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Reconstructing the Katian seawater lithium isotope signature from carbonate-evaporite sequences and formation brines

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Carbonates and evaporites are promising archives for reconstructing the Lithium (Li) history of seawater. However, these efforts are complicated by conflicting information on the mechanisms controlling Li uptake and isotope fractionation into marine carbonate minerals (aragonite and calcite) and evaporites (halite and gypsum/anhydrite), as well as by post-depositional alteration during diagenesis and Li contamination by detrital minerals released during sample preparation.

Fortunately, Li has a ~1 million year residence time in the ocean, meaning that seawater should remain resistant to changes in its Li composition over several million years, far longer than the duration of 3rd order (0.1–1 Myr) sequences, thus, allowing multiple genetically-related sedimentary archives (limestone, evaporite, and early diagenetic dolomite) to be analyzed within a single sequence framework without concern that seawater δ^7Li value or Li concentrations changed over the duration of the studied sequences.

In the Red River Formation, there are four repeating brining-upwards sequences: D, C, B and A, from bottom to top. Here, we employ the 3rd order 'C' Member sequence in the Red River Formation of the Williston Basin, composed of Late Ordovician (Katian Stage) burrow-mottled carbonate with dolomitized burrows and limestone matrix, overlain by laminated dolomite and the base of the 'B' Member sequence anhydrite. Previous work using Ca and Mg isotopes has shown that the 'C' Member carbonates record large proximal-to-distal gradients in δ^{44}Ca values. The limestone gradient is interpreted to reflect changes from fluid- to sediment-buffered diagenesis in the direction of depositional deepening. The dolomite gradient reflects two dolomitization events: (1) early diagenetic dolomite formation by brines that filtered down from the overlying evaporite basin, and (2) burial dolomite formed by fluid-rock interactions between early diagenetic dolomite and hot fluids ascending from the deep structural center of the basin at a younger age. Here we show how Li isotopic data from limestone, burrow-dolomite, anhydrite, and formation brines can be combined to create a snapshot of the δ^7Li value of Katian seawater and give insight into the fractionation factors, uptake mechanisms, and diagenetic considerations required to bring to focus this picture of the δ^7Li value of seawater.