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Mo isotope chemostratigraphy of the 2.93 Ga Red Lake Carbonate Platform

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Three billion years ago, the Earth system was dramatically different from today, and the earliest oceans were largely anoxic, except for possible local oxygen oases in shallow seas. This study reports the first detailed molybdenum (Mo) stable isotope chemostratigraphy through Earth's earliest carbonate platform, preserved in the 2.93-billion-year-old (Ga) Ball Assemblage of the Red Lake Greenstone Belt (Ontario, Canada). The analyses were performed on 81 samples from two correlative drill cores in order to evaluate the presence of trace amounts of O_2, as previously reported Mo stable isotope data from a limited number of outcrop carbonate samples from Red Lake have been interpreted to reflect the presence of an oxygen oases at this locality.

In the fresh drill core samples, Mo isotopes showed important variations throughout the different lithologies in both cores relative to the average continental crust, ranging from -2.22 ‰ to 0.53 ‰ in $\delta^{98/95}$Mo, clearly demonstrating Mo isotope fractionation as far back to 2.93 Ga. However, in the carbonate samples, Mo concentrations determined by isotope dilution were largely below crustal values, and Mo stable isotopes were largely unfractionated, indicating a seawater $\delta^{98/95}$Mo value of near 0 ‰ at the time of deposition. Banded iron formation and shale samples showed isotopically lighter values consistent with fractionation during Mo adsorption onto Fe-oxides or partial uptake by reducing sediments, respectively, from seawater that was similarly near 0 ‰. Combined, this evidence argues against important oxidative processing of Mo during the deposition of the Red Lake platform, and points to a largely unfractionated seawater Mo reservoir derived from anoxic chemical weathering or low temperature hydrothermal sources. Considering that Fe-oxides do not need O_2 to precipitate, and that the studied carbonates and BIF are not obvious witnesses to oxidative Mo processing, it would appear that the previously analyzed outcrop carbonate samples showing heavy Mo isotope compositions may constitute a false positive due to surface weathering for the presence of O_2. Some rare samples from this study show Mo isotope systematics that may be explained by trace amounts of free O_2, but further study would be required.