



Using regional datasets of isotope geochemistry to resolve complex groundwater flow and formation connectivity in northeastern Alberta, Canada

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ABSTRACT

In the southern Athabasca Oil Sands (SAOS) Region, located in Alberta Canada, individual in-situ oil sands operators have conducted local geochemical and isotope groundwater studies to establish baseline characteristics and to improve understanding of the connectivity of water supply and disposal formations within individual leases. Canada's Oil Sands Innovation Alliance (COSIA) initiated this study to combine the data from these individual studies along with public information into a comprehensive unified dataset to evaluate conceptual models of regional groundwater flow and the degree of interaction and separation between important water supply and disposal aquifers. The unified dataset comprised over 293 groundwater samples from the main water source and disposal hydrostratigraphic units and included geochemical and isotopic tracers that can be used to identify sources ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) and age of water (^3H) and associated solutes ($^{14}\text{C}_{\text{DIC}}$, ^{36}Cl), as well as the sources of salinity and diagenetic processes ($\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{34}\text{S}_{\text{SO}_4}$, $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{11}\text{B}$, $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$) and dissolved organics ($\delta^{13}\text{C}_{\text{DOC}}$). The TDS and stable isotope composition ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) of groundwater from several Cretaceous formations were used to identify three main mixing controls. i) Areas where locally recharged groundwater mixes with glaciogenic water were identified by lower $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values, high TDS, Cl:Br and $\delta^{34}\text{S}_{\text{SO}_4}$, $^{87}\text{Sr}/^{86}\text{Sr}$, and $\delta^{37}\text{Cl}$ values consistent with dissolution of evaporites. These areas were situated where vertical pathways through otherwise competent formations are likely to occur. ii) Mixing with paleo-waters characterized by high TDS and higher $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signatures indicating groundwater recharged under warmer climate periods and/or evaporative enrichment were identified in the south, and southwestern portions of the study area. The presence of these paleo-waters indicate slow-moving groundwater zones with limited lateral and vertical connectivity. iii) Areas with potential connectivity to shallow aquifers were identified by their lower TDS values, modern meteoric $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signatures, HCO_3^- type waters, and $\delta^{34}\text{S}-\text{SO}_4$ and $^{87}\text{Sr}/^{86}\text{Sr}$ signatures, consistent with weathering of shallow aquifer material. Geochemical and isotopic indicators suggest that in areas where the Colorado Group aquitard is thin or absent, there is greater connectivity between the Grand Rapids Formation and the shallower aquifers. Interpretation of the new unified dataset has improved understanding of the extent that glacial recharge had on Devonian aquifers, and overlying Cretaceous formations, and identified zones with relatively stagnant groundwater flow, both of which have implications for regional groundwater resource development, monitoring and potential wastewater disposal.

1. Introduction

The Athabasca oil sands deposits are located at the terminus of the

Western Canadian Sedimentary Basin. Large sedimentary basins are often the setting for conventional and unconventional petroleum resources, but there is still debate on the controls on brine evolution and

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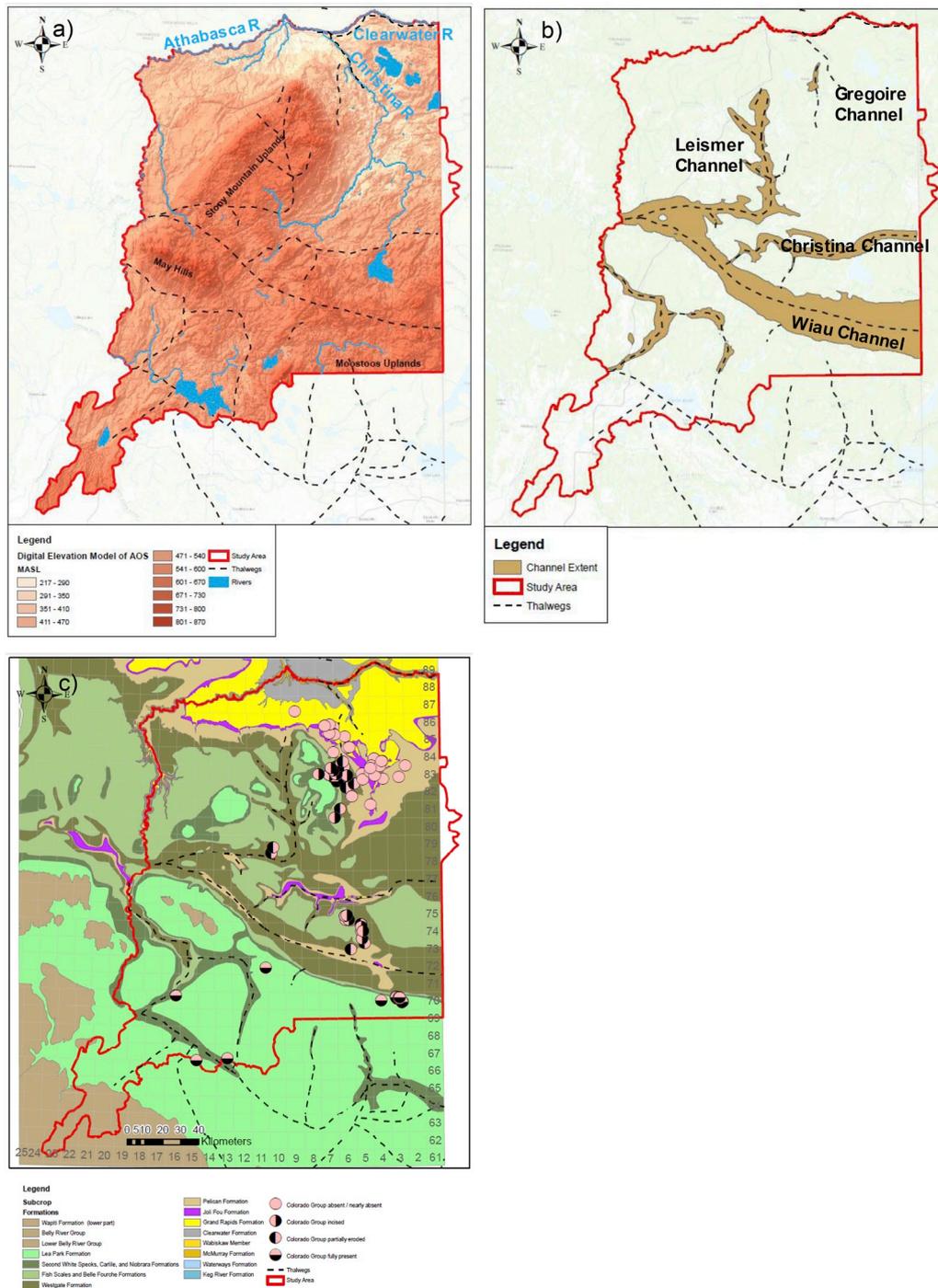


Fig. 1. a) Topography of the study region, b) outlines of major buried channels showing the thalwegs and channel deposit extents (Andriashek, 2003) and c) bedrock geology (symbols indicate the location of Grand Rapid samples and degree of Colorado Group cover) (AGS, 2013).

degree of flushing in these systems (Ferguson et al., 2018), which can have important implications for the sustainability of water withdrawals and stability of storage or disposal zones. The substantial influence of continental glaciations on groundwater dynamics has also been recently considered (Ferguson et al., 2018; Lemieux et al., 2008; McIntosh et al., 2011; Person et al., 2007), and has also been shown to significantly influence geochemistry of groundwater in both shield regions (Clark et al., 2005) and sedimentary basins worldwide (Babre et al., 2016; Grasby et al., 2000; Grasby and Betcher, 2002; McIntosh and Walter, 2006). Development of the oil sands deposits of Alberta has been an important part of Canada's economic success, but there are challenges related to public perception around water use and waste disposal.

Although oil sands surface mining development is at the forefront of these concerns, the majority of the oil sands deposits (about 80%) are too deep to access from surface, and therefore must be developed using in situ technologies (Alberta Energy Regulator, 2015). The most common approach thus far has been thermal stimulation using high temperature steam injected into the bitumen-bearing formations to mobilize the highly viscous bitumen and facilitate recovery to surface for processing and eventual sales. The comprehensive geochemical datasets compiled across this region were originally collected by industry with the objective of improving understanding of the local hydrogeological setting of individual operations, but they have been compiled in this study to test regional hydrogeological conceptual

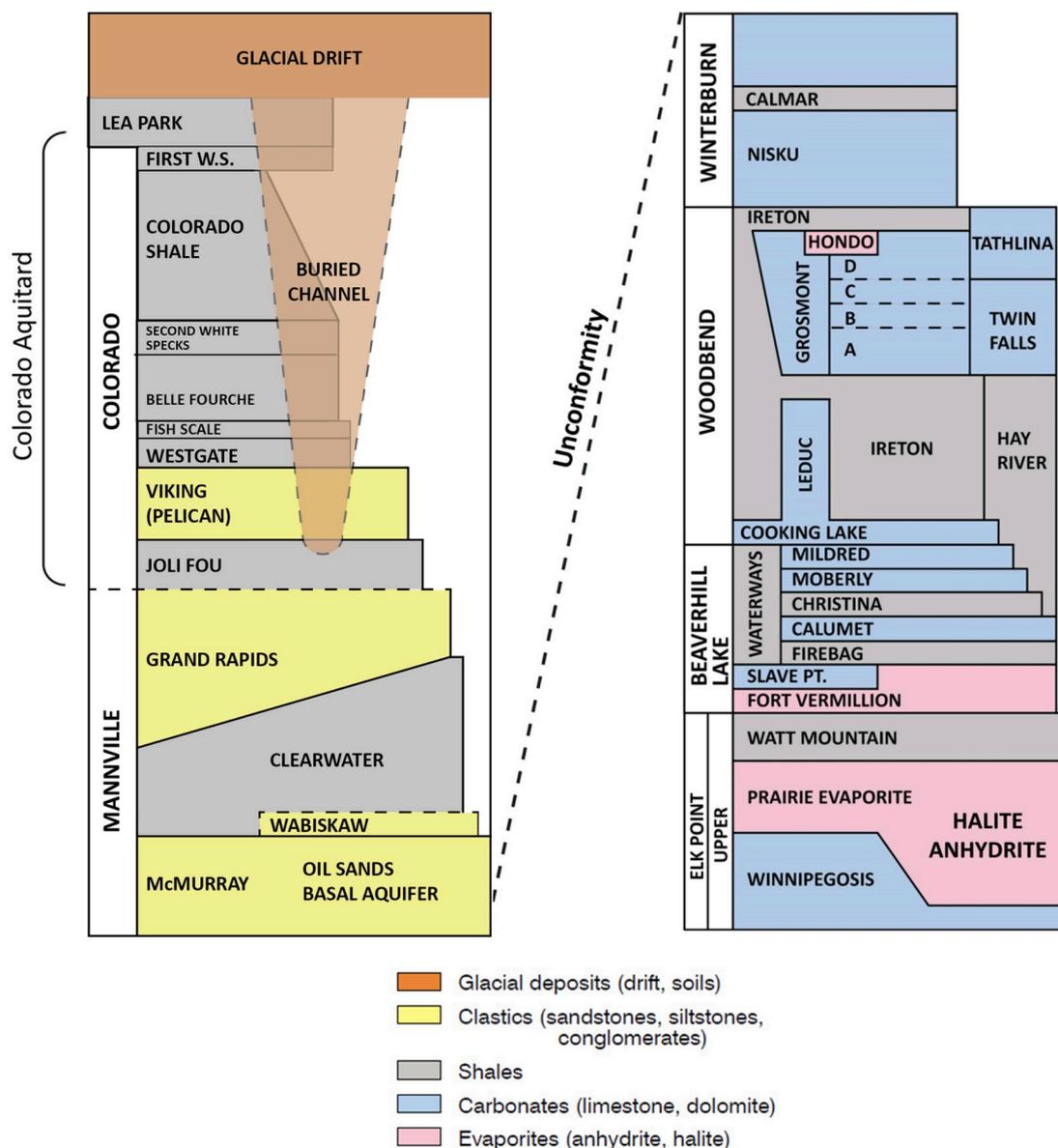


Fig. 2. Stratigraphy of the SAOS region from surface to the Middle Devonian (adapted from AER Table of Formations, Alberta).

models of groundwater flow. Globally, data-rich examples of geochemical interactions occurring in sedimentary basins under the influence of glaciogenic processes are limited, and as such, this case study is expected to be a valuable contribution to understanding these processes on a global scale.

Groundwater is used to produce the steam required to mobilize the bitumen (e.g., 0.4–0.5 m³ of water per m³ of bitumen produced (RSC, 2010). The majority of this water is withdrawn from the Cretaceous permeable sandstone formations (65 million years old or greater), while a minor amount is obtained from younger, confined sand and gravel aquifers (less than 1 million years old) (Matrix, 2016).

Much of the water is returned to surface with the produced bitumen and recycled (greater than 90–95%, RSC, 2010). Treatment of the water prior to steam generation is usually required to remove components such as Ca, Mg, Ba, Fe, Si, and dissolved organics. Disposal of the liquid waste streams generated during the treatment process is typically achieved by downhole disposal into geologically-isolated saline (poor water quality) bedrock formations.

Thermal in situ bitumen recovery is employed in all three of Alberta's oil sands deposits (i.e. Peace River, Cold Lake and Athabasca).

Most of the development activity has been occurring in the Cold Lake and Southern Athabasca Oil Sands (SAOS) regions. The SAOS has been the subject of numerous studies to understand the hydrogeologic environment and the potential implications of past, current, and future oil sands development including groundwater extraction and downhole disposal (Matrix, 2013, 2016; Worley Parsons, 2010). Results to date have indicated a complex system of groundwater flow with variable geochemical conditions within the various aquifer intervals beneath the region.

To provide further understanding of the hydrogeologic setting of the SAOS region, a working group of Canada's Oil Sands Innovation Alliance (COSIA) initiated a study to consolidate existing geochemical information and review, and re-assess the results to support an enhanced regional interpretation of these data. The objectives of this regional geochemistry study were to: i) compile all available geochemical and isotope data for the SAOS region (both public and industry-related), ii) interpret the unified dataset of information to refine knowledge regarding the origin of pore waters in various formations extending from surface down to the upper Devonian, and iii) assess the evolutionary history and age of groundwater within the Cretaceous-

aged aquifers (McMurray, Clearwater, and Grand Rapids Formations) used to support thermal in situ operations. Improved understanding of the connectivity between the main aquifers in this region, particularly the aquifers used for water supply and potential fluid waste disposal, can be used by oil sands operators and industry regulators to ensure that existing water management plans minimize potential impacts and environmental monitoring programs are properly designed and executed.

2. Background

The terrain of the SAOS region is characterized by broad, rolling uplands and adjacent low-lying plains (Fig. 1a). Surficial deposits consist of large accumulations of peat and recent soils formed since the final retreat of the continental ice sheets around 10,000 to 15,000 years ago. Beneath the surficial deposits is a veneer of unconsolidated sediments comprising tills, lacustrine clays, and fluvial sands and gravels of glacial and pre-glacial origin (Andriashek, 2003). These are commonly referred to as drift deposits, which are typically on the order of 10 m–30 m thick, however they can exceed 100 m or more in the deepest parts of pre-glacial and glacial channels (Fig. 1b) eroded into the bedrock surface (Andriashek and Atkinson, 2007).

Beneath the drift deposits are various consolidated bedrock formations of the Cretaceous Period (Fig. 1c) resting unconformably on upper Devonian deposits (Fig. 2). The aquifers of the Mannville Group, which include (in descending order) the Grand Rapids, Clearwater, and McMurray formations, are of particular interest since they are used as industrial-grade lower quality water sources. Although somewhat variable in composition, the hydrocarbon-rich formations of the Mannville Group are typically dominated by very fine-to fine-grained sandstones with intervening intervals of siltstone and shale. In turn, these formations are capped by shale-dominated formations of the Colorado Group. Beneath the Mannville Group sediments are carbonate-rich to shale-dominated deposits of the Wabamun, Winterburn, Woodbend and Beaverhill Lake groups (upper Devonian) – some of which are bitumen-bearing as well (Barson et al., 2001).

A prominent structural feature in the SAOS region is the dissolution edge of the deeper Prairie Evaporite Formation from the Middle Devonian (Broughton, 2013, Broughton, 2015). Removal of the soluble salts in that interval (halite and anhydrite) is responsible for a reversal in the usual south-west dip on the overlying Mannville Group formations to a north-easterly dip, forming a structural trap for hydrocarbons. The reversal of dip is suspected to have created some connectivity between water-bearing intervals of the Devonian and shallower formations resulting from formation collapse due to the dissolution of salts. The degree of connectivity is complicated by the presence of the low permeability bitumen deposits in the McMurray formation, where present. Other notable features influencing the potential for cross-formational groundwater flow are the buried channels of pre-glacial and glacial origin (Fig. 1b) eroded into, and in one area, through the underlying bedrock formations as deep as the upper Devonian (Andriashek, 2003).

2.1. Conceptual models of groundwater flow

The SAOS region is located near the eastern edge of the Western Canadian Sedimentary Basin. Regional groundwater flow is generally to the northeast towards the edge of the basin (Bachu, 1996; Bachu et al., 1991, 1993; Bachu and Underschlutz, 1993). Beneath the Devonian Prairie Evaporite Formation the hydrostratigraphic units comprise a regional flow system that originates from the Rocky Mountain overthrust belt and flows eastward with discharge occurring in northeastern Alberta and Saskatchewan (Bachu et al., 1993). Deep basin brines within the Western Canadian Sedimentary Basin are typically characterized geochemical and isotopic signatures that are consistent with the original evaporated seawater composition overprinted with

evidence of water/rock interaction, fluid migration and mixing-dilution (Hitchon and Friedman, 1969; Connolly et al., 1990a, 1990b; Simpson, 1999). Regional-scale groundwater flow in the overlying units is similarly towards the northeast, but is more affected by topographic variability and related physiographic features. This has led to the development of local- and intermediate-scale systems with variable flow directions and rates.

Groundwater springs with glaciogenic signatures (very low $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values) and very high salinity, provided the basis for a conceptual model for the Athabasca region developed by Grasby and Chen (2005). This conceptual model suggests that modern-day flow systems in the region may not be indicative of the historical groundwater flow systems. Grasby and Chen suspected that high permeability carbonate units in the Western Canadian Sedimentary Basin acted as preferential subglacial drains during the Pleistocene Epoch. The characteristics of groundwater sampled from springs sampled along the Athabasca River had Na–Cl type waters, elevated salinity and very low $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values, supporting their idea of temporary reversal of the regional groundwater flow pattern by intruding Pleistocene glacial meltwater (under high pressure at the base of the continental ice sheet). These intruding waters would have interacted with, and dissolved, portions of the Prairie Evaporite Formation, resulting in the characteristically high salinity groundwater with lower $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signatures (Grasby and Chen, 2005). The return of these saline waters to surface, under re-established regional flow conditions, and eventual discharge into watercourses like the Athabasca and Clearwater rivers from springs and river bed groundwater discharge has been documented by others (Birks et al., 2018; Gibson et al., 2013; Gue, 2012; Gue et al., 2015). Glacial meltwater has been identified in a number of sedimentary basins across North America, diluting and displacing remnant basin brines (Grasby et al., 2000; McIntosh and Walter, 2006) and there is growing recognition of the impacts glacial meltwater has had on basin scale groundwater flow (Lemieux et al., 2008; McIntosh et al., 2011; Person et al., 2007).

In general, the pattern of lateral groundwater flow is radially or semi-radially outward from the major upland areas towards the adjacent low-lying areas, with eventual discharge occurring in the low-land areas and at major drainage features, the Clearwater, Athabasca, and Christina Rivers. The occurrence of saline springs and saline groundwater seepage areas in and near the rivers provides evidence of this discharge (Birks et al., 2018; Gibson et al., 2013; Gue et al., 2015).

Groundwater flow patterns extending as deep as the upper Devonian (Barson et al., 2001) are largely defined by the presence of broad topographic upland areas including the Stony Mountain Upland and May Hills to the west and southwest, and the Mostoos Hills Upland to the south (Fig. 1a). A secondary influence on regional groundwater flow patterns is the presence of large buried channels beneath the study area – the main ones being the north-south trending Leismer Channel located in the north, and the west-east trending Wiau and Christina channels in the central and western portion (Fig. 1b). These channels have a significant influence on lateral groundwater flow patterns, given their comparatively higher hydraulic conductivity and overall draining characteristics, but also affect vertical flow conditions by providing permeable conduits for downward flow into the bedrock formations. The buried channel thalwegs shown in Fig. 1b are inferred from topographic lows in the bedrock surface, as mapped by Andriashek (2003). However, it is important to note that these thalwegs do not necessarily coincide with the presence of high permeability sand and gravel deposits. The Wiau, Christina, and Leismer Channels are filled extensively with permeable sand and gravel deposits, whereas permeable deposits are much less extensive in the Gregoire Channel and do not continue over the full length of this erosional feature (Fig. 1b).

Given this complex groundwater flow configuration, there is potential for zones of relatively stagnant, slow-moving groundwater to form in areas where divergent or convergent conditions occur in all directions. These zones would be isolated from flushing by the local and

Table 1
Summary of geochemical parameters used in this study.

| Questions Answered | Parameters Used |
|--|--|
| Residence time of water and associated solutes | <ul style="list-style-type: none"> • ^{14}C (up to 40,000 years) • ^3H (post-1950 recharge) |
| Indicators of source waters and occurrence of groundwater-surface water interactions | <ul style="list-style-type: none"> • Major ion chemistry, TDS (calculated and gravimetric), alkalinity, hardness • Metals and trace elements • $\delta^{18}\text{O}$, $\delta^2\text{H}$ |
| Indicators of solute source and associated geochemical processes | <ul style="list-style-type: none"> • Selected ion ratios (e.g. $\text{Cl}:\text{Br}$, $\text{Cl}:\text{SO}_4$) • $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{13}\text{C}_{\text{DOC}}$, $\delta^{34}\text{S}_{\text{SO}_4}$, $\delta^{18}\text{O}_{\text{SO}_4}$, $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{37}\text{Cl}$, $\delta^{11}\text{B}$ |

regional flow systems and could manifest themselves as aquifer intervals with different hydrochemistry compared to adjacent aquifer intervals due to the extended residence time of the pore water and related water-rock interaction. The groundwater present in these areas would have been excluded from significant advective mixing with the glaciogenic recharge (inferred by the [Grasby and Chen \(2005\)](#) conceptual model), and modern recharge, or even lateral mixing within the aquifer. The geochemical and isotopic composition of waters within these slower flowing zones could be altered by diffusion with the adjacent aquifer porewater ([Hendry et al., 2013](#)), and water-rock interactions with aquifer materials, but one would not expect these more isolated waters to have undergone the same degree of mixing and flushing as portions of the aquifer more directly connected to the local and regional flow systems. These saline formation waters may contain some of the original connate water present during formation (paleo-seawater for marine formations, paleo-recharge for non-marine), but some post-depositional alteration of the original composition is likely to have occurred prior to hydraulic isolation as the evolution of the Western Canadian Sedimentary Basin progressed, or via diffusion with adjacent zones ([Hendry et al., 2013](#)). The geochemical and isotopic characteristics of connate water, as the end-member of cross-formation mixing, has been well demonstrated ([Hitchon et al., 1969](#); [Connolly et al., 1990a & 1990b](#); [Simpson, 1999](#); [Grasby and Chen, 2005](#)).

Vertical groundwater flow conditions in the SAOS are predominantly downward from the unconsolidated Quaternary deposits towards the upper Devonian formations, as evidenced by pressure versus depth profiles, groundwater chemistry, and the presence of porewater with relatively younger radiogenic ages in some areas of Cretaceous and Devonian formations ([Bachu et al., 1993](#); [Hackbarth and Nastasa, 1979](#)). However, localized areas of upward flow are still possible depending on location within the regional, intermediate, and local scale flow systems. Regional flow systems exist in hydrostratigraphic units beneath the Prairie Evaporite Formation and to a lesser extent in the Upper Devonian aquifers (Beaverhill Lake Group), and upward groundwater flow occurs as groundwater flows updip from the southwest to the northeast. The overlying Cretaceous and Quaternary aquifers typically have more local flow regimes with recharge occurring in upland areas, and discharge zones (and upward groundwater flow) occurring in localized areas near major erosional features (e.g. Athabasca River) ([Bachu et al., 1993](#)). The presence of upward hydraulic gradients and associated cross-formational groundwater flow between Devonian and McMurray Formation has been inferred in the vicinity of the Prairie Evaporite dissolution scarp from anomalous salinity measurements (i.e., Na, Cl, and SO_4) in the basal McMurray Formation consistent with pore waters originating from dissolution of halite and anhydrite present in the Middle Devonian formations and was attributed to re-equilibration of subsurface pore pressures following off-loading of the last continental ice sheet ([Cowie et al., 2015](#)).

3. Methods

The SAOS geochemical and isotopic data were compiled using available published datasets ([Cowie, 2013](#); [Gibson et al., 2013](#); [Gue et al., 2015](#); [Lemay, 2002a, 2002b](#); [Stewart and Lemay, 2011](#); [Moncur](#)

[et al., 2015](#)) and those compiled by individual COSIA members. The industry data were generated following various sampling campaigns, and the descriptions of the sampling and analytical methods were made available to assess the integrity and comparability of individual data sources. The industry data included geochemical and isotopic analyses of samples collected from water wells, groundwater seeps, and surface waters bodies within the study area. To ensure that only groundwater samples representative of baseline conditions were assessed, only data from background wells (i.e. located away from the immediate vicinity of operations, and outside the area where any effects of operations would be expected), or data obtained prior to extensive aquifer use were included in the dataset. Each industrial contributor was asked to submit groundwater data for their lease that they thought would not have any potential impacts from their activities, and the study relied on their more detailed knowledge of their operations to select the appropriate background wells for inclusion in the database. The main focus of this study was the Mannville Formation aquifers, but information from the Quaternary and Devonian aquifers was also included, where available, to identify potential areas of hydraulic and hydrochemical interaction between Cretaceous formations and the adjacent near-surface and deep environments. The resulting unified dataset included parameters helpful in evaluating source, origin, relative age, and mixing relationships between various groundwaters ([Table 1](#)).

In all cases, stable isotope analyses were undertaken by standard isotope ratio mass spectrometry (IRMS), and ^{14}C was analyzed by accelerator mass spectrometry (AMS). Samples were collected, filtered (either in the field or in the lab) using 0.45 μm cellulose nitrate filters, and preserved accordingly. Selected samples were also analyzed for ^{36}Cl ; however, the predominance of radiogenically “dead” Cl sourced from the 380 + million year old evaporite deposits in the Devonian negated its utility for age dating purposes. Therefore, assessment of groundwater residence times principally relied upon ^{14}C . Once compiled, data integrity was evaluated using a variety of approaches and associated acceptance criteria, those being: i) ion balance ($\pm 10\%$), ii) pH range (6 to 9 standard units), and iii) presence of ^3H (< 0.8 TU for ^{14}C activities).

The presence of measureable ^3H activity was used to identify groundwater samples with evidence of post-1950's recharge or impacts from residual drilling fluids. The presence of short-lived radioisotopes in seemingly older water can be explained by mixing. Deeper samples with ^3H activities $> 1\text{TU}$ were considered unrepresentative of formation conditions, and the associated results were treated with caution. Particular scrutiny to ^3H activities was applied during ^{14}C residence time corrections, and only samples without detectable tritium were used.

The Grand Rapids Formation was the key aquifer of interest in this study, due to its importance for industrial water supply and potential as a future disposal zone. Therefore, the data from this formation was further subdivided based on the thickness of overlying Colorado Group (aquitard) cover ([Fig. 1c](#)), so that groundwater samples from the Grand Rapids aquifer with minimal overlying Colorado Group cover could be distinguished from locations where the Grand Rapids is present at greater depths and with a more substantive aquitard cover ([Fig. 3c](#)). The Grand Rapids category with the least Colorado Group cover

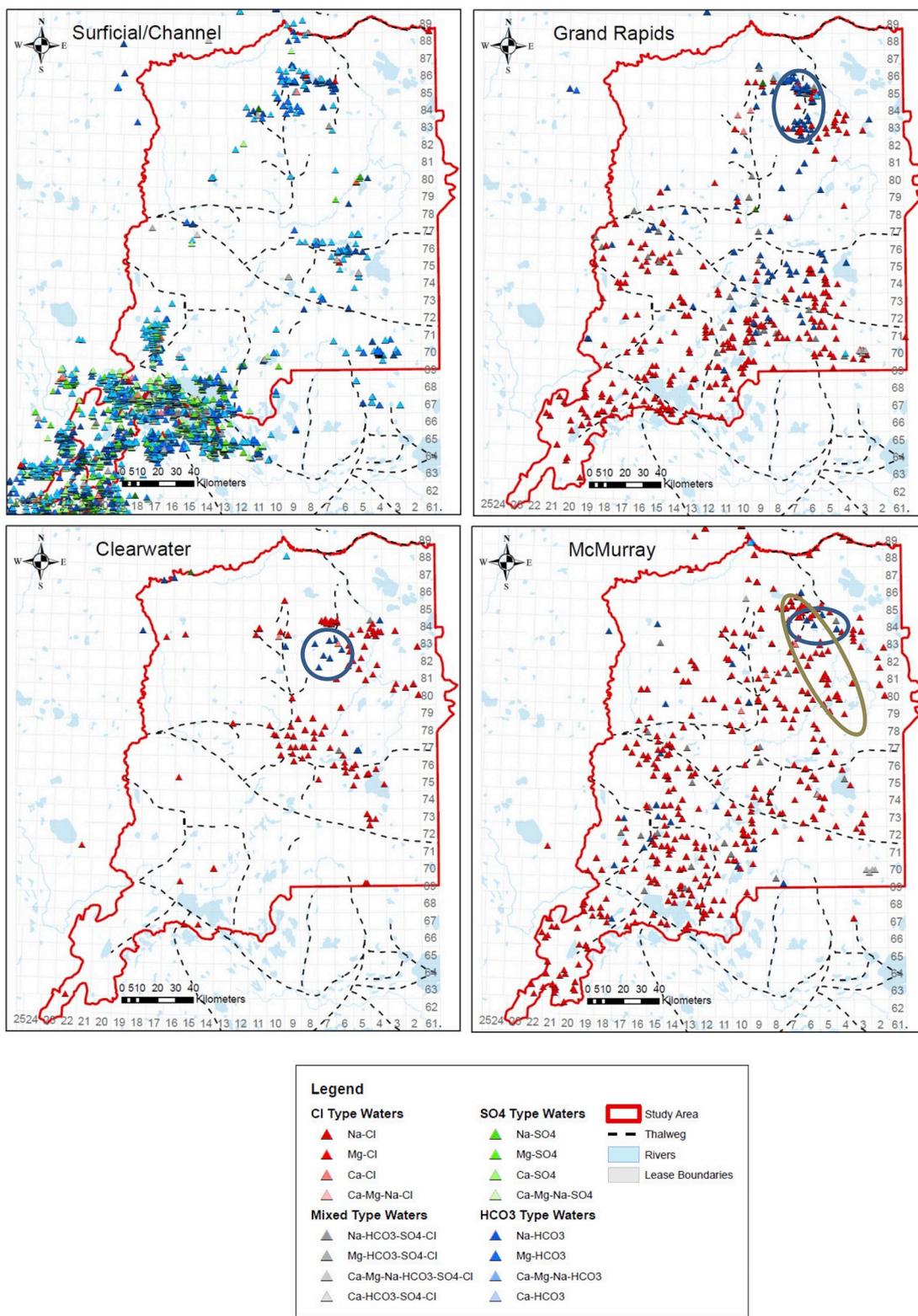


Fig. 3. Spatial distribution of hydrochemical facies. Areas with possible evidence of mixing with shallower groundwater are shown by blue ellipses. The area with higher TDS (from Fig. S1) is shown with the brown ellipse. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

included wells where the Colorado Group was entirely absent, or where it overlain by the Pelican (Viking Formation equivalent) and Joli Fou Formations (Fig. 2). The Pelican Formation is a sandstone unit that acts as an aquifer (Viking aquifer) and was not expected to function as a substantial hydraulic barrier. The other categories of Grand Rapids

wells listed in order of increasing Colorado Group cover included: incised (eroded to Westgate Formation), partially eroded (eroded to Second White Specks Formation), and fully present, where the full Colorado Group package (Lea Park to Joli Fou Formations) is present.

Inverse geochemical modeling, using the computer program

NETPATH, was applied to estimate the ^{14}C groundwater residence times (Plummer et al., 1991, 1994; Parkhurst and Charlton, 2008). NETPATH can be used to model the processes of mineral dissolution or precipitation, ion exchange, oxidation/reduction reactions, degradation of organic compounds, incongruent reactions, gas exchange, mixing, evaporation, and dilution, and can be used to adjust radiocarbon data for geochemical reactions to refine estimates of time since recharge (e.g. Plummer and Sprinkle, 2001; Aravena et al., 1995; Van der Kemp et al., 2000; McMahon et al., 2008; Bayari et al., 2008). Measured ^{14}C activity values were converted to modelled groundwater residence times using the models of Vogel (1970), Ingerson and Pearson (1964), Fontes and Garnier (1979) and Tamers (1975) and available geochemistry and $\delta^{13}\text{C}$ signatures to account for dissolved inorganic carbon sources, related reservoir effects, carbonate dissolution, sulfate reduction, methanogenesis, and geogenic carbon sources.

4. Results

Summaries of the major ion and isotopic data for the unified dataset (including both COSIA and public data sources) are presented in Tables 2 and 3, respectively and are discussed below. The dataset is available by request from COSIA (<http://www.cosia.ca/>).

4.1. Major ion typology

Typical evolution of groundwater along a flow path progresses from lower TDS waters with Ca– HCO_3 type compositions near the recharge area, towards a more Na– HCO_3 or SO_4 -dominated groundwater type in some cases, and eventually toward deeper basin brines where the Cl

anion dominates. Along such flow paths one would expect the TDS to gradually increase due to dissolution of soluble minerals, with the types of minerals playing a key role in the resulting solution chemistry. The most soluble minerals in the SAOS are the evaporites of the middle Devonian, which are extensive across much of the region towards the southwest. The distribution of dissolved solutes, including hydrochemical facies (Fig. 3) and concentrations (Table 2, Fig. S1), were used to identify areas characterized by differing degree of geochemical evolution in each aquifer. The spatial distribution of hydrochemical facies and TDS have many of the same trends consistent with differing degrees of groundwater evolution in the shallow and Cretaceous aquifers. Visualizing these facies types across each individual aquifer was simplified by dividing the water types into four major anion categories: i) HCO_3 (+ CO_3) dominated, ii) SO_4 dominated, iii) Cl dominated, and ix) mixed (Fig. 3).

In general, the surficial and buried channel groundwaters are characterized by low TDS concentrations (Fig. S1) and HCO_3 as the dominant anion (Fig. 3), typical of groundwater that has not undergone significant water-rock interactions. Anomalies to these trends include individual or small clusters of wells with $-\text{SO}_4$ or $-\text{Cl}$ type groundwaters and elevated TDS. The Grand Rapids Formation is characterized with TDS concentrations that increase towards the SW (Fig. S1) and Na–Cl type-waters, but there are areas with lower TDS and mixed HCO_3 –Cl type waters indicating an increased influence from alkalinity, likely associated with weathering of natural organic material or methanogenesis (Fig. 3). These areas with HCO_3 -type waters (blue ellipses on Fig. 3) could indicate mixing with fresher, less hydrochemically-evolved, groundwaters more typical of the overlying surficial deposits. Similar occurrences are noted for the underlying Clearwater, and

Table 2

Statistics for dissolved major ion concentrations measured from groundwater aquifers in the Southern Athabasca Oil Sands Region. Number of samples analyzed is given as n.

| Formation | EC | TDS | HCO_3 | SO_4 | Cl | Ca | Mg | K | Na |
|---------------------|-------------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| | $\mu\text{S}/\text{cm}$ | mg L^{-1} |
| Quaternary | | | | | | | | | |
| Average | 953 | 554 | 528 | 38 | 34 | 72 | 23 | 5 | 110 |
| Maximum | 6090 | 2300 | 2100 | 330 | 460 | 291 | 68 | 66 | 950 |
| Minimum | 289 | 231 | 0.3 | 0.1 | 0.3 | 0.5 | 0.4 | 0.8 | 3.5 |
| n | 140 | 140 | 147 | 141 | 148 | 135 | 133 | 132 | 133 |
| Channel | | | | | | | | | |
| Average | 1214 | 670 | 531 | 53.0 | 59.2 | 40.5 | 8.5 | 4.4 | 237 |
| Maximum | 4866 | 1446 | 853 | 270 | 400 | 291 | 29 | 16 | 610 |
| Minimum | 353 | 130 | 2.5 | 0.3 | 0.3 | 4.8 | 0 | 1.7 | 6.2 |
| n | 22 | 22 | 23 | 21 | 23 | 19 | 18 | 18 | 18 |
| Grand Rapids | | | | | | | | | |
| Average | 8724 | 8368 | 671 | 121 | 4498 | 108 | 51.9 | 27.7 | 3003 |
| Maximum | 57,000 | 58,273 | 2436 | 9000 | 33,400 | 1435 | 685 | 741 | 19,600 |
| Minimum | 627 | 349 | 0.3 | 0.1 | 1.3 | 0.3 | 0.1 | 0.3 | 46 |
| n | 122 | 466 | 462 | 443 | 470 | 462 | 454 | 346 | 463 |
| Clearwater | | | | | | | | | |
| Average | 10,124 | 9486 | 782.2 | 91.5 | 4565 | 59.6 | 42.6 | 23.5 | 3225 |
| Maximum | 41,400 | 140,000 | 3230 | 2525 | 40,600 | 900 | 575 | 439 | 25,638 |
| Minimum | 1040 | 595 | 163 | 0.1 | 13 | 1.6 | 0.3 | 1.3 | 240 |
| n | 59 | 137 | 139 | 133 | 139 | 136 | 136 | 89 | 132 |
| McMurray | | | | | | | | | |
| Average | 18,077 | 13,875 | 1159 | 169 | 7535 | 168 | 96.9 | 52 | 4995 |
| Maximum | 80,800 | 278,652 | 5016 | 5380 | 171,800 | 1893 | 594 | 782 | 101,563 |
| Minimum | 369 | 153 | 29.3 | 0.2 | 0.2 | 0.6 | 0.5 | 0.5 | 2.8 |
| n | 57 | 611 | 426 | 598 | 617 | 608 | 598 | 453 | 613 |
| Devonian | | | | | | | | | |
| Average | 103,540 | 110,081 | 641 | 2195 | 66,261 | 5495 | 956 | 662 | 35,836 |
| Maximum | 492,000 | 337,000 | 2600 | 13,300 | 214,000 | 81,600 | 10,100 | 9680 | 106,501 |
| Minimum | 3220 | 1700 | 2.5 | 8.9 | 150 | 0.7 | 2.1 | 24 | 450 |
| n | 9 | 23 | 23 | 21 | 24 | 22 | 21 | 17 | 24 |

Table 3

Statistics for available regional isotopic data for the SAOS. Number of samples analyzed is given as n.

| Formation | ^3H (TU) | ^{14}C pMC | $\delta^{18}\text{O}$ ‰ (VSMOW) | $\delta^2\text{H}$ ‰ (VSMOW) | $\delta^{13}\text{C}_{\text{DIC}}$ ‰(VPDB) | $\delta^{34}\text{S}_{\text{SO}_4}$ ‰(VCDT) | $\delta^{18}\text{O}_{\text{SO}_4}$ ‰ (VSMOW) | $\delta^{11}\text{B}$ ‰ | $^{87}\text{Sr}/^{86}\text{Sr}$ | $\delta^{37}\text{Cl}$ ‰ (VSMOC) | $\delta^{81}\text{Br}$ ‰ (SMOB) | $\delta^{13}\text{C}_{\text{DOC}}$ ‰ (V-PDB) |
|---------------------|-------------------|---------------------|------------------------------------|---------------------------------|---|---|--|-------------------------|---------------------------------|-------------------------------------|------------------------------------|---|
| Quaternary | | | | | | | | | | | | |
| Average | 1.5 | 38.1 | -18.4 | -144.4 | -14.6 | 8 | 10.9 | 19 | 0.709954 | -0.2 | -0.3 | -26.8 |
| Maximum | 10 | 74.8 | -15.2 | -128.6 | 22.1 | 45.9 | 40.3 | 43 | 0.716735 | 0.6 | 0.7 | -21.7 |
| Minimum | < 0.8 | 1.5 | -21.4 | -161.8 | -23 | -7.1 | 3 | 1 | 0.707917 | -1 | -1.4 | -30.5 |
| n | 79 | 27 | 119 | 119 | 56 | 48 | 22 | 22 | 42 | 25 | 12 | 29 |
| Channel | | | | | | | | | | | | |
| Average | < 0.8 | 25.7 | -19 | -148.7 | -16.1 | 13.3 | 7.8 | 24.2 | 0.708508 | -1.1 | - | -27 |
| Maximum | < 0.8 | 45.4 | -17.1 | -140 | -12.4 | 44.6 | 7.8 | 38 | 0.709180 | -0.2 | - | -26.6 |
| Minimum | < 0.8 | 3.3 | -20.9 | -163.8 | -21.5 | 2 | 7.8 | 17 | 0.707970 | -3.2 | - | -27.5 |
| n | 12 | 11 | 21 | 22 | 21 | 12 | 1 | 5 | 14 | 9 | 0 | 10 |
| Grand Rapids | | | | | | | | | | | | |
| Average | 0.8 | 4.5 | -19.1 | -149.9 | -5.8 | 14.6 | - | 29 | 0.708002 | -0.3 | - | -26.7 |
| Maximum | 14.5 | 74.1 | -15.1 | -122 | 22.7 | 30.8 | - | 44 | 0.711180 | 0.6 | 2 | -16.8 |
| Minimum | < 0.8 | 0.2 | -22.8 | -176 | -24.6 | 2.1 | - | 8 | 0.707350 | -1.4 | -2 | -49.7 |
| n | 87 | 102 | 119 | 120 | 110 | 21 | 0 | 24 | 65 | 55 | 29 | 61 |
| Clearwater | | | | | | | | | | | | |
| Average | 0.8 | 2.7 | -19.9 | -154.9 | -3.9 | 20 | - | 30.7 | 0.708026 | 0 | 0.7 | -25.7 |
| Maximum | 3.8 | 16.6 | -16.7 | -118 | 16.3 | 79.7 | - | 43 | 0.709109 | 0.7 | 1.8 | -17 |
| Minimum | < 0.8 | 0.2 | -22 | -170 | -21.5 | -15.5 | - | 21 | 0.707170 | -1 | -1.8 | -30.3 |
| n | 47 | 48 | 59 | 59 | 55 | 19 | 0 | 18 | 49 | 38 | 24 | 33 |
| McMurray | | | | | | | | | | | | |
| Average | 1.4 | 11.2 | -19.7 | -154.5 | 2.8 | 15 | 7.1 | 26.4 | 0.708559 | 0.1 | 0.7 | -27.6 |
| Maximum | 7.6 | 83.5 | -4.7 | -127.7 | 28.2 | 36.3 | 14 | 50 | 0.710340 | 0.8 | 1.2 | -16.6 |
| Minimum | < 0.8 | 0.4 | -23.1 | -177.2 | -21.7 | -2.8 | 4.3 | 11.4 | 0.707650 | -0.8 | 0.4 | -55.6 |
| n | 45 | 37 | 58 | 58 | 52 | 17 | 5 | 13 | 26 | 23 | 9 | 37 |
| Devonian | | | | | | | | | | | | |
| Average | 1.4 | 5.3 | -21.1 | -168 | 4.7 | 30.4 | - | 37.7 | 0.708521 | 0.1 | 0.4 | -31.2 |
| Maximum | 2.9 | 16.9 | -15.2 | -158.3 | 12.5 | 41.5 | - | 43.5 | 0.709155 | 0.2 | 0.4 | -27 |
| Minimum | < 0.8 | 0.7 | -23.1 | -176.4 | -10.7 | 19.3 | - | 34.3 | 0.708183 | 0.1 | 0.4 | -38.7 |
| n | 6 | 4 | 8 | 8 | 6 | 2 | 0 | 3 | 4 | 3 | 1 | 6 |

McMurray formations in areas around the Christina River and between the Gregoire and Leismer Channels. The McMurray Formation consists primarily of Na–Cl type waters, with areas of elevated TDS occurring coincident with the Prairie Evaporite dissolution scarp (Fig. S1, location shown by brown ellipse in Fig. 3) as noted by Cowie et al. (2015). Salinity originating from a typical seawater source will yield a Cl:Br ratio of around 290, whereas salinity originating from the dissolution of Devonian evaporites will typically yield values greater than 1000, and as high as 20,000 (Freeman, 2007). In contrast, Cl:Br values less than 200 have been noted for groundwater samples from shallow groundwater flow systems in Alberta (Freeman, 2007). Almost all of the samples assessed in this study had Cl:Br mass ratios greater than 290 indicating some degree of influence from evaporite dissolution (Fig. S4).

4.2. Stable isotopes of water

The stable isotope signatures of oxygen and hydrogen ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) in the SAOS groundwater samples were used to identify mixing trends between locally-recharged, modern groundwater and other isotopically-distinct sources of water, such as glaciogenic or paleo-groundwaters (Fig. 4). Comparisons between the SAOS data and modern Global and Local Meteoric Water Lines (GMWL Craig, 1961; and LWML Baer et al., 2016) and paleo formation water lines (Cretaceous Formation Water Line, Connolly et al., 1990b; Hitchon Friedman Formation Water Line, Hitchon and Friedman, 1969) were used to identify mixing between modern and paleo waters.

In the study area, recharge from modern precipitation would be expected to have $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signatures similar to the weighted mean of annual precipitation ($\delta^{18}\text{O} = -17.5$ ‰ and $\delta^2\text{H} = -142$ ‰, Baer et al., 2016; -17.7 and -135 ; Birks et al., 2002). Pleistocene glacial

meltwaters in western Canada have $\delta^{18}\text{O}$ values in the range of -25 – 24 ‰ (Ferguson and Jasechko, 2015; Remenda et al., 1994). Therefore, groundwater samples with $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signatures that are depleted in the heavy isotopes relative to modern precipitation (lower $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values) indicate the presence of water recharged during colder climate periods (e.g. glaciogenic sources). In contrast, groundwater samples with signatures that are more enriched in the heavy isotopes than mean annual precipitation (i.e. higher $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values) that plot below the GMWL and LMWL can indicate the presence of paleo-waters recharged during warmer climate periods or water that has undergone open-system evaporation. Evaporative signatures would be expected in modern surface waters, or in paleo-waters of marine origin.

$\delta^{18}\text{O}$ values for groundwater sampled within the study area ranged from -23.1 ‰ to -15.1 ‰, while $\delta^2\text{H}$ values ranged from -177.2 ‰ to -118.0 ‰ (Fig. 4, Table 4). The mean isotopic composition of groundwater in the study area is approximately -19 ‰ for $\delta^{18}\text{O}$ and -142 ‰ for $\delta^2\text{H}$. Some samples plot below the GMWL indicating some evaporative enrichment, or mixing with an evaporatively enriched source such as: i) surface waters (lakes, rivers) exposed to the contemporary atmosphere, and ii) paleo-seawater present as formation water, which acquired an evaporative signature when exposed to the atmosphere during warmer climate periods. Deeper in the Western Canadian Sedimentary Basin Cretaceous formation waters have the latter type of evaporative signature, and typically plot along a Cretaceous Formation Water Line (CFWL, $\delta^2\text{H} = 3.57 \times \delta^{18}\text{O} - 62.1$) proposed by Connolly et al. (1990b) and the Hitchon Friedman Formation Water Line (HFFWL, $\delta^2\text{H} = 3.81 \times \delta^{18}\text{O} - 72.8$, Hitchon and Friedman, 1969) with $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values > -10 ‰– 100 ‰ respectively. The HFFWL overlaps with the modern Local Evaporation Line (LEL) obtained from lake datasets in the region (Gibson et al., 2011),

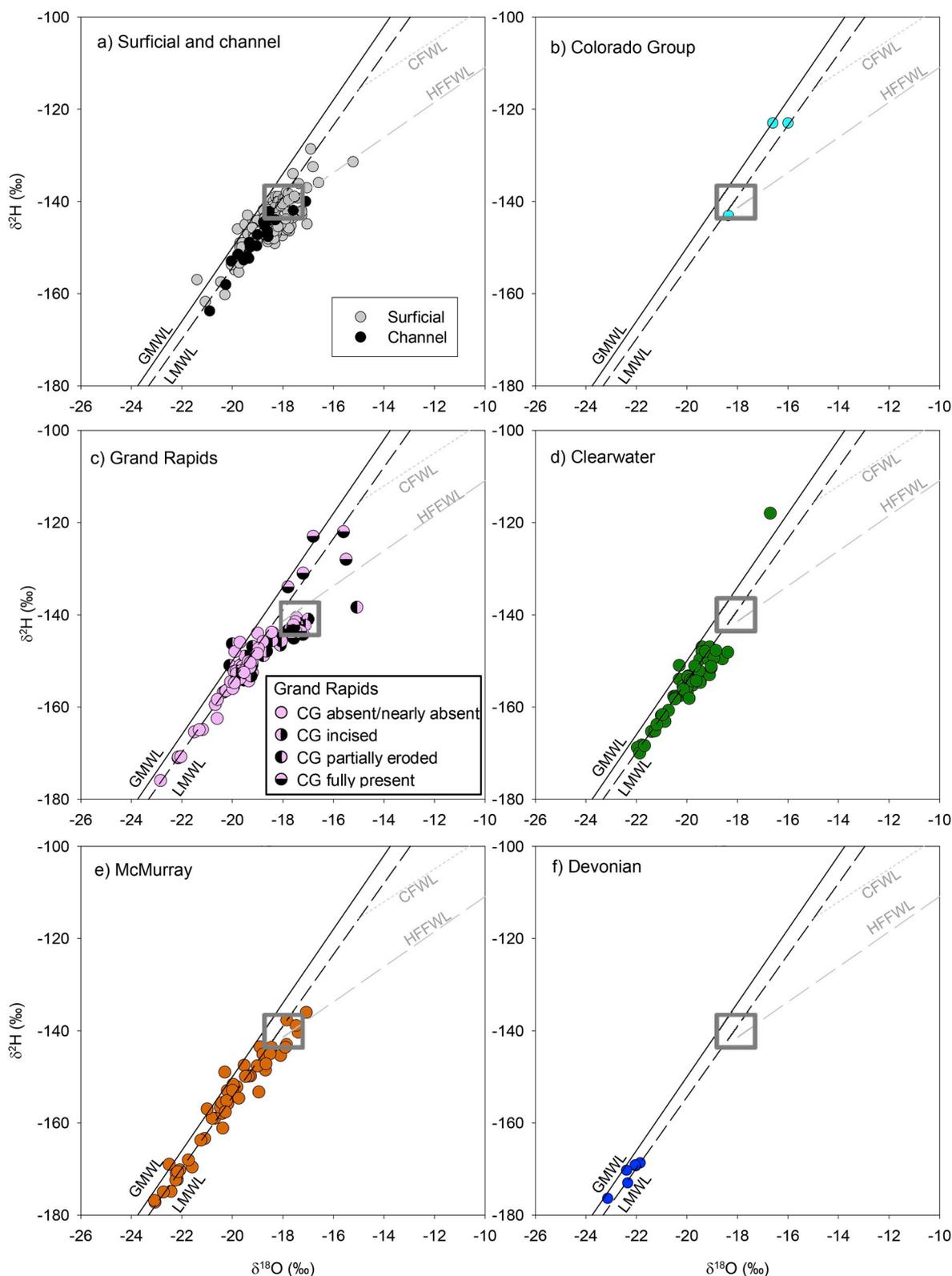


Figure 4. $\delta^{18}\text{O}$ - $\delta^2\text{H}$ data separated by formation and plotted against the Global Meteoric Water Line (GMWL), a Local Meteoric Water Line (LMWL), a Cretaceous Formation Water Line (CFWL) and the Hitchon and Friedman Formation Water Line (HFFWL). Grey squares show the approximate range of modern precipitation.

however, these evaporatively enriched modern surface waters can be differentiated from evaporatively enriched paleo-waters by their very low TDS, and ages (presence of ^3H and high ^{14}C activity).

The average ranges of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values for the individual aquifers become lower with depth (Table 3), with the highest average

values occurring in the Quaternary deposits and the lowest in the Devonian aquifers. Groundwater samples collected from the surficial deposits tend to plot along a LMWL with values close to that of modern precipitation (Fig. 4a). Samples collected from the buried channel deposits exhibit slightly lower $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values suggesting mixing

Table 4
Summary of key isotopic shifts expected with different modifying geochemical processes occurring in aquifers in the SAOS.

| Geochemical reaction | Isotopic shift | Geochemical changes |
|--|--|--|
| <i>Sulfide Oxidation (eg. pyrite)</i> $\text{FeS}_2 + 15/4\text{O}_2 + 7/2\text{H}_2\text{O}$ $\rightarrow 2\text{SO}_4^{2-} + \text{Fe}(\text{OH})_3 + 4\text{H}^+$ | $\downarrow \delta^{34}\text{S}_{\text{SO}_4}$ | $\uparrow \text{SO}_4$ |
| <i>Carbonate Dissolution</i> $\text{CaCO}_3 \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{HCO}_3^-$ | $\uparrow \delta^{13}\text{C}$ | $\uparrow \text{HCO}_3^-$ |
| <i>Bacterial Sulfate Reduction (BSR)</i> $2\text{CH}_3\text{COO}^- + \text{SO}_4^{2-} \rightarrow 2\text{HCO}_3^- + \text{HS}^-$ | $\uparrow \delta^{34}\text{S}_{\text{SO}_4}$, $\downarrow \delta^{13}\text{C}_{\text{DIC}}$ | $\downarrow \text{SO}_4$, $\uparrow \text{HCO}_3^-$, $\downarrow \text{DOC}$ |
| <i>Methanogenesis</i> $\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{CH}_4$ | $\uparrow \delta^{13}\text{C}_{\text{DIC}}$ | $\uparrow \text{HCO}_3^-$, $\downarrow \text{DOC}$ |

with older groundwater with a glaciogenic influence. Groundwater collected from some of the surficial deposits yielded higher $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values relative to the weighted mean average of modern precipitation, that also plotted below the LMWL along a LEL. The higher $\delta^{18}\text{O}$ values, combined with the fairly low TDS and high ^{14}C activities indicating low residence time within the aquifer suggest greater connectivity to surface water or shallower aquifer systems rather than mixing with ^{18}O enriched paleo-waters.

The unified dataset includes a small number of samples collected from Colorado Group formations (Fig. 4b). The two Colorado Group samples, with higher $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values, are both from the Viking (Pelican) Formation (Lemay 2002a) south of the Mostoos Hills Upland and on the southern flank of the SAOS. The higher $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values have been interpreted as indicating the presence of groundwater recharged during a warmer climatic period (Lemay 2002a). The only industry data available for the Colorado Group within the SAOS region is from a well completed in the Second White Specks. In this case the isotopic values are lower (i.e. $\delta^{18}\text{O} = -18.37\text{‰}$ and $\delta^2\text{H} = -143.1\text{‰}$) than those reported for the deeper Viking interval.

The Grand Rapids Formation exhibited the greatest range in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values (Fig. 4c), which can be explained by differing degrees of mixing with glaciogenic or paleo-waters. There are three distinct groups of Grand Rapids samples evident within the dataset: (i) samples plotting below and to the right of the LMWL, indicating mixing with an evaporated source, (ii) samples that plot along the LMWL, but more enriched in the heavy isotopes than modern precipitation, and (iii) samples that are depleted in heavy isotopes relative to modern precipitation, suggesting mixing with glaciogenic water. These grouping within the Grand Rapids groundwater samples also appear to coincide with the degree of Colorado Group cover, with most of the evaporated samples (i) occurring in areas where the Colorado Group is fully present or only partially eroded and most of the samples with low $\delta^{18}\text{O}$ values (iii) occurring in areas where the Colorado Group sediments are thin or absent (Fig. 4c).

Groundwater samples collected from the Clearwater Formation generally fall along the LMWL, ranging from -22‰ to -18‰ for $\delta^{18}\text{O}$ (Fig. 4d). There is also one anomalous sample collected from the Wabiskaw Member of the Lower Mannville Group southwest of the Mostoos Hills Upland (in Lemay 2002a; -16.7‰ , -118.0‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively) that is more enriched in the heavy isotopes of oxygen and hydrogen than the rest of the samples assessed. This sample plots near the intersection of the CFWL and the GMWL.

Groundwater collected from the McMurray Formation generally plotted along the LMWL between -23‰ and -16‰ for $\delta^{18}\text{O}$ (Fig. 4e). Although there are very few results for the Devonian formations, the data have noticeably lower $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values relative to the overlying Cretaceous formations (less than -20‰ for $\delta^{18}\text{O}$) (Fig. 4f) and consistent with a glaciogenic influence.

Overall, the spatial distribution of $\delta^{18}\text{O}$ signatures values provides useful information about the sources of water in the different aquifers and the potential interactions between them (Fig. 5). The lower $\delta^{18}\text{O}$

values (indicating more of a glaciogenic influence) tend to occur in the Grand Rapids, Clearwater and McMurray Formations near the Christina River where the Colorado Group cover is thin (Fig. 5 – blue circles).

The Grand Rapids Formation samples with $\delta^{18}\text{O}$ values that were higher than modern meteoric values indicating evidence of mixing with evaporatively enriched paleo-waters (i.e. that plot along the HFFWL line in Fig. 4c) are mainly identified in the southern portion of the study area (Fig. 5 – red circles). The combination of evaporatively-enriched water isotope values, Na–Cl type waters, and elevated TDS are consistent with the presence of some original formation water of marine origin, similar to those observed by Connolly et al. (1991a, 1991b) in the Western Canadian Sedimentary Basin. The other paleo-waters that were characterized by more enriched $\delta^{18}\text{O}$ values, those that are higher than modern meteoric water but that plot along the GMWL (Fig. 4c), are located in the southwestern portion of the study area (Fig. 5– orange circles).

The relationship between $\delta^{18}\text{O}$ values and TDS concentrations highlights (Fig. 6) two prominent mixing trends; groundwater samples with evidence of mixing with isotopically enriched (higher $\delta^{18}\text{O}$ and $\delta^2\text{H}$) paleo-waters and those with evidence of mixing with glaciogenic waters. Both of these mixing trends emanate from $\delta^{18}\text{O}$ values for locally-recharged Cretaceous formation water in the region (black square in Fig. 6). One group of samples (blue arrow in Fig. 6) indicates a trend where higher TDS concentrations are associated with lower $\delta^{18}\text{O}$ values, consistent with mixing of Cretaceous groundwaters with a saline, glaciogenic endmember. At the endpoint of this trend are groundwaters sampled from the Devonian aquifers—where the high TDS and glaciogenic signature has been attributed to injection of glacial meltwater and dissolution of Prairie Evaporite Formation (Grasby and Chen, 2005). The samples that plot along this trend include groundwaters from the McMurray, Clearwater and Grand Rapids formations. All of the Grand Rapids samples with evidence of glaciogenic influence are from portions of the aquifer with limited or no Colorado Group cover. Vertical hydraulic connectivity has been inferred between the McMurray Formation and the underlying Devonian aquifers based on the correlation between high TDS areas within the McMurray Formation aquifer and the partial dissolution front of the Prairie Evaporite Formation (Cowie et al., 2015), but the data from the unified SAOS dataset indicate that mixing with glaciogenic sources can also be detected in some of the overlying Cretaceous aquifers.

The other group of samples (red arrow in Fig. 6) indicates a trend where higher TDS groundwaters are associated with higher $\delta^{18}\text{O}$ values. This trend of increasing TDS with higher $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values is similar to what has been observed in Western Canadian Sedimentary Basin waters (Connolly et al., 1990b) that have been interpreted as indicating the presence of formation waters of marine origin. The SAOS samples that plot along the paleo-water mixing trend are all from the Grand Rapids Formation in the southern portion of the study area where the Colorado Group is fully present, or only partially eroded (Fig. 5). The presence of a relatively thick and impermeable cover of Colorado Group sediments above, and lower permeability bitumen-impregnated sandstones of the McMurray Formation below may have created a confining interval where enhanced hydraulic isolation preserved the paleo-waters and limited mixing with shallower aquifers, or glaciogenic waters. The higher TDS and more enriched $\delta^{18}\text{O}$ values indicate that these paleo-waters could include formation waters of marine origin (Connolly et al., 1990b) or paleo-waters recharged under warmer climate conditions (Lemay, 2002a).

4.3. Solute isotopes

The isotopic labelling of $\delta^{13}\text{C}_{\text{DIC}}$ (Figs. 7 and 8b, and S2), $\delta^{34}\text{S}_{\text{SO}_4}$ (Fig. 8a and b), $^{87}\text{Sr}/^{86}\text{Sr}$ (Fig. 9a), and $\delta^{37}\text{Cl}$ (Fig. 9b), were used to identify sources of solutes and geochemical processes occurring in the main Cretaceous aquifers (Table 3). More limited datasets for $\delta^{11}\text{B}$, $\delta^{81}\text{Br}$, and $\delta^{13}\text{C}_{\text{DOC}}$ were also compiled (Table 3), but are not discussed here.

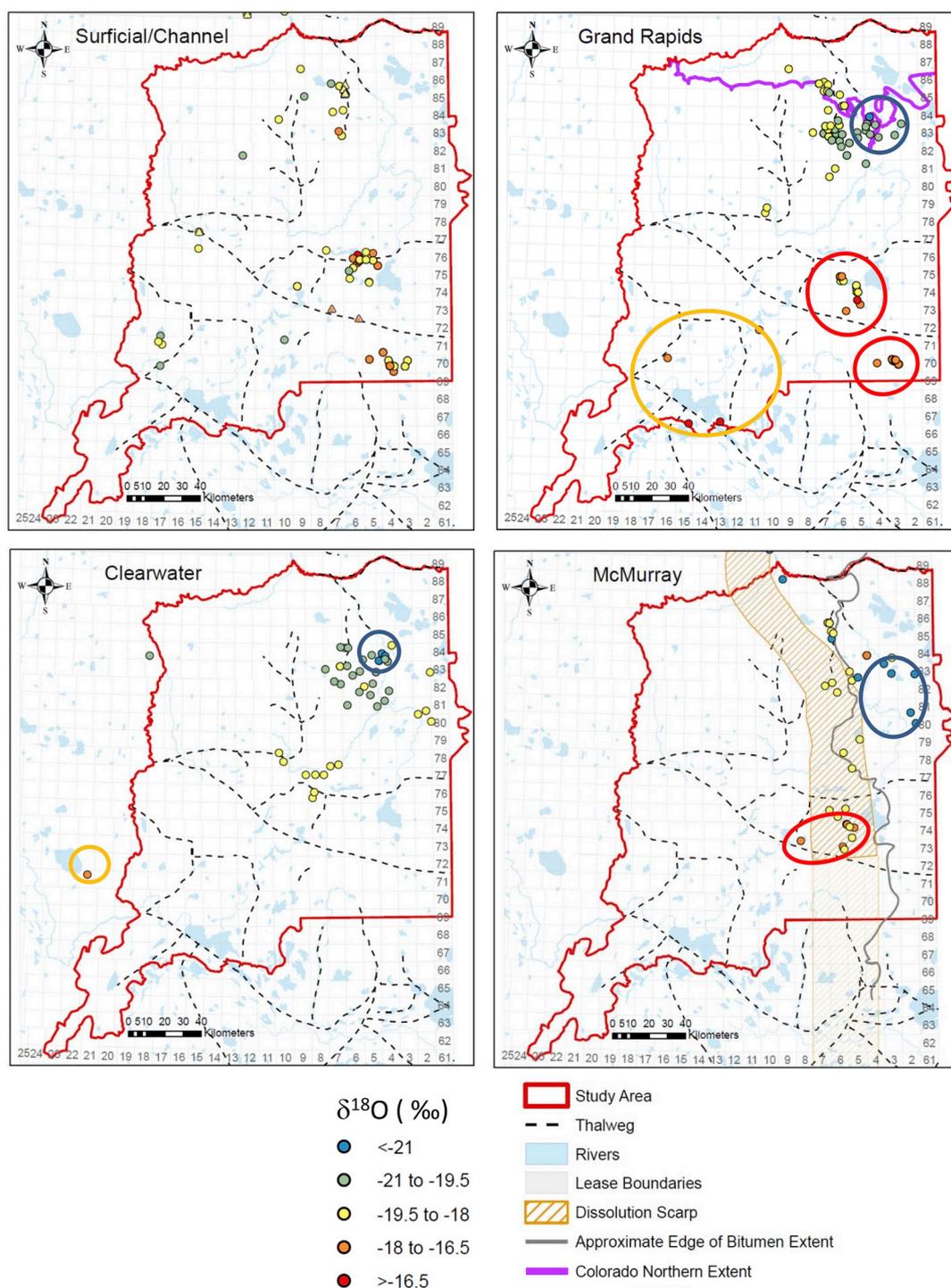


Fig. 5. Spatial distribution of $\delta^{18}\text{O}$ values by formation. Note in the Surficial/Channel panel that triangles identify wells completed within channel deposits, on the Grand Rapids panel the purple line shows the northern extent of the Colorado Group (Joli Fou Formation outcrop), and that McMurray panel denotes the zero-bitumen edge as a grey line and the dissolution scarp (Broughton, 2013) with hatching. Circles show the locations where glaciogenic (blue), evaporated paleo-waters (red) and non-evaporated paleo water (orange) influence has been inferred. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

The $\delta^{13}\text{C}$ values in the dissolved inorganic carbon (DIC) fraction had an extremely wide range, varying from -24.6‰ to $+28.2\text{‰}$ (Fig. 7). There was a general trend towards higher $\delta^{13}\text{C}_{\text{DIC}}$ values with higher total alkalinity concentrations. The $\delta^{13}\text{C}_{\text{DIC}}$ values tended to fall within three general ranges: i) -20 to -10‰ ; ii) around 0‰ and iii) greater than 10‰ . The samples with $\delta^{13}\text{C}_{\text{DIC}}$ values in range i) -20 to -10‰ are consistent with DIC formed in the soil zone, ($\delta^{13}\text{C}_{\text{DIC}}$ values around -15‰ , with lower values possible if disconnected from the

atmosphere). Higher $\delta^{13}\text{C}_{\text{DIC}}$ signatures found in the other ranges are usually consistent with ii) dissolution of marine carbonates ($\sim 0\text{‰}$) or iii) secondary biogeochemical processes, such as methanogenesis ($> 10\text{‰}$). All Quaternary groundwater samples (both surficial deposits and buried channels) were found to have similar $\delta^{13}\text{C}_{\text{DIC}}$ values (around -15‰), suggesting natural weathering of soil carbon (Fig. 7). Groundwater from the Grand Rapids and Clearwater formations tended to plot within two groups (Fig. 7): i) groundwater with low alkalinity

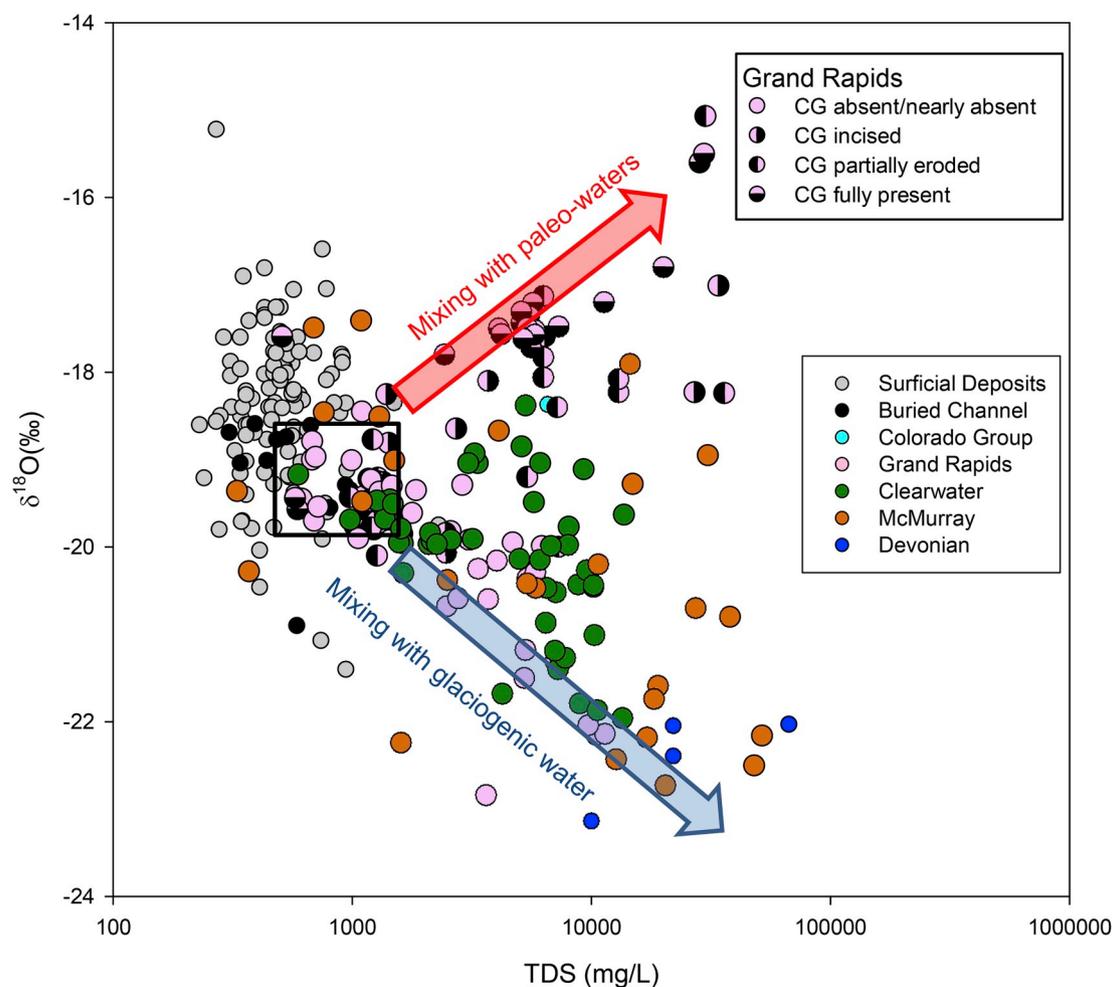


Fig. 6. Relationship between $\delta^{18}\text{O}$ signatures and TDS in groundwater samples. The arrows indicate two potential mixing lines originating from the general negative TDS– $\delta^{18}\text{O}$ correlations and some exceptions which are characterized by elevated TDS and enriched $\delta^{18}\text{O}$ signatures. Note that Grand Rapids Formation sample symbols are further distinguished by extent of Colorado Group cover.

(roughly $250\text{--}700\text{ mg L}^{-1}$) and $\delta^{13}\text{C}_{\text{DIC}}$ values in the -20 to -10% range, or ii) groundwater with higher total alkalinity values (around $700\text{--}1200\text{ mg L}^{-1}$) yielding $\delta^{13}\text{C}_{\text{DIC}}$ values in the -5 to $+5\%$ range. The samples with the $\delta^{13}\text{C}_{\text{DIC}}$ values in the -5 to $+5\%$ range (ii) are indicative of a more evolved groundwater with higher alkalinities due to secondary processes such as carbonate dissolution, bacterial sulfate reduction (BSR), or possibly methanogenesis. These two groups of Grand Rapids and Clearwater samples have some spatial patterns, with the lower $\delta^{13}\text{C}_{\text{DIC}}$ values, those consistent with DIC formed in the soil zone, occurring in the northeastern portion of the study area, near the Christina River (blue ellipses on Fig. S2), and the intermediate $\delta^{13}\text{C}_{\text{DIC}}$ values present just south of that area (yellow ellipses on Fig. S2). Groundwater sampled from the McMurray Formation spanned the entire range of $\delta^{13}\text{C}_{\text{DIC}}$ values and total alkalinity concentrations, with some overlap with soil zone, and carbonate dissolution ranges, as well as some with higher $\delta^{13}\text{C}_{\text{DIC}}$ values ($> 20\%$) consistent with methanogenic conditions (Figs. 7 and S2). The McMurray Formation samples with the lower $\delta^{13}\text{C}_{\text{DIC}}$ values were sampled in the northeastern portion of the study area, and the high $\delta^{13}\text{C}_{\text{DIC}}$ values ($> 20\%$) occurred along a north-south trend (Fig. S2), roughly aligned with the areas of high TDS (Fig. S1), and the Prairie Evaporite dissolution scarp (shown on Fig. 5).

The $\delta^{34}\text{S}_{\text{SO}_4}$ can be used to determine the source(s) of sulfate as well as biogeochemical processes occurring in the subsurface (Fig. 8). Sulfate originating from the dissolution of anhydrite have $\delta^{34}\text{S}_{\text{SO}_4}$ values $> 20\%$ (Sasaki and Krouse, 1969; Hitchon and Krouse, 1972;

Horita et al., 1996), whereas sulfate originating from the oxidation of sulfide minerals typically have $\delta^{34}\text{S}_{\text{SO}_4}$ values less than 0% (Mayer, 2005). These original isotopic signatures can be altered during bacterially mediated sulfate reduction, resulting in a decrease in sulfate concentrations and a corresponding increase in $\delta^{34}\text{S}_{\text{SO}_4}$ values. Groundwater from surficial deposits tended to have lower sulfate concentrations and $\delta^{34}\text{S}_{\text{SO}_4}$ values (generally $< 5\%$) typical of sulfate originating from the oxidation of sulfide minerals. The samples with the highest sulfate concentrations were sourced from the Cretaceous or Devonian formations, and tended to have higher $\delta^{34}\text{S}_{\text{SO}_4}$ values (Fig. 8). Extremely high $\delta^{34}\text{S}$ values ($> 50\%$), beyond what is typically found in evaporite minerals, were measured in groundwater sampled from the Clearwater Formation, and could indicate modification of the original $\delta^{34}\text{S}$ signature due to secondary sulfate reduction.

Geochemical processes, such as sulfide oxidation, carbonate dissolution bacterial sulfate reduction and methanogenesis can alter concentrations of sulfate, bicarbonate and dissolved organic carbon (DOC) and result in predictable shifts in the isotopic labelling of these solutes (Table 4). The ranges of $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{34}\text{S}_{\text{SO}_4}$ in the unified SAOS groundwater dataset can be used to identify where these processes are occurring. The range of $\delta^{13}\text{C}_{\text{DIC}}$ values for the Grand Rapids and Clearwater formations are related to the relative importance of carbonate dissolution and methanogenesis, both of which can result in higher $\delta^{13}\text{C}_{\text{DIC}}$ values. The $\delta^{34}\text{S}_{\text{SO}_4}$ labelling of the Cretaceous formation groundwaters provides additional insight into the geochemical processes occurring in the samples with $\delta^{13}\text{C}_{\text{DIC}}$ values in the -20 to

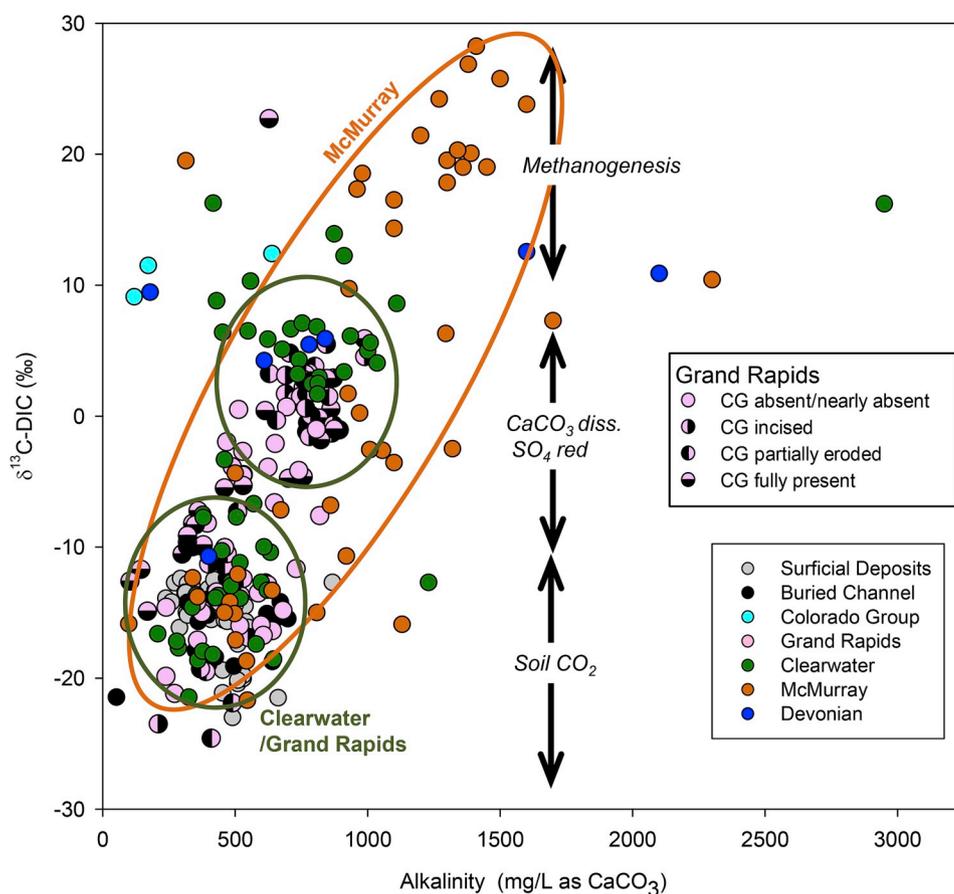


Fig. 7. $\delta^{13}\text{C}_{\text{DIC}}$ versus alkalinity concentrations. Note that Grand Rapids Formation sample symbols are further distinguished by the extent of Colorado Group (CG) cover. Green circles show the grouping of Clearwater and Grand Rapids formations samples; the orange ellipse shows the range of McMurray Formation samples. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

–10‰. The $\delta^{13}\text{C}$ labelling is consistent with DIC formed in the soil zone, but the higher $\delta^{34}\text{S}_{\text{SO}_4}$ signatures for some of the Cretaceous formation groundwater samples are interpreted to be the result of BSR, facilitated by the decomposition of organic matter, which could include natural hydrocarbons (Fig. 8b).

Systematic variations in strontium isotopes $^{87}\text{Sr}/^{86}\text{Sr}$ have been established for the Phanerozoic oceans, which can allow the weathering source-formation to be identified. Typical reference ranges for Devonian carbonates (0.7078–0.7083; ± 0.00004), Cretaceous carbonates (0.7070–0.7077; ± 0.00004) and Quaternary carbonates (0.7080–0.7090; ± 0.00004) (Faure, 1986) were used to evaluate the potential sources of Sr in the unified dataset (Fig. 9a). The range for Devonian carbonates are similar to the range reported for anhydrite from the Prairie Evaporite Formation 0.70781 to 0.70789 (Horita et al., 1996). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of groundwater samples collected from different hydrostratigraphic units plot along two mixing trends: i) low TDS groundwaters with Cl concentrations less than 500 mg L^{-1} plotting along a mixing line between Quaternary and Cretaceous sources of Sr (Fig. 10 grey arrow), and ii) higher TDS groundwaters with Cl concentrations greater than 500 mg L^{-1} plotting along a mixing line between Cretaceous and Devonian sources of Sr (Fig. 9a red arrow). Groundwater samples from buried channel aquifers tended to have lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than the near surface deposits (Fig. 9a). Many of these channels are eroded into Cretaceous formations and may have interacted with the adjacent formations over geologic time which would explain the greater proportion of Cretaceous and Devonian sourced Sr. Some Cretaceous formation groundwaters had high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios more typical of Quaternary sources of Sr, and these may indicate areas greater interactions with shallow aquifers. Most of the samples that plot along the mixing line between Cretaceous and Devonian sources of Sr were from Cretaceous or Devonian wells. The

Grand Rapids groundwater samples from locations with limited or no Colorado Group cover plotted along both of the mixing trends, but the Grand Rapids samples with the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, those that fall within the range typical of Cretaceous sources of Sr, are primarily from Grand Rapids sampling locations where the Colorado Group cover is fully present.

The $\delta^{37}\text{Cl}$ values reported for SAOS groundwaters range from –3.2‰ to +0.8‰ (Table 3, Fig. 9b). Groundwaters from the surficial deposits and channel had the lowest Cl concentrations ($< 10 \text{ mg L}^{-1}$) and $\delta^{37}\text{Cl}$ values spanned the range expected for Prairie Evaporite Formation halite ($\delta^{37}\text{Cl} = -0.2$ to +0.5‰; Zhang et al., 2014), but also lower $\delta^{37}\text{Cl}$ values ($< -2\%$) consistent with chloride present in rain water ($\delta^{37}\text{Cl} = -3.5\%$ to -1.2% ; Koehler and Wassenaar, 2010). The Devonian samples had the highest Cl concentrations and $\delta^{37}\text{Cl}$ that were consistent with the Prairie Evaporite Formation. The most enriched $\delta^{37}\text{Cl}$ value (+1.5‰) was measured on a sample from the Colorado Group, from a well completed in the Second White Specks Formation. The remaining Cretaceous groundwater samples plot along a trend of lower $\delta^{37}\text{Cl}$ values associated with decreasing Cl concentrations. The Cretaceous samples with the lowest $\delta^{37}\text{Cl}$ values were measured in Grand Rapid Formation with Colorado Group cover and in some Clearwater Formation samples. The combination of low $\delta^{37}\text{Cl}$ values and low chloride concentrations could indicate mixing with more recent meteoric water, or more likely given the thickness of the overlying Colorado Group cover, diffusive fractionation. During diffusive transport between a higher salinity aquitard and adjacent aquifer, the lighter isotopes of Cl tend to migrate faster, leaving the residual groundwater in the aquitard enriched in the heavy isotope and resulting in lower $\delta^{37}\text{Cl}$ values in the adjacent aquifer (Desaulniers et al., 1986; Eggenkamp, 1994).

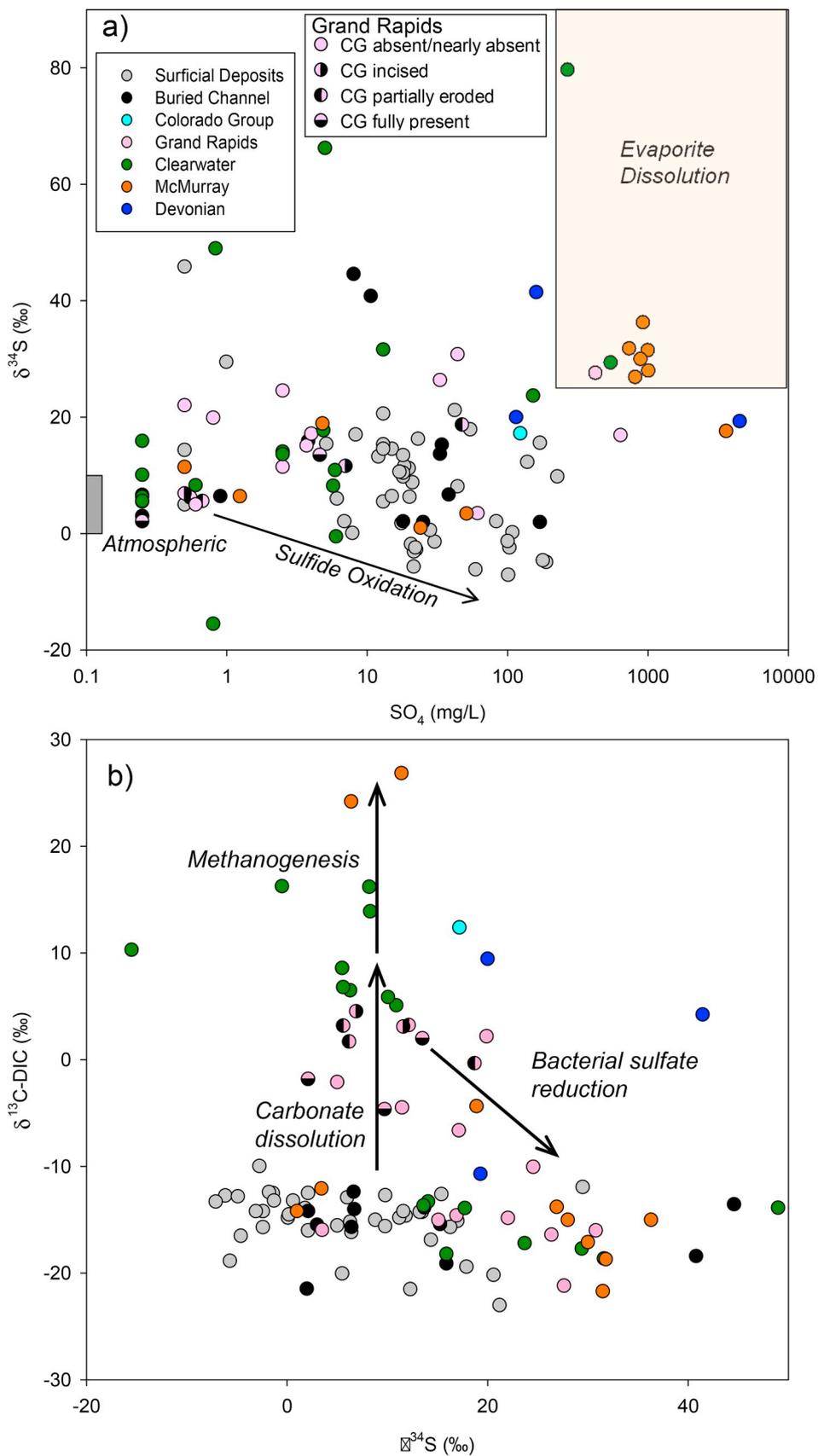


Fig. 8. a) $\delta^{34}\text{S}_{\text{SO}_4}$ versus sulfate concentrations with typical ranges for $\delta^{34}\text{S}$ relating to dissolution of evaporites ($> 20\text{‰}$) and sulfide mineral oxidation ($< 10\text{‰}$). Note that Grand Rapids Formation sample symbols are further distinguished by the extent of Colorado Group (CG) cover. b) $\delta^{13}\text{C}_{\text{DIC}}$ versus $\delta^{34}\text{S}_{\text{SO}_4}$ showing the effects of methanogenesis and bacterial sulfate reduction.

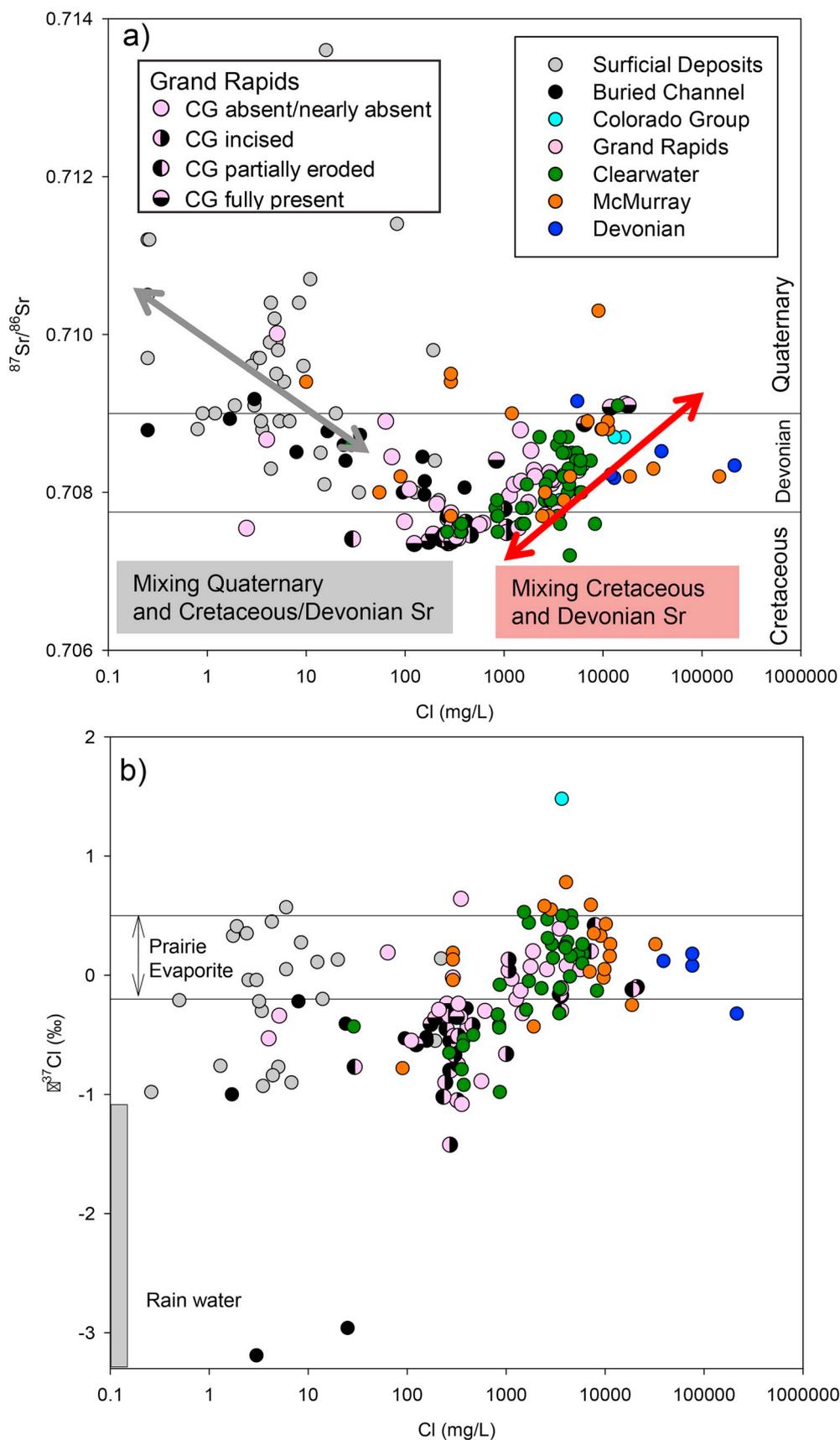


Fig. 9. a) The $^{87}\text{Sr}/^{86}\text{Sr}$ composition and Cl concentration of groundwaters in the region. Ranges typical for Quaternary, Devonian and Cretaceous Sr sources are included for comparison. b) The $\delta^{37}\text{Cl}$ and Cl concentrations of groundwaters are shown with the ranges of $\delta^{37}\text{Cl}$ values measured in the Prairie Evaporite Formation (Zhang et al., 2014) and rain water shown for comparison (Koehler and Wassenaar, 2010).

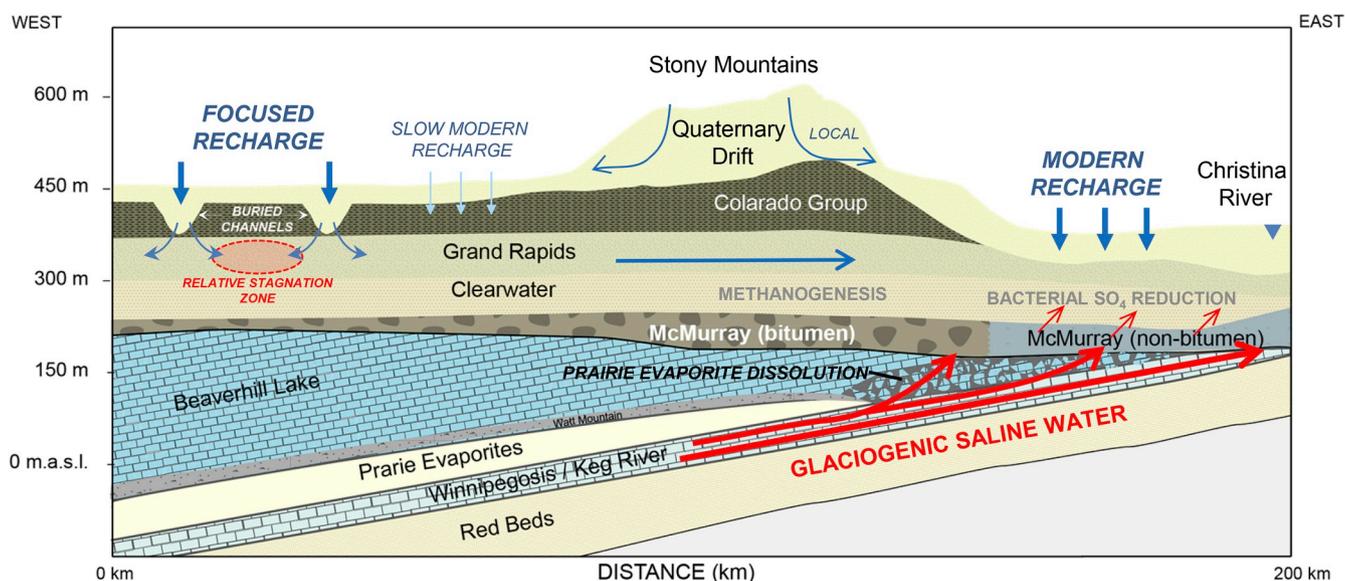


Fig. 10. a) Schematic showing a conceptual model groundwater flow from an east west cross-section through the study area after the regional flow system returned to from the temporary reversal during glacial conditions (modified from Gibson et al., 2012).

4.4. ^{14}C

The ^{14}C abundances indicate greater proportions of modern carbon in the surficial and channel deposits (Table 4) and lower percentages in the Cretaceous and Devonian aquifers. Only samples with no detectable ^3H were used in the ^{14}C residence time corrections (see Supplemental Material section 1.3), however, ^3H was not available for all samples and the average modelled residence times include many that are near the maximum for use of ^{14}C age dating. However, some general trends in the distribution of ^{14}C activities, and modelled residence times are useful for evaluating the mixing trends identified from the water and solute isotope distributions. Relatively short ^{14}C residence times were identified in the Grand Rapids, Clearwater, and McMurray Formations in the northeastern portion of the study area (Fig. S3), where these formations are present at shallow depths, and with a greater influence of post-glacial meteoric water. The shallower Quaternary aquifers, for the most part, contain waters with shorter residence times than the deeper Cretaceous formations, while deposits in the buried channels have longer residence times, consistent with a deeper position in the stratigraphic column and influence from paleo-water. In turn, groundwater sampled from the Lower Grand Rapids Formation is variable in ^{14}C activity, but, but the lowest are generally associated with areas where the Colorado Group aquitard remains relatively thick, whereas shorter residence times are noted where this confining interval is thin or absent.

5. Discussion

Interpretation of the unified dataset has identified geochemical and isotopic indicators of connectivity and source water mixing that can be inferred over the geologic history that can be used to update some of the models about groundwater flow and history in the SAOS (Fig. 10).

5.1. McMurray formation

Groundwater flow in the McMurray Formation is influenced by the topographic highs and lows, with flow generally occurring radially outward from major upland areas towards the Athabasca, Christina, and Clearwater Rivers (Barson et al., 2001; Matrix Solutions Inc. 2016). In turn, mineralization of the groundwater generally follows the distribution of water-types, with higher concentrations associated with

higher TDS, Na–Cl type waters in the southwestern portion of the study area (Figs. S1 and 3), consistent with greater isolation of the aquifer due to deeper burial and thicker confining cover. There are other areas of higher TDS groundwaters that roughly coincide with the dissolution edge of the Prairie Evaporite Formation (Cowie et al., 2015). However, the major ion composition of groundwater is highly variable near the dissolution edge, where higher TDS, Na–Cl groundwaters are frequently encountered in fairly close proximity to lower TDS, Na– HCO_3 groundwaters (Figs. S1 and 3). The lower $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in McMurray Formation groundwater are evidence of a greater influence from glaciogenic waters and occur east of the bitumen extent and dissolution scarp, in areas where bitumen would not limit mixing with underlying formations (Fig. 5).

The $\delta^{34}\text{S}$, $^{87}\text{Sr}/^{86}\text{Sr}$, and $\delta^{37}\text{Cl}$ signatures and Cl:Br ratios (see Supplemental Material) in the McMurray groundwaters are typical of solutes originating from the Prairie Evaporite Formation, but the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signatures show influence of glaciogenic water. The spatial distribution of $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{34}\text{S}$ values provides additional insight about where carbonate dissolution, methanogenesis, and BSR may be occurring. Comparatively higher $\delta^{13}\text{C}_{\text{DIC}}$ values identify areas where methanogenesis is suspected to be occurring within the bitumen-bearing zones; these are roughly aligned with the Prairie Evaporite dissolution scarp and the bitumen extent (Fig. S2).

Within the McMurray Formation there are geochemical and isotopic indicators of potential vertical connectivity that do not appear to be related to present vertical head differences and associated hydraulic gradients between aquifers. Instead, they appear to be very generally associated with vertical pathways inferred to occur near the dissolution scarp of the Prairie Evaporite Formation. Elevated TDS and Na–Cl type waters are noted in this area, immediately adjacent pockets of glaciogenic water characterized by lower $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values near buried channels and river valleys incised into the bedrock formations.

5.2. Clearwater Formation

Within the Clearwater Formation, groundwater flows north towards the Clearwater River, and northwest and west towards the Athabasca River (Barson et al., 2001; Matrix Solutions Inc. 2016). The TDS data for this hydrostratigraphic interval are not as abundant as other intervals, but their distribution does show higher concentrations in the southwestern portion of the study area (Fig. S1), and in similar areas

where Na–Cl type groundwaters tend to dominate (Fig. 3). This is again consistent with greater isolation of the aquifer where it is more deeply buried. There are other smaller areas of higher TDS in the northeastern portion of the study area (Fig. S1). The groundwater in these areas is dominated by a Na–Cl types, except for small areas where Na–HCO₃ types are noted (i.e. Fig. 3 - Townships 81–83, Range 6–7 W4M). The range of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values is less variable than the other Mannville Group formations (Fig. 4d), but does indicate values consistent with a glaciogenic water influence near the Christina River (Figs. 5 and 10). Higher $\delta^{13}\text{C}_{\text{DIC}}$ values also occur in groundwaters sampled near the Christina and Leismer Channels supporting the occurrence of methanogenic conditions in that interval (Fig. S2).

5.3. Grand Rapids

Within the Grand Rapids Formation, groundwater flows north towards the Clearwater River and northwest and west towards the Athabasca River (Barson et al., 2001; Matrix Solutions Inc. 2016). TDS concentrations increase in the southwestern portion of the study area (Fig. S1), where the formation is at its deepest, and where Na–Cl type groundwaters dominate (Fig. 3) and where Cl:Br ratios consistent with seawater are more prevalent (Fig. S4). The most prevalent water types in this interval are Na–HCO₃–Cl and Na–Cl, but there are a few anomalous mixed cation-HCO₃ waters present in this formation.

Groundwater from the Grand Rapids Formation exhibits the largest range in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values (Fig. 4c), showing evidence of mixing between two isotopically distinct end-member waters (Fig. 6). Comparatively low $\delta^{18}\text{O}$, and associated $\delta^2\text{H}$, values near the Christina River (Fig. 5) indicate mixing with a glaciogenic source, and this mixing pattern is associated with portions of the aquifer with little to no Colorado Group cover. The $\delta^{34}\text{S}_{\text{SO}_4}$, $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{37}\text{Cl}$ and Cl:Br values for these waters are within the ranges expected for solutes originating from dissolution of the Devonian Evaporites, consistent with the conceptual model of subglacial meltwater injection (Grasby and Chen, 2005).

The Grand Rapids groundwater samples that plot along the mixing line with more enriched paleo-waters (Fig. 6) include:

- samples that plot below the GMWL, indicating mixing with a paleo-water with evaporative signatures, and
- samples that plot along the GMWL, but with $\delta^{18}\text{O}$ and $\delta^2\text{H}$ indicative or recharge under warmer climate conditions (Fig. 4c).

All the Grand Rapids groundwater samples that plot along the mixing line with paleo-waters are from areas where the Colorado Group is fully present or only partially eroded, and are located in south and southwestern portions of the SAOS study area (Fig. 5). The elevated TDS values, and evaporatively-enriched $\delta^{18}\text{O}$ and $\delta^2\text{H}$ composition of the samples collected from groundwater from the area around Townships 73–74, and Ranges 4–5 support the interpretation that this is a relatively stagnant groundwater zonewhithin the aquifer, where paleo-waters (formation waters of marine origin) are still present, however, the Cl:Br ratios for these samples are still within the range indicating evaporite dissolution (Fig. S4). Detailed hydraulic head data are available for this location, and has shown that convergent flow conditions created by the surrounding buried channels may have created a zone of relative isolation from the regional flow system (Brewster, 2016). Unfortunately, there are limited solute isotope data for the other samples that show influence of an evaporatively enriched $\delta^{18}\text{O}$ source, so comparison of all the solute isotope labelling was not possible. However, principle component analysis (PCA) of the geochemical and isotopic data available for the Grand Rapids Formation wells have shown the distinctiveness of the group of evaporatively-enriched samples (Supplementary Material Fig. S5). These samples are distinguished from other Grand Rapids Formation samples by the higher $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values, and elevated concentrations of Na, Cl, conductivity, and hardness (Table S1).

5.4. Revised conceptual model

Based on previous investigations in the region (Barson et al., 2001; Grasby and Chen, 2005), and the enhanced perspective gained from the unified geochemical and isotopic dataset presented herein, a revised conceptual model of groundwater flow conditions in the SAOS was developed (Fig. 10). Notably, the revised model incorporates additional details such as the vertical connectivity between Devonian aquifers and the McMurray Formation in the vicinity of the Prairie Evaporite dissolution scarp (Cowie et al., 2015), the presence of glacial meltwater into Cretaceous formations, and the associated geochemical processes and role of both the Colorado Group and bitumen layer as aquitards preventing complete flushing of the groundwater system. In deeper portions of the sedimentary basin, where the Grand Rapids is present at greater depths the revised conceptual model also includes slow-moving, relatively stagnant groundwater zones that still show evidence of mixing with pre-glacial formation waters. Focused recharge via buried Quaternary channels that fully or partially penetrate the Colorado Group may lead to locally convergent groundwater flow and zones of relative stagnation (Fig. 10). Geochemical and isotopic evidence suggests glacial meltwater injection effectively flushed the eastern margin of the Western Canadian Sedimentary Basin (likely between about 125Ka and 10Ka during the last glaciation), followed by a period of groundwater reversal and exfiltration, peaking at the time of deglaciation and diminishing to the present. During glaciation, pressurized glacial meltwater was likely injected against the prevailing hydraulic gradient, particularly along high-permeability Devonian strata, leading to extensive dissolution of evaporites and formation of high salinity groundwater (Fig. 10). While high permeability units such as the Devonian carbonates sub-cropping in NE Alberta and Manitoba are presumed to have been preferred conduits for meltwater, a general increase in pressurized recharge to all units likely occurred at this time. During early deglaciation, as glaciers receded from west to east in this region, migration of saline water from Devonian units into overlying Cretaceous strata may have occurred under much higher hydraulic gradients than today. After the regional flow system resumed towards the east (Fig. 10), relaxation of hydraulic gradients may have allowed further upward movement of saline groundwater into Cretaceous strata, although at reduced rates. Note that the bitumen layer within the McMurray Formation acts as an aquitard limiting upward migration of saline water in the western portion of the SAOS region.

For Cretaceous formations in the Stony Mountains region, the presence of the low-permeability Colorado Group above and bitumen-impregnated sands of the McMurray Formation below are hypothesized as major hydraulic barriers for meteoric and glaciogenic water influence. The hydraulic isolation provided by the relatively low permeability overlying and underlying formation preserved the original formation waters and limited mixing with shallower aquifers, or glaciogenic waters in areas where evaporative influences were detected. Similarly, areas where mixing with younger groundwaters from overlying surficial deposits or glaciogenic groundwater tended to be located in aquifer areas where these confining layers were not present. Areas associated with less evolved groundwaters (HCO₃-dominated) are typically located in the vicinity of the buried channel aquifers that incise into, or through, the Cretaceous formations and areas to the northeast where Colorado Group is thin or absent. These glacially influenced groundwaters were detected in the McMurray, Clearwater and Grand Rapids formations, indicating that vertical flow may have occurred between these formations.

Several dominant geochemical patterns affecting formation water hydrochemistry are explained by this model: i) mixing with glaciogenic waters (i.e. comparatively low $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values, higher TDS values, Cl:Br ratios, and $\delta^{34}\text{S}_{\text{SO}_4}$, $^{87}\text{Sr}/^{86}\text{Sr}$, and $\delta^{37}\text{Cl}$ values consistent with evaporite dissolution), ii) mixing with paleo-waters (i.e. higher TDS values and higher $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values), and iii) mixing with shallow aquifers (i.e. $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values consistent with more meteoric HCO₃-

dominated water, and $\delta^{34}\text{S}_{\text{SO}_4}$, $^{87}\text{Sr}/^{86}\text{Sr}$ values consistent with weathering of materials associated with the Quaternary and more recent sediments). None of the waters sampled in this study had geochemical or isotopic signatures of the original connate end-members, but there are isolated pockets (slow moving zones of relative stagnation) that appear to have been exempt from the glaciogenic flushing experienced in other areas, where mixing with a more evaporated paleowater was preserved.

The distribution of geochemical and isotopic parameters assessed in this study supports the conclusion that greater potential for vertical connectivity and mixing between otherwise discrete formation waters occurs where buried channels have thinned or completely incised through Cretaceous units (particularly the low permeability Colorado Group interval). This study used the location of thalwegs and mapped channel deposits to approximate these areas, although additional channels influencing connectivity may yet to be identified across the SAOS region.

The ability for saline brines to persist in large sedimentary basins despite regional flow systems has been explained by basin geometry and brine density, with the recent review of data from North American sedimentary basins showing that in some basins there is insufficient topography to drive dense fluids from the bottom of deep sedimentary basins (Ferguson et al., 2018). The driving force ratios determined for the Alberta Basin (Ferguson et al., 2018) predicts that there should be a range of groundwater salinities due to a combination of flushing by regional groundwater flow, glacial meltwater ingress and low initial salinities. This prediction is consistent with data available from deeper in the basin where connate waters have been identified (Hitchon et al., 1969; Connolly et al., 1990a & 1990b; Simpson, 1999; Grasby and Chen, 2005) as well as data compiled for locations closer to the discharge edge of the basin (this study, Grasby and Chen, 2005), which clearly show evidence of glacial water ingress and evaporite dissolution.

In other sedimentary basins the influx of glaciogenic water has been found to have significant impacts on the distribution of salinity and geochemical processes. In the Athabasca Region, dissolution of evaporites by glaciogenic water has been presumed as the source of high TDS waters in regional springs (Grasby and Chen, 2005; Gue et al., 2015), groundwater seepage zones in the Athabasca river (Birks et al., 2018; Gibson et al., 2013). It is also interpreted to be the cause of numerous collapse and blowout features observed in the region (Broughton, 2013), and influential in creating the modern TDS distributions in the McMurray Formation (Cowie et al., 2015). The results from this study indicate that mixing with glaciogenic water can also be identified in overlying aquifers (Clearwater and Grand Rapids) in areas where there are no vertical barriers to upward flow.

In addition, the $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ data from the SAOS suggest that methanogenesis and sulfate reduction may also be related to the presence of bitumen and extent of glaciogenic water influx. In other sedimentary basins, the presence of glaciogenic water has been linked to the degradation of crude oil (Grasby et al., 2000; McIntosh et al., 2002; McIntosh and Walter, 2006; Williston Basin) and gas generation (Shurr and Ridgely, 2002). The heavy oil present in the Athabasca and Cold Lake oil sands deposits is thought to be the result of biodegradation of conventional oil, due to an influx oxygenated meteoric water (Creaney et al., 1994; Hayes et al., 1994). The injection of glacial meltwater into Devonian formations and migration upward to the Mannville deposits via dissolution and collapse features in this area may have been a source of oxygenated meteoric water.

6. Conclusions

Consolidation and re-interpretation of geochemical and isotopic datasets for the SAOS made available here, has allowed substantial refinement of existing knowledge of the region's groundwater flow

systems, and may serve to enhance and challenge previous conceptual and numerical models applied in northeastern Alberta for groundwater management. Complex groundwater flow systems influenced by paleo-flow conditions, topographic features, and geological structures (e.g. buried channels, salt dissolution collapse features, and stratigraphic changes) are often difficult to resolve using physical parameters alone. In such cases, the geochemical and isotopic parameters may be useful, as demonstrated, for constraining groundwater provenance and history. This extensive geochemical and isotopic groundwater dataset provides examples of geochemical interactions occurring in sedimentary basins under the influence of continental ice sheets, and as such, this study is expected to form a valuable resource for understanding and interpreting glaciogenic influence on groundwaters globally.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apgeochem.2018.12.013>.

References

- Alberta Energy Regulator, 2015. Accessed 5 October 2017 at: <http://www.oscaalberta.ca/wp-content/uploads/2017/06/Alberta-Energy-Regulator-FAQs.pdf>.
- Alberta Geological Survey, 2013. Bedrock Geology of Alberta (GIS Data, Polygon Features), DIG_2013.0013. http://ags.aer.ca/document/DIG/DIG_2013.0018.zip.
- Andriashuk, L.D., 2003. Quaternary geological setting of the Athabasca oil sands (in situ) area, northeast Alberta. In: Earth Sciences Report 2002-03. Alberta Geological Survey. Alberta Energy Utilities Board 286 pp.
- Andriashuk, L.D., Atkinson, N., 2007. Buried Channels and Glacial-drift Aquifers in the Fort McMurray Region, Northeast Alberta; Alberta Energy and Utilities Board, EUB/AGS Earth Sciences Report 2007-01. 170 pp.
- Aravena, R., Wassenaar, L.L., Plummer, L.N., 1995. Estimating ^{14}C groundwater ages in a methanogenic aquifer. *Water Resour. Res.* 31, 2307–2317.
- Babre, A., Kalvāns, A., Popovs, K., Retiķe, I., Dēliņa, A., Vaikmāe, R., Martma, T., 2016. Pleistocene age paleo-groundwater inferred from water-stable isotope values in the central part of the Baltic Artesian Basin. *Isot. Environ. Health Stud.* 52 (6), 706–725. <https://doi.org/10.1080/10256016.2016.1168411>.
- Bachu, S., 1996. Regional Subsurface Hydrogeology in Northeast Alberta. Alberta Geological Survey Open File Report 1996-14. 149pp.
- Bachu, S., Underschultz, J.R., 1993. Hydrogeology of formation waters, northeastern Alberta Basin. *AAPG Bull.* 77, 1745–1768.
- Bachu, S., Underschultz, J.R., Hitchon, B., Cotterill, D., 1993. Regional-scale Subsurface Hydrogeology in Northeast Alberta. Alberta Geological Survey, Alberta Research Council, Bulletin No. 61. 44 pp.
- Bachu, S., Underschultz, J.R., McPhee, D., Cotterill, D.K., 1991. Regional Geology and Hydrostratigraphy in Northeast Alberta. Alberta Geological Survey Open File Report 1996-16. 162 pp.
- Baer, T., Barbour, S.L., Gibson, J.J., 2016. The stable isotopes of site wide waters at an oil sands mine in northern Alberta, Canada. *J. Hydrol.* 541B, 1155–1164. <https://doi.org/10.1016/j.jhydrol.2016.08.017>.
- Barson, D., Bachu, S., Esslinger, P., 2001. Flow systems in the Mannville Group in the east-Central Athabasca area and implications for steam-assisted gravity drainage (SAGD) operations for in situ bitumen production. *Bull. Can. Petrol. Geol.* 49, 376–392.
- Bayari, C.S., Ozyurt, N.N., Kilani, S., 2008. Radiocarbon age distribution of groundwater in the konya closed basin, central anatolia, Turkey. *Hydrogeol. J.* 17 (2), 347–365.
- Birks, S.J., Gibson, J.J., Gourcy, L., Aggarwal, P.K., Edwards, T.W.D., 2002. Maps and animations offer new opportunities for studying the global water cycle. *Trans. AGU EOS* 83 (37), 406–407. plus electronic supplement. http://www.agu.org/eos_elec/20082e.html.

- Birks, S.J., Moncur, M.C., Gibson, J.J., Yi, Y., Fennell, J., Taylor, E.B., 2018. Origin and hydrogeological setting of saline groundwater discharges to the Athabasca River: geochemical and isotopic characterization of the hyporheic zone. *Appl. Geochem.* 98, 172–190.
- Brewster, M., 2016. Exploration and Development of a New Water Disposal Zone for Steam Assisted Gravity Drainage. WaterTech, Banff, Canada 2016.
- Broughton, P.L., 2015. Collapse-induced fluidization structures in the lower cretaceous Athabasca oil sands deposit, western Canada. *Basin Res.* 1–29. <https://doi.org/10.1111/bre.12120>.
- Broughton, P.L., 2013. Devonian salt dissolution-collapse breccias flooring the Cretaceous Athabasca oil sands deposit and development of lower McMurray Formation sinkholes, northern Alberta Basin, Western Canada. *Sediment. Geol.* 283, 57–82.
- Clark, I.D., Douglas, M., Raven, K., Bottomley, D., 2005. Recharge and preservation of Laurentide glacial melt water in the Canadian shield. *Groundwater*.
- Connolly, C.A., Walter, L.M., Baadsgaard, H., Longstaffe, F.J., 1990a. Origin and evolution of Formation waters, Alberta Basin, western Canada sedimentary basin. I. Chemistry. *Appl. Geochem.* 5, 375–395.
- Connolly, C.A., Walter, L.M., Baadsgaard, H., Longstaffe, F.J., 1990b. Origin and evolution of formation waters, Alberta Basin, Western Canada Sedimentary Basin. II. Isotope systematics and water mixing. *Appl. Geochem.* 5, 397–413.
- Cowie, B.R., 2013. Stable Isotope and Geochemical Investigation into the Hydrogeology and Biogeochemistry of Oil Sands Reservoir Systems in Northeastern Alberta, Canada. Ph.D. Thesis. University of Calgary, Canada.
- Cowie, B.R., James, B., Mayer, B., 2015. Distribution of total dissolved solids in McMurray Formation water in the Athabasca oil sands region, Alberta, Canada: implications for regional hydrogeology and resource development. *AAPG (Am. Assoc. Pet. Geol.) Bull.* 99 (1), 77–90.
- Craig, H., 1961. Isotopic variations in meteoric waters. *Science* 133, 1702–1703.
- Creaney, S., Allan, J., Cole, K.S., Fowler, M.G., Brooks, P.W., Osadetz, K.G., et al., 1994. Petroleum generation and migration in the Western Canada sedimentary basin. In: Mossop, G., Shetson, I. (Eds.), *Geological Atlas of the Western Canada Sedimentary Basin*. Canadian Society of Petroleum Geologists and Alberta Research Council, Edmonton, pp. 455–468.
- Desaulniers, D.E., Kaufmann, R.S., Cherry, J.A., Bentley, H.W., 1986. ^{37}Cl - ^{35}Cl variations in a diffusion-controlled groundwater system. *Geochem. Cosmochim. Acta* 50, 1757–1764.
- Eggenkamp, H.G.M., 1994. $\delta^{37}\text{Cl}$, the Geochemistry of Chlorine Isotopes. Doctoral thesis. Univ. Utrecht, Utrecht, Netherlands 150 pp.
- Faure, G., 1986. *Principles of Isotope Geology*, second ed. John Wiley & Sons, New York 589 pp. ISBN 0-471-86412-9.
- Ferguson, G., McIntosh, J.C., Grasby, S.E., Hendry, M.J., Jsechko, S., Lindsay, M.B.J., Luijendijk, E., 2018. The persistence of brines in sedimentary basins. *Geophys. Res. Lett.* <https://doi.org/10.1029/2018GL078409>.
- Ferguson, G., Jasechko, S., 2015. The isotopic composition of the Laurentide Ice Sheet and fossil groundwater. *Geophys. Res. Lett.* 42, 4856–4861. <https://doi.org/10.1029/2015SL064106>.
- Fontes, J.C., Garnier, J.M., 1979. Determination of the initial ^{14}C activity of the total dissolved carbon: a review of the existing models and a new approach. *Water Resour. Res.* 15, 399–413.
- Freeman, J.T., 2007. The use of bromide and chloride mass ratios to differentiate salt-dissolution and formation brines in shallow groundwaters of the Western Canadian Sedimentary Basin. *Hydrogeol. J.* 15 (7), 1377–1385.
- Gibson, J.J., Birks, S.J., Moncur, M., Yi, Y., Tattrie, K., Jasechko, S., Richardson, K., Eby, P., 2011. Isotopic and geochemical tracers for fingerprinting process-affected waters in the oil sands industry: a pilot study. In: *Oil Sands Research and Information Network, OSRIN Report No. TR-12*. University of Alberta, Edmonton April 2011, 109pp.
- Gibson, J.J., Fennell, J., Birks, S.J., Yi, Y., Moncur, M., Hansen, B., Jasechko, S., 2013. Evidence of discharging saline formation water to the Athabasca River in the northern Athabasca oil sands region. *Can. J. Earth Sci.* 50 (2013), 1244–1257. <https://doi.org/10.1139/cjes-2013-0027>.
- Gibson, J.J., Birks, S.J., Yi, Y., Moncur, M., Jasechko, S., Tattrie, K., Richardson, K., Szabova, M., Cendon, D., Marandi, A., 2012. Isotopic tracing of surface/groundwater interactions, groundwater age and salinity in the the South Athabasca Oil Sands area: final report on baseline surveys. In: *Technical Report Prepared under Contract to Conocophillips Canada Inc., and Nexen Inc., Finalized 2012*, 90 pp. + appendices.
- Grasby, S.E., Osadetz, K., Betcher, R., Render, F., 2000. Reversal of the regional-scale flow system of the Williston Basin in response to the Pleistocene glaciation. *Geology* 29, 635–638.
- Grasby, S.E., Betcher, R., 2002. Regional hydrogeochemistry of the carbonate rock aquifer, southern Manitoba. *Can. J. Earth Sci.* 39, 1053–1063.
- Grasby, S.E., Chen, Z., 2005. Subglacial recharge into the Western Canada Sedimentary Basin – impact of Pleistocene glaciation on basin hydrodynamics. *GSA Bull.* 117, 500–514.
- Gue, A., 2012. The Geochemistry of Saline Springs in the Athabasca Oil Sands Region and Their Impact on the Clearwater and Athabasca Rivers. M.Sc. Thesis. University of Calgary 173 pp.
- Gue, A.E., Mayer, B., Grasby, S.E., 2015. Origin and geochemistry of saline spring waters in the Athabasca oil sands region, Alberta, Canada. *Appl. Geochem.* 61, 132–145.
- Hayes, B., Christopher, J., Rosenthal, L., Los, G., Mc Kercher, B., Minken, D., Tremblay, Y., Fennell, J., Smith, D., 1994. Cretaceous Mannville group of the western Canada Sedimentary Basin, geological atlas of the western Canada Sedimentary Basin. *Can. Soc. Petrol. Geol. Alberta Res. Coun.* 4, 317–334.
- Hackbarth, D.A., Nastasa, N., 1979. The hydrogeology of the Athabasca oil sands area, Alberta. *Alberta Res. Coun. Bull.* 38 39 pp.
- Hendry, J.M., Barbour, S.L.O., Novakowski, K., Wassenaar, L.I., 2013. Paleohydrogeology of the Cretaceous sediments of the Williston Basin using stable isotopes of water. *Water Resour. Res.* v49 (8), 4580–4592.
- Hitchon, B., Friedman, I., 1969. Geochemistry and origin of formation waters in the Western Canada Sedimentary Basin - i. Stable isotopes of hydrogen and oxygen. *Geochem. Cosmochim. Acta* 33, 1321–1349.
- Hitchon, B., Levinson, A.A., Reeder, S.W., 1969. Regional variations of river water composition resulting from halite dissolution, Mackenzie River drainage basin, Canada. *Water Resour. Res.* 5 (6), 1395–1403.
- Hitchon, B., Krouse, H., 1972. Hydrogeochemistry of surface waters of the Mackenzie River drainage basin, Canada - iii. stable isotopes of oxygen, carbon and sulfur. *Geochem. Cosmochim. Acta* 36, 1337–1357.
- Horita, J., Weinberg, A., Das, N., Holland, H.D., 1996. Brine inclusions in halite and the origin of the middle Devonian Prairie Evaporites of western Canada. *J. Sediment. Res.* 66 (5), 956–964.
- Ingerson, C.W., Pearson, F.J., 1964. Estimation of age and rate of motion of groundwater by the ^{14}C method. In: *Recent Researches in the Field of Hydrosphere, Atmosphere, and Nuclear Geochemistry, Sugawara Festival Volume*. Maruzen Company, Tokyo, Japan, pp. 263–283.
- Koehler, G., Wassenaar, L.I., 2010. The stable isotopic composition ($^{37}\text{Cl}/^{35}\text{Cl}$) of dissolved chloride in rainwater. *Appl. Geochem.* 25, 91–96.
- Lemay, T.G., 2002a. Geochemical and Isotope Data for Formation Water from Selected Wells, Cretaceous to Quaternary Succession, Athabasca Oil Sand (In-situ) Area, Alberta. EUB/AGS Geo-note 2002-02. pp. 1–30.
- Lemay, T.G., 2002b. Carbon-14 Dating of Groundwater from Selected Wells in Quaternary and Quaternary-tertiary Sediments, Athabasca Oil Sands (In Situ) Area, Alberta; Alberta Energy and Utilities Board, Alberta Geological Survey, Geo-note 2002-03. 15 pp.
- Lemieux, J.M., Sudicky, E.A., Peltier, W.R., Tarasov, L., 2008. Dynamics of groundwater recharge and seepage over the Canadian landscape during the Wisconsinian glaciation. *J. Geophys. Res.* 113, F01011. <https://doi.org/10.1029/2007JF000838>, 2008.
- Matrix Solutions Inc. (Matrix), 2013. Framework for Development of a Regional Groundwater Monitoring Network - Interim Report, Southern Athabasca Oil Sands Area. Report prepared for Alberta Environment. 107 pp.
- Matrix Solutions Inc. (Matrix), 2016. Predictive Simulations Using the 3D Southern Athabasca Oil Sands Groundwater Flow Model, Regional Groundwater Solutions Project. Canadian Oil Sands Innovation Alliance (COSIA) 14 pp + Appendices.
- Mayer, B., 2005. Assessing sources and transformations of sulphate and nitrate in the hydrosphere using isotope techniques. In: Aggarwal, P.K., Gar, J.R., Froehlich, K.F.O. (Eds.), *Isotopes in the Water cycle: Past, Present, and Future of a Developing Sciences*, pp. 67–89.
- 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. *Geochem. Cosmochim. Acta* 70, 2454–2479.
- 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, 18–33.
- McIntosh, J.C., Walter, L.M., Martini, A.M., 2002. Pleistocene recharge to midcontinent basins: effects on salinity structure and microbial gas generation. *Geochem. Cosmochim. Acta* 66 (10), 1681–1700.
- McMahon, P.B., Böhlke, J.K., Christenson, S.C., 2008. Geochemistry, radiocarbon ages, and paleorecharge conditions along a transect in the central High Plains aquifer, southwestern Kansas, USA. *Appl. Geochem.* 19, 1655–1686.
- Moncur, M.C., Paktunc, D., Birks, S.J., Ptacek, C.J., Welsh, B., Thibault, Y., 2015. Source and distribution of naturally occurring arsenic in groundwater from Alberta's Southern Oil Sands Regions. *Appl. Geochem.* 62, 171–185.
- Parkhurst, D.L., Charlton, S.R., 2008. NetpathXL – an Excel Interface to the Program NETPATH: U.S. Geological Survey Techniques and Methods 6-A-26. pp. 11.
- 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. *Rev. Geophys.* 45, RG3007. <https://doi.org/10.1029/2006RG000206>.
- Plummer, L.N., Sprinkle, C.L., 2001. Radiocarbon dating of dissolved inorganic carbon in groundwater from confined parts of the Upper Floridan aquifer, Florida, USA. *Hydrogeol. J.* 9, 127–150.
- Plummer, L.N., Prestemon, E.C., Parkhurst, D.L., 1991. An Interactive Code (NETPATH) for Modeling NET Geochemical Reactions along a Flow PATH: U.S. Geological Survey Water-resources Investigations Report 91-4078.
- Plummer, L.N., Prestemon, E.C., Parkhurst, D.L., 1994. An Interactive Code (NETPATH) for Modeling NET Geochemical Reactions along a Flow PATH, Version 2.0: U.S. Geological Survey Water-resources Investigations Report. pp. 94–4169.
- Remenda, V., Cherry, J., Edwards, T., 1994. Isotopic composition of old groundwater from Lake Agassiz: implications for late Pleistocene climate. *Science* 266 (5193), 1975–1978.
- Royal Society of Canada Expert Panel (RSC), 2010. Environmental and Health Impacts of Canada's Oil Sands Industry. 438 pp.
- Sasaki, A., Krouse, H.R., 1969. Sulphur isotopes and the Pine Point lead-zinc mineralization. *Econ. Geol.* 64, 718–730.
- Shurr, G., Ridgely, J.L., 2002. Unconventional shallow biogenic gas systems. *Am. Assoc. Pet. Geol.* 86 (110). <https://doi.org/10.1306/61EEDDC8-173E-11D7-8645000102C1865D>.
- Simpson, G.P., 1999. Sulfate Reduction and Fluid Chemistry of the Devonian Leduc and Nisku Formations in Southcentral Alberta [Ph.D. Thesis]. Alberta, University of Calgary 228 pp.
- Stewart, S.A., Lemay, T.G., 2011. Inorganic Water Chemistry of Saline Fens in Northeastern Alberta (NTS 74D). Energy Resources Conservation Board, Open File Report 2011-09. 6pp.

- Tamers, M.A., 1975. Validity of radiocarbon dates on ground water. *Geophys. Surv.* 2, 217–239.
- Van der Kemp, W.J.M., Appelo, C.A.J., Walraevens, K., 2000. Inverse chemical modeling and radiocarbon dating of palaeogroundwaters: the Tertiary Ledo-Paniselian aquifer in Flanders, Belgium. *Water Resour. Res.* 36, 1277–1287.
- Vogel, J.C., 1970. Carbon-14 dating of groundwater. In: *Isotope Hydrology 1970*, IAEA Symposium 129, March 1970, Vienna, pp. 225–239.
- Worley Parsons, 2010. Groundwater Flow Model for the Oil Sands (In-situ) Area South of Fort McMurray, Phase 2. Report Prepared for Alberta Environment 351pp.
- Zhang, M., Eby, P., Birks, S.J., Gibson, J.J., Bistran, R., 2014. Determination of Chlorine Isotopic Composition of Evaporites from the Western Canadian Sedimentary Basin. Alberta Innovates Technology Futures Technical Report 36 pp.