

Origin and significance of Li isotope composition in epeiric marine carbonates and formation brine

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Carbonates and evaporites are potentially valuable archives for recording Li cycling in the geological past. But conflicting information on the magnitude of the isotopic fractionations associated with facies-dependent cycling, diagenetic alteration, and the leaching methods employed to release Li from carbonates hamper the accurate reconstruction of the Li isotopic records in seawater in the geological past. Here, we employ a lithostratigraphic time-slice (the ‘C’ Member limestone of the Red River Formation) composed of Late Ordovician burrow mottled carbonate with dolomitized burrows and limestone matrix, overlain by laminated dolomite and bedded anhydrite.

Previous work using Ca and Mg isotopes has shown that the ‘C’ Member carbonates record large proximal-to-distal gradients in $\delta^{44}\text{Ca}$ 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 later (2) burial of diagenetic dolomite formed by hot ascending Mg- and Ca-bearing fluids.

To mitigate uncertainty and evaluate proxy reliability, lateral facies variations in limestones, dolomites, anhydrite and formation brines were studied using $\delta^7\text{Li}$ values.

Though the long oceanic Li residence time implies uniform Li isotopic compositions at any one time in the geological past, our findings show that the studied limestones record 6‰ gradients in $\delta^7\text{Li}$ values, with low values near the basin edge and high values near the basin centre, while the dolomites record smaller oppositely configured gradients. Formation brines with geochemical signatures of evaporatively concentrated seawater yielded $\delta^7\text{Li}$ values of 20‰, falling in the range of the studied carbonates (16–22‰). Data from these different proxy materials will be used to provide a more reliable estimate of the contemporaneous seawater $\delta^7\text{Li}$ value.