

Integrated geochemical-sedimentological tests for the preservation of seawater paleo-redox signals in carbonates

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The application of novel isotope and trace metal geochemistry to ancient sedimentary successions has been instrumental in the characterization of the Earth's oxygenation. However, with much recent attention focused on obtaining large geochemical data sets to derive these redox histories, there has been less attention paid to the preservation of an original depositional signal in these sediments. Here we show that a variety of diagenetic processes may significantly alter trace metal and isotope compositions of carbonates.

Uranium and chromium isotope systems in carbonates are two newly developed paleo-redox proxies that may reveal the redox state of ancient oceans. However, carbonates are susceptible to a range of sedimentary and diagenetic processes including detrital contamination, recrystallization and dolomitization, which may alter their chemical composition. We have used case studies of trace metals, U and Cr isotopes from a suite of marine carbonates with a range of diagenetic histories to demonstrate the importance of careful sample selection.

Neoproterozoic carbonates of Australia show a large range in U and Cr isotope composition between components (including ooids, microbialites, marine cements and late-stage cements). Single hand samples of the Cryogenian (Balcanoona) reefal dolomites show almost the entire range of U isotopes ever documented. In these reefs, early marine dolomitization of aragonite has preserved the original U isotope composition of samples, and is within error of the $\delta^{238}\text{U}$ value of primary dolomite marine cements (-0.23‰), suggesting ferruginous ocean conditions at this time. In contrast, the U and Cr isotope compositions of Devonian microbialites and other Paleozoic limestones are significantly altered by late-stage, fluid-driven diagenesis and saddle dolomitization.

These results suggest petrographic and stratigraphic analysis is necessary to determine if an original seawater geochemical value has been preserved in marine carbonates.