

# **Geological Introduction to Lithium-Rich Formation Water with Emphasis on the Fox Creek Area of West-Central Alberta (NTS 83F and 83K)**

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## Abstract

The idea of a green mining operation—one that extracts minerals from waste oil-field water for eco-friendly products—is appealing. Devonian formation waters associated with producing oil and gas wells in the Fox Creek area of west-central Alberta contain up to 140 mg/L lithium. This value is significant considering the average and median values of lithium in Alberta formation waters are 10 mg/L and 0.2 mg/L, respectively (based on 1511 analyses). The high-lithium brines also contain elevated potassium (up to 8000 mg/L), boron (up to 270 mg/L) and bromine (up to 410 mg/L), such that industry is considering the feasibility of a multi-commodity extraction plant.

The occurrence of lithium in the world's oil-field waters is poorly understood and inadequately represented in the literature. The objectives of this report, therefore, are to illustrate where lithium-rich formation waters occur in Alberta and to understand the source environment, mobilization and transport of lithium and related minerals to form these unique brines. Major ion and Sr, Pb and Li isotopic geochemistry show Alberta's lithium-rich brines form prior to halite precipitation, lack a freshwater source and involve alteration of silicates (particularly Li- and K-bearing minerals).

In the Fox Creek area, viable lithium-source models should invoke direct mobilization of silicate-bearing fluids from either the crystalline basement or the immature siliciclastics deposited above the basement (basal Cambrian sandstone, Granite Wash or the Gilwood Member), to the Devonian Swan Hills, Leduc and Beaverhill Lake formation waters.

A number of thermal, potential-field and tectonic features in west-central Alberta are reviewed in this introductory investigation of lithium-rich oil-field waters that may one day become an economically viable resource for Alberta.

# 1 Introduction

Lithium is the lightest solid metal (atomic number of 3), is highly reactive (resembles sodium in its chemical behaviour), malleable (hardness of 0.6), and is a good conductor of heat and electricity. These properties contribute to its widely varying uses, including

- medical (e.g., mood-stabilizer, bipolar disorder treatment, preventing Alzheimer's disease),
- electrical (e.g., batteries, telecommunications),
- chemical (e.g., desiccants, polymerisation and organic synthesis),
- general engineering (e.g., high-temperature lubricants and soaps, flux for welding/soldering, CO<sub>2</sub> scale prevention),
- high strength-to-weight alloys (e.g., high-performance aircraft parts),
- optics (e.g., focal lenses, infrared and ultraviolet applications),
- rocketry (e.g., propellant),
- nuclear (e.g., fusion material in power plants and weaponry), and
- environmental (e.g., a substitute for environmentally unfriendly elements such as fluorine).

Perhaps most significantly, automobile manufacturers are on the verge of mass-producing electrical vehicles. Lithium-ion batteries represent a viable lightweight, durable power source for at least the first generation of eco-friendly vehicles. Subsequent demand has caused lithium commodity prices to surge and introduced speculation about whether sufficient volumes of lithium are available to sustain global Li-ion battery production (Evans, 2008, 2010).

Economic concentrations of lithium typically form in residual late-stage granitic pegmatite melts, and continental brine and clay (Garrett, 2004). In addition, some oil-field waters have moderate to high lithium content, including those found in the Devonian formations in the Williston Basin in North Dakota, the Jurassic Smackover Formation in the US Gulf Coast, and the Cretaceous reservoirs in Texas (e.g., Collins, 1976; Garrett, 2004). Exploration companies have recently expressed interest in the lithium potential of Alberta's oil-field waters. The awareness is largely due to a government study that reviewed nearly 130 000 chemical analyses of Cambrian to Triassic formation waters from the Alberta Basin, for economic industrial-mineral potential (Hitchon et al., 1993). These authors reported anomalous lithium concentrations of up to 140 mg/L\* in the Devonian carbonate buildups of the Fox Creek area in west-central Alberta (Table 1; Figure 1). The Li-rich oil-field waters occur in the Leduc (Woodbend Group) and Swan Hills (Beaverhill Lake Group) formations at depths of approximately 2500–3900 m below surface. Bachu et al. (1995) provided a historical (i.e., non-National Instrument 43-101 compliant) lithium resource estimate for the Swan Hills, Leduc and Beaverhill Lake formation waters of 515 000 t, over an area of 4000 km<sup>2</sup>.

During 2009 and 2010, at least three exploration companies reported high levels of lithium (up to 112 mg/L) from brine-sampling programs of producing wells in the Fox Creek area, confirming the presence of Li-rich formation waters in the area. In addition to lithium, these companies also reported elevated boron (223 mg/L), potassium (5870 mg/L) and bromine (412 mg/L), suggesting the potential for a multi-element separation plant.

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\* 1 mg/L equals 1 part per million

The Alberta Geological Survey obtained Li-rich and Li-poor formation waters from the Fox Creek area and conducted standard water geochemical, and Li, Pb and Sr isotopic analysis on the samples. Because the source, transportation and residence of lithium in oil-field waters is poorly understood and inadequately covered in the literature, our objective was to obtain Li-rich oil-field waters in Alberta, conduct a preliminary evaluation of the Fox Creek area brine geochemistry and provide some geological context for the origin and history of lithium in the formation waters of the Fox Creek area.

**Table 1. Summary of lithium in Cambrian to Triassic formation waters in west-central Alberta (Hitchon et al., 1993).**

<b>Stratigraphic Unit</b>	<b>Lithium Max (mg/L)</b>
Triassic	
Baldonnel Formation	60
Charlie Lake Formation	68
Halfway Formation	58
Montney Formation	60
Carboniferous-Mississippian	
Rundle Group	60
Banff Formation	52
Devonian	
Wabamun Group	115
Winterburn Group	90
Woodbend Group	140
Beaverhill Lake Group	130
Watt Mountain Formation	98
Keg River Formation	95
Lower Elk Point Group	71
Cambrian	81

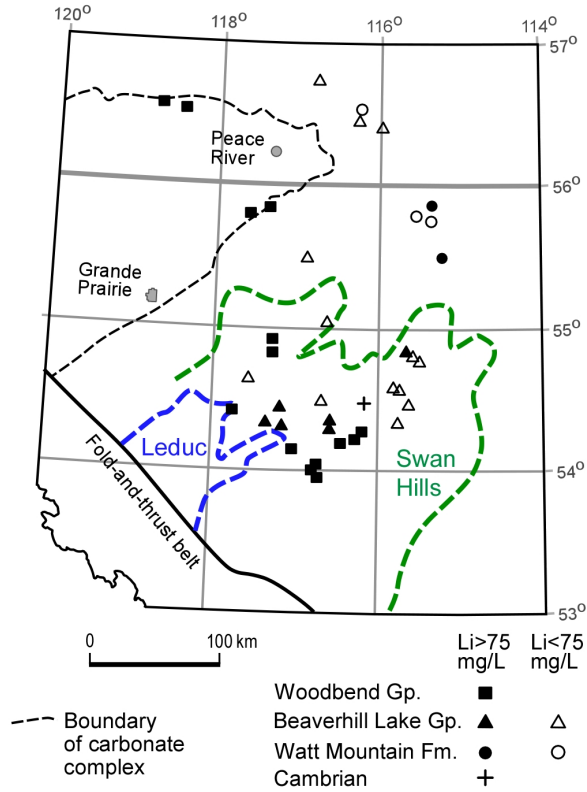
## 2 Theory of Lithium Origin and Host Environments

The estimated average Li content of the Earth's upper crust is between 7 and 70 ppm (Bach et al., 1967; Vine, 1980; Deberitz, 1993; Kamienski et al., 1995). Economic concentrations of lithium are known to form in either endogenous (e.g., granitic pegmatites) or exogenous (e.g., salt flats, brine and clay) environments (Garrett, 2004). Although these host environments differ in most aspects, they both form under conditions that permit slow development, a commonality that promotes lithium accumulation because it is more soluble than most other cations. Thus, when liberated and mobilized into a slow-forming system, lithium can concentrate after the fractionation or precipitation of less-soluble elements to form an economic deposit.

Before this process occurs, however, the lithium must be derived from a source. Lithium occurs in a variety of rock types, brines and waters, but usually at low concentration (Garrett, 2004). Deberitz (1993) documented at least 145 different minerals containing >0.002% Li<sub>2</sub>O and 25 minerals with >2% Li<sub>2</sub>O. Spodumene (LiAlSi<sub>2</sub>O<sub>6</sub>), lepidolite (lithium mica, K[Li,Al]<sub>3</sub>[Si,Al]<sub>4</sub>O<sub>10</sub>[F,OH]<sub>2</sub>), petalite (LiAlSi<sub>4</sub>O<sub>10</sub>) and amblygonite (LiAlPO<sub>4</sub>[F,OH]) are the most common lithium minerals.



a)



b)

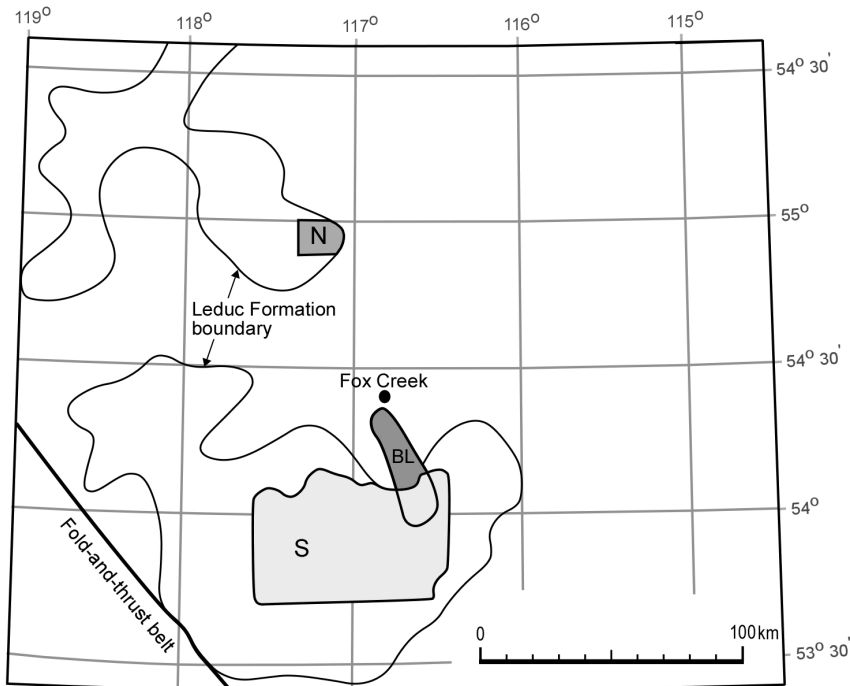


Figure 1. Government data from the mid-1990s depicting the lithium potential of west-central Alberta: a) distribution of lithium in formation water associated with the Leduc and Swan Hills carbonate complexes (modified from Hitchon et al., 1993); b) estimated areas of producible lithium formation water in the Leduc Formation (N, North; S, South) and the Beaverhill Lake Group (BL) strata (Bachu et al., 1995).

Granitic pegmatite provides the greatest abundance of lithium-containing minerals, with spodumene and petalite being the most commercially viable sources (Kamienski et al., 1995). Lithium-rich pegmatite is thought to be formed when pegmatite magma migrates upward through and interacts with its host granitic rock. Initial crystallization of the flowing magma subsequently results in the precipitation of less soluble compounds (Fe- and Mn-silicates), leaving a residual fractionated granitic-type melt characterized by more soluble and lower-melting lithium silicate.

The origin of continental brine deposits formed in exogenous environments remains speculative. Lithium may be introduced via high-lithium geothermal springs that flow into and mix with seawater in a closed, volcanically active basin. Geothermal and/or volcanic associations are the favoured mechanisms for introducing lithium into continental basins because lithium-rich brines often exist in areas of volcanic activity (e.g., Imperial Valley, California; Reykjanes field, Iceland; Taupo Volcanic Zone, New Zealand). The lithium deposit at the Silver Peak mine (Chemetall Foote Corp.) in Clayton Valley, Nevada, likely formed sequentially through Pliocene volcanism, Sierra Nevada Pleistocene uplift, water-rock interaction and runoff, formation of temporary lakes and, finally, evaporation and concentration of impurities such as lithium during interpluvial periods. This process epitomizes the exogenous liberation, mobilization and concentration of lithium in slow-forming systems. Similarly, potash, which forms by evaporation of seawater in a restricted basin, acquires lithium when there is a geothermal or volcanic contribution to the basin. Some examples of continental brine deposits that have lithium enrichment include Russia's Angara-Lena Basin (1600–1900 ppm Li), Utah's Paradox Basin (66–173 ppm Li), Michigan's Sylvania Formation (66–173 ppm Li) and northern England's Zechstein Formation (7–65 ppm Li; Garrett, 2004).

Another potential source of exogenous lithium is magnesium- and lithium-bearing silicate clay (hectorite,  $\text{Na}_{0.3}[\text{Mg},\text{Li}]_3\text{Si}_4\text{O}_{10}[\text{F},\text{OH}]_2$ ). The type locality for hectorite is at Hector, California, which is 120 km east of a large geothermal spring–formed borax deposit at Boron. Hectorite is a trioctahedral smectite clay, derived from volcanic tuff and ash, in which lithium is substituted for magnesium in the lattice (Deer et al., 1962). It is often associated with hot spring activity (e.g., Higashi et al., 2007). Smaller occurrences of hectorite have also been found in Nevada, Arizona, New Mexico and Montana.

The least understood potential source of lithium occurs within some of the world's oil-field waters, which contain moderate to high lithium concentrations. Lithium enrichment of oil-field brines and saline formation waters is known to occur worldwide in sedimentary basins of various age, including the Cambrian Siberian Platform, Russia (Shouakar-Stash et al., 2007); Devonian Michigan Basin (Wilson and Long, 1993); Mississippian–Pennsylvanian reservoirs of the Illinois Basin (Stueber et al., 1993); Pennsylvanian Paradox Basin, Utah (Garrett, 2004); Triassic strata of the Paris Basin, France (Fontes and Matray, 1993); and Jurassic basal strata from the Gulf Coast, Arkansas and Texas (Moldovanyi et al., 1993). The Smackover oil-field brines in the US Gulf Coast have localized zones of high-Na and CaCl that contain up to 572 ppm Li, with the Texas and Arkansas brines averaging 386 and 365 ppm Li, respectively (Collins, 1976; Garrett, 2004).

The source of lithium in oil-field waters remains subject to debate. Most explanations generally conform with models proposed for Li-rich brine solutions that include recycling of earlier deposits/salars, mixing with pre-existing subsurface brines, weathering of volcanic and/or basement rocks, and mobilizing fluids associated with hydrothermal volcanic activity (e.g., Garret, 2004). However, none of these hypotheses has identified the ultimate source for the anomalous values of Li in oil-field waters. In a comprehensive investigation of Li-isotope and elemental data from Li-rich oil-field brines in Israel, Chan et al. (2002) suggested that these brines evolved from seawater through a process of mineral reactions, evaporation and dilution. In this case, brines that were isotopically lighter than seawater were associated with lithium mobilized from sediment.

### 3 Identification of a Lithium Anomaly in Formation Water in West-Central Alberta

Hitchon et al. (1993) reviewed a dataset comprising nearly 130 000 formation-water analyses from the Alberta Basin for potential economic industrial-mineral interest. The study identified anomalously high values of certain elements in the Devonian strata of Alberta, including

- Ca, Mg, K and Br in the Lower Elk Point Group of northern Alberta;
- Ca, Mg, K and Br in the Beaverhill Lake Group of southern Alberta; and
- Li in Devonian carbonate complexes of west-central Alberta.

In the Fox Creek area of west-central Alberta, Hitchon et al. (1993) identified Li above the detailed exploration threshold (75 mg/L) in 16 samples (to a maximum of 140 mg/L; Figure 1). The Li-rich formation waters appear to be associated with carbonate buildups in the Leduc Formation of the Woodbend Group and the Swan Hills Formation of the Beaverhill Lake Group. The Woodbend Group carbonates, including the Leduc and Cooking Lake formations, reach thicknesses of >300 m, whereas the Beaverhill Lake carbonate platform varies in thickness from >150 m in the southern reef portion to 50 m in the northwest. However, in the Fox Creek area, the carbonate platform of the Cooking Lake Formation and the reefs of the Leduc Formation directly overlie the Beaverhill Lake Group carbonates, such that differentiating between the various formation waters is difficult. Nevertheless, Hitchon et al. (1993) suggested that lithium is of potential economic interest in the formation waters of the Woodbend aquifers (found at the Sturgeon Lake South, Bonnie Glen and Homeglen-Rimbey fields), with particularly high concentrations associated with the Windfall–Swan Hills carbonate complexes.

Further modelling by Underschultz et al. (1994) depicted two areas of ‘significant lithium resources’ corresponding to areas of thickened Leduc strata. These authors suggested that the geographic extent of Li-rich formation water in west-central Alberta covers approximately 75 000 km<sup>2</sup> at prospective depths between 2700 and 4000 m. Based on Li concentrations and rock properties (porosity and permeability), Bachu et al. (1995) identified three areas with potential for economic Li extraction: northern Leduc reef (N), southern Leduc reef (S), and Beaverhill Lake Group strata (BL; Figure 1b). These authors suggest the potentially productive interval in the

- northern Leduc reef (N) has an average thickness of 12 m, an average porosity of 6% and an average permeability of  $3.5 \times 10^{-14}$  m<sup>2</sup> (35 mD);
- southern Leduc reef (S) has an average thickness of 25 m, an average porosity of 6% and an average permeability of  $2 \times 10^{-14}$  m<sup>2</sup> (20 mD); and
- Beaverhill Lake Group (BL) has an average thickness of 46 m, an average porosity of 7% and an average permeability of  $4.3 \times 10^{-14}$  m<sup>2</sup> (43 mD).

Bachu et al. (1995) calculated resource estimates by multiplying the concentration of any element by the thickness and porosity of the host stratum. Their estimates are deemed historical, or resource estimates that are not compliant with National Instrument 43-101. The estimates of potentially economic lithium vary between 10 and 570 g/m<sup>2</sup> (t/km<sup>2</sup>) in the Leduc reef (S) area, and between 34 and 340 g/m<sup>2</sup> (t/km<sup>2</sup>) in the northern Leduc reef (N) area (Bachu et al., 1995). Resource estimates for lithium in the Beaverhill Lake (BL) water vary between 11 and 918 g/m<sup>2</sup> (t/km<sup>2</sup>). The high variability of Bachu et al. (1995) estimates is related to the variability of the rock properties in the reef complexes. Nevertheless, they provided a lithium resource estimate of 515 000 tonnes for Leduc and Beaverhill Lake formation waters in west-central Alberta. This estimate covers a cumulative area of 3980 km<sup>2</sup>, representing about  $2 \times 10^{-6}$  (or 0.0002%) of the host-rock mass.

## 4 Revised Distribution Map of Lithium-Rich Formation Water

To enable mineral exploration companies working in Alberta, presently and in the future, to better evaluate their targets and characterize resource estimates, Eccles and Jean (2010) released a geochemical dataset of lithium-bearing ground and formation water. In total, there are 1511 records. A revised distribution map of lithium-rich formation water was created by analyzing the Eccles and Jean (2010) dataset with the surface representation grid module from VIEWLOG 3.0 software by Earthfx Inc.

We used the full kriging interpolation algorithm to provide an unbiased estimate, minimize overall estimation variance, and to allow us to examine the spatial variability of the data to determine the best-fit variogram. A reasonably good match between theoretical and experimental variograms was achieved using fit options that included a maximum distance of 100 000 with the number of intervals set to 20, such that between 0 and 100 000, there are 20 intervals or lag distances. To better fit an idealized curve through the data, semivariogram parameters were defined with nugget (0.01), sill (0.13) and range (130 000). We investigated both culled (data verified for quality assessment based on the culling criteria of Hitchon and Brulotte, 1994) and non-culled data. Because there were no discernible changes in the outcome of the data presentation, the gridding process included both culled and non-culled data.

Of the 1511 records, the average and median lithium values are 10 and 0.2 mg/L, respectively, providing a background estimate that demonstrates the uniqueness of elevated lithium formation waters in west-central Alberta. Forty-eight records have >75 mg/L Li; higher lithium values are dispersed predominantly through west-central to northwestern Alberta (Table 2). Not surprisingly, Figure 2 confirms the area of anomalous lithium formation water depicted originally by Hitchon et al. (1993) in the Fox Creek area of west-central Alberta. This anomaly comprises the largest concentration of high-lithium formation water values in Alberta, with over 21 analyses having >75 mg/L and 8 analyses having >100 mg/L Li (up to 140 mg/L). The Fox Creek lithium anomaly encompasses most of the southern half of NTS 83K and the northernmost part of 83F, and occurs at depths that place the waters within strata of the Middle to Late Devonian Beaverhill Lake, Woodbend and Winterburn groups. The Li-rich waters also contain elevated potassium (up to 8000 mg/L) and boron (270 mg/L) confirming industries perception that these wells contain other extractable elements, potentially of economic value.

The second largest geographic area of elevated lithium values is in the central part of NTS 83O and southernmost part of 84B. This area, which is north of Lesser Slave Lake in the Utikuma Uplands, includes 23 analyses from Li formation water in the Elk Point and Beaverhill Lake groups, with two analyses having >70 mg/L Li and one value having 95 mg/L. Other minor concentrations of Li-rich formation water include isolated occurrences in the Peace River Arch area (NTS 83M, 83N and 84D) and in south-central Alberta (NTS 82P, 83A and 83B). The Peace River Arch area includes approximately 65 water analyses with 4 samples having values >75 mg/L Li, including samples in the Woodbend and Winterburn groups with up to 96 mg/L Li. The south-central cluster of anomalous Li-rich water occurs in the Woodbend and Winterburn groups, and includes 16 analyses with >75 mg/L Li, 8 analyses with >100 mg/L, and some analyses with values of up to 140 mg/L Li. The south-central cluster has high-lithium values similar to the Fox Creek anomaly and covers a larger geographic area.

Table 2. Alberta formation waters with lithium values >75 mg/L (from Eccles and Jean, 2010).

AGS Site ID	Dataset <sup>1</sup>	Location <sup>2</sup>			Ground Elevation (m asl)	Kelly Bushing Elevation (m asl)	Sample Depth <sup>3</sup>				Culled Status <sup>4</sup>	Cation-Anion Balance	Lithium (mg/L)	Formation Name <sup>5</sup>
		Well ID	Latitude	Longitude			Top (m asl)	Bottom (m asl)	Top (m)	Bottom (m)				
57948	AGSWDB	00/11-14-042-02W5-0	52.620122	-114.183919	900.7	904.6	-1479.5	-1482.3	2384.1	2386.9	No	-0.015311	140	Woodbend Gp.
66141	AGSWDB	00/05-21-047-27W4-0	53.066504	-113.900835	846.4	850.1	-1292.6	-1294.5	2142.7	2144.6	No	-0.008968	140	Woodbend Gp.
104497	AGSWDB	00/13-27-068-22W5-0	54.921378	-117.277563	672.1	676.0	-1929.4	-1935.5	2605.4	2611.5	No	-0.004446	140	Winterburn Gp.
53964	AGSWDB	00/13-21-040-24W4-0	52.461494	-113.408228	892.5	894.3	-1019.8	-1020.8	1914.1	1915.1	No	-0.018250	135	Winterburn Gp.
36913	AGSWDB	00/11-14-028-25W4-0	51.397312	-113.420484	923.8	927.8	40.8	31.7	887.0	896.1	Yes	0.018106	130	n/a
51416	AGSWDB	00/02-22-039-21W4-0	52.363495	-112.938422	813.2	817.2	-900.7	-912.5	1717.9	1729.7	Yes	0.016712	130	Woodbend Gp.
93742	AGSWDB	00/14-14-060-17W5-0	54.195694	-116.438929	841.2	846.1	-1811.1	-1819.4	2657.2	2665.5	Yes	-0.032922	130	Woodbend Gp.
95839	AGSWDB	00/10-13-062-18W5-0	54.363791	-116.561507	873.6	879.4	-2197.6	-2225.0	3077.0	3104.4	No	-0.014845	130	Beaverhill Lake Fm.
42113	AGSWDB	00/13-24-033-26W4-0	51.850832	-113.568684	964.4	968.7	-1310.9	-1311.8	2279.6	2280.5	No	-0.015004	120	Woodbend Gp.
92004	AGSWDB	00/02-10-058-19W5-0	53.993493	-116.735110	1222.9	1226.5	-2250.7	-2231.8	3477.2	3458.3	Yes	-0.012735	120	Winterburn Gp.
92921	AGSWDB	02/11-36-059-21W5-0	54.145639	-117.014931	1021.4	1027.0	-2298.4	-2345.6	3325.4	3372.6	Yes	-0.001763	120	Woodbend Gp.
96055	AGSWDB	00/07-11-062-23W5-0	54.346071	-117.333820	1001.0	1005.2	-2618.9	-2633.5	3624.1	3638.7	Yes	0.045338	118	Woodbend Gp.
94938	AGSWDB	00/07-36-061-18W5-0	54.317010	-116.558730	876.0	880.6	-2215.3	-2228.4	3095.9	3109.0	Yes	-0.005946	115	Beaverhill Lake Fm.
109007	AGSWDB	00/04-28-074-02W6-0	55.433365	-118.254909	633.7	637.9	-2032.1	-2048.9	2670.0	2686.8	No	-0.063851	115	Wabamun Gp.
90822	AGSWDB	00/10-23-057-19W5-0	53.942913	-116.710982	1133.2	1137.5	-2259.8	-2280.2	3397.3	3417.7	Yes	0.006507	100	Woodbend Gp.
112065	AGSWDB	00/01-16-079-22W5-0	55.841676	-117.371475	576.7	580.9	-1473.5	-1475.0	2054.4	2055.9	No	-0.001142	100	Winterburn Gp.
110084	AGSWDB	00/08-27-076-08W5-0	55.611848	-115.145462	677.0	681.2	-1106.8	-1129.3	1788.0	1810.5	Yes	0.004239	98	n/a
92014	AGSWDB	00/16-22-058-19W5-0	54.033290	-116.732016	1035.4	1040.3	-2307.9	-2339.9	3348.2	3380.2	No	-0.000465	97	Woodbend Gp.
117051	AGSWDB	00/07-21-087-05W6-0	56.556875	-118.729399	719.6	723.6	-1402.4	-1420.4	2126.0	2144.0	No	0.000392	96	Winterburn Gp.
112055	AGSWDB	00/11-09-079-22W5-0	55.834706	-117.385181	571.8	575.8	-1182.9	-1192.0	1758.7	1767.8	Yes	-0.003886	95	Wabamun Gp.
113503	AGSWDB	00/02-24-081-10W5-0	56.030755	-115.419885	653.5	658.1	-1078.7	-1082.9	1736.8	1741.0	Yes	0.000074	95	n/a
128853	AGSWDB	00/11-25-116-06W6-0	59.104510	-118.872412	388.0	392.3	-1092.1	-1095.7	1484.4	1488.0	No	-0.010672	95	Keg River Fm.
111331	AGSWDB	00/07-35-078-24W5-0	55.800535	-117.605451	472.7	477.0	-1384.4	-1473.7	1861.4	1950.7	Yes	-0.075000	94	Wabamun Gp.
97206	AGSWDB	00/10-18-063-21W5-0	54.453469	-117.159623	827.2	831.8	-2473.5	-2485.6	3305.3	3317.4	Yes	0.008089	93	Beaverhill Lake Fm.
62971	AGSWDB	00/10-36-045-05W5-0	52.926574	-114.588935	924.2	927.8	-1490.8	-1547.2	2418.6	2475.0	Yes	-0.028836	90	Winterburn Gp.

AGS Site ID	Dataset <sup>1</sup>	Location <sup>2</sup>			Ground Elevation (m asl)	Kelly Bushing Elevation (m asl)	Sample Depth <sup>3</sup>				Culled Status <sup>4</sup>	Cation-Anion Balance	Lithium (mg/L)	Formation Name <sup>5</sup>
		Well ID	Latitude	Longitude			Top (m asl)	Bottom (m asl)	Top (m)	Bottom (m)				
112933	AGSWDB	00/07-30-080-11W6-0	55.960843	-119.705266	660.2	666.0	-2586.8	-2638.0	3252.8	3304.0	Yes	-0.001866	89	Wabamun Gp.
93729	AGSWDB	00/15-25-060-16W5-0	54.222957	-116.260846	810.2	814.4	-1765.1	-1768.8	2579.5	2583.2	No	-0.017455	86	Winterburn Gp.
50334	AGSWDB	00/10-08-038-03W5-0	52.256285	-114.390057	947.6	951.9	-1816.3	-1831.5	2768.2	2783.4	No	-0.025231	85	Winterburn Gp.
62920	AGSWDB	00/07-08-045-04W5-0	52.862944	-114.541468	998.2	1002.8	-1504.2	-1519.4	2507.0	2522.2	No	-0.008095	85	Winterburn Gp.
103513	AGSWDB	00/14-24-067-19W5-0	54.819059	-116.763958	763.2	767.5	-1497.2	-1536.2	2264.7	2303.7	Yes	0.023190	84	Winterburn Gp.
103550	AGSWDB	00/07-27-067-22W5-0	54.826875	-117.266683	672.4	676.4	-1977.8	-1979.0	2654.2	2655.4	No	0.012438	84	Winterburn Gp.
103416	AGSWDB	00/10-32-067-11W5-0	54.845891	-115.636088	1114.0	1118.0	-1510.9	-1582.5	2628.9	2700.5	Yes	0.016701	83	Beaverhill Lake Fm.
114166	AGSWDB	00/11-29-082-05W6-0	56.141087	-118.749844	624.5	627.9	-1504.5	-1506.3	2132.4	2134.2	Yes	-0.009318	83	n/a
94864	AGSWDB	00/15-17-061-15W5-0	54.280913	-116.208906	856.5	861.7	-1873.9	-1885.8	2735.6	2747.5	No	0.009597	82	Woodbend Gp.
97250	AGSWDB	00/12-05-063-25W5-0	54.423358	-117.754093	879.0	883.3	-2651.8	-2659.4	3535.1	3542.7	Yes	-0.007730	82	Woodbend Gp.
98349	AGSWDB	00/10-33-064-12W5-0	54.583796	-115.748866	999.4	1003.7	-1692.6	-1727.3	2696.3	2731.0	No	-0.001282	82	Beaverhill Lake Fm.
111331	AGSWDB	00/07-35-078-24W5-0	55.800535	-117.605451	472.7	477.0	-1546.9	-1592.6	2023.9	2069.6	Yes	-0.073097	82	Winterburn Gp.
94864	AGSWDB	00/15-17-061-15W5-0	54.280913	-116.208906	856.5	861.7	-2143.9	-2158.3	3005.6	3020.0	No	0.010194	81	Cambrian system
114668	AGSWDB	00/11-08-083-06W6-0	56.185025	-118.916081	625.8	629.4	-1609.7	-1663.9	2239.1	2293.3	No	0.051797	79	Wabamun Gp.
57756	AGSWDB	00/04-24-042-23W4-0	52.624635	-113.191830	858.0	863.2	-845.2	-848.6	1708.4	1711.8	No	0.015586	78	Winterburn Gp.
83576	AGSWDB	00/15-36-053-26W4-0	53.626873	-113.699500	659.6	659.6	-750.1	-751.6	1409.7	1411.2	No	-0.007451	78	Winterburn Gp.
37717	AGSWDB	00/16-33-029-21W4-0	51.529252	-112.892031	781.5	784.3	-888.4	-890.3	1672.7	1674.6	No	-0.016064	77	Winterburn Gp.
164320	AGSWDB	F1/03-32-079-08W5-0	55.885325	-115.217505	n/a	645.0	-1143.6	-1150.0	1788.6	1795.0	No	0.027075	77	Elk Point Gp.
23731	AGSWDB	02/06-01-019-07W4-0	50.578984	-110.850699	787.6	791.9	-921.1	-942.4	1713.0	1734.3	Yes	-0.005123	76	Elk Point Gp.
53804	AGSWDB	00/07-07-040-23W4-0	52.424707	-113.300526	879.3	883.3	-937.6	-939.4	1820.9	1822.7	No	0.025155	76	Winterburn Gp.
53949	AGSWDB	00/03-21-040-24W4-0	52.450926	-113.402321	896.4	900.4	-1018.0	-1018.9	1918.4	1919.3	No	-0.010327	76	Winterburn Gp.
95008	AGSWDB	00/07-31-061-21W5-0	54.318252	-117.136265	925.7	929.9	-2563.1	-2569.2	3493.0	3499.1	Yes	-0.022558	76	Beaverhill Lake Fm.
117024	AGSWDB	00/04-08-087-03W6-0	56.525635	-118.451906	865.3	869.3	-1401.5	-1444.1	2270.8	2313.4	Yes	-0.007596	76	Woodbend Gp.

<sup>1</sup> AGSWDB: internal database of oil and gas wells.

<sup>2</sup> Datum used is NAD83.

<sup>3</sup> Calculated from Kelly bushing for AGS dataset (AGSWDB).

<sup>4</sup> Culled data verified with a quality assessment using various culling criteria (e.g., Hitchon and Brulotte, 1994).

<sup>5</sup> Formation name as shown in AGSWDB.

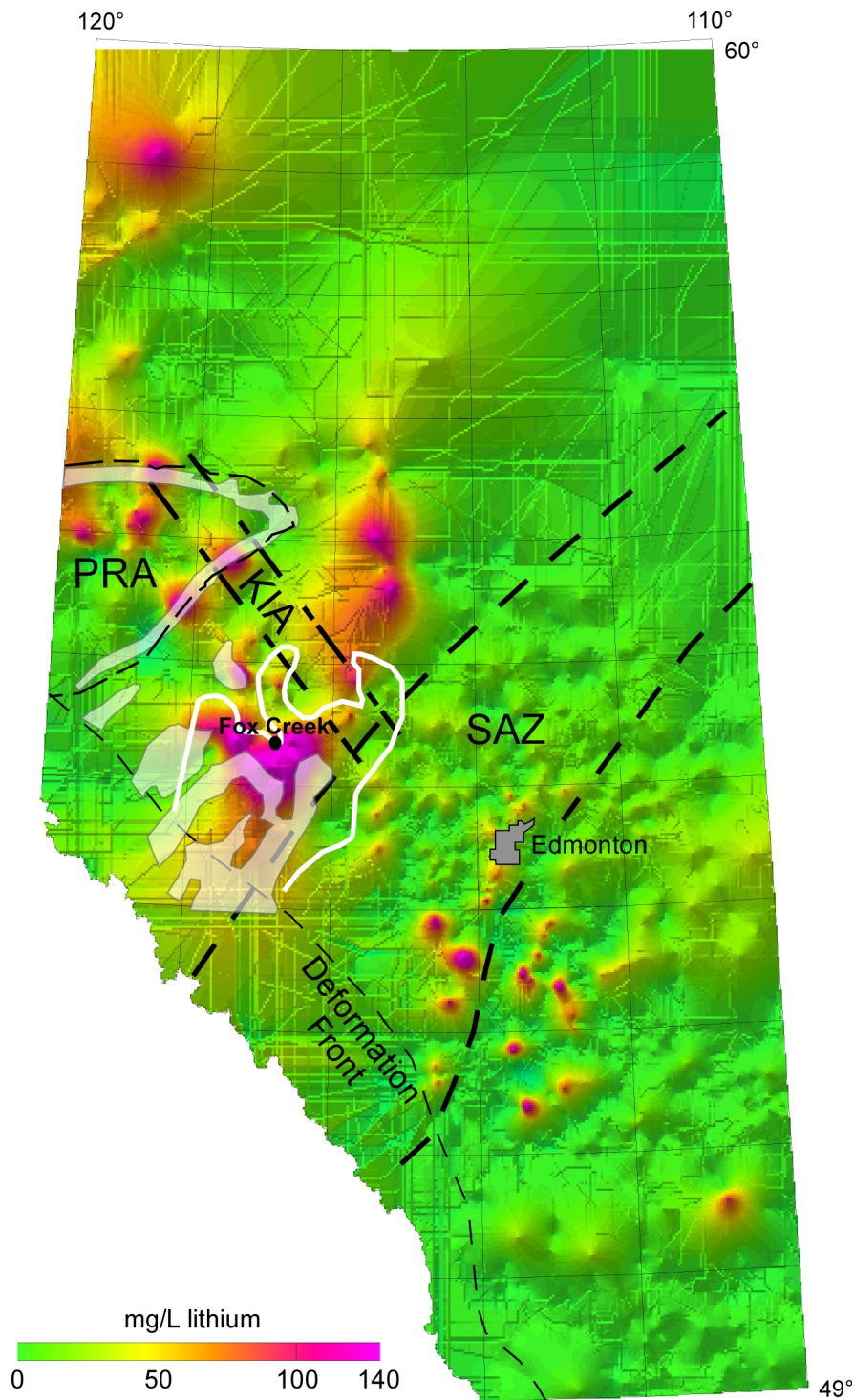


Figure 2. Shaded contour map of lithium-bearing formation waters in west-central Alberta. The map is generated from a dataset totalling 1511 analyses (Eccles and Jean, 2010). Nineteen analyses with >100 mg/L Li (up to 140 mg/L) occur within the Middle to Late Devonian Leduc (Woodbend Group) and Swan Hills (Beaverhill Lake Group) carbonate complexes in west-central Alberta. Abbreviations for selected west-central Alberta tectonic features: KIA, Kimiwan isotopic anomaly; PRA, boundary of the Devonian Peace River Arch; SAZ, Snowbird Anomaly Zone. White solid line represents the boundary of the Swan Hills (Beaverhill Lake Group) carbonate complex (Oldale et al., 1994). White, semi-transparent polygons represent Leduc (Woodbend Group) carbonate complexes (Switzer et al., 1994).

## 5 Geochemical Methodology

To investigate the origin and history of lithium in the Fox Creek area formation waters, the Alberta Geological Survey received formation-water samples and geochemical data (from sample splits identical to the donated water samples) from two mineral companies exploring in the Fox Creek area. The samples and their respective geochemical data were obtained from 18 operating oil-field wells in the Fox Creek area (Appendix). The samples were collected by the exploration companies using clean plastic vessels and analyzed at AGAT Laboratories and Exova Group Ltd. (Edmonton, Alberta) by routine water-analysis techniques including ion chromatography and inductively coupled plasma–mass spectrometry (ICP-MS). Because these data were donated without the details of certified standards, control samples and blanks, the authors are unable to report on the accuracy and precision of the analyses.

The donated geochemical data were divided into two groups, represented as Li-rich (80–112 mg/L; n = 13; n, number of samples) and Li-poor (10–43 mg/L; n = 5) water samples. To bolster our dataset, the industry-generated geochemical data are compared with 195 geochemical analyses from Li-bearing Devonian formation waters throughout Alberta (Eccles and Jean, 2010), which were also grouped into high-Li (100–140 mg/L), moderate-Li (50–100 mg/L) and low-Li (<50 mg/L) concentrations.

Of the 18 water samples, 13 were analyzed for Li, Pb and Sr isotopes at Queen’s University, Canada (Queen’s Facility for Isotopic Research, QFIR). These samples were selected based on geochemical data and include 8 Li-rich and 5 Li-poor water samples (Appendix 1). Three basement-rock powders from west-central Alberta (variations of biotite-plagioclase-microcline-hornblende-gneiss) were also analyzed for isotopic comparison. These samples were from an archived collection at the University of Alberta. For Li-isotope analysis, rock samples were dissolved in a 3:1 mixture of concentrated HF:HNO<sub>3</sub> and refluxed twice with concentrated HCl, prior to dilution with 5 ml 0.6 M<sup>†</sup> HCl. Water samples were evaporated to near dry and converted to their chlorine form by adding 1 ml of concentrated HCl at 120°C. The residue was dissolved with 5 ml 0.6 M HCl prior to ion-exchange separation. HCl and HNO<sub>3</sub> were double-distilled using a Savillex® sub-boiling still. All reagents were prepared using ≥18.2 MΩ water obtained from a Millipore® purification system. The exchange columns are made of quartz glass with an internal diameter of 8 mm and a resin height of 200 mm. The resin employed is Bio-Rad AG® 50W-X8, 100–200 mesh. The resin was cleaned by repeated rinses with 7 M HCl and de-ionized water. A large resin volume was used to ensure quantitative recovery during elution of the samples. Prior to use, the resin was conditioned with two column volumes of 0.6 M HCl. After loading the samples on the column, 13 ml of 0.6 M HCl was discarded and the Li was totally eluted with 30 ml of 0.6 M HCl. As isotope fractionation occurs during ion exchange, quantitative recovery of Li is critical. Therefore, 10 ml of 0.6 M HCl were added and checked for the complete recovery of Li. For the water samples, the Li fraction was reprocessed twice through the column because of the high-Na content. Isotopic measurements were made on a NEPTUNE™ multi-collector ICP-MS (Thermo-Finnigan) at QFIR. Measurements of <sup>6</sup>Li and <sup>7</sup>Li were performed by static multiple collection with Faraday cups. The introduction interface consisted of a CETAC ASX-100 auto-sampler, an ESI concentric Teflon nebulizer operating at 100 µL/min<sup>-1</sup>, standard Al cones and a Scott double-pass cyclonic spray chamber. A gain calibration was performed before each analysis session. Blanks (2% HNO<sub>3</sub>) were measured before each group of four samples and their corresponding bracketing standards, and monitored throughout the running sequence.

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<sup>†</sup> 1 M equals 1 mol per litre



The samples and standards were blank subtracted online. The results were reported in the conventional delta notation of stable isotopes where

$$\delta^7\text{Li}(\text{‰}) = \left( \frac{[{}^7\text{Li}/{}^6\text{Li}]_{\text{sample}} - [{}^7\text{Li}/{}^6\text{Li}]_{\text{Av.reference}}}{[{}^7\text{Li}/{}^6\text{Li}]_{\text{Av.reference}}} \right) \times 1000$$

*Av.reference* is the average of the two LSVEC bracketing standards, measured before and after the sample. The error in  $\delta^7\text{Li}$  for rock samples is less than 1‰ and for the water samples is approximately 1.5‰.

With respect to Pb and Sr isotopes, rock samples were dissolved in a 3:1 mixture of concentrated HF:HNO<sub>3</sub>, and refluxed twice with concentrated HNO<sub>3</sub>. The dried residue was then dissolved with 2 ml of 3 M HNO<sub>3</sub> for ion exchange. Water samples were evaporated to near dry, refluxed with concentrated HCl and dissolved with 25 ml of 2.2 M HCl. A first-step purification, using Bio-Rad AG® 50W-X8, 100–200 mesh, was necessary due to the high concentration in Na. The resulting samples were dried, refluxed with 3 ml of concentrated HNO<sub>3</sub>, evaporated and re-dissolved in 2 ml of 3 M HNO<sub>3</sub>, and loaded onto ion-exchange columns packed with 500 µL Eichrom™ Sr-Spec resin, specific to retaining Pb and Sr ions. All other ions were washed out with 3 ml of 3 M HNO<sub>3</sub> before eluting Sr with 1 ml of 0.05 M HNO<sub>3</sub>. Lead was eluted separately with 1 ml of H<sub>2</sub>O and 1 ml of 0.1 M ammonium oxalate. After drying at 70°C, the Pb and Sr residues were dissolved in 0.5 ml of hot, concentrated HNO<sub>3</sub> and a few drops of 30% H<sub>2</sub>O<sub>2</sub> to oxidize the remaining oxalate and resin from the solution. Strontium and Pb solutions were evaporated at 70°C, and then the residue dissolved in 2 ml of 2% HNO<sub>3</sub> for isotope-ratio measurements on a Thermo-Finnigan™ NEPTUNE multi-collector ICP-MS. Lead samples were spiked with 10 ppb Tl to correct for mass bias, using the <sup>205</sup>Tl/<sup>203</sup>Tl ratio. Mass bias of Sr analyses was corrected using the <sup>88</sup>Sr/<sup>86</sup>Sr ratio.

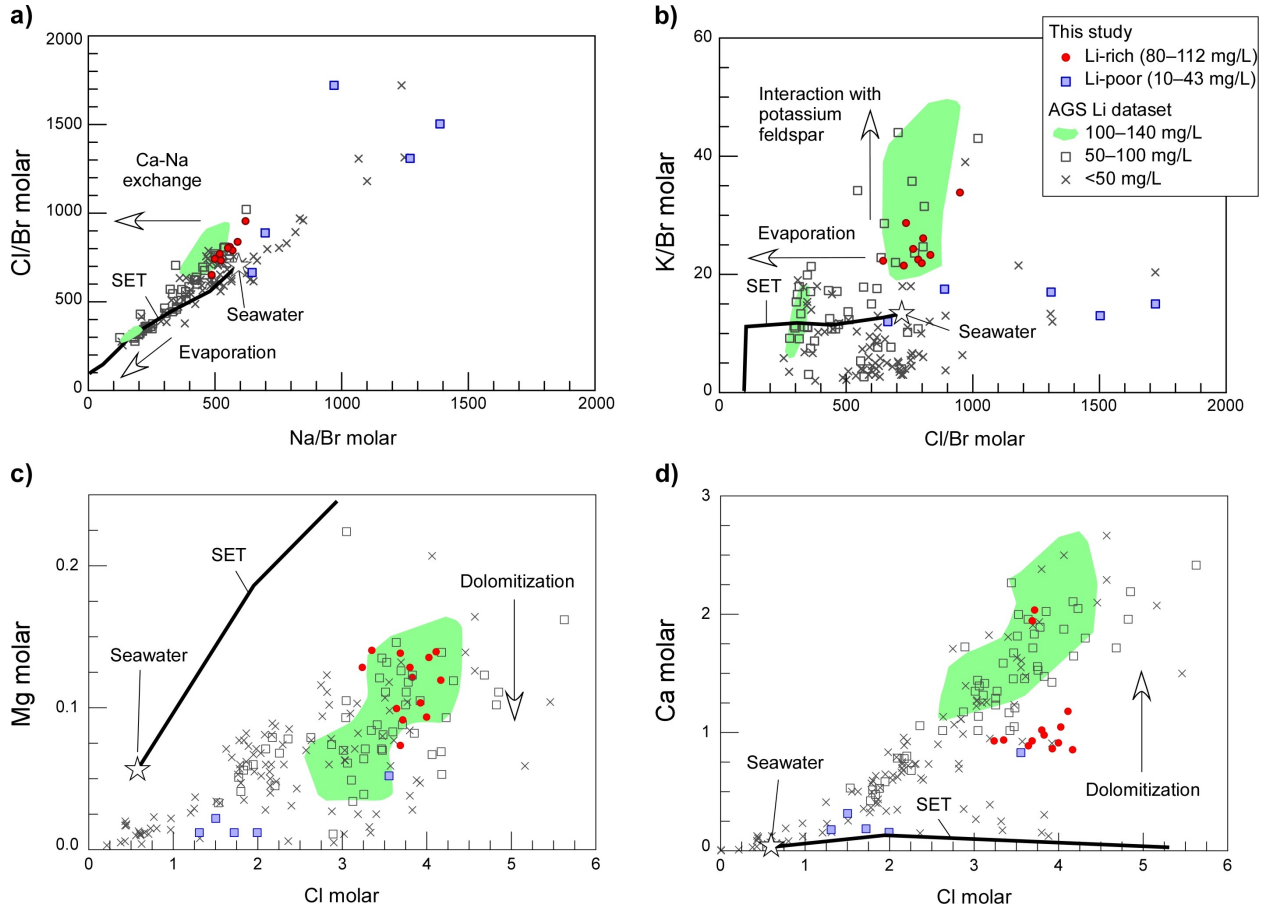
Measurement accuracy was monitored using the National Institute of Standards and Technology standard reference materials (NIST SRM® 981 for Pb and NIST SRM® 987 for Sr). The average ratios measured for 100 ppb SRM 981 are <sup>206</sup>Pb/<sup>204</sup>Pb = 16.927 ± 0.011, <sup>207</sup>Pb/<sup>204</sup>Pb = 15.478 ± 0.015, and <sup>208</sup>Pb/<sup>204</sup>Pb = 36.658 ± 0.044 (2 sd, standard deviation), based on 44 runs between November 2009 and August 2010. Measurements of NIST SRM® 987 returned <sup>87</sup>Sr/<sup>86</sup>Sr ratios of 0.71029 ± 1.3 × 10<sup>-5</sup> (n = 28). The error on the Pb isotope ratios for the water samples, which had much lower lead contents than standards, was 1%–2%.

## 6 Major Ion Geochemical Results

The majority (92%) of the combined data from the Alberta Geological Survey data holdings and this study are hypersaline Na-Ca-Cl-type water typical of Devonian aquifer systems. Based on Cl/Br ratios, Figure 3a shows there is not much deviation from the seawater evaporation trajectory (SET; Fontes and Matray, 1993). Starting as seawater, the brine has evaporated up to the point of halite formation with little evidence of halite dissolution or dilution with meteoric water. A small cluster of >100 mg/L Li waters from the Cooking Lake carbonate platform, located ~275 km southeast of Fox Creek, has evaporated past halite precipitation, possibly as a product of advanced evaporation similar to processes responsible for potash precipitation.

Based on an evaluation of Devonian to Neogene formation waters in west-central Alberta, Michael and Bachu (2001) suggested highly saline, low Na/Cl ratio Devonian waters are partly the product of albitization of feldspar as waters refluxed through the crystalline basement. When sodium of Li-bearing Devonian water is evaluated against SET, however, there is only slight deviation from SET and evidence

of Ca-Na exchange (albitization). Rather, Figure 3b shows Li-rich brine experienced significant potassium enrichment, which suggests water-rock interactions involved silicate alteration. In addition, Mg and Ca are far removed from the SET suggesting these brines were highly influenced by dolomitization, which requires Mg and expels Ca, resulting in the low Mg/high Ca brine relative to seawater (Figure 3c and d).

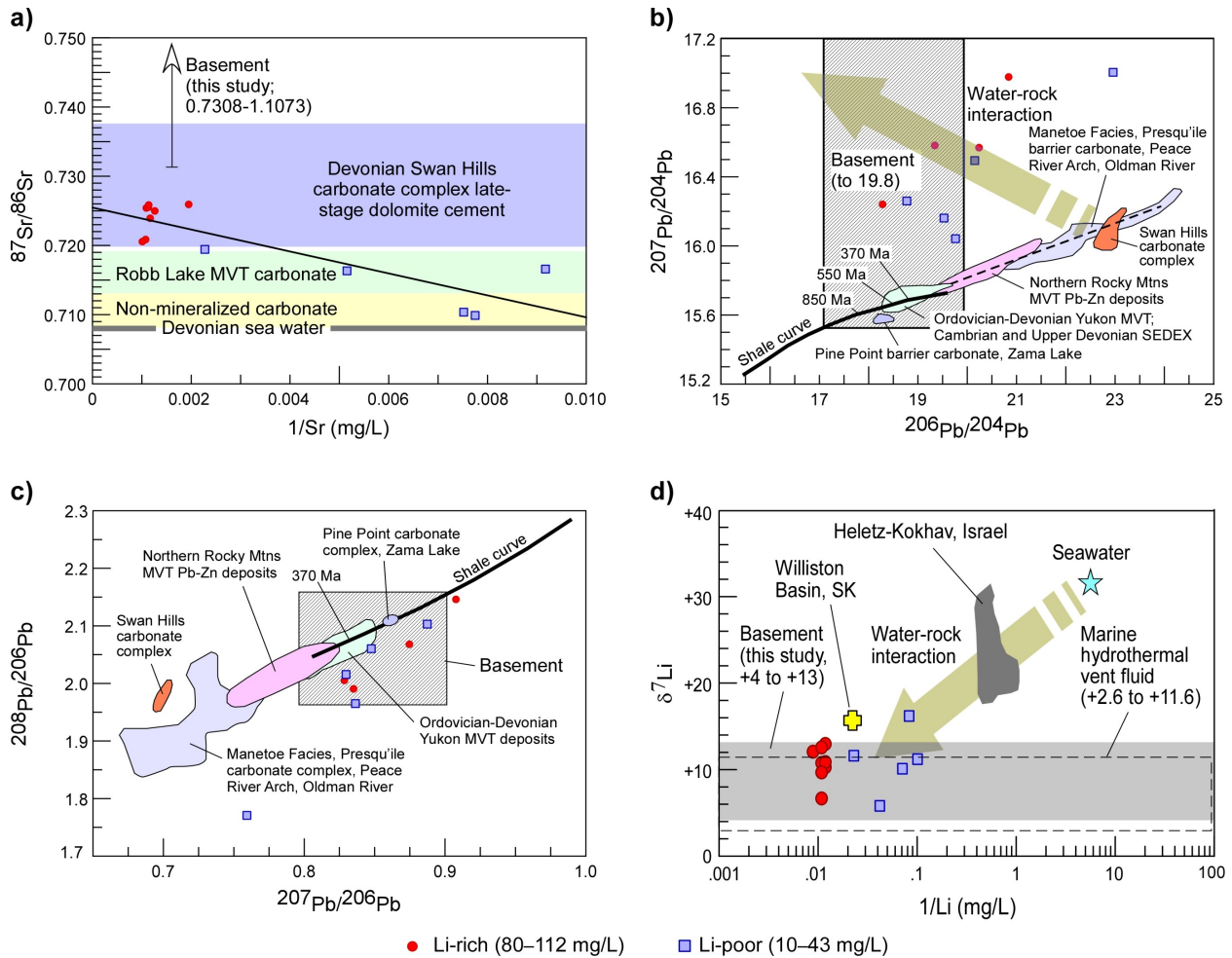


**Figure 3.** Plot of Na-Cl-Br, K-Cl-Br, Mg-Cl and Ca-Cl systematics of lithium-bearing formation waters in the Fox Creek area (this study, solid symbols) and Alberta Devonian formation waters (grouped according to Li concentrations; Eccles and Jean, 2010). Heavy solid line represents the modern day seawater evaporation trajectory (SET) from Fontes and Matray (1993).

## 7 Isotopic Geochemical Results

Radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  (0.720465–0.725840) characterizes 8 Li-rich formation-water samples, whereas the Li-poor formation water ( $n = 5$ ) is less radiogenic (0.70988–0.71942) and approaches the Sr isotopic composition of Devonian seawater (Figure 4a). This appears to define two end-members in our dataset for which normal seawater trends toward radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  associated with water-silicate interaction. The Pb isotope data are generally scattered, but have elevated  $^{207}\text{Pb}/^{204}\text{Pb}$  (16.04–19.17) and  $^{207}\text{Pb}/^{206}\text{Pb}$  (majority between 0.83 and 0.91) relative to selected Devonian carbonate rocks, such that they either mimic our basement samples (e.g.,  $^{207}\text{Pb}/^{206}\text{Pb}$  between 0.80 and 0.90) or plot between basement and the Swan Hills carbonate Pb isotope values from Duggan (1997; e.g.,  $^{206}\text{Pb}/^{204}\text{Pb}$  between 22.5 and 23.3; Figure 4b and c). The  $\delta^7\text{Li}$  isotope values range from +6‰ to +16‰, forming a tight cluster between +10‰ and +13‰ (Figure 4d). These  $\delta^7\text{Li}$  values are substantially lighter than seawater and the Heletz-Kokhav, Israel oil-field brines (Chan et al., 2002), which represent the only known Li-isotope work

completed on oil-field brine and were interpreted to form by interaction with siliciclastic sediments in an exchange process that included diagenetic reactions. The Fox Creek formation water has similar  $\delta^7\text{Li}$  to our basement samples and/or hydrothermal vent fluids, providing further evidence that these waters experienced significant silicate interaction and, possibly, are associated with hydrothermal fluids.



**Figure 4.** Plot of Sr, Pb and Li isotope systematics for Li-rich and Li-poor formation waters from the Fox Creek area of Alberta: a)  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratio versus the inverse of Sr. For comparison, Devonian sea water (Denison et al., 1997), Devonian Manetoe Facies, Presqu'île barrier reef, and Western Canada Sedimentary Basin Cambrian nonmineralized carbonate, mineralized dolomite, and saddle dolomite from the Robb Lake Mississippi Valley-Type (MVT) deposit (Pană, 2006); and late-stage 'pure' calcite and dolomite cement from burial dolomite at the Swan Hills Simonette Reef (Duggan et al., 2001); b) and c) lead isotope systematics; for comparison, Western Canada Mississippi Valley-Type Pb-Zn deposits and carbonate-hosted sphalerite and galena occurrences in the Western Canada Sedimentary Basin and northern Rocky Mountains from Paradis et al. (2006); d)  $\delta^7\text{Li}$  versus the inverse of Li; for comparison, Heletz-Kokhav, Israel oil-field brine (Chan et al., 2002); Williston Basin brine (Bottomley et al., 1999); and marine hydrothermal-vent fluid (Tomascak, 2004).

## 8 Summary and Discussion

### 8.1 Geochemical Summary

Geological processes in the Fox Creek area have created Li-rich brines in the Beaverhill Lake, Woodbend and Winterburn aquifer systems. The source of the lithium is ultimately unknown, but it precludes halite precipitation, lacks a meteoric water source, involves alteration of silicates (particularly Li- and K-bearing minerals), and appears to correlate with dolomitization. As tempting as it is to consider  $\text{Li}^+$  to  $\text{Mg}^{2+}$  substitution due to their similar ionic ratios followed by expulsion of the charge imbalanced Li during the Mg-hungry dolomitization process, temporal and even spatial association between silicate-leachate and dolomitization are not necessarily required to produce Li-rich brine. We suspect that it is unlikely even the ‘dirtiest’ carbonate could have sequestered enough monovalent cations of  $\text{Li}^+$  and  $\text{K}^+$  prior to, or during dolomitization, to produce potentially economic Li-bearing brine. A more viable scenario involves either direct contact between Devonian waters and basement, or mobilization of silicate-bearing fluids to the aquifer. The following text expands upon this hypothesis.

### 8.2 Previous Models for Dolomitization of Swan Hills Carbonates

At least two dolomitization models are applicable to the Swan Hills carbonate complex: the squeegee flow model (Machel et al., 2001) and the fault-controlled dolomitization model (Duggan et al., 2001). Both models advocate silicate interaction between the brines and either direct reflux mixing with the Precambrian basement or with immature siliciclastics (such as the Granite Wash, Cambrian basal sandstone, and the Devonian Gilwood Member of the Watt Mountain Formation), deposited above the basement. The squeegee model contends that  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope values are unusually high adjacent to the deformation front and decrease into the foreland basin. Machel et al. (2001) proposed that this progressive reduction of radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  is related to tectonic expulsion of formation fluids, with radiogenic Sr being derived from Proterozoic Miette Group rocks from the deformed belt adjacent to the Rocky Mountains.

In the fault-controlled dolomitization model, plume-like dolomitization is related to hydrothermal fluids that are restricted to laterally confined flow systems associated with faults. The fault-controlled dolomitization model seems more appropriate to form the relatively isolated Li-rich formation waters in the Fox Creek area than the regional concept of the squeegee model; however, fluids emanating from both models could have contributed Li, K and B.

### 8.3 Potential Role of West-Central Alberta Basement and Tectonic Features

An important consideration for the introduction of lithium into an exogenous setting, such as the Fox Creek area formation waters, involves volcanic and/or hydrothermal activity. However, both processes are difficult to detect due to the thickness of the Phanerozoic wedge and depth at which these formation waters occur. Nevertheless, any model involving basement-water interaction and silicate mobilization in the Fox Creek area of west-central Alberta, must consider thermal, potential field, and tectonic features in the basement and the overlying strata. Summarized below are some spatially coincidental features that may have implications for lithium enrichment in the Fox Creek area.

- **Thermal anomaly at the base of the sedimentary column:** The temperature at the base of the sedimentary column in the Fox Creek–Swan Hills area is anomalously high (more than 120°C, Bachu and Burwash, 1994). In northern Alberta, temperatures this high usually correspond to areas where the thickest Phanerozoic rocks overlie the basement (e.g., Caribou and Birch mountains). However, the sedimentary cover in the Fox Creek–Swan Hills area is not sufficiently thick enough to explain this particular temperature increase (Bachu and Burwash, 1994).

- Precambrian high-geothermal regime: A small-scale, moderately high radiogenic heat anomaly (4–6  $\mu\text{W}/\text{m}^3$ ) in the Fox Creek–Swan Hills area may relate to a localized zone of radiogenic heat generation at the top of the Precambrian basement (Bachu and Burwash, 1994).
- Horizontal gravity gradient anomaly: A distinctly localized, high horizontal gravity gradient anomaly occurs in the Fox Creek–Swan Hills area (Ross et al., 1994). The width of the anomaly and contrasting high to low gravity pattern over short distances is similar to gravity anomalies associated with the Snowbird Tectonic Zone in east-central Alberta (Ross et al., 1994) and the Trout Mountain pluton in north-central Alberta (Burwash and Power, 1990). In a study that examined deep-migrated seismic profiles, Bouzidi et al. (2002) recognized a correlation between the Snowbird Tectonic Zone’s linear, sharply contrasting gravity anomaly and topographic displacement of up to 10 km in the Moho.
- Peace River Arch: The Peace River Arch is an area of prominent structural disturbance in west-central Alberta that formed in three phases, each phase being characterized by a main structural manifestation: Precambrian to Early Carboniferous arch formation, Early Carboniferous to Jurassic embayment, and Jurassic and Cretaceous enhanced subsidence in the foreland basin (O’Connell et al., 1990; Figure 5). The western portion of the arch is characterized by large-scale, broad grabens and half-grabens orientated both parallel (west-southwest) and normal (north-northwest) to the arch axis.
- Kimiwan isotopic anomaly: With respect to basement domains, a sharp aeromagnetic boundary separates the Chinchaga Terrane from the Buffalo Head Terrane on the east and the Ksituan Terrane on the west, possibly suggesting a faulted contact on both sides of the Chinchaga Terrane (Ross et al., 1994). This aeromagnetic boundary also coincides with a zone of significantly depleted  $\delta^{18}\text{O}$  standard mean ocean water (SMOW) values that led Muehlenbachs et al. (1993) and Burwash et al. (2000) to suggest the anomaly, known as the Kimiwan isotopic anomaly, formed by interaction of basement rocks with surface-derived fluids in a northwest-trending zone of crustal extension (Figure 5). A LITHOPROBE Peace River Arch Industry Seismic Experiment (PRAISE) across the Kimiwan isotopic anomaly disclosed pre-1.8 Ga extensional faults penetrating to depths of at least 35 km (and probably to the Moho; Hope and Eaton, 2002).
- Northern edge of the Snowbird Anomaly Zone: The northern edge of the Snowbird Anomaly Zone, which represents the main regional northeast-trending magnetic and gravity anomaly band in central Alberta, is proximal to the Fox Creek area (Lyatsky and Paná, 2003; Figure 5). On the exposed part of the Canadian Shield, the Snowbird Tectonic Zone represents a pronounced 2000 km long zone of ductile deformation separating the Rae and Hearne crustal provinces (Hoffman, 1990; Lewry and Collerson, 1990; Hanmer et al., 1994).

To reiterate, any link between these features and the Li-rich formation waters is speculative. For the purposes of discussion, however, it is worth pointing out interesting coincidences. First, there is a potential link between thermal anomalies (top of the Precambrian basement) and a horizontal gravity gradient anomaly. This association may imply a pluton and/or a geothermal system, both of which could readily act as a silicate source. An endogenous granitic pegmatite system, in particular, could liberate the Li- and K-bearing minerals observed in the Fox Creek brine geochemistry.

Second, any model that explains Li-accumulation in the Fox Creek formation waters should consider tectonic features in west-central Alberta, including the Peace River Arch, Kimiwan isotopic anomaly and Snowbird Anomaly Zone (Figure 5a and b). Perhaps more importantly, erosion of the arch prior to its inundation in the Late Devonian generated layers of immature siliciclastics at its periphery. These permeable clastic wedges could then act as pathways for the mobilization and transportation of altered silicate materials/fluids to the Leduc and Beaverhill Lake aquifers in the Fox Creek area (Figure 5c).

The Fox Creek area correlates with the intersection and apparent termination of the southeast-trending Kimiwan isotopic anomaly together with the northern edge of the southern continuation of the northeast-trending Snowbird Anomaly Zone (Figure 5). Both of these systems could source silicate fluids and/or act as fluid pathways. Collectively, these tectonic features could work in concert or in isolation to liberate and mobilize Li-rich fluids to the Fox Creek brines (Figure 5c).

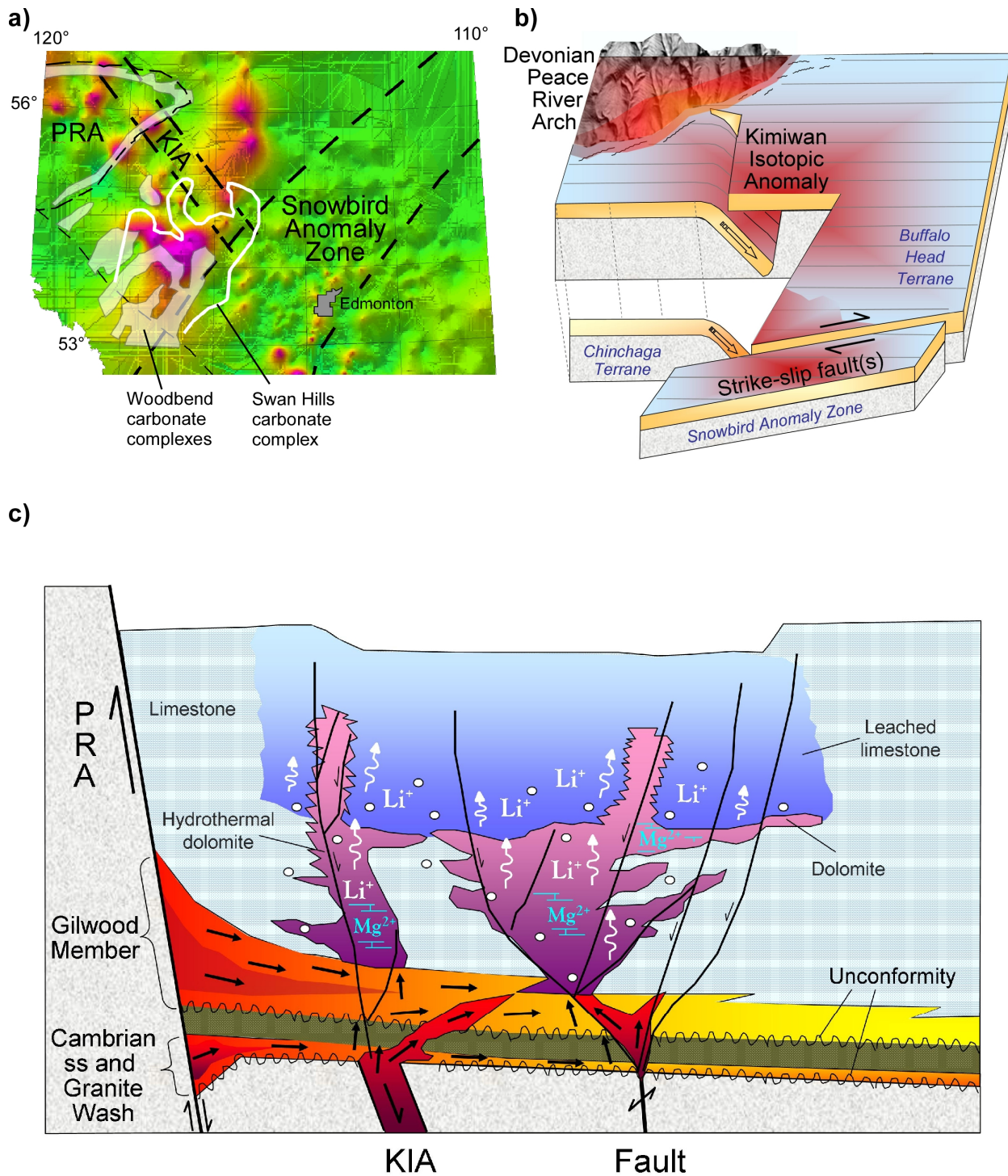


Figure 5. Potential associations between tectonic features and lithium accumulation in aquifers of the Leduc and Beaverhill Lake reef complexes, west-central Alberta: a) inferred locations of the Peace River Arch (PRA), Kimiwan isotopic anomaly (KIA) and Snowbird Anomaly Zone in relation to the Leduc and Swan Hills reef complexes (These features are displayed on the shaded contour map of lithium-bearing formation waters in Alberta, see Figure 2.); b) an oblong cartoon of the Peace River Arch, Kimiwan isotopic anomaly, and strike-slip faults of the Snowbird Anomaly Zone to show how they could potentially act in concert to mobilize altered silicates and/or fluids; c) a schematic model to illustrate mobilization of fluids along immature siliciclastics deposited above the basement and entry into the Fox Creek aquifers via fault and fracture systems.

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**Appendix – Results of Li, Pb and Sr Isotopic Analysis on Li-Rich and Li-Poor Formation Water Samples (West-Central Alberta) and Selected Geochemical Data Contributed to this Study by the Minerals Industry**

Sample	Well Identifier	<sup>207</sup> / <sub>206</sub> Pb	Error	<sup>208</sup> / <sub>206</sub> Pb	Error	<sup>206</sup> / <sub>204</sub> Pb	Error	<sup>207</sup> / <sub>204</sub> Pb	Error	<sup>208</sup> / <sub>204</sub> Pb	Error	<sup>87</sup> / <sub>86</sub> Sr	Error	d <sup>7</sup> Li/ <sup>6</sup> Li <sup>1</sup>	d <sup>7</sup> Li/ <sup>6</sup> Li (Rerun)
1	00/04-13-058-18W5/0														
2	00/10-02-059-18W5	0.83544	0.0060	1.98952	0.013	20.85235	0.22	16.97503	0.17	40.77883	0.39	0.72077	0.000002	12.01	
3	00/10-11-059-18W5/0														
4	00/10-15-059-18W5/0	0.59472	0.0048	1.36375	0.015	32.24639	0.33	18.89638	0.23	43.49350	0.56	0.72047	0.000003	10.24	10.4
5	00/05-23-059-18W5/0	0.31821	0.0023	0.66513	0.004	61.91346	0.39	19.17206	0.14	40.48178	0.33	0.72384	0.000003	10.73	
6	00/10-22-059-18W5/0														
7	00/10-21-059-18W5/0	0.57998	0.0045	1.33452	0.010	31.61759	0.26	18.03728	0.15	41.74669	0.38	0.72490	0.000003	12.92	13.3
8	00/09-27-059-18W5/0	0.82889	0.0051	2.00427	0.014	20.25238	0.14	16.56563	0.13	40.23554	0.35	0.72532	0.000002	10.82	
9	00/10-29-059-18W5/0	0.56594	0.0038	1.30567	0.010	31.36611	0.19	17.62651	0.13	40.77699	0.40	0.72543	0.000002	9.57	
10	00/04-03-060-18W5/2	0.90819	0.0055	2.14514	0.017	18.29473	0.10	16.23706	0.07	38.66026	0.29	0.72575	0.000002	12.53	
11	100/04-08-060-18W5/0														
12	100/10-07-060-18W5/0														
13	100/01-18-060-18W5/0	0.87503	0.0060	2.06710	0.015	19.35360	0.12	16.57810	0.11	39.44602	0.27	0.72584	0.000004	6.64	
14	12-10-64-19W5	0.82969	0.0054	2.01561	0.011	19.76385	0.11	16.04130	0.08	39.27147	0.20	0.70988	0.000005	5.81	6.3
15	4-30-65-13W5	0.84767	0.0055	2.06024	0.014	19.52798	0.12	16.16089	0.08	39.60447	0.22	0.71942	0.000002	11.65	9.2
16	10-4-67-18W5	0.75932	0.0054	1.77071	0.013	22.96181	0.19	17.00500	0.13	39.99982	0.34	0.71035	0.000007	10.10	10.6
17	3-19-65-10W5	0.88742	0.0058	2.10288	0.011	18.77568	0.16	16.25999	0.13	38.86802	0.32	0.71658	0.000002	11.22	
18	7-4-71-18W5	0.83634	0.0065	1.96491	0.013	20.15288	0.15	16.49380	0.12	39.06593	0.33	0.71632	0.000002	16.25	

<sup>1</sup> Lithium isotope compositions expressed in per mil relative to the manufactured Li<sub>2</sub>CO<sub>3</sub> standard L-SVEC (NIST SRM-8545).

<sup>2</sup> TDS (calc), total dissolved solids (calculated).

Sample	Well Identifier	K	Li	B	Mg	Ba	Br	Fe	Mn	Ca	Na	Cl	HCO <sub>3</sub>	SO <sub>4</sub>	TDS (calc) <sup>1</sup>	pH	Alkalinity
1	00/04-13-058-18W5/0	3904	91.5	177	1780	2250	91	trace	2.18	23300	48600	130959	610.7	trace	208909	6.44	610.67
2	00/10-02-059-18W5	3098	112.0	223	2210	408	0	trace	0.82	24400	54700	131959	733.3	78.2	216885	6.76	733.33
3	00/10-11-059-18W5/0	4850	79.5	194	3410	2090	0	trace	0.58	11200	54900	118963	821.5	95.7	194240	6.93	673.33
4	00/10-15-059-18W5/0	5610	85.8	187	3350	896	412	trace	1.84	11100	57600	130959	686.7	62.9	209093	7.15	686.67
5	00/05-23-059-18W5/0	4720	93.9	181	2930	1130	378	trace	1.30	11700	59900	135958	469.3	54.6	215544	7.00	469.33
6	00/10-22-059-18W5/0	4350	77.2	153	3120	1450	390	trace	2.14	11100	56200	114964	624.0	21.4	190129	7.12	624.00
7	00/10-22-059-18W5/0	5290	86.8	173	3120	1390	353	6.00	2.28	12200	57300	134958	616.0	51.3	213288	7.14	616.00
8	00/09-27-059-18W5/0	5070	86.4	158	3270	1400	377	5.30	1.40	12500	64500	142956	422.8	69.9	228619	6.99	422.67
9	00/10-29-059-18W5/0	5500	87.3	163	3390	1190	17	trace	0.52	14100	66200	145955	517.3	7.5	235462	7.05	517.33
10	00/04-03-060-18W5/2	4530	87.1	154	2890	1290	364	trace	0.48	10200	68000	147954	523.3	69.9	233957	6.97	523.33
11	100/04-08-060-18W5/0	4170	86.8	149	2410	1180	408	5.90	1.32	10600	60400	129371	728.7	14.5	210008	6.13	597.33
12	100/10-07-060-18W5/0	4390	86.2	148	2500	197	378	trace	0.42	10300	65700	139439	746.6	10.8	223730	6.38	612.00
13	100/01-18-060-18W5/0	4260	87.5	140	2250	538	413	5.90	0.53	10900	63600	141956	752.3	15.0	225200	6.55	616.67
14	12-10-64-19W5	1420	24	84.9	298	12	200	2	1.1	1870	44600	70700	377	300	114000	7.02	309
15	4-30-65-13W5	2720	42.9	121	1260	5.3	280	767	9.7	9960	64200	126000	<5	640	201000	3.36	<5
16	10-4-67-18W5	668	14	46.5	299	1.1	100	2.9	0.1	2140	29200	46400	225	990	77900	7.09	185
17	3-19-65-10W5	591	9.92	32	294	0.95	90	93.8	1.3	2240	22300	61000	17	740	98100	5.58	14
18	7-4-71-18W5	499	12	28.5	546	2.8	100	7	<0.1	3780	31900	53300	206	1000	89800	6.98	169

<sup>1</sup> TDS (calc), total dissolved solids (calculated).