Deciphering the carbonate record of Mesoproterozoic biospheric oxygenation: insights from chromium and uranium isotopes

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The 'boring billion' has been described as the "dullest time in Earth history"—however, major global events did occur, from the initial diversification of eukaryotes to the assembly of the supercontinent Rodinia. These events unfolded against the backdrop of an ocean-atmosphere system whose redox landscape remains largely unknown. In recent years, debate has centered around atmospheric pO_2 and the seafloor distribution of redox environments. Isotope proxies such as molybdenum (Mo), chromium (Cr), and uranium (U) have provided a wealth of new information, but they have largely been applied to black shale and iron-rich sedimentary rocks, which are relatively sparse in the Mesoproterozoic sedimentary record. Here, we present Cr- and U-isotope data from marine carbonate rocks, which are plentiful in the geologic record of this interval. Extracting primary redox information from carbonate rocks is challenging because of low concentrations of these elements, potential detrital masking of seawater signatures, and the inherent reactivity of carbonate minerals during diagenesis. We review current approaches to mitigating these challenges, and present a compilation of isotopic data from six successions spanning the interval between 1.5 and 0.9 Ga. $\delta^{53}Cr$ values range from unfractionated to highly positively fractionated, indicating periods of atmospheric pO_2 both below and above the threshold required for Cr-isotope fractionation during continental weathering (~0.1 to 1 % PAL). Average $\delta^{238}U$ values are -0.39 ± 0.20 ‰ (1 s.d.), which is similar to the modern seawater value of -0.41 ‰. Accounting for potential fractionation during carbonate precipitation, these data are consistent with a larger degree of ocean anoxia compared to the modern ocean, but are inconsistent with an entirely anoxic deep ocean. Combined with previous proxy investigations, Cr- and U-isotope data suggest a more dynamic Mesoproterozoic redox landscape than previously envisaged, against the backdrop of a generally low O_2 world.