

# Geochemistry of Duperow Formation brines: Mechanisms of enrichment and obstacles for direct Li extraction

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## Introduction

As energy production shifts away from carbon-derived forms, other elements and minerals will be increasingly relied upon, raising their demand. Lithium (Li) is an example of such an element. Due to its role in clean energy technologies stemming from its high energy density, Li is set to be of increasing importance because of its applications for energy storage in Li-ion batteries, specifically in electric vehicles (Tarascon, 2010; Dugamin et al., 2023). At current rates of production, it is estimated that the supply-demand balance for Li will become overwhelmed by the year 2030 (Benson et al., 2017). Increased demand has sparked exploration for undeveloped Li resources, including non-traditional sources such as brine-hosted Li deposits from sedimentary basins, or “petro-lithium”. Brine-hosted Li deposits have been historically overlooked as potential Li sources due to low Li concentrations and high salinities (Quist-Jensen et al., 2018). However, advancements in direct lithium extraction (DLE) technologies have the potential to allow exploration from previously non-exploitable Li sources, including brines (Boroumand & Razmjou, 2024). These advancements could play a role in promoting Li exploration and production within the Western Canada Sedimentary Basin (WCSB), where brines of the Duperow Formation have been observed to contain economic levels of Li, reaching as high as 259 ppm (EMP Metals, 2023). Despite its increasing potential, there are still some knowledge gaps related to the development and well-informed exploitation of Duperow Formation brines and Li-bearing brines from across the WCSB. The conditions of formation of continental Li brines are relatively well understood, but how closely the development of brine-hosted Li within sedimentary basins follows that of continental brines has yet to be fully constrained, including the mechanism by which Li is liberated from the source rocks, leading to enriched brines (Li et al., 2019). By extension, the composition of formation waters most favourable to the formation of a Li-bearing brine have not been identified (Lee et al., 2023). Likewise, more information is necessary regarding the implementation of DLE in the extraction of Li from enriched brines (Murphy & Haji, 2022). Inherently, some aspects of DLE will likely need to be tailored on a brine-by-brine basis, as competing ions are present in varying amounts. These competing ions pose issues when, as the brine cools to surface temperatures, they may yield precipitates, that could block or otherwise damage the DLE technology, limiting its permeability, lifetime, and effectiveness (Xiao et al., 2022). The potential for mineral precipitation and its subsequent effects must be considered for DLE technology, but a study on potential precipitates from the Duperow Formation brine has yet to be completed.

With these current knowledge gaps in mind, this research is split into two separate studies. The first uses geochemical modelling to predict the dissolved ion speciation and mineral species that are likely to precipitate from the Duperow Formation brine across varying temperature, Eh, pH, and activity conditions. The second portion of this study is centered around elucidating the conditions that can lead to Li release from sediments into the brines and further constrain the source within the Duperow Formation.

## Methods

For the first study, average chemical concentrations of the Duperow Formation brine were compiled (Jensen, 2011; Jensen, 2016; Jensen & Rostron, 2018; Jensen & Rostron, 2017) and input into the geochemical modelling software PHREEQ-C to derive the activities of the various constituents. This activity data was then used in the Tact and Act2 modules of the Geochemist's Workbench Community Edition, to identify mineral species trending towards saturation.

The leaching experiment followed methods previously performed by Bishop et al. (2023). Sediments from the Duperow, Birdbear, and Souris River formations were suspended in solutions of Ca, K, and Mg to determine the effects of each ion on leaching Li from the sediments. Samples were allowed to equilibrate with synthetic brines for a seven-day-period, at 20°C and 75°C and at a pH of 5.8. Following this seven-day period, samples were filtered and analyzed by ICP-MS.

## Results

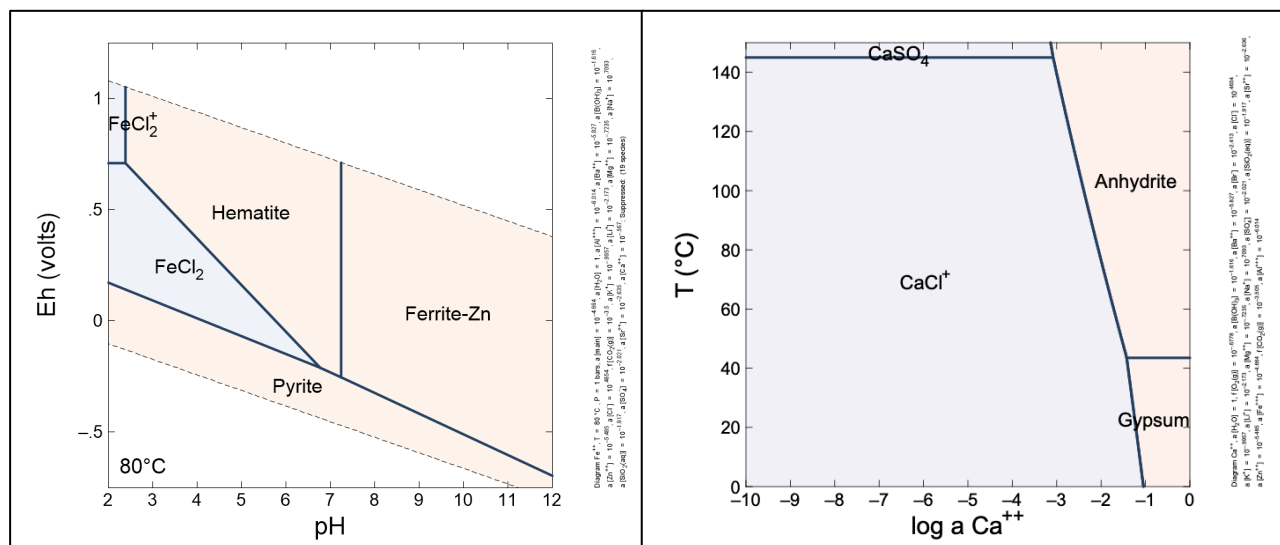


Figure 1: Fe- and Ca- mineralizations from the Li-bearing Duperow Formation brines.

The geochemical modelling study identified that Ca- and Fe-species (Figure 1) are most likely to precipitate from the Li-bearing Duperow Formation brine. These findings provide new insight to the development of a brine specific DLE for the Duperow Formation brine, indicating that steps may need to be taken to reduce or eliminate the potential for precipitation of these phases during the DLE process. This modelling has utility for assisting in the effective exploitation of this potential Li resource since DLE is one of the biggest bottlenecks in turning these brine-hosted Li deposits into an economic resource.

Results from the leaching experiments provide insight into the source of the Li within the Duperow Formation brine as well as the geochemical conditions which could lead to Li enrichments. Additionally, information was gained into the mechanism of enrichment of Li-bearing brines. This allows for more accurate constraints to be placed on the extent of this resource.

## References

- Benson TR, Coble MA, Rytuba JJ, Mahood GA. 2017. Lithium enrichment in intracontinental rhyolite magmas leads to Li deposits in caldera basins. *Nature Communications*, **270**.
- Bishop BA, Shivakumar KR, Alessi DS, Robbins LJ. 2023. Insights into the rare earth element potential of coal combustion by-products from western Canada. *Environmental Science: Advances*, **2**: 529-542.
- Boroumand Y & Razmjou. 2024. Adsorption-type aluminum-based direct lithium extraction: The effect of heat, salinity, and lithium content. *Desalination*, **577**.
- Coffey DM, Munk LA, Ibarra DE, Butler KL, Boutt DF, Jenckes J. 2021. Lithium Storage and Release from Lacustrine Sediments: Implications for Lithium Enrichment and Sustainability, in Continental Brines. *Geochemistry, Geophysics, Geosystems*.
- Dugamin EJ, Cathelineau M, Boiron MC, Richard A, Despinois F. 2023. Lithium enrichment processes in sedimentary formation waters. *Chemical Geology*, **635**.
- EMP Metals. 2023. EMP Metals discovers record lithium in brine concentrations – up to 259 mg/l at Viewfield.
- Jensen GK & Rostron BJ. 2017. Investigating the mineral potential of brines in Saskatchewan: results from the 2017 field season for the brine sampling project; in Summary of Investigations 2017, Volume 1, Saskatchewan Geological Survey, Saskatchewan Ministry of the Economy, Miscellaneous Report 2017-4.1, Paper A-1, 6p.
- Jensen GK & Rostron BJ. 2018. Investigating the mineral potential of brines in Saskatchewan: new results from the brine sampling project for 2018; in Summary of Investigations 2018, Volume 1, Saskatchewan Geological Survey, Saskatchewan Ministry of Energy and Resources, Miscellaneous Report 2018-4.1, Paper A-5, 8p.
- Jensen GK. 2011. Investigating the Mineral Potential of Brines in Southeastern Saskatchewan. Summary of Investigations 2011, Volume 2, Saskatchewan Geological Survey, Sask Ministry of Energy and Resources, Misc. Rep.
- Jensen GK. 2016. Results from the 2016 field season for the brine sampling project: investigating the mineral potential of brines in Saskatchewan in Summary of Investigations 2016, Volume 1, Saskatchewan Geological Survey, Saskatchewan Ministry of the Economy, Miscellaneous Report 2016-4.1, Paper A-3, 7p.
- Lee KJ, You J, Gao Y, Terlier T. 2023. Release, transport, and accumulation of lithium in shale brines. *Fuel*, **356**.
- Morissette CL. 2012. The Impact of Geological Environment on the Lithium Concentration and Structural Composition of Hectorite Clays. Master's Thesis, *University of Nevada, Reno*.
- Murphy O & Haji MN. 2022. A review of technologies for direct lithium extraction from low Li<sup>+</sup> concentration aqueous solutions. *Frontiers in Chemical Engineering*.

- Quist-Jensen CA, Aamer A, Drioli E, Macedonio F. 2018. Perspectives on mining from sea and other alternative strategies for minerals and water recovery – The development of novel membrane operations. *Journal of the Taiwan Institute of Chemical Engineers*, **94**: 129-134.
- Tarascon JM. 2010. Is lithium the new gold? *Nature Chemistry*.
- Xiao H, Chai M, Abdollahzadeh M, Ahmadi H, Chen V, Gore DB, Asadnia M, Razmjou A. 2022. A lithium ion selective membrane synthesized from a double layered Sr based metalorganic framework (MOF-on-MOF) thin film. *Desalination*, **532**.