

Lithium concentrations in brine springs near Lake Winnipegosis, west-central Manitoba (parts of NTS 63C, 62N16, 62O12, 13)

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In Brief:

- Brine springs along Lake Winnipegosis contain low levels of lithium, averaging 1263 ppb
- Groundwater mixing has diluted the lithium concentration coming out from the springs
- Deep subsurface Winnipeg Formation brines have good potential as a lithium source

Citation:

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Summary

The most common and cost-effective source of lithium within the brine deposits are deep brines in continental sedimentary basins. Southern Manitoba has a complex groundwater aquifer system, with salinities ranging from brines in the deeper aquifers and brine springs to freshwater in the shallower and eastern aquifers. The brine springs occur along and near the shores of Lake Winnipegosis on large salt flats and have chemical signatures indicative of mixed halite dissolution brine and freshwater. Lithium concentrations in these brines range from 150 to 6300 ppb, with an average of 1263 ppb.

Introduction

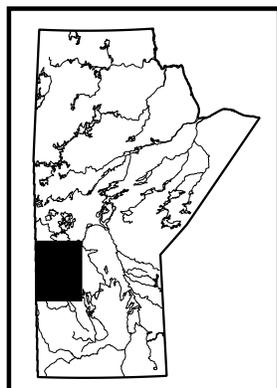
Saline groundwater in continental sedimentary basins are generated from evaporitic concentration and/or halite dissolution, where the former is a primary process and the latter is a secondary (diagenetic) process (Clayton et al., 1966; Walter et al., 1990). Both these mechanisms provide opportunities for trace elements to accumulate, potentially reaching economic concentrations. In Manitoba, the mineral potential of brines remains largely under-explored and little understood, as exemplified by the current level of knowledge about lithium concentrations in these saline groundwater systems. Active exploration for this element in deep saline waters found in continental sedimentary basins is presently occurring in the Province, and the lithium values it reveals may prove these waters to be a cost-effective source of this element.

Southern Manitoba has a complex groundwater aquifer system, with salinities ranging from brines in the deeper western aquifers to freshwater in the shallower eastern aquifers (Grasby and Betcher, 2002; Grasby and Chen, 2005; Nicolas, 2017). Oil and gas operations in Manitoba produce large quantities of these brines, which contain a wide range of trace elements. Although few in number, preliminary results indicate that the lithium concentrations in Manitoba's brines are low. However, extrapolation of better, more comprehensive results from Saskatchewan suggests that there is potential for lithium concentrations to be higher than currently recorded in Manitoba and that more work needs to be done to evaluate the deeper aquifers (Nicolas, 2017). In addition, little is known about the potential of brine springs, which occur in west-central Manitoba.

Nicolas (2017) reported on the known lithium concentrations in the deep brines, as well as shallow freshwater aquifers, and this paper focuses on the lithium content of brine springs that are located near and along the shores of Lake Winnipegosis in west-central Manitoba.

Southern Manitoba hydrogeology

Grasby et al. (2000) and Grasby and Chen (2005) described the complex history of the hydrodynamics of the Western Canada Sedimentary Basin (WCSB) over the last 50 m.y.; their findings are summarized here. The deep basin waters represent original evaporated sea waters that have remained as interstitial brines since near the time they were deposited. During the Laramide orogeny (50–84 Ma ago), uplift of the western portion of the WCSB allowed influx of freshwater from the topographic highs in the northwestern United States at the western edge of the basin. Travelling through the porous sediments, these



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freshwaters dissolved portions of the Prairie Evaporite in southwestern Saskatchewan, and the resulting hydraulic pressures pushed existing deep saline groundwater to partially migrate northward and eastward. To this day, these deep brines display chemical signatures indicative of evaporated seawater affected by rock–water interactions and have never been mixed with freshwater. On the eastern side of the basin, flow of groundwater in southwestern Manitoba during the Laramide orogeny followed regional topographical gradients, similar to modern day, with a northeastern flow direction. As the uppermost sediments of the WCSB eroded, the gradient decreased, but with little change in groundwater flow direction. During the last ice age, thick glacial ice over Manitoba resulted in a reversal of the topographic gradient and groundwater flow. Of great importance was the fact that the basal meltwater of the glacier significantly increased hydraulic pressures, forcing large volumes of freshwater into the porous Devonian carbonate rocks present at the basal-ice surface. This freshwater influx penetrated deeply into the carbonate succession toward the southwest, resulting in partial dissolution of the Prairie Evaporite. Upon glacial retreat, and the subsequent glacial rebound, the groundwater again reversed its flow path, back to the current northeastern direction. The brine springs near and along the shores of Lake Winnipegosis are the surface seeps of this saline groundwater. Grasby and Chen (2005) identified the hydrochemistry of these brine springs as bearing the signatures of mixed halite dissolution brine and freshwater.

In southern Manitoba, a hydrological divide separates two regional groundwater-flow systems (Figure GS2018-10-1). West of the divide, the groundwater matches the saline water system described above and hosts the brine springs, whereas east of the divide the groundwater is freshwater (Grasby and Betcher, 2002). The eastern flow system is the carbonate-rock aquifer and consists of gently west-dipping, carbonate-dominated strata from the Ordovician Red River Formation up to the Souris River Formation (Grasby and Betcher, 2002).

Hydro- and lithostratigraphy

The brine springs are located within Devonian-aged carbonate rock outcrops of the Winnipegosis, Dawson Bay and Souris River formations (Figure GS2018-10-1). These formations fall within the Winnipegosis aquifer and Devonian aquifer (Dawson Bay and Souris River combined) of Bachu and Hitchon (1996), or equally the Winnipegosis aquifer and Manitoba aquifer (Dawson Bay and Souris River combined) of Palombi (2008), and are separated by the Prairie aquiclude in the deep subsurface. Once past the Prairie Evaporite formation edge to the

north and east, these aquifers combine into one open aquifer system, which is exposed at the land surface and which discharges brine waters as springs.

Nearby outcrops of the McArdle salt flat (also referred to as the Red Deer River salt spring; Figure GS2018-10-2a) suggest that Winnipegosis Formation reefs may underlie most, if not all, brine springs (Bezys and McCabe, 1996; Bezys et al., 1997). These reefs are known for having high water drives in the subsurface, essentially concentrating fluid flow upward. They are often associated with collapse structures overtop due to the localized rapid dissolution of the Prairie Evaporite, which results in overlying formations draping overtop of these structures, creating zones of enhanced permeability. In those areas where the Prairie Evaporite was not present, and which were therefore not affected by dissolution, draping of the overlying carbonate rocks on the reefs would have the same effect on permeability due to natural compaction of the rocks over time.

Salt-flat and brine-spring morphology

The morphology of the salt flats varies in size from small sites to large flat-lying, uniform, treeless, iron-stained to whitish grey expanses (Figure GS2018-10-2b). Brine pools, which are clear with a light blue substrate (Figure GS2018-10-2c), and brine boils (shallower ponds with percolating gas bubbles; Figure GS2018-10-2d) occur at the discharge sites and are commonly surrounded by red to green algae, algal mats, and brine-loving vegetation and bacteria (Bezys et al., 1997; Grasby and Londry, 2007). The sites are often littered with glacially transported boulders and erratics, and are often extensively corroded (Bezys et al., 1997).

Brine spring sampling

Over the course of three years (1998–2000) a total of 46 samples were collected from brine springs near Lake Winnipegosis, and major element and isotope values were originally reported in Grasby and Chen (2005). Lithium concentrations were recorded but not reported at the time of publication; sampling methods are described in Appendix 1 of Grasby and Chen (2005).

Lithium concentrations

The hydrochemistry of the saline groundwater in the basin is variable and is dependent on location within the basin, which is itself related to the generative mechanism that characterizes these brines, be it evaporitic concentration (of seawater) or halite dissolution (of existing salt deposits). Nicolas (2017) summarized the variable lithium concentrations in Manitoba's groundwater, with

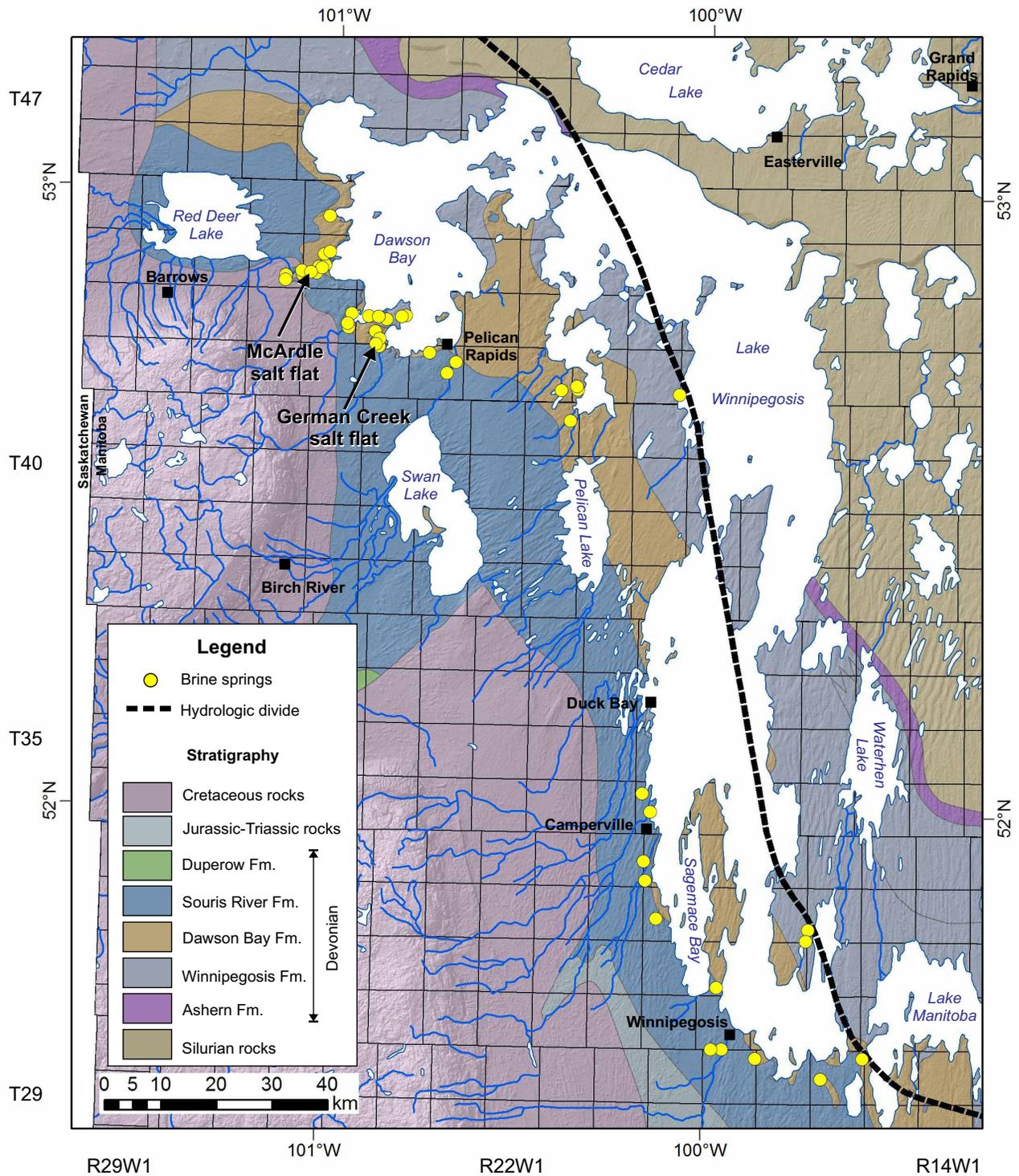


Figure GS2018-10-1: Regional geology of the study area in west-central Manitoba with digital elevation model (United States Geological Survey, 2002), showing the hydrological divide (which follows the 2000 mg/L dissolved-solids contour) and the location of the brine springs samples.



Figure GS2018-10-2: Field photographs of **a)** the McArde salt flat, in west-central Manitoba, also referred to as the Red Deer River salt spring, and collection location of sample M983075; **b)** the German Creek salt flat, in west-central Manitoba, showing large salt-flat and discharge-site morphology; **c)** a close up of a brine pool; **d)** brine boils (scale card shows size in centimetres). Sample M993016 was collected at this salt flat.

values from brines in the oil wells ranging from 0.258 to 7.32 ppm, values from freshwater to brackish water wells ranging from 0.01 ppb to 0.3 ppm, and values from shallow saline waters to brines in monitoring wells ranging from 0.488 to 3.84 ppm. Despite the small number of analytical results from deep brines, lithium concentrations in Manitoba's groundwater are low, with overall higher concentrations in the deep Jurassic and Paleozoic brines of southwestern Manitoba's oil region. Shallower brines and saline waters measured from the groundwater monitoring wells have lower lithium concentrations compared with the brines derived from deep oil wells. Freshwater-dominated Cambro-Ordovician aquifers along the eastern erosional edge of the Williston Basin, and located east of the hydrological divide, have extremely low lithium concentrations.

The lithium concentrations for the 46 brine springs that occur near and along the shores of Lake Winnipegosis are listed in Table GS2018-10-1. The lithium concentrations range from 150 to 6300 ppb, with an average of 1263 ppb. These values are comparable to or slightly higher than those reported in Nicolas (2017) from

groundwater east of the hydrological divide within the Cambro-Ordovician aquifer (carbonate-rock aquifer).

Discussion and conclusions

The lithium values from the brine springs are extremely low, falling far below economic limits for economic extraction from brines, which is estimated to be approximately 100 ppm (Munk et al., 2016). All but three of the reported values are above the mean lithium concentrations of seawater of 183 ppb (Riley and Tongudai, 1964), indicating some degree of lithium enrichment into the system. Since the brine springs consist of mixed brine waters from halite dissolution (likely dominated by the dissolution of the Prairie Evaporite, with minor influence from thinner evaporite beds in other Devonian formations) and freshwater, the source of this lithium enrichment is uncertain. The enrichment could come from a combination of lithium-bearing salt minerals and impurities within the Prairie Evaporite, and/or from freshwater enriched with lithium from the numerous lithium-bearing pegmatite occurrences in the Precambrian in Manitoba.

Table GS2018-10-1: Lithium concentrations from brine springs.

Sample Number	Sec	Twp	Rge (W1)	Latitude	Longitude	Li (ppb)
M983073		24	20	51.92644	-100.156393	770
M983074	17	35	19	52.00679	-100.141327	860
M983075		45	25	52.86719	-101.054513	1500
M983076		45	25	52.87543	-101.039318	1200
M983077		45	25	52.90154	-101.018757	980
M983078B		44	24	52.79866	-100.885302	1300
M983079	13	44	25	52.78675	-100.967345	830
M993008	24	44	25	52.80285	-100.956783	1500
M993009		44	24	52.79950	-100.911783	1600
M993010		45	25	52.88052	-101.030283	1300
M993011		45	25	52.87672	-101.048100	1400
M993012		45	25	52.89797	-101.033833	180
M993013		44	24	52.80175	-100.812500	1600
M993014		44	24	52.79505	-100.863617	1400
M993015		44	24	52.77542	-100.892683	150
M993016		44	24	52.75143	-100.882100	1400
M993017	12	44	25	52.78003	-100.964200	610
M993019		45	26	52.86253	-101.136100	1500
M993020		45	26	52.85482	-101.135983	1400
M993021		43	23	52.72865	-100.676367	530
M993022		43	24	52.71053	-100.699300	560
M993024		43	23	52.74282	-100.747700	170
M993025		44	24	52.76343	-100.880750	6300
M993026		45	25	52.86305	-101.089867	1400
M993027		45	20	52.68765	-100.349800	1300
M993028		45	20	52.69268	-100.352933	1300
M993029		45	21	52.63725	-100.368667	1400
M993030		45	21	52.68613	-100.393467	2700
M993031		43	19	52.68155	-100.079967	1400
M993032	6	34	19	51.89552	-100.151133	500
M993033	17	33	19	51.83398	-100.121750	550
M993034	4	32	18	51.72317	-99.961533	1100
M993035	4	31	18	51.62373	-99.946283	1400
M993036	36	30	18	51.60950	-99.859033	1200
M993037	5	31	18	51.62382	-99.974533	1300
M993038	4	31	18	51.81832	-99.724883	1200
M993039	1	33	17	51.80000	-99.729867	750
M993040	36	30	16	51.60998	-99.580883	3200
M993041	30	25	19	52.03652	-100.162567	420
M003001	17	30	16	51.57663	-99.688408	470
M003002		45	26	52.86985	-101.092713	1300
M003003		45	25	52.86839	-101.069483	1500
M003004		45	24	52.75444	-100.890475	970
M003005		44	24	52.79962	-100.823825	1600
M003006		44	24	52.79866	-100.885302	1400
M003007		46	25	52.95979	-101.021657	690

Although these are lower than optimal concentration values often considered as targets for exploration, brines in this region may present less challenges for lithium extraction due to their relatively low calcium concentrations (when compared to deep-basin brines to the west). High calcium in brines can be problematic, causing a common ion effect that inhibits extraction of lithium carbonate, such that sodium-rich brines are a preferable exploration target. In a similar sense, other sodium-rich brines, which are known to occur in the Winnipeg Formation, may prove a better exploration target given their known lower calcium contents (Ferguson et al., 2005).

Economic considerations

Lithium has been identified as a critical element (United States Geological Survey, 2018) since its demand has grown substantially over the last few years, mainly because of its use in rechargeable batteries, and is currently experiencing an exploration boom.

Extraction of lithium from brines using emerging technologies continues to push the boundaries and lower the minimum concentration required for deposits to be economic. Although lithium concentrations in Manitoba's deep brines are low, the water chemistry of the brine springs, as well as of the deeper brines of the Winnipeg Formation, marks these as favourable for lithium extraction.

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References

Bachu, S. and Hitchon, B. 1996: Regional-scale flow of formation waters in the Williston Basin; *American Association of Petroleum Geologists Bulletin*, v. 80, p. 248–264.

Bezys, R.K. and McCabe, H.R. 1996: Lower to middle Paleozoic stratigraphy of southwestern Manitoba; *Geological Association of Canada–Mineralogical Association of Canada, Joint Annual Meeting, Winnipeg, Manitoba, May 27–29, 1996, Field Trip Guidebook B4*, p. 92.

Bezys, R.K., Ducharme, E.B., Bamburak, J.D. and Fedikow, M.A.F. 1997: A geochemical study of saline brine sediments as a guide to prairie-type micro-disseminated mineralization and other precious metals in west central Manitoba (NTS 63C); *in Report of Activities 1997, Manitoba Energy and Mines, Geological Services*, p. 118–122.

Clayton, R.N., Friedman, I., Graf, D.L., Mayeda, T.K., Meents, W.F. and Shrimp, N.F. 1966: The origin of saline formation waters: 1. Isotopic composition; *Journal of Geophysical Research*, v. 71, p. 3869–3882.

Ferguson, G., Betcher, R.N. and Grasby, S.E. 2005: Water chemistry of the Winnipeg Formation in Manitoba; *Geological Survey of Canada, Open File 4933*, 37 p.

Grasby, S.E. and Betcher, R.N. 2002: Regional hydrogeochemistry of the carbonate rock aquifer, southern Manitoba; *Canadian Journal of Earth Sciences*, v. 39, p. 1053–1063.

Grasby, S.E. and Chen, Z. 2005: Subglacial recharge into the Western Canada Sedimentary Basin — impact of Pleistocene glaciation on basin hydrodynamics; *Geological Society of America Bulletin*, v. 117, p. 500–514.

Grasby, S.E. and Londry, K.L. 2007: Biogeochemistry of hypersaline springs supporting a mid-continent marine ecosystem: an analogue for Martian springs?; *Astrobiology*, v. 7, p. 662–683.

Grasby, S.E., Betcher, R., Osadetz, K.G. and Render, F. 2000: Reversal of the regional flow system of the Williston Basin in response to Pleistocene glaciation; *Geology*, v. 28, p. 635–638.

Munk, L.A., Hynek, S.A., Bradley, D.C., Boutt, D., Labay, K. and Jochens, H. 2016: Lithium brines: a global perspective; *Review in Economic Geology*, v. 18, p. 339–365.

Nicolas, M.P.B. 2017: Preliminary investigation of the potential for lithium in groundwater in sedimentary rocks in southwestern Manitoba; *in Report of Activities 2017, Manitoba Growth, Enterprise and Trade, Manitoba Geological Survey*, p. 183–190.

Palombi, D.D. 2008: Regional hydrogeological characterization of the northeastern margin in the Williston Basin; M.Sc. thesis, University of Alberta, Edmonton, Alberta, 196 p.

Riley, J.P. and Tongudai, M. 1964: The lithium content of sea water; *Deep Sea Research and Oceanographic Abstracts*, v. 11, p. 563–568.

United States Geological Survey 2002: Shuttle Radar Topography Mission, digital topographic data, Manitoba; United States Geological Survey, URL <ftp://edcsgs9.cr.usgs.gov/pub/data/srtm/>, portions of files N48W88W.hgt.zip through N60W102.hgt.zip, 1.5 Mb (variable), 90 m cell, zipped hgt format [March 2003].

United States Geological Survey 2018: Draft critical minerals list—summary of methodology and background information—United States Geological Survey technical input document in response to Secretarial Order No. 3359; United States Department of the Interior, United States Geological Survey; Open-file Report 2018-1021, 26 p.

Walter, L.M., Stueber, A.M. and Huston, T.J. 1990: Br-Cl-Na systematics in Illinois basin fluids: constraints on fluid origin and evolution; *Geology*, v. 18, p. 315–318.