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The molybdenum isotope composition of modern and ancient stromatolites

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The primitive Earth was characterized by an oxygen-poor ocean–atmosphere system [1,2,3], and experienced a significant increase in oxygen concentrations during the Great Oxidation Event (GOE) ca 2.45 Ga [4]. This event is generally believed to be linked to oxygenic photosynthesis by bacteria [2,5]. However, it is becoming commonly accepted that "whiffs" of oxygen existed before the GOE [2,6,7,8,9,10]. To shed new light on this emerging paradigm, here we present molybdenum (Mo) isotopic data from stromatolitic carbonates of different ages. In modern oceans, Mo is the most abundant transition metal, is redox-sensitive, and displays heavy isotope enrichment, with δ98/95Mo = 2.63‰ ± 0.1 (2σ; relative to NIST SRM 3134) for mean ocean water Mo (MOMo) [11], primarily as the result of Mn and Fe oxide sinks that select against the heavy isotope [12]. No fractionation has been observed between no skeletal carbonate and the water from which they were precipitated [13], making carbonates an important potential archive of ancient seawater δ98/95Mo and thus redox evolution. In our study, we examined modern stromatolites from Bacalar lagoon, Mexico, and Precambrian stromatolites deposited ca. 1.88 Ga (Gunflint, Canada), 2.52 Ga (Ghaap Group, South Africa), 2.8 Ga (Steep Rock, Canada), and 2.96 Ga (Red Lake, Canada). Modern samples record a molybdenum isotope signature that appears related to the water from which they grew, supporting the idea that the molybdenum isotopic composition of carbonates is a robust proxy for examining paleo-redox conditions of environments where carbonates were precipitated. Ancient stromatolites reveal evidence for oxygen in the environment at 2.8 Ga, while stromatolites from the Ghaap Group (2.52 Ga) and Red Lake (2.96 Ga) appear to have grown under poorly-oxygenated conditions. This data reaffirms suggestions that oxygenic photosynthesis existed at least 0.35 Ga before the rise of atmospheric oxygen. Moreover, the consistent signal for oxygen in the environment at this time could be indicative of a constant period of mild oxygenation, rather than local oases as previously proposed.

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