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GEOLOGICAL SURVEY OF CANADA
OPEN FILE 9237

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Recommended citation
Kingston, A. and Jiang, C., 2025. Lithium enrichment in produced water from the Triassic Montney Formation, Western Canada Sedimentary Basin; Geological Survey of Canada, Open File 9237. 29 p. https://doi.org/10.4095/pd08hxw2f4

ISSN 2816-7155
ISBN 978-0-660-76586-0
Catalogue No. M183-2/9237E-PDF
https://doi.org/10.4095/pd08hxw2f4

Abstract:

As the world endeavors to transition to a low-carbon economy the need for energy storage devices such as lithium (Li) batteries becomes increasingly important. To respond to the rapidly increasing demand for rechargeable batteries, new sources of Li must be developed. Brines hosted in sedimentary basins offer an attractive option as fluids are currently produced from existing hydrocarbon extraction operations. Previous studies indicate these brines can be enriched in Li and are widespread in deep sedimentary basins. Despite this, our understanding of the processes responsible for Li enrichment in basinal brines is lacking. In this report, we show that the Montney Formation in the Western Canadian Sedimentary Basin hosts brines with appreciable Li concentrations. Water Na-Cl-Br systematics suggest that halite dissolution, as opposed to evapo-concentration, is responsible for brine development. Lithium isotope composition indicates that the siliciclastic fraction of basin sediments is the main source of Li to brines. A strong correlation between Li concentrations and clay content in Montney core samples suggests clay minerals are a likely source of Li. Oxygen isotope composition of brines provides evidence for equilibrium with clay minerals confirming the importance of water-rock exchange. The results of this study show that fine-grained sediment in the Montney Fm. is rich in muscovite, which can host significant Li content. We propose that muscovite dissolution mediated by organic acids and/or H_2S results in metal cation leaching, providing another potential source of Li 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. In addition to the Devonia Leduc reef formation in Alberta and its equivalent Duperow carbonate formation in Saskatchewan, the Montney Triassic siliciclastic formation in the northeastern British Columbia can be another source of sedimentary brine with economic grade of Li contents for producing the critical mineral in Western Canada.

1. Introduction

The current transition towards a low-carbon economy accompanied by a decreasing reliance on fossil fuels has triggered an increase in global demand for energy storage systems. Lithium-ion batteries are crucial for electric vehicles and are also widespread in many consumer electronics such as mobile phones. Lithium (Li) is critical for production of these modern high energy density batteries and, as a consequence, the demand for Li has increased dramatically in the past few years.

Currently, the dominant source of Li is spodumene deposits in Australia where large open pit mines produce more than 50% of global supply (World Economic Forum, 2023). Closed basin near-surface brines or salars such as those found in the Atacama Desert of South America are the second largest source of Li (USGS, 2023). However, open pit mining for spodumene and development of salar deposits come with significant socio-environmental impacts (Leece and Jiang, 2023 and references therein) including intense water utilization. In contrast, extraction of Li from subsurface brines does not produce mine tailings and the effluent can be reinjected into the subsurface to avoid surface water contamination. As such, sedimentary brines are increasingly being evaluated for their Li resource potential including brines within the Montney Formation of the Western Canadian Sedimentary Basin (WCSB).

The evolution of formation water in the WCSB has been well studied as it has significant implications for hydrocarbon production. Compared with typical fresh water and seawater, elevated Li concentrations were identified in the 1970s by Hitchon et al. (1971) and within a series of reports by the Energy Resources Conservation Board leading to follow-up studies aimed at evaluating the potential for Li extraction from formational brines in the WCSB (Hitchon, 1984; Hitchon et al., 1993; Underschultz et al., 1994; Bachu et al., 1995; Eccles and Berhane, 2011; Huff, 2016; 2019). A thorough review of past Li resource assessments in the WCSB is provided by Lyster et al. (2022) and is only briefly summarized here. Most previous work focused on Devonian strata where the highest Li concentrations have been measured. Devonian brine geochemistry suggests that elevated Li is associated with either the evapo-concentration of connate waters through time (Huff, 2016; 2019; Rostron et al., 2022) or basin-scale mixing of fluids which previously interacted with crystalline basement rocks via hydrothermal and tectonic activity (Eccles and Berhane, 2011).

However, despite widespread assessments of Li within Devonian strata of the WCSB (e.g., Eccles and Berhane, 2011; Huff, 2016; 2019; Lyster et al., 2022; Rostron et al., 2022), limited effort has been made on the Triassic strata. Several previous studies (Lyster et al., 2022; Kingston et al., 2023; Reimert, 2023) indicate that Li concentrations in the early Triassic Montney Formation can have appreciable concentrations of Li (Fig. 1), which have economic potential using modern direct Li extraction technology contingent on grade (Leece and Jiang, 2023). The Montney Formation is a highly productive unconventional hydrocarbon reservoir within the WCSB which produced large volumes of wastewater annually. If economic grades of Li are found in the wastewater, Li recovery would present a value-added benefit to a waste product that currently requires costly treatment and disposal. Additionally, it could represent a pathway for re-investment of energy profits into green technology, a potential strategy for offsetting the effects of greenhouse gases on climate change (Sanderson, 2023).

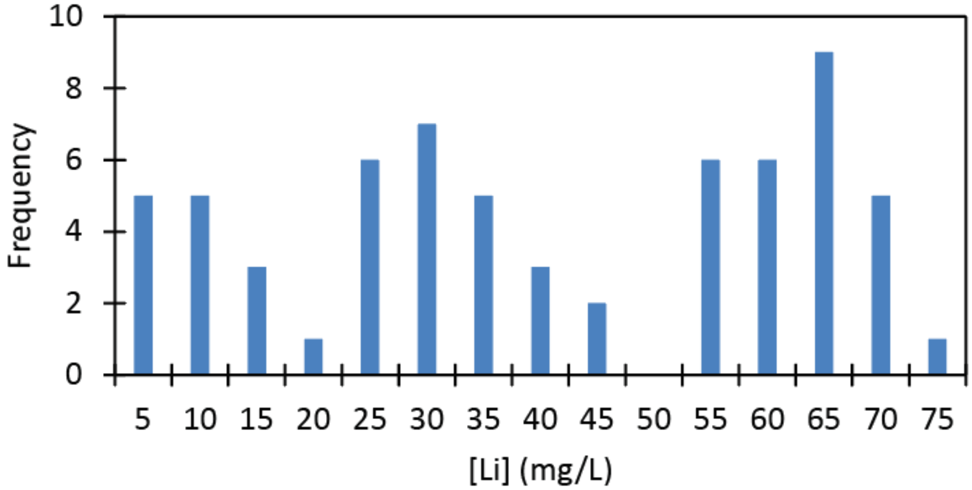

Figure 1: Histogram of lithium concentrations for Early Triassic Montney Formation brines from oil and gas production wells. Data from Reimert et al. (2023) and this study.

In this study we explore the occurrence of Li-enriched brines hosted in the Montney Formation. First, water geochemistry derived from the Alberta Geological Survey and the Geological Survey of Canada brine geochemistry datasets are used to evaluate the origin of Montney pore fluids and potential geochemical processes responsible for Li-enrichment. Then using bulk rock mineralogy and geochemistry from a full Montney core we explore potential lithologic sources of Li. Finally, we suggest several mechanisms which may be responsible for enriching Li in pore waters from these lithologic sources.

2. Geologic Setting

For this study formational brines and core samples were collected from the Montney Formation (Fig. 2) within the WCSB. The WCSB straddles the border between Alberta and British Columbia and is composed of a westward-thickening sedimentary wedge up to 6 km in thickness adjacent to the present day Canadian Rocky Mountains and thinning to an erosional edge along the Canadian Shield in the east (Price, 1994; Wright et al., 1994; Tufano and Pietras, 2017). Sediments that make up the Montney

Formation were deposited on a clastic ramp on the northwestern margin of the supercontinent Pangea (Golonka, 2007) within a collisional retro-foreland basin (Rohais et al., 2018). The Montney Formation overlies the Permian Belloy Formation bounded by an unconformity and underlies the Middle Triassic Doig Formation again via an unconformity (Davies et al., 2018; Zonneveld and Moslow, 2018).

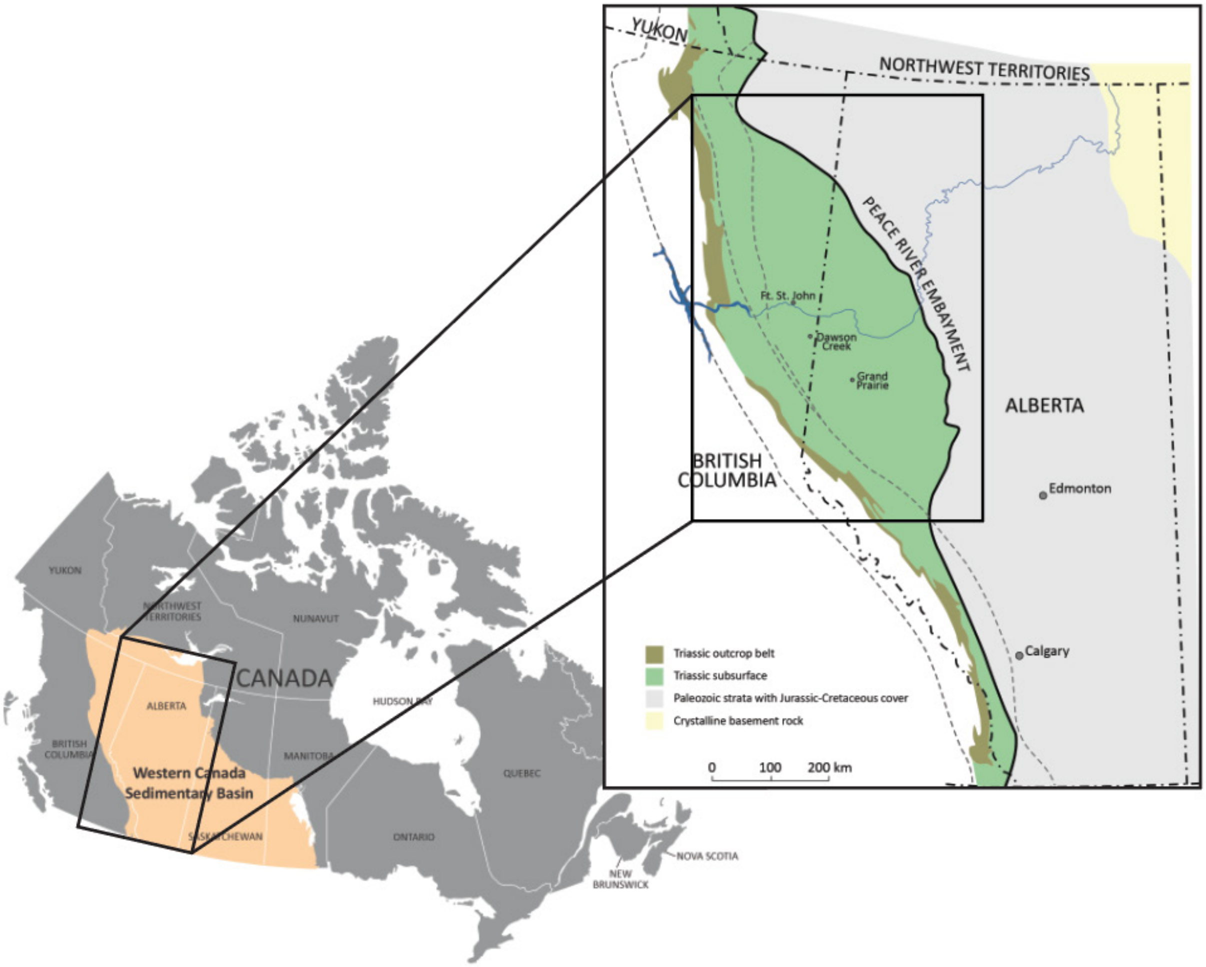

Figure 2: Location of the Early Triassic Montney Formation within the Western Canadian Sedimentary Basin straddling the border of the provinces of Alberta and British Columbia in Canada.

Lithologically, the Montney Formation is often described as dolosiltstone where authigenic and detrital dolomite make up 10 to 45 wt.% (Davies et al., 1997). The Montney contains extensive evidence of diagenetic alteration including albitization of feldspar minerals, illitization of smectite clays (Vaisblat et al., 2021), alteration of sulfate and sulfide minerals (Liseroudi et al., 2020; 2021), and carbonate diagenesis (Davies et al., 1997; Liseroudi et al., 2022). Diagenesis initiated during the Early Triassic soon after deposition and evolved significantly through to the Late Cretaceous associated with maximum burial (Ness, 2001; Ducros et al., 2017; Rohais et al., 2018). Dolomite cements formed early prior to compaction (Davis et al., 1997) reducing porosity. Volumetrically, authigenic clay minerals comprise only a minor part of the Montney (Davies et al., 2018) and most clay minerals are detrital in origin making up roughly 2 to 33 wt.% (Davies et al., 2018; Vaisblat et al., 2021). Muscovite is the dominant form of detrital mica (Vaisblat et al., 2021), occurs at up to 10 wt.% in the Montney, and is strongly correlated with the silt-size fraction (Davies et al., 1997) resulting in higher concentrations in siltstones and lower in sandstones (Davies et al., 2018). The Montney Formation has a high detrital feldspar component (10-31 wt.%) with roughly equal proportions of potassium feldspar and plagioclase (Davies, 1997). Preservation of detrital feldspars, which are likely derived from an arid continental setting, may be influenced by aeolian processes (Davies, 1997).

Water in the Montney formation is characterized by high total dissolved solids (TDS). Due to the marine clastic depositional setting, the source of high salinity is thought to be external migration of fluids, potentially high salinity residual brines from the Charlie Lake Formation (Kirste et al., 1997) or migrated Devonian fluids (Liseroudi et al., 2022). In general, TDS is lowest along the eastern sub-crop edge and highest along the western deformation front in the deepest parts of the basin. Heterogeneity of water chemistry in Lower Triassic waters suggest isolation developed at some point, likely related to permeability (Kirste et al., 1997).

Fluid flow models in the WCSB include topography-driven flow or tectonic-induced flow, where either topographic relief or compression-induced expulsion of fluids drives basin scale fluid movement (Garven et al., 1999). Isotopic analysis of carbonate and anhydrite cements in the Montney Formation indicate the presence of both tectonic- and topography-driven diagenetic fluids along with hydrothermal fluid flow (Liseroudi et al., 2022). Networks of deep-seated faults provide fluid conduits between Devonian and Triassic formations (Mei, 2009, and references therein) allowing the migration of fluids from underlying strata, some of which may have mixed with the Precambrian basement, to interact with connate fluids of the Montney (Liseroudi et al., 2022).

Migration of this water must have occurred early and prior to the development of the tight, low permeability conditions currently in the Montney known to extend back until at least the Late Cretaceous (Kingston et al., 2022). Basin modeling projects that the Montney underwent burial during the Late Jurassic followed by uplift during the Early Cretaceous (Watt et al., 2022) and that hydrocarbon migration may have occurred during this period (Cesar et al., 2023). This tectonic activity and hydrocarbon fluid migration may also represent the timing of brine emplacement. Indeed, this region has experienced consistently active tectonism including extensional faulting in the Devonian to Triassic followed by compressional faulting during the Jurassic to Cretaceous (O'Connell et al., 1990; Hope et al., 1999; Mei, 2009). This activity was postulated to control migration of sulfate-containing fluids into the Montney based on the Devonian sulfur isotope signatures of Montney-hosted diagenetic sulfates (Liseroudi et al., 2020).

3. Methods

3.1.Brine and core sampling and data sources

Produced brine samples were derived from several sources including: a) a time series of produced waters collected during this study; b) a collection of produced water samples from industry; and c) a dataset of formation water generated by the Alberta Geological Survey.

A 12-month time series of produced water samples was collected during a hydraulic fracturing (HF) operation from the onset of production with analysis of the samples occurring immediately following sampling. This dataset includes 13 samples collected in the first week following production and then 11 monthly samples. These water samples are also paired with core analysis from the same well.

The collection of produced water samples donated from industry consists of over 200 samples, some of which have extended shelf life, with one to two years of refrigerated storage followed by about twelve months of ambient storage. Therefore, not all geochemical species are considered to accurately reflect composition in the subsurface due to post-sampling alterations during storage. Caution must be used when assessing the composition of these samples, especially with regards to those weathering- and redox-sensitive components such as Fe^{2+}; however, Li concentrations are likely to remain unaltered. These data can be found in Kingston et al. (2023).

Data released by the Alberta Geological Survey (DIG 2022-0052; Reimert et al., 2023) provide extended water chemistry for produced waters from many formations within the WCSB in Alberta. In this study we incorporate our data with data from the Triassic in this Digital Data download.

Core samples were collected from several cores of the Montney Formation including: a) a full Montney core that was collected prior to hydraulic stimulation of the well; b) another full Montney core from a similar region to the previous core also before HF operations; and c) a collection of core samples derived from the vicinity of other brine samples.

3.2. Aqueous geochemistry

Aqueous geochemistry was performed by the Applied Geochemistry Group at the University of Calgary. All water samples were filtered through a 0.45 μm nitrocellulose filter (Millipore Corporation) prior to analysis. Total alkalinity (bicarbonate) was determined using an Orion 960 Titrator (Thermo Electron Corporation). A 10 mL aliquot of each sample was titrated with 0.01 M sulfuric acid (Fisher

Scientific) until a pH of 2.5 was reached. End-point determination was accomplished via double differentiation of titration results.

Water for cation analysis was filtered through a 0.45 µm nitrocellulose syringe filter (Millipore Corporation), diluted (1:100, 1:1000) with deionized water, and placed in 15 mL Falcon tubes. Major/minor cations (Al, B, Ba, Ca, Fe, K, Li, Mg, Mn, Na, Si and Sr) were analyzed using a Varian 725-ES Inductively Coupled Plasma Optical Emission Spectrophotometer (ICP-OES). The spectrophotometer was calibrated ($r^2 > 0.99$) via serial dilution of certified standards (BDH Ltd.) of each individual element. Analytical precision and accuracy for cation analysis is typically ± 5.0%. Detailed results can be found in Kingston et al. (2023).

Water for anion analysis was filtered through a 0.45 µm nitrocellulose syringe filter (Millipore Corporation), diluted (1:100, 1:1000) with deionized water and placed in 2.0 mL glass vials prior to analysis. Major/minor anions (Br^-, Cl^-, and SO_4^{2-}) were analyzed using a Thermo-Dionex ICS 2000 ion chromatograph (Thermo Fisher Scientific Inc.). A 25 µL aliquot of each sample was injected onto an Ion Pac AS18 anion column (Thermo Fisher Scientific Inc.) and then separated by isocratic elution using 35.0 mM potassium hydroxide, a flow rate of 1.1 mL/min, and column temperature of 30°C. Analytical precision and accuracy for anion analysis is typically ± 5.0%. Detailed results are also available in Kingston et al. (2023).

3.3. Isotopic Analysis

Oxygen and hydrogen isotope analysis of waters

Produced waters are often contaminated with other components from the subsurface including H_2S from sour gas and dissolved organics from hydrocarbons and must be treated prior to isotope analysis. In the lab, 25 mL aliquots of water were sub-sampled and treated with copper rods to remove dissolved H_2S and activated charcoal powder to remove dissolved organics. Hydrogen and oxygen isotope analysis of waters was conducted by headspace equilibration. For hydrogen isotope analysis, 250 µL of water was placed into an Exetainer vial (Labco p/n 038W) along with a Hokko bead stick and then flushed with a 2% H_2 balanced with helium gas mixture for 10 minutes. Samples were then placed in a heated block at 25°C and left for 2 hours to allow for headspace equilibration. For oxygen isotope analysis, 250 µL of water was placed into an Exetainer vial and flushed with a mixture of 0.5% CO_2 with a balance of helium for 10 min and then placed in the heated block at 25°C for 20 hours. Hydrogen and oxygen isotope analysis was performed using a Thermo Gasbench II coupled to a Thermo Delta V^{Plus} isotope ratio mass spectrometer housed in the Isotope Science Laboratory at the University of Calgary. Internal reference materials were analyzed multiple times during each analytical sequence to normalize the data and correct for instrument drift. Internal reference materials were periodically calibrated against international reference materials from the IAEA to ensure accuracy with the VSMOW-VSLAP scale. All results are reported in the standard delta notation in per mill relative to VSMOW.

3.4. X-ray Diffraction

Aliquots of core material were removed using a rock saw to cut out 50 g samples. This material was washed to remove drilling muds or other contaminants and then sub-sampled for various analyses. For XRD analysis, 10 g of sample was powdered and then 2 g of this was subsampled for bulk XRD analysis and clay separation. The clay-sized fraction (<3 μm) was separated using centrifugation. Samples were deflocculated with sodium hexametaphosphate and then centrifuged in two stages (600 rpm and 3000 rpm) in order to first separate the coarse fraction from the clay fraction and then settle the clay fraction for analysis. Dried samples were then mounted on glass slides and analyzed using a Bruker D4 X-ray diffractometer equipped with a cobalt K-alpha radiation X-ray generator at 40 mA and 35 kV. Samples were run from 3° to 75° 2θ and monitored for instrumental drift using a suite of certified reference materials at regular intervals.

3.5. Statistical and compositional data analysis

Compositional data analysis of raw concentration data is known to be prone to spurious correlations and artifacts owing to the fact that the concentration of different chemical species does not vary independently and instead is related to the abundance of all other chemical species. This is particularly important for sedimentary brines because the mass of the solutes makes up a large percentage of the total mass (Engle and Rowan, 2013). One approach to overcome this is use log-ratio transformations which converts data to Euclidean geometry allowing for accurate interpretation of compositional data (Aitchison, 1986). Here we use an isometric log-ratio (ilr) transformation of the Na-Cl-Br concentrations in brines using a method outlined in Engle and Rowan (2013) as this allows us to create a partition matrix with geochemical significance. Transformed data is represented by two variables: z1 (y-axis) provides a measure of the Na gain or loss relative to Cl; and z2 (x-axis) provides a measure of the Br exclusion related to halite dissolution.

4. Results and Discussion

4.1. The source of pore water in the Montney Formation

Sodium-chloride-bromide (Na-Cl-Br) systematics are often used to evaluate sedimentary brine history differentiating brine sources, evaporative evolution, and effects related to halite dissolution/precipitation (e.g., Connolly et al., 1990; Rowan et al., 2015). Analysis of Na-Cl-Br chemistry of resultant brines during the evaporation of seawater reveals that Br is increasingly enriched in residual water as it is essentially excluded from incorporation in the halite lattice (McCaffery et al., 1987). Therefore, comparison of brine Na-Cl-Br chemistry with trends from evaporative seawater provides a measure of the extent of evaporative processes as well as potential Na-Cl contributions from halite dissolution. These relationships are illustrated in plots of Na/Br against Cl/Br (Fig. 3a). Brines that have undergone evaporative concentration plot along the seawater evaporation trend (lower left of plot), whereas brines that plot above and right of this trend have elevated Na and Cl compared with seawater indicating halite dissolution. All Montney samples plot in the halite dissolution zone except for three samples from the AGS dataset. However, one of the main issues with this interpretation is the absence of halite in the Montney Formation, suggesting that an alternative mechanism(s) or external water source may also be influencing Na-Cl-Br brine chemistry.

Isometric log ratio transformed Montney data is plotted alongside the seawater evaporation trend in Fig. 3b. In this space brines which have undergone halite dissolution should be close to 0 on the y-axis and have values higher than seawater (i.e., >5.2) on the x-axis, as they are depleted in Br compared with evaporative seawater. Montney brine samples plot to the right of seawater on the x-axis suggesting they have been influenced by halite dissolution. However, they are generally below the line for halite dissolution indicating depleted Na compared with Cl, potentially implicating Na loss through water-rock interactions. Consumption of Na via albitization of plagioclase feldspars is a potential mechanism for Na loss. Previous studies of diagenesis in the Montney Formation reveals significant albitization which occurred during the late burial to uplift stage (Vaisblat et al., 2021). Dissolution of K-feldspars is associated with this process, which would provide a source of K and help explain the positive correlation between K and Li (Fig. 4a). High K occurring alongside high Li is similar to previous findings from Devonian brines in the WCSB (Eccles and Berhane, 2011; Huff, 2019). Montney porosity measurements from Ghanizadeh et al. (2015) range between 2 and 6%, which equate to a potential maximum rock/water ratio 19:1. This high rock/water ratio means water-rock interactions such as the albitization of feldspars, and others described below, will have a strong influence on formation water chemistry.

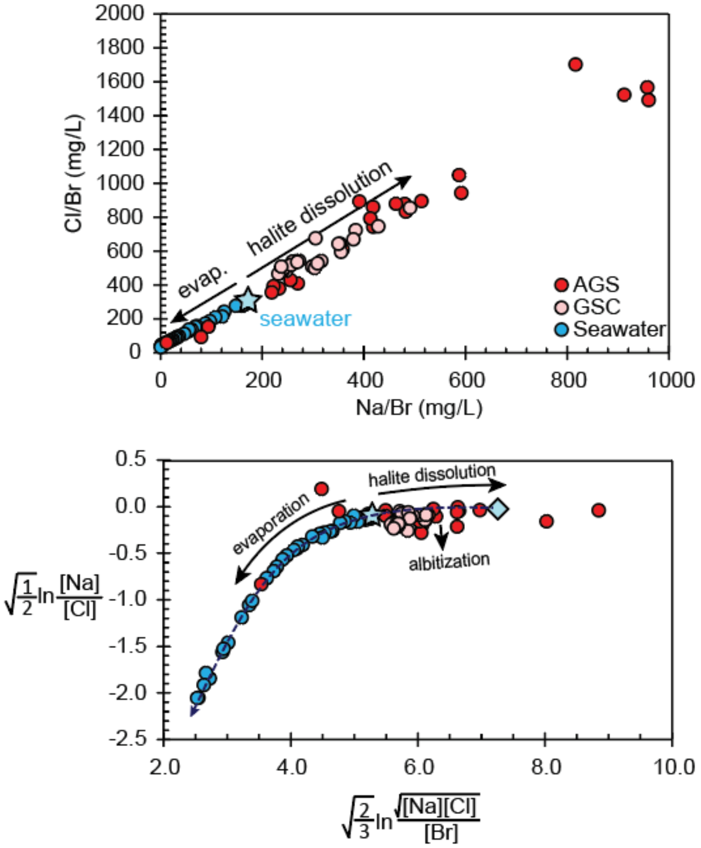

Figure 3: Na-Cl-Br systematics of Montney waters. Note that most water has a Na/Br to Cl/Br relationship consistent with halite dissolution and not seawater evaporation. Isometric log-ratio transformation of Na-Cl-Br concentrations (Engle and Rowan, 2013) of Montney water further supports halite dissolution and also indicates Na-loss implicating water-rock reactions such as albitization of feldspars.

The Montney Formation does not contain halite or other syndepositional evaporitic minerals. Therefore, Montney-hosted brines must at least partially consist of migrated fluids as previously suggested (Kirste et al., 1997). The Upper Triassic Charlie Lake Formation and several Devonian Formations contain significant evaporitic deposits suggesting one of these may contribute to the original sources of Montney formation water. While currently we are unable to determine whether the original source of Montney brine is Devonian or Triassic, what is clear is that the Montney formation hosts migrated brines with strong evidence of evaporite dissolution signatures.

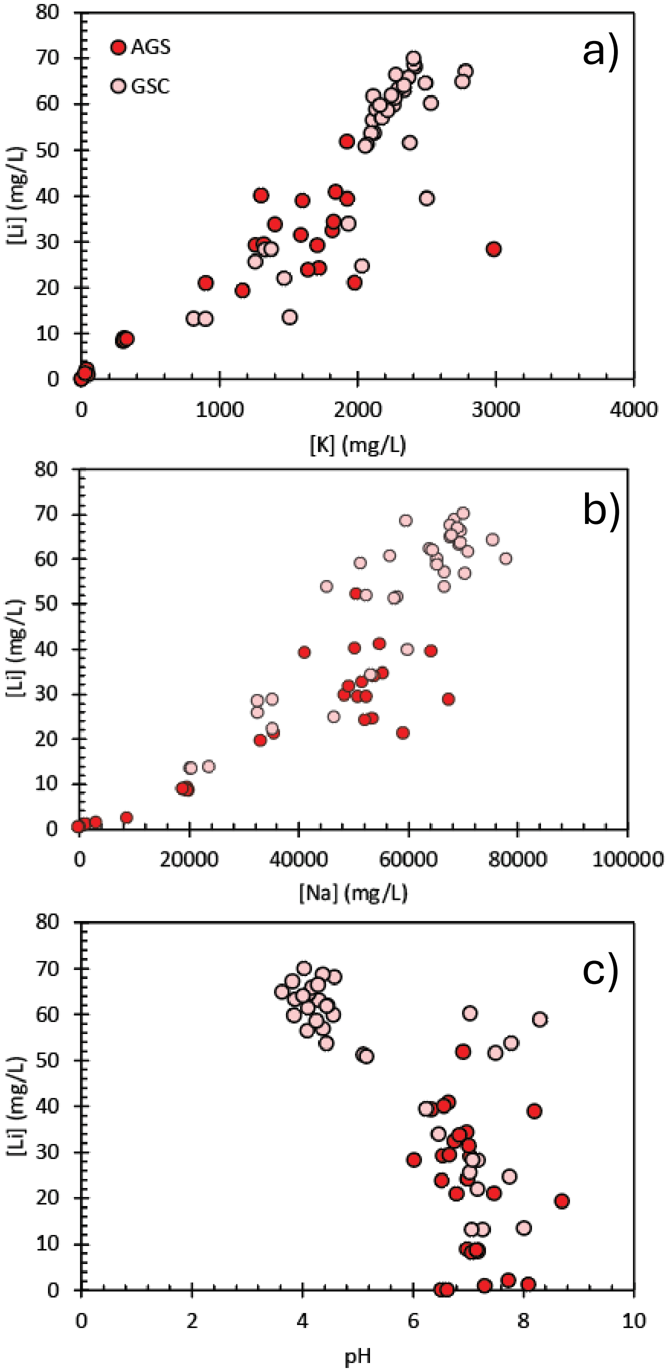

Figure 4: The relationship of lithium concentration with a) potassium (K), b), sodium (Na), and c) pH in Montney water.

4.2. Origin of Li in formation waters

The origin of Li in oilfield brines is still an active area of research. Previous reviews of the origins of Li in brines suggests that all elevated Li must come from hydrothermal fluids (Garrett, 2004). This is based in part on laboratory experimental data showing that Li extraction/leaching from Li-bearing minerals is difficult. Experiments using water-based extractions from granitic rocks at ambient temperatures show effectively no enrichment of Li in the waters. Only when water is heated to temperatures of 275 to 600°C is there minimal extraction (Dibble and Dickson, 1976). Furthermore, Li might be adsorbed onto rather than leached from surface rocks when Li exists in the fluid at high abundance due to equilibration effect. Sedimentary brines in the WCSB are not associated with hydrothermal fluids except potentially in some unique circumstances. For example, Li-enriched brines in Devonian strata were originally shown to have elevated $^{87}Sr/^{86}Sr$ values suggesting inputs from radiogenic sources thought to be the result of the circulation of fluids interacting with basement rocks (Eccles and Berhane, 2011). However, further investigations revealed that not all Li-enriched brines have elevated $^{87}Sr/^{86}Sr$ values (Huff, 2019). Elevated Li concentrations in Montney waters are not correlated with radiogenic $^{87}Sr/^{86}Sr$ signatures (Fig. 5), indicating that hydrothermal fluids are not a major source of Li in the Montney.

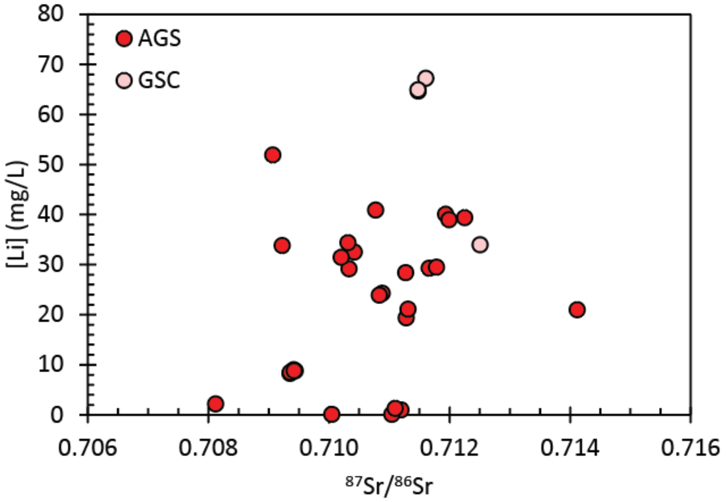

Figure 5: Lithium concentrations are not correlated with $^{87}Sr/^{86}Sr$ values suggesting Li is not derived from geothermal fluids in the Montney Formation.

4.3. Lithium isotope composition of brines

Lithium isotope analysis offers a promising tool for fingerprinting the sources and geochemical cycling of Li in formational brines; however, owing to their low charge and small size Li ions are highly mobile, and consequently primary δ^7Li signatures are rarely preserved (Tomascak et al., 2016). Therefore, caution must be applied as Li isotope chemistry reflects a combination of the mixing of various reservoirs along with a plethora of water-rock reactions which are difficult to separate (Millot et al., 2007). When Li partitions into the aqueous phase it undergoes positive isotope fractionation as ^7Li preferentially moves into the aqueous phase and ^6Li remains in the solid phase, hence seawater has a high δ^7Li value of 31‰ (Millot et al., 2004).

Lithium is often exchanged within the interlayer sites of clays such as smectite (Decarreau et al., 2012), providing a major reservoir for Li in sedimentary systems (Tomascak et al., 2016). During this process ^{6}Li is preferentially incorporated into the crystal structure of the clay (Tomasack, 2004; Vigier et al., 2006; Millot et al., 2010). The δ^7Li values of Montney formation brines range from 5.1 to 15.5‰ with an average value of 13.2‰ (±3.7, 1 σ) (Fig. 6). Therefore, they have δ^7Li values significantly lower than seawater, implying that seawater is an unlikely source of Li in formational brines. Measured δ^7Li values in modern pelagic clays range from -1.6 to +5‰ (Chan et al., 2006) and are similar to that of the suspended sediments in the Mackenzie River Basin, -1.7 to +3.2‰ (Millot et al., 2010). Within the Mackenzie River Basin, which overlies the Montney Formation, Li isotope composition of water is controlled by the degree of weathering with more intense water-rock interactions resulting in δ^7Li values ranging from approximately 10‰ to 15‰ (Millot et al., 2010), consistent with the bulk of δ^7Li values measured in Montney water (Fig. 6). Therefore, Triassic brine δ^7Li values are more consistent with Li derived from intense water-rock interactions with silicate minerals (including the formation of secondary clay minerals) developed over long residence times. Additionally, δ^7Li values exhibit no relationship with Li concentration, therefore, it is likely that similar process(es) are responsible for enriching Li in the ancient sediments independent of current Li concentration.

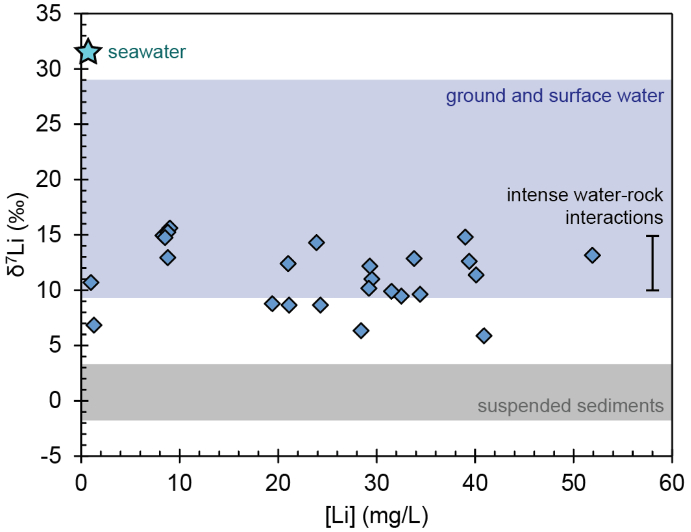

Figure 6: Lithium isotope composition of Montney waters plotted against Li concentration. Ranges of Li isotope values in suspended sediment, ground and surface waters, and water-rock interactions compiled from surveys of Western Canada's Mackenzie River Basin groundwater and lithic sources (Millot et al., 2010).

4.4. Lithological source of Li in the Montney Formation

Evidence from Li isotope geochemistry supports water-rock interactions with siliciclastic materials as the main source of Li in formation brines, necessitating an evaluation of Li within the Montney sediments. Comparison of bulk rock geochemistry with brine geochemistry of waters from Devonian, Triassic, and Cretaceous formations in the WCSB illustrates that bulk Li concentrations in rocks do not reflect the concentration of Li in the pore waters they contain (Fig. 7). Lithium contents of core material from Cretaceous, Triassic and Devonian strata show that Cretaceous rocks contain the highest Li contents (up to 175 ppm) and that most Triassic and Devonian rocks have Li concentrations <40 ppm (Fig. 7a). This Li distribution reflects the dominant rock lithology as Cretaceous strata are dominated by siliciclastics including many shale units deposited in an epeiric sea setting. The Devonian is dominated by carbonates and the Triassic is a mix of carbonates, evaporites, and siliciclastics. Conversely, formation waters hosted by Cretaceous strata have lower Li contents compared with Triassic and Devonian formation waters (Fig. 7b). This suggests that burial history and physio-chemical processes are more important in controlling the Li content of sedimentary brines rather than host rock Li concentration. Diagenetic processes responsible for controlling Li concentrations in sedimentary brine deposits may include cation exchange with clay minerals, illitization of smectite, mineral leaching and dissolution, and/or other processes associated with burial history.

4.5. Clay minerals as a source of lithium in Montney Formation brines

Smectite is an expanding clay with interlayer water where Li ions can exchange with other cations in contrast to illite, which is non-expanding and without interlayer water. This is partially responsible for the higher cation exchange capacity of smectite (80-120 meq/100 g) compared with illite (10-40 meq/100 g) (Kumari and Mohan, 2021). Therefore, Li can more readily exchange within smectite where it also substitutes into octahedral sites. During burial, increasing temperatures result in the transformation of smectite to illite, referred to as illitization. This process begins around 70-90°C and reaches completion around 120°C (Nicot et al., 2018; and references therein). This transformation results in an overall reduction in the cation exchange capacity of clay minerals in formation sediments and release of interlayer cations into interstitial brines. The Montney Formation has undergone significant burial exposing clay minerals to temperatures in excess of 140°C (Ness, 2001; Ducros et al., 2017; Rohais et al., 2018; Kingston et al., 2022), and as such, has extensive evidence of illitization of clay minerals. Around 70-98% of the clays in the Montney are illite and mixed layer illite-smectite (MLIS) with an illite:smectite ratio of 95:5 (Vaisblat et al., 2021). Clay concentrations in the Montney range from 1.5 wt.% to 37 wt.% with an average of 14 wt.% with the main clay mineral being MLIS along with minor authigenic kaolinite and fibrous illite (Vaisblat et al. 2021).

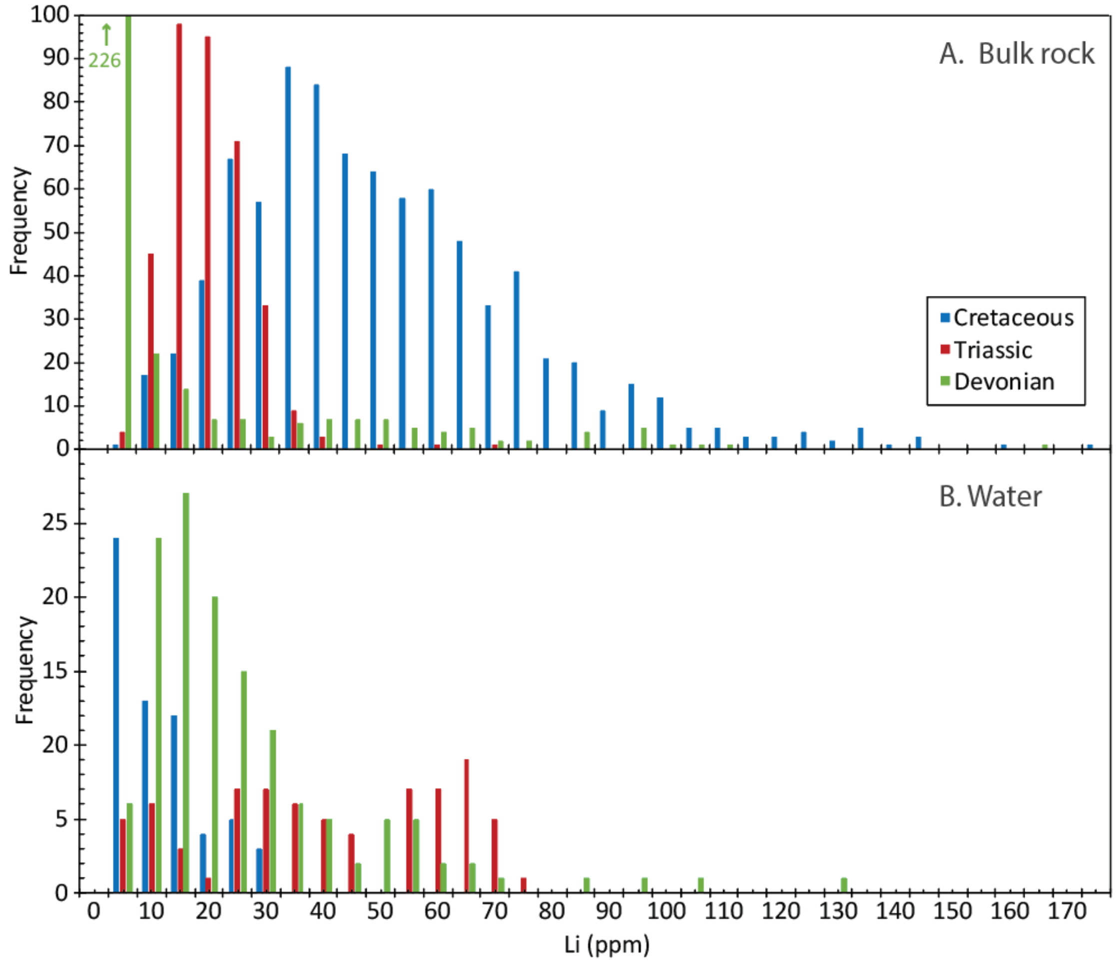

Figure 7: Histograms of Li content of A) core material from Cretaceous, Triassic and Devonian strata; and B) formation waters (Reimert et al., 2023). Cretaceous rocks contain the highest Li contents but Cretaceous waters have the lowest Li concentrations indicating that bulk Li contents in rocks are not a strong control on Li concentrations in brines.

Dehydration of clay minerals associated with smectite to illite conversion releases water enriched in ^{18}O resulting in increased δ^{18}O value of pore waters (Suchecki and Land, 1983; Tremosa et al., 2021). Unfortunately, oxygen isotope analysis of clay minerals from Triassic strata in the WCSB is lacking; however, a study of Upper Cretaceous Belly River clay minerals reported illite/smectite δ^{18}O values of +10.9 to +13.7‰ (Ayalon and Longstaffe, 1988) and Lower Cretaceous Viking Formation illite/smectite have δ^{18}O values ranging from +13.8 to +16.5‰ for the same basin (Longstaffe and Ayalon, 1987). Therefore, formation waters with enriched δ^{18}O values beyond seawater composition and lacking evidence of evapo-concentration (e.g., Na-Cl-Br systematics detailed earlier) may represent water-rock interactions with ^{18}O-enriched clays. A strong correlation between Li concentrations and δ^{18}O values (Fig. 8) of formation brines suggests that the intensity of water-rock interactions may be a critical control on Li partitioning from minerals to brine in the WCSB.

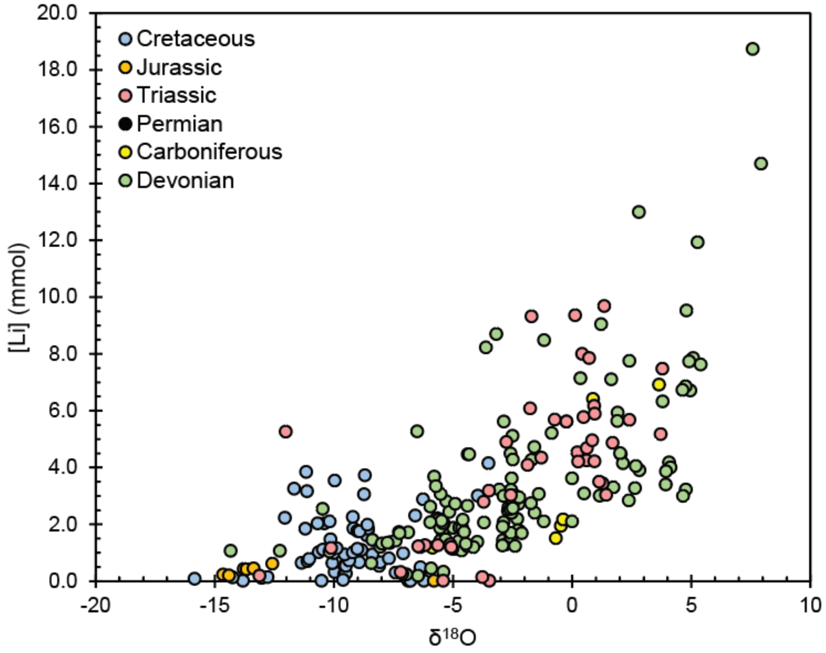

Figure 8: Lithium concentration vs. oxygen isotope composition for basinal waters from the Western Canadian Sedimentary Basin. Data from this study and Alberta Geological Survey DIG 2022-052.

To evaluate the potential for exchange between reservoir water and clay minerals a model of expected $\delta^{18}O$ values of formation water was developed based on formation temperature and equilibrium oxygen isotope fractionation relationships between water and both clays and carbonates (Kharaka and Carothers, 1986; Engle et al., 2020). Formation temperatures were estimated using the Li-Mg geothermometer (Kharaka and Mariner, 1989) and compare well with measured/modelled Montney reservoir temperatures (e.g., Ness, 2001; Ducros et al., 2017; Kingston et al., 2022), indicating that water chemistry is consistent with water-rock interactions at reservoir conditions (Engle et al., 2020). The $\delta^{18}O$ of water in equilibrium with clay and carbonate minerals was modelled using the a) illite relationship of Savin and Lee (1988), b) smectite relationship of Escande (1983), c) calcite relationship of Friedman and O'Neil (1977), and d) the dolomite relationship of Land (1983). The $\delta^{18}O$ composition of illite/smectite was assumed to be close to Lower Cretaceous clays (+13.8‰; Longstaffe and Ayalon, 1987), an initial $\delta^{18}O_{water}$ of 0‰ (e.g., seawater) was used, and an illite proportion of 95% (Vaisblat et al., 2021) were input into the model resulting in the curves presented in Fig. 9. Measured Montney $\delta^{18}O_{water}$ values agree well with modeled water from smectite and illite equilibration curves, consistent with an interpretation of pore water equilibrium with clays at reservoir temperatures (Fig. 9). This provides further evidence of the strong influence that water-rock interactions at reservoir conditions have in controlling the geochemical properties of Montney formation water.

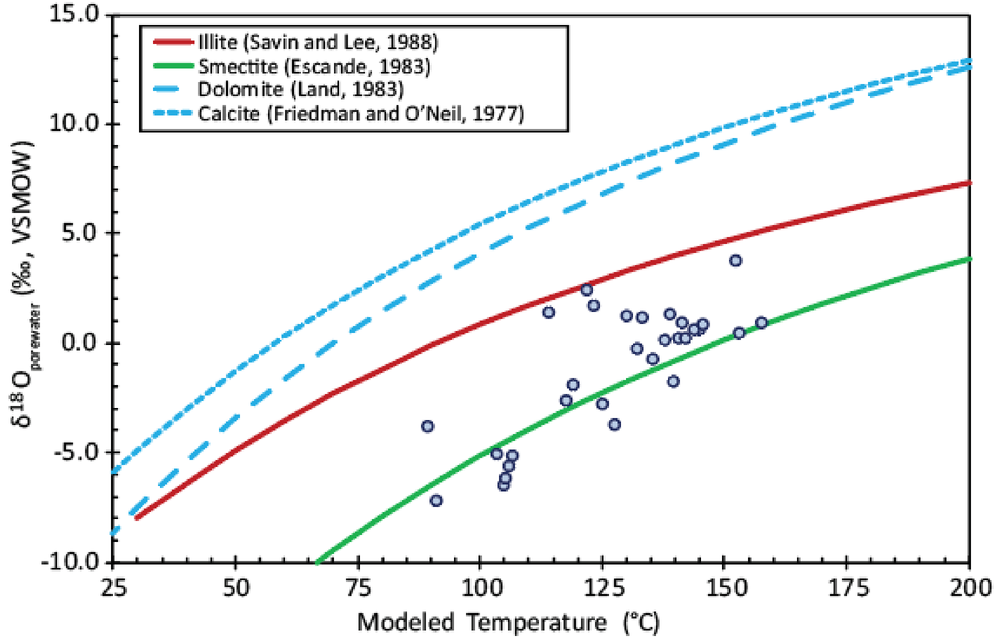

Figure 9: Montney formation water $\delta^{18}O$ plotted alongside equilibrium oxygen isotope fractionation curves between smectite, illite, and carbonate minerals (calcite and dolomite). Modeled temperatures from Mg-Li geothermometer (Kharaka and Mariner, 1988). Note that Montney formation water $\delta^{18}O$ are consistent with equilibrium with clay $\delta^{18}O$.

Elemental analysis of a full Montney core illustrates that bulk rock Li concentrations are strongly correlated with clay content (Fig. 10). Sediment gravity flow deposits within the top section of the core have the highest Li concentration and consist of fine-grained terrestrial-derived material transported from the shoreface environment. During the early Triassic this western margin of Pangea was climatically arid, consistent with the formation of extensive evaporites and early-diagenetic dolomitization (Davies, 1997a). Magnesium-rich clay minerals, dolomites, and gypsum formed in arid environments are all enriched in Li (Tardy et al., 1972) and may be a key source of Li in this system.

4.6. Detrital muscovite as another potential lithium source

Lithium is also a common minor element in micas that can be implicated in the transport of Li within clays as they are often fine grained and inseparable from clay minerals (Starkey, 1982). Muscovite is the dominant form of detrital mica (Vaisblat et al., 2021) and occurs at up to 10 wt.% in the Montney and is strongly correlated with the silt size fraction (Davies et al., 1997), resulting in higher concentrations in siltstones and lower in sandstones (Davies et al., 2018). In the top section of the Montney core, interbedded siltstone and sandstone beds associated with sediment gravity flows show similar cyclical variations in potassium (K) and Li, with higher K and Li concentrations observed in siltstone beds (Fig. 10). It is difficult to differentiate between fine-grained muscovite and illite minerals using XRD (Mashrur, personal communication). Therefore, in these samples high abundances of clay could also represent high abundances of muscovite and/or mixtures of both. As muscovite is K-rich it may represent a potential source of both high K and Li concentrations observed in the formation brines.

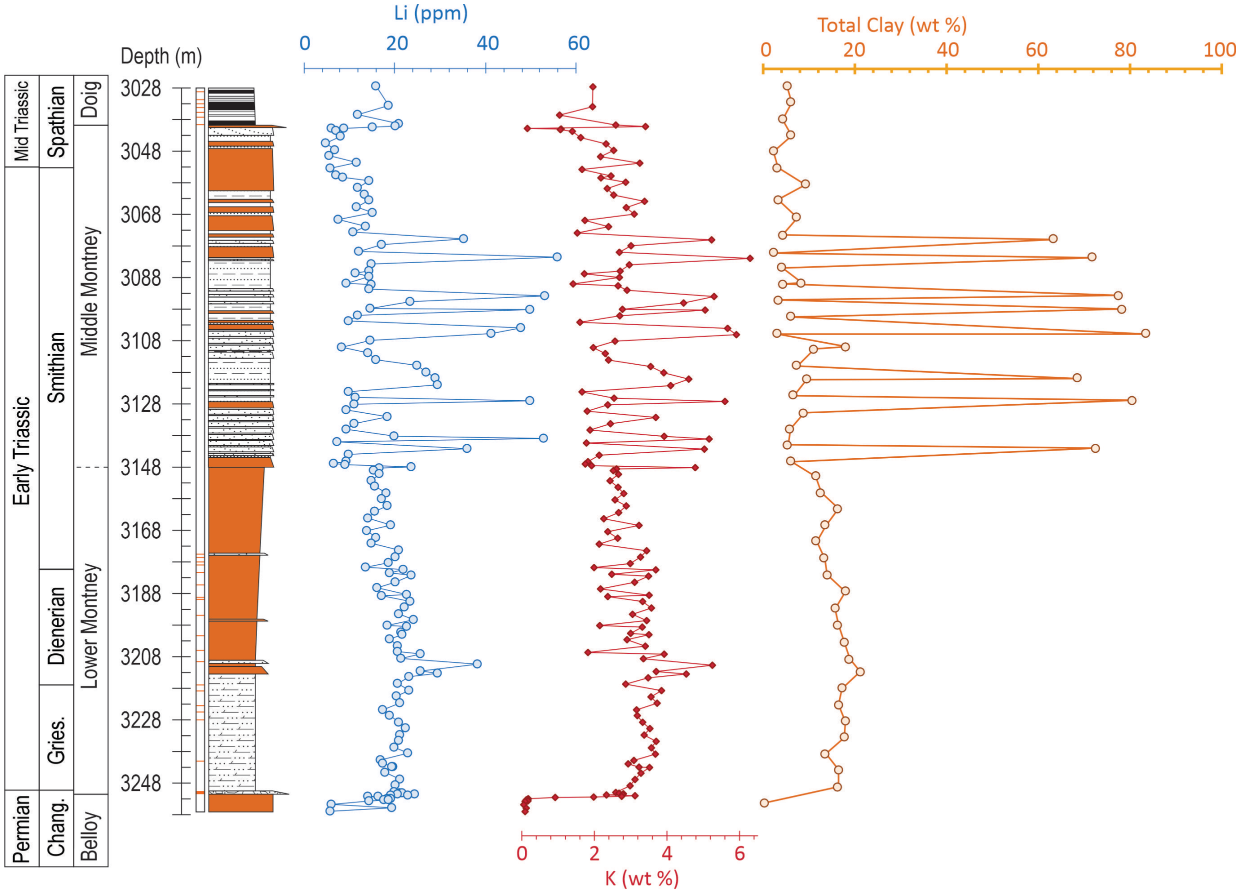

Figure 10: Vertical profile of the Li, K, and total clay content within a Montney core.

Lithium ions on the surface of delaminated muscovite are readily exchangeable with other alkali metal ions such as Na, K, Rb, and Cs (Osman et al., 1999), highlighting the importance of high salinity (i.e., high Na concentrations) for driving Li extraction from micas into brines. Lithium is at the bottom of the alkali metals for ion exchange on muscovite mica (Lawrence, 1958, Carroll, 1959) and therefore will be replaced by other cations within pore waters. Weathering and water-rock interactions are known to release Li from clays and micas (Starkey, 1982). Alteration and dissolution of micas provides a primary source for other monovalent cations such as K, Na, Rb, and Cs (Aylmore et al., 2018), potentially associated with diagenetic alteration over geologic time scales.

4.7. Role of pH: Organic matter degradation and H_2S

Taken together these observations suggest that oilfield brines likely derive their Li from water-rock interactions involving clay or micaceous minerals; however, the conditions required for Li enrichment are still poorly understood. Previous water-rock interaction studies indicate temperatures in excess of 275°C are required for Li partitioning between granite and water (Dibble and Dickson, 1976), which far exceeds burial temperature models for the Montney Formation (e.g., Ness, 2001; Ducros et al., 2017). However, under burial conditions increased pressure and the chemical alteration of organic matter and other compounds such as calcium sulfates have strong influences on pore water chemistry including pH.

A common factor for all oilfield brines that has yet to be evaluated is the role of bio-chemical degradation of organic matter (OM) during diagenesis and thermal maturation of OM during catagenesis including hydrocarbon generation and degradation. OM degradation during early diagenesis results in the production of organic acids. Organic acids are currently being assessed for their ability to recover Li from spent batteries (e.g., Golmohammadzadeh et al., 2018) where they can lead to >90% recovery of Li. Short-chain aliphatic acid concentrations of up to 932 mg/L have been measured in basinal brines of the WCSB (Connolly et al., 1990). The exposure of muscovite to even mildly acidic organic acids promotes muscovite dissolution (Oelkers et al., 2008). This may partly explain why the highest Li concentrations are found in Montney brines with the lowest pH (Fig. 4c).

Another trend within oilfield brines enriched in Li is the presence of H_2S and sulfates either within the formation or in adjacent formations. A prime example is the Smackover Formation along the US Gulf Coast, which has the highest measured Li concentrations of any oilfield brines and H_2S concentrations in gas samples of 78% (Heydari, 1997). Similarly, brines in the Duperow Formation in Saskatchewan and Montana and North Dakota have the highest Li content of any basinal fluids in the Williston Basin (Rostron et al., 2022) and contain gas H_2S concentrations up to 38% (Rowe et al., 1978). Within the WCSB, several Devonian formations including the Nisku and Leduc host Li enriched brines (Eccles and Berhane, 2011; Huff, 2016; 2019; Lyster et al., 2022) and are also known for high concentrations of H_2S (Machel et al., 1994). As shown previously, brines hosted in the Montney Formation are also enriched in Li (Kingston et al., 2023) and contain widespread occurrences of elevated H_2S (Kingston et al., 2021). The occurrence of H_2S within hydrocarbon reservoirs is by no means rare; however, the combination of Li-bearing minerals (e.g., muscovite, clays, etc.) along with H_2S and sulfates may provide the reaction mechanisms to promote Li-enrichment in sedimentary brines.

At formation pressures (>35 bar) mica wettability exhibits a pronounced alteration to become H_2S-wet, meaning the surfaces of mica minerals have a preference for being in contact with aqueous H_2S (Broseta et al., 2012) potentially resulting in enhanced degradation of muscovite grains. The muscovite dissolution reaction (1) of Oelkers et al. (2008) illustrates how the breakdown of muscovite at low pH also releases K ions into solution.

$$KAl_3Si_3O_{10}(OH)_2 + 10H^+ \leftrightarrow K^+ + 3Al^{+3} + 3SiO_2(aq) + 6H_2O \qquad (1)$$

Li^+, Na^+, and K^+ all have similarly lower metal-oxygen bond energies (1468.6, 1347.2, 1251.0 kJ mol^{-1}, respectively) especially in comparison to Si (13091.7 kJ mol^{-1}) (Huggins and Sun, 1946), therefore, they are more susceptible to acid-related leaching of metal cations (Terry, 1983). Notably Li, Na, and K all exhibit strong correlations in Montney brines (Fig. 4a,b).

Besides H_2S other sulfur compounds may affect Li enrichment as well. For example, when calcium sulfate interacts with muscovite it can weaken the structure followed by dissolution of the interlayer cations producing charge imbalances, which exposes additional surfaces for cation leaching or exchange (Xue et al., 2017). Currently there is a lack of experimental work on the role that sulfur compounds play in the Li enrichment process. However, the simulation of reservoir conditions will be essential for recreating the pressure-temperature and chemical conditions responsible for Li enrichment in sedimentary brines. This work may prove critical for our understanding of the distribution of Li-enriched brines in the subsurface and potentially to enable in situ Li extraction via selective electrochemical processing of brines within the reservoir itself (Haddad, 2023).

5. Conclusions

The evidence presented in this report indicates that the Montney Formation hosts brines with appreciable Li concentrations and the enrichment likely originates from water-rock interactions during burial. Although brine Na-Cl-Br systematics suggest that water chemistry is dominated by halite dissolution as opposed to evapo-concentration, Li isotope compositions are consistent with intensive water-rock interactions with the siliciclastic fraction of basin sediments as being the main source of Li. A strong correlation between Li concentrations and clay content in Montney core samples further suggests clay minerals are a likely source of Li. Oxygen isotope composition of brines provides evidence for equilibrium with clay minerals, confirming the importance of water-rock exchange. Fine-grained sediment in the Montney is also rich in muscovite, which can host significant Li contents. Muscovite dissolution mediated by organic acids and/or H_2S results in metal cation leaching providing another potential source of Li within Montney brines. Deep burial conditions combined with a reduction in brine pH associated with either organic matter degradation or H_2S production are likely essential for the enrichment of Li within sedimentary basinal brines.

We postulate that the highest concentrations of Li in sedimentary brines, including the Montney Formation, will be found in regions where intensive deposition of terrestrial detrital material occurred along with deep burial resulting in organic matter degradation and the production of H_2S.

Acknowledgements

Natural Resources Canada's Critical Minerals Geoscience and Data (CMGD) and GeoEnergy research programs are acknowledged for funding this research.

References

Aitchison, J. (1982). The statistical analysis of compositional data. Journal of the Royal Statistical Society: Series B (Methodological), 44(2), 139-160.

Ayalon, A., & Longstaffe, F. J. (1988). Oxygen isotope studies of diagenesis and pore-water evolution in the Western Canada sedimentary basin; evidence from the Upper Cretaceous basal Belly River Sandstone, Alberta. Journal of Sedimentary Research, 58(3), 489-505.

Aylmore, M. G., Merigot, K., Quadir, Z., Rickard, W. D., Evans, N. J., McDonald, B. J., Catovic, E., & Spitalny, P. (2018). Applications of advanced analytical and mass spectrometry techniques to the characterisation of micaceous lithium-bearing ores. Minerals Engineering, 116, 182-195.

Bachu, S., Yuan, L.P. and Brulotte, M. (1995): Resource estimates of industrial minerals in Alberta formation waters; Alberta Research Council, Alberta Geological Survey, Open File Report 1995-01, 59 p., https://ags.aer.ca/publication/ofr-1995-01

Broseta, D., Tonnet, N. and Shah, V. (2012). Are rocks still water-wet in the presence of dense CO_2 or H_2S? *Geofluids*, *12*(4), pp.280-294.

Cesar, J., Ardakani, O.H., Watt, E., Song, Y., Kingston, A. and Ahad, J. (2023) Paleo-biodegradation and hydrocarbon mixing in a major hybrid petroleum reservoir. Scientific Reports 13 (1), 4357.

Connolly, C.A., Walter, L.M., Baadsgaard, H. and Longstaffe, F.J., (1990). Origin and evolution of formation waters, Alberta basin, western Canada sedimentary basin. I. Chemistry. Applied Geochemistry, 5(4), pp. 375-395.

Davies, G. R. (1997a). The Triassic of the Western Canada Sedimentary Basin: tectonic and stratigraphic framework, paleogeography, paleoclimate and biota. Bulletin of Canadian Petroleum Geology, 45(4), 434–460. https://doi.org/10.35767/gscpgbull.45.4.434

Davies, G. R. (1997b). Aeolian sedimentation and bypass, Triassic of western Canada. Bulletin of Canadian Petroleum Geology, 45(4), 624–642.

Davies, G. R., Moslow, T. F., & Sherwin, M. D. (1997). The lower Triassic Montney formation, west-central Alberta. Bulletin of Canadian Petroleum Geology, 45(4), 474-505.

Davies, G.R., Watson, N., Moslow, T.F. and MacEachern, J.A. (2018). Regional subdivisions, sequences, correlations and facies relationships of the Lower Triassic Montney Formation, west-central Alberta to northeastern British Columbia, Canada—with emphasis on role of paleostructure. Bulletin of Canadian Petroleum Geology, 66(1), 23–92.

Decarreau, A., Vigier, N., Pálková, H., Petit, S., Vieillard, P., & Fontaine, C. (2012). Partitioning of lithium between smectite and solution: An experimental approach. Geochimica et Cosmochimica Acta, 85, 314-325.

Desrocher, S., Hutcheon, I., Kirste, D., Henderson, C.M., 2004. Constraints on the generation of H2S and CO2 in the subsurface Triassic, Alberta basin, Canada. Chem. Geol. 204, 237–254.

Dibble, W.E., Dickson, F.W., (1976). The behavior of lithium in experimental rock-water interaction studies. Geological Survey Professional Paper, (1005), 142-147.

Ducros, M., W. Sassi, R. Vially, T. Euzen, and V. Crombez, (2017), 2-D Basin Modeling of the Western Canada Sedimentary Basin across the Montney-Doig System: Implications for Hydrocarbon Migration Pathways and Unconventional Resources Potential, in Mahdi A. AbuAli, Isabelle Moretti, and Hege M. Nordgård Bolås, eds., Petroleum Systems Analysis—Case Studies: AAPG Memoir 114, p. 117–134.

Eccles, D.R. and Berhane, H., (2011). Geological introduction to lithium-rich formation water with emphasis on the Fox Creek area of west-central Alberta (NTS 83F and 83K); Energy Resources Conservation Board, Alberta Geological Survey, Open File Report 2011-10, 22 p., URL https://ags.aer.ca/publication/ofr-2011-10

Engle, M. A., & Rowan, E. L. (2013). Interpretation of Na–Cl–Br systematics in sedimentary basin brines: comparison of concentration, element ratio, and isometric log-ratio approaches. Mathematical Geosciences, 45(1), 87-101.

Engle, M.A., Doolan, C.A., Pitman, J.A., Varonka, M.S., Chenault, J., Orem, W.H., McMahon, P.B. and Jubb, A.M. (2020). Origin and geochemistry of formation waters form the lower Eadle Ford Group, Gulf Coast Basin, south central Texas. Chemical Geology, 550 (2020) 119754.

Garrett, D. E. (2004). Handbook of lithium and natural calcium chloride. Elsevier.

Garven, G., Appold, M.S., Toptygina, V.I., Hazlett, T.J., 1999. Hydrogeologic modeling of the genesis of carbonate-hosted lead-zinc ores. Hydrogeol. J. 7, 108–126. https://doi.org/10.1007/s100400050183.

Ghanizadeh, A., Clarkson, C. R., Aquino, S., Ardakani, O. H., & Sanei, H. (2015). Petrophysical and geomechanical characteristics of Canadian tight oil and liquid-rich gas reservoirs: II. Geomechanical property estimation. Fuel, 153, 682-691.

Golonka, J., (2007). Late Triassic and Early Jurassic palaeogeography of the world. Palaeogeography, Palaeoclimatology, Palaeoecology 244, 297–307. https://doi.org/10.1016/j.palaeo.2006.06.041

Haddad, A. Z., Hackl, L., Akuzum, B., Pohlman, G., Magnan, J. F., & Kostecki, R. (2023). How to make lithium extraction cleaner, faster and cheaper—in six steps. Nature, 616(7956), 245-248.

Heydari, E., 1997. The role of burial diagenesis in hydrocarbon destruction and H2S accumulation, Upper Jurassic Smackover Formation, Black Creek Field, Mississippi. *AAPG Bulletin*, *81*(1), pp.26-45.

Hitchon, B., Billings, G. K., & Klovan, J. E. (1971). Geochemistry and origin of formation waters in the western Canada sedimentary basin—III. Factors controlling chemical composition. Geochimica et Cosmochimica Acta, 35(6), 567-598.

Hitchon, B. (1984): Formation waters as a source of industrial minerals in Alberta; in The Geology of Industrial Minerals in Canada, G.R. Guillet and W. Martin (ed.), Canadian Institute of Mining and Metallurgy, Special Volume 29, p. 247–249.

Hitchon, B., Underschultz, J.R. and Bachu, S. (1993): Industrial mineral potential of Alberta formation waters; Alberta Research Council, Alberta Geological Survey, Open File Report 1993-15, 92 p., https://ags.aer.ca/publication/ofr-1993-15

Huff, G. F. (2016). Evolution of Li-enriched oilfield brines in Devonian carbonates of the south-central Alberta Basin, Canada. Bulletin of Canadian Petroleum Geology, 64(3), 438-448.

Huff, G.F., (2019). Origin and Li-enrichment of selected oilfield brines in the Alberta Basin, Canada; Alberta Energy Regulator / Alberta Geological Survey, AER/AGS Open File Report 2019-01, 29 p., https://ags.aer.ca/publication/ofr-2019-01

Huggins, M.L., and Sun, K.H., 1946. Energy additivity in oxygen containing crystals and glasses, J. Phys. Chem., 50 pp.319-328.

Kharaka, Y.K., Carothers, W.W. (1986). Oxygen and hydrogen isotope geochemistry of deep basin brines. In: Fritz, P., Fontes, J.P. (Eds.), Handbook of Environmental Isotope Geochemistry. II. Elsevier B.V, pp. 305–360. https://doi.org/10.1016/B978-0-444-42225-5.50013-9.

Kingston, A.W., Mort, A., Deblonde, C. and Ardakani, O.H., 2021. Hydrogen sulfide (H2S) distribution in the Triassic Montney Formation of the Western Canadian Sedimentary Basin. Geological Survey of Canada.

Kingston A, Ardakani OH, Watt E and Samson IM (2022) Evidence of Hydrocarbon Generation and Overpressure Development in an Unconventional Reservoir Using Fluid Inclusion and Stable Isotope Analysis From the Early Triassic, Western Canadian Sedimentary Basin. Front. Earth Sci. https://doi.org/10.3389/feart.2022.918898.

Kingston, A; Jiang, C., Wang, X., Hobbs, T E. (2023). Chemical compositions of flowback and produced water from the Duvernay shale and Montney tight reservoir developments in Western Canada: potential for lithium resources from wastewater. Geological Survey of Canada, Open File 8974, 2023, 25 pages, https://doi.org/10.4095/331878.

Kirste, D., Desrocher, S., Spence, B., Hoyne, B., Tsang, B., Hutcheon, I., 1997. Fluid flow, water chemistry, gas chemistry and diagenesis in the subsurface Triassic in Alberta and British Columbia. Bull. Can. Petrol. Geol. 45, 742–764.

Kumari, K.R. and Mohan, C. (2021). Basics of Clay Minerals and Their Characteristic Properties. In Clay and Caly Minerals. *http://dx.doi.org/10.5772/intechopen.97672*

Lafuente B, Downs R T, Yang H, Stone N (2015). The power of databases: the RRUFF project. In: Highlights in Mineralogical Crystallography, T Armbruster and R M Danisi, eds. Berlin, Germany, W. De Gruyter, pp 1-30.

Leece, A.S., Jiang, C., (2023). A preliminary techno-economic assessment of lithium extraction from flowback and produced water from unconventional shale and tight hydrocarbon operations in Western Canada. Geological Survey of Canada, Open File OF8975, 119 p.

Liseroudi, M.H., Ardakani, O.H., Sanei, H., Pedersen, P.K., Stern, R.A. and Wood, J.M., (2020). Origin of sulfate-rich fluids in the Early Triassic Montney Formation, Western Canadian Sedimentary Basin. Marine and Petroleum Geology, 114, p.104236

Liseroudi, M. H., Ardakani, O. H., Pedersen, P. K., Stern, R. A., Wood, J. M. and Sanei, H. (2021). Microbial and Thermochemical Controlled Sulfur Cycle in the Early Triassic Sediments of the Western Canadian Sedimentary Basin. Journal of the Geological Society, 55(1), jgs2020-175. https://doi.org/10.1144/jgs2020-175

Liseroudi, M. H., Ardakani, O. H., Pedersen, P. K. and Sanei, H. (2022). Fluid flow and water/rock interaction during the Early Triassic evolution of the western Canada sedimentary basin as revealed by carbonate diagenesis. Marine and Petroleum Geology, 142 (2022) 105765.

Liu, Z. R. R., Zhou, M. F., Williams-Jones, A. E., Wang, W., & Gao, J. F. (2019). Diagenetic mobilization of Ti and formation of brookite/anatase in early Cambrian black shales, South China. Chemical Geology, 506, 79–96. https://doi.org/10.1016/j.chemgeo.2018.12.022

Longstaffe, F. J., & Ayalon, A. (1987). Oxygen-isotope studies of clastic diagenesis in the Lower Cretaceous Viking Formation, Alberta: implications for the role of meteoric water. Geological Society, London, Special Publications, 36(1), 277-296.

Lyster, S., Hauck, T.E., Lopez, G.P., Playter, T.L., Reimert, C., Palombi, D. and Schultz, S.K., (2022). Lithium and helium in Alberta: data compilation and preliminary observations; Alberta Energy Regulator / Alberta Geological Survey, AER/AGS Open File Report 2021-04, 36 p.

Machel, H.G., Krouse, H.R., Foght, J.M., Riciputi, L.R. and Cole, D.R., 1994. Sour Gas in the Nisku Formation of Central Alberta: Geochemical Evidence for Biological and Thermochemical Sulphate Reduction. (https://archives.datapages.com/data/cspg_sp/data/CSPG-SP-016/016001/427_cspgsp160427.htm)

Maneta, V., & Baker, D. R. (2019). The potential of lithium in alkali feldspars, quartz, and muscovite as a geochemical indicator in the exploration for lithium-rich granitic pegmatites: A case study from the spodumene-rich Moblan pegmatite, Quebec, Canada. Journal of Geochemical Exploration, 205, 106336.

McCaffrey, M.A., Lazar, B. and Holland, H.D., (1987). The evaporation path of seawater and the coprecipitation of Br^- and K^+ with halite. Journal of Sedimentary Research, 57(5), pp. 928-937.

Mei, S. (2009). New insights on faults in the Peace River Arch region, northwest Alberta, based on existing well-log data and refined trend surface analysis. Can. J. Earth Sci. 46, 41–65. https://doi.org/10.1139/E09-006.

Millot, R., Guerrot, C., & Vigier, N. (2004). Accurate and high-precision measurement of lithium isotopes in two reference materials by MC-ICP-MS. Geostandards and Geoanalytical Research, 28(1), 153-159.

Millot, R., Negrel, P., & Petelet-Giraud, E. (2007). Multi-isotopic (Li, B, Sr, Nd) approach for geothermal reservoir characterization in the Limagne Basin (Massif Central, France). Applied Geochemistry, 22(11), 2307-2325.

Millot, R., Vigier, N., & Gaillardet, J. (2010). Behaviour of lithium and its isotopes during weathering in the Mackenzie Basin, Canada. Geochimica et Cosmochimica Acta, 74(14), 3897-3912.

Morad, S., & Aldahan, A. A. (1982). Authigenesis of titanium minerals in two Proterozoic sedimentary rocks from southern and central Sweden. Journal of Sedimentary Petrology, 52(4), 1295–1305. https://doi.org/10.1306/212f8120-2b24-11d7-8648000102c1865d

Ness, S.M., (2001). The Application of Basin Analysis to the Triassic Succession, Alberta Basin: an Investigation of Burial and Thermal History and Evolution of Hydrocarbons in Triassic Rocks (M.Sc. thesis), University of Calgary, Canada, 192 pp.

Nicot, J.-P., Gherabati, A., Darvari, R. and Mickler, P. (2018). Salinity reversal and water freshening in the Eagle Ford Shale, Texas, USA. ACS Earth and Space Chemistry 2 (11), 1087–1094. https://doi.org/10.1021/acsearthspacechem.8b00095.

Osman, M.A., Moor, C., Caseri, W.R. and Suter, U.W., 1999. Alkali metals ion exchange on muscovite mica. *Journal of colloid and interface science*, *209*(1), pp.232-239.

Pe-Piper, G., Karim, A., & Piper, D. J. W. (2011). Authigenesis of titania minerals and the mobility of Ti: New evidence from pro-deltaic sandstones, Cretaceous Scotian Basin, Canada. Journal of Sedimentary Research, 81(10), 762–773. https://doi.org/10.2110/jsr.2011.63

Price, R., (1994). Cordilleran tectonics and the evolution of the Western Canada sedimentary basin. In: Geological Atlas of Western Canada. G.D. Mossop and I. Shetsen (Comps.). Calgary, Canadian Society of Petroleum Geologists/ Alberta Research Council, pp. 13–24.

Reimert, C., Lyster, S. and Palombi, D. (2023): Brine geochemical data, Mineral Mapping Program, 2022 (tabular data, tab delimited format); Alberta Energy Regulator / Alberta Geological Survey, AER/AGS Digital Data 2022-0052.

Rohais, S., Crombez, V., Euzen, T., Zonneveld, J.P., (2018). Subsidence dynamics of the Montney formation (Early Triassic, Western Canada Sedimentary Basin): Insights for its geodynamic setting and wider implications. Bulletin of Canadian Petroleum Geology 66, 128–160.

Rostron, B., Maurer, Z., Hillier, C., Caplan, M., Kreis, L.K., 2022. Lithium in saline brines from the Duperow Aquifer in southeastern Saskatchewan. Saskatchewan Geological Open House 2022. Saskatoon, SK. Nov. 28-30, 2022.

Rowan, E.L., Engle, M.A., Kraemer, T.F., Schroeder, K.T., Hammack, R.W. and Doughten, M.W., (2015). Geochemical and isotopic evolution of water produced from Middle Devonian Marcellus shale gas wells, Appalachian basin, Pennsylvania. AAPG Bulletin, 99(2), pp. 181-206.

Rowe, H.L., McADAMS, J.B. and MERCER, R.F., 1978. Hydrocarbon Well Logging in the Williston Basin—Cross-Sections of Case Histories. (https://archives.datapages.com/data/mgs/mt/data/0034/0407/0407.html)

Sanderson, K. (2023). How oil companies' soaring profits compare with green-energy investments. Nature. May 15, 2023.

Schulz, H. M., Wirth, R., & Schreiber, A. (2016). Nano-crystal formation of TiO2 polymorphs brookite and anatase due to organic-inorganic rock-fluid interactions. Journal of Sedimentary Research, 86(2), 59–72. https://doi.org/10.2110/jsr.2016.1

Suchecki, R.K., Land, L.S. (1983). Isotopic geochemistry of burial-metamorphosed volcanogenic sediments, Great Valley sequence, northern California. Geochem. Cosmochim. Acta 47 (8), 1487–1499. https://doi.org/10.1016/0016-7037(83) 90308-3.

Tardy, Y., Krempp, G. and Trauth, N., 1972. Le lithium dans les minéraux argileux des sédiments et des sols. *Geochimica et Cosmochimica Acta*, *36*(4), pp.397-412.

Terry, B., 1983. The acid decomposition of silicate minerals part I. Reactivities and modes of dissolution of silicates. *Hydrometallurgy*, *10*(2), pp.135-150.

Tomascak, P. B. (2004). Developments in the understanding and application of lithium isotopes in the earth and planetary sciences. Reviews in Mineralogy and Geochemistry, 55(1), 153-195.

Tomascak, P. B., Magna, T., & Dohmen, R. (2016). Advances in lithium isotope geochemistry (pp. 1-195). Cham, Switzerland: Springer International Publishing.

Tremosa, J., Gaucher, E. C., & Gailhanou, H. (2021). Overpressure generation by smectite dehydration in sedimentary basins constrained by salinity dilution and stable isotopes. Applied Geochemistry, 131, 105035.

Tufano, B.C., Pietras, J.T., 2017. Coupled flexural-dynamic subsidence modeling approach for retro-foreland basins: Example from the Western Canada Sedimentary Basin. GSA Bulletin 1622-1635. https://doi.org/10.1130/b31646.1

Underschultz, J.R., Yuan, L.P., Bachu, S., Cotterill, D.K. and Hitchon, B. (1994): Industrial mineral resources in Alberta formation waters; Alberta Research Council, Alberta Geological Survey, Open File Report 1994-13, 71 p.

USGS (2023). Mineral Commodity Summaries: https://www.usgs.gov/centers/national-minerals-information-center/lithium-statistics-and-information, 2023

Vaisblat, N., Harris, N. B., Ayranci, K., Power, M., DeBhur, C., Bish, D. L., Chalaturnyk, R., Krause, F., Crombez, V., Euzen, T., & Rohais, S. (2021). Compositional and diagenetic evolution of a siltstone, with implications for reservoir quality; an example from the Lower Triassic Montney Formation in western Canada. Marine and Petroleum Geology, 129, 105066. https://doi.org/10.1016/J.MARPETGEO.2021.105066

Vigier, N., Gislason, S. R., Burton, K. W., Millot, R., & Mokadem, F. (2009). The relationship between riverine lithium isotope composition and silicate weathering rates in Iceland. Earth and Planetary Science Letters, 287(3-4), 434-441.

Walter, L. M., Stueber, A. M. & Huston, T. J., (1990). Br-Cl-Na systematics in Illinois basin fluids: Constraints on fluid origin and evolution. Geology, 18, p. 315-318.

Watt, E.A., Laycock, D.P., Michael, E., Tobin, R.C., Kelly, S., Johnston, M.N. (2022). Hydrocarbon charge and petroleum system evolution of the Montney Formation: a multidisciplinary case study of the Blueberry sub-play in Northeast British Columbia, Canada. Bullet. Canadian Energy Geosci. 69, 21–50.

World Economic Forum (2023). https://www.weforum.org/stories/2023/01/chart-countries-produce-lithium-world/

Wright, G.N., McMechan, M.E., Potter, D.E.G., (1994). Structure and Architecture of the Western Canada Sedimentary Basin. In: Geological Atlas of Western Canada. G.D. Mossop and I. Shetsen

(Comps.). Calgary, Canadian Society of Petroleum Geologists/ Alberta Research Council, pp. 25–40.

Yan, Q., Li, X., Wang, Z., Wu, X., Guo, H., Hu, Q., Peng, W., & Wang, J. (2012). Extraction of valuable metals from lepidolite. Hydrometallurgy, 117, 116-118.

Zonneveld, J.P., Moslow, T.F., (2018). Palaeogeographic setting, lithostratigraphy, and sedimentary framework of the Lower Triassic Montney Formation of western Alberta and northeastern British Columbia. Bulletin of Canadian Petroleum Geology 66, 93–127.