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Primary evidence for redox cycling in 2.8-billion-year-old microbialites

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Archean carbonate sediments are important archives of the redox state of ancient seawater and can potentially provide important insights into early microbial life, such as the timing of the evolution of microbial metabolisms prior to the Great Oxidation Event (~2.4 Ga). Unfortunately, extensive diagenesis and/or metamorphic alteration has often modified the primary geochemical signals. These post-depositional processes are major obstacles for our ability to accurately infer the emergence, extent, and impacts of microbial metabolisms on early Earth. For example, due to the complications associated with diagenesis and metamorphism, interpretations of Archean geochemical records fail to converge on a consistent estimate for the evolution of oxygenic photosynthesis. To resolve this controversy, a deeper understanding of the post-depositional history of Archean sedimentary rocks is essential, including geochemical constraints on the timing of carbonate recrystallization, chemistry and redox state of the pore-waters during early diagenesis, and composition of late-stage burial fluids. In this study, we provide more accurate constraints on the redox conditions and elemental cycling in Archean seawater by interrogating the diagenetic history of ~2.8 Ga old sediments, the Mosher Carbonate, from Northwest Ontario. We combine petrographic observations with targeted fabric-specific analysis of Ca isotope (δ44/40Ca), C isotopes (δ13C), major and trace elemental ratios (Mg/Ca, Sr/Ca, Mg/Ca), and Rare Earth Element (REE+Y) patterns. Despite having been recrystallized, we find that carefully screened carbonate fabrics preserve pristine geochemical records of the Archean environment, containing hints of both early diagenetic Mn-redox cycling across the sediment-water interface and the major elemental composition of Archean seawater. These findings suggest that Archean surface-seawater locally had prominent Ce-anomalies, high Mn concentrations, depleted δ44/40Ca values, and δ13C values similar to the modern ocean.