

A 3-Billion-Year Lithium Isotope Record from Marine Dolostones

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Changes in the global lithium cycle, as recorded by seawater Li concentrations ($[Li^+]_{sw}$) and isotopic compositions (δ^7Li_{sw}), have emerged as a promising tracer for reconstructing the long-term controls of seawater chemistry and Earth's geologic carbon and silicon cycles. Recent δ^7Li_{sw} records from marine fossil shells show a $\sim 8\text{--}9\text{‰}$ increase over the past 60 million years (Ma) [1, 2, 3]. Bulk measurements of shallow-water marine carbonates have extended the δ^7Li record back to 3 billion years ago (Ga), indicating a noisy but dramatic unidirectional increase in mean δ^7Li_{sw} by $\sim 24\text{‰}$ over the Phanerozoic and $\sim 29\text{‰}$ since 3 Ga [4]. However, studies of bulk shallow-water carbonate sediments, including drill cores from modern carbonate platforms [5,6], show $\sim 0\text{--}15\text{‰}$ offset from the seawater δ^7Li values due to diagenesis (e.g., marine vs. meteoric) under fluid- or sediment-buffered conditions, mineralogy (e.g., calcite vs. aragonite), and clay contamination [7]. Early dolomitized shallow-water carbonates under fluid-buffered conditions in marine settings record the heaviest endmember of the diagenetic spectrum, approaching the seawater-equilibrium δ^7Li values [5,8]. Here, we present δ^7Li of bulk marine dolostones from samples that were previously used to document $\delta^{26}Mg_{sw}$ [9] and $\delta^{44/40}Ca_{sw}$ [10] to reconstruct δ^7Li_{sw} for the past 3 Ga. Dolostones show non-linear δ^7Li evolution and have heavier values compared to shallow-water carbonates. The δ^7Li_{sw} curve from dolostones overlaps with δ^7Li_{sw} trends from foraminifera [1], brachiopods [2], and corals [3] over the Mesozoic and Cenozoic, and fluid inclusions in halites over the Neoproterozoic and Phanerozoic Eras [11]. Dolostones suggest modest non-linear changes in the δ^7Li_{sw} ($<17\text{‰}$) over the past 3 Ga with minima during the Cretaceous, Cambrian, and Archean and maxima during the Tonian, Permian, and Quaternary Periods.

[1] Misra and Froelich, 2012; [2] Washington et al., 2020; [3] Murphy et al., 2019; [4] Kalderon-Asael et al., 2021; [5] Murphy et al., 2022; [6] Wei and Zhang, 2024; [7] Dellinger et al., 2020; [8] Liu et al., 2023; [9] Xia et al., 2024; [10] Blättler and Higgins, 2017; [11] Weldeghebriel et al., 2024