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Testing a new strategy for reconstructing seawater Li isotope compositions using Devonian age dolomite and anhydrite in the Williston Basin

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In the Willison Basin, brines from the Late Devonian (Frasnian) Duperow Formation are prospective for Lithium (Li), with maximum reported concentrations of 258 mg/L in the Wymark D aquifer but lower concentrations in the Wymark A–C aquifers (~90-150 mg/L) from the same location. However, the source of brine Li and the mechanisms by which brines may reach different levels of enrichment is poorly understood.

The restricted marine setting of the Duperow Formation, together with its dolomites, evaporites, and brines with the chemistry of evaporatively concentrated seawater, is consistent with a seawater Li source. But, with enrichments of just 24 mg/L through the evaporation to halite facies in the Devonian (predicted using seawater Devonian Li concentration [1]), another source of Li is required to balance the Li budget within each aquifer. Here we propose to determine the δ^7Li value of the added Li source by mass balance, which requires a reliable estimate of the δ^7Li value of Frasnian seawater. Because the δ^7Li history of seawater is imprecisely known over most of the Phanerozoic, its value in the Frasnian must be determined using: (1) limestone and dolomite from the Wymark aquifers, and (2) anhydrite from the intervening aquitards, bearing in mind that the seawater δ^7Li value may be offset by fractionation or altered by diagenesis in these materials. Our results, thus far, are limited to anhydrite, which appears to contain two populations of Li. By analogy with halite [2], these are tentatively consigned to: (1) a seawater-derived pool of structurally bound Li that is strongly isotopically fractionated (9.7‰), and (2) a brine-based pool of Li in fluid inclusions that is unfractionated (20.0‰). All of the anhydrite samples record seawater $^{87}Sr/^{86}Sr$ ratios. The δ^7Li value of the Wymark D aquifer is 13.5‰. If 20.0‰ is the true value of Frasnian seawater, the δ^7Li value of the added source of Li is 12.8‰, which rules out continentally derived clay minerals (0 ±3‰) as the source of added Li.

[1] Weldeghebriel et al. (2024) EGU24, 13908.
[2] Y. Li et al. (2024) Chemical Geology 668, 122326.