

**HYDROGEOCHEMICAL EVOLUTION OF GROUNDWATERS IN THE  
WILLISTON BASIN, CANADA**

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By

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## ABSTRACT

Glacial cycles over the last two million years have successfully altered deep groundwater flow in the Williston Basin, Canada. Mixing with evaporated paleoseawater has resulted in unique geochemical signatures in formation waters with spatial and temporal trends, however the timing of glaciogenic recharge into the Williston Basin and spatial understanding of the flow system is loosely constrained. I examine timing and effect of glaciogenic recharge by using an integration of fluid chemistry, stable isotope data, and transport modeling. Results demonstrate that meltwater arrived at depths of ~600 to 1000 m in the northcentral region of the Williston Basin at two separate time periods, 75 to 150 ka and 300 ka. Spatial analysis of geochemical data illustrates that meltwater recharge extended to a continuous recharge belt along the northern margin of the Williston Basin, greater than previously anticipated. Individual and multi-variate analysis of isotope and solute geochemistry exhibit trends that contribute to fractionation of  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $\delta^{37}\text{Cl}$ , and  $\delta^{81}\text{Br}$ , and validates the importance of water origin and variation in mineral composition on solute concentrations and isotope values. Although overprinting and mixing interactions may present challenges in geochemical interpretation, the inter-disciplinary approach used in this research contributes to a greater understanding of how glacial meltwater recharge altered geochemical landscapes during large-scale salt dissolution in the Williston Basin.

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## LIST OF ABBREVIATIONS

TDS	Total dissolved solids
‰	Per mille
VSMOW	Vienna Standard Mean Ocean Water
SMOC	Standard Mean Ocean Chloride
SMOB	Standard Mean Ocean bromide
SRM	Standard reference material
GMWL	Global Meteoric Water Line
LMWL	Local meteoric water line
HDPE	High Density Polyethylene
GC-CF-IRMS	Gas chromatography continuous flow isotope ratio mass spectrometry
PCA	Principal component analysis

## CHAPTER 1: INTRODUCTION

Major geologic events must ensue for continental-scale groundwater flow systems to be altered. Glacial cycles over the last two million years were successful in greatly altering these flow systems by increasing hydraulic heads and recharging subglacial meltwaters to kilometre depths in permeable formations (Grasby et al., 2000; Person et al., 2007; McIntosh et al., 2012). From dilution to complete flushing of remnant paleo-evaporated fluids, the hydrogeologic landscape of sedimentary basins was changed over the last two million years.

Glacial recharge has impacted sedimentary basins across the northern hemisphere as evidenced by using physical geography and geochemical observations (Boulton et al., 1996; Grasby et al., 2000) resulting in major changes to loading structures and instabilities in near-surface formations. In particular, in North America where glacial activity has occurred along mid-latitudes in the Western Canada Sedimentary Basin and Michigan/Illinois/Appalachian basins (Grasby et al., 2000; Person et al., 2007; McIntosh et al., 2012), massive regions of salt dissolution have resulted in vastly different geochemical signatures and major changes to energy and mineral resources.

The Williston Basin, located in the Western Canada Sedimentary Basin, is no exception to the effects of Pleistocene glaciation (Grasby et al., 2000; Person et al., 2007). However, timing of glaciogenic recharge responsible for flushing evaporated and dissolution of evaporites remain vaguely constrained. Previous studies highlight the importance of the eastern margin of the Williston Basin for these recharge events, but evidence suggests there is a similar amount of recharge occurring along the northern margin as well. Additionally, minimal research has been

done to construct how the hydrostratigraphy in regions across the Williston Basin vary together, or as separate entities, and how the geochemical variables evolve with glaciogenic flushing and mineral dissolution.

### **1.1 Research Hypothesis and Objectives**

This thesis examines the timing and extent of glaciogenic recharge and relative effects on remnant saline fluids in deep, subsurface aquifers of the Williston Basin. This is observed by simulating meltwater recharge in the last two million years to the Williston Basin, and collecting mine solute and isotope geochemistry data to understand statistical and qualitative correlations between selected variables. Specifically, these objectives include:

- Objective 1: simulate 1–D vertical transport in Devonian carbonate aquifers to the Williston Basin to confirm the ages of glaciogenic-origin groundwater, and map the transport ages to estimate flow paths and recharge zones along the Williston Basin margin.
- Objective 2: use bivariate and multivariate analysis to understand the variation in geochemistry between glaciogenic and brine sources.

### **1.2 Thesis Organization**

This manuscript-style thesis consists of one published research paper (Chapter 2), a second research chapter (Chapter 3), and summary of observations (Chapter 5). The first research paper (Chapter 2) analyzes the variability in timing and transport of Pleistocene meltwater recharge to regional aquifers in the Williston Basin. Following the study conducted in Chapter 2, questions arose regarding the ability of various geochemical and isotopic tracers to evolve with different sources of saline fluids (e.g. from salt dissolution or paleoevaporated seawater). Therefore, the second chapter (Chapter 3) explores the geochemical variation in

solutes and isotope systems between evaporated paleoseawater and glaciogenic sourced groundwaters in the Williston Basin. The results from Chapter 2 and 3 compliment each other in identifying trends in solute and isotope chemistry and the driving factors to geochemical changes in deep, subsurface aquifers of the Williston Basin.

## **CHAPTER 2: VARIABILITY IN TIMING AND TRANSPORT OF PLEISTOCENE MELTWATER RECHARGE TO REGIONAL AQUIFERS**

### **Abstract**

The impacts of Pleistocene glaciation on groundwater flow systems in sedimentary basins are widely recognized, but the timing and distribution of subglacial recharge events remain poorly constrained. We investigate the spatial and temporal variability of recharge events from glaciations over the last two million years in the Williston Basin, Canada. Integration of fluid chemistry, stable isotope data, and transport modeling indicate that meltwater arrived at depths of ~600 to 1000 m in the northcentral region of the Williston Basin at two separate time periods, 75 to 150 ka and 300 ka, which we attribute to permeability differences between stacked aquifer systems. Our findings indicate that meltwater recharge extended along the northern margin of the Williston Basin as well as previously identified recharge areas to the east. Given the distance of measurements from recharge areas, evidence of recharge from the early to mid-Pleistocene appears to be preserved in the Williston Basin.

### **2.1 Introduction**

Pleistocene glaciation profoundly altered continental-scale groundwater flow systems by increasing hydraulic heads and recharging fresh subglacial meltwaters to kilometre depths in underlying sedimentary basins (Grasby et al., 2000; Person et al., 2007; McIntosh et al., 2012). Advance and retreat of ice sheets produced multiple subglacial recharge events, which flushed and diluted remnant saline fluids (McIntosh et al., 2012) and extensively dissolved evaporites (Grasby and Chen, 2005; McIntosh and Walter, 2006) in sedimentary basins of North America and Europe

(Boulton et al., 1994; Kloppmann et al., 2001). The few studies that have attempted to constrain the timing of subglacial recharge using age tracers (e.g., Mazor and Bosch, 1987; Schlegel et al., 2011) have been relatively coarse and focus on single aquifer or confined aquifer systems, while many of these sedimentary basins contain extensive stacked aquifers that were likely recharged intermittently over the past two million years.

Pleistocene glacial meltwaters are an important fresh groundwater resource in glaciated continental and coastal regions across the northern hemisphere (Grasby et al., 2000; Edmunds and Milne, 2001; Person et al., 2007; Person, 2007; McIntosh et al., 2011). Infiltration and recharge of meltwaters have implications for long-term radioactive waste and CO<sub>2</sub> storage (Lemieux et al., 2008; Lemieux et al., 2011), energy resources via stimulation of microbial methanogenesis in shales and coalbeds (Martini et al., 2008; McIntosh et al., 2012), and mineral resources via dissolution of potash deposits in the Williston Basin (Grasby et al., 2000). Thus, determining the timing and flowpaths of subglacial recharge is vital for assessing resource sustainability and understanding the paleohydrogeology of sedimentary basins.

Previous studies have used age tracers like radiocarbon (<sup>14</sup>C), helium (<sup>4</sup>He), and krypton (<sup>81</sup>Kr) to constrain the timing of Pleistocene recharge (McIntosh and Walter, 2006; Cloutier et al., 2006; Schlegel et al., 2011; Hendry et al., 2013; Gerber et al., 2017). However, radiocarbon dating is limited to <~50,000 years and existing noble gas data is relatively sparse. As an alternative, stable isotopes of water ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) data are more widely available (Ferguson and Jasechko, 2015; Jasechko, 2019), enabling higher-resolution studies. These data are also effective indicators of groundwater sources as modern meteoric waters, Pleistocene recharge, and evaporated paleoseawater typically exhibit distinct  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  signatures. Previous studies using numerical models estimated the arrival time of waters with distinct isotopic signatures (e.g., subglacial

meltwater recharge) at specified locations within the Williston Basin (Hendry et al., 2013; Hendry and Harrington, 2014). The numerical transport modeling solves for the time period(s) which has passed since the Pleistocene meltwater arrived in the region and, fitted to high-resolution  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  data, can effectively constrain the timing of subglacial meltwater arrival.

The impacts of Pleistocene glaciation on basinal-scale flow systems in the Williston Basin are widely recognized (Grasby et al., 2000; Person et al., 2007). However, the timing of meltwater recharge events responsible for flushing evaporated and dissolution of evaporites remain ambiguous. Evaporated paleoseawater, positioned deep within the Williston Basin, are highly saline ( $>350 \text{ g L}^{-1}$  TDS) and have elevated  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values characteristic of evaporated paleoseawater (Wittrup and Kyser, 1990). However, recharge of fresh Pleistocene meltwaters, with low  $\delta^{18}\text{O}$  values, along the north to east margins of the Williston Basin flushed evaporated paleoseawater and generated new salinity via extensive salt dissolution (Wittrup and Kyser, 1990; Grasby et al., 2000; Grasby and Chen 2005; Tipton, 2018). Using 1-D transport modeling of  $\delta^{18}\text{O}$ -depth profiles, Hendry et al. (2013) estimated Pleistocene subglacial recharge for the Cretaceous Mannville aquifer in southeast Saskatchewan, Canada arrived between 240 and 430 ka. The variation in arrival times to the Mannville aquifer may be attributed to local and regional discontinuities between locations, the distance to different recharge areas, and (or) changes in hydraulic properties (e.g. hydraulic conductivity or porosity).

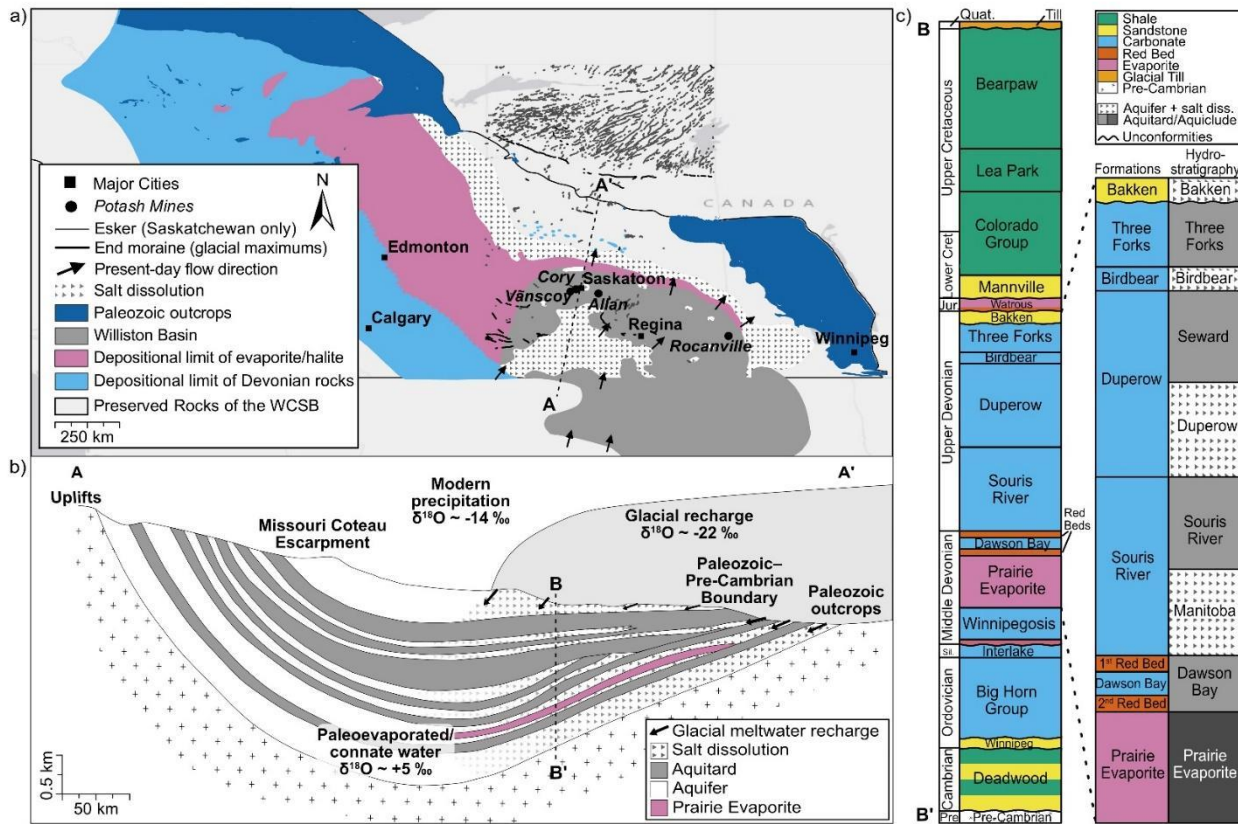
Here, we explore the timing of Pleistocene meltwater recharge into a deep, stacked carbonate aquifer system at different locations within the Williston Basin to gain a more basin-scale perspective using a combination of high-resolution  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  data with groundwater transport modeling. We show that arrival times varied incoherently with spatial location and aquifer position in the carbonates, but that it consistently occurred within two separate time periods and from areas

along a continuous recharge belt along the north to east margin of the basin. This contributes a greater understanding of glacial meltwater recharge and flowpaths in the Williston Basin, and also its relevant applicability to other sedimentary basins impacted by glaciation in the northern hemisphere.

## **2.2 Regional Hydrogeology**

The Williston Basin is an intracratonic sedimentary basin centered in North Dakota, USA. The basin extends north into southcentral Saskatchewan and southwest Manitoba in Canada, and west and south into Montana and South Dakota, respectively, in the USA. The basin is structurally bound by the Sweetgrass Arch to the west, the Canadian Shield to the north, the Manitoba Escarpment to the east, and various uplifts in Montana and South Dakota to the south (Kent and Christopher, 1994) (Figure 2–1). The Williston Basin consists of sedimentary rocks conformably and unconformably overlain by each other. Middle and upper Devonian (mid-Paleozoic) strata are composed of stacked aquifers, aquitards, and aquicludes that were deposited during carbonate transgressive and regressive episodes. These strata include the Prairie Evaporite aquiclude, Manitoba aquifer, Souris River aquitard, Duperow aquifer, Seward aquitard, Birdbear aquifer, and Three Forks aquitard (Figure 2–1).





**Figure 2–1:** Overview of (a) Western Canada Sedimentary Basin and relevant geologic features with present–day regional flow directions, (b) cross section for the Williston Basin between A–A' with meltwater infiltration and mixing process during glacial impact, and (c) stratigraphic column of the Williston Basin between B–B' with the Devonian inset with more detailed geology and hydrostratigraphy surrounding the aquifers examined in this study.

The Williston Basin has been intermittently overlain by continental ice sheets over the past two million years (Christiansen and Sauer, 2001). Increases in the hydraulic head associated with ice sheets and subsequent influx of glacial meltwater into Paleozoic carbonate aquifers significantly altered groundwater flow patterns in the basin (Grasby et al., 2000). Groundwater within these carbonate aquifers, which are relatively isolated at-depth between adjacent confining units of shale and bedrock, retain a distinct geochemical and isotopic signature characteristic of Pleistocene meltwaters (Grasby and Betcher, 2002; Grasby and Chen, 2005). These characteristics include  $\delta^{18}O$  and  $\delta^2H$  values that plot on the Global Meteoric Water Line (GMWL) but more  $^{18}O$

and  $^2\text{H}$ -depleted with respect to modern precipitation. They also exhibit a molar Na:Cl ratio of  $\sim 1$  and Cl:Br ratios  $\sim 10$  times greater than seawater, indicative of halite and salt dissolution (Grasby and Betcher, 2000)

Following retreat of the Laurentide Ice Sheet, hydraulic heads in the Williston Basin likely returned to the present, quasi-equilibrium state (Hitchon, 1969a; Grasby and Chen, 2005). Present-day regional groundwater flow is from topographic highs in the southwest, including the Black Hills in South Dakota, to topographic lows near the boundary of the Canadian Shield in the northeast (Figure 2–1a). The deepest hydrostratigraphic units of the Williston Basin exhibit little evidence of meteoric water circulation (Palombi, 2008). Instead, these Na-Cl to Na-Ca-Cl type waters exhibit characteristics of evaporated paleoseawater including molar Na:Cl ratios  $< 0.85$ , Cl:Br ratios comparable to evaporated seawater, and  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values that plot below the GMWL (Grasby and Betcher, 2002; Grasby and Chen, 2005; Ferguson et al., 2007; Tipton, 2018). Stagnation of evaporated paleoseawater within deep sedimentary basins is attributed to negative buoyancy associated with high TDS waters (Bachu and Hitchon, 1996; Palombi, 2008; Ferguson et al., 2018).

## **2.3 Methods**

### ***2.3.1 Sample collection and analysis***

Formation fluids were collected in November 2016 and March 2018 from active seeps over short time intervals in mine shafts and mine workings at the Vanscoy, Cory, Allan, and Rocanville potash mines in southcentral Saskatchewan (Figure 2–1). These seeps primarily originated from the middle to upper Devonian strata from the Birdbear formation ( $\sim 600$  m) to the Prairie formation ( $\sim 1100$  m), which corresponds to mine level (Table A1). Fluids were collected into clean 250 mL or 1000 mL HDPE bottles and stored at ambient room temperature until analysis.

Dissolved Cl<sup>-</sup> and Br<sup>-</sup> concentrations were determined by ion chromatography in the Environmental Analytical Laboratory at the Saskatchewan Research Council (Saskatoon, Canada). The  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values were determined using CO<sub>2</sub>-H<sub>2</sub>O and H<sub>2</sub>-H<sub>2</sub>O equilibration methods, respectively, at the Saskatchewan Isotope Laboratory (Saskatoon, Canada) and results are reported as the relative difference between the <sup>18</sup>O/<sup>16</sup>O and <sup>2</sup>H/<sup>1</sup>H abundance ratios normalized to Vienna Standard Mean Ocean Water (VSMOW), expressed in per mille (‰) notation. Accuracies of  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  are 2‰ and 0.2‰, respectively, but this methodology does not account for the salt effect in highly saline waters (Sofer and Gat, 1972; Sofer and Gat, 1975; Koehler et al., 2013). Corrections for the salt effect, which produces discrepancies in measured isotope compositions in high activity brines as outlined by Sofer and Gat (1972; 1975) and Koehler et al. (2013), were applied to the  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values. Additional data (Cl, Br,  $\delta^{18}\text{O}$ , and  $\delta^2\text{H}$ ) is from Tipton (2018) to increase data coverage.

### ***2.3.2 Model setup***

A simplified hydrostratigraphic column (Figure 2–2a) was constructed based on local geology using GeoHub Saskatchewan (Marsh and Love, 2014) for Prairie Evaporite (mine level) to surface. Simulation of measured  $\delta^{18}\text{O}$  data follows a similar procedure as detailed by Hendry et al. (2013) to develop a diffusion model using the finite element model software CTRAN/W and SEEP/W (GeoStudio 2018 R2, v. 9.1.1.16749). In this approach, we simulate 1–D vertical transport from Devonian carbonate aquifers into adjacent aquitards by assigning a step change in aquifer groundwater concentration when meltwater first arrives in the study site via regional groundwater flow (Figure 2–2a-b). These models, which used a spacing between nodes of 10 m, assumes that prior to the arrival of meltwater, the vertical distribution of  $\delta^{18}\text{O}$  was controlled by diffusion over tens of millions of years due to presence of relatively low regional groundwater

flow rates. Therefore, the arrival time of glacial meltwater recharge to the study region before present day,  $t = 0$  ka, is the simulation period length which best fits observed data ( $t > 0$  ka).

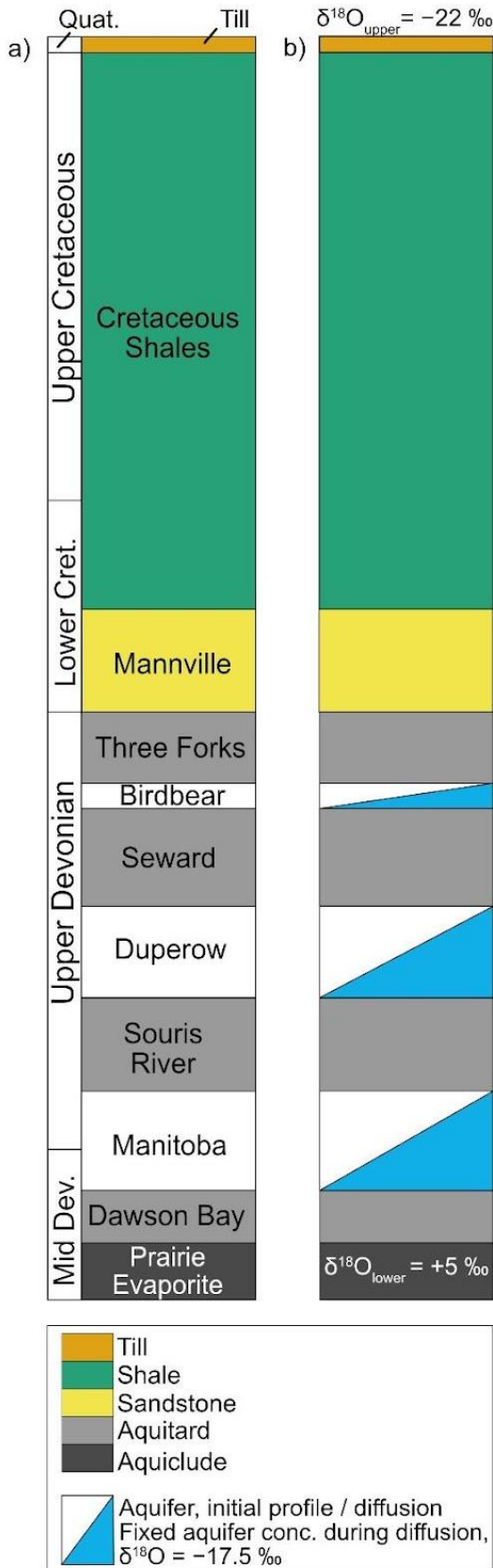
Solute transport is calculated based on:

$$(1) \frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z}$$

$$(2) v = \frac{q}{n_e},$$

where  $C$  is concentration,  $t$  is time,  $D_e$  is the effective diffusion coefficient,  $z$  is vertical distance,  $v$  is average linear velocity,  $q$  is specific discharge, and  $n_e$  is effective porosity.

We used  $n_e$  values reported by Hendry et al. (2013) based on laboratory measurements for the Quaternary glacial till (0.24), Cretaceous shales (0.33), lower Cretaceous sandstones (0.34), Devonian carbonates (0.10), and the Prairie Evaporite (0.33) based on measurements on core from a commercial database (IHS Energy, 2017). We used  $D_e$  values of  $2.3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  for glacial till, shale and sandstone units (Hendry and Wassenar, 1999),  $1.32 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  for the Devonian carbonate aquifers, and  $6.0 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$  for the Prairie Evaporite (Boudreau, 1996; Boudreau and Meysman, 2006; Hendry et al., 2009). We increased  $D_e$  to  $9 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  for the Devonian carbonate aquifers in the diffusion model set-up (Figure 2–2c).



**Figure 2–2:** Conceptual build of 1-dimensional finite element model software in CTRAN/W and SEEP/W (GeoStudio 2018 R2, v. 9.1.1.16749). (a) initial profile with only upper and lower boundary conditions, and (b) diffusion-only profile set-up with upper and lower boundary conditions and constant concentration at each carbonate aquifer.

The initial hydrogeochemical profile, representing pre-glaciation conditions and (or) zero recharge, is simulated based on a diffusion-only transport setting (i.e.,  $v = 0$ ) after Hendry et al. (2013) between two fixed boundaries (Figure 2–2). Zero pressure was assigned to the top of the hydrostratigraphic column, and a bottom pressure head was assigned to the bottom of the column equivalent to the depth of the Prairie Evaporite formation (i.e. hydrostatic conditions): (Cory) 1025 m, (Vanscoy) 1025 m, (Allan) 1000 m, and (Rocanville) 950 m. The  $\delta^{18}\text{O}$  values used for the constant concentrations of the upper and lower boundaries correspond to minimum and maximum isotope compositions recorded in the Western Canada Sedimentary Basin. We defined the upper boundary,  $\delta^{18}\text{O}_{\text{upper}}$ , for surface recharge  $-22\text{‰}$  to reflect subglacial meltwater (Grasby and Chen,

2005; Ferguson et al., 2007; Ferguson and Jasechko, 2015) and the lower fixed boundary,  $\delta^{18}\text{O}_{\text{lower}}$  at the Prairie Evaporite as +5‰ to represent evaporated paleoseawater (Grasby and Chen, 2005; Ferguson et al., 2007) (Figure 2–2a). The model simulated diffusive distribution from the upper to lower boundary for  $t = 100$  million years until it reached steady state. However, the simulation matched unperturbed  $\delta^{18}\text{O}$  data at  $t = 25$  million years, and we used this profile as the initial concentration input for subsequent simulations (Figure S1). Next, we simulated vertical distribution between the aquifers and aquitards following arrival of subglacial meltwater recharge at the study sites. We performed a transient solute transport simulation of vertical diffusive transport (Figure 2–2b) over one million years from  $t_{\text{initial}}$  to  $t_{\text{final}}$ . This range covers the time period examined by Hendry et al. (2013) in their study of a shallower regional aquifer in our study area and encompasses much of the time where continental ice sheets covered this area of North America during the Pleistocene Epoch (Ehlers et al., 2008). In this scenario, we maintained the  $\delta^{18}\text{O}_{\text{upper}}$  and  $\delta^{18}\text{O}_{\text{lower}}$  values that defined the upper and lower boundary conditions, and defined the fixed aquifer concentrations,  $\delta^{18}\text{O}_{\text{aquifer}}$ , as  $-17.5\text{‰}$  to reflect an average  $\delta^{18}\text{O}_{\text{aquifer}}$  value for our dataset. Lastly, we increased  $D_e$  to  $9 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  for the Devonian carbonate aquifers to reflect the effect of increased flow and mixing during a large recharge event. The best fit of meltwater arrival time(s) for each location were decided based on the qualitative and quantitative results between measured and simulated  $\delta^{18}\text{O}$ –depth profiles using root mean squared error (RMSE).

## 2.4 Results

### 2.4.1 Geochemical Results

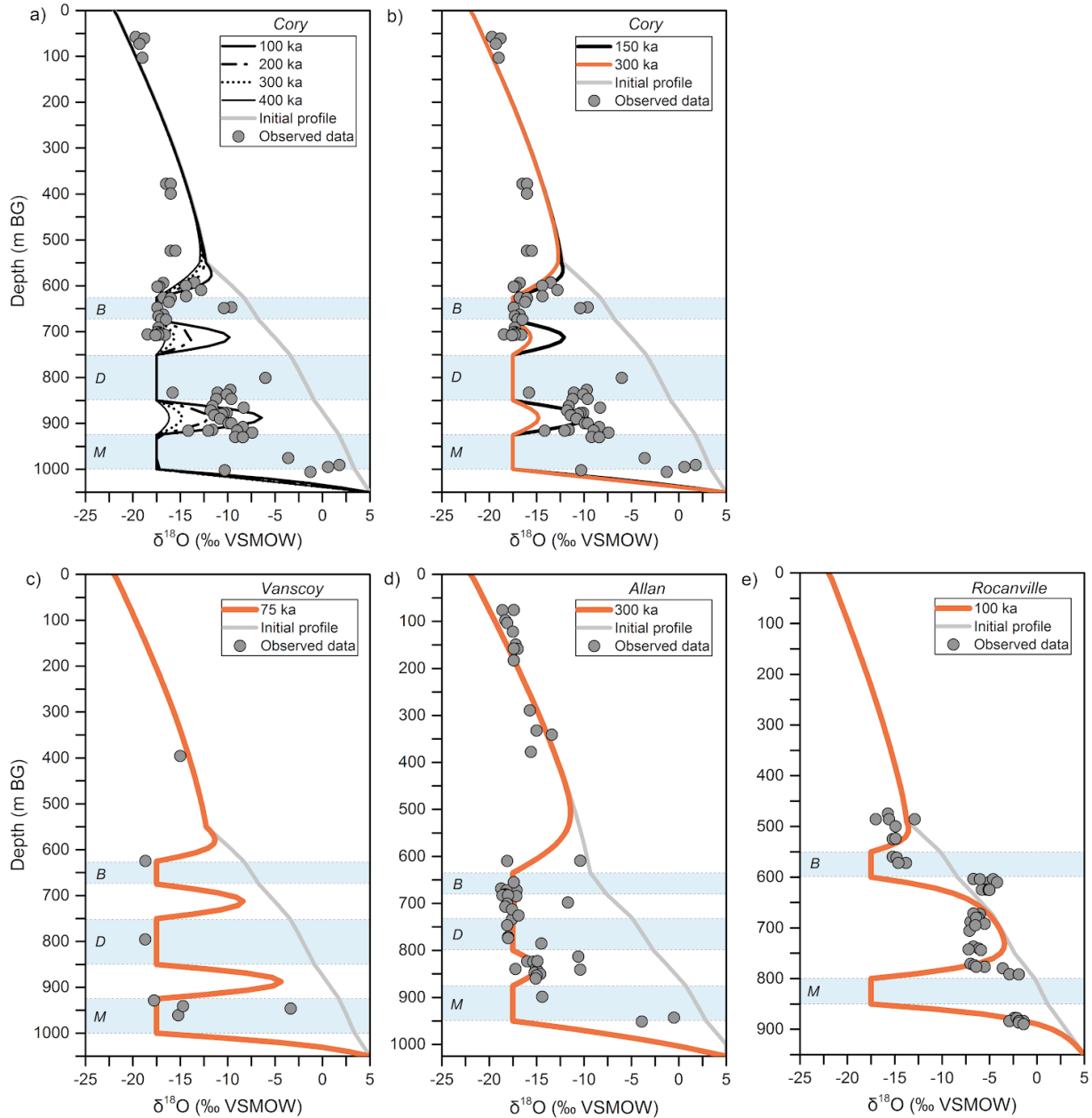
The  $\delta^{18}\text{O}$  values tended to be lower within aquifer units than in aquitards (Figure 2–3; Table A1), with these lower values generally falling on the GMWL (Figure 2–4a).  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values fell along a mixing trend between the GMWL at a value consistent with a Pleistocene signature

(Ferguson and Jasechko, 2015) and a brine endmember resembling evaporated seawater (Figure 2–4a). Samples plotting near the GMWL tended to have high molar Cl:Br, while values below the GMWL had low molar Cl:Br (Figure 2–4b).

#### **2.4.2 Model Results**

The initial profile, describing the pre-glaciation conditions and (or) zero recharge, shows the best-fit to unperturbed  $\delta^{18}\text{O}$  values at 25 million years and deviates greatly from the measured data after 40 million years (Figure S1). The upper and lower  $\delta^{18}\text{O}$  boundary conditions ( $-22\text{‰}$  and  $+5\text{‰}$ , respectively) provide a reasonable approximation of the estimated and known  $\delta^{18}\text{O}$  values for glacial recharge (Grasby and Chen, 2005; Ferguson et al., 2007; Ferguson and Jasechko, 2015) and evaporated paleoseawater (Grasby and Chen, 2005; Ferguson et al., 2007). It is evident from the initial depth profile (Figure 2–3) that additional transport processes must be imparted on this stacked aquifer system to closely replicate the observed present-day  $^{18}\text{O}$  values by simulating a diffusion-dominated environment with perturbation by a  $^{18}\text{O}$ -depleted source into carbonate aquifers in the last million years. These results indicate that meltwater arrived non-uniformly into Devonian stacked aquifers (deepest Manitoba, middle Duperow, and uppermost Birdbear) at given locations in the Williston Basin (Figure 2–3b-d). In each simulation, the model demonstrates the aquitard(s) response to meltwater that was transported from the aquitards ( $\delta^{18}\text{O}_{\text{aquitard}} = 17.5\text{‰}$ ) as  $t$  increases, and eventually creating a best-fit to observed data.

Our diffusion models provide the following arrival times to our study locations: (Cory) 150 ka and 300 ka, (Vanscoy) 75 ka, (Allan) 300 ka, and (Rocanville) 100 ka (Figure 2–3). There was no detectable shift in  $\delta^{18}\text{O}$  values reflective of glacial meltwaters in the Duperow aquifer at Rocanville.

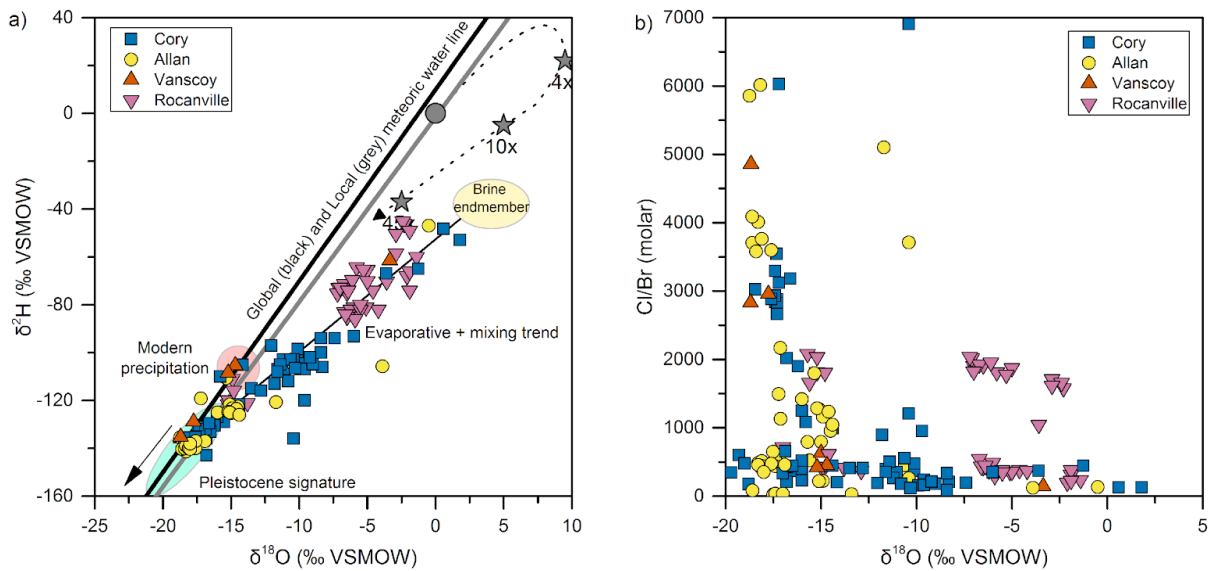


**Figure 2–3:**  $\delta^{18}\text{O}$ –depth profile results for (a) simulation of diffusion into aquitards between 100 ka and 400 ka at Cory with the initial profile included (light grey), and final best-fits of observed data for (b) Cory, (c) Vanscoy, (d) Allan, and (e) Rocanville. B = Birdbear, D = Duperow, and M = Manitoba aquifers.

These results, displaying perturbation of a freshwater source in carbonate aquifers, are complemented by  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values that fall along the GMWL (Figure 4a) and higher Cl:Br



values, which indicate halite and salt dissolution (Figure 2–4b). In contrast, formation waters in the carbonate aquitards plot to the right of the GMWL (Figure 2–4a) and have relatively low Cl:Br values (< 2000; less than seawater) (Figure 2–4b). These brines derived from evaporation of paleoseawater (i.e., brine endmember in Figure 2–4a) which have been diluted by Pleistocene meltwaters, as indicated by the linear mixing trend in Figure 2–4a.



**Figure 2–4:** (a)  $\delta^{18}\text{O}$  versus  $\delta^2\text{H}$  values of formation waters from stacked carbonate aquifers from the four study sites relative to with the global (black) and local (grey) meteoric water lines, general evaporation sequence of seawater (grey circle and stars with amount of evaporation) to form brines, and endmember ranges for the Williston Basin evaporated paleoseawater, present-day meteoric water, and Pleistocene glacial meltwater. (b)  $\delta^{18}\text{O}$  versus molar Cl:Br molar ratios.

## 2.5 Discussion

The distribution of  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values and molar Cl:Br found at depth in Devonian carbonate aquifers in this study are consistent with other studies that have found preserved Pleistocene age groundwaters in the Williston Basin (Grasby et al., 2000; Ferguson et al., 2007; Hendry et al., 2013; Ferguson and Jasechko, 2015). The lowest  $\delta^{18}\text{O}$  values are higher than the lowest values documented in the region (less than  $-24\text{‰}$ ; Ferguson and Jasechko, 2015), (Figure

2–4) which likely reflects variability in the isotopic composition of ice sheets both spatially and temporally during the Pleistocene. However, the Pleistocene endmember ( $-17.5\text{‰}$ ) is similar to other studies examining mixing between older brines and subglacial recharge (Grasby et al., 2000; Hendry et al., 2013) and is represented by a large portion of our data (Figure 2–4). The lowest  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values are present in the Duperow, Manitoba and Birdbear aquifers at Cory, Vanscoy and Allan (Figure 2–3), while the aquitards at those sites have higher  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values, indicating that the aquitards have retained some component of older, paleoevaporated seawater. At Rocanville, Pleistocene waters appear to have only arrived in the Birdbear and Manitoba aquifers, but not in the Duperow aquifer. The variability between stratigraphic positions and geographic locations is likely a function of local heterogeneity in geology and hydraulic properties.

The arrival times of subglacial meltwater to our study locations varied in two groups – a younger 75 ka to 150 ka and an older 300 ka (Figure 2–3). The arrival times are consistent with Pleistocene recharge as previously established by others (Grasby et al., 2000; Person et al., 2007; McIntosh et al., 2012). These provide minimum estimates of groundwater ages for these waters and does not account for time required for transport from their recharge areas, which are likely a few hundred kilometers to the north and northeast. If we account for the transport time from the recharge areas to our study regions, we expect groundwater recharge events to likely correspond to glacial events that occurred in the early to mid-Pleistocene (Person et al, 2007). Subglacial recharge with similar ages is likely preserved in other sedimentary basins that experienced multiple advances of Pleistocene continental ice sheets. Groundwater flowpaths in the Williston Basin and previously glaciated regions across the northern hemisphere would have varied substantially during these multiple advances due to changes in glacial thicknesses, temperatures of basal ice, and evolving hydrostratigraphy, making reconstruction of past hydrogeologic conditions difficult.

Modelled arrival times do not reveal a coherent relationship by geographic location, but – except for Cory – the times are similar between stratigraphic positions. Local variations in hydraulic properties, such as those associated with dissolution features in the Williston Basin (Christiansen et al., 1982; Christiansen and Sauer, 2001; Grasby et al., 2000; Tipton, 2018), likely resulted in the preferential movement of subglacial recharge in our study region and within the Williston Basin. These variations are also consistent with previous studies that have demonstrated the role of ice sheets in creating transient and complex flow patterns in sedimentary basins by effectively reorganizing groundwater flow over the past two million years (Person, 2007; Bense and Person, 2008). For example, groundwaters at depth in the Illinois Basin show a mixing zone between evaporated paleoseawater and Pleistocene meltwater dating up to 1.2 Ma (Siegel, 1991; McIntosh et al., 2002; McIntosh and Walter, 2006), while other aquifers in the Illinois Basin and Michigan Basin record groundwater ages greater than 50 ka (McIntosh and Walter, 2006). Additionally, previous studies provide evidence for emplacement of high volumes of Pleistocene-sourced groundwaters in deep aquifers of the Williston Basin between 135 ka and 430 ka (Hendry, 2013; Schmeling, 2014).

The extent of transport of meltwater recharge into the Williston Basin was previously approximated to be 300 km from major outcrop zones to the east and northeast in Manitoba (Grasby et al., 2000). Rocanville has been affected by meltwater influx more recently than study locations that are westward, demonstrating a lack of an east–west trend in the flowpaths. The lack of an east–west trend in our modelled arrival times suggests that recharge arriving at Cory, Vanscoy, and Allan likely occurred from the north near the Paleozoic–Precambrian boundary of the basin. In Rocanville, low molar Cl:Br values (< 2000 molar Cl:Br), which are associated with a paleo-evaporated source, and  $^{18}\text{O}$ -enriched groundwater (Figure 2–4) is opposite to the expected

trend if meltwater recharged solely from the east and was transported west–southwest. Instead, the observed salt dissolution across the northern edge of the Williston Basin (Marsh and Love, 2014) along with higher molar Cl:Br values, which result from addition of Cl by dissolution of halite, and  $^{18}\text{O}$ –depleted groundwater at Cory, Vanscoy, and Allan (Figure 2–4) suggests a continuous recharge belt along the northern margin of the Williston Basin from Saskatchewan into Manitoba (Figure 2–1a). This finding is consistent with observations of widespread salt dissolution and mixing zones between evaporated paleoseawater and meltwater recharge in the northcentral region of the basin (Grasby and Chen, 2005; Tipton, 2018; Woroniuk et al., 2018). Esker distribution in northern Saskatchewan supports this hypothesis by demonstrating a sharp change in permeability at the boundary of Precambrian and sedimentary rocks (Figure 2–1; Grasby and Chen, 2005) where high-permeability sedimentary rocks will facilitate enhanced recharge. Anomalous TDS concentrations and Na:Cl ratios (Tipton, 2018) bolster interpretations of regionally variable flow paths across the Williston Basin and further illustrates the complexity in stacked carbonate sequences and subglacial recharge over several million years.

## **2.6 Conclusion**

A combination of high-resolution stable isotope data,  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ , with groundwater transport modeling provided a useful dating approach to resolve ambiguity concerning timing of emplacement of Pleistocene waters at depth into the Williston Basin. This technique allows us to present a constrained range of groundwater arrival times and an updated view of flowpaths and paleohydrogeology of the basin. Here, we demonstrate that the arrival times of glacial meltwater to our study regions were variable – between 75 ka to 150 ka and 300 ka – which emphasizes the complexity of this aquifer system. The simulations produce best-fits for the same arrival times at each individual study site, but we did not identify coherent trends between the geographic locations

as a whole. Our results support previously identified recharge from the east in Manitoba, but we also determine the likelihood of recharge from the north to form a continuous recharge belt along the entire north-to-east margin of the Williston Basin.

The arrival times found in this study provide a constraint on the timing of subglacial recharge. Given the distance of the measurements from where Paleozoic carbonates subcrop (Figure 2–1), subglacial recharge from the early to mid-Pleistocene appear to be preserved in the Williston Basin. However, the exact recharge locations and groundwater flow patterns are unknown and likely varied throughout the Pleistocene Epoch. Subglacial recharge of similar ages is likely preserved in many glaciated areas of the northern hemisphere. Multiple glacial advances would have affected groundwater flow patterns in the Williston Basin and other similar environments. Application of the approach used here, along with improving our understanding of glacial advances and noble gas sampling, may provide insights into how other environments evolved during the Pleistocene and shifted to present-day conditions.

## **2.7 Acknowledgments and Data**

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All data included in this manuscript are included in Tipton (2018), Table A1, and (or) at the following DOI: [10.5281/zenodo.5363453](https://doi.org/10.5281/zenodo.5363453).

## **CHAPTER 3: GEOCHEMICAL EVOLUTION OF BRINES IN THE WILLISTON BASIN, CANADA**

### **Abstract**

Mixing between multiple fluid sources has led to distinct geochemical signatures in solute and isotope geochemistry of formation waters at depth in the Williston Basin, Canada. Observations of spatial and temporal trends in isotope and solute data identify three groups of formation waters at four different locations that can be explained by mixing between glaciogenic meteoric waters and paleoevaporated seawater. Results from this study help constrain groundwater flow paths and extent of glaciogenic perturbation (i.e., dilution/flushing of remnant saline fluids) between the four study sites. The results suggest that glaciogenic perturbation is greater from the northern margin versus from the eastern margin, migrating towards the center of the Williston Basin. Additionally, results demonstrate that Devonian carbonates formation waters at Allan and Cory have been the most impacted by meteoric flushing events, while Rocanville has been the least impacted by the most recent glaciogenic perturbation.

### **3.1 Introduction**

The geochemistry of fresh glaciogenic waters contrasts greatly against paleoevaporated seawater-derived groundwaters (Grasby et al., 2000; McIntosh et al., 2012; Birks et al., 2019). Past studies on formation water geochemistry in the Williston Basin have largely focused on “fingerprinting” fluids from specific stratigraphic units but lack synthesis of the available geochemical data and how the geochemical systems are related or evolve during new mineral interactions or large-scale salt dissolution. Previous studies have reported data for sedimentary

basins that contributes to the overall knowledge of the hydrogeochemistry of sedimentary basins – mostly, these studies have used solute composition like Na, Cl, and Br, and stable isotopes of water (Rostron and Holmden, 2000; Jensen et al., 2006; Tipton, 2018). There have been a few studies to-date that have utilized novel solute isotope tracers to distinguish the sources of salinity and fluid-rock reactions (Marza et al., 2022; Eggenkamp et al., 1995; Shouakar-Stash, 2008), but the data is sparse. Thus, pairing these solute isotope tracers with higher-density solute composition data enhances our knowledge of how these groundwater flow systems are affected by large-scale salt dissolution and mixing of geochemically distinct water sources related to glaciogenic influx.

This study synthesizes new results of solute and isotope geochemistry in deep groundwater of the Williston Basin at several different locations (Cory, Vanscoy, Allan, and Rocanville potash mines) to understand the effect of extensive salt dissolution on the geochemical systems and improve our understanding of flow paths and fluid evolution in the Williston Basin. This research demonstrates local and regional variation in solute and isotope geochemistry and shows mixing of glacial meltwater and remnant paleoevaporated seawater, and salt dissolution. Although overprinting of basinal fluid signatures by glacial recharge in the last two million years may present challenges, this study combines multiple geochemical and isotopic tools to contribute to a greater understanding of the hydrologic landscape of the Williston Basin.

### **3.2 Regional geology**

Details on the hydrogeology of the Williston Basin is outlined extensively in chapter 2, Figure 2–1. Briefly, the Williston Basin is a sedimentary basin centered in North Dakota, USA. Deep stacked aquifers, aquitards, and aquicludes are relatively isolated from the surface, which retains unique geochemical and isotopic signatures in the groundwater that allows us to discern



major geologic events. In this chapter, the lithology of the Williston Basin is important in understanding mineral dissolution and water-rock interactions during glacial meltwater recharge.

The Williston Basin is made up of sedimentary rocks: carbonates, evaporites, sandstones, and shales (figure 2–1). Evaporite deposits are interlayered within the carbonate sequences during deposition of these sediments. The main evaporite minerals present are sylvite (KCl) and halite (NaCl), with small amounts of carnallite ( $\text{KMgCl}_3 \cdot 6(\text{H}_2\text{O})$ ), anhydrite ( $\text{CaSO}_4$ ) and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ); minor evaporite layers may be interbedded in units above the Prairie Evaporite consisting mostly of anhydrite (Holter, 1969). Potash-bearing Prairie Evaporite units are intermittent within the Williston Basin and thus the mineral composition strongly controls the geochemical signature of formation waters and ability of glaciogenic waters to dissolve evaporites.

### 3.3 Methods

Groundwater samples were collected into clean 250 mL or 1000 mL HDPE bottles from seeps within mine shafts and mine workings at the Vanscoy, Cory, Allan, and Rocanville potash mines. Dissolved ion concentrations ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{F}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{Br}^-$ ,  $\text{Li}^+$ ,  $\text{Sr}^{2+}$ ) were determined by ion chromatography in the Environmental Analytical Laboratory at the Saskatchewan Research Council (Saskatoon, Canada). The  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values were determined using  $\text{CO}_2\text{--H}_2\text{O}$  and  $\text{H}_2\text{--H}_2\text{O}$  equilibration methods, respectively, at the Saskatchewan Isotope Laboratory (Saskatoon, Canada) and results are reported as the relative difference between the  $^{18}\text{O}/^{16}\text{O}$  and  $^2\text{H}/^1\text{H}$  abundance ratios normalized to Vienna Standard Mean Ocean Water (VSMOW), expressed in per mille (‰) notation. Accuracies of  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  are 2‰ and 0.2‰, respectively. Corrections for the salt effect, as outlined by Sofer and Gat (1972; 1975) and Koehler et al. (2013), were applied to the  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values.

The  $^{87}\text{Sr}/^{86}\text{Sr}$  values were analyzed at the Saskatchewan Isotope Laboratory (Saskatoon, Canada) using a Finnigan Triton mass spectrometry instrument in static multi-collection mode, with instrumental mass fractionation that was corrected for  $^{86}\text{Sr}/^{88}\text{Sr}$  of 0.1194. External precision of the  $^{87}\text{Sr}/^{86}\text{Sr}$  measurements performed for these samples was  $\pm 8$  ppm ( $2\sigma$ ) based on repeated measurements of NIST SRM 987, with quality control measurements of  $0.710263 \pm 0.000010$ .

The  $\delta^{37}\text{Cl}$  and  $\delta^{81}\text{Br}$  values were determined using gas chromatography continuous flow isotope ratio mass spectrometry (GC-CF-IRMS) in the Environmental Isotope Laboratory at the University of Waterloo (Waterloo, Canada).  $\delta^{37}\text{Cl}$  and  $\delta^{81}\text{Br}$  values are reported as the relative difference between the  $^{37}\text{Cl}/^{35}\text{Cl}$  and  $^{81}\text{Br}/^{79}\text{Br}$  abundance ratios normalized to the Standard Mean Ocean Chloride (SMOC) and Standard Mean Ocean Bromide (SMOB), respectively, expressed in per mille (‰) notation. Accuracy for both  $\delta^{37}\text{Cl}$  and  $\delta^{81}\text{Br}$  is 0.1‰.

Results for dissolved ion concentrations,  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $\delta^{37}\text{Cl}$ , and  $\delta^{81}\text{Br}$  may be found in Table B2.

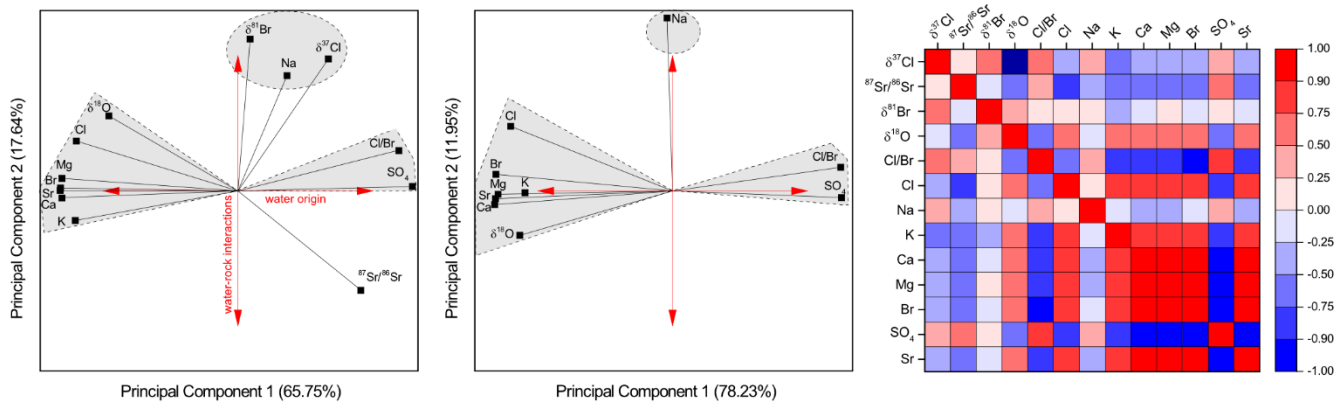
The data is separated into three groups to better understand how basinal fluids evolve over time and space: glaciogenic/meteoric (group 1); mixed brine and glaciogenic (group 2); and paleo-evaporated seawater-derived brine (group 3). These groups are defined based on  $\delta^{18}\text{O}$  values (figure 3–2): group 1:2 boundary occurs at  $\delta^{18}\text{O} = -14\text{‰}$  and group 2:3 boundary is  $\delta^{18}\text{O} = -5\text{‰}$ .

Variation in solute and isotope geochemistry may be described using multivariate statistical analyses like Principal Component Analysis (PCA). In short, PCA reduces the dimensionality of the dataset to understand which variable(s) have the largest influence on the dataset (IMDEX, 2019). Data transformation is performed on the solute geochemistry while isotope chemistry is already along a normal distribution. While performing PCA, the sample population was reduced

as a result of fewer samples collected for isotope analysis. PCA was completed via ioGAS software (v. 7.2.1).

### 3.4 Results and Discussion

A multivariate analysis of the geochemical data supports that there are two main factors controlling the geochemistry of deep groundwaters in the Williston Basin: (1) water origin (glaciogenic or brine), and (2) water-rock interactions (Figure 3–1). While the sample populations were decreased during PCA, Figure 3–1b demonstrates that solute-and-isotope and solute-only PCA have similar relationships and, as such, the isotope sample population is sufficient to draw conclusions.



**Figure 3–1:** Principal Component Analysis and correlative analysis (ioGAS version v. 7.2.1, Table B1) for (a) component 1 and component 2 depicting the relationships between all solute and isotope variables ( $n_{\text{samples}} = 15$ ), and (b) component 1 and component 2 for solute variables only ( $n_{\text{samples}} = 60$ ), and (c) covariance matrix of all solute and isotope variables.

The majority of this data is explained by the water origin and glaciogenic waters are responsible for the majority of salt dissolution, represented by the negative relationship between Cl:Br (molar) ratios and  $\text{SO}_4$ , and  $\delta^{18}\text{O}$ , Cl, M, Br, Sr, Ca, and K (Figure 3–1, Table B1). However, mineral interactions and mineral composition appear to be an important factor for the novel

isotopes, observed by a cluster for Na,  $\delta^{37}\text{Cl}$ , and  $\delta^{81}\text{Br}$ .  $^{87}\text{Sr}/^{86}\text{Sr}$  values appear to have mixed influence with no clear correlation with other solutes or isotope tracers.

### ***3.4.1 General composition of water sources***

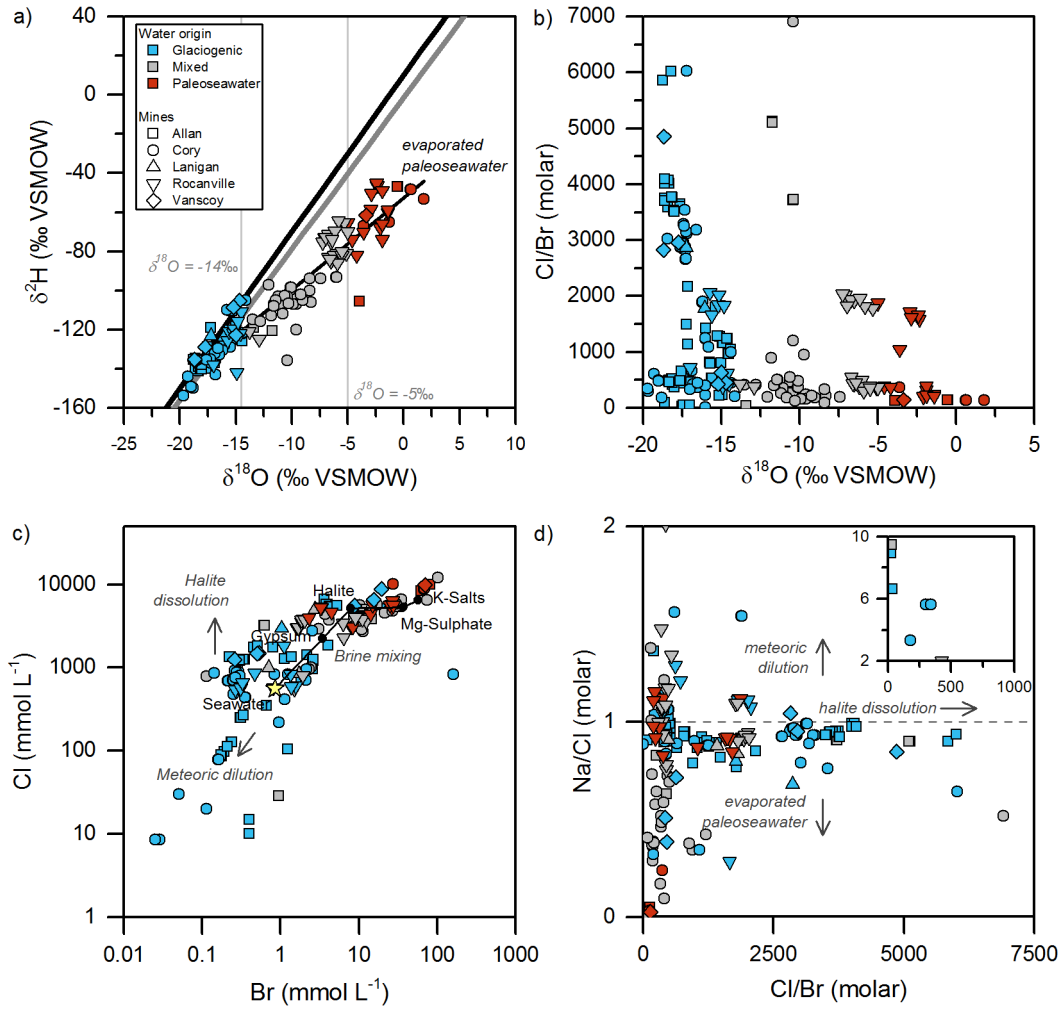
Solute composition can be directly linked to salinity and water origin (McIntosh, 2012) and in deep subsurface settings, the composition of Na, Br, and Cl aids in identifying mixing between paleo-evaporated sources and a glaciogenic source via salinity structure (Grasby and Chen, 2005; Tipton, 2018). The sensitive nature of geochemical solutes to mineral precipitation and dissolution reactions makes it difficult to use Na, Cl, or Br to determine a precise mixing line and (or) proportions of mixing between different sources; however, these variables are useful in comparing and contrasting extents of mixing and determining where there has been perturbation and extensive salt dissolution in deep subsurface settings. In addition to solute composition,  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  are proven to be valuable in understanding deep subsurface settings altered in the last 1 Ma (Mowat et al., 2021).

The data presented shows widespread values of Cl, Br, and Na observed in the Williston Basin (Figure 3–2). Formation waters that originated from highly evaporated seawater, past halite saturation/precipitation) are enriched in Na, Cl and Br, with Cl:Br values less than seawater (~650) and Na:Cl <0.85 (Connolly et al., 1990) (Figure 3–2c,d). In contrast, glaciogenic waters have relatively low Br concentrations, and high Cl:Br ratios from dissolution of halite, which does not contain appreciable Br. Glaciogenic waters that have dissolved mostly halite salt will also exhibit molar Na:Cl ~ 1. Formation waters in this study have Na:Cl values > 1 with Cl:Br ratios mostly < 500 (figure 3–2d), maybe a result of the glaciogenic groundwaters being relatively fresh with low amounts of halite dissolution.

$\delta^{18}\text{O}$  values range between  $-19.6\text{‰}$  and  $+1.8\text{‰}$ , following along the GMWL and to the right, along the evaporation and mixing trend with remnant evaporated paleoseawater-derived brines, respectively. Cory data displays the most glaciogenic signature ( $\delta^{18}\text{O} = -19.6\text{‰}$ ), as well as the most remnant brine signature of  $\delta^{18}\text{O} = +1.8\text{‰}$ . Allan has the largest percent (84%) of  $\delta^{18}\text{O}$  values indicative of glaciogenic waters ( $\delta^{18}\text{O} \leq -14\text{‰}$ ) while Rocanville has the greatest percentage of  $\delta^{18}\text{O}$  values (30%) falling within the range of remnant evaporated paleoseawater-derived brines ( $\delta^{18}\text{O} \geq -5\text{‰}$ , Figure 3-2a). In comparison, Allan only has 4% of its  $\delta^{18}\text{O}$  values classified as evaporated paleoseawater, and Rocanville only has 19% classified as glaciogenic. Mixed waters, where  $-14\text{‰} < \delta^{18}\text{O} < -5\text{‰}$ , accounts for approximately 32% of all  $\delta^{18}\text{O}$  values (Appendix B). These three fluid types – brine, mixed, and glaciogenic – are generally consistent with molar Cl:Br values where there is clear synchronicity between glaciogenic waters which are  $^{18}\text{O}$ -depleted with the highest molar Cl:Br value of  $\sim 6000$  (median = 670), versus evaporated paleoseawater which are  $^{18}\text{O}$ -enriched which have a maximum molar Cl:Br value of 1900 (median = 230).

Regionally, groundwater fluid samples collected from Devonian carbonates at Allan and Cory are the most impacted by a glaciogenic source, evidenced by a high proportion of data within glaciogenic range ( $\delta^{18}\text{O} < -14\text{‰}$ ) and molar Cl:Br values greater than seawater. This suggests that groundwaters at Allan and Cory have been affected more by glacial recharge than Vanscoy or Lanigan groundwaters, which have strong preservation of both glaciogenic and paleo-evaporated waters, and (or) Rocanville groundwaters where there is minor glaciogenic perturbation based on Na, Cl, Br, and  $\delta^{18}\text{O}$  data. These observations may be explained by multiple scenarios, including: (1) lack of extensive glacial flushing in the area of Rocanville and the center of the basin in comparison to Allan or Cory, (2) Rocanville groundwaters have not been perturbed and flushed as

recently as other locations, or (3) Rocanville did not experience as much salt dissolution due to local and regional salt discontinuity. Our results identify flow paths throughout the Williston Basin, concluding that there has likely been a greater flushing towards the center of the Williston



**Figure 3–2:** Geochemical results for all available data, attributed by water origin (color) and mine (shape) for: (a)  $\delta^{18}\text{O}$  versus  $\delta^2\text{H}$  values relative to the global (black) and local (grey) meteoric water lines, (b)  $\delta^{18}\text{O}$  versus Cl:Br values, (c) molar Br versus Cl with the seawater evaporation trajectory, and (d) Cl:Br values versus molar Na:Cl values.

Basin along the north to northeast in comparison to the eastern margin. The east-northeastern margin experienced glacial meltwater recharge; however it is possible that it has not been as

extensively flushed into the center of the basin. These observations have also been identified via solute composition and hydraulic head maps in Tipton (2018) and 1-D profile modeling (Mowat et al., 2021), and they are likely a function of differences in permeability at a regional level resulting in differences in timing and intensity of salt dissolution.

### 3.4.2 *Strontium Isotopes ( $^{87}\text{Sr}/^{86}\text{Sr}$ )*

$^{87}\text{Sr}/^{86}\text{Sr}$  signatures are well-described in the literature throughout geologic history (McArthur et al., 2012) and, although very deep subsurface paleo-evaporated brines may experience  $^{87}\text{Sr}/^{86}\text{Sr}$  overprinting by migration and (or) mixing interaction, a general trend between water-origin and mixing reactions has been observed in  $^{87}\text{Sr}/^{86}\text{Sr}$  values in sedimentary basins which experienced glacial recharge and salt dissolution (McNutt et al., 1987; Connolly et al., 1990; Birks et al., 2019; Marza et al., 2022). Particularly, groundwater that is distinctly different from the paleo-evaporated brine source geochemistry and surrounding host rocks is clear evidence that there has been a long fluid migration to the present location. Chaudhuri and Clauer (1993) identify fluid migration and dilution as a main source of radiogenic signatures in sedimentary basins as a result of water-rock interactions with marine carbonate and sulfate minerals during the fluid transport process, such as the fluid pathways glaciogenic waters have taken in the Williston Basin.

Results from this study indicate that evaporated paleoseawater are less radiogenic with lower  $^{87}\text{Sr}/^{86}\text{Sr}$  values (median = 0.7083, maximum = 0.7084), while glaciogenic sources are more radiogenic with higher  $^{87}\text{Sr}/^{86}\text{Sr}$  values (median = 0.7087, maximum = 0.7088) because of water-rock interactions. Due to lower data density, evaluating  $^{87}\text{Sr}/^{86}\text{Sr}$  signatures at a stratigraphic level proves to be difficult – however, observed correlative analysis between solute variables and

$^{87}\text{Sr}/^{86}\text{Sr}$  values demonstrates that molar Cl:Br values and  $\text{SO}_4$  are reasonable options for comparing glaciogenic and evaporated paleoseawater.

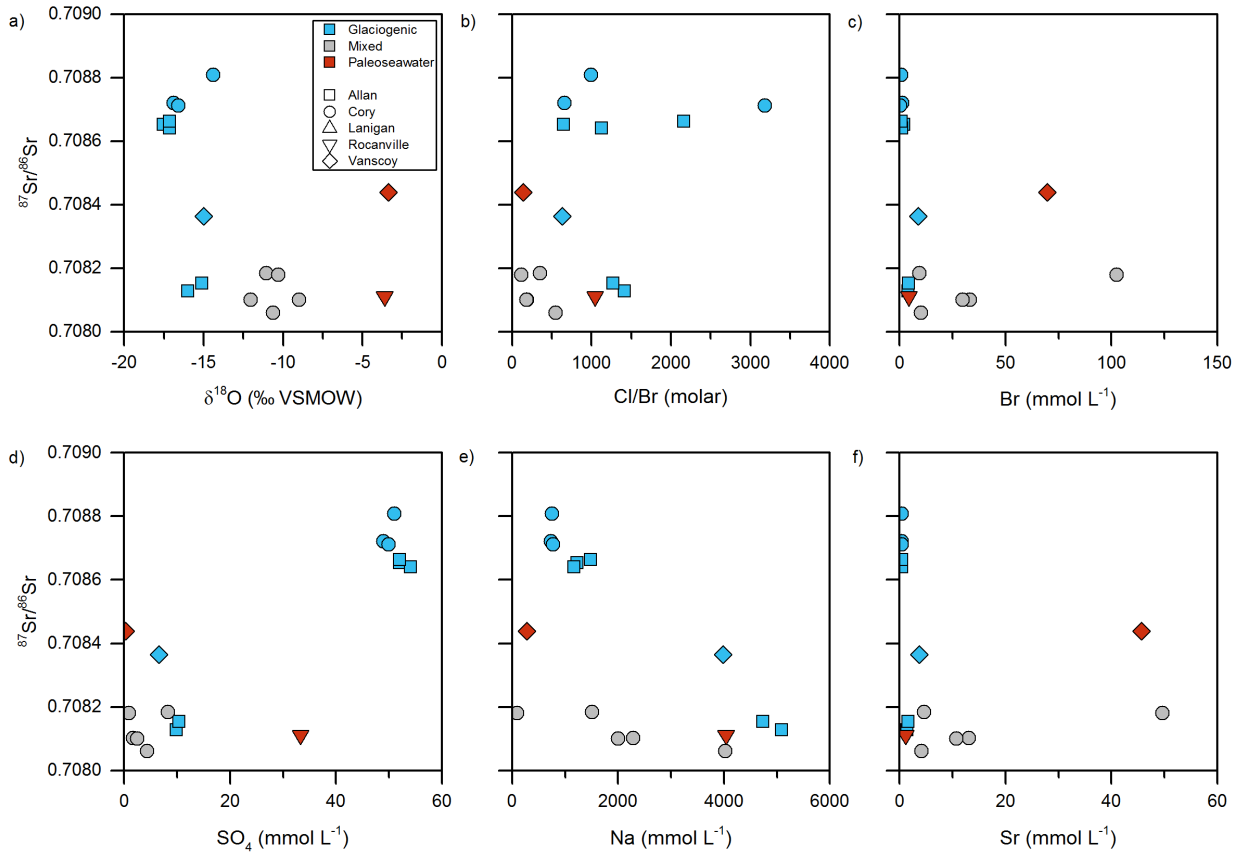
**Table 1:** Minimum, maximum, and median values of  $^{87}\text{Sr}/^{86}\text{Sr}$  for glaciogenic waters, mixed, and paleoseawater.

	$^{87}\text{Sr}/^{86}\text{Sr}$		
	Glaciogenic	Mixed	Paleoseawater
$n_{\text{samples}}$	9	5	2
Minimum	0.70813	0.70806	0.70811
Maximum	0.70881	0.70818	0.70844
Median	0.70865	0.70810	0.70828

$^{87}\text{Sr}/^{86}\text{Sr}$  versus molar Cl:Br ratios demonstrate a positive relationship until approximately Cl:Br ~ 1500 where  $^{87}\text{Sr}/^{86}\text{Sr}$  values reach a maximum of 0.7078 while there is still a steady increase in molar Cl:Br. Group 1 locations with the most radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  values (Cory, Allan) also have the greatest salt dissolution with high molar Cl:Br values indicating intensive water-rock interactions and dissolution of low-evaporitic sulfate-rich salts (anhydrite, gypsum; high  $\text{SO}_4$  concentrations). The Rocanville sample (Figure 3–3a, 3–3b) is the least radiogenic where the effects of salt dissolution also appear lowest based on solute geochemistry. These results suggest that relatively radiogenic Sr is being released to formation waters during dissolution of Ca-bearing evaporites.

Maximum  $^{87}\text{Sr}/^{86}\text{Sr}$  values for the suite of Devonian carbonates in the Williston Basin is 0.7082 (McArthur et al., 2012) which agrees with the evaporated paleoseawater values in this study (Figure 3–3). However, many of the glaciogenic group 1 samples – expected to be more radiogenic – have low  $^{87}\text{Sr}/^{86}\text{Sr}$ , evidence that a glaciogenic source dissolving radiogenic minerals is not the only factor in estimating  $^{87}\text{Sr}/^{86}\text{Sr}$  values. Principal component analysis verifies that there





**Figure 3–3:** Geochemical results attributed by water origin (color) and mine (shape) for  $^{87}\text{Sr}/^{86}\text{Sr}$  versus (a)  $\delta^{18}\text{O}$ , (b) Cl/Br, (c) Br, (d)  $\text{SO}_4$ , (e) Na, and (f) Sr.

is no single variable that can explain  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (Figure 3–1), and that  $^{87}\text{Sr}/^{86}\text{Sr}$  is dependent on both water origin and intensity of salt dissolution and water-rock interactions.

### 3.4.3 Chlorine and Bromine Isotopes ( $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ )

The data for  $\delta^{37}\text{Cl}$  and  $\delta^{81}\text{Br}$  reveal synonymous patterns between water types: glaciogenic waters exhibit a large range in values ( $-0.155 < \delta^{37}\text{Cl} < 0.352$  and  $0.157 < \delta^{81}\text{Br} < 1.649$ ) while evaporated paleoseawaters have less variance in values ( $-0.096 < \delta^{37}\text{Cl} < 0.052$  and  $0.685 < \delta^{81}\text{Br} < 1.069$ ) (Table 1).

	$\delta^{37}\text{Cl}$			$\delta^{81}\text{Br}$		
	Glaciogenic	Mixed	Paleoseawater	Glaciogenic	Mixed	Paleoseawater
<i>n</i> <sub>samples</sub>	24	6	2	24	6	2
Minimum	-0.155	-0.323	-0.096	0.157	0.236	0.685
Maximum	0.352	0.219	0.200	1.649	0.968	1.069
Median	0.062	-0.125	0.052	0.529	0.392	0.877

**Table 2:** Minimum, maximum, and median values of  $\delta^{37}\text{Cl}$  and  $\delta^{81}\text{Br}$  for glaciogenic waters, mixed, and paleoseawater.

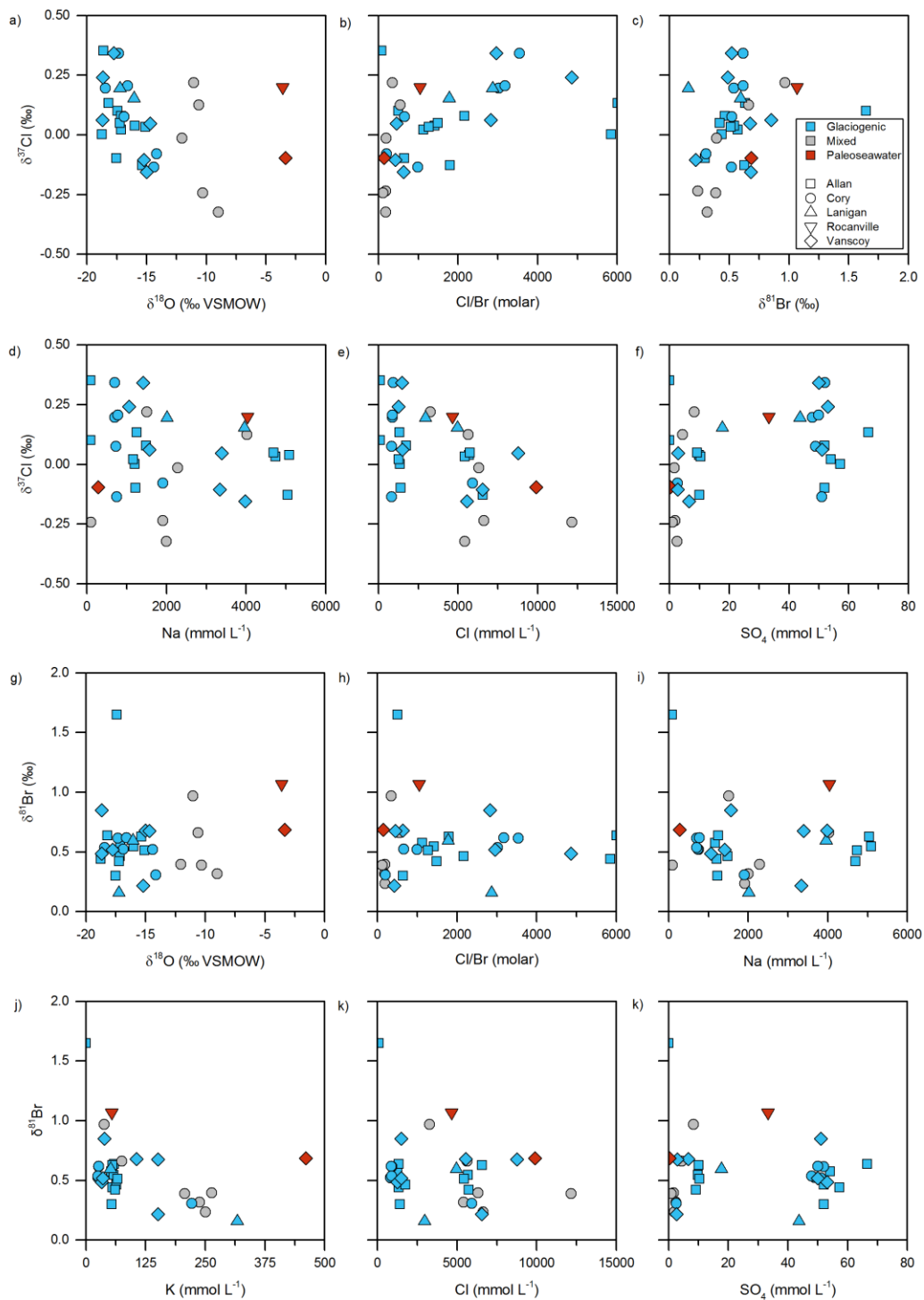
It is challenging to conclude trends between locations due to low sample density; however, there is a notable negative and positive correlation between water origin versus  $\delta^{37}\text{Cl}$  and  $\delta^{81}\text{Br}$  values, respectively. The main correlations based on water origin (groups 1–3) between  $\delta^{37}\text{Cl}$  and  $\delta^{81}\text{Br}$  isotopes with other variables based on PCA include:  $\delta^{37}\text{Cl}$  versus molar Cl:Br, Cl,  $\delta^{81}\text{Br}$ , and  $\text{SO}_4$ , and  $\delta^{81}\text{Br}$  versus K. Principal component analysis indicates that halite dissolution is the driving factor controlling  $\delta^{37}\text{Cl}$  and  $\delta^{81}\text{Br}$  values: there is a positive correlation with Na, and a positive correlation with molar Cl:Br due to these variables being largely dependent on the extent of salt dissolution and (or) variation of halite that is being dissolved (e.g. where Br has been substituted into the mineral lattice in the latest stages of mineral precipitation (McCaffrey et al., 1987)) (Figure 3–1, Figure 3–4).

$\delta^{37}\text{Cl}$  values and molar Cl:Br ratios have the strongest affinity together until Cl:Br ~ 4000, and then the trend reverses. The point of inflection for molar Cl:Br values indicates the dissolution of the most concentrated halite (e.g. dissolution of halite which formed in the latest stages of mineral precipitation and contain Br), Mg-salts, and K-salts (Figure 3–4b, Figure 3–2c). The influence of water origin is highlighted here, as glaciogenic groundwater will have the greatest ability to dissolve salts while paleoevaporated brines may already be at (or near) saturation; in this

case, it is positively supported by a weak negative relationship between  $\delta^{18}\text{O}$  and  $\delta^{37}\text{Cl}$  (Figure 3-1, Figure 3-4g).

The values of  $\delta^{81}\text{Br}$  suggest that they are dependent on water origin, although there is no correlation observed between  $\delta^{81}\text{Br}$  and the rest of the variables. The strongest correlation is between  $\delta^{81}\text{Br}$  and K, while there is a weak correlation between  $\delta^{81}\text{Br}$  and  $\delta^{18}\text{O}$  where there is a general increase of  $\delta^{81}\text{Br}$  based on water origin (Figure 3-4g, 4h).

Overall, there is little known about the effects on  $\delta^{37}\text{Cl}$  and  $\delta^{81}\text{Br}$  when mixing groundwater sources, although some research has hypothesized the possible patterns relate to isotope fractionation in paleo-evaporated sources. Literature states that during large scale evaporation and mineral precipitation,  $\delta^{37}\text{Cl}$ ,  $\delta^{81}\text{Br}$ , and relative molar Cl:Br values are recorded in halite and other Cl and Br rich minerals (McCaffrey et al., 1987; Eggenkamp et al., 1995; Shouakar-Stash, 2008; Stotler et al., 2010), and the remnant paleo-evaporated groundwater will exhibit enriched  $\delta^{37}\text{Cl}$  and  $\delta^{81}\text{Br}$  values. During glacial meltwater perturbation and major halite salt dissolution,  $^{37}\text{Cl}$ -depleted and  $\delta^{81}\text{Br}$ -depleted signatures preserved in halite will be recorded in the glaciogenic and mixed groundwater. The Williston Basin is host to extensive evaporative minerals beyond halite, therefore knowledge of water origin is helpful to understand the effects on  $\delta^{37}\text{Cl}$  and  $\delta^{81}\text{Br}$  geochemistry.



**Figure 3-4:** Geochemical results attributed by water origin (color) and mine (shape) for  $\delta^{37}\text{Cl}$  versus (a)  $\delta^{18}\text{O}$ , (b) Cl/Br, (c)  $\delta^{81}\text{Br}$ , (d) Na, (e) Cl, and (f) SO<sub>4</sub>, and  $\delta^{81}\text{Br}$  versus (g)  $\delta^{18}\text{O}$ , (h) Cl/Br, (i) Na, (j) K, (k) Cl, and (l) SO<sub>4</sub>.

### 3.5 Conclusions

A combination of new isotope and solute geochemistry of formation waters in the Williston Basin helps inform the differences between glaciogenic and evaporated paleoseawater-derived waters at depth. Although mixing and water–rock interactions can present challenges by modifying fluid chemistry and obscuring sources, this study combines multiple tracers to better understand novel isotope fractionation processes. The results support a continuous recharge belt along the north-to-eastern margins of the Williston Basin (Mowat et al., 2021), and shows that strong glacial recharge signatures are preserved deep into the Williston Basin.

Comparing isotope systems to solute and stable isotope geochemistry informs trends that contribute to fractionation of  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $\delta^{37}\text{Cl}$ , and  $\delta^{81}\text{Br}$ . Results show the importance of variation in salt and mineral composition on the concentrations and values of molar Cl:Br,  $\delta^{37}\text{Cl}$ , and  $\delta^{81}\text{Br}$ , or the sensitivity of  $^{87}\text{Sr}/^{86}\text{Sr}$  values to overprinting and water-rock interaction processes. A combination of statistical and correlative analysis tools established the variation in geochemistry between glaciogenic and brine sources. Application of this multi-tracer approach using large datasets and data mining for other sedimentary basins may provide further insights into the signatures of novel isotope tracers and the mixing and evolution of multiple water sources.

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Saskatchewan Queen Elizabeth II Centennial Aboriginal Scholarship. All data included in this manuscript are included in Appendix B, and (or) at the following DOI: [10.5281/zenodo.7749457](https://doi.org/10.5281/zenodo.7749457)

## CHAPTER 4: CONCLUSION

Glacial recharge has impacted sedimentary basins across the northern hemisphere and the Williston Basin in the Western Canada Sedimentary Basin is no exception. Massive regions of salt dissolution along the northeast to east margin of the Williston Basin has resulted in vastly different geochemical signatures of formation waters and major changes to energy and mineral resources including oil, gas, and potash potential.

This thesis examined the effects of glaciogenic recharge to deep subsurface aquifers in the Williston Basin and approximated the age of recharge perturbations using an interdisciplinary approach between geochemistry, geology, and computational modeling. Here, we conclude that glaciogenic recharge occurred during two separate time periods, 75 to 150 ka and 300 ka, to the northcentral regions of the Williston Basin. Spatial reconstruction between observed trends in the Williston Basin indicated that there was a much larger impact by subglacial recharge along the north to northeast margin than previously anticipated.

Geochemistry in this deep, isolated aquifer system of the Williston Basin is differentiated into two categories: glaciogenic recharge and paleo-evaporated brines. Strong trends are observed for Molar Cl:Br,  $\delta^{18}\text{O}$ , and  $\delta^2\text{H}$  values, and moderate trends are observed for  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $\delta^{37}\text{Cl}$ , and  $\delta^{81}\text{Br}$  values despite a smaller sample density and less literature to describe the trends. Qualitative tools, like statistical and correlative analysis, and quantitative tools were used to discern the main influences to brine geochemistry in the data set: water-rock interactions and water origin. In conclusion, this study provided new insights into the timing and variability in recharge of

glaciogenic waters and the geochemical variation in solutes and isotope systems between paleoevaporated and glaciogenic sourced groundwaters in the Williston Basin.

In anticipation of further research, additional samples should be collected to increase the data density for solute geochemistry, prioritizing additional sampling for novel isotopes included in this study to more rigorously constrain the isotope fractionation, mixing, and water-rock interactions influencing these variables. Sample collection and analysis for noble gases ( $^4\text{He}$  and  $^{81}\text{Kr}$ ) would also be useful to help better constrain the residence time of groundwaters and timing of subglacial recharge.



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## APPENDIX

APPENDIX A

Table A1: Compilation of data.

Source	Mine	Formation/ Group	Aquifer/ Aquitard	Depth (m BG)	δ18O	δD	Cl (mg L <sup>-1</sup> )	Na (mg L <sup>-1</sup> )	Br (mg L <sup>-1</sup> )
This study	Allan	Bearpaw		76	-17.4	-135.8	3460	2170	15.4
This study	Allan	Bearpaw		76	-18.6	-134.7	3700	2170	100
Jensen et al. (2006)	Allan	Cret. Shales		98	-18.3	-140.6	3021	2015	14
Jensen et al. (2006)	Allan	Cret. Shales		104	-18.1	-138.9	3181	1959	14
Nutrien internal database	Allan	Cret. Shales		122	-17.5	-129	354	2050	32
Wittrup and Kyser (1990)	Allan	Cret. Shales		122	-17.5	-129	354	2050	32
Jensen et al. (2006)	Allan	Cret. Shales		149	-17.2	-133.2	4529	2689	19
Wittrup and Kyser (1990)	Allan	Cret. Shales		158	-17.4	-136	530	2280	32
Nutrien internal database	Allan	Cret. Shales		159	-17	-136	530	2280	32
Jensen et al. (2006)	Allan	Cret. Shales		183	-17.4	-135.2	3978	2494	17
Jensen et al. (2006)	Allan	Cret. Shales		290	-15.7	-121.3	8784	5396	25
Jensen et al. (2006)	Allan	Cret. Shales		332	-15	-118.5	9519	5712	27
Wittrup and Kyser (1990)	Allan	Cret. Shales		341	-13.4	-119	1020	6250	76
Jensen et al. (2006)	Allan	Cret. Shales		378	-15.6	-120.5	12364	7948	53
Jensen et al. (2006)	Allan	Watrous		610	-10.4	-105.7	37863	22193	23
Nutrien internal database	Allan	Watrous		610	-18.1	-138	26700	15500	148
Wittrup and Kyser (1990)	Allan	Birdbear		655	-17.4	-136	31000	19800	160
This study	Allan	Birdbear		669	-17.5	-135	50200	28200	174
This study	Allan	Birdbear		669	-18.7	-135.5	47800	27800	18.4
This study	Allan	Birdbear		672	-17.1	-134.3	45100	26900	90
This study	Allan	Birdbear		672	-18.2	-136.4	47500	28800	17.8
Jensen et al. (2006)	Allan	Duperow	Seward	681	-18.3	-141.3	42714	27391	24
Jensen et al. (2006)	Allan	Duperow	Seward	683	-18.4	-140.1	44482	27219	28
Jensen et al. (2006)	Allan	Duperow	Seward	683	-18.6	-140.3	44363	27348	27
Jensen et al. (2006)	Allan	Duperow	Seward	683	-18.6	-140.4	43532	27459	24
Wittrup and Kyser (1990)	Allan	Duperow	Seward	683	-18	-139	33800	24200	207
This study	Allan	Duperow	Seward	685	-17.1	-132.2	62200	34200	64.7
Jensen et al. (2006)	Allan	Duperow	Seward	698	-11.7	-120.7	113177	66035	50
Wittrup and Kyser (1990)	Allan	Duperow	Seward	701	-18.1	-138	40900	25700	208
Wittrup and Kyser (1990)	Allan	Duperow	Seward	707	-18.3	-139	42700	24900	211
Wittrup and Kyser (1990)	Allan	Duperow	Seward	713	-17.6	-140	44500	27000	211
Wittrup and Kyser (1990)	Allan	Duperow	Seward	726	-16.9	-137	65900	39300	323
Jensen et al. (2006)	Allan	Duperow	Duperow	734	-17.6	-137	62219	38283	39
Jensen et al. (2006)	Allan	Duperow	Duperow	747	-18.1	-140	61739	36858	37
Jensen et al. (2006)	Allan	Duperow	Duperow	772	-18	-140.3	63816	38493	410
Wittrup and Kyser (1990)	Allan	Duperow	Duperow	774	-18	-138		46600	318
Jensen et al. (2006)	Allan	Duperow	Duperow	786	-14.5	-122.6	47510	24280	112
Jensen et al. (2006)	Allan	Souris River	Souris	813	-10.6	-103	139802	56956	696
Wittrup and Kyser (1990)	Allan	Souris River	Souris	823	-14.9	-124	180000	120000	1810
This study	Allan	Souris River	Souris	823	-16	-125	202000	117000	321
This study	Allan	Souris River	Souris	824	-15.3	-110.7	233000	116000	292
This study	Allan	Souris River	Souris	839	-15.1	-121.7	193000	109000	342
This study	Allan	Souris River	Souris	839	-17.2	-119.2	204000	108000	308
Wittrup and Kyser (1990)	Allan	Souris River	Souris	841	-10.4	-105	136000	73000	1170
Jensen et al. (2006)	Allan	Souris River	Souris	843	-14.9	-123.3	184797	107056	359
Jensen et al. (2006)	Allan	Souris River	Souris	847	-15.2	-124.8	192092	111132	337
Jensen et al. (2006)	Allan	Souris River	Souris	850	-14.6	-123.6	190769	111667	348
Nutrien internal database	Allan	Souris River	Souris	854	-15	-125.3	201924	118552	
Wittrup and Kyser (1990)	Allan	Souris River	Souris	860	-15.1	-125	196000	173000	2030

Jensen et al. (2006)	Allan	Souris River	Souris	899	-14.4	-126	195319	109579	422
Jensen et al. (2006)	Allan	Souris River	Souris	943	-0.5	-47	296602	9844	5050
Jensen et al. (2006)	Allan	Souris River	Souris	952	-3.9	-105.7	348725	4598	6520
Jensen et al. (2006)	Cory	Glacial till		58	-19.7	-154	305	1111	2
Wittrup and Kyser (1990)	Cory	Glacial till		61	-18.8	-150	709	1520	9
Nutrien internal database	Cory	Glacial till		73	-19.3	-144	1067	1080	4
Jensen et al. (2006)	Cory	Cret. Shales		103	-19	-149.2	2764	1902	13
Nutrien internal database	Cory	Cret. Shales		378	-16.5	-129	14790	4907	91
Nutrien internal database	Cory	Cret. Shales		378	-16	-129	7800	5240	77
Jensen et al. (2006)	Cory	Cret. Shales		399	-16	-125.9	15542	8857	28
Wittrup and Kyser (1990)	Cory	Three Forks		524	-15.5	-129		20720	200
Wittrup and Kyser (1990)	Cory	Three Forks		524	-16	-128	28500	19500	160
Wittrup and Kyser (1990)	Cory	Birdbear		593	-13.5	-115	35600	28000	196
Nutrien internal database	Cory	Birdbear		594	-16.8	-135			
Nutrien internal database	Cory	Birdbear		600	-14.4	-122	32000	17300	162
Jensen et al. (2006)	Cory	Birdbear		602	-17.2	-134.9	24916	15996	18
Jensen et al. (2006)	Cory	Birdbear		603	-17.4	-132.5	24819	14990	17
Nutrien internal database	Cory	Birdbear		610	-12.8	-116	33800	2100	186
This study	Cory	Duperow	Seward	623	-14.4	-121.6	29600	17300	67
Wittrup and Kyser (1990)	Cory	Duperow	Seward	626	-16.8	-143	29200	17000	155
Wittrup and Kyser (1990)	Cory	Duperow	Seward	627	-16	-127	29600	17000	129
Jensen et al. (2006)	Cory	Duperow	Seward	635	-16.2	-130.5	16845	16845	20
Wittrup and Kyser (1990)	Cory	Souris River	Souris	647	-9.6	-120	96400	3600	906
Jensen et al. (2006)	Cory	Duperow	Seward	648	-17.4	-135.6	25213	15520	20
Nutrien internal database	Cory	Duperow	Seward	649	-10.4	-136	27890	9396	9
Wittrup and Kyser (1990)	Cory	Duperow	Seward	663	-16.8	-136			
Jensen et al. (2006)	Cory	Duperow	Seward	667	-17.3	-133.8	26803	16757	21
Wittrup and Kyser (1990)	Cory	Duperow	Seward	673	-17	-134	24900	18000	168
Nutrien internal database	Cory	Duperow	Seward	674	-16.5	-133	33800	18300	173
Jensen et al. (2006)	Cory	Duperow	Duperow	692	-17.3	-134.3	27458	16940	22
This study	Cory	Duperow	Duperow	701	-17.3	-131.3	32700	16100	21
Jensen et al. (2006)	Cory	Duperow	Duperow	701	-17.4	-135.8	28584	17250	22
Nutrien internal database	Cory	Souris River	Souris	704	-17.2	-137	30490	12707	11
This study	Cory	Duperow	Duperow	705	-16.9	-132.1	29200	16800	100
This study	Cory	Duperow	Duperow	706	-18.4	-135.6	31400	16100	23
This study	Cory	Duperow	Duperow	707	-16.6	-129.6	30900	17800	22
Jensen et al. (2006)	Cory	Duperow	Duperow	707	-17.3	-135.1	28348	16980	24
Jensen et al. (2006)	Cory	Duperow	Duperow	708	-17.6	-135.5	26874	16875	21
Jensen et al. (2006)	Cory	Souris River	Souris	801	-6	-93.2	153325	51474	995
Nutrien internal database	Cory	Souris River	Souris	827	-9.7	-102	103260	23039	245
This study	Cory	Souris River	Souris	833	-11	-106.9	116000		746
Nutrien internal database	Cory	Souris River	Souris	833	-15.8	-110	98170	21919	205
Jensen et al. (2006)	Cory	Souris River	Souris	837	-10.1	-99.8	110998	34890	691
Nutrien internal database	Cory	Souris River	Souris	847	-9.6	-120	96400	36000	906
Wittrup and Kyser (1990)	Cory	Souris River	Souris	847	-11.2	-103	101000	42000	863
Jensen et al. (2006)	Cory	Souris River	Souris	863	-11.6	-107.1	140537	53624	803
Nutrien internal database	Cory	Souris River	Souris	866	-8.3	-106	160000	103500	1720
Wittrup and Kyser (1990)	Cory	Souris River	Souris	866	-8.3	-106	160000	103500	1720
Nutrien internal database	Cory	Souris River	Souris	872	-11.8	-113	131870	32227	333
Jensen et al. (2006)	Cory	Souris River	Souris	877	-10.1	-98.6	183311	86260	873
Nutrien internal database	Cory	Souris River	Souris	877	-10.4	-103	157060	43280	294
This study	Cory	Souris River	Souris	880	-10.6	-102.9	200000	92500	818
Jensen et al. (2006)	Cory	Souris River	Souris	882	-11.4	-105	167620	75078	754

Nutrien internal database	Cory	Souris River	Souris	890	-10.8	-112	171000	81000	2157
Nutrien internal database	Cory	Souris River	Souris	900	-9.9	-107	194000	173000	2804
Wittrup and Kyser (1990)	Cory	Souris River	Souris	900	-9.6	-107	199000	130000	2800
Nutrien internal database	Cory	Souris River	Souris	908	-8.4	-100	203150	22565	1366
Nutrien internal database	Cory	Souris River	Souris	914	-11.6	-108			
This study	Cory	Souris River	Souris	916	-12	-97.1	224000	52500	2660
This study	Cory	Souris River	Souris	916	-9	-105	192000	46000	2390
This study	Cory	Souris River	Souris	916			235000	44000	2800
This study	Cory	Souris River	Souris	916	-14.1	-105.1	210000	43800	2350
Jensen et al. (2006)	Cory	Souris River	Souris	920	-7.4	-94	207984	52233	2390
Nutrien internal database	Cory	Souris River	Souris	930	-9.2	-102	207000	51000	2206
Wittrup and Kyser (1990)	Cory	Souris River	Souris	930	-8.4	-94	228000	60000	5950
Nutrien internal database	Cory	Dawson Bay		976	-3.6	-67	355000	54870	2174
Jensen et al. (2006)	Cory	Dawson Bay		991	1.8	-53	310760	6986	5400
Jensen et al. (2006)	Cory	Dawson Bay		995	0.6	-48.3	318746	6947	5490
This study	Cory	Dawson Bay		1002	-10.3	-106.6	431000	2300	8200
Nutrien internal database	Cory	Dawson Bay		1006	-1.3	-65			
Jensen et al. (2006)	Rocanville	Lodgepole Fm.		475	-15.7	-125.7	19384	13514	21
Wittrup and Kyser (1990)	Rocanville	Lodgepole Fm.		486	-12.9	-125	19600	13300	119
Wittrup and Kyser (1990)	Rocanville	Lodgepole Fm.		486	-15.6	-121	64715	11970	88
Wittrup and Kyser (1990)	Rocanville	Lodgepole Fm.		486	-17	-138	20400	16000	64
Wittrup and Kyser (1990)	Rocanville	Lodgepole Fm.		500	-14.9	-142	21300	14600	125
Wittrup and Kyser (1990)	Rocanville	Three Forks Gr.		524	-14.9	-111	21000	15600	110
Jensen et al. (2006)	Rocanville	Three Forks Gr.		525	-15.2	-121.6	20116	14603	25
Jensen et al. (2006)	Rocanville	Birdbear		560	-15.2	-119.9	23480	16918	26
Jensen et al. (2006)	Rocanville	Birdbear		562	-14.8	-115.9	30441	21908	38
Wittrup and Kyser (1990)	Rocanville	Birdbear		572	-13.8	-121	28500	21700	154
Wittrup and Kyser (1990)	Rocanville	Birdbear		572	-14.6	-122	29600	24700	108
Nutrien internal database	Rocanville	Duperow	Seward	604	-6.7	-83	120800	105000	500
Wittrup and Kyser (1990)	Rocanville	Duperow	Seward	604	-4.6	-74	110000	79900	647
Wittrup and Kyser (1990)	Rocanville	Duperow	Seward	604	-6	-81	182000	138000	840
Jensen et al. (2006)	Rocanville	Duperow	Seward	610	-5	-65.4	108179	78475	130
Wittrup and Kyser (1990)	Rocanville	Duperow	Seward	610	-4.2	-82	110000	76400	673
Jensen et al. (2006)	Rocanville	Duperow	Seward	625	-5.3	-65.3	107206	76085	136
Jensen et al. (2006)	Rocanville	Duperow	Seward	625	-5.8	-64.3	107764	76584	134
Wittrup and Kyser (1990)	Rocanville	Duperow	Seward	625	-5.1	-81	138700	97000	880
Wittrup and Kyser (1990)	Rocanville	Duperow	Seward	625	-5	-70	81400	52400	510
Nutrien internal database	Rocanville	Duperow	Duperow	672	-6.7	-83	120800	105000	500
Wittrup and Kyser (1990)	Rocanville	Duperow	Duperow	672	-6.7	-83	120800	105000	500
Nutrien internal database	Rocanville	Duperow	Duperow	673	-6	-81	182000	138000	840
Wittrup and Kyser (1990)	Rocanville	Duperow	Duperow	680	-6.2	-82	139000	90000	828
Wittrup and Kyser (1990)	Rocanville	Duperow	Duperow	680	-6.4	-84	142400	69700	720
Jensen et al. (2006)	Rocanville	Duperow	Duperow	688	-7	-73.4	129236	77199	153
Wittrup and Kyser (1990)	Rocanville	Duperow	Duperow	692	-5.5	-82	153500	93000	906
Jensen et al. (2006)	Rocanville	Duperow	Duperow	693	-6.5	-75	125647	74851	148
Wittrup and Kyser (1990)	Rocanville	Duperow	Duperow	695	-6.5	-85	148000	193000	780
Jensen et al. (2006)	Rocanville	Duperow	Duperow	706	-7.1	-73	136019	83187	152
Jensen et al. (2006)	Rocanville	Duperow	Duperow	737	-6.7	-71.3	133343	78930	156
Jensen et al. (2006)	Rocanville	Duperow	Duperow	741	-6.1	-69.6	136196	82190	157
Jensen et al. (2006)	Rocanville	Duperow	Duperow	743	-7.2	-75.3	133061	79230	147

Wittrup and Kyser (1990)	Rocanville	Duperow	Seward	744	-5.9	-86	130000	84000	992
Jensen et al. (2006)	Rocanville	Souris River	Souris	771	-7	-72.8	131987	77271	163
Wittrup and Kyser (1990)	Rocanville	Souris River	Souris	774	-6.6	-84	144900	102000	750
Wittrup and Kyser (1990)	Rocanville	Souris River	Souris	777	-5.5	-80	136000	130000	880
Wittrup and Kyser (1990)	Rocanville	Souris River	Souris	777	-6.4	-74	142400	72100	720
This study	Rocanville	Duperow	Duperow	780	-3.6	-70.3	165000	92900	356
Jensen et al. (2006)	Rocanville	Souris River	Souris	792	-2.9	-58.6	140646	77243	185
Wittrup and Kyser (1990)	Rocanville	Souris River	Souris	792	-1.9	-74	157000	99000	1120
Jensen et al. (2006)	Rocanville	Dawson Bay		878	-2.3	-46.3	187092	111345	267
Jensen et al. (2006)	Rocanville	Dawson Bay		878	-2.4	-45.1	190709	113057	259
Wittrup and Kyser (1990)	Rocanville	Dawson Bay		878	-2.1	-68	186000	118000	2110
Jensen et al. (2006)	Rocanville	Dawson Bay		884	-2.9	-50.4	186902	111553	261
Wittrup and Kyser (1990)	Rocanville	Dawson Bay		884	-1.4	-60	227000	135000	2160
Wittrup and Kyser (1990)	Rocanville	Dawson Bay		884	-1.9	-49	201500	108000	1190
Wittrup and Kyser (1990)	Rocanville	Dawson Bay		887	-1.9	-66	200600	150000	2000
Wittrup and Kyser (1990)	Rocanville	Dawson Bay		890	-1.4	-59	199000	143000	2200
This study	Vanscoy	Cret. Shales		396	-15	-122.8	197000	91500	702
This study	Vanscoy	Duperow	Seward	625	-18.7	-136	44400	24400	21
This study	Vanscoy	Souris River	Souris	796	-18.7	-135.2	53200	36000	42
This study	Vanscoy	Souris River	Souris	929	-17.8	-128.9	52500	32400	40
This study	Vanscoy	Souris River	Souris	941	-14.7	-105.3	311000	77900	1550
This study	Vanscoy	Souris River	Souris	946	-3.4	-61.6	351000	6400	5570
This study	Vanscoy	Souris River	Souris	961	-15.2	-108.6	232000	76700	1240

**Table A2:** Model setup parameters.

Stratigraphy	Depth (m BG)*						
	Cory	Vanscoy	Allan	Rocanville	n	De**	
Glacial Till	0	0	0	0	0.24	2.3E-10	
Shales	11	11	11	11	0.33	2.3E-10	
Mannville	485	485	485	375	0.34	2.3E-10	
Three Forks	550	550	560	490	0.1	1.32E-10	
Birdbear	590	590	635	530	0.15	9E-10	
Seward	625	625	680	550	0.1	1.32E-10	
Duperow	675	675	730	625	0.15	9E-10	
Souris River	800	800	785	700	0.1	1.32E-10	
Manitoba	910	910	875	775	0.15	9E-10	
Evaporite	1025	1025	1100	950	0.33	0	

\*Depths from Marsh and Love (2014).

\*\*De = 1.32E-10 for Three Forks to Manitoba in initial profile.

APPENDIX B

Table B1-1: PCA Plots Fig 3-1a

PCA Report: Transform None, Scaling true (15 rows)

Summary Count  
PCA Report: Transform None, Scaling true (15 rows)

Summary Count  
Rows 15  
Columns 13

	87/86Sr	81Br	d18O	Cl/Br_LOG	Cl_ppm_LOG	Na_ppm_LOG	K_ppm_LOG	Ca_ppm_LOG	Mg_ppm_LOG	Br_ppm_LOG	SO4_ppm_LOG	Sr_ppm_LOG	
37Cl	1	0.03208	0.7092	-0.1224	0.5955	-0.2843	0.4313	-0.5761	-0.462	-0.4004	-0.4925	0.4441	-0.4421
87/86Sr	0.03208	1	-0.2123	-0.5453	0.45	-0.8541	-0.4104	-0.5073	-0.6435	-0.6949	-0.7085	0.6094	-0.6491
81Br	0.7092	-0.2123	1	0.4957	0.1678	0.06798	0.2228	-0.2709	-0.0907	0.00512	-0.0609	0.08357	-0.0351
d18O	-0.1224	-0.5453	0.4957	1	-0.5928	0.6732	-0.108	0.5957	0.6331	0.7115	0.6955	-0.6568	0.6935
Cl/Br_LOG	0.5955	0.45	0.1678	-0.5928	1	-0.6463	0.4348	-0.7759	-0.8773	-0.8704	-0.9159	0.8361	-0.8755
Cl_ppm_LOG	-0.2843	-0.8541	0.06798	0.6732	-0.6463	1	0.01811	0.8015	0.8602	0.862	0.8982	-0.8669	0.8787
Na_ppm_LOG	0.4313	-0.4104	0.2228	-0.108	0.4348	0.01811	1	-0.2453	-0.3344	-0.2516	-0.2409	0.2995	-0.3391
K_ppm_LOG	-0.5761	-0.5073	-0.2709	0.5957	-0.7759	0.8015	-0.2453	1	0.8641	0.8532	0.8685	-0.8904	0.8758
Ca_ppm_LOG	-0.462	-0.6435	-0.0907	0.6331	-0.8773	0.8602	-0.3344	0.8641	1	0.9824	0.9578	-0.9744	0.9949
Mg_ppm_LOG	-0.4004	-0.6949	0.00512	0.7115	-0.8704	0.862	-0.2516	0.8532	0.9824	1	0.9547	-0.9593	0.9861
Br_ppm_LOG	-0.4925	-0.7085	-0.0609	0.6955	-0.9159	0.8982	-0.2409	0.8685	0.9578	0.9547	1	-0.9375	0.9664
SO4_ppm_LOG	0.4441	0.6094	0.08357	-0.6568	0.8361	-0.8669	0.2995	-0.8904	-0.9744	-0.9593	-0.9375	1	-0.9782
Sr_ppm_LOG	-0.4421	-0.6491	-0.0351	0.6935	-0.8755	0.8787	-0.3391	0.8758	0.9949	0.9861	0.9664	-0.9782	1

Scaled Coordinates	PC1	PC2
37Cl	0.5011	0.7323
87/86Sr	0.6828	-0.5532
81Br	0.06734	0.8429
d18O	-0.7193	0.4146
Cl/Br_LOG	0.8926	0.2234
Cl_ppm_LOG	-0.8989	0.2756
Na_ppm_LOG	0.2729	0.6394
K_ppm_LOG	-0.9049	-0.1648
Ca_ppm_LOG	-0.98	-0.03904
Mg_ppm_LOG	-0.979	0.06815
Br_ppm_LOG	-0.9869	0.0163
SO4_ppm_LOG	0.9693	0.02262
Sr_ppm_LOG	-0.989	5.32E-04

Table B1-2: PCA Plots Fig 3-1b

PCA Report: Transform None, Scaling true (60 rows)

Summary Count  
PCA Report: Transform None, Scaling true (60 rows)

Summary Count  
Rows 60  
Columns 10

Correlation	d18O	Cl/Br_LOG	Cl_ppm_LOG	Na_ppm_LOG	K_ppm_LOG	Ca_ppm_LOG	Mg_ppm_LOG	Br_ppm_LOG	SO4_ppm_LOG	Sr_ppm_LOG
d18O	1	-0.8271	0.6679	-0.1608	0.6332	0.8129	0.8117	0.8094	-0.732	0.8406
Cl/Br_LOG	-0.8271	1	-0.7462	0.07167	-0.6671	-0.9164	-0.9078	-0.9497	0.8811	-0.9266
Cl_ppm_LOG	0.6679	-0.7462	1	0.3514	0.7718	0.8699	0.8607	0.9171	-0.8429	0.8661
Na_ppm_LOG	-0.1608	0.07167	0.3514	1	-0.02045	-0.01708	0.013	0.1224	-0.05561	-0.04832
K_ppm_LOG	0.6332	-0.6671	0.7718	-0.02045	1	0.8037	0.7682	0.7625	-0.7176	0.7859
Ca_ppm_LOG	0.8129	-0.9164	0.8699	-0.01708	0.8037	1	0.9763	0.9578	-0.9246	0.9906
Mg_ppm_LOG	0.8117	-0.9078	0.8607	0.013	0.7682	0.9763	1	0.9484	-0.8779	0.9683
Br_ppm_LOG	0.8094	-0.9497	0.9171	0.1224	0.7625	0.9578	0.9484	1	-0.924	0.9622
SO4_ppm_LOG	-0.732	0.8811	-0.8429	-0.05561	-0.7176	-0.9246	-0.8779	-0.924	1	-0.9401
Sr_ppm_LOG	0.8406	-0.9266	0.8661	-0.04832	0.7859	0.9906	0.9683	0.9622	-0.9401	1

Scaled Coordinates	PC1	PC2
d18O	0.8491	-0.248
Cl/Br_LOG	-0.9353	0.1298
Cl_ppm_LOG	0.9017	0.3574
Na_ppm_LOG	0.03182	0.9855
K_ppm_LOG	0.8201	-0.01026
Ca_ppm_LOG	9.86E-01	-0.0432
Mg_ppm_LOG	9.71E-01	-0.01996
Br_ppm_LOG	9.84E-01	0.09043
SO4_ppm_LOG	-9.38E-01	-0.03742
Sr_ppm_LOG	9.89E-01	-0.07612







Wittrup and Kvaer (1990)	12	Corv	539	35600	28000	1360	1964	870	196	1.2129	409.36382	-13.5	-115
Wittrup and Kvaer (1990)	117	Corv	569	25200	17000	430	1954	820	155	0.89781	424.53699	-16.8	-143
Wittrup and Kvaer (1990)	19	Corv	570	29600	17000	430	2202	670	12900	0.88668	5.17151	-16	-127
Wittrup and Kvaer (1990)	119	Corv	588	96400	36000	710	22180	6600	906	0.5759	238.80839	-9.6	-120
Wittrup and Kvaer (1990)	145	Corv	603									-16.9	-136
Wittrup and Kvaer (1990)	118	Corv	612	24800	18000	540	2010	830	168	1.11479	334.04548	-17	-134
Wittrup and Kvaer (1990)	411	Allan	621	33800	24200	1240	2098	530	207	1.10412	368.01192	-18	-139
Wittrup and Kvaer (1990)	412	Allan	637	40900	25700	1390	2059	520	208	0.96901	443.17525	-18.1	-138
Wittrup and Kvaer (1990)	45	Allan	643	42700	24900	1250	2037	330	211	0.89927	456.10992	-18.3	-139
Wittrup and Kvaer (1990)	46	Allan	648	44500	27000	1370	2245	510	211	0.93567	475.32766	-17.6	-140
Wittrup and Kvaer (1990)	413	Allan	650	65900	39300	1930	2355	610	323	0.91966	459.83119	-16.9	-137
Wittrup and Kvaer (1990)	47	Allan	704		46600	2280	2770	650	318			-18	-138
Wittrup and Kvaer (1990)	414	Allan	748	180000	120000	1740	5109	2060	1810	1.02808	224.13489	-14.9	-124
Wittrup and Kvaer (1990)	48	Allan	765	136000	73000	2410	2370	2400	1170	0.82776	261.98026	-10.4	-105
Wittrup and Kvaer (1990)	110	Corv	770	101000	42000	940	24500	4800	863	0.64128	263.77043	-11.2	-103
Wittrup and Kvaer (1990)	49	Allan	782	196000	173000	1810	8160	2810	2030	1.36116	217.60835	-15.1	-125
Wittrup and Kvaer (1990)	14	Corv	787	160000	103000	2220	21740	5650	1720	0.39756	209.65589	-8.3	-106
Wittrup and Kvaer (1990)	121	Corv	818	199000	130000	2290	22640	1500	2600	1.00742	160.18084	-9.6	-107
Wittrup and Kvaer (1990)	122	Corv	845	228000	60000	6300	68500	18300	5950	0.40582	86.36413	-8.4	-94