

Ca-Mg-Li isotope variations in 2.8 Ga carbonate sediments from Steep Rock, Canada: Constraints on seawater composition and temperature and global weathering regimes in the late Archean

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Ocean chemistry is sensitive to numerous processes linked to the long-term evolution of Earth's surface environment, including climatic- and tectonic-driven variations in chemical and physical weathering of emerged continental crust. We have examined Li-, Ca-, and Mg-isotope variations in a suite of well-preserved carbonate samples from the ~2.8 Ga Steep Rock Formation, Canada to constrain the isotopic composition of Archean seawater during a period that records significant changes in average crustal composition and may reflect the global transition to a plate tectonic regime.

$d^{44}\text{Ca}_{\text{SRM915a}}$ in non-dolomitic samples is negatively correlated with both $d^{26}\text{Mg}$ and Sr/Ca, with $d^{44}\text{Ca}$ ranging from -0.1 to +1.5‰. These correlations are consistent with differences in the isotopic fractionation factors and carbonate/fluid $K_D(\text{Sr}/\text{Ca})$ between aragonite and calcite. These trends may result from variable mixing of calcite and aragonite in primary sediments, with isotopic signals preserved during sediment-buffered diagenesis and conversion of aragonite to calcite. Alternatively, they may reflect incomplete re-equilibration with seawater-derived fluids during fluid-buffered diagenesis. In either case the trends allow retrieval of seawater Ca, Mg, and Li isotopic compositions at the time of sediment deposition and compaction. Assuming seawater temperature of ~30 °C, the observed trend is consistent with seawater Mg- and Ca-isotope composition similar to modern values (e.g., $d^{44}\text{Ca} \gg 1.95\text{‰}$). Significantly higher Archean seawater temperatures, suggested by previous studies, would require a fortuitous counterbalancing shift in seawater $d^{44}\text{Ca}$ to lower values, a non-parsimonious scenario.

$d^7\text{Li}_{\text{LSVEC}}$ values range from 3.3 to 10.7‰, except for one dolomitic sample (16.5‰). This sample is also shifted off the $d^{26}\text{Mg}$ - $d^{44}\text{Ca}$ trend to higher $d^{26}\text{Mg}$ values, consistent with lower isotopic fractionation for Ca, Mg, and Li between dolomite and aqueous fluids than for low-Mg carbonate phases. $d^7\text{Li}$ values are well below modern carbonate values (>20‰), consistent with lower flux of Li to the Archean ocean from continental weathering and/or reduced isotopic fractionation of weathered products due to congruent weathering regimes.

These results suggest that seawater Ca and Mg cycles were fundamentally similar at 2.8 Ga to today, as were global temperatures, but support a diminished role for terrestrial and marine clay formation in the global Li cycle.