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Key Points:
- Groundwater derived from the LIS had variable $\delta^{18}O$ values
- Groundwater $\delta^{18}O$ values are correlated with GCM output
- The bulk LIS $\delta^{18}O$ is lower than most fossil groundwater values

Supporting Information:
- Figure S1 and Tables S1–S3

Correspondence to:
G. Ferguson,
grant.ferguson@usask.ca

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The isotopic composition of the Laurentide Ice Sheet and fossil groundwater

Grant Ferguson[1] **and Scott Jasechko**[2]

[1]Department of Civil and Geological Engineering, University of Saskatchewan, Saskatoon, Saskatchewan, Canada,
[2]Department of Geography, University of Calgary, Calgary, Alberta, Canada

Abstract Stable isotopes have been used to study large-scale changes in hydrology during the Pleistocene epoch. Many of these efforts have required an estimate of the $\delta^{18}O$ value of runoff generated by melting ice sheets. There is no consensus on representative values. Here we examine $\delta^{18}O$ values from fossil groundwater samples and isotope-enabled general circulation models (GCMs) to better understand the isotopic composition of the Laurentide Ice Sheet (LIS). Groundwater $\delta^{18}O$ values ranged from -12.5 to -25.3‰ and tended to increase southward. The $\delta^{18}O$ precipitation values predicted by GCMs follow a similar trend but increase more steeply southward. The difference in groundwater and GCM output can be explained by invoking movement of glacial ice and meltwater, along with mixing within groundwater systems. Most groundwater $\delta^{18}O$ values are higher than an average LIS $\delta^{18}O$ value of -25.4 ± 2.5‰ calculated based on estimated ice sheet volumes and sea level data.

1. Introduction

Stable isotopes of oxygen and hydrogen have been used in a number of studies to quantify impacts of Pleistocene glaciations on global water fluxes and ocean circulation [*Shackleton*, 1987; *Rahmstorf*, 2002]. However, the isotopic composition of the Laurentide Ice Sheet (LIS) remains elusive, with bulk paleo ice sheet $\delta^{18}O$ estimates varying from values as high as -15 down to -38‰ and often with no attempt to incorporate spatial variability [*Lambeck and Chappell*, 2001; *Flower et al.*, 2004; *Refsnider et al.*, 2012; *Wickert et al.*, 2013].

Liquid water has been observed beneath modern glaciers in a variety of settings [*Bell*, 2008]. This meltwater is produced where temperatures are sufficiently high due to various combinations of the insulating effect of overlying ice, geothermal gradients, pressure-induced melting, and heat generated by friction between the ice and the substrate. Rates of meltwater generation and the partitioning of meltwater into subglacial runoff and groundwater recharge are poorly constrained, although a variety of modeling approaches have been attempted [*Lemieux et al.*, 2008].

Stable isotopes of oxygen and hydrogen are commonly used to delineate fossil groundwater [*Clark and Fritz*, 1997]. In precipitation, oxygen and hydrogen vary in their stable isotope concentrations seasonally and by geographic location. In precipitation, δ^2H and $\delta^{18}O$ values usually plot on or near the global meteoric water line (GMWL) defined as $\delta^2H = 8 \times \delta^{18}O + 10$ [*Craig*, 1961]. Values plotting on or near the GMWL, but having δ^2H and $\delta^{18}O$ values that are lower than modern precipitation, are commonly interpreted as Pleistocene recharge [*Beyerle et al.*, 1998; *McIntosh et al.*, 2012]. Other lines of evidence, such as dating with radioisotopes [*Klump et al.*, 2008] and salinity [*Grasby et al.*, 2000], are also used to delineate groundwater with a subglacial or periglacial origin. The isotopic signals of recharge are not always preserved in the subsurface because of mixing with groundwater from other sources. These other sources are typically saline connate water, with an isotopic signal resembling marine sources, and modern precipitation. Both of these sources have $\delta^{18}O$ values that are typically much higher than Pleistocene ice sheets. Therefore, groundwater values may represent an upper bound for the $\delta^{18}O$ values of LIS-derived groundwater recharge. Nevertheless, some hydrogeological settings better preserve Pleistocene recharge. The Winnipeg Formation in Manitoba, a deep sandstone aquifer confined by a low-permeability shale layer, contains groundwater with lower $\delta^{18}O$ values than the overlying carbonate rock aquifer, which is semiconfined [*Ferguson et al.*, 2007]. The low-permeability Lake Agassiz clays overlying the carbonate rock aquifer also contain lower $\delta^{18}O$ values [*Remenda et al.*, 1994].

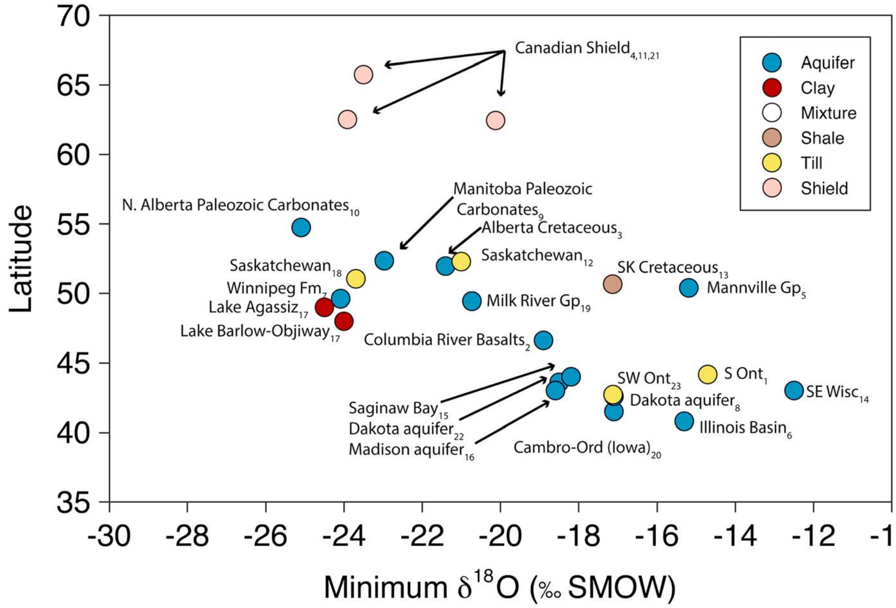

Figure 1. Distribution of minimum δ^{18}O values from groundwater studies with latitude. See Table S1 for sources.

Here we synthesize groundwater samples interpreted as glacial in origin from Canada and the northern United States along with isotope-enabled general circulation models (GCMs) [*Hoffmann et al.*, 1998; *Yoshimura et al.*, 2003; *LeGrande et al.*, 2006; *Risi et al.*, 2010; *Pausata et al.*, 2011; *Werner et al.*, 2011; *Jasechko et al.*, 2015]. The relationships between δ^{18}O values in groundwater and GCM output are compared to identify possible spatial trends in the δ^{18}O composition of the LIS.

2. Subglacial and Periglacial Groundwater Recharge

In this study we compiled δ^{18}O data from a number of groundwater studies spanning North America that invoked subglacial or preglacial recharge to explain low δ^{18}O values (Figure 1 and Table S1). There is evidence of a strong north-south trend in these data (Figures 1 and 2). The minimum δ^{18}O value of -25.1‰ is found in Northern Alberta, and values lower than -20‰ are found in both aquifers and aquitards throughout the Canadian Prairies. Values of -12.5 to -18‰ are found in groundwater in Iowa, Michigan, South Dakota, and Southern Ontario. In most aquifers, tills and clays, dispersion is thought to have had a minimal impact on the minimum δ^{18}O values. However, for some aquifers, such as the Mannville Group of Western Canada [*Hendry et al.*, 2013], the δ^{18}O values may reflect older glacial events or there may have been mixing with brines. Samples from the Canadian Shield in Northern Canada are the result of mixing subglacial water with in situ brine and are suggestive of a subglacial end-member of approximately -28‰ [*Clark et al.*, 2000; *Greene et al.*, 2008].

3. GCM Output

Output from five GCMs of the Last Glacial Maximum (LGM) was synthesized in this study: (a) CCSM3 [*Pausata et al.*, 2011] (b) European Centre/Hamburg (ECHAM) [*Hoffmann et al.*, 1998; *Werner et al.*, 2011] (c) Goddard Institute for Space Studies (GISS) [*LeGrande et al.*, 2006], (d) IsoGSM [*Yoshimura et al.*, 2003], and (e) LMDZ4 [*Risi et al.*, 2010]. The models span a range of spatial and temporal resolutions and isotopic/atmospheric parameterizations detailed within the above references. In brief, the isotopic composition of simulated precipitation is controlled by air mass mixing and by isotope effects during phase changes. Hydroclimatic processes influencing the isotopic composition of precipitation include sea surface meteorology, air mass trajectories, continental moisture recycling, and precipitation seasonality. Intermodel differences in parameterizations of these processes and isotope effects will lead to differences in simulated precipitation isotopic compositions. However, simulated precipitation δ^{18}O overlying the Laurentide Ice Sheet at the

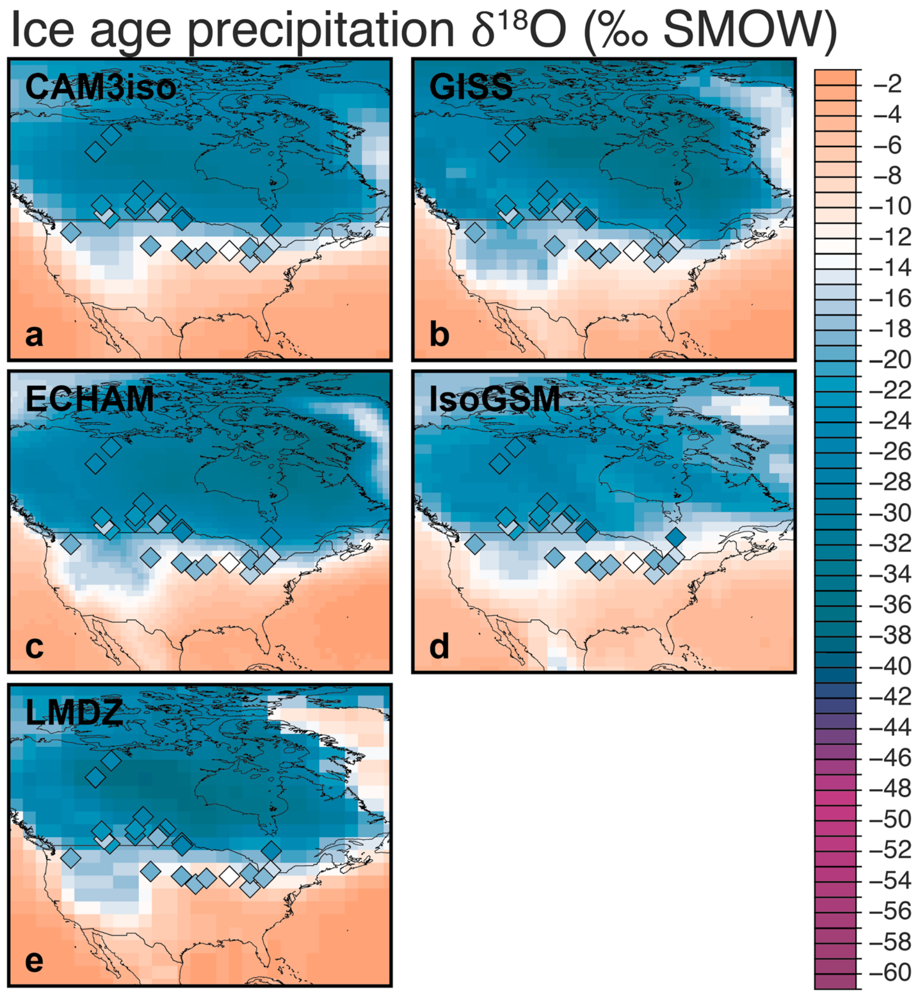

Figure 2. Output of δ^{18}O for the LGM from isotope-enabled GCMs: (a) CCSM3 [*Pausata et al.,* 2011], (b) ECHAM [*Hoffmann et al.,* 1998; *Werner et al.,* 2011], (c) GISS [*LeGrande et al.,* 2006], (d) IsoGSM [*Yoshimura et al.,* 2003], and (e) LMDZ4 [*Risi et al.,* 2010]. Diamonds represent δ^{18}O from groundwater samples. Both GCM and groundwater data use the same color scale.

LGM values amongst the various models is highly correlated (Table S2). R^2 values vary from 0.83 and 0.93 between the five models.

Simulated δ^{18}O precipitation values for the grid cells containing the minimum groundwater δ^{18}O values were collected. Groundwater δ^{18}O values and δ^{18}O values from GCMs at similar locations show high intermodel variability (Figure 2). The R^2 correlations between the output of simulations were significant at the $p < 0.05$ level in all cases, with $R^2 > 0.38$. IsoGSM- and ECHAM-simulated δ^{18}O values match observed groundwater δ^{18}O most closely (Figure S1 and Table S1), with $R^2 = 0.48$ in both cases. While the trends were captured reasonably well by all models, the RMS error was relatively high, ranging from 3.57‰ to 6.02‰.

4. Relationship Between Groundwater, GCM, and LIS δ^{18}O

The range of δ^{18}O in subglacial recharge is less than that in GCM output (Figure 2). Groundwater δ^{18}O values tend to be higher than simulated precipitation at higher latitudes and lower than simulated precipitation at lower latitudes (Figure 3). Movement of ice sheets and, depending on the situation, subglacial and/or periglacial runoff could be responsible for this discrepancy. Subglacial runoff is thought to be favored over subglacial recharge where the Canadian Shield was present beneath the Laurentide Ice Sheet [*Breemer et al.,* 2002; *Grasby and Chen*, 2005]. Recharge will be low in this region due to the low hydraulic conductivities of igneous and metamorphic rocks in the Canadian Shield. Between ice sheet

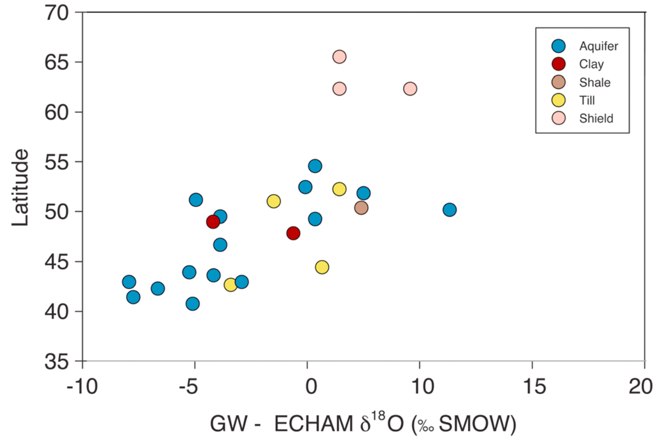

Figure 3. Minimum $\delta^{18}O$ values observed in groundwater are greater than $\delta^{18}O$ in precipitation from ECHAM output at higher latitudes. At lower latitudes, $\delta^{18}O$ in precipitation from ECHAM output exceeds observed groundwater $\delta^{18}O$ values.

movement and runoff, recharged water may integrate precipitation over distances reaching several hundred kilometers toward the center of the ice sheet. In regional flow systems, this water was often transported hundreds of kilometers away from the recharge area [*Grasby et al.,* 2000; *Person et al.,* 2007]. Regional flow systems were affected by glacial loading, favoring further movement of recharge away from the ice center in or near Hudson Bay [*Grasby et al.,* 2000; *Person et al.,* 2012]. These processes would allow for mixing that would decrease the $\delta^{18}O$ values in southern regions (Figure 3).

Movement of ice and meltwater is further complicated by variations in the isotopic composition of precipitation over time. Measurements from ice cores from Greenland indicate that between 40 ka and 15 ka, $\delta^{18}O$ varied by as much as 7‰ [*Blunier and Brook*, 2001], that is approximately 50% of the variation found in all groundwaters examined in this study. Models of the Greenland Ice Sheet have shown similar distributions of $\delta^{18}O$ with depth over time [*Clarke and Marshall*, 2002; *Lhomme et al.,* 2005]. Accretion of basal meltwater to the base of the ice sheet will also increase the $\delta^{18}O$ value of the ice sheet relative to precipitation [*Sugden et al.,* 1987; *Iverson and Souchez*, 1996]. The higher $\delta^{18}O$ values in the north (Figure 3) reflect melting of ice with a higher $\delta^{18}O$ value than precipitation at the LGM, which should coincide with a local minimum in the $\delta^{18}O$ record. Variations in $\delta^{18}O$ value in glacial ice will be less prominent in areas covered by the LIS for shorter periods of time, which includes lower latitudes [*Marshall et al.,* 2002].

Seawater $\delta^{18}O$ was 1.0 ± 0.1‰ higher than present at the LGM (as based on seafloor pore water samples [*Schrag et al.,* 1996]). Similarly, terrestrial ice volumes were 52,000,000 km^3 greater than today's (on the basis of eustatic sea level change [*Lambeck et al.,* 2000]). Applying an isotope mass balance means that the average isotope composition of additional ice at the Last Glacial Maximum was -25.4 ± 2.55‰, a lower value than 67% of subglacial groundwater samples compiled in this study (supporting information Tables S1 and S2). The poor spatial coverage of groundwater isotope samples in northern areas could explain this discrepancy. The estimated value of the subglacial component of groundwater in the Northwest Territories, Canada [*Clark et al.,* 2000], (−28‰) is slightly less than the estimated bulk value of the LIS, supporting this idea. The $\delta^{18}O$ measurements of Late Wisconsinan ice from ground ice in Yukon, Canada (−32 to −29‰) [*Kotler and Burn*, 2000], and the Barnes Ice Cap, Nunavut, Canada (−35‰) [*Refsnider et al.,* 2012], also indicate that groundwater samples from the south may not be representative of the bulk LIS $\delta^{18}O$ value. Further, greater than modern polar ice volumes embedded within the Antarctic and Greenland Ice Sheets [*Huybrechts*, 2002] with expectedly low $\delta^{18}O$ values may also partly reconcile this discrepancy (modern Greenland and Antarctic ice $\delta^{18}O$ range of −20‰ to −60‰). Future work using paleo ice sheet models equipped with stable isotope parameterizations could be used to constrain ice volumes of Northern Hemisphere versus polar ice sheet volumes that currently have large uncertainty (Table S3).

5. Conclusions

Groundwater recharged by the LIS shows a clear geographic trend that is related to the distribution of isotopes in precipitation and glacial processes. This is remarkable, given that the ages of these waters are variable and the cacophony of processes involved with subglacial hydrology. The isotopic data from groundwater suggest that it is generally not possible or useful to attempt to ascribe a single end-member

$\delta^{18}O$ (or δ^2H) value to the LIS, as commonly applied in current isotope-based deglaciation models. Future model development could incorporate this new data synthesis to better understand spatial heterogeneities of past ice sheets and embed these data into hydrologic models to constrain processes leading to the collapse of large, Northern Hemisphere ice sheets.

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