Introduction to Special Issue

Oxygen and life in the Precambrian

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This special issue of *Geobiology* traces Earth's biogeochemistry from the very earliest sedimentary rocks in Greenland to the late Proterozoic in papers that range from field and laboratory studies to computer models of the atmosphere. The thematic link between all papers is the impact of the rise of atmospheric oxygen through the Precambrian on life and environments. The solicitation of papers for this themed issue grew out of a session of the *Earth System Processes 2* conference in Calgary, Canada, 8–11 August 2005, generously sponsored by the NASA Astrobiology Institute.

The earliest sedimentary rocks that can tell us about life come from the Isua Supracrustal Belt in Greenland. Papineau & Mojzsis (in this issue) investigate sulfur isotopes from >3.77 Ga Isua rocks. In recent years, a key development in examining the history of oxygen has been the discovery of mass-independent fractionation of sulfur isotopes (S-MIF) in ancient rocks (Farquhar *et al.* 2000). In most processes, isotopes are fractionated in proportion to their mass difference. Hence, ^{34}S is usually fractionated about twice as much as ^{33}S with respect to ^{32}S because the mass difference between ^{34}S and ^{32}S is twice that between ^{33}S and ^{32}S. Photochemistry in an anoxic atmosphere can produce S-MIF, where the relative sulfur isotope abundances deviate from simple proportionality. Papineau & Mojzsis (in this issue) present 54 new analyses that show mass-dependent fractionation ($\delta^{34}S$) close to zero. Microbial fractionation becomes evident at seawater sulfate concentrations >0.2 mM (Habicht *et al.* 2002), so limited mass-dependent fractionation means either that sulfur-reducing microbes were absent or that the Archean ocean had very low levels of sulfate. In examining the three-isotope system (^{32}S, ^{33}S and ^{34}S), Papineau & Mojzsis (in this issue) detect S-MIF, which is consistent with a largely anoxic and weakly reducing atmosphere at >3.77 Ga.

There is abundant evidence that the atmosphere became oxygenated between 2.4 and 2.2 Ga (e.g. Catling & Claire 2005), but what was the ultimate trigger? At first sight, one might suggest the contemporaneous origin of oxygenic photosynthesis (e.g. Kopp *et al.* 2005), which is the only significant source of free O_2 molecules. However, biomarker evidence suggests that there was lag of at least 300 Myr between the

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origin of O_2-producing cyanobacteria and abundant O_2 in the atmosphere (Brocks *et al.* 2003; Summons *et al.* 2006). Claire *et al.* (in this issue) present a quantitative biogeochemical model that simulates Earth's atmospheric transition to an O_2-rich state. They start by laying out general equations for quantifying atmospheric O_2 levels, which express the competition between sources and sinks of O_2. These equations are solved to obtain O_2 levels as a function of time. The paper by Claire *et al.* (in this issue) is the first to produce a self-consistent numerical model for the 2.4–2.2 Ga rise of O_2. Their basic hypothesis is that the rise of O_2 was caused by a decreasing flux from the solid planet of reduced gases and reduced hydrothermal cations. One numerical solution involves a decline in the flux of reductants driven by irreversible secular oxidation of the crust caused by time-integrated hydrogen escape to space from the pre-oxygenated atmosphere. This produces a collapse of CH_4 and a rise of O_2. An alternative version of the model, where fluxes of reducing hydrothermal cations from the Archean seafloor consume O_2, produces an essentially identical atmospheric history. Claire *et al.* (in this issue) also present climate calculations showing that when CH_4 collapses, 'Snowball Earth' ensues.

Between 2.45 and 2.32 Ga, the S-MIF signature disappeared, which has been attributed to the creation of the O_2-rich atmosphere (Pavlov & Kasting 2002). Zahnle *et al.* (in this issue) convincingly overturn that idea. As well as the very low oxygen levels, the production of S-MIF relies on an atmosphere with a sufficient amount of reducing gas to reduce volcanic SO_2 to elemental sulfur particles. These insoluble particles rain out of the atmosphere and preserve the S-MIF signal. Zahnle *et al.* (in this issue) show that a decrease of atmospheric methane levels from hundreds of p.p.m.v. to below ~10 p.p.m.v. would eliminate the S-MIF signal. This scenario would be consistent with the onset of low-latitude ('Snowball Earth') glaciation around ~2.4 Ga. Zahnle *et al.* (in this issue) suggest that methane perhaps decreased because the biogenic flux of methane was throttled by an increase in oceanic sulfate even before atmospheric O_2 had risen to detectable levels. Oxygen only significantly accumulated in the atmosphere after CH_4 collapsed, which would explain why classical indicators of oxygen, such as red beds, occur after ~2.3 Ga. Zahnle *et al.*'s (in this issue)

modelling predicts a testable sequence of events. CH_4 goes down first, the drawdown of CH_4 then allows the transition from low to high O_2 to occur, and the resulting increase in O_2 and stratospheric ozone actually allows CH_4 to recover because the troposphere is shielded from solar ultraviolet radiation.

A sleeping giant in our knowledge of the history of oxygen concerns the co-evolution of the nitrogen cycle. Oxygenation of the Earth's atmosphere forced the deep ocean to change from an iron-enriched state to a hypothesized sulfidic state (Canfield 1998). A sulfidic Proterozoic ocean would have limited both oceanic iron and molybdenum that are essential components of the nitrogenase enzyme used in bacterial nitrogen fixation. It has been suggested that this may have diminished rates of Proterozoic nitrogen fixation and primary production (Anbar & Knoll 2002). Zerkle *et al.* (this issue) investigate the effect of the concentrations of trace metals on nitrogen fixation in cultures of the bacterium *Azotobacter vinelandii*. They report low rates of nitrogen fixation in cultures with low [Fe] and [Mo]. However, they find rates similar to those observed in fully oxygenated conditions with low [Fe] and relatively higher [Mo], which they take as representative of the mid-Proterozoic ocean. Because metals are also important in denitrification and eukaryotic nitrate assimilation, further work is needed to get a complete picture of the early nitrogen cycle and how it influenced the rates of photosynthetic oxygen production.

Finally, the Proterozoic history of oxygen needs to be related to the level of carbon dioxide so that the effect of both gases on the biosphere can be evaluated. Riding (in this issue) suggests a two-step process in the Proterozoic consistent with previously published estimates of CO_2 and O_2. First, a fall in CO_2 mixing ratio to below 1% (or 33 times the present levels) would have allowed calcium carbonate crystals to nucleate adjacent to cyanobacteria, which may account for carbonate muds that began to appear at 1.4–1.3 Ga. Second, CO_2-concentrating mechanisms promote *in vivo* sheath calcification in modern cyanobacteria when CO_2 falls below ~0.4% (or 10 times the present levels), while high levels of O_2 may also favour CO_2-concentrating mechanisms. Riding proposes that the first appearance of the sheath calcified cyanobacteria at 0.75–0.7 Ga constrains CO_2 to less than 0.4% at this time. After Neoproterozoic 'Snowball Earth' events, Riding (in this issue) argues that rising O_2 and higher temperatures were responsible for further inducing *in vivo* sheath calcification among diverse cyanobacteria in the early Cambrian.

This collection of papers addresses the evolution of the redox state of the environment, a core area of the emerging discipline of geobiology. The timing, causes, and magnitude of atmospheric oxygenation are still very much the subjects of active discussion within the geobiological community. The advances in this special issue provide new evidence and new interpretations that will significantly improve our understanding of the co-evolution of Earth's environment and life.

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