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Evidence for Oxygenic Photosynthesis Half a Billion Years Before the Great Oxidation Event

Noah Planavsky, Chris Reinhard, Dan Asael, Tim Lyons, Axel Hofmann, and Olivier Rouxel
noah.planavsky@yale.edu

Despite detailed investigations over the past 50 years, there is still intense debate about when oxygenic photosynthesis evolved. Current estimates span over a billion years of Earth history, ranging from prior to 3.7 Ga, the age of the oldest sedimentary rocks, to 2.4-2.3 Ga, coincident with the rise of atmospheric oxygen ("The Great Oxidation Event" or GOE). As such, a new, independent perspective is needed. We will provide such a perspective herein by using molybdenum (Mo) isotopes in a novel way to track the onset of manganese(II)oxidation and thus biological oxygen production.

The oxidation of Mn(II) in modern marine setting requires free dissolved oxygen. Mn is relatively unique in its environmental specificity for oxygen as an electron acceptor among the redox-sensitive transition metals, many of which, like Fe, can be oxidized under anoxic conditions either through a microbial pathway and/or with alternative oxidants such as nitrate. There are large Mo isotope fractionations associated with the sorption of Mo (as a polymolybdate complex) onto Mn-oxyhydroxides, with an approximately -2.7‰ fractionation in d98Mo associated with Mo sorption onto Mn-oxyhydroxides (e.g., birnessite, vernadite). In contrast, sorption of Mo onto the Fe-oxyhydroxide (e.g., ferrihydrite) results in a fractionation of only -1.1‰ or less. Because of this difference in Mo isotope fractionation, Mo isotope values should become lighter with increasing Mn content, if Mn oxidation occurred during deposition and is an important vector of Mo transfer to the sediment.

We find a strong positive correlation between d98Mo values and Fe/Mn ratios in iron formations deposited before and after the Great Oxidation Event. Most strikingly, Mo isotope data and Fe/Mn ratios correlate over a 2.5‰ range in d98Mo values in the Mn-rich (0.1 – 6%) iron formation of the 2.95 Ga Sinqeni Formation, South Africa. The large isotopic shifts occur over a relatively thin (3 meter thick) horizon, reflecting short-term variations in the degree of Mn oxidation that are consistent with localized oxygen generation and rapid consumption in a geochemical backdrop that was otherwise reducing. The observed range in d98Mo values and the correlation between d98Mo values and Fe/Mn ratios is statistically identical to that found in the ca. 1.89 Ga iron formations from the Lake Superior region, Animikie basin, which were deposited well after the rise of atmospheric oxygen.

Our work and other recent geochemical work on the Pongola Supergroup reconcile geochemical and molecular records for the emergence of oxygenic photosynthesis and provide strong evidence that there was biological oxygen production well before its permanent accumulation in the atmosphere around 2.4-2.3 Ga.