

Lithium Concentration in the Duperow Formation: Preliminary Results of Geochemical Analysis of Core Samples from Two Wells in Southeastern Saskatchewan



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Abstract

In 2011 the Saskatchewan Geological Survey began a program of sampling brine from producing wells in the province as a response to the demand for lithium and other trace elements that could potentially be derived from basinal brines. During the field seasons since then, samples of brine were collected from numerous wells that produced from Paleozoic-aged formations in the oil-producing region of Saskatchewan and sent for geochemical analysis of their trace elements. The results of analyses on the brines from the formations that were sampled show that lithium concentration varies among the formations, and there are spatial variations in lithium content within the formations.

In 2019, 21 samples were taken from core from two wells that had produced from the Duperow Formation in southeastern Saskatchewan, one of which had been sampled previously for its produced brines. The lithium concentration in the brine from the Duperow well sampled previously represents the highest lithium value of all samples analyzed during this program. The core samples were analyzed for their trace element concentrations, and the core itself was logged. Analytical results show a large variation in lithium concentration in the core, ranging from 1 ppm to 120 ppm. Core logging resulted in the identification of seven facies. Of these seven facies, a green shale possesses the greatest lithium concentrations in both cores. Conversely, the lowest concentrations of lithium are from the anhydrites and from the oil-saturated zones of the cores.

This stage of the brine sampling project is the first step in determining the source of the lithium in the brines of Saskatchewan. Further work is being completed on cores from other oil-producing formations in southeastern Saskatchewan.

Keywords: Williston Basin, lithium, brine, geochemistry, industrial minerals

1. Introduction

The rapid expansion in the use of electric vehicles, and a growing demand to transition away from carbon-based energy sources has driven the demand for and increase in the price of lithium in the form of lithium carbonate, which is the main component for lithium-ion batteries that power electric vehicles. Currently, lithium is produced by two different mining processes: mining of a pegmatite rock that is rich in lithium (the majority of this production takes place in Australia); 2) evaporation of a lithium-rich brine, which takes 18 to 24 months. The second means of production occurs in South America, in a region known as the "Lithium Triangle," which includes Chile, Argentina and Bolivia, where the concentration of lithium in the brines ranges from 300 to 600 milligrams per litre (mg/L). In the salars of northern Chile, researchers have suggested that the lithium in the brines is of volcanic origin (Ericksen *et al.*, 1990).

The increase in demand is driving a search for other sources of lithium. One such alternate source of lithium may be from subsurface brines in sedimentary basins. Previous research by the Saskatchewan Geological Survey found lithium concentrations as high as 190 mg/L in produced brines from oil wells in the province (Jensen, 2011, 2015, 2016; Jensen and Rostron, 2017, 2018). These brine resources have the potential to create a new industry for the province. The origin of the lithium in formation waters is not well documented, but it is believed to be produced by interactions between bedrock and fluids migrating through it, since the concentration of lithium in seawater is very low, ranging from 0.1 mg/L to 1.17 mg/L (Choubey *et al.*, 2017). Previous research on the potential for the development of a brine resource in the province of Saskatchewan focused on sampling the brine produced from oil wells throughout the province (Jensen, 2011, 2015, 2016; Jensen and Rostron, 2017, 2018). The focus of the research presented in this paper is to investigate the concentration of lithium in the framework of the rock cored in producing oil wells, as all of the previous lithium values are from lithium that is in solution (*i.e.*, produced brines). Cores from two wells producing from the Duperow Formation (Figure 1) were chosen as a starting point, because the samples of brines from the Duperow had the highest lithium concentrations observed in the province to date (Jensen, 2011, 2015, 2016). Fortunately, core is available for the Duperow well with the highest concentration of lithium (well 41/14-12-7-11W2; 03J253), as examination and testing of this core provided an opportunity to observe if there is a correlation between the lithium present in the produced formation waters and the lithium present in the rock itself.

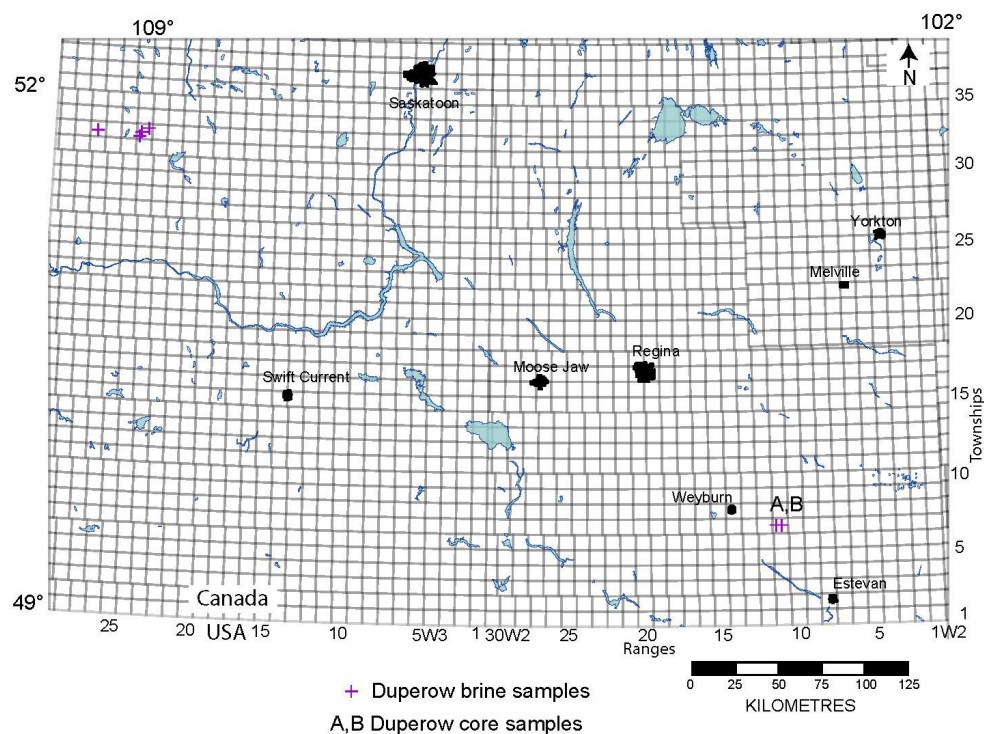


Figure 1 – Location of the Duperow Formation wells that were sampled for this project. All samples were obtained from wellheads that were currently producing within the Williston Basin. The two Duperow cores that were sampled, indicated by the letters A and B, correspond to the wells whose analytical results are presented in Table 1 and Appendix 1, which accompanies this paper.

2. Methodology

A total of 21 samples were taken for this study, from two Duperow Formation cores. Sampling was completed in two stages. Initially, 12 samples were taken from well 41/14-12-007-11W2; 03J253 and sent for analysis. Once the results of these analyses were received, it was concluded that more sampling was required to better understand the vertical variability, so an additional six samples were collected from well 41/14-12-007-11W2; 03J253, along with three samples from well 41/15-12-007-11W2; 03F509, another well that had produced from the Duperow Formation and that lies approximately 350 metres east of the first well, to determine if the vertical variability in lithium concentration could be correlated between the two wells.

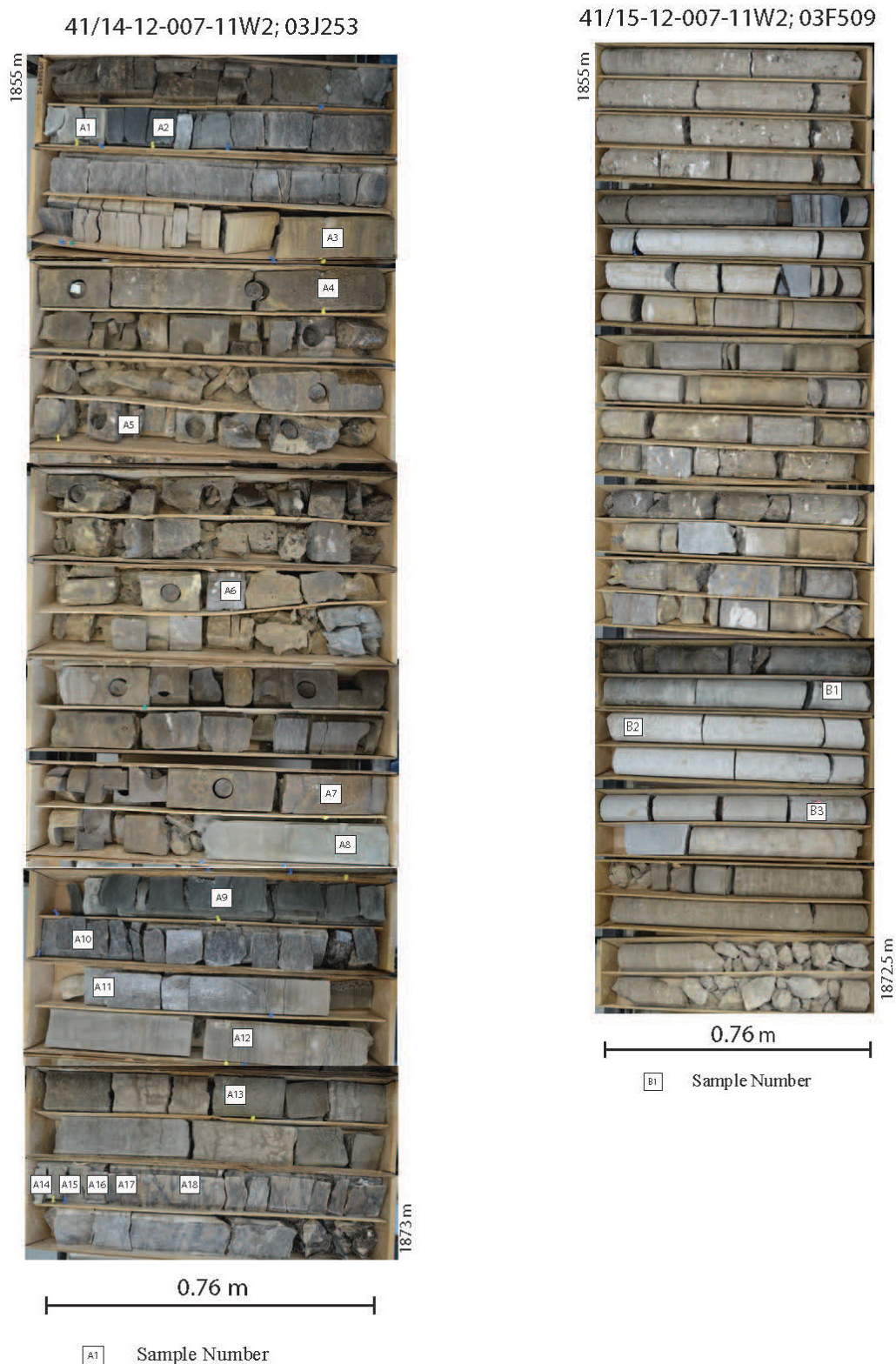


Figure 2 – Photos of core from Duperow Formation wells 41/14-12-007-11W2; 03J253 (**left**; well A in Figure 1), and 41/15-12-007-11W2; 03F509 (**right**; well B on Figure 1) showing locations of samples collected. The sample numbers in this figure are also correlated to the interpreted facies on Figure 3, and to the analytical results in Table 1 and Appendix 1. Darker areas on the core are zones of oil saturation.

The core to be sampled was laid out in the viewing room of the Saskatchewan Geological Subsurface Laboratory in Regina. Samples were chosen to ensure that all lithologies present in the core were represented, including oil-saturated zones. Core samples were taken with a carbide drill bit. The drill bit was washed with de-ionized water after each sample and allowed to dry before the next sample was taken. Figure 2 shows photos of the core for wells 41/14-12-007-11W2; 03J253 (well A in Figure 1) and 41/15-12-007-11W2; 03F509 (well B in Figure 1), with sample locations marked.

The powdered rock resulting from the drilling was placed into vials—5 grams each for the first 12 samples, then roughly 1.2 grams each for the second-stage samples after it was determined that a smaller amount would suffice—and sent to the Saskatchewan Research Council (SRC) in Saskatoon for analysis of the major and trace element content. The sample preparation and analytical procedures followed by the SRC are outlined below. The results of the analyses are given in Table 1 (lithium concentration only) and Appendix 1 (all analytical results), which accompanies this paper.

Sample Preparation

Rock samples were dried in their original containers, then crushed in a jaw crusher. A subsample was split out using a sample riffler. The subsample was pulverized using a puck-and-ring grinding mill. The pulp was transferred to a barcode-labeled plastic snap-top vial and then either total digestion for inductively coupled plasma–optical emission spectrometry (ICP-OES) analysis or partial digestion for inductively coupled plasma–mass spectrometry (ICP-MS) analysis was carried out.

Geochemical Analysis by ICP-OES: Multi-Element Total Digestion

Total digestion analysis was performed on samples to determine the dilution required prior to analysis by ICP-MS. An aliquot of pulp was digested to dryness in a HotBlock™ digestion system using a mixture of ultra-pure concentrated acids (HF:HNO₃:HClO₄). The residue was dissolved and made to volume using de-ionized water prior to analysis. Instruments were calibrated using certified commercial solutions. The instrument used was Perkin Elmer Optima 5300DV.

The following elements were analyzed only by ICP-OES for total digestion leaching: Al₂O₃, CaO, Fe₂O₃, K₂O, MgO, MnO, Na₂O, P₂O₅, TiO₂, Ba, Ce, Cr, La, Li, Sr, S, V, and Zr.

Geochemical Analysis by ICP-MS: Partial Digestion

A partial digestion analysis was performed on the elements As, Ge, Hg, Sb, Se and Te, as these elements are not suited to total digestion analysis. An aliquot of pulp in a digestion tube was digested in a mixture of ultra-pure concentrated nitric and hydrochloric acids (HNO₃:HCl) in a hot water bath and then diluted using de-ionized water prior to analysis. The ICP-MS instruments used were Perkin Elmer Elan DRC II or Perkin Elmer NEXION.

3. Sedimentology of the Duperow Formation, and Facies Interpretation

The sediments forming the Duperow Formation were laid down during the third phase of Devonian deposition, in the middle to late Frasnian (~380 to 370 Ma; Christopher *et al.*, 1971; Dunn, 1975; Yang, 2015). The portion of the Duperow Formation examined for this study was deposited along the eastern edge of the Elk Point Basin, which, at that time, represented very shallow restricted marine waters, with deposition occurring on a broad tidal flat. The facies identified in cores from wells 14-12-007-11W2; 03J253 and 15-12-007-11W2; 03F509 are a product of this depositional environment.

The following seven facies were identified from the examination of the two Duperow cores in this study. They are distinguished by lithology, sedimentary structures, fossils and grain size, as described below and illustrated in Figure 3.

Facies 1 – Nodular anhydrite: Dark green to brown interspersed with white, Facies 1 has a ‘chicken wire’ fabric and is structureless. Facies 1 can be up to 2 metres thick, and is repeated within the study area’s stratigraphic section (Figure 3). Facies 1 is interpreted as a coastal sabkha, deposited during periods of high evaporation rates of hypersaline waters.

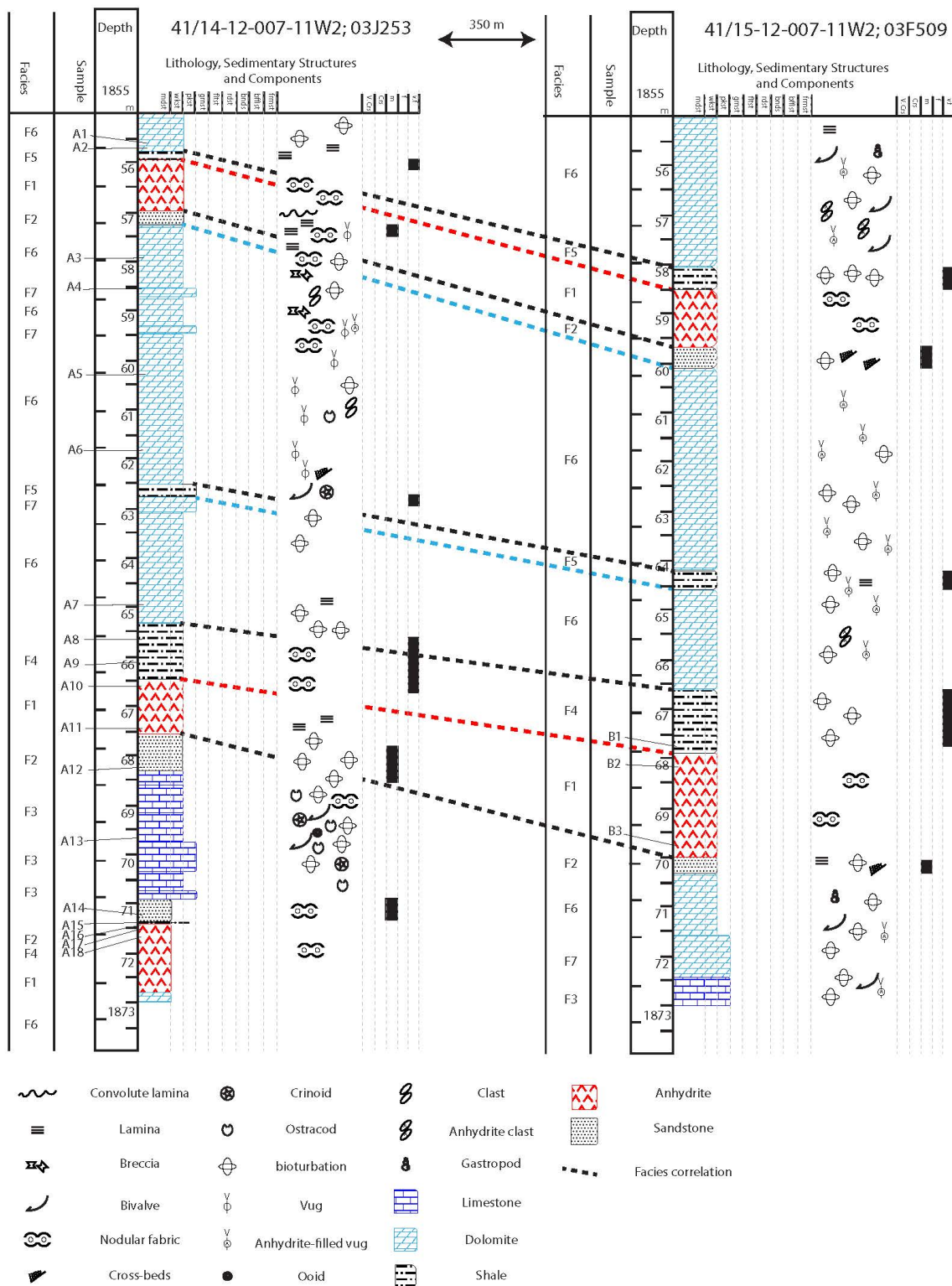


Figure 3 – Correlation of the lithology and interpreted facies in the two Duperow cores examined in this study. Locations of samples are shown in Figure 2; analytical results for the samples are in Table 1 and Appendix 1. Abbreviations for rock type: *frmst* – framestone, *bflst* – baffestone, *bnds* – bindstone, *rdst* – rudstone, *flst* – floatstone, *grnst* – grainstone, *pkst* – packstone, *wkst* – wackestone, *mdst* – mudstone. Abbreviations for grain size: *V.f* – very fine, *f* – fine, *m* – medium, *Crs* – coarse, *V.Crs* – very coarse.

Facies 2 – Quartz lithic wackestone: This facies is tan to brown in colour, and fine to medium grained with planar cross-bedding, giving the rock a laminated appearance. Facies 2 locally comprises angular cross-bedding. Facies 2 is repeated in the stratigraphic section and can be identified at three different depths (Figure 3). Facies 2 is interpreted as a tidal flat channel deposit, deposited during periods of low to moderate hydrodynamic energy. The hydrodynamics reworked and distributed continentally derived siliciclastic material.

Facies 3 – Skeletal wackestone: Brown to dark brown in colour, Facies 3 is a bioturbated limestone comprising ostracods, bivalve and crinoid fragments; ooids and planar cross-beds are present locally. Facies 3 displays vuggy porosity, with a relatively even distribution between open porosity and porosity occluded by anhydrite. The fragmented allochems and planar cross-beds are evidence of tidal translocation and reworking of sediments from production sites to depositional sites. The vuggy porosity is a diagenetic fabric initiated during early-stage meteoric diagenesis, with pore enhancement affected and often occluded by anhydrite during late-stage burial diagenesis. Facies 3 is interpreted as carbonate deposition on a shallow tidal flat inundated by restricted marine waters.

Facies 4 – Green shale: Facies 4 is light green to dark green in colour and is commonly heavily burrowed at the base, gradually becoming less burrowed toward the top. Facies 4 is interpreted as a eutrophic deposit that was bioturbated in a reducing environment. The lack of sedimentary structures may be attributed to bioturbation in a lagoonal setting.

Facies 5 – Grey shale: Bluish grey in colour, Facies 5 can be up to 60 cm thick and displays a finely laminated texture with polymictic pebbles and clasts. Facies 5 is a relatively thin unit that may represent a punctuated input of continentally derived siliciclastic material that was focused in localized areas of accommodation.

Facies 6 – Dolomitic wackestone: This facies is tan to brown in colour and comprises fine-grained sucrosic dolomite, gastropod fragments, burrows, metasomatic anhydrite, with vuggy porosity occluded by bladed anhydrite. The vugs with porosity occluded by bladed anhydrite are up to 6 cm in size. Facies 6 is interpreted as carbonate deposition in a restricted marine environment, with early-stage dolomitic replacement of the muddy carbonate sediments, accompanied by depositional sucrosic dolomite in restricted magnesium-rich waters. The depositional dolomite may represent a localized embayment that was not regularly refreshed by normal marine waters.

Facies 7 – Skeletal dolomitic packstone: Brown to dark brown in colour, Facies 7 comprises crinoid fragments, bivalves, angular cross-beds, subrounded rip-up clasts and burrows. Facies 7 has vuggy porosity that is occluded by bladed anhydrite. Facies 7 is interpreted as a moderate-energy tidal deposit, evidenced by the cross-beds and fragmented allochems. The dolomitic texture is from diagenetic replacement of the carbonate sediments during early- to middle-stage reflux diagenesis of magnesium-rich waters.

The close proximity of the two wells (only roughly 350 metres apart) allows for direct correlation of the facies. Figure 3 illustrates the relationship between the facies of the two wells. The figure shows the anhydrite and siliciclastic facies thicken in well 15-12-007-11W2; 03F509. The thickening of these sediments is attributed to deepening of the site of deposition and increase in accommodation space of the facies compared to well 14-12-007-11W2; 03J253. The shallowing of the facies in well 14-12-007-11W2; 03J253 may be interpreted as this well being located on the flank of a tidal channel, whereas the facies in well 15-12-007-11W2; 03F509 may have been deposited at a deeper locale, toward the channel thalweg.

4. Lithium Concentration in the Duperow Formation: Results and Discussion

For the scope of this paper, only the results of the lithium analyses are discussed; all other elemental data are in Appendix 1, which accompanies this paper.

Lithium concentration in the 21 core samples analyzed ranges from 1 parts per million (ppm) to 120 ppm (Table 1). There are three observed heightened concentrations in lithium ($\text{Li} > 50$ ppm) in well 14-12-007-11W2; 03J253. These elevated concentrations occur in the following facies (from top to bottom of core): Facies 6 (sample A1, 57 ppm), Facies 4 (samples A8, 76 ppm and A9, 83 ppm), and Facies 2 (sample A14, 114 ppm). In well 15-12-007-11W2; 03F509, three samples were taken in order to determine if the high lithium concentration observed in sample A14

(114 ppm) was present in this core, and if it could be correlated to the first well. Sample B1 from well 15-12-007-11W2; 03F509 had a lithium concentration of 120 ppm; this is the highest lithium concentration from the two cores (Table 1). The highest lithium concentrations were in samples that were taken from Facies 2 and 4 in well 14-12-007-11W2; 03J253 and from Facies 2 in well 15-12-007-11W2; 03F509 (Figure 3).

Table 1 – Concentration of lithium in the samples collected from the two Duperow cores examined in this study. ‘Sample ID’ is keyed to Figures 2 and 3; the facies are described in the text and illustrated in Figure 3. Location coordinates are in North American Datum 1983 (NAD83), Zone 13.

	Depth (m)	Sample ID	Facies	Li (ppm)
Well A	1855.8	A1	F6	57
UWI 41/14-12-007-11W2/00; 03J253	1856.0	A2	F6	44
Sample interval: 1855.5 to 1872 m	1857.7	A3	F2	5
Longitude (NAD83): -103.37447	1858.5	A4	F6	8
Latitude (NAD83): 49.55059	1860.5	A5	F6	9
UTM Easting (NAD83): 617576.4697	1861.8	A6	F6	3
UTM Northing (NAD83): 5489936.566	1865.0	A7	F6	5
	1865.7	A8	F4	76
	1866.1	A9	F4	83
	1866.6	A10	F1	1
	1867.5	A11	F1	1
	1868.4	A12	F2	14
	1869.7	A13	F3	40
	1871.2	A14	F2	114
	1871.3	A15	F1	19
	1871.4	A16	F1	16
	1871.5	A17	F1	2
	1871.7	A18	F1	14
Well B	1867.8	B1	F4	120
UWI 41/15-12-007-11W2/00; 03F509	1868.2	B2	F1	1
Sample interval: 1867 to 1869.5 m	1869.8	B3	F1	6
Longitude (NAD83): -103.36966				
Latitude (NAD83): 49.55048				
UTM Easting (NAD83): 617937.4496				
UTM Northing (NAD83): 5489942.151				

Three of the four highest lithium values occur in Facies 4 (Figure 3), a green shale. Other facies that display high levels of lithium are Facies 2 (quartz lithic wackestone) and Facies 6 (dolomitic wackestone; Figure 3) with concentrations of 114 ppm and 57 ppm, respectively. The lower lithium values are typically observed in the anhydrites and in the oil-saturated zones of the cores.

The produced brines are being drawn from the portions of the cores that are oil saturated; these zones have the lowest concentrations of lithium observed in the samples taken. The exact nature of the source of the lithium is presently unknown, but it is suspected to be in the produced brines as a result of rock-water interactions since deposition. It is believed that the low concentration of lithium in the rock of the oil-saturated zones is a result of the lithium being dissolved from the rock and becoming enriched in the produced brine. Further research needs to be completed to better understand the source of the lithium in brines of Saskatchewan.

5. Future Work

- Sampling of other Lower Paleozoic formations in southeastern Saskatchewan will be carried out to investigate if there is a variation in lithium concentration between formations as well as the vertical variation within formations that has already been detected.
- Other Duperow wells that have core will be tested to determine if there is a spatial variation in lithium concentration within the Duperow Formation.

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