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Investigating reservoir-scale heterogeneity in Li-enriched oil field brines of the Devonian Leduc and Nisku formations, Alberta Basin, Canada

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ABSTRACT

Securing a North American lithium (Li) pipeline is pivotal to the clean energy transition and national security. The low-temperature sedimentary basin brines of the Devonian Alberta Basin, Canada are emerging as a promising unconventional domestic Li resource. This study integrates new and published geochemical and isotopic datasets from the Devonian Leduc and Nisku formation oil field brines to investigate brine origin, evolution, and Li enrichment mechanisms at the reservoir scale. Despite receiving considerably less attention than the Leduc Formation, the Nisku Formation brines display broadly similar geochemical and isotopic characteristics, suggesting common Li enrichment processes. Here we subdivide the Leduc and Nisku brines into geochemically distinct groups associated with four Devonian carbonate reef reservoirs (Redwater, Leduc, Chedderville, Bashaw) and evaluate the combined behavior of Li–B-radiogenic Sr–O–H isotope systems and major-element chemistry. Shallow reef complexes in hydraulic communication with surrounding formations contain low $\delta^{2}H$ and $\delta^{18}O$ values (avg. −78‰ and −3‰, respectively) and Li concentrations (avg. ~32 mg/L), suggesting meteoric infiltration caused dilution of the Li resource. Brines from structurally deep reef complexes approaching the Rocky Mountain deformation front display high Li concentrations (avg. ~67 mg/L), high $\delta^{18}O$ (avg. 3.4‰) and radiogenic strontium values (avg. 0.70899), and low $\delta^{11}B$ and $\delta^{7}Li$ values (avg. 24‰ and 15‰, respectively), consistent with interaction between brines and marine shales. Results suggest that Li enrichment and preservation are controlled by distinct but related processes, where shale-fluid interactions likely contribute Li to the basin brines while hydrologic isolation controls the preservation of elevated Li concentrations.

1. Introduction

Lithium (Li) is a critical mineral pivotal to the clean energy transition (U.S. Department of Energy, 2023). Demand for Li-ion batteries in electric vehicles and renewable energy grid storage applications has driven an exponential increase in Li production since the Paris Climate Agreement in 2016 (Ambrose and Kendall, 2020; IEA, 2023). Economic grade conventional Li deposits (hard-rock pegmatites and closed-basin brines) are scarce in North America and are resource-intensive to develop (Bibienne et al., 2020). As a result, the U.S. and Canada are net importers of Li, raising supply-chain and energy-security concerns (Natural Resources Canada, 2022; U.S. Geological Survey, 2023). Sedimentary basin Li brines (e.g., oil field brines) are quickly emerging as a potentially more sustainable and readily available domestic Li resource.

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Although Li grades are on average lower than conventional Li deposits, the large volume of sedimentary basin brines yield resource estimates on par with traditional resources (Butler et al., 2025; Dugamin et al., 2021). Additionally, sedimentary basin Li brines associated with oil fields have the unique advantage of pre-existing petroleum infrastructure, including large federally managed geochemical oil field brine datasets (e.g., Alberta Geological Survey Formation Water Database, U.S. Geological Survey National Produced Waters Geochemical Database).

The Western Canadian Sedimentary Basin (WCSB) hosts Devonian oil reservoirs that span much of the Alberta Basin (estimated at ~75,000 km^2; Fig. 1a) and associated brines exhibit a broad range of Li concentrations (0-140 mg/L; Bachu, 1995; Underschultz et al., 1994). Zones of elevated Li enrichment (generally >50-75 mg/L) were first identified in the 1990s in the Swan Hills and Leduc Formation reservoirs (Bachu, 1995; Hitchon et al., 1993; Underschultz et al., 1994). Subsequent work has investigated Li enrichment from the perspective of brine chemistry, basin hydrogeologic history, diagenetic processes, and other contexts (Bishop and Robbins, 2025; Butler et al., 2025; Eccles and Berhane, 2011; Eccles and Jean, 2013; Huff, 2016, 2019; Lazowski et al., 2025). Brine sampling campaigns have been undertaken by several lithium brine exploration companies (e.g., E3 Lithium Ltd., Lithium Exploration Group, MGX Minerals Inc., LithiumBank Corp). These assessments have historically focused on the Devonian Leduc Formation brines, with concentrations ranging from 29 to 91 mg/L across the basin (Butler et al., 2025). Similarly elevated Li concentrations also occur in the Devonian Nisku Formation reservoir brines (up to 87 mg/L; E3 Lithium Ltd., 2024). Spatial heterogeneity in Li grade, both across the basin and between reservoir units, confounds Li resource exploration, valuation, and production strategies. Additionally, variations in brine chemistry can affect Li recovery and separation during direct lithium extraction (DLE) processes due to competing dissolved ions or high salinities (Vera et al., 2023).

Several mechanisms have been proposed to explain Li enrichment in Devonian Alberta Basin brines. Early work interpreted brines as connate or highly evolved formation waters modified by evaporation, halite dissolution, gypsum dewatering, sulfate reduction, and mixing with meteoric waters (Connolly et al., 1990a, 1990b; Gupta et al., 2012; Huff, 2019). Li enrichment has been attributed to prolonged fluid-rock interaction and diagenetic reactions during burial (Hitchon et al., 1993), regional hydrodynamic transport along stratigraphic and structural pathways (Bachu, 1995), brine recycling during burial and sediment compaction (Eccles and Jean, 2013), hydrothermal fluids upwelling along basement fault systems (Eccles and Berhane, 2011; Huff, 2019), and dissolution of Li-bearing evaporite minerals or fluid

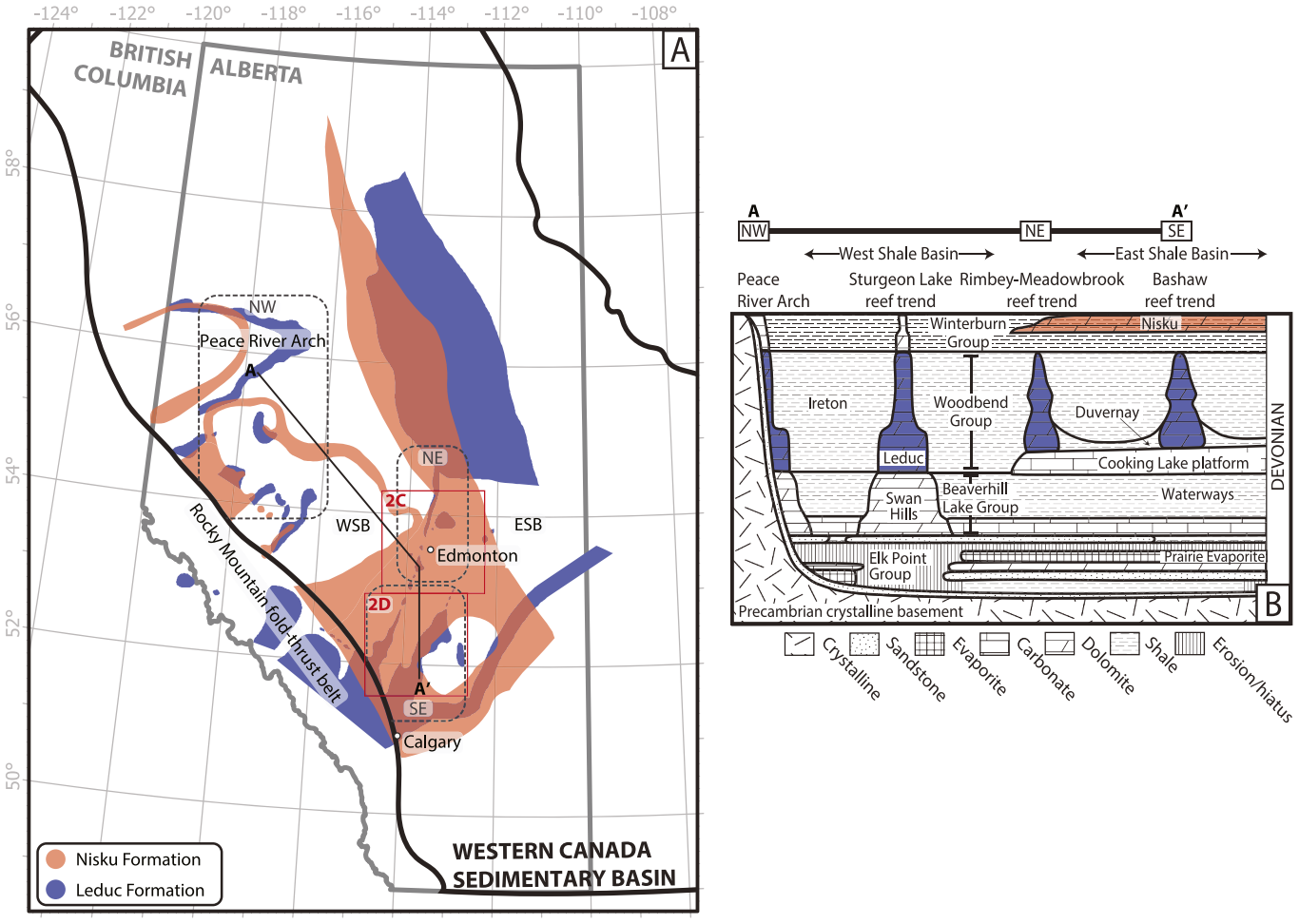

Fig. 1. (A) Map of Alberta Basin major structural features, formation extents from Switzer et al. (1994), regional brine groups (NW: northwest, NE: northeast, SE: southeast) from Butler et al. (2025), and study areas outlined in red. (B) Cross section from A to A′ in Fig. 1a, modified from Stacey et al. (2020).

inclusions (Underschultz et al., 1994;Huff, 2016, 2019).

More recent studies emphasize the role of marine shales in Li accumulation and release through burial diagenesis, water-rock interaction, and shale dewatering (Bishop and Robbins, 2025; Butler et al., 2025; Lazowski et al., 2025). Alberta Basin brines, particularly those hosted in Devonian carbonate reservoirs, have long been hypothesized to be influenced by clay mineral transformations and leaching reactions with basinal shale units (Connolly et al., 1990a; Hitchon et al., 1993). Bishop and Robbins (2025) compile brine data across the WCSB and interpret water-rock interactions with Li-rich clay intervals in shale as a significant Li source to basin brines. Lazowski et al. (2025) identified elevated Li concentrations in clay-sized particles deposited in supratidal environments of the Devonian halite sequences near Peace River Arch (avg. 304 ppm Li) suggesting that fine-grained siliciclastic material may act as a Li reservoir during burial and diagenesis. Butler et al. (2025) identified three regionally distinct groups from the Leduc Formation brines–northeast (NE), southeast (SE), and northwest (NW) – each with unique brine formation pathways and modification histories, but all broadly suggestive of the addition of Li via water-rock interactions between shales and shale pore waters. These spatially distinct brine chemistries highlight the complexity of Li enrichment mechanisms across the basin and invite higher resolution investigation of brine formation and modification. The distribution and interconnectivity of the Devonian carbonate reef complexes is highly complex, meaning individual reef reservoirs may experience varying magnitudes of brine modification processes. Here, we integrate five published datasets of subsurface brine geochemistry for the Leduc and Nisku Formation brines (215 brine samples; Alberta Energy Regulator databases: Butler et al., 2025; Huff, 2019; Huff et al., 2012, 2011; Reimert et al., 2025) with new geochemical and isotopic data from 7 Nisku Formation brine samples to evaluate whether the geochemical and isotopic characteristics identified in Li-enriched Leduc brines are common to the Nisku Formation. We further investigate how reef-specific characteristics influence Li enrichment and preservation at the reservoir level to avoid lateral variations inherent to larger-scale studies.

2. Geological background

The Alberta Basin is comprised of a Cambrian-Cenozoic succession of sedimentary units that structurally dip southwest toward the Rocky Mountain fold-and-thrust front and overlie Precambrian crystalline basement (Fig. 1b; Mossop et al., n.d.). Basin stratigraphy comprises a Paleozoic to Cenozoic succession (Wright et al., 1994). The Paleozoic section consists largely of carbonates with minor evaporites (halite, anhydrite) deposited in shallow-marine and sabkha environments (Switzer et al., 1994). The overlying Mesozoic section comprises thick sequences of marine and non-marine sandstones, shales, and coals derived from erosion of the Cordilleran orogeny units to the west (Wright et al., 1994). Cenozoic deposits are primarily unconsolidated sediments related to glacial and fluvial processes (Fulton et al., 1986).

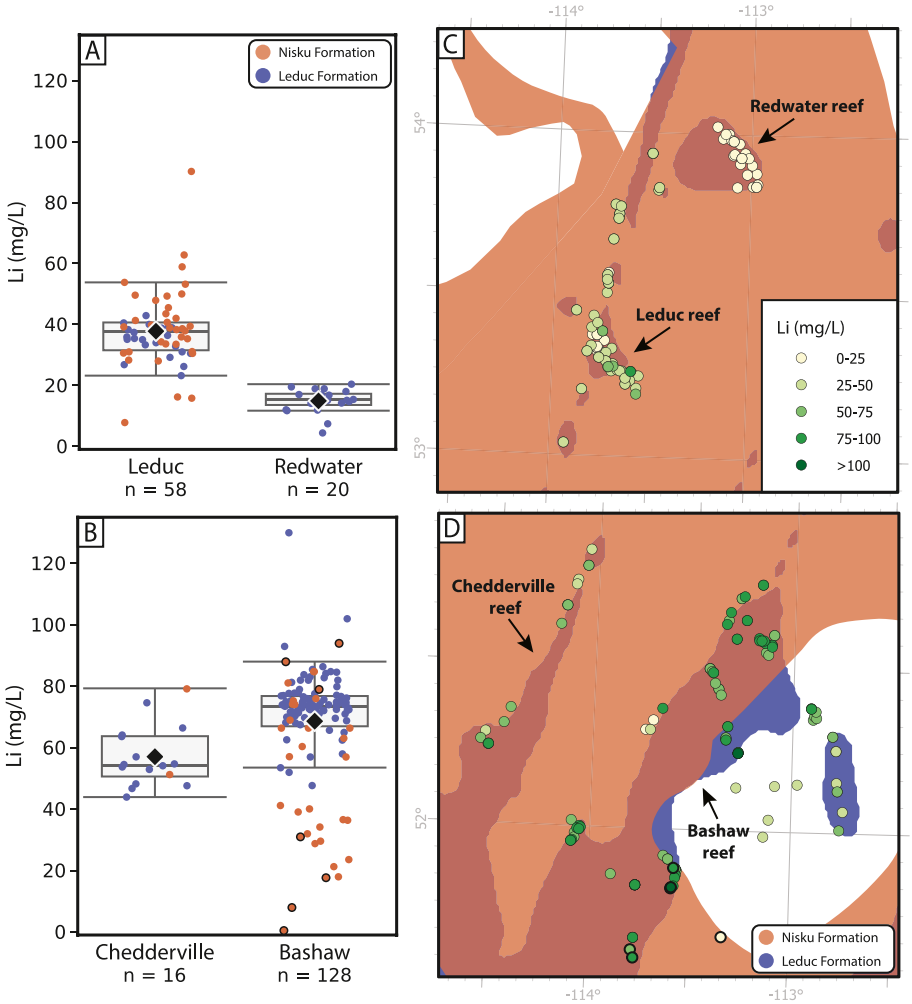

Fig. 2. (A, B) Box plots of brine lithium concentrations separated by reef reservoir and colored by formation. Data for brine samples is compiled from Huff et al. (2011, 2012, 2019), Reimert et al. (2025), Butler et al. (2025), and this study. (C, D) Maps of study areas (see Fig. 1) displaying discrete reefs in each region with brine samples colored by lithium concentration. Samples from this study are shown in bold.

The highest average aqueous Li concentrations (typically ranging from ~50 to 90 mg/L) of Alberta Basin oil field brines are found in Middle to Upper Devonian carbonate reef complexes, particularly the Swan Hills, Leduc, and Nisku formations (Fig. 2; Bachu, 1995; Eccles and Berhane, 2011; Hitchon et al., 1993; Underschultz et al., 1994). The Leduc and Nisku carbonate reef complexes are pervasively dolomitized, while the Swan Hills carbonate reef complexes preserve primary limestone and dolomite facies (Mossop et al., n.d.). These units were deposited on a shallow, frequently restricted reef-rimmed carbonate platform in an epeiric seaway (Switzer et al., 1994; Wendte, 1992). The partial restriction of marine inflow and the overall shallow depth of the continental basin drove evaporative concentration along the basin margins, where extensive evaporites formed throughout the Devonian (e.g., Prairie Evaporite, Muskeg Formations; Meijer Drees, 1994). Thick sequences of marine shales encase the Devonian platform and reef complexes (e.g., Ireton Formation, Duvernay Formation; Stoakes, 1979; Switzer et al., 1994). Rapid burial during the Late Devonian – Early Mississippian Antler Orogeny initiated extensive dolomitization of Devonian carbonate units (Stacey et al., 2020). Eastward propagation of the Laramide Orogeny fold and thrust belt steepened the basin's westward dip and generated the Devonian petroleum system (Price, 1981; Qing and Mountjoy, 1994). Deep geothermal fluids likely migrated along basement-penetrating faults, particularly in the Peace River Arch region, generating localized saddle dolomitization (Fig. 1; Machel and Cavell, 1999; Qing and Mountjoy, 1994).

3. Methods

For a regional perspective on brine heterogeneity, we compiled published brine geochemical data for the Devonian Leduc and Nisku reservoirs (Alberta Energy Regulator databases: Huff, 2019; Huff et al., 2011, 2012; Reimert et al., 2025; Butler et al., 2025) and screened using a ±10% cation-anion charge balance cutoff; the resulting dataset includes 215 previously published brine samples. Most of the Li concentration data from the Alberta Basin were measured by industrial labs using inductively coupled plasma optical emission spectroscopy (ICP-OES) or inductively coupled plasma mass spectrometry (ICP-MS) instruments and reported in milligrams per liter (mg/L). Major cation, anion, and trace-metal concentrations for 7 new Nisku brine samples were collected by Bureau Veritas Labs on behalf of E3 Lithium. After removal of H_2S gas from the brines, the brines underwent acid digestion to dissolve any suspended solids and were analyzed for total Li concentrations via ICP-OES at SGS Canada, Lakefield, Ontario. The complete dataset is provided in the supplementary material (Table 1 in Appendix A).

8 shale samples were selected from Devonian shale sediment cores across the Alberta Basin; well identification numbers and locations are provided in the supplementary material (Table 2 in Appendix A). Li concentrations of bulk shale powders were analyzed using an MC-ICP-MS by ALS Reno (Reno, Nevada). Li isotopes were analyzed using a ThermoScientific Neptune Plus multicollector (MC)-ICP-MS by ALS Scandinavia (Aurora, Sweden). Shales were powdered and digested by $HFNO_3$ and evaporated to dryness with aqua regia before measurement.

Water isotope ratios ($\delta^{18}O$, $\delta^{2}H$) were analyzed for the 7 Nisku Formation brines using a Picarro L2140-*i* isotopic water analyzer at the Critical Zone Hydrology Lab, University of Georgia. The analyzer is attached to a high-precision vaporizer, micro-combustion module (MCM), and autosampler. The MCM was used to destructively remove potential organic contaminants from liquid water samples, thereby ensuring maximum measurement precision and accuracy. The system was operated in the 'MCM High Precision' mode. For each sample vial, nine injections were run; the first six were discarded to minimize memory effects, and $\delta^{18}O$ and $\delta^{2}H$ were calculated from the mean of the final three injections. This approach addresses memory effects, which are typically greater for $\delta^{2}H$ than for $\delta^{18}O$, ensuring that by the 7th injection, approximately 98% for $\delta^{2}H$ and 99% for $\delta^{18}O$ of the true isotope difference is attained. Analytical precision (1σ) was 0.025‰ for $\delta^{18}O$ and 0.100‰ for $\delta^{2}H$. ChemCorrect post-processing flagged no samples for potential organics.

Boron concentrations were measured for the 7 Nisku brine samples on a ThermoFisher X-series II ICP-MS at Duke University. All samples were diluted to an approximate TDS of 200 mg/L prior to analysis and accuracy of measurements was monitored with regular measurements of the IAPSO Atlantic Seawater standard.

$\delta^{11}B$ measurements were measured for the 7 Nisku brine samples with a Thermo Fisher TRITON thermal ionization mass spectrometer (TIMS) in negative mode at Duke University, Durham, NC. Methods followed those published in Leslie et al. (2014) and Williams et al. (2025) and per mil values are reported relative to NIST 951. Each sample was prepared in a B free fume hood and reacted with H_2O_2 at room temperature for a minimum of 24 h to break down organic matter. Approximately 4 ng of B were loaded onto single Re filaments with a B-free synthetic seawater solution. B was ionized as BO_2^- and CN^- was monitored as a proxy for CNO^- interference. Repeated analysis of the IAPSO Atlantic seawater standard during the run period yield a mean value of 39.5 ± 0.5‰ (2SD) (n = 7) in agreement with the accepted value of 39.61‰ for seawater (Foster et al., 2010).

Lithium isotope measurements for the 7 Nisku brine samples were made on a ThermoScientific Neoma MC-ICP-MS in low mass resolution using a sample-standard bracketing technique. Samples were yield-checked (>99%) and concentration-matched to the NIST LSVEC standard and measured at 0.5 ppb (~0.5 V on ^{7}Li) with 10^{13} Ω amplifiers using high-sensitivity Jet sample and X skimmer cones. Solutions were aspirated using a PFA nebulizer and APEX Omega HF desolvator with an uptake rate of 134 μL/min. We also adopted the technique used in Bohlin et al. (2018) and recently verified in Zhang et al. (2025) to reduce Li background by conditioning the cones with a 10 ppm Na solution for 10 min before measurement, resulting in an average background of 2 mV on ^{7}Li. $\delta^{7}Li$ were bracketed and are reported relative to LSVEC. Analytical uncertainty for $\delta^{7}Li$ based on ≥3 measurement of column splits and a secondary solution standard was ≤ ±0.3‰ (2 SD). Precision was verified by measurements of aliquots of IAPSO (n = 1) and Atlantic Seawater (n = 2) seawater standards processed in parallel to the brine samples, which gave $\delta^{7}Li$ values of 31.80 ± 0,28‰; 32.55 ± 0.27‰ and 31.38 ± 0.17‰ (2SD), in agreement with literature values (Li et al., 2022; Millot et al., 2004), as well as self-bracketed LSVEC $\delta^{7}Li$ measurements of 0.00 ± 0.25‰ (2SD). Secondary solution standard GHPS and IV-1643 (Inorganic Ventures; IV-STOCK-1643-125ML) processed in parallel to the brine samples produced $\delta^{7}Li$ values of 7.48 ± 0.24‰ and 18.34 ± 0.06‰ (2SD), respectively.

The 7 Nisku brine samples were also purified for Sr isotope analysis at Brown University in the Trace Metal Clean Lab. Aliquots of brines containing 200 ng Sr were taken and evaporated to dryness in acid-cleaned Savillex vials, re-dissolved in 1 mL 3 N HNO_3 for purification, and chromatographically separated using Eichrom Sr-specific resin. Sr isotope ratios were measured at the Mass Spectrometer Analytical Facility at Brown University on a ThermoScientific Neptune Plus MC-ICP-MS and are reported relative to the $^{87}Sr/^{86}Sr$ NBS SRM 987 of 0.71024 (Mallick et al., 2023; Muñoz et al., 2024). Four aliquots of two water standards were processed and measured in parallel to the brine samples. SLRS-6 (National Research Council Canada) gave an $^{87}Sr/^{86}Sr$ value of 0.712087 ± 0.000012 (2SD), in agreement with previous literature values (Lee and Ko, 2023; Yeghicheyan et al., 2021) and IV-1643 (Inorganic Ventures; IV-STOCK-1643-125ML) gave values of 0.708724, 0.708714 and 0.708728 ± 0.000012 (2SD).

4. Results

4.1. Lithium concentrations

Lithium concentrations range widely in the Nisku and Leduc Formation brines (0.5-94 mg/L and 4.4-130 mg/L, respectively; Fig. 2).

Brines can be separated into distinct geochemical groups that spatially correspond to four Devonian reef reservoirs: the Redwater reef (4.4-20.4 mg/L, avg. 14.9 mg/L), the Leduc reef (7.8-90.2 mg/L, avg. 37.8 mg/L), the Chedderville reef (43.9-79.3 mg/L, avg. 57.0 mg/L), and the Bashaw reef (0.5-130 mg/L, avg. 68.3 mg/L). Lower Li concentrations in the Bashaw reef area (<~60 mg/L) are associated with Nisku Formation brines located off the reef complex (Fig. 2B). Li concentrations are broadly similar between the Nisku and Leduc Formations in all reef groups, particularly the Leduc reef brines (avg. 32 and 35 mg/L, respectively). Only two brine samples are available from the Nisku Formation in the Chedderville reef, but the Li concentrations are within the range exhibited by the Leduc Formation brines (avg. 65 and 56 mg/L, respectively). The Bashaw reef brines display the most notable variation between the Nisku and Leduc Formations (avg. 59 and 74 ppm, respectively). No brine samples are available from the Nisku Formation in the Redwater reef.

4.2. Brine oxygen and hydrogen isotopes

Stable oxygen and hydrogen isotopes of Nisku and Leduc brines reveal four distinct geographic groups differentiated by reef reservoirs (Fig. 3). The Redwater reef brines range from −96.4 to −70.0‰ δD and −12.3 to −4.91‰ $\delta^{18}O$ and represent the lowest values on average. The Leduc reef brines range from −118 to −48.9‰ δD and −11.1 to 4.13‰ $\delta^{18}O$. The Chedderville reef brines range from −56.1 to −49.6‰ δD and 3.78 to 6.22‰ $\delta^{18}O$ and are the most tightly clustered in isotopic values. The Bashaw reef brines range from −113 to −21.1‰ δD and −10.9 to 13.0‰ $\delta^{18}O$ and are the highest values on average. All brines exhibit lower values than the δD value of modern seawater (Vienna standard mean ocean water, VSMOW) and the likely range of Devonian seawater isotopic composition reconstructed from primary carbonate values (approx. 19‰; Carpenter et al., 1991; Popp et al., 1986) and lie along a subparallel compositional trend compared to expected seawater evaporation trajectory of modern seawater. Generally, northeast brines (Redwater and Leduc reefs) have lower values than southeast brines (Chedderville and Bashaw reefs). The Nisku Formation brines from the Bashaw reef area are notably lower in isotopic value than the Leduc Formation brines in the same region.

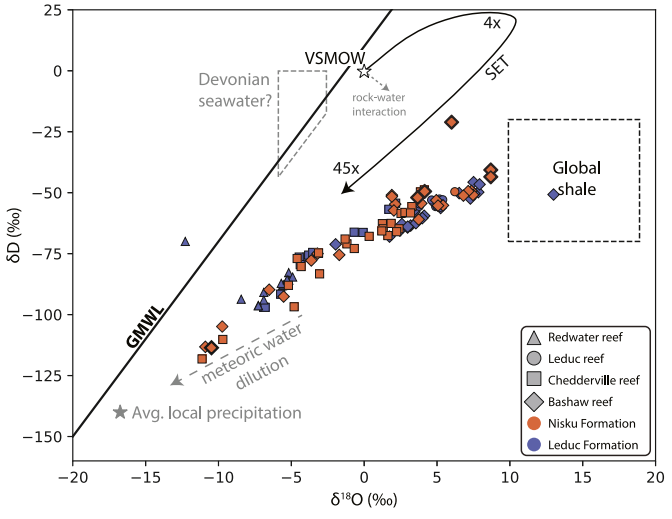

Fig. 3. Stable water isotope (δD versus $\delta^{18}O$) values of Nisku and Leduc brines, Vienna standard mean ocean water (VSMOW), average Calgary, Alberta meteoric water (Peng et al., 2004), possible Devonian seawater (Popp et al., 1986; Carpenter et al., 1991), and global shales (Faure, 1997), alongside the global meteoric water line (GMWL) and seawater evaporation trajectory (SET; Knauth and Beeunas, 1986). Grey lines represent potential trajectories of meteoric water dilution (Gat, 1996) and rock-water interactions (Taylor, 1974), respectively. Samples from this study are shown in bold.

4.3. Strontium concentrations and radiogenic strontium isotopes

Radiogenic strontium isotope ratios of the Redwater reef, Leduc reef, and Bashaw reef brines display similar behavior between reef groups (Fig. 4). The Redwater reef brines are by far the lowest in Sr concentration (58.3-236 mg/L, avg. 168 mg/L), and $^{87}Sr/^{86}Sr$ values range from 0.708654 to 0.709744. Chedderville reef brines have the highest average strontium concentration (800-1330 mg/L, avg. 1147 mg/L), and $^{87}Sr/^{86}Sr$ values range from 0.70869 to 0.70930. The Bashaw reef brines vary widely in strontium concentrations (11.7-1420 mg/L, avg. 799 mg/L), and $^{87}Sr/^{86}Sr$ values range from 0.70822 to 0.71262. The Leduc reef brines display the widest array of $^{87}Sr/^{86}Sr$ values (0.70869 to 0.71319) and show Nisku brines to be notably more radiogenic than underlying Leduc brines. All brine $^{87}Sr/^{86}Sr$ values are more radiogenic than Devonian seawater (0.7078–0.7090; Prokoph et al., 2008) or the Prairie Evaporite (0.70781–0.70789; Horita et al., 1996), but significantly less radiogenic than rocks in the underlying Precambrian basement units (0.74307–1.3097; Connolly et al., 1990b). The range of all brine $^{87}Sr/^{86}Sr$ values overlap with the range of reflux dolomites (0.7079–0.7120; Amthor et al., 1993; Buschkuehle and Machel, 2002; Green and Mountjoy, 2005; Machel et al., 1996; Machel and Cavell, 1999) and all but the most radiogenic Leduc reef brines are less radiogenic than the maximum strontium isotope ratio measured in basinal shales (Machel and Cavell, 1999).

4.4. Lithium isotopes

Lithium isotope values of all the brine samples are broadly similar, with no clear separation between formations or reef reservoirs (Fig. 5). Brine $\delta^{7}Li$ values range from 8.3 to 26.67‰, significantly lower than modern seawater (31‰; Chan et al., 1992), similar to or lower than the potential isotopic value of Devonian seawater (avg. carbonate values of 16 ± 12‰; Kalderon-Asael et al., 2021; Wang et al., 2023), and slightly higher or similar to global shale values (avg −0.2‰; Macpherson et al., 2014) and the Alberta Basin shale values (avg. 4.5‰, this study).

4.5. Boron concentrations and isotopes

Boron isotope values of the brines show a clear negative correlation between boron concentrations and $\delta^{11}B$ (Fig. 6). The Redwater reef

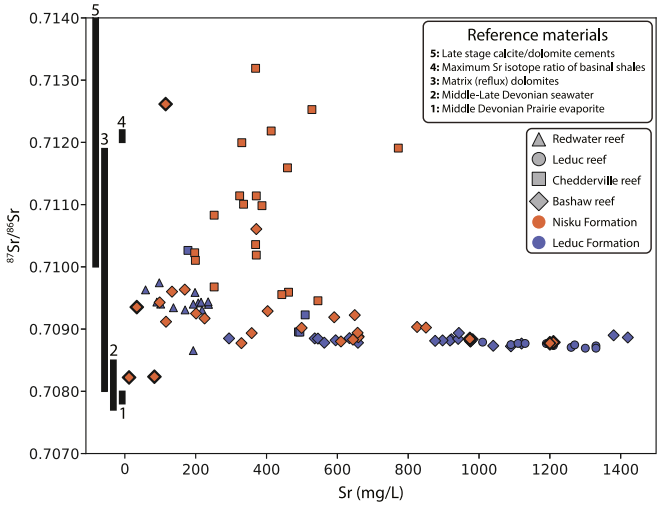

Fig. 4. Radiogenic strontium isotope ratios for the Nisku and Leduc brines. Strontium isotope ratios for reference materials from the Alberta Basin were compiled from Burke et al. (1982), Connolly et al. (1990b), Mountjoy et al. (1992), Amthor et al. (1993), Machel et al. (1996), Horita et al. (1996), Machel and Cavell (1999), Buschkuehle and Machel (2002), and Green and Mountjoy (2005). Samples from this study are shown in bold.

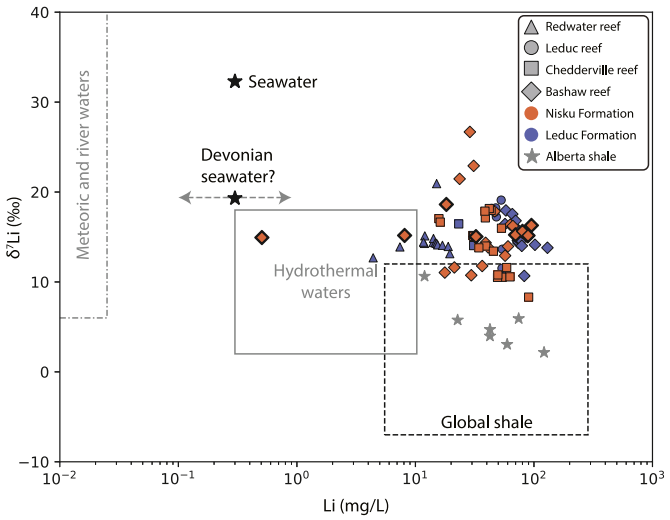

Fig. 5. Lithium isotope values versus lithium concentrations for the Nisku and Leduc brines. Geochemistry of reference materials was assembled from Holland (1984), Moriguti and Nakamura (1998), Teng et al. (2004), Tomascak (2004), Chan et al. (2002), Ketris and Yudovich (2009), Araoka et al. (2014), Romer et al. (2014), Phan et al. (2016), and Marza et al. (2024). Composition of Devonian seawater was estimated after Butler et al. (2025), who used Devonian carbonate isotope signatures from Kalderon-Asael et al. (2021) and Wang et al. (2023) to calculate average Devonian seawater lithium isotope composition assuming a fractionation factor of −9 to 0‰ (Marriott et al., 2004; Pogge von Strandmann et al., 2019; Day et al., 2021). Samples from this study are shown in bold.

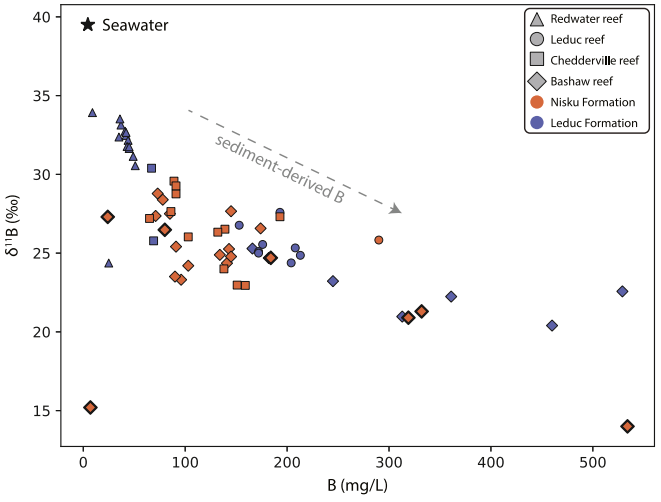

Fig. 6. Boron isotope values versus boron concentrations for the Nisku and Leduc brines. Grey dashed arrow indicates the effect of added sediment-derived boron. Boron isotope composition of modern seawater taken from Foster et al. (2010). Samples from this study are shown in bold.

brine contains the lowest concentrations of boron (9-51 mg/L, avg. 39 mg/L) and highest $\delta^{11}B$ values (24.4-33.9‰), slightly below the $\delta^{11}B$ value of modern seawater (39.6‰; Foster et al., 2010). The Leduc reef brines are more enriched in boron (38-193 mg/L, avg. 96 mg/L) and display lower $\delta^{11}B$ values (23.0-30.4‰) than Redwater reef brine. The Chedderville reef brines have similar $\delta^{11}B$ values (24.4-27.6‰) to north Rimbey brines but have higher average concentrations of boron (153-290 mg/L, avg. 195 mg/L). Bashaw reef brines contain the highest concentrations of boron (7-534 mg/L, avg. 189 mg/L) and the lowest $\delta^{11}B$ values (14.0-28.8‰).

5. Discussion

5.1. Brine origin and modification

Stable water isotope values indicate evaporative processes influenced the Nisku and Leduc formation brines, suggesting evaporative concentration of seawater or halite dissolution as the most likely sources of high salinity. Halogen compositions can be used to differentiate between primary (evapoconcentrated seawater) and secondary (halite-dissolution) brine formation pathways (Fig. 7). Brine Cl/Br values that plot along the seawater evaporation trajectory (SET) suggest a primary brine origin, whereas elevated ratios indicate a secondary origin. Compositions below the SET may be achieved via meteoric water dilution (Fontes and Matray, 1993; Kharaka and Hanor, 2003). Cl/Br ratios of the Redwater reef brines point to secondary or mixed origins, while all the other brines display Cl/Br ratios indicative of a primary origin with varying amounts of meteoric water dilution. There is much debate around whether halogen relationships, particularly Cl/Br ratios, are reliable indicators of origin due to the confounding effects of halite recrystallization or fluid mixing (Engle and Rowan, 2013; Gupta et al., 2012). However, Cl/Br ratios remain a useful and widely used tool for constraining regional-scale geochemistry when used with caution and should be verified by other independent geochemical proxies.

Water stable isotope values and Cl/Br ratios suggest the brines are derived from evaporatively concentrated seawater with variable degrees of evaporite dissolution (e.g., Redwater reef) and meteoric water dilution (e.g., Redwater reef, Leduc reef). Brine oxygen and deuterium isotopic values are increasingly lower up structural dip (to the northeast and away from the Rocky Mountain deformation front, Fig. 1a) suggesting dilution may be related to meteoric water infiltration at shallower structural levels. Solute transport models by Gupta et al. (2015) propose that meteoric water enters through permeable units and pathways at the basin margin to the northeast and diffuses into older brines via topography-driven flow. Hydraulic head and formation pressure data suggest that potential hydraulic communication exists between the Redwater reef and shallower Cretaceous units (e.g., Lower Mannville; Bachu et al., 2008). The structurally deeper SE region brines are consistently high in $\delta^{18}O$ value relative to VSMOW and Devonian seawater, consistent with evaporation in more isolated hydrologic settings and prolonged water–rock interactions at elevated temperatures (Newman et al., 2023).

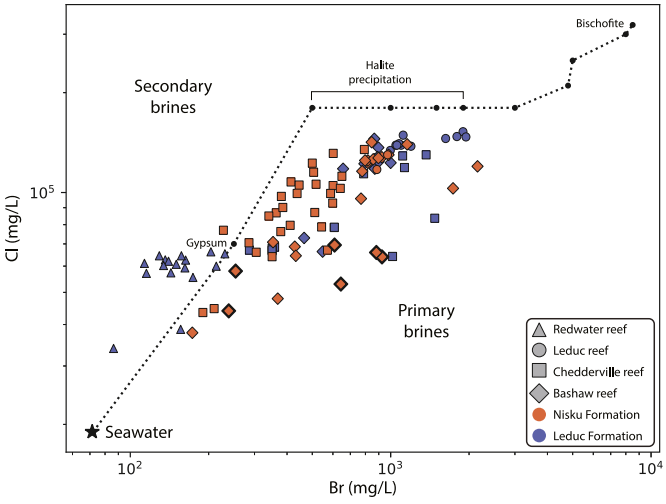

Fig. 7. Chloride concentration versus bromide concentration of Nisku and Leduc brine. Dotted black line represents the seawater evaporation trajectory (SET) of modern seawater from Fontes and Matray (1993). Deflection below the SET suggests dilution via meteoric water (Kharaka and Hanor, 2003). Samples from this study are shown in bold.

5.2. Regional-scale lithium enrichment mechanisms

Previous work has proposed multiple potential Li sources and enrichment pathways for the Alberta Basin brines: evapoconcentrated seawater (Eccles and Berhane, 2011; Connolly et al., 1990a, 1990b), deep hydrothermal fluids (Connolly et al., 1990a, 1990b; Machel et al., 1996; Huff, 2015), fault-associated fluids from adjacent or underlying siliciclastic units (Stacey et al., 2020), dissolution of marine evaporite units such as the Devonian Prairie Evaporite (Huff, 2016, 2019), and prolonged rock-water interactions between brine and marine shales (Machel et al., 1996; Machel and Cavell, 1999; Butler et al., 2025; Bishop and Robbins, 2025). It is likely that more than one of these processes contributed Li to the Devonian brines; however, the brine geochemical and isotopic characteristics can elucidate which of these sources are significant at the basin and discrete reef reservoir scale. Notably, similar Li concentrations, elemental relationships, and isotopic compositions are observed in both the Nisku and Leduc formations, suggesting that common basin-scale enrichment processes operate across both units.

Lithium concentrations in the majority of Nisku and Leduc brines are an order of magnitude higher than expected for seawater evaporatively concentrated up to bischofite saturation (Fig. 7). The Alberta Basin Devonian seawater would need to have been significantly enriched in Li relative to modern seawater for the brine Li concentrations to be generated solely through evapoconcentration of Devonian seawater. Additionally, brines with similar total dissolved solids display a wide range of Li concentrations (up to ~75 mg/L difference), suggesting that Li enrichment is decoupled from salinity evolution. It is possible that localized mechanisms may have elevated Li concentrations of the Alberta Basin Devonian seaway, including aeolian/fluvial transport and subsequent dissolution of Li-rich sediments (Lazowski et al., 2025), distal ashfall, localized hydrothermal springs, or that global Devonian seawater was elevated in Li. Data from Horita et al. (1996) shows fluid inclusions within Prairie Evaporite Formation reach Li/Br molar ratios of 0.10 to 0.15, much higher than modern seawater (approx. 0.003; Drever, 1988).

Hydrothermal fluids and fluids associated with basement-derived siliciclastic units are plausible sources of Li in structurally complex areas of Alberta Basin, especially near major fault zones (e.g., northwest brines associated with Peace River Arch, Fig. 1a; Butler et al., 2025). These fluids are likely to be characterized by highly radiogenic strontium isotope values due to rock-water interactions with crustal materials, and their addition would notably increase brine $^{87}Sr/^{86}Sr$ values. An example of this is the radiogenic strontium isotope ratios of brines associated with the Peace River Arch in central Alberta, which range from 0.72244 to 0.72898 (Butler et al., 2025). Despite comparable Li concentrations, brines evaluated in this study display $^{87}Sr/^{86}Sr$ values between 0.70822 and 0.71319, only marginally more radiogenic than Devonian seawater (0.7078–0.7090; Prokoph et al., 2008) and evaporites (0.70781–0.70789; Horita et al., 1996). Additionally, hydrothermal fluids are predicted to have been highly localized and likely did not flow more than 100-200 km from the Rocky Mountains deformation front (Machel and Cavell, 1999). This suggests that hydrothermal fluids are unlikely to serve as the dominant mechanism for Li enrichment in the northeast and southeast brine regions (Fig. 1a), although localized contributions remain possible.

Another suggested Li source is the dissolution of evaporite units, which may store Li either by incorporation into evaporite minerals (e.g., Li-carnallite) or in Li-rich fluid inclusions trapping during evaporite formation. However, Li is highly conservative in solution and is rarely incorporated into the halite crystal lattice, indicating the formation of Li-salts is unlikely outside of extreme conditions (Fontes and Matray, 1993). It is more likely that Li in evaporites would be sourced from Li-rich fluid inclusions. Li concentrations of Middle Devonian Prairie evaporite fluid inclusions measured by Horita et al. (1996) average ~42 mg/L, which could contribute Li to halite-derived brines. However, halogen compositions broadly suggest a seawater origin for brines in this study, and Li does not strongly positively covary with Na or Cl (Fig. 8). Evaporite dissolution may contribute Li locally but does not fully explain the observed regional and reservoir-scale heterogeneity in Li concentrations.

Water-rock interactions with marine Devonian shales have been proposed by multiple authors as a likely Li enrichment mechanism based on several geochemical indices (Machel et al., 1996; Machel and Cavell, 1999; Butler et al., 2025). Li has been observed to readily adsorb to clay minerals under saline conditions (e.g., Li and Liu, 2022) and can be incorporated into the interlayer and octahedral sites of authigenic clay minerals during burial diagenesis (e.g., Williams and Hervig, 2005). Clay minerals preferentially take up ^{6}Li, which significantly fractionates structurally bound Li (14-24‰) and, to a lesser degree, adsorbed Li (0–12‰; Pogge von Strandmann et al., 2020). Fine-grained marine shales encasing Devonian carbonate reef complexes likely would have captured a portion of the available Li from Devonian seawater. During burial, increased temperature and pressure would have promoted the release of Li from clay minerals into pore fluids through desorption and possible clay mineral transformations, modifying Li isotope compositions of the pore waters to more closely resemble those of the shale (Williams and Hervig, 2005; Chan et al., 1994). Burial at depths of roughly 1-3 km dewaters shales via physical compaction, smectite-illite transformations, and clay mineral dehydration, which mobilizes pore fluids (Eberl, 1993). This process is consistent with the strong positive covariation between Li, B, and K brine concentrations: elements commonly associated with the diagenesis of fine-grained sediments (Fig. 8). If covariation in these elements were controlled solely by salinity, Li would have similarly strong positive correlations to Na, Cl, and/or Br; however, these relationships are much weaker than those between Li, B, and K (Fig. 8). Additionally, Li isotopes of basinal shales from Alberta Basin in this study range between 1.5 and 10.6‰, in the upper range of global shale average values (Fig. 5). While fractionation of Li between brines and shales is highly dependent on the clay mineral type, the difference between brine and shale Li isotope values may reasonably be explained by this mechanism.

Similar to Li isotopes, boron isotopes are valuable tracers for fine-grained sediment-fluid interactions. Boron behaves similarly to Li as a highly mobile element commonly adsorbed in clay sediments, and a positive covariation can be observed between the two elements in all brines (Fig. 8). Fine-grained sediments preferentially adsorb the isotopically lighter borate ion ($B(OH)_4^-$) over boric acid ($B(OH)_3$), even when borate concentrations in solution are low; the magnitude of sorbed boron is dependent on pH, with alkaline seawater providing conditions for maximum adsorption (Ring et al., 2025). Boron mobilized from subsurface sediments under increased temperatures and pressures would therefore decrease brine isotope value by the addition of isotopically light borate ions, as seen in similar sedimentary basin settings (e.g., Texas Gulf Coast Basin; Williams et al., 2001). While lithium and boron isotopes cannot uniquely identify a single Li source, their behavior is compatible with mixing between seawater-derived brine and Li released from clays in fine-grained sediments during burial and diagenesis.

The B–Li-radiogenic strontium isotope systems provide complementary constraints on Li enrichment mechanisms. Radiogenic strontium isotope values do not support input from basement-derived hydrothermal fluids, low $\delta^{11}B$ values of Li-enriched brines are consistent with the desorption of ions from subsurface fine-grained sediments, and lithium isotope values may be explained by prolonged water-rock interaction with Alberta Basin Devonian marine shales. Together, these isotope systems are consistent with Li mobilization through interaction between seawater-derived brines and marine shales during burial and diagenesis.

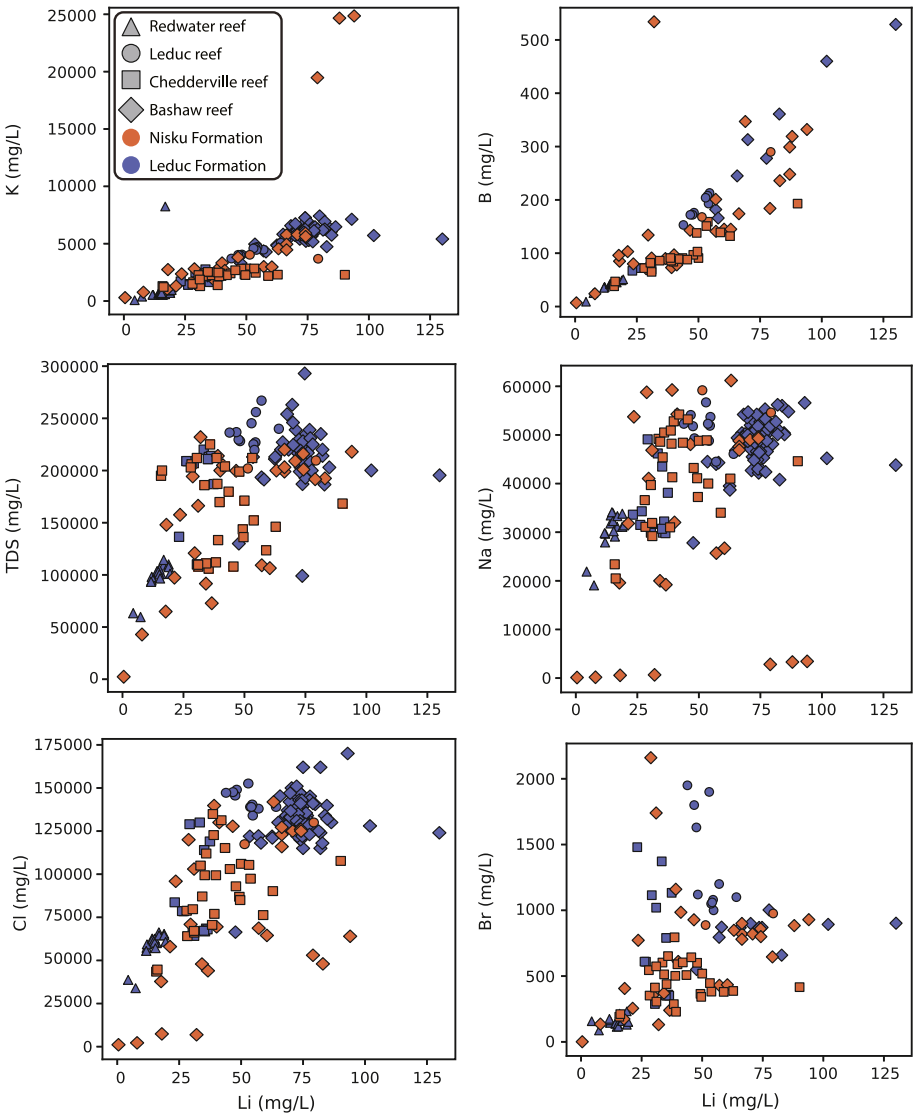

Fig. 8. Lithium concentrations versus potassium, boron, total dissolved solids (TDS), sodium chloride, and bromide concentrations of Nisku and Leduc brines.

5.3. Reef reservoir specific formation and enrichment of the devonian brines

The Nisku and Leduc Formation brines across the four Devonian reef reservoirs share general similarities in geochemistry that point to basin-scale brine genesis and Li enrichment mechanisms. However, systematic differences in salinity, isotope values, and Li concentrations indicate that reef reservoir-specific processes, such as local stratigraphy and hydrogeologic connectivity and fluid flow history, are important controls on Li enrichment and preservation. The observed variability is best described as a system with two endmembers: (1) hydrologically open reservoirs affected by meteoric water intrusion that dilutes brines and (2) hydrologically isolated reservoirs that preserve evolved brines and elevated Li concentrations (Fig. 9).

Brines from the Redwater reef are the least saline and on average the lowest in δD and $\delta^{18}O$ values suggesting dilution by meteoric waters. This is consistent with the relatively shallow structural position (~1000 m depth; Sodagar and Lawton, 2009), proximity to the basin margin and hydraulic connectivity with the overlying permeable Cretaceous units (Bachu et al., 2008). Li concentrations are correspondingly low; despite a similar depositional environment and age to other reefs, Li-enriched brine was either not well preserved (diluted or flushed out) or not able to accumulate in the reservoir. This suggests that meteoric dilution and hydraulic connectivity may limit Li preservation even where regional Li enrichment processes have occurred.

The Leduc reef brines display moderate salinities and low to moderate concentrations of Li. The overlying Nisku Formation brines appear to experience more extensive mixing with fluids sourced from surrounding shales or other siliciclastics, with notably elevated brine radiogenic strontium isotope values. These observations suggest a reservoir more hydrologically isolated than the Redwater reef, but still exhibits stratigraphically variable degrees of hydraulic connectivity to surrounding units. The broadly similar geochemical and isotopic characteristics of the Nisku and Leduc brines suggest that both formations experienced comparable basin-scale enrichment processes, but local differences in hydraulic connectivity influenced the degree of brine modification and Li preservation.

Brines from the Chedderville reef exhibit relatively high salinities, show little evidence for meteoric water dilution, and have moderate Li concentrations. These observations are consistent with a more isolated hydrologic setting, where Li-enriched brines were allowed to accumulate and were relatively well-preserved. The transition from the Redwater and Leduc reefs to the Chedderville reef suggests that increasing hydrologic isolation promotes the preservation of evolved brines and elevated Li concentrations.

Finally, the Bashaw reef brines display the highest salinities, Li

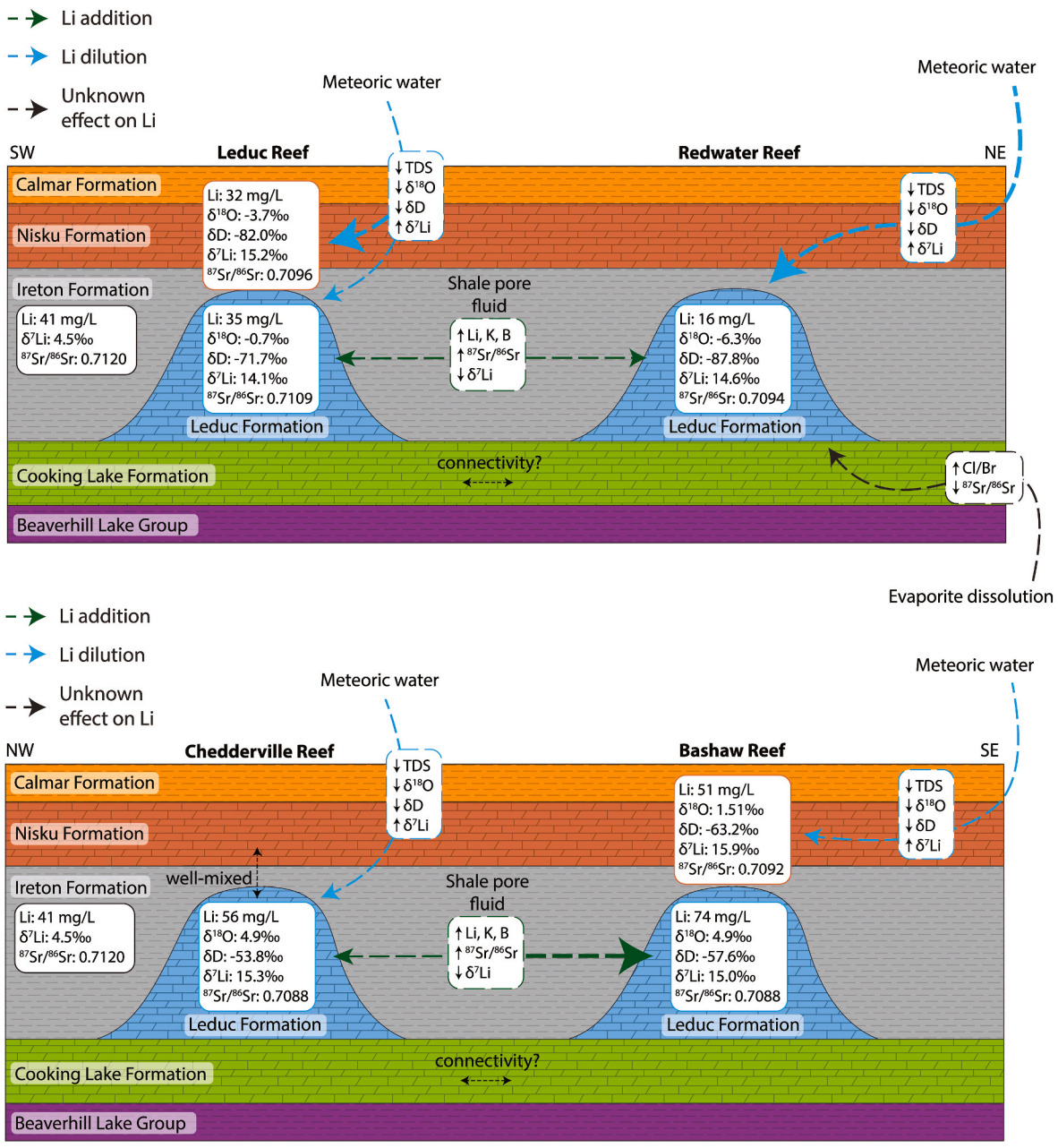

Fig. 9. Conceptual model evaluating the varying lithium addition and dilution mechanics present in each reef. Arrow magnitudes represent degree of influence on each reservoir. Boxes with solid outlines represent average geochemical characteristics of each reservoir, while boxes with dotted outlines represent the observed geochemical effects of each mechanism.

concentrations, and highest δD and $\delta^{18}O$ values of the four reef complexes. Additionally, the Leduc Formation Bashaw brines contain significantly higher concentrations of boron than the other reef brines, alongside the lowest $\delta^{11}B$ values. Together, these observations identify Bashaw reef as the most well-preserved brine reservoir of the four reefs, and may also indicate the greatest accumulation of marine shale-derived Li. The Bashaw reef represents the ideal end member for Li preservation, where hydrologic isolation appears to have facilitated both prolonged water-rock interaction and preservation of evolved Li-enriched brines.

6. Conclusions

Across all reef reservoirs, brine Li concentrations correlate with ions commonly released during marine shale diagenesis (K, B, Ca), brine Li isotope values resemble those of global shales, boron isotope values suggest desorption of boron from subsurface sediments, and radiogenic strontium isotope values are inconsistent with a hydrothermal Li source. These relationships point to clay–fluid interactions as a major basin-scale control on Li enrichment in brine. Similar geochemical and isotopic relationships are observed in both the Nisku and Leduc formations, suggesting that these processes are not restricted to a single Devonian reservoir unit. Results support a model in which Alberta Basin brines are largely derived from evaporatively concentrated seawater stored as shale pore waters and are subsequently enriched in Li through shale dewatering, clay mineral reactions, and associated water-rock interactions during burial, following the mechanism proposed for the Leduc Formation brine origin and enrichment by Butler et al. (2025). Hydrocarbon generation and extensive replacement dolomitization throughout the basin provide further evidence for post-depositional fluid circulation between reservoir carbonates and connate marine

fluids of multiple formations, including surrounding shale units. Therefore, it is plausible that fluids released from shales play a notable role in basin-scale Li transport and accumulation. However, the distribution of Li between reef reservoirs suggests that Li enrichment and preservation are controlled by distinct processes.

Li-enriched oil field brines within the Alberta Basin have regional geochemical and isotopic signatures that suggest similar origins and Li enrichment mechanisms across multiple brine reservoirs. However, reef-specific characteristics (e.g., hydraulic connectivity, structural depth, surrounding stratigraphic units) have clear controls on Li accumulation and preservation. Brines associated with hydrologically open reef systems show greater evidence of meteoric water dilution and lower Li concentrations, while deeper and more hydrologically isolated reef systems preserve elevated Li concentrations and geochemical signatures consistent with greater fluid-rock interaction.

1. The Redwater reef's shallow depth and connectivity with surrounding permeable units has allowed for meteoric water dilution, which likely prevented significant Li accumulation and/or preservation despite broadly similar regional Li enrichment mechanisms.
2. The Leduc reef brines show evidence for meteoric water dilution, particularly in the overlying Nisku Formation, but to a lesser degree than the Redwater reef. Low to moderate Li concentrations are present, possibly due to greater rock-water interactions with surrounding marine shales.
3. The Chedderville reef brines show evidence for meteoric water dilution to a lesser degree than the Redwater and Leduc reefs, likely due to the reef's increased structural depth. Moderate Li concentrations are present.
4. The Bashaw reef brines exhibit the least meteoric water dilution, likely due to the reef's structural depth. Brine geochemistry suggests the greatest degree of shale-fluid interaction, which likely contributed Li. These brines have the most elevated lithium concentrations.

Using multiple geochemical and isotopic methods helps quantify the effects of these geologic characteristics to inform higher resolution decision making for Li exploration, resource characterization, and direct Li extraction methods. These results demonstrate that reservoir-scale hydrogeologic features are an important control on Li resource quality and should be considered alongside regional brine evolution models during exploration and resource evaluation. Future research should focus on refining whole-rock geochemical and isotopic constraints for Alberta Basin Devonian shales and reservoir carbonates, to better quantify the role of shale composition and diagenetic processes in Li storage and release and present-day brine geochemistry. Subsequent work developing reactive transport models of basinal fluid flow would be highly valuable in verifying the role of reef-specific characteristics on Li enrichment and preservation.

CRediT authorship contribution statement

M.R. Blake: Visualization, Writing – original draft. **K.L. Butler:** Conceptualization, Supervision, Writing – review & editing. **L.A. Munk:** Conceptualization, Writing – review & editing. **D.F. Boutt:** Conceptualization, Writing – review & editing. **N. Morris:** Resources, Writing – review & editing. **J. Kennedy:** Resources, Writing – review & editing. **P. Saha:** Resources, Writing – review & editing. **J. Serotta:** Investigation, Writing – review & editing. **H. Tompkins:** Investigation, Writing – review & editing. **G. Williams:** Investigation, Writing – review & editing. **A. Vengosh:** Investigation, Writing – review & editing. **J. Evaristo:** Investigation, Writing – review & editing. **D.E. Ibarra:** Investigation, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apgeochem.2026.106973.

Data availability

The full dataset is available in Appendix A, Tables 1 and 2.

References

Ambrose, H., Kendall, A., 2020. Understanding the future of lithium: part 1, resource model. J. Ind. Ecol. 24, 80–89. https://doi.org/10.1111/jiec.12949.

Amthor, J.E., Mountjoy, E.W., Machel, H.G., 1993. Subsurface dolomites in Upper Devonian leduc formation buildups, central part of rimbey-meadowbrook reef trend, Alberta, Canada. Bull. Can. Petrol. Geol. 41, 164–185. https://doi.org/10.35767/gscpgbull.41.2.164.

Araoka, D., Kawahata, H., Takagi, T., Watanabe, Y., Nishimura, K., Nishio, Y., 2014. Lithium and strontium isotopic systematics in playas in Nevada, USA: constraints on the origin of lithium. Miner. Deposita 49, 371–379. https://doi.org/10.1007/s00126-013-0495-y.

Bachu, S., 1995. Synthesis and model of formation-water flow, Alberta basin, Canada. AAPG (Am. Assoc. Pet. Geol.) Bull. 79, 1159–1178. https://doi.org/10.1306/8D2B2209-171E-11D7-8645000102C1865D.

Bachu, S., Buschkuehle, M., Haug, K., Michael, K., 2008. Subsurface Characterization of the Edmonton-area acid-gas Injection Operations. Edmonton, Alberta.

Bibienne, T., Magnan, J.-F., Rupp, A., Laroche, N., 2020. From mine to mind and mobiles: society's increasing dependence on lithium. Elements 16, 265–270. https://doi.org/10.2138/gselements.16.4.265.

Bishop, B.A., Robbins, L.J., 2025. Overview of brine-hosted lithium mineral resources, distribution, and genesis in the Western Canada sedimentary basin. The Canadian Journal of Mineralogy and Petrology. https://doi.org/10.3749/2400035.

Bohlin, M.S., Misra, S., Lloyd, N., Elderfield, H., Bickle, M.J., 2018. High-precision determination of lithium and magnesium isotopes utilising single column separation and multi-collector inductively coupled plasma mass spectrometry. Rapid Commun. Mass Spectrom. 32, 93–104. https://doi.org/10.1002/rcm.8020.

Burke, W.H., Denison, R.E., Hetherington, E.A., Koepnick, R.B., Nelson, H.F., Otto, J.B., 1982. Variation of seawater 87Sr/86Sr throughout Phanerozoic time. Geology 10, 516–519. https://doi.org/10.1130/0091-7613(1982)10%253C516:VOSSTP%253E2.0.CO;2.

Buschkuehle, B.E., Machel, H.G., 2002. Diagenesis and paleofluid flow in the Devonian southesk-cairn carbonate complex in Alberta, Canada. Marine and Petroleum Geology, Origin, Characterization and Significance of Fluids in Sedimentary Basins 19, 219–227. https://doi.org/10.1016/S0264-8172(02)00014-4.

Butler, K.L., Munk, L.A., Boutt, D.F., Morris, N., Kennedy, J., Saha, P., Blake, M.R., Custado, M.J., Ibarra, D.E., 2025. The origin and enrichment of sedimentary basin lithium brines: a case study from the Upper Devonian leduc formation, Alberta basin, Canada. Econ. Geol. 120, 649–662. https://doi.org/10.5382/econgeo.5151.

Carpenter, S.J., Lohmann, K.C., Holden, P., Walter, L.M., Huston, T.J., Halliday, A.N., 1991. δ18O values, 87Sr86Sr and Sr/Mg ratios of late Devonian abiotic marine calcite: implications for the composition of ancient seawater. Geochem. Cosmochim. Acta 55, 1991–2010. https://doi.org/10.1016/0016-7037(91)90038-7.

Chan, L.-H., Starinsky, A., Katz, A., 2002. The behavior of lithium and its isotopes in oilfield brines: evidence from the heletz-kokhav field, Israel. Geochem. Cosmochim. Acta 66, 615–623. https://doi.org/10.1016/S0016-7037(01)00800-6.

Chan, L.H., Edmond, J.M., Thompson, G., Gillis, K., 1992. Lithium isotopic composition of submarine basalts: implications for the lithium cycle in the oceans. Earth Planet Sci. Lett. 108, 151–160. https://doi.org/10.1016/0012-821X(92)90067-6.

Connolly, C.A., Walter, L.M., Baadsgaard, H., Longstaffe, F.J., 1990a. Origin and evolution of formation waters, Alberta basin, Western Canada sedimentary basin. I. Chemistry. Applied Geochemistry 5, 375–395. https://doi.org/10.1016/0883-2927(90)90016-X.

Connolly, C.A., Walter, L.M., Baadsgaard, H., Longstaffe, F.J., 1990b. Origin and evolution of formation waters, Alberta basin, Western Canada sedimentary basin. II. Isotope systematics and water mixing. Appl. Geochem. 5, 397–413. https://doi.org/10.1016/0883-2927(90)90017-Y.

Day, C.C., Pogge von Strandmann, P.A.E., Mason, A.J., 2021. Lithium isotopes and partition coefficients in inorganic carbonates: proxy calibration for weathering reconstruction. Geochem. Cosmochim. Acta 305, 243–262. https://doi.org/10.1016/j.gca.2021.02.037.

Drever, J.I., 1988. The Geochemistry of Natural Waters, second ed. Prentice Hall, Englewood Cliffs, New Jersey.

Dugamin, E.J.M., Richard, A., Cathelineau, M., Boiron, M.-C., Despinois, F., Brisset, A., 2021. Groundwater in sedimentary basins as potential lithium resource: a global prospective study. Sci. Rep. 11, 21091. https://doi.org/10.1038/s41598-021-99912-7.

E3 Lithium Limited, 2024. The Future of Canadian Lithium.

Eberl, D.D., 1993. Three zones for illite formation during burial diagenesis and metamorphism. Clays Clay Miner. 41, 26–37. https://doi.org/10.1346/CCMN.1993.0410103.

Eccles, D.R., 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), ERCB/AGS Open File Report 2011. Energy Resources Conservation Board.

Eccles, D.R., Jean, G.M., 2013. Lithium Groundwater and Formation-Water Geochemical Data.

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. Math. Geosci. 45, 87–101. https://doi.org/10.1007/s11004-012-9436-z.

Faure, G., 1997. Principles and Applications of Geochemistry. Pearson, Upper Saddle River, N.J.

Fontes, J.Ch, Matray, J.M., 1993. Geochemistry and origin of formation brines from the paris basin, France: 2. Saline solutions associated with oil fields. Chem. Geol. 109, 177–200. https://doi.org/10.1016/0009-2541(93)90069-U.

Foster, G.L., Pogge von Strandmann, P.a.E., Rae, J.W.B., 2010. Boron and magnesium isotopic composition of seawater. G-cubed 11. https://doi.org/10.1029/2010GC003201.

Fulton, R.J., Fenton, M.M., Rutter, N.W., 1986. Summary of Quaternary stratigraphy and history, Western Canada. Quat. Sci. Rev. 5, 229–241. https://doi.org/10.1016/0277-3791(86)90189-7.

Gat, J.R., 1996. Oxygen and hydrogen isotopes in the hydrologic cycle. Annu. Rev. Earth Planet Sci. 24, 225–262. https://doi.org/10.1146/annurev.earth.24.1.225.

Green, D.G., Mountjoy, E.W., 2005. Fault and conduit controlled burial dolomitization of the Devonian west-central Alberta deep basin. Bull. Can. Petrol. Geol. 53, 101–129. https://doi.org/10.2113/53.2.101.

Gupta, I., Wilson, A.M., Rostron, B.J., 2012. Cl/Br compositions as indicators of the origin of brines: hydrogeologic simulations of the Alberta basin, Canada. GSA Bulletin 124 (1), 200–212. https://doi.org/10.1130/B30252.

Gupta, I., Wilson, A.M., Rostron, B.J., 2015. Groundwater age, brine migration, and large-scale solute transport in the Alberta basin, Canada. Geofluids 15, 608–620. https://doi.org/10.1111/gfl.12131.

Hitchon, B., Underschultz, J.R., Bachu, S., 1993. Industrial Mineral Potential of Alberta Formation Waters (No. OFR 1993-15), ARC/AGS Open File Report 1993. Alberta Research Council.

Holland, H.D., 1984. The chemical evolution of the atmosphere and oceans. Princeton Series in Geochemistry. Princeton University Press, Princeton, New Jersey.

Horita, J., Weinberg, A., Das, N., Holland, H.D., 1996. Brine inclusions in halite and the origin of the middle Devonian prairie evaporites of Western Canada. J. Sediment. Res. 66, 956–964. https://doi.org/10.1306/D4268450-2B26-11D7-8648000102C1865D.

Huff, G.F., 2016. Evolution of Li-enriched oilfield brines in Devonian carbonates of the south-central Alberta basin, Canada. Bull. Can. Petrol. Geol. 64, 438–448. https://doi.org/10.2113/gscpgbull.64.3.438.

Huff, G.F., 2019. Origin and Li-Enrichment of Selected Oilfield Brines in the Alberta Basin, Canada (No. OFR 2019-01), AER/AGS Open File Report 2019. Alberta Geological Survey/Alberta Energy Regulator.

Huff, G.F., Bechtel, D.J., Stewart, S.A., Brock, E., Heikkinen, C., 2012. Water Geochemical Data, Saline Aquifer Project, 2011, ERCB/AGS Digital Dataset 2012. Energy Resources Conservation Board.

Huff, G.F., Lopez, G.P., Weiss, J.A., 2019. Water Geochemistry of Selected Formation Brines in the Alberta Basin, Canada (Tabular Data, tab-delimited Format) (No. DIG 2019-0002), AER/AGS Digital Data 2019. Alberta Energy Regulator/Alberta Geological Survey.

Huff, G.F., Stewart, S.A., Riddell, J.T.F., Chisholm, S., 2011. Water Geochemical Data, Saline Aquifer Project, ERCB/AGS Digital Dataset 2011. Energy Resources Conservation Board.

IEA, 2023. Critical Minerals Market Review [WWW Document], 2023. . IEA. URL. https://www.iea.org/reports/critical-minerals-market-review-2023. accessed 2.12.26.

Kalderon-Asael, B., Katchinoff, J.A.R., Planavsky, N.J., Hood, A. v S., Dellinger, M., Bellefroid, E.J., Jones, D.S., Hofmann, A., Ossa, F.O., Macdonald, F.A., Wang, C., Isson, T.T., Murphy, J.G., Higgins, J.A., West, A.J., Wallace, M.W., Asael, D., Pogge von Strandmann, P.A.E., 2021. A lithium-isotope perspective on the evolution of carbon and silicon cycles. Nature 595, 394–398. https://doi.org/10.1038/s41586-021-03612-1.

Ketris, M.P., Yudovich, YaE., 2009. Estimations of clarkes for carbonaceous biolithes: world averages for trace element contents in Black shales and coals. Int. J. Coal Geol. 78, 135–148. https://doi.org/10.1016/j.coal.2009.01.002.

Kharaka, Y.K., Hanor, J.S., 2003. Deep fluids in the continents: I. Sedimentary basins. Treatise on geochemistry 5, 605.

Knauth, L.P., Beeunas, M.A., 1986. Isotope geochemistry of fluid inclusions in Permian halite with implications for the isotopic history of ocean water and the origin of saline formation waters. Geochem. Cosmochim. Acta 50, 419–433. https://doi.org/10.1016/0016-7037(86)90195-X.

Lazowski, C.N., Kalderon-Asael, B., Asael, D., Arizaleta, M.L., Melnyk, S., Wilson, S., Alessi, D.S., Planavsky, N.J., Konhauser, K.O., Gingras, M.K., 2025. Lithium isotopes of the peace river arch in the Western Canada sedimentary basin: a framework for resolving deep basin lithium sources. GSA Bulletin 137 (1), 4993–5008. https://doi.org/10.1130/B38102.

Lee, S.-G., Ko, K.-S., 2023. Development of an analytical method for accurate and precise determination of rare Earth element concentrations in geological materials using an MC-ICP-MS and group separation. Front. Chem. 10. https://doi.org/10.3389/fchem.2022.906160.

Leslie, D., Berry Lyons, W., Warner, N., Vengosh, A., Olesik, J., Welch, K., Deuerling, K., 2014. Boron isotopic geochemistry of the McMurdo dry valley lakes, Antarctica. Chem. Geol. 386, 152–164. https://doi.org/10.1016/j.chemgeo.2014.08.016.

Li, X., Han, G., Zhang, Q., Qu, R., Miao, Z., 2022. Accurate lithium isotopic analysis of twenty geological reference materials by multi-collector inductively coupled plasma mass spectrometry. Spectrochim. Acta B Atom Spectrosc. 188, 106348. https://doi.org/10.1016/j.sab.2021.106348.

Li, W., Liu, X.-M., 2022. Mineralogy and fluid chemistry controls on lithium isotope fractionation during clay adsorption. Sci. Total Environ. 851, 158138. https://doi.org/10.1016/j.scitotenv.2022.158138.

Machel, H.G., Cavell, P.A., Patey, K.S., 1996. Isotopic evidence for carbonate cementation and recrystallization, and for tectonic expulsion of fluids into the Western Canada sedimentary basin. GSA Bulletin 108 (2), 1108–1119. https://doi.org/10.1130/0016-7606(1996)108%253C1108:IEFCCA%253E2.3.CO.

Machel, H.G., Cavell, P.A., 1999. Low-flux, tectonically-induced squeegee fluid flow ("hot flash") into the rocky Mountain foreland basin. Bull. Can. Petrol. Geol. 47, 510–533. https://doi.org/10.35767/gscpgbull.47.4.510.

Macpherson, G.L., Capo, R.C., Stewart, B.W., Phan, T.T., Schroeder, K., Hammack, R.W., 2014. Temperature-dependent li isotope ratios in appalachian Plateau and gulf Coast sedimentary basin saline water. Geofluids 14, 419–429. https://doi.org/10.1111/gfl.12084.

Mallick, J., Shukla, A., Panda, S.K., Manglam, M.K., Biswal, S.K., Pradhan, L.K., Kar, M., 2023. Enhanced ferroelectricity and electrocaloric effect of Sm modified BSTO with temperature stability near room temperature. J. Appl. Phys. 133, 064102. https://doi.org/10.1063/5.0131458.

Marriott, C.S., Henderson, G.M., Belshaw, N.S., Tudhope, A.W., 2004. Temperature dependence of δ7Li, δ44Ca and Li/Ca during growth of calcium carbonate. Earth Planet Sci. Lett. 222, 615–624. https://doi.org/10.1016/j.epsl.2004.02.031.

Marza, M., Ferguson, G., Thorson, J., Barton, I., Kim, J.-H., Ma, L., McIntosh, J., 2024. Geological controls on lithium production from basinal brines across North America. J. Geochem. Explor. 257, 107383. https://doi.org/10.1016/j.gexplo.2023.107383.

Meijer Drees, N.C., 1994. Devonian elk point group of the Western Canada sedimentary basin. In: Geological Atlas of the Western Canada Sedimentary Basin. Canadian Society of Petroleum Geologists, Alberta Research Council.

Millot, R., Guerrot, C., Vigier, N., 2004. Accurate and high-precision measurement of lithium isotopes in two reference materials by MC-ICP-MS. Geostand. Geoanal. Res. 28, 153–159. https://doi.org/10.1111/j.1751-908X.2004.tb01052.x.

Moriguti, T., Nakamura, E., 1998. Across-arc variation of li isotopes in lavas and implications for crust/mantle recycling at subduction zones. Earth Planet Sci. Lett. 163, 167–174. https://doi.org/10.1016/S0012-821X(98)00184-8.

Mossop, G.D., Shetsen, I., comp., n.d. Geological Atlas of the Western Canada Sedimentary Basin. Canadian Society of Petroleum Geologists and Alberta Research Council.

Mountjoy, E.W., Qing, H., McNutt, R.H., 1992. Strontium isotopic composition of Devonian dolomites, Western Canada sedimentary basin: significance of sources of dolomitizing fluids. Appl. Geochem. 7, 59–75. https://doi.org/10.1016/0883-2927(92)90015-U.

Muñoz, S., Jenckes, J., Ramos, E.J., Munk, L.A., Ibarra, D.E., 2024. Hydrologic and Landscape Controls on Rock Weathering Along a Glacial Gradient in South Central Alaska, USA. Journal of Geophysical Research: Earth Surface 129 (3), e2023JF007255. https://doi.org/10.1029/2023jf007255. https://agupubs.onlinelibrary.wiley.com/doi/10.1029/2023JF007255. (Accessed 2 March 2024).

Natural Resources Canada, 2022. Lithium facts [WWW Document]. URL. https://natural-resources.canada.ca/minerals-mining/mining-data-statistics-analysis/minerals-metals-facts/lithium-facts. accessed 2.12.26.

Newman, C.P., Walton-Day, K., Runkel, R.L., Wilkin, R.T., 2023. Mechanisms of water-rock interaction and implications for remediating flooded mine workings elucidated from environmental tracers, stable isotopes, and rare Earth elements. Appl. Geochem. 157, 105769. https://doi.org/10.1016/j.apgeochem.2023.105769.

Peng, H., Mayer, B., Harris, S., Krouse, H.R., 2004. A 10-yr record of stable isotope ratios of hydrogen and oxygen in precipitation at Calgary, Alberta, Canada. Tellus B 56, 147–159.

Phan, T.T., Capo, R.C., Stewart, B.W., Macpherson, G.L., Rowan, E.L., Hammack, R.W., 2016. Factors controlling Li concentration and isotopic composition in formation waters and host rocks of marcellus shale, appalachian basin. Chem. Geol. 420, 162–179. https://doi.org/10.1016/j.chemgeo.2015.11.003.

Pogge von Strandmann, P.A.E., Kasemann, S.A., Wimpenny, J.B., 2020. Lithium and lithium isotopes in Earth's surface cycles. Elements 16, 253–258. https://doi.org/10.2138/gselements.16.4.253.

Pogge von Strandmann, P.A.E., Schmidt, D.N., Planavsky, N.J., Wei, G., Jones, C.L.C., Baumann, K.-H., 2019. Assessing bulk carbonates as archives for seawater Li isotope ratios. Chem. Geol. 530, 119338. https://doi.org/10.1016/j.chemgeo.2019.119338.

Popp, B.N., Anderson, T.F., Sandberg, P.A., 1986. Textural, elemental, and isotopic variations among constituents in Middle Devonian limestones, North America. J. Sediment. Res. 56, 715–727. https://doi.org/10.1306/212F8A26-2B24-11D7-8648000102C1865D.

Price, R.A., 1981. The Cordilleran Foreland Thrust and Fold belt in the Southern Canadian Rocky Mountains, 9. Geological Society, London, Special Publications, pp. 427–448. https://doi.org/10.1144/GSL.SP.1981.009.01.39.

Qing, H., Mountjoy, E.W., 1994. Formation of coarsely crystalline, hydrothermal dolomite reservoirs in the Presqu'ile barrier, Western Canada sedimentary basin. AAPG (Am. Assoc. Pet. Geol.) Bull. 78, 55–77. https://doi.org/10.1306/BDFF9014-1718-11D7-8645000102C1865D.

Reimert, C., Lyster, S., Palombi, D., Bernal, N., 2025. Brine Geochemical Data, Mineral Mapping Program, 2021–2024 (Tabular Data, tab-delimited Format).

Ring, S.J., Henehan, M.J., Blukis, R., von Blanckenburg, F., 2025. Adsorption pathways of boron on clay and their implications for boron cycling on land and in the ocean. Geochem. Cosmochim. Acta 389, 74–83. https://doi.org/10.1016/j.gca.2024.08.014.

Romer, R.L., Meixner, A., Hahne, K., 2014. Lithium and boron isotopic composition of sedimentary rocks — the role of source history and depositional environment: a 250 Ma record from the Cadomian orogeny to the Variscan orogeny. Gondwana Res. 26, 1093–1110. https://doi.org/10.1016/j.gr.2013.08.015.

Sodagar, T.M., Lawton, D.D.C., 2009. Seismic modeling of fluid substitution in redwater reef, Alberta. CREWES Research Report.

Stacey, J., Hollis, C., Corlett, H., Koeshidayatullah, A., 2020. Burial dolomitization driven by modified seawater and basal aquifer-sourced brines: insights from the middle and Upper Devonian of the Western Canadian sedimentary basin. Basin Res. 33, 648–680. https://doi.org/10.1111/bre.12489.

Stoakes, F.A., 1979. Sea Level Control of carbonate-shale Deposition during Progradational basin-filling: the Upper Devonian Duvernay and Ireton Formations of Alberta. Canada. University of Calgary, Calgary, Canada. https://doi.org/10.11575/PRISM/19984.

Switzer, S.B., Holland, W.G., Christie, D.S., Graf, G.C., Hedinger, A.S., McAuley, R.J., Wierzbicki, R.A., Packard, J.J., 1994. Devonian woodbend-winterburn strata of the Alberta basin. In: Geological Atlas of the Western Canada Sedimentary Basin. Canadian Society of Petroleum Geologists, Alberta Research Council.

Taylor Jr., H.P., 1974. The application of oxygen and hydrogen isotope studies to problems of hydrothermal alteration and ore deposition. Econ. Geol. 69, 843–883. https://doi.org/10.2113/gsecongeo.69.6.843.

Teng, F.-Z., McDonough, W.F., Rudnick, R.L., Dalpé, C., Tomascak, P.B., Chappell, B.W., Gao, S., 2004. Lithium isotopic composition and concentration of the upper Continental crust. Geochem. Cosmochim. Acta 68, 4167–4178. https://doi.org/10.1016/j.gca.2004.03.031.

Tomascak, P.B., 2004. Developments in the understanding and application of lithium isotopes in the Earth and planetary sciences. Rev. Mineral. Geochem. 55, 153–195. https://doi.org/10.2138/gsrmg.55.1.153.

Underschultz, J.R., Yuan, L.P., Bachu, S., Cotterill, D.K., Hitchon, B., 1994. Industrial Mineral Resources in Alberta formation Waters, ARC/AGS. Alberta Research Council.

Geological Survey, U.S., 2023. Mineral commodity summaries 2023 (No. 2023). Mineral Commodity Summaries. U.S. Geological Survey. https://doi.org/10.3133/mcs2023.

Wang, Y.-Y., Liang, K., Xiao, Y., Chen, B., Shan, E., Yang, T., Zhang, M., Sun, H., Gu, H.-O., Tong, F., Fu, L., Li, D.-Y., Lu, Y., Qie, W., 2023. Carbonate lithium isotope systematics indicate cooling triggered mass extinction during the Frasnian-Famennian transition. Global Planet. Change 230, 104284. https://doi.org/10.1016/j.gloplacha.2023.104284.

Wendte, J.C., 1992. Overview of the Devonian of the Western Canada sedimentary basin. In: Wendte, J., Stoakes, F.A., Campbell, C.V. (Eds.), Devonian-Early Mississippian Carbonates of the Western Canada Sedimentary Basin: a Sequence Stratigraphic Framework. SEPM Society for Sedimentary Geology. https://doi.org/10.2110/scn.92.28.0001.

Williams, G.D.Z., Nativ, P., Vengosh, A., 2025. The role of boron in controlling the pH of lithium brines. Sci. Adv. 11. https://doi.org/10.1126/sciadv.adw3268.

Williams, L.B., Hervig, R.L., 2005. Lithium and boron isotopes in illite-smectite: the importance of crystal size. Geochem. Cosmochim. Acta 69, 5705–5716. https://doi.org/10.1016/j.gca.2005.08.005.

Wright, G.N., McMechan, M.E., Potter, D.S., 1994. Structure and architecture. In: Geological Atlas of the Western Canada Sedimentary Basin. Canadian Society of Petroleum Geologists and Alberta Research Council.

Yeghicheyan, D., Grinberg, P., Alleman, L.Y., Belhadj, M., Causse, L., Chmeleff, J., Cordier, L., Djouraev, I., Dumoulin, D., Dumont, J., Freydier, R., Mariot, H., Cloquet, C., Kumkrong, P., Malet, B., Jeandel, C., Marquet, A., Riotte, J., Tharaud, M., Billon, G., Trommetter, G., Séby, F., Guihou, A., Deschamps, P., Mester, Z., 2021. Collaborative determination of trace element mass fractions and isotope ratios in AQUA-1 drinking water certified reference material. Anal. Bioanal. Chem. 413, 4959–4978. https://doi.org/10.1007/s00216-021-03456-8.

Zhang, T., Lin, J., Zhu, X., Yang, A., Deng, K., Hu, Z., Liu, Y., 2025. Investigating the mechanism that reduces the memory effect of li on MC-ICP-MS. J. Anal. At. Spectrom. 40, 1220–1230. https://doi.org/10.1039/D5JA00031A.