In-Situ Water-Rock Interactions as the Source of Brine-Hosted Lithium: Implications for Developing a Deposit Model

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Summary

Decarbonization of the transportation sector will significantly increase the demand for battery metals, such as Li. This could lead to a significant Li supply gap in the coming years, requiring the development of new sources of this critical mineral. Deep subsurface brines from sedimentary basins, or brine-hosted Li deposits, could help to close this gap and have attracted significant interest from industry, academia, and government. In the Western Canada Sedimentary Basin (WCSB), numerous companies are exploring and looking to produce Li from brines, primarily from the Frasnian-aged Duperow Formation of Saskatchewan and the Leduc and Nisku formations of Alberta. To date, the majority of the exploration and mineral tenure has been centered around areas where there is existing geochemical brine data from historical hydrocarbon or water source wells. Most of this data is from well-head sampling programs conducted by the Alberta and Saskatchewan geological surveys but these programs were restricted to locations where there was active production. As such, there could be other locations, both geographically and stratigraphically, which could contain economic Li concentrations but have yet to be discovered. However, without a fluid sample, assessing the Li potential of an area or interval is difficult, if not impossible. A deposit model, similar to what exists for petroleum or ore deposits, does not yet exist and could assist in further exploration where samples cannot be easily collected. One of the first steps in developing such a model is identifying the Li source in these brines.

The two leading hypotheses for the enrichment of Li in WCSB brines are related to seawater evaporation and basement contributions. Based on halogen systematics, brines from the Duperow Formation of southeastern Saskatchewan were observed to derive their salinity from seawater evaporation, and therefore this was interpreted to also lead to the observed Li enrichments. However, it has been found that brines with high Li concentrations can also plot in the evaporite dissolution field (Bishop and Robbins, 2022). Furthermore, significant evapo-concentration rates would be required to achieve the observed concentrations of up to 259 ppm, and late stage evaporites are not common in drill core of the Duperow Formation to provide evidence for extreme evapo-concentration. Alternatively, due to the proximity of the Leduc Formation reefs to the Precambrian basement in northwestern Alberta, either direct contact of Leduc Formation fluids with the basement or the infiltration of hydrothermal fluids was proposed as the Li source (Eccles and Berhane, 2011). However, in Saskatchewan, this would require fluid migration through the thick, impermeable Elk Point Group, and Li enrichments would also be expected in intermediary formations such as the Deadwood and Winnipegosis formations. Additionally, elevated Li concentrations were observed across the basin, not restricted to a discrete geographical area (Bishop et al., 2022). In light of these findings, these mechanisms are unlikely to solely account for the high Li concentrations observed in the WCSB (Bishop et al., 2024). There is, however, a growing body of evidence, including from Eccles and Berhane (2011), that point towards water-rock interactions as the significant factor contributing Li to these brines. In this work, we present new geochemical and isotopic data from both brines and drill core to

provide evidence that in-situ water-rock interactions are critical to generating the high Li enrichments observed in the Duperow Formation.

Methods and Data

Brine geochemical data for this work was compiled from previous studies (Rostron et al., 2002; Iampen 2003; Jensen 2006, 2012, 2016; Jensen and Rostron 2017, 2018; Lyster et al., 2022; Bishop et al., 2024). Sediment samples were collected from drill core at the Saskatchewan Geological Subsurface Laboratory in Regina, SK. Sediment samples were analyzed for bulk geochemistry and selected sediment and brine samples were analyzed for their Li isotopic composition following the methods of Kalderon-Asael et al. (2021).

In-Situ Water-Rock Interactions as a Lithium Source

Water-rock interactions have been proposed as the source of Li in continental brine deposits of South America (Munk et al., 2016, p. 20) as well as formation waters from the Appalachian Basin, USA (Macpherson, 2015; Phan et al., 2016), the Qaidam Basin, China (He et al., 2020), and Germany (Mertineit and Schramm, 2019). Here, we present evidence to support these findings for brines of the WCSB and provide a new model for Li enrichment.

Based on the δD vs $\delta^{18}O$ ratios of brines from Frasnian-aged formations in Alberta and Saskatchewan, most brines display a strong evaporation trend with increasingly isotopically heavy δD and $\delta^{18}O$. However, the majority of the samples with the highest Li concentrations plot to the right of this trend which is likely due to ^{18}O exchange through water-rock interactions which likely supply the waters with Li.

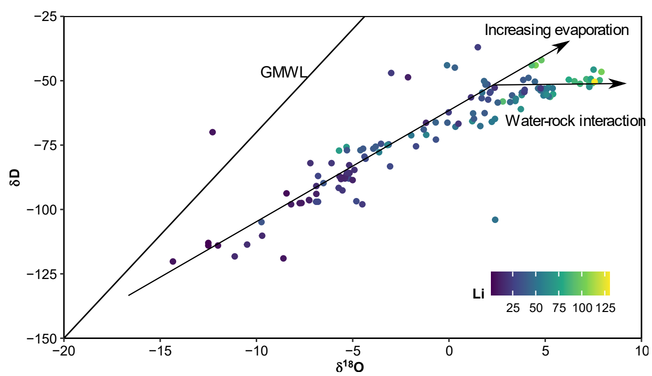

Figure 1 Stable isotope ratios of brines from Frasnian-aged formations in the WCSB.

Similar to the continental brine deposits, the Li could be derived from enriched clay intervals within the formation of interest. Evidence for Li-enriched clay intervals in the Duperow Formation have been observed by (Jensen et al., 2020) as well as in this study. Thin clay-rich beds are significantly enriched in Li, in some cases >200 ppm, while Li concentrations in the evaporites and carbonates is <20 ppm. Additionally, work performed by industry found certain intervals within the Wymark Member of the Duperow Formation can contain brines with over 200 ppm Li. Comparison of the δ^7Li of the clays and brines provides strong evidence that Li in the brines is being enriched through water-rock interactions with the clays. However, elevated Li concentrations have also been observed in clays from the overlying Birdbear Formation, yet the Li concentrations in the brine are significantly lower than the Duperow Formation at ~40 ppm.

This could indicate that there is an unknown mechanism which releases Li from the sediments, such as dolomitization or another geochemical process. Finally, determining the ultimate source of these Li beds, whether related to Devonian volcanism or weathering of a Li-rich source, is also an important consideration and will be the focus of future work.

This work on determining the Li source will be incorporated into a broader framework which includes other variables such as stratigraphy, hydrodynamics, and paleogeography, to assist in developing a deposit model which can be applied to assess the Li potential of other areas within the WCSB, and potentially other basins around the world.

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