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$$\delta^{34}S = \frac{[(^{34}S/^{32}S)_{sam} - (^{34}S/^{32}S)_{CDT}]}{(^{34}S/^{32}S)_{CDT}} \times 10^3$$

where sam is the sample. The symbol δ is used only to present isotopic values relative to CDT. In many cases isotopic values are presented or discussed relative to some specified secondary reference point such as seawater sulfate or the S^0 used in the experiments.
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15. Model lines are generated from the following expression:

$$\delta^{34}S_t[X]_t = \delta^{34}S_{t-1}[X]_{t-1} + \delta^{34}S_{SR}\Delta[X]_{SR} + \delta^{34}S_{disp}\Delta[X]_{disp}$$

where $[X]_t$ is the measured concentration of either AVS or SO_4^{2-} at time t, $\delta^{34}S_t$ is the model predicted isotopic composition of X, and $\delta^{34}S_{t-1}[X]_{t-1}$ is the product $\delta^{34}S_t[X]_t$ from the previous time point; $\delta^{34}S_{t-1}$ is the isotopic composition of X either removed or added as a result of sulfate reduction (SR). In the control experiments sulfate reduction produced sulfide depleted in ^{34}S by 20 per mil relative to sulfate, and this value has been used. The quantity $\Delta[X]_{SR}$ is the change in the concentration of X between t and $t-1$; $\Delta[X]_{disp}$ is the change in X due to disproportionation, and $\delta^{34}S_{disp}$ is the isotopic composition of X added as a result of the fractionations accompanying disproportionation. This is the variable in the equation, and the lines are generated for different values of this parameter.
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Isotopic Composition of Old Ground Water from Lake Agassiz: Implications for Late Pleistocene Climate

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A uniform oxygen isotope value of −25 per mil was obtained from old ground water at depths of 20 to 30 meters in a thick deposit of clay in the southern part of the glacial Lake Agassiz basin. The lake occupied parts of North Dakota and southern Manitoba at the end of the last glacial maximum and received water from the ice margin and the interior plains region of Canada. Ground water from thick late Pleistocene–age clay deposits elsewhere, a till in southern Saskatchewan, and a glaciolacustrine deposit in northern Ontario show the same value at similar depths. These sites are at about 50°N latitude, span a distance of 2000 kilometers, and like the Lake Agassiz sites, have a ground-water velocity of less than a few millimeters per year. The value of −25 per mil is characteristic of meltwater impounded in the southern basin of Lake Agassiz. This value corresponds to an estimated air temperature of −16°C, compared with the modern temperature of 0°C for this area.

At some locations in the glaciated regions of North America and elsewhere, the stable-isotope content of old ground water provides a terrestrial record of pre-Holocene climate. Old ground water is usually associated with large confined aquifers with long residence times and long flow paths. However, complex mixing may dampen climate signals. Old ground water in thick unfractured aquitards also has long residence times but short travel paths and limited mixing. These aquitards may preserve isotopic signatures characteristic of the water that was incorporated at the time of deposition. On the basis of field measurements of hydraulic gradients and hydraulic conductivities and calculations of average linear ground-water velocities, we anticipate that original pore water is still present in thick aquitards deposited during the last glaciation (*1*). The isotopic signature of pore water from such aquitards could potentially yield climate information from the late Pleistocene.

In this report, we describe ground-water conditions at four field sites located in the aquitard deposited in the southern basin of glacial Lake Agassiz (Fig. 1). At the end of the last glacial maximum, Lake Agassiz occupied parts of North Dakota and southern Manitoba and was the receiving body for meltwater coming directly from the ice margin and from meltwater channels originating in western Canada (*2*). The sediments comprising the aquitard were deposited from about 11,700 to 9500 years ago, following a southward readvance of the ice sheet. The sediments range in thickness from about 10 to 80 m.

At the Montcalm site, about 50 km south of Winnipeg, 40 m of glaciolacustrine clay overlie 30 m of till. Dolostone underlies the glacial sediments. At the Emerson site, less than 1 km north of the Canada–United States boundary, 30 m of glaciolacustrine clay and 30 m of till overlie the same dolostone. At the Drayton site, 50 km south of the international boundary and 21 km west of the Red River, 76 m of Lake Agassiz deposits overlie 18 m of till and shale. At the Manvel site, 100 km south of the border, 28 m of clay overlie a thin till (1 to 2 m thick) underlain by sandstone.

At the Montcalm, Emerson, and Manvel sites, sediment cores were obtained. Monitoring wells were installed in vertical clusters through the clay (*3*), except at Emerson, where one till and one bedrock well were

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installed (*4*). At Montcalm, Manvel, and Drayton, rising head response tests were done to determine the hydraulic conductivity K (*5*). At Montcalm and Manvel, laboratory values of K were determined from core samples taken from the same depth interval at which each monitoring well was screened.

Water samples were obtained periodically from all of the monitoring wells that yielded enough water for samples. Groundwater samples from Montcalm, Drayton, and Manvel were analyzed for ^{18}O, ^{2}H, and ^{3}H. Pore water squeezed from core samples from Montcalm was analyzed for ^{3}H and ^{18}O. Pore water squeezed from core samples from Emerson was analyzed for ^{18}O (*6*).

Laboratory and field tests show that the values of K for the sediments deeper than 10 m are 3×10^{-11} m/s or less. Above 10 m, the values of K range from 1×10^{-10} to 5×10^{-10} m/s, presumably enhanced by fractures. Fractures, identified by oxide coatings, are common near the ground surface in most clayey deposits and can increase field K to values as much as two orders of magnitude greater than those measured on core samples (*7, 8*). At Montcalm, Drayton, and Manvel, the close agreement between field- and laboratory-measured values of K shows that the zone of abundant fractures does not extend more than a few meters below the ground surface.

At both Montcalm and Emerson, the average annual water table currently lies about 3 m below ground surface. Measured hydraulic heads are above ground surface in wells screened at depths ranging from 5 to 30 m in the clay at Montcalm and wells completed in the till and bedrock below the clay at Emerson. The calculated vertical hydraulic gradient i is 0.15 at Montcalm and 0.1 at Emerson. The water in the underlying dolostone aquifer is brackish and unsuitable as a water supply; therefore, it is unlikely that these gradients have been disturbed by pumping. For Montcalm, the average linear ground-water velocity v calculated from the mean field-measured K, $i = 0.15$, and the measured porosity $n = 0.5$ is 13 m per 10^4 years (*9*). The same calculation with the laboratory-measured K gives 9 m per 10^4 years. For Emerson, the same ranges of K give v from 9 to 6 m per 10^4 years. For these velocities and thicknesses of clay (40 m at Montcalm and 30 m at Emerson), little advective displacement of original Lake Agassiz pore water should have occurred at either site since deposition.

At Drayton, where there are 76 m of clay, measured hydraulic heads from wells screened at depths ranging from 5 to 28 m are at or above ground surface, and $i = 0.03$. Assuming that this gradient has been undisturbed by pumping and using the measured $K = 1 \times 10^{-11}$ m/s and $n = 0.5$, we find v to be 1 m per 10^4 years.

The artesian Dakota aquifer underlies the Manvel site. The hydraulic head of the aquifer has decreased in this century because of unchecked exploitation (*10*). The best estimate of hydraulic head in the aquifer before pumping is 14 m above ground surface on the basis of a record for one well in the town of Manvel (*11*), less than 1 km from the Manvel site. The present mean gradient is 0.2. For this gradient, $v = 25$ m per 10^4 years. For a hydraulic head of 14 m above ground surface and the present depth to the water table of about 3.5 m, the estimated paleogradient is 0.63 and $v = 80$ m per 10^4 years. In this case, upward ground-water flow would have displaced all or most of the original pore water in the clay with water from the underlying Dakota aquifer.

At Montcalm, ^{3}H concentrations (*6*) measured on water extracted from core samples from depths of 7 to 30 m (0.8 to 1.6 TU, with one sample at 3.5 TU) were near the nominal counting detection limit (± 0.8 TU). Considering the extraction and counting procedure, these levels are insignificant. At Manvel, ^{3}H concentrations measured on samples from wells screened at 10 and 19 m below ground surface were also insignificant ($<0.8 \pm 0.5$ TU). The lack of significant ^{3}H below the surficial weathered zone is an indication that modern water (from after 1963) has not penetrated into the unweathered clay.

In the southern basin of Lake Agassiz, modern meteoric precipitation has average values of -13 to -14 per mil (*12*). Late Pleistocene precipitation in this region should have had considerably lower $\delta^{18}O$ values because of a much colder climate. The $\delta^{18}O$ values in ground water are unlikely to be altered by mineral-water reactions below 50°C (*13, 14*).

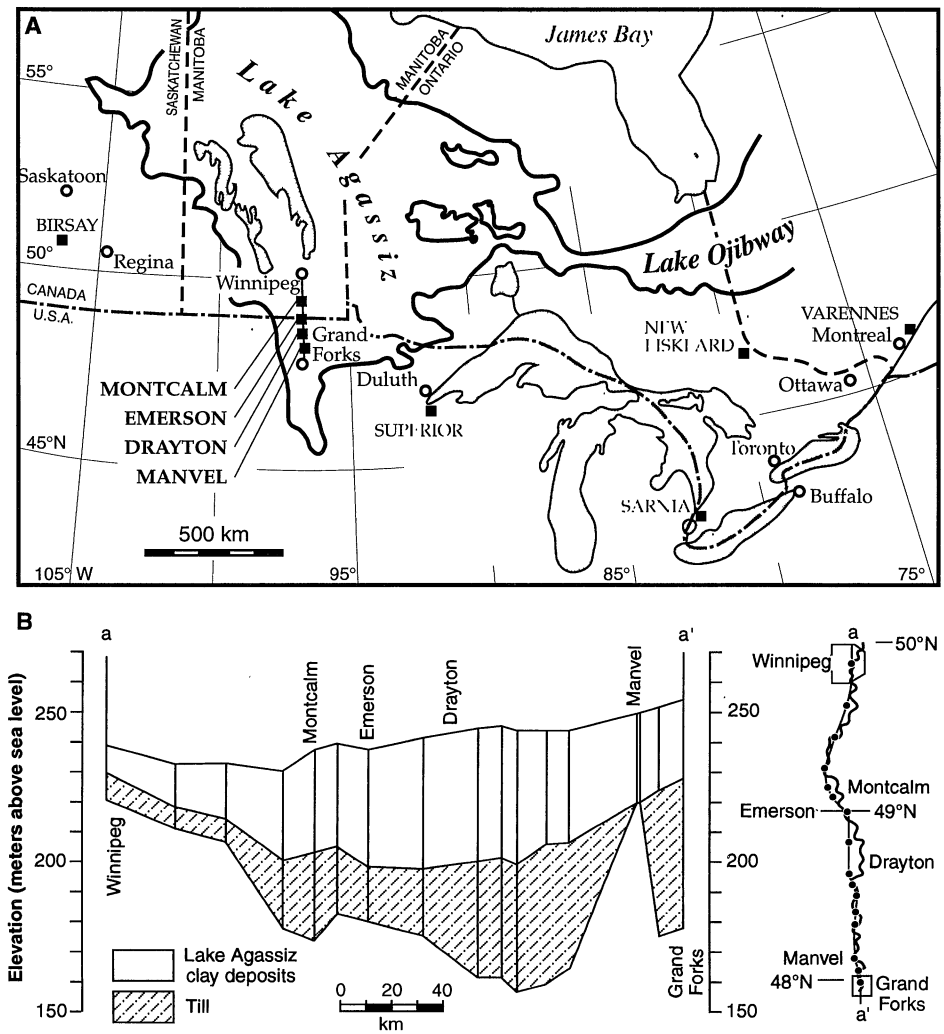

Fig. 1. (**A**) The maximum of extent of glacial Lake Agassiz (*2*) with locations of aquitard field sites (■). Additional sites in glacially deposited aquitards are located in southern Saskatchewan, northern Wisconsin, southwestern Ontario, northern Ontario, and Quebec. (**B**) The cross section from Winnipeg, Manitoba, to Grand Forks, North Dakota, shows the thickness of deposited clay, underlying till, and bedrock under the glacial lake.

From the hydraulic conditions at Montcalm, Emerson, and Drayton, we expect that late Pleistocene water is present deep in the clay at these sites (*15*). At Manvel, however, hydraulic conditions suggest that the original pore water has been mixed with or replaced by water flowing upward from the underlying aquifer.

The profiles of $\delta^{18}O$ values at Montcalm, Emerson, and Drayton (Fig. 2) are essentially the same. The $\delta^{18}O$ values in the shallow ground water are at or slightly below the average value for modern precipitation. The values decrease with depth to a uniform value of −24.5 per mil between 20 and 30 m. At both Montcalm and Emerson, there is a subsequent increase in $\delta^{18}O$ in the underlying till. There are no wells below 30 m at Drayton. The substantial contrast between the zone of depleted $\delta^{18}O$ at depth and that at ground surface and in the underlying till at Montcalm and Emerson suggests that little displacement of pore water has occurred. This is consistent with the ground-water velocity estimates from the hydraulic data. Because the same depleted $\delta^{18}O$ value is found deep in the clay at the three sites, which span a distance of 60 km, we conclude that the range of −24 to −25 per mil is characteristic of the water impounded in the southern part of the Lake Agassiz basin at the end of the late Pleistocene.

At Manvel, $\delta^{18}O$ in the shallow ground water is similar to meteoric water. The $\delta^{18}O$ value decreases to −19.6 per mil at depth and increases to about −18 per mil near the interface of the till and underlying Dakota aquifer (Fig. 2). The $\delta^{18}O$ values of several samples of Dakota aquifer water from Grand Forks County are −18 per mil (*16*). The lowest $\delta^{18}O$ value measured at Manvel, −19.6 per mil, is higher than the low value of −24.5 per mil measured at Montcalm, Emerson, and Drayton. Together with the velocity calculation, this higher value suggests that the pore water has been displaced by or mixed with water from the underlying Dakota aquifer.

Except for one core sample, $\delta^{18}O$ and $\delta^{2}H$ values of core samples from Montcalm and well samples from Montcalm, Manvel, and Drayton lie along the local meteoric water line (MWL) for Gimli, Manitoba (*12*), and within 1σ of the global MWL (*17*) (Fig. 3). This indicates that there has been no significant alteration of the isotopic signature as a result of evaporation, mineral exchange, or invasion by an isotopically different water.

The $\delta^{18}O$ values for shallow ground water, deep ground water, and average meteoric precipitation compiled for other sites in thick late Pleistocene–age aquitards in northern North America (Fig. 4) show that the greatest difference between $\delta^{18}O$ values for shallow ground water and deep ground water occur at the Lake Agassiz sites. Shallow ground water and average precipitation are similar in most areas, although in semiarid Saskatchewan, shallow ground water is somewhat enriched compared with the average annual precipitation, probably as a result of evapotranspiration before or during recharge.

The very depleted values of −24 to −25 per mil from Montcalm, Emerson, and Drayton are similar to values from deep ground water in glacial till at the Birsay site in southern Saskatchewan (−25.1 per mil; 50°N) (*18*) and in a glaciolacustrine deposit at the New Liskeard site in northern Ontario (−24 per mil; 48°N) (*19*).

Of these five sites, four, including New Liskeard, are situated in glaciolacustrine sediments deposited at the end of the last glacial maximum; Birsay is situated in glacial till that was deposited in the previous glaciation. Although these sites occur at roughly the same latitude, they are separated by a distance of 2000 km. The presence of the same negative $\delta^{18}O$ values in thick unweathered deposits ranging from Saskatchewan to Ontario suggests that −24 or −25

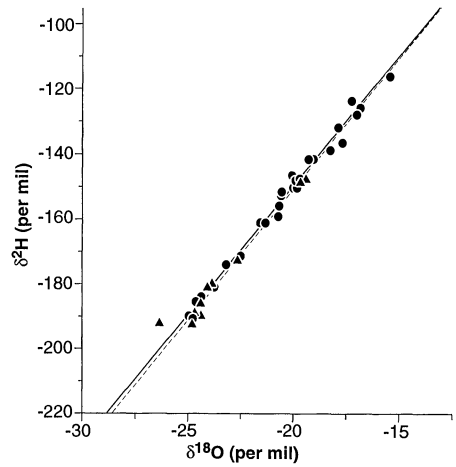

Fig. 3. Plot of $\delta^{18}O$ versus $\delta^{2}H$ for water samples taken from monitoring wells installed at Drayton, Montcalm, and Manvel (●) and for pore water squeezed from clay samples at Montcalm (▲). The Gimli MWL [solid line; $\delta^{2}H = 7.8\ \delta^{18}O + 6.2$ (*12*)] is indistinguishable from the global MWL [dotted line; $\delta^{2}H = 8\ \delta^{18}O + 10$ (*17*)].

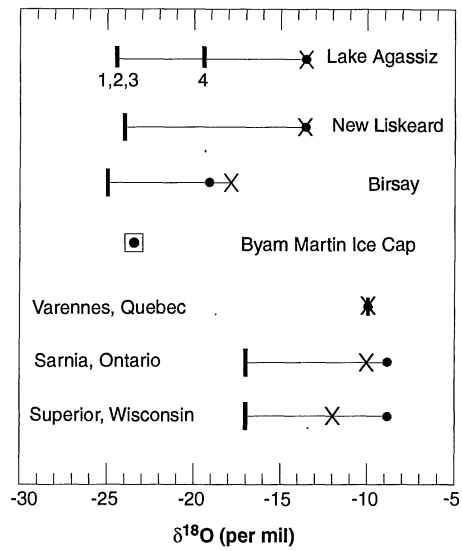

Fig. 4. Summary of $\delta^{18}O$ values (relative to VSMOW) of shallow (×) and deep (|) ground water and of average precipitation (●) at field locations in aquitards in northern North America (*1, 18, 19, 24*). Numbers 1, 2, 3, and 4 in the Lake Agassiz data refer to the Montcalm, Drayton, Emerson, and Manvel sites, respectively. The boxed point is from glacier runoff from the Byam Martin Ice Cap (*22*).

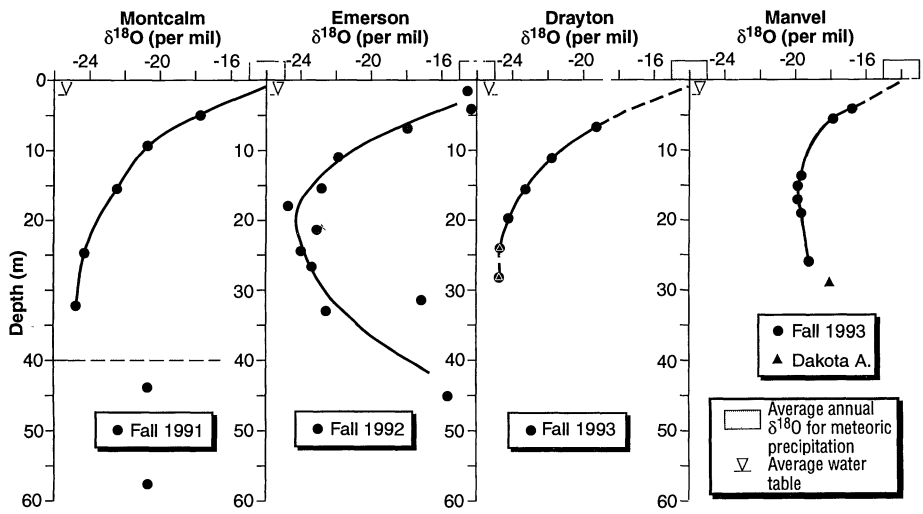

Fig. 2. The $\delta^{18}O$ values (relative to VSMOW) of ground water sampled from monitoring wells at Montcalm, Drayton, and Manvel and from cores at Emerson. A reading from the Dakota aquifer is included in the Manvel data.

per mil was the average $\delta^{18}O$ signature of melting glacial ice at the end of the late Pleistocene in a zone of 48° to 50°N.

Although the relation between air temperature and the $\delta^{18}O$ value of precipitation is not always straightforward, the observed $\delta^{18}O$ values of −24 and −25 per mil yield paleotemperature estimates of −15.0° to −16.4°C (*20*). These values fall within the range of estimates from paleoclimate simulations that indicate that mean annual surface air temperature in the region (north-central North America) increased from about −18°C at 12,000 years ago to about −10°C at 10,000 years ago (*21*). A shift of 10 per mil in the $\delta^{18}O$ value of precipitation (from −24 to −25 per mil to the present value of −13 to −14 per mil) and a warming of 10° to 18°C gives a slope of 0.55 to 1.1 per mil per degree Celsius, which is within the expected slope of $\delta^{18}O$ with temperature at mid- to high latitudes. Equivalent modern conditions of depleted $\delta^{18}O$ (−24 per mil) and low temperature (−15°C) currently exist 2500 km north of the study area at the southern margin of the Byam Martin Ice cap, Bylot Island (73°N) (*22*).

These results indicate that thick, unweathered clayey deposits can maintain ^{18}O signatures in pore water over 10,000 or more years because ground-water flow and mineral-water interaction are insignificant. Under the favorable hydrogeologic conditions provided by these thick aquitards, isotopic signatures of deep ground water can be related to climatic conditions of the late Pleistocene.

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3. At Montcalm, five polyvinyl chloride (PVC) monitoring wells with outer diameters of 1.9 cm were installed in a cluster through the clay. The method of installation is detailed in (*23*). Additional monitoring wells were installed in till and bedrock by hydraulic rotary methods. The till and bedrock wells were pumped to remove drilling fluid that might have contaminated ground–water samples. Water levels were monitored from June 1991 to October 1992. At Emerson, one well was installed in the till and one in the bedrock. At Drayton, six wells were driven into the clay, the deepest of which was 28 m below ground surface, and the remaining five were installed at intervals of 4.3 m. The method of installation was detailed by W. W. Woessner, V. H. Remenda, R. Ingleton, and V. Kuhnel [in *Proceedings of the North Dakota Water Quality Symposium* (North Dakota State University Extension Service, Bismarck, 1991), pp. 292–301]. Water levels have been monitored biweekly since the time of installation. At Manvel, 14 single monitoring wells (90 series) were installed as above at 2-m intervals to a depth of 26 m. An additional eight wells were driven into the clay (91 series), the deepest of which was 25 m below ground surface. Water levels in the 90 series have been measured weekly, and water levels in the 91 series have been measured biweekly since their installation.
4. R. N. Betcher, unpublished data.
5. Response tests were performed in each monitoring well by either monitoring the equilibration of newly installed wells or by removing a slug of water and recording the time for reequilibration. The method of M. J. Hvorslev ["Time Lag and Soil Permeability in Ground Water Observations," *Waterways Exp. Stn. Bull. 36* (U.S. Army Corps of Engineers, Vicksburg, MI, 1951)] was used to determine K. At both Montcalm and Manvel, core samples taken from the same interval over which each well was screened were used for laboratory hydraulic conductivity testing. This allowed a direct comparison of laboratory- and field-measured values of K. Montcalm core samples were tested with a triaxial cell that closely approximated field conditions. Laboratory hydraulic conductivity (consolidation) tests on cores from selected depths at the Manvel site were performed by the root time method [R. F. Craig, *Soil Mechanics* (Chapman & Hall, London, ed. 4, 1987)].
6. The ^{18}O and ^{2}H analyses were performed at the University of Waterloo Environmental Isotope Laboratory following the method of S. Epstein and T. K. Mayeda [*Geochim. Cosmochim. Acta* **4**, 213 (1953)]. The results are expressed in the δ per mil notation relative to Vienna standard mean ocean water (VSMOW). The analytical precision for $\delta^{18}O$ was better than ±0.15 per mil and for $\delta^{2}H$ was better than ±1.5 per mil. The ^{3}H analyses were performed at the University of Waterloo Environmental Isotope Laboratory by liquid scintillation counting on water samples. Water samples were enriched by distillation before counting to improve the detection limit (0.5 to 1.1 TU). The ^{3}H values are expressed as TU, where one TU is equal to one ^{3}H atom in 10^{18} ^{1}H atoms.
7. Field measurements may underestimate K because the well screens fail to intersect hydraulically conductive features (*23*) or because the clay is smeared around the drivepoint. Laboratory measurements may overestimate K because the samples are disturbed or there are small leaks in consolidation equipment [C. E. Neuzil, *Water Resour. Res.* **30** (no. 2), 145 (1994)].
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9. The average linear ground-water velocity $v = -(Ki)/n$ is used to estimate a theoretical displacement of water and does not account for mixing as a result of mechanical dispersion or diffusion. We use the measured total porosity n to represent the solute transport porosity rather than an effective hydraulic porosity n' because the value of n' cannot be measured independent of a tracer. In the only study of solute transport porosity of Pleistocene clayey sediments of which we are aware (*19*), ^{3}H and ^{36}Cl were advected at high hydraulic gradients through core samples of two different media, one a silty clay till and the other a glaciomarine clay. In the case of the silty clay till, the elution curves of ^{3}H and ^{36}Cl were identical and provided a transport volume equal to the total porosity measured (0.64). For the glaciomarine clay, ^{36}Cl was eluted faster than ^{3}H, suggesting that the solute transport porosity (n' = 0.49) for ^{36}Cl was smaller than the total porosity (n = 0.64). The tracer in our study is ^{18}O, and as part of the water molecule, it is not expected to be expelled from pore spaces as a negatively charged species might be. In addition, because advection is small and diffusion is the dominant transport mechanism, all of the pore spaces are available for tracer movement. One-dimensional analytical transport simulations in the form of sensitivity analyses were performed for the Manvel and Montcalm sites (*18*), the Birsay site in Saskatchewan (*19*), and the New Liskeard site in Northern Ontario (*20*). For each site, the initial $\delta^{18}O$ of the pore water was taken to be −24 or −25 per mil. At the upper boundaries, the input $\delta^{18}O$ ranged from values corresponding to modern meteoric precipitation for that area (−13 to −14 per mil for Lake Agassiz and New Liskeard; −19 per mil for Birsay) to the value found in shallow ground water (−16 to −15 per mil in Lake Agassiz and New Liskeard; −17.5 per mil at Birsay). The effective diffusion coefficients ranged from 1×10^{-10} to 5×10^{-11} m^2/s, which is within the expected range. The calculated v and known times (ranging from 11,000 to 9500 years ago) were used. The simulations show that with the exception of the Manvel site, diffusion is the dominant transport mechanism and advection is minor or negligible. The simulations are sensitive to the initial $\delta^{18}O$ value of the pore water, and the present-day distribution can be simulated only with initial values in the range of −25 per mil. Neither lower nor higher initial values provide a reasonable match to the observed distributions.
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15. The geologic record of the study area shows no evidence for the burial of or glacier advance over the sediments that form the aquitard. Thus, changes in porosity would have occurred only as a result of compaction caused by the weight of the overlying water and, after lake retreat, the weight of the sediments themselves. Once the lake drained, the strong gradients from the underlying bedrock formations would have likely prevented the downward movement of pore fluid; therefore, fluid released during consolidation would have migrated upwards. The upward migration of water would have hindered the downward movement of $\delta^{18}O$ enriched relative to that found in the original pore fluid.
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20. A target air temperature can be estimated as $\delta^{18}O = 0.695T - 13.6$, where $\delta^{18}O$ is annual mean $\delta^{18}O$ of precipitation and T is average annual surface air temperature in degrees Celsius [W. Dansgaard, *Tellus* **16** (no. 4), 436 (1964)], assuming that this relation is valid for the late Pleistocene. That the aquitard was deposited during lake phases that occurred as a result of the melting of a southward readvance of the ice sheet suggests that the water represents, for the most part, precipitation from the region north of the lake. For a $\delta^{18}O$ value of −24.5 per mil, the average air temperature is −16°C, which is about 17°C colder than the current mean average air temperature (~0°C) in southern Manitoba and northern North Dakota. The modern value of $\delta^{18}O$ for annual precipitation of −13 or −14 per mil gives a calculated temperature of ~0°C. The same relation used to calculate air temperature from $\delta^{18}O$ of −23 to −24 per mil for Byam Martin Ice Cap, Bylot Island, gives −14°C; the measured mean annual air temperature is −15°C (*22*).
21. J. E. Kutzbach, in *North America and Adjacent Oceans During the Last Deglaciation*, W. F. Ruddiman and H. E. Wright Jr, Eds., vol. K-3 of *Geology of North America* (Geological Society of America, Denver, CO, 1986), pp. 425–446.
22. M. Elver and F. Michel, abstract in the program from the Joint Annual Meeting of the Geological Association of Canada and the Mineralogical Association of Canada, Waterloo, Ontario, 16 to 18 May 1994, p. A33.
23. A. Y. D'Astous, W. W. Ruland, J. R. G. Bruce, J. A. Cherry, R. W. Gillham, *Can. Geotech. J.* **26**, 43 (1989).
24. D. E. Desaulniers and J. A. Cherry, *ibid.*, p. 80.

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