



# Geophysical Research Letters

#### RESEARCH LETTER

10.1029/2021GL094285

#### **Key Points:**

- Pleistocene glacial meltwater recharge migrated non-uniformly within and between stacked Paleozoic aquifers of the Williston Basin
- Deep, stacked, carbonate aquifers were impacted by Pleistocene recharge at two arrival intervals, attributed to permeability differences
- The arrival times of subglacial recharge are constrained to early to mid-Pleistocene and appear fully preserved in the Williston Basin

#### **Supporting Information:**

Supporting Information may be found in the online version of this article.

#### Correspondence to:

A. C. Mowat and G. A. G. Ferguson, aidan.mowat@usask.ca; grant.ferguson@usask.ca

#### Citation:

Mowat, A. C., Francis, D. J., McIntosh, J. C., Lindsay, M. B. J., & Ferguson, G. A. G. (2021). Variability in timing and transport of Pleistocene meltwater recharge to regional aquifers. *Geophysical Research Letters*, 48, e2021GL094285. https://doi.org/10.1029/2021GL094285

Received 10 MAY 2021 Accepted 30 SEP 2021

# Variability in Timing and Transport of Pleistocene Meltwater Recharge to Regional Aquifers

Aidan C. Mowat<sup>1</sup>, Daniel J. Francis<sup>1</sup>, Jennifer C. McIntosh<sup>2,3</sup>, Matthew B. J. Lindsay<sup>1</sup>, and Grant A. G. Ferguson<sup>2,3</sup>

<sup>1</sup>Department of Geological Sciences, University of Saskatchewan, Saskatoon, SK, Canada, <sup>2</sup>Department of Hydrology and Atmospheric Sciences, University of Arizona, Tucson, AZ, USA, <sup>3</sup>Department of Civil, Geological and Environmental Engineering, University of Saskatchewan, Saskatoon, SK, Canada

**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 2 million years in the Williston Basin, Canada. Integration of fluid chemistry, stable isotope data, and transport modeling indicate that meltwater arrived at depths of  $\sim\!600-1000$  m in the northcentral region of the Williston Basin at two separate time periods, 75–150 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.

**Plain Language Summary** Continental glaciations can reorganize large-scale groundwater flow systems, but the timing of recharge events is not well known. We investigated local and regional variations in groundwater flow and the timing of meltwater influx resulting from glaciations over the last 2 million years in a deep aquifer system in the Williston Basin, Canada. Isotopic signatures of groundwaters indicate the presence of subglacial meltwater and older marine-derived brines within these aquifers. These isotopic signatures were used to constrain groundwater transport models and estimate arrival times of Pleistocene meltwater recharge at study sites in the northcentral Williston Basin. We identified two arrival time periods (i.e., 75,000 to 150,000 and 300,000 years before present) and attribute these to local and regional variations in aquifer properties. Our results also indicate that recharge occurred at the northern margin of the Williston Basin, along with the eastern margin, to form a continuous recharge belt.

#### 1. Introduction

Pleistocene glaciation profoundly altered continental-scale groundwater flow systems by increasing hydraulic heads and recharging fresh subglacial meltwaters to kilometer depths in underlying sedimentary basins (Grasby et al., 2000; McIntosh et al., 2012; Person et al., 2007). 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 & Chen, 2005; McIntosh & Walter, 2006) in sedimentary basins of North America and Europe (Boulton et al., 1995; Kloppmann et al., 2001). The few studies that have attempted to constrain the timing of subglacial recharge using age tracers (e.g., Mazor & 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 2 million years.

Pleistocene glacial meltwaters are an important fresh groundwater resource in glaciated continental and coastal regions across the northern hemisphere (Edmunds & Milne, 2001; Grasby et al., 2000; McIntosh et al., 2011; Person, 2007; Person et al., 2007). Infiltration and recharge of meltwaters have implications for long-term radioactive waste and  $CO_2$  storage (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

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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 ( $^{14}$ C), helium ( $^{4}$ He), and krypton ( $^{81}$ Kr) to constrain the timing of Pleistocene recharge (Cloutier et al., 2006; Gerber et al., 2017; Hendry et al., 2013; McIntosh & Walter, 2006; Phillips & Castro, 2013; Schlegel et al., 2011). However, radiocarbon dating is limited to  $<\sim50,000$  years and existing noble gas data is relatively sparse. As an alternative, stable isotopes of water ( $\delta^{18}$ O and  $\delta^{2}$ H) data are more widely available (Ferguson & Jasechko, 2015; Jasechko, 2019), enabling higher-resolution studies to indirectly support dating studies. These data are also effective indicators of ground-water sources as modern meteoric waters, Pleistocene recharge, and connate brines typically exhibit distinct  $\delta^{18}$ O and  $\delta^{2}$ 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 & Harrington, 2014; Hendry et al., 2013). The numerical transport modeling inherently considers elapsed time since the Pleistocene meltwater arrived in the region and, fitted to high-resolution  $\delta^{18}$ O and  $\delta^{2}$ 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 connate brines and dissolution of evaporites remain ambiguous. Connate brines, positioned deep within the Williston Basin, are highly saline (>350 g L<sup>-1</sup> TDS) and have elevated  $\delta^{18}$ O and  $\delta^{2}$ H values characteristic of paleoevaporated seawater (Wittrup & Kyser, 1990). However, recharge of fresh Pleistocene meltwaters, with low  $\delta^{18}$ O values, along the north to east margins of the Williston Basin flushed connate brines and generated new salinity via extensive salt dissolution (Grasby & Chen, 2005; Grasby et al., 2000; Wittrup & Kyser, 1990). Using 1–D transport modeling of  $\delta^{18}$ 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  $\delta^{18}O$  and  $\delta^{2}H$  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.

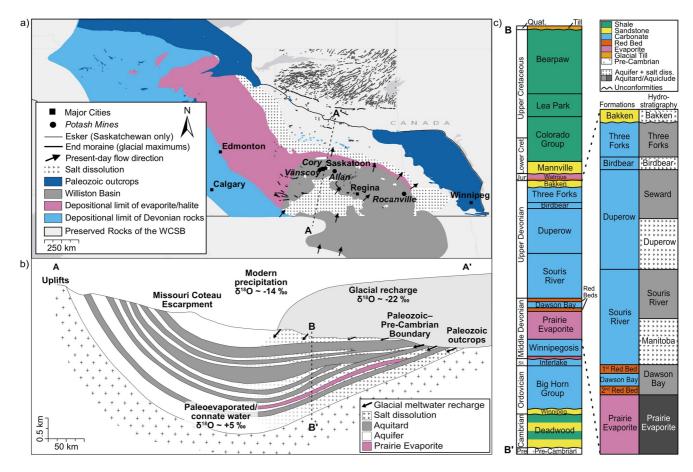
# 2. Regional Hydrogeology

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 & Christopher, 1994) (Figure 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 1).

The Williston Basin has been intermittently overlain by continental ice sheets over the past 2 million years (Christiansen & 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

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**Figure 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.

isotopic signature characteristic of Pleistocene meltwaters (Grasby & Betcher, 2000; Grasby & Chen, 2005). These characteristics include  $\delta^2H$  and  $\delta^{18}O$  values that plot on the Global Meteoric Water Line (GMWL) but more  $^{18}O$  and  $^2H$ -depleted with respect to modern precipitation. They also exhibit a molar Na:Cl ratio of  $\sim 1$  and molar Cl:Br ratios  $\sim 10$  times greater than seawater, indicative of halite (salt) dissolution (Grasby & Betcher, 2000)

Following retreat of the Laurentide Ice Sheet, hydraulic heads in the Williston Basin likely returned to the present, quasi-equilibrium state (Grasby & Chen, 2005; Hitchon, 1969). 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 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 paleoevaporated seawater including molar Na:Cl ratios <0.85, molar Cl:Br ratios comparable to evaporated seawater, and  $\delta^{18}$ O values that plot below the GMWL (Ferguson et al., 2007; Grasby & Betcher, 2000; Grasby & Chen, 2005). Stagnation of connate brines within deep sedimentary basins is attributed to negative buoyancy associated with high TDS waters (Bachu & Hitchon, 1996; Palombi, 2008; Ferguson et al., 2018).

#### 3. Methods

### 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

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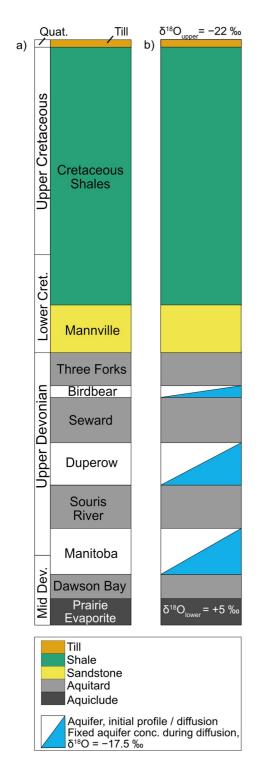


Figure 2. Conceptual build of 1-dimensional finite element model software in CTRAN/W and SEEP/W (GeoStudio, 2018 R2, v. 9.1.1.16749). (a) Basic geology and, (b) the initial profile and diffusion-only profile set-up with upper and lower boundary conditions. The diffusion-only profile accounts for upper and lower boundary conditions and constant concentration at each carbonate aquifer ( $\delta^{18}O_{aquifer} = -17.5\%$ ).

southcentral Saskatchewan (Figure 1). These seeps primarily originated from the middle to upper Devonian strata from the Birdbear Formation ( $\sim$ 600 m) to the Prairie Formation ( $\sim$ 1,100 m), which corresponds to mine level (Table S1). Fluids were collected into clean 250 mL or 1,000 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  $\delta^{18}O$  and  $\delta^{2}H$  values were determined using CO<sup>2</sup>–H<sup>2</sup>O and H<sup>2</sup>–H<sup>2</sup>O equilibration methods, respectively, at the Saskatchewan Isotope Laboratory (Saskatoon, Canada) and results are reported as the relative difference between the  $^{18}O/^{16}O$  and  $^{2}H/^{1}H$  abundance ratios normalized to Vienna Standard Mean Ocean Water (VSMOW), expressed in per mil (‰) notation. Accuracies of  $\delta^{2}H$  and  $\delta^{18}O$  are 2‰ and 0.2‰, respectively, but this methodology does not account for the salt effect in highly saline waters (Koehler et al., 2013; Sofer & Gat, 1972, 1975). Corrections for the salt effect, which produces discrepancies in measured isotope compositions in high activity brines as outlined by Koehler et al. (2013) and Sofer and Gat (1972, 1975), were applied to the  $\delta^{18}O$  and  $\delta^{2}H$  values. Additional data (Cl, Br,  $\delta^{18}O$ , and  $\delta^{2}H$ ) are from Jensen et al. (2006) and Wittrup and Kyser (1990) to increase data coverage.

#### 3.2. Model Setup

A simplified hydrostratigraphic column (Figure 2a) was constructed based on local geology using GeoHub Saskatchewan (Marsh & Love, 2014) for Prairie Evaporite (mine level) to surface. Simulation of measured  $\delta^{18}O$  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 aguifer groundwater concentration when meltwater first arrives in the study site via regional groundwater flow (Figure 2b. These models, which used a spacing between nodes of 10 m, assumes that prior to the arrival of meltwater, the vertical distribution of  $\delta^{18}O$  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:

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

$$v = \frac{q}{n},\tag{2}$$

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

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We used  $n_e$  values reported by Hendry et al. (2013), which are based on measurements from a commerical data base (IHS Energy, 2017), 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). We used  $D_e$  values of  $2.3 \times 10^{-10}$  m<sup>2</sup> s<sup>-1</sup> for glacial till, shale and sandstone units (Hendry & Wassenaar, 1999),  $1.32 \times 10^{-10}$  m<sup>2</sup> s<sup>-1</sup> for the Devonian carbonate aquifers, and  $6.0 \times 10^{-11}$  m<sup>2</sup> s<sup>-1</sup> for the Prairie Evaporite (Boudreau, 1996; Boudreau & Meysman, 2006; Hendry et al., 2009). We increased  $D_e$  to  $9 \times 10^{-10}$  m<sup>2</sup> s<sup>-1</sup> for the Devonian carbonate aquifers in the diffusion model set-up (Figure 2b).

The initial hydrogeochemical profile, representing pre-glaciation conditions and (or) zero recharge, is simulated based on a diffusion-only transport setting (i.e.,  $\nu = 0$ ) after Hendry et al. (2013) between two fixed boundaries (Figure 2a). 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  $\delta^{18}$ 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,  $\delta^{18}O_{upper}$ , for surface recharge -22% to reflect subglacial meltwater (Ferguson et al., 2007; Ferguson & Jasechko, 2015; Grasby & Chen, 2005) and the lower fixed boundary,  $\delta^{18}O_{lower}$ , at the Prairie Evaporite as +5% to represent paleoevaporated seawater (Ferguson et al., 2007; Grasby & Chen, 2005; Figure 2b). 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  $\delta^{18}$ 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 2b) over 1 million years from  $t_{initial}$  to  $t_{final}$ . 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 & Gibbard, 2008). In this scenario, we maintained the  $\delta^{18}O_{upper}$  and  $\delta^{18}O_{lower}$ values that defined the upper and lower boundary conditions, and defined the fixed aquifer concentrations,  $\delta^{18}O_{aquifer}$ , as -17.5% to reflect an average  $\delta^{18}O_{aquifer}$  value for our dataset. Lastly, we increased  $D_e$  to  $9 \times 10^{-10}$  m<sup>2</sup> s<sup>-1</sup> 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  $\delta^{18}O$ -depth profiles using root mean squared error (RMSE).

#### 4. Results

#### 4.1. Geochemical Results

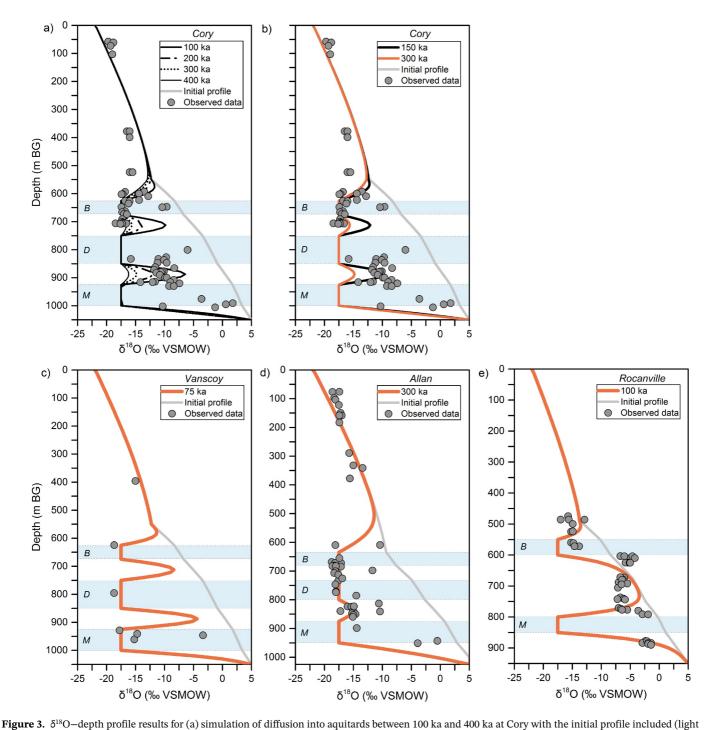
The  $\delta^{18}$ O values tended to be lower within aquifer units than in aquitards (Figure 3; Table S1), with these lower values generally falling on the GMWL (Figure 4a).  $\delta^{2}$ H and  $\delta^{18}$ O values fell along a mixing trend between the GMWL at a value consistent with a Pleistocene signature (Ferguson & Jasechko, 2015) and a brine endmember resembling evaporated seawater (Figure 4a). Samples plotting near the GMWL tended to have high Cl:Br, while values below the GMWL had low Cl:Br (Figure 4b).

#### 4.2. Model Results

The initial profile, describing the pre-glaciation conditions and (or) zero recharge, provides the best-fit to unperturbed  $\delta^{18}$ O values at 25 million years and deviates greatly from the measured data after 40 million years (Figure S1). The upper and lower  $\delta^{18}$ O boundary conditions (-22% and +5%, respectively) provide a reasonable approximation of the estimated and known  $\delta^{18}$ O values for glacial recharge (Ferguson et al., 2007; Ferguson & Jasechko, 2015; Grasby & Chen, 2005) and paleoevaporated seawater (Ferguson et al., 2007; Grasby & Chen, 2005). It is evident from the initial depth profile (Figure 3) that additional transport processes must be imparted on this stacked aquifer system to closely replicate the observed present-day  $\delta^{18}$ O values by simulating a diffusion-dominated environment with perturbation by a  $^{18}$ O-depleted source

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gray), 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.

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 (Figures 3b–3d). In each simulation, the model demonstrates the aquitard(s) response to meltwater that was transported from the aquitards ( $\delta^{18}O_{aquifer} = -17.5\%$ ) as t increases, and eventually creating a best-fit to observed data.

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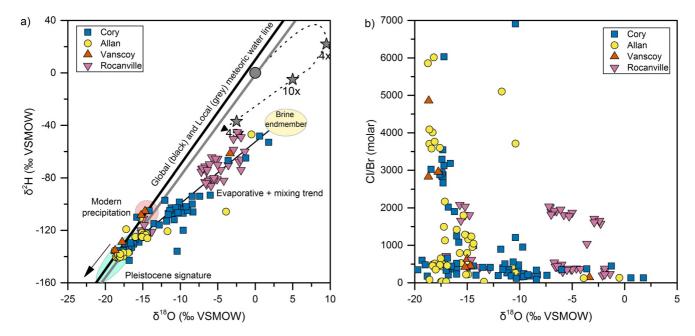


Figure 4. (a)  $\delta^{18}$ O versus  $\delta^{2}$ H values of formation waters from stacked carbonate aquifers from the four study sites relative to with the global (black) and local (gray) meteoric water lines, general evaporation sequence of seawater (gray circle and stars with amount of evaporation)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

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 3). There was no detectable shift in  $\delta^{18}$ O values reflective of glacial meltwaters in the Duperow aquifer at Rocanville.

These results, displaying perturbation of a freshwater source in carbonate aquifers, are complemented by  $\delta^{18}O$  and  $\delta^{2}H$  values that fall along the GMWL (Figure 4a) and higher molar Cl:Br values, which indicate halite and salt dissolution (Figure 4b). In contrast, formation waters in the carbonate aquitards plot to the right of the GMWL (Figure 4a) and have relatively low molar Cl:Br values (<2000; less than seawater) (Figure 4b). These brines derived from evaporation of paleoseawater (i.e., brine endmember in Figure 4a), which have been diluted by Pleistocene meltwaters, as indicated by the linear mixing trend in Figure 4a.

### 5. Discussion

The distribution of  $\delta^2H$  and  $\delta^{18}O$  values and 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 (Ferguson & Jasechko, 2015; Ferguson et al., 2007; Grasby et al., 2000; Hendry et al., 2013). The lowest  $\delta^{18}O$  values are higher than the lowest values documented in the region (less than -24%; Ferguson & Jasechko, 2015; Figure 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%) 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 4). The lowest  $\delta^2H$  and  $\delta^{18}O$  values are present in the Duperow, Manitoba, and Birdbear aquifers at Cory, Vanscoy, and Allan (Figure 3), while the aquitards at those sites have higher  $\delta^2H$  and  $\delta^{18}O$  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 75–150 ka and an older 300 ka (Figure 3). The arrival times are consistent with Pleistocene recharge as previously es-

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tablished by others (Grasby et al., 2000; McIntosh et al., 2012; Person et al., 2007). 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 advances that occurred in the early to mid-Pleistocene. 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.

Modeled 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 Willison Basin (Christiansen et al., 1982; Christiansen & Sauer, 2001; Grasby et al., 2000), 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 2 million years (Bense & Person, 2008; Person, 2007). For example, groundwaters at depth in the Illinois Basin show a mixing zone between paleoevaporated seawater and Pleistocene meltwater dating up to 1.2 Ma (McIntosh et al., 2002; McIntosh & Walter, 2006; Siegel, 1991), while other aquifers in the Illinois Basin and Michigan Basin record groundwater ages greater than 50 ka (McIntosh & 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 and 430 ka (Hendry et al., 2013; Schmeling, 2014).

The extent of meltwater recharge transport 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 modeled 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 Cl:Br values (<2000 Cl:Br), which are associated with a paleoevaporated source, and <sup>18</sup>O-enriched groundwater (Figure 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 & Love, 2014) along with higher Cl:Br values, which result from addition of Cl by dissolution of halite, and <sup>18</sup>O-depleted groundwater at Cory, Vanscoy, and Allan (Figure 4) suggests a continuous recharge belt along the northern margin of the Williston Basin from Saskatchewan into Manitoba (Figure 1a). This finding is consistent with observations of widespread salt dissolution and mixing zones between paleoevaporated seawater and meltwater recharge in the northcentral region of the basin (Grasby & Chen, 2005). Esker distribution in northern Saskatchewan supports this hypothesis by demonstrating a sharp change in permeability at the boundary of Precambrian and sedimentary rocks (Figure 1; Grasby & Chen, 2005) where high-permeability sedimentary rocks will facilitate enhanced recharge. Anomalous TDS concentrations and Na:Cl ratios 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.

#### 6. Conclusion

A combination of high-resolution stable isotope data,  $\delta^{18}O$  and  $\delta^{2}H$ , 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 75–150 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 geo-

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graphic 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 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.

# **Data Availability Statement**

All data included in this manuscript are included in Table S1, and (or) at the following DOI: 10.5281/zenodo.5363453.

## Acknowledgments References

Funding was provided to G. Fergu-

Natural Sciences and Engineering

son by Global Water Futures and the

Research Council of Canada (NSERC)

(Grant No. CRDPJ 500161-16), and to

M. Lindsay by (NSERC) (Grant No.

RGPIN-2020-05172). Additional sup-

port is awarded to A. Mowat from the

- Master's Program (NSERC CGS-M),

the NSERC Postgraduate Scholarship

- Doctoral (NSERC PGS-D) Program

(PGSD3-546592-2020), the University

of Saskatchewan Dean's Scholarship,

and the Saskatchewan Oueen Elizabeth

II Centennial Aboriginal Scholarship.

We are grateful to Dr. S. L. Barbour for

assistance in transport modeling, to K.

data, and to Tanner Soroka (Nutrien)

for assistance with sample collection.

We also acknowledge two anonymous

reviewers who provided constructive

feedback that improved this paper.

Tipton for consultation about additional

NSERC Canadian Graduate Scholarship

Bachu, S., & Hitchon, B. (1996). Regional-scale flow of formation waters in the Williston Basin. AAPG Bulletin, 80(2), 248–264. https://doi.org/10.1306/64ED87A0-1724-11D7-8645000102C1865D

Bense, V. F., & Person, M. A. (2008). Transient hydrodynamics within intercratonic sedimentary basins during glacial cycles. *Journal of Geophysical Research*, 113(4), 1–17. https://doi.org/10.1029/2007JF000969

Boudreau, B. P. (1996). The diffusive tortuosity of fine-grained unlithified sediments. *Geochimica et Cosmochimica Acta*, 60(16), 3139–3142. https://doi.org/10.1016/0016-7037(96)00158-5

Boudreau, B. P., & Meysman, P. J. R. (2006). Predicted tortuosity of muds. Geology, 34(8), 693-696. https://doi.org/10.1130/G22771.1

Boulton, G. S., Caban, P. E., & Gijssel, V. K. (1995). Groundwater flow beneath ice sheets: Part 1 – Large scale patterns. *Quaternary Science Reviews*, 14, 545–562. https://doi.org/10.1016/0277-3791(95)00039-R

Christiansen, E. A., Gendzwill, D. J., & Meneley, W. A. (1982). Howe lake: A hydrodynamic blowout structure. Canadian Journal of Earth Sciences, 19(6), 1122–1139. https://doi.org/10.1139/e82-097

Christiansen, E. A., & Sauer, E. K. (2001). Stratigraphy and structure of a Late Wisconsinan salt collapse in the Saskatoon Low, south of Saskatoon, Saskatchewan, Canada: An update. *Canadian Journal of Earth Sciences*, 38(11), 1601–1613. https://doi.org/10.1139/cjes-38-11-160110.1139/e01-038

Cloutier, V., Lefebvre, R., Savard, M. M., Bourque, D., & Therrien, R. (2006). Hydrogeochemistry and groundwater origin of the Basses-Laurentides sedimentary rock aquifer system, St. Lawrence Lowlands, Que'bec, Canada. *Hydrogeology Journal*, 14, 573–590. https://doi.org/10.1007/s10040-005-0002-3

 $Edmunds, W. M., \& \ Milne, C. J. \ (2001). \ Palaeowaters in coastal \ Europe: Evolution \ of \ groundwater since \ the \ late \ Pleistocene \ (p. 189). \ Geological \ Society Special \ Publications. \ https://doi.org/10.1144/GSL.SP.2001.189$ 

Ehlers, J., & Gibbard, P. (2008). Extent and chronology of Quaternary glaciation. *Episodes*, 31(2), 211–218. https://doi.org/10.18814/epiiugs/2008/v31i2/004

Ferguson, G., Betcher, R. N., & Grasby, S. E. (2007). Hydrogeology of the Winnipeg formation in Manitoba, Canada. *Hydrogeology Journal*, 15(3), 573–587. https://doi.org/10.1007/s10040-006-0130-4

Ferguson, G., & Jasechko, S. (2015). The isotopic composition of the Laurentide Ice Sheet and fossil groundwater. *Geophysical Research Letters*, 42(12), 4856–4861. https://doi.org/10.1002/2015GL064106

Ferguson, G., McIntosh, J. C., Grasby, S. E., Hendry, M. J., Jasechko, S., Lindsay, M. B. J., & Luijendijk, E. (2018). The persistence of brines in sedimentary basins. *Geophysical Research Letters*, 45(10), 4851–4858. https://doi.org/10.1029/2018GL078409

GeoStudio computer software. (2018). Version 9.1.1.16749. Retrieved from www.geoslope.com

Gerber, C., Vaikmäe, R., Aeschbach, W., Babre, A., Jiang, W., Leuenberger, M., et al. (2017). Using <sup>81</sup>Kr and noble gases to characterize and date groundwater and brines in the Baltic Artesian Basin on the one-million-year timescale. *Geochimica et Cosmochimica Acta*, 205, 187–210. https://doi.org/10.1016/j.gca.2017.01.033

Grasby, S. E., & Betcher, R. N. (2000). Regional hydrogeochemistry of the carbonate rock aquifer, southern Manitoba. Canadian Journal of Earth Sciences, 39(7), 1053–1063. https://doi.org/10.1139/e02-021

Grasby, S. E., & Chen, Z. (2005). Subglacial recharge into the Western Canada sedimentary basin—Impact of Pleistocene glaciation on basin hydrodynamics. *Bulletin of the Geological Society of America*, 117(3–4), 500–514. https://doi.org/10.1130/B25571.1

Grasby, S. E., Hutcheon, I., & Krouse, H. R. (2000). The influence of water-rock interaction on the chemistry of thermal springs in western Canada. *Applied Geochemistry*, 15, 439–454. https://doi.org/10.1016/S0883-2927(00)00020-2

Hendry, M. J., Barbour, S. L., Boldt-Leppin, B., Reifferscheid, L., & Wassenaar, L. I. (2009). A comparison of laboratory and field based determinations of molecular diffusion coefficients in a low permeability geologic medium. *Environmental Science and Technology*, 43(17), 6730–6736. https://doi.org/10.1021/es901036p

Hendry, M. J., Barbour, S. L., Novakowski, K., & Wassenaar, L. I. (2013). Paleohydrogeology of the Cretaceous sediments of the Williston Basin using stable isotopes of water. Water Resources Research, 49(8), 4580–4592. https://doi.org/10.1002/wrcr.20321

Hendry, M. J., & Harrington, G. A. (2014). Comparing vertical profiles of natural tracers in the Williston Basin to estimate the onset of deep aquifer activation. Water Resources Research, 50(8), 6496–6506. https://doi.org/10.1002/2014WR015652

MOWAT ET AL. 9 of 10



- Hendry, M. J., & Wassenaar, L. I. (1999). Implications of transport of dD in porewaters for groundwater flow and the timing of geologic events in a thick aquitard system. *Water Resources Research*, 35, 1751–1760. https://doi.org/10.1029/1999wr900046
- Hitchon, B. (1969). Fluid flow in the Western Canada Sedimentary Basin: 2. Effect of topography. Water Resources Research, 5(1), 186–195. https://doi.org/10.1029/WR005i001p00186
- IHS Energy. (2017). IHS AccuMap: Commercial database. IHS Energy.
- Jasechko, S. (2019). Glocal Isotope Hydrogeology—Review. Reviews of Geophysics, 57, 835–965. https://doi.org/10.1029/2018RG000627
- Jensen, G. K. S., Rostron, B. J., Duke, M. J. M., & Holmden, C. (2006). Chemical Profiles of Formation Waters from Potash Mine Shafts, Saskatchewan. Saskatchewan Geological Survey Summary of Investigations, 1.
- Kent, D. M., & Christopher, J. E. (1994). Geological History of the Williston Basin and Sweetgrass Arch. In G. D. Mossop, & I. Shetsen (Eds.), *Geological Atlas of the Western Canada sedimentary basin* (pp. 421–430). Canadian Society of Petroleum Geologists and Alberta Research Council. Retrieved from https://ags.aer.ca/reports/atlas-of-the-western-canada-sedimentary-basin.html
- Kloppman, W., Negrel, P., Casanova, J., Klinge, H., Schelkes, K., & Guerrot, C. (2001). Halite dissolution derived brines in the vicinity of a Permian salt dome (N German Basin): Evidence from boron, strontium, oxygen, and hydrogen isotopes. *Geochimica et Cosmochimica Acta*, 65(22), 4087–4101. https://doi.org/10.1016/S0016-7037(01)00640-8
- Koehler, G., Wassenaar, L. I., & Hendry, J. (2013). Measurement of stable isotope activities in saline aqueous solutions using optical spectroscopy methods. *Isotopes in Environmental and Health Studies*, 49(3), 378–386. https://doi.org/10.1080/10256016.2013.815183
- Lemieux, J.-M., Sudicky, E. A., Peltier, W. R., & Tarasov, L. (2011). Simulating the impact of glaciations on continental groundwater flow systems: 2. Model application to the Wisconsinian glaciation over the Canadian landscape. *Journal of Geophysical Research*, 113, F03018. https://doi.org/10.1029/2007JF000929
- Marsh, A., & Love, M. (2014). Regional stratigraphic framework of the Phanerozoic in Saskatchewan; Saskatchewan Phanerozoic Fluids and Petroleum Systems Project. Saskatchewan Ministry of Energy and Resources, Saskatchewan Geological Survey.
- Martini, A. M., Walter, L. M., & McIntosh, J. C. (2008). Identification of microbial and thermogenic gas components from Upper Devonian black shale cores, Illinois and Michigan basins. *American Association of Petroleum Geologists Bulletin*, 92(3), 327–339. https://doi.org/10.1306/10180706037
- Mazor, E., & Bosch, A. (1987). Noble gases in formation fluids from deep sedimentary basins: A review. *Applied Geochemistry*, 2(5–6), 621–627. https://doi.org/10.1016/0883-2927(87)90014-X
- McIntosh, J. C., Garven, G., & Hanor, J. S. (2011). Impacts of Pleistocene glaciation on large-scale groundwater flow and salinity in the Michigan Basin. *Geofluids*, 11(1), 18–33. https://doi.org/10.1111/j.1468-8123.2010.00303.x
- Mcintosh, J. C., Schlegel, M. E., & Person, M. (2012). Glacial impacts on hydrologic processes in sedimentary basins: Evidence from natural tracer studies. *Geofluids*, 12(1), 7–21. https://doi.org/10.1111/j.1468-8123.2011.00344.x
- McIntosh, J. C., & Walter, L. M. (2006). Paleowaters in Silurian-Devonian carbonate aquifers: Geochemical evolution of groundwater in the Great Lakes region since the Late Pleistocene. *Geochimica et Cosmochimica Acta*, 70(10), 2454–2479. https://doi.org/10.1016/j.gca.2006.02.002
- McIntosh, J. C., Walter, L. M., & Martini, A. M. (2002). Pleistocene recharge to mid-continent basins: Effects on salinity structure and microbial gas generation. *Geochimica et Cosmochimica Acta*, 66(10), 1681–1700. https://doi.org/10.1016/S0016-7037(01)00885-7
- Palombi, D. D. (2008). Regional hydrogeological characterization of the northeastern margin in the Williston Basin (Master of Science, thesis). Edmonton: University of Alberta.
- Person, M. (2007). Pleistocene Hydrogeology of the Atlantic Continental Shelf, New England. In P. G. Knight (Ed.), Glacier Science and environmental change (Vol. 11, pp. 68–70). https://doi.org/10.1002/9780470750636.ch13
- Person, M., McIntosh, J., Bense, V., & Remenda, V. H. (2007). Pleistocene hydrology of North America: The role of ice sheets in reorganizing groundwater flow systems. *Reviews of Geophysics*, 45(3), 1. https://doi.org/10.1029/2006RG000206
- Phillips, F. M., & Castro, M. C. (2013). Groundwater Dating and Residence-Time Measurements. In H. D. Holland, & K. K. Turekian (Eds.), Treatise on Geochemistry (2nd ed., Vol. 7, pp. 361–400). https://doi.org/10.1016/B978-0-08-095975-7.00513-1
- Schlegel, M. E., Zhou, Z., McIntosh, J. C., Ballentine, C. J., & Person, M. A. (2011). Constraining the timing of microbial methane generation in an organic-rich shale using noble gases, Illinois Basin, USA. Chemical Geology, 287(1-2), 27-40. https://doi.org/10.1016/j.chemgeo.2011.04.019
- Schmeling, E. E. (2014). Characterization of the hydrogeology and solute transport in a geologically complex, fractured, late-Cretaceous shale, Fort a la Corne kimberlite field, Saskatchewan, Canada (Master of Science, thesis). Saskatoon: University of Saskatchewan.
- Siegel, D. I. (1991). Evidence for dilution of deep, confined groundwater by vertical recharge of isotopically heavy Pleistocene water. *Geology*, 19, 4332–4436. https://doi.org/10.1130/0091-7613(1991)019<0433:efdodc>2.3.co;2
- Sofer, Z., & Gat, J. R. (1972). Activities and concentrations of O-19 in concentrated aqueous salt solutions: Analytical and geophysical implication. Earth and Planetary Science Letters, 15, 232–238. https://doi.org/10.1016/0012-821X(72)90168-9
- Sofer, Z., & Gat, J. R. (1975). The isotope composition of evaporating brines: Effect of the isotopic activity ratio in saline solutions. Earth and Planetary Science Letters, 26(2), 179–186. https://doi.org/10.1016/0012-821X(75)90085-0
- Wittrup, M. B., & Kyser, T. K. (1990). The petrogenesis of brines in Devonian potash deposits of western Canada. *Chemical Geology*, 82, 103–128. https://doi.org/10.1016/0009-2541(90)90077-K

MOWAT ET AL. 10 of 10