2.45 billion years contain a large degree of mass-independent fractionation (MIF) of sulphur isotopes; rocks younger than 2.32 billion years show essentially none[5] (Fig. 1). Many processes on Earth discriminate between the isotopes of elements, but usually the discrimination depends on the mass of the isotope. Processes that lead to MIF of sulphur are rare, and large MIF effects are restricted to gas-phase photochemical reactions in the upper atmosphere. The signature of MIF sulphur photochemistry is small and is rapidly homogenized in the modern oxidizing atmosphere. By contrast, in an oxygen-free atmosphere, large MIF effects are preserved, resulting in contrasting isotopic compositions of reduced and oxidized sulphur species that are deposited from the atmosphere and incorporated into sedimentary rocks.

To preserve the MIF signature, three conditions are needed: very low atmospheric oxygen, sufficient sulphur gas in the atmosphere, and substantial concentrations of reducing gases. Numerical modelling by Zahnle *et al.*[6] has shown that the latter, in particular the atmospheric methane level, is the primary requirement for preserving MIF. Indeed, Zahnle *et al.* posit that the contraction of the spread in MIF values at ~2.45 billion years ago (Fig. 1) was the direct result of a collapse in atmospheric methane levels. This loss of 'greenhouse warming' is then invoked to explain the ensuing first major glaciation in Earth's history, perhaps of 'snowball Earth' proportions[7] with ice extending to the tropics. In the scenario proposed by Zahnle *et al.*[6], the decrease in methane would account for the increase in atmospheric oxygen, an alternative to the previously proposed scenario in which the rise in oxygen is proposed to have caused the collapse of the methane 'greenhouse'[8]. Given the high reactivity of methane and oxygen, the rise of oxygen and the demise of methane must have been inextricably linked; unravelling cause and effect will continue to be a challenge.

On closer inspection[9,10], the Archaean (pre-2.5 billion years ago) MIF record displays an extended interval between 3.2 and 2.8 billion years ago (the Mesoarchaean) during which the spread of MIF values seems to be smaller. During this period[11], was there a failed attempt at atmospheric oxygenation or a collapse of atmospheric methane, or is this simply an artefact of a sparse geological record? Trace gases, such as methane and carbon dioxide, are important in biogeochemical cycles, and their atmospheric concentrations have fluctuated significantly on geological timescales. Is it unreasonable to presume that when oxygen was a trace gas, it too varied substantially in response to imbalances between production and consumption? The most recent analysis of the MIF record indicates persistent anoxia throughout the Archaean, with some other change in atmospheric chemistry accounting for lower MIF values during the Mesoarchaean[12], although geochemical evidence suggests a 'whiff of oxygen' might have appeared at the close of the Archaean, 50 million years before the permanent increase in oxygen[13].

From when to why

Future work on the evolution of atmospheric oxygen will focus on these intriguing aspects of the time before its ultimate rise at 2.45 billion years ago. It will seek to explain why the increase in oxygen occurred when it did, and to develop proxy indicators of oxygen levels so that the history of atmospheric oxygen evolution can be established.

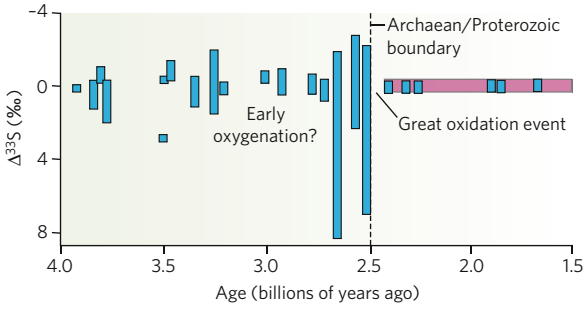

Figure 1 | Range of MIF of sulphur over time. The great oxidation event occurred ~2.45 billion years ago, and an early, failed, oxygenation event might have occurred around 3.2 billion years ago (but this is hotly debated). The degree of MIF (blue) is indicated by $\Delta^{33}S$, which is the parts per thousand (‰) deviation of the standardized $^{33}S/^{32}S$ ratio from the value predicted from the $^{34}S/^{32}S$ ratio and mass-dependent fractionation. The range of values from samples of a given age is shown by vertical bars. The pink bar shows the range of variability in $\Delta^{33}S$ that is due to mass-dependent effects, indicating only small variations during the past 2.32 billion years.

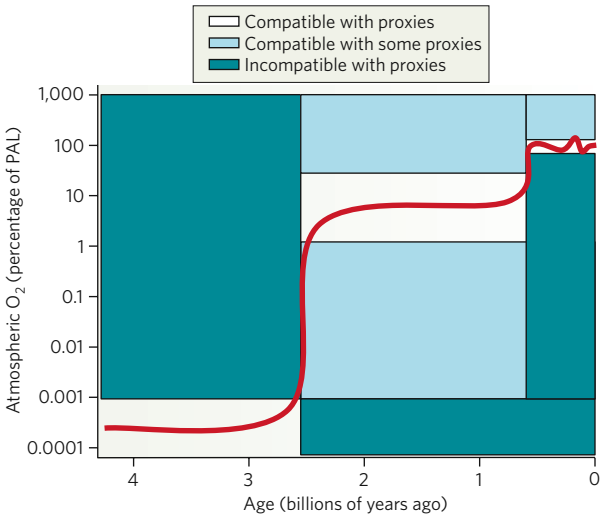

Figure 2 | Prevailing view of atmospheric oxygen evolution over time. The red line shows the inferred level of atmospheric oxygen bounded by the constraints imposed by the proxy record of atmospheric oxygen variation over Earth's history[2,20]. The signature of mass-independent sulphur-isotope behaviour sets an upper limit for oxygen levels before 2.45 billion years ago and a lower limit after that time. The record of oxidative weathering after 2.45 billion years ago sets a lower limit for oxygen levels at 1% of PAL, whereas an upper limit of 40% of PAL is inferred from the evidence for anoxic oceans during the Proterozoic. The tighter bounds on atmospheric oxygen from 420 million years ago to the present is set by the fairly continuous record of charcoal accumulation[19]: flames cannot be sustained below an oxygen level of 60% of PAL, and above about 160% of PAL the persistence of forest ecosystems would be unlikely because of the frequency and vigour of wildfires[21].

Why oxygen levels rose when they did remains an understudied problem in atmospheric evolution. This time interval has traditionally been associated with the establishment of large, thick and stable continental land masses. Did a resultant change in the style of plate tectonics decrease the overall demand for oxygen as it reacted with volcanic[14] or metamorphic[15] outgassings? Or did cyanobacteria simply evolve oxygenic photosynthesis at this time[7], perhaps in response to some new selective pressure arising from the stabilization of continents? Biomarker evidence for cyanobacteria (2-methylhopanes) and their waste product oxygen (in the form of steranes, which probably require oxygen for their synthesis) exists in rocks that formed 200 million years before the increase in atmospheric oxygen[16]. Taken together with other geological data, these biomarkers suggest that oxygen was being produced at prodigious rates before 2.5 billion years ago but was consumed faster than it was produced. However, 2-methylhopanes are no longer considered diagnostic of cyanobacteria[17], and alternative pathways of sterane synthesis are possible[7]. So additional proxies must be sought. Fossilized microbial mats might hold the clue to the early origin of oxygen photosynthesis if it can be demonstrated that the expected strong redox gradients[18] existed and produced isotopic or compositional variations that can be recovered from Archaean rocks.

Reconstructing ancient oxygen levels

Most geological indicators of ancient atmospheric oxygen levels imply only presence or absence (Fig. 2). MIF disappears when oxygen levels reach 0.001% of the present atmospheric level (PAL)[8], and iron is retained in ancient lithified soils when oxygen is at 1% of its PAL[3]. Persistent anoxia of the oceans in the Proterozoic (from 1.8 to 0.5 billion years ago) is argued to require oxygen levels below 40% of PAL[2]. Fire is sustained only above about 60% of PAL, so the more-or-less continuous geological record of charcoal over the past 450 million years sets this as a lower limit for atmospheric oxygen since the advent of forests on Earth. The interesting exception is the Middle to Late Devonian, ~380 million years ago, which shows a charcoal gap[19] coincident with widespread evidence for marine anoxia. The other available redox indicators are from marine sediments, requiring that internal ocean processes that affect deep-ocean oxygen levels be untangled before inferences about atmospheric oxygen level can be made.

A promising approach to reconstructing ancient oxygen levels looks at the effect that oxygen has on carbon-isotope fractionation[20], but the signal is convolved with all the other factors that affect isotopic discrimination in plants and algae. Greater focus on the physiological effects of, adaptations to, and defences against oxygen in plants and animals is likely to lead to additional proxies. As we explore new proxies and seek out new sites for geological discovery, we will undoubtedly develop a more complete history of the multibillion-year evolution of atmospheric oxygen. ■

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1. Lovelock, J. E. *The Ages of Gaia* (Norton, New York, 1988).
2. Canfield, D. E. The early history of atmospheric oxygen: homage to Robert M. Garrels. *Annu. Rev. Earth Planet. Sci.* **33,** 1–36 (2005).
3. Holland, H. D. in *Early Life on Earth* (ed. Bengston, S.) 237–244 (Columbia Univ. Press, New York, 1994).
4. Farquhar, J., Bao, H. & Thiemens, M. Atmospheric influence of Earth's earliest sulfur cycle. *Science* **289,** 756–758 (2000).
5. Bekker, A., *et al.* Dating the rise of atmospheric oxygen. *Nature* **427,** 117–120 (2004).
6. Zahnle, K., Claire, M. & Catling, D. The loss of mass-independent fractionation in sulfur due to a Palaeoproterozoic collapse of atmospheric methane. *Geobiology* **4,** 271–283 (2006).
7. Kopp, R. E., Kirschvink, J. L., Hilburn, I. A. & Nash, C. Z. The paleoproterozoic snowball Earth: a climate disaster triggered by the evolution of oxygenic photosynthesis. *Proc. Natl Acad. Sci. USA* **102,** 11131–11136 (2005).
8. Pavlov, A. A. & Kasting, J. F. Mass-independent fractionation of sulfur isotopes in Archean sediments: strong evidence for an anoxic Archean atmosphere. *Astrobiology* **2,** 27–41 (2002).
9. Ono, S., Beukes, N. J., Rumble, D. & Fogel, M. L. Early evolution of atmospheric oxygen from multiple-sulfur and carbon isotope records of the 2.9 Ga Mozaan Group of the Pongola Supergroup, Southern Africa. *S. Afr. J. Geol.* **109,** 97–108 (2006).
10. Ohmoto, H., Watanabe, Y., Ikemi, H., Poulson, S. R. & Taylor, B. E. Sulphur isotope evidence for an oxic Archaean atmosphere. *Nature* **442,** 908–911 (2006).
11. Knauth, L. P. Signature required. *Nature* **442,** 873–874 (2006).
12. Farquhar, J. *et al.* Isotopic evidence for Mesoarchean anoxia and changing atmospheric sulfur chemistry. *Nature* **448,** 1033–1036 (2007).
13. Anbar, A. D. *et al.* A whiff of oxygen before the Great Oxidation Event? *Science* **317,** 1903–1906 (2007).
14. Kump, L. R. & Barley, M. E. Increased subaerial volcanism and the rise of atmospheric oxygen 2.5 billion years ago. *Nature* **448,** 1033–1036 (2007).
15. Catling, D. C. & Claire, M. W. How Earth's atmosphere evolved to an oxic state: a status report. *Earth Planet. Sci. Lett.* **237,** 1–20 (2005).
16. Brocks, J. J., Logan, G. A., Buick, R. & Summons, R. E. Archean molecular fossils and the early rise of eukaryotes. *Science* **285,** 1033–1036 (1999).
17. Rashby, S. E., Sessions, A. L., Summons, R. E. & Newman, D. K. Biosynthesis of 2-methylbacteriohopanepolyols by an anoxygenic phototroph. *Proc. Natl Acad. Sci. USA* **104,** 15099–15104 (2007).
18. Herman, E. K. & Kump, L. R. Biogeochemistry of microbial mats under Precambrian environmental conditions: a modelling study. *Geobiology* **3,** 77–92 (2005).
19. Scott, A. C. & Glasspool, I. J. The diversification of Paleozoic fire systems and fluctuations in atmospheric oxygen concentration. *Proc. Natl Acad. Sci. USA* **103,** 10861–10865 (2006).
20. Berner, R. A., Beerling, D. J., Dudley, R., Robinson, J. M. & Wildman, R. A. Phanerozoic atmospheric oxygen. *Annu. Rev. Earth Planet. Sci.* **31,** 105–134 (2003).
21. Watson, A., Lovelock, J. E. & Margulis, L. Methanogenesis, fires, and the regulation of atmospheric oxygen. *Biosystems* **10,** 293–298 (1978).

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