

Are microbial carbonates reliable archives for the redox state of the Precambrian oceans and atmosphere?

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Microbial carbonates (microbialites) form in shallow-water depositional settings at the interface with the atmosphere and are ideal candidates for the application of redox-sensitive, non-traditional isotope systems, such as uranium isotopes ($^{238}\text{U}/^{235}\text{U}$), to improve our understanding of Earth's redox history. However, the redox cycling of elements such as U by microbes may induce additional isotope fractionation and lead to spurious interpretations regarding paleoredox states. In addition, there may be a distinct isotopic offset for a particular microbial community at a given environmental setting. Many important early examples of Archean stromatolites formed in open marine, semi-restricted marine and volcanic rift settings. The presence of living microbialites in similar modern environments allows us to assess the U isotope signature associated with each setting. In the hypersaline, restricted marine embayment of Shark Bay, Western Australia, modern stromatolite (laminated microbialites) crusts exhibited a $\delta^{238}\text{U}$ offset of ca. +0.1‰ from seawater whilst deeper and older stromatolite laminae exhibited offsets up to +0.4‰. In the open marine setting of Schiermonnikoog, an island in the North Sea, microbial mats faithfully

recorded the $\delta^{238}\text{U}$ of (ca. -0.4‰). However, microbialites in the volcanic rift setting of Lake Chew Bahir, Ethiopia (volcanic rift) produced a wide range of $\delta^{238}\text{U}$ that were both above and below the value of modern lakewater (ca. -0.3‰), indicating enhanced redox cycling of U. These findings demonstrate the strong control of the local environment on microbialite $\delta^{238}\text{U}$ that are independent of the atmospheric redox state. This highlights the need to carefully interpret the depositional environment of Precambrian stromatolites when applying paleoredox proxies, particularly in ancient volcanic rift settings.