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The origin and mechanisms of lithium enrichment in Montney Formation brines of the Western Canadian Sedimentary Basin

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Introduction

The transition to a low-carbon economy requires increased production of energy storage devices currently dominated by lithium (Li) batteries. Therefore in response to this rapid increase in the demand for Li, new sources of Li must be developed especially those in regions with appropriate ESG practices. Oilfield brines hosted within sedimentary basins offer an attractive option as brines are currently produced as a byproduct of existing hydrocarbon extraction operations and therefore Li extraction from these fluids would represent value added to a current waste product. Previous studies indicate these brines can be enriched in Li and are widespread in deep sedimentary basins (for Western Canadian Sedimentary Basin see review in Lyster et al., 2022). Despite this, our understanding of the processes responsible for Li enrichment in basinal brines is incomplete. In this study, we utilize isotopic and geochemical data from Montney Formation flowback and produced water to evaluate the sources of Li and the processes responsible for Li enrichment in these brines.

Results, Observations, Conclusions

Montney Formation water Na-Cl-Br systematics suggest that halite dissolution, as opposed to seawater evapo-concentration, is responsible for brine development (Fig. 1). Additionally, many samples show evidence of Na loss through water-rock interactions potentially implicating Na consumption via albitization of plagioclase feldspars. Lithium isotope analysis offers a promising tool for fingerprinting the sources and geochemical cycling of Li in formation brines (e.g., Millot et al., 2010). All Montney brines have lithium isotope composition consistent with a siliciclastic source as opposed to seawater (Fig. 2), indicating fine-grained silts and clay fractions are likely the main source of Li in the Montney brines. Comparison of the Li concentrations and clay content within a Montney core indicates a strong positive correlation consistent with clay minerals being the main source of Li within the sediment. Modeled formation water oxygen isotope composition based on equilibrium fractionation relationships with clays at Montney formation temperatures agree well with measured oxygen isotope composition of formation brines. Furthermore, positive correlations between the oxygen isotope composition of brines and Li concentrations provides additional evidence for equilibrium of brines with clay minerals. Combined evidence confirms the importance of water-rock exchange reactions in the enrichment of Li in Montney brines.

The Montney Formation contains abundant mixed layer illite-smectite clays dominated by illite (illite:smectite of 95:5; Vaisblat et al., 2021), additionally silt size fractions are known to contain up to 10 wt. % muscovite (Davies et al., 1997). Within muscovite, Li can substitute for Al and K at up to 1.5% (by mass) without disrupting the muscovite crystal structure. We propose that muscovite dissolution mediated by organic acids and/or sulfur bearing compounds (e.g., H_2S, sulfates, etc.) results in metal cation leaching, providing a potential mechanism for Li enrichment

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within Montney brines. Deep burial conditions combined with a reduction in water pH associated with either organic matter degradation or H_2S production are likely essential for the enrichment of Li within sedimentary basinal brines.

Our work indicates that, in addition to the Devonian Leduc reef formation in Alberta and its equivalent Duperow carbonate formation in Saskatchewan, portions of the Triassic Montney Formation in the northeastern British Columbia may also represent a source of sedimentary brine with economic Li concentrations in Western Canada. We postulate that the highest concentrations of Li in Montney brines will be found in regions where the deposition of terrestrial detrital material rich in micaceous minerals occurred along with deep burial and either the degradation of organic matter and/or the presence of elevated H_2S concentrations mediating intensive water-rock interactions leaching Li to *in situ* brines.

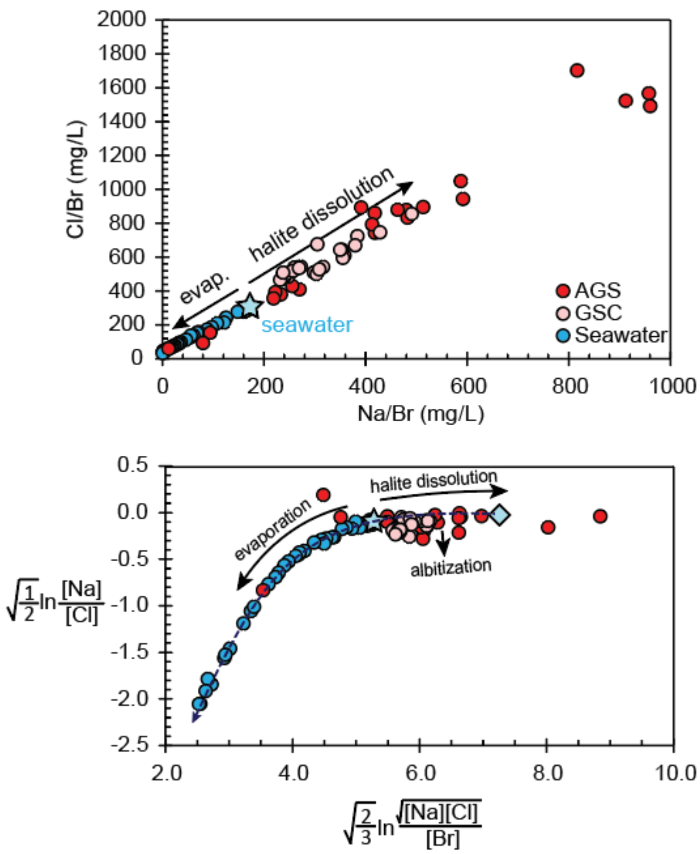

Figure 1: Na-Cl-Br systematics for Montney Brines indicating most formation waters show evidence of halite dissolution as opposed to evapo-concentration. Data derived from the Alberta Geological Survey and Geological Survey of Canada Brine Chemistry datasets.

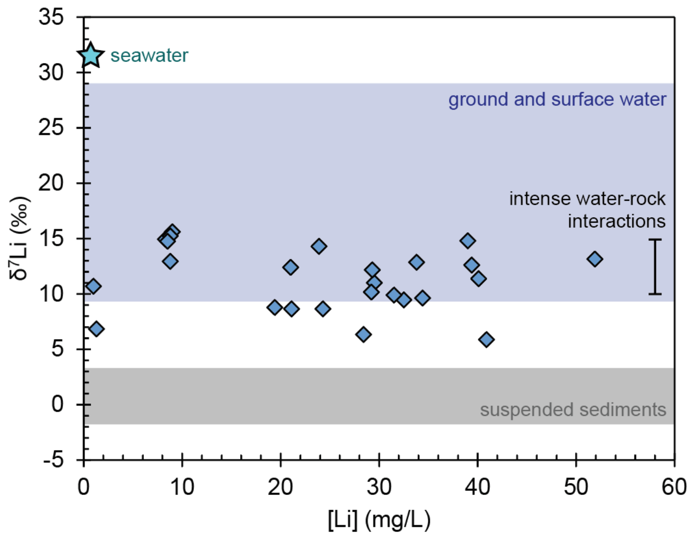

Figure 2: Lithium isotope composition of Montney waters plotted against Li concentration. Ranges of Li isotope values in suspended sediment, ground and surface waters, and water-rock interactions compiled from surveys of Western Canada's Mackenzie River Basin groundwater and lithic sources (Millot et al., 2010).

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