Cracking the Neoproterozoic atmosphere?

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It is often said that the Earth is a planet that records its own history. While this is certainly true of the solid and liquid Earth, the archives are less well kept for the atmosphere. We have excellent records of atmospheric composition from gas bubbles in ice cores as far back as one million years (Higgins et al., 2015). In the absence of older, intact ice, different approaches are required to develop a quantitative understanding of atmospheric evolution for the more distant past. Geochemists have developed proxies to infer changes in atmospheric composition from the marine and terrestrial sedimentary rock record. No atmospheric constituent has received more attention than molecular oxygen, which has increased from levels in the Archean below 0.001% of present atmospheric level (PAL) to ~21% of the atmosphere in the modern world (Kump, 2008; Lyons et al., 2014). This transition is intimately tied to the evolution of life, as photosynthetic organisms ultimately generate the atmosphere’s O₂, and animals require it both for biosynthesis of key macromolecules and for respiration.

The emergence of eukaryotic diversity and complex multicellular life in the Neoproterozoic Era (Xiao and Laflamme, 2009; Erwin et al., 2011; Cohen and Macdonald, 2015) makes this a critical interval for reconstructing atmospheric oxygen levels. Geochemical records of carbon and sulfur isotope ratios (Fike et al., 2006; McFadden et al., 2008), iron speciation (Canfield et al., 2007), and the abundance of redox-sensitive trace metals such as Mo, U, and V (Partin et al., 2013; Reinhard et al., 2013), have all pointed to a significant rise in oxygen levels in the Ediacaran Period, bolstering the contention that the evolution of animal life could not occur until oxygen was plentiful in the environment. However, unraveling the timing and magnitude of changes in oxygen levels is complicated by differential responses of each geochemical proxy, uncertainties in the models used that link proxy measurements to quantitative estimates of oxygen in the environment, and questions regarding possible diagenetic alteration of the proxies.

In this context, Blamey and colleagues (2016, p. 651 in this issue of *Geology*) now contribute to the debate by reporting the first direct measurements of putatively primary Neoproterozoic atmospheric gases, obtained from gas inclusions in evaporite sedimentary rocks from the Officer Basin in Australia. They measured the oxygen content at ~50% PAL in rocks deposited during the Tonian Period, ca. 810 Ma. Based on petrographic screening and independent geochemical analyses, the authors argue atmospheric gas was trapped in the mineral halite as it crystallized on the surface of an evaporating water body, and that the gases remained undisturbed since the burial of the halite. Gas inclusion analysis is a relatively new analytical technique, which here is being used to address a fundamental question in Earth history. Blamey et al. support the validity of their approach by analyzing halite crystals precipitating in modern evaporative environments, demonstrating that the gas inclusions capture the composition of the modern atmosphere. However further systematic work will still be necessary to understand and quantify the full range of possible post-depositional effects, including the production and consumption of O₂ by halophilic microbes, gas diffusion through the crystal lattice, and gas exchange along mineral cleavage planes.

How might this result add to our understanding of Proterozoic O₂ levels? Quantitative reconstruction of the Mesoproterozoic and early Neoproterozoic atmosphere has traditionally placed O₂ levels between 1% PAL and 40% PAL. The lower limit is a constraint based on O₂ requirements to generate oxidative weathering patterns observed in sedimentary rocks, such as the retention of iron in paleosols and the absence of redox-sensitive detrital grains, such as pyrite or uraninite (Rye and Holland, 1998; Johnson et al., 2014). The upper limit is a modeled boundary condition necessary to maintain the anoxic deep oceans that are thought to have dominated the Proterozoic (Canfield, 1998). Oxygen in the deep ocean is supplied by sinking surface waters and consumed by aerobic respiration of organic matter. Therefore, nutrient availability and primary production exert a strong control on the oxygenation state of the deep ocean. Building on a simple biogeochemical box model of the modern ocean (Sarmiento et al., 1988), Canfield (1998) established an upper limit of ~40%–50% PAL O₂ in the Proterozoic atmosphere to maintain an anoxic deep ocean. Although this result is sensitive to the latitude of deep-water formation, the temperature structure of the surface ocean, and nutrient availability, it demonstrates that the surface and deep ocean can have widely different equilibrium oxygenation states. In this context, the new halite gas inclusion data pushes against the upper limit of widely accepted models and may indicate some combination of a warmer surface ocean or a greater respiration demand at depth in the Tonian ocean.

Much of the evidence for anoxic deep oceans during the Proterozoic comes from the iron speciation proxy (reviewed by Poulton and Canfield, 2011). This approach uses the relative abundances of various iron-bearing compounds in marine sedimentary rocks to identify the ancient local environment as oxic or anoxic, with anoxic water columns further subdivided into ferruginous (free dissolved iron) or euxinic (free dissolved sulfide). Early iron speciation data from Newfoundland seemed to indicate a switch from ferruginous deep oceans to oxic deep oceans coinciding with the termination of the ca. 580 Ma Gaskiers glaciation and the appearance of the Ediacaran biota (Canfield et al., 2007); this provided an exciting possible link between ocean oxygenation and evolution of complex multicellular life. However, recent work from the Mackenzie Mountains paints a more complex relationship between the appearance of the Ediacaran biota and deep ocean redox changes based on iron speciation data (Sperling et al., 2016), and there is no trend toward increased deep ocean oxygenation over the course of the Proterozoic (Sperling et al., 2015). These studies of deep basin facies provide a glimpse of local conditions in the deepest parts of sedimentary basins; whether or not these conditions represent conditions in the abyssal global ocean remains an open question. Nevertheless, an oxic surface ocean is inferred to have coexisted with persistently anoxic deep water throughout most of the Neoproterozoic (Canfield et al., 2008).

The stable isotopic composition of chromium in marine sedimentary rocks has recently emerged as a promising new proxy for quantifying atmospheric O₂ levels directly, without relying on inferences from reconstructions of the deep-ocean redox state (Frei et al., 2009; Crowe et al., 2013). An isotopic fractionation is imparted during terrestrial chromium oxidation mediated by Mn oxides. Oxidative weathering generates mobile oxidized Cr species enriched in the heavy Cr isotope. Authigenic minerals precipitated from oxidatively weathered Cr are therefore distinguishable from the low and uniform Cr isotope ratios in crustal source rocks. Models suggest that the isotopic signal of oxidative weathering may develop when O₂ exceeds 0.1% PAL (Planavsky et al., 2014), although a 1% threshold is...
also possible (Crowe et al., 2013). The Cr isotope record of marine shales and ironstones indicates that the oxidative threshold was not reached until ca. 810 Ma (Planavsky et al., 2014; Cole et al., 2016), which is in good agreement with the timing of the first appearance of several eukaryotic groups (Cohen and Macdonald, 2015) and estimates for the divergence of early animals (Erwin et al., 2011). As the Neoproterozoic Cr isotope database expands, it will be important to calibrate the proxy in modern environments, refine the quantification of the oxidation threshold, as well as to evaluate the importance of H$_2$O$_2$-mediated Cr oxidation during serpentinization (Oze et al., 2016).

The emerging picture therefore is one of dramatically increasing atmospheric O$_2$ levels in the Tonian while deep ocean anoxia persisted. The chromium isotope data indicate that O$_2$ first exceeded 1% PAL between 900 Ma and 800 Ma (Planavsky et al., 2014; Cole et al., 2016). Blamey et al.'s new halite gas inclusion data yield ~50% PAL at ca. 810 Ma. If both results prove to be robust, it will be a major challenge to explain the magnitude, rate, and timing of this Tonian Oxidation Event. Although the geologic record of evaporites is not continuous, a series of data points from globally distributed evaporite units with excellent stratigraphic correlation could greatly augment our quantitative understanding of the oxygenation of Earth’s atmosphere. Well-preserved Tonian evaporites of the Shaler Supergroup in northwest Canada (Thomson et al., 2015) stand out as promising candidates for further study. Future work would need to elucidate the biogeochemical and oceanographic processes that delayed the oxygenation of the deep ocean until the late Neoproterozoic and early Paleozoic.

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REFERENCES CITED


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