

## Isotopic characteristics of ice cover in a large northern river basin

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### Abstract:

Isotope stratigraphy of river-ice covers can be applied to reconstruct time-series of the stable isotopic composition of winter streamflow, although careful attention to ice type, morphology and location of sampling is required to obtain useful results. Ice surveys conducted in the Liard River Basin, northwestern Canada, suggest that the isotopic composition of winter streamflow is relatively invariant along the main river stem. However, systematic isotopic enrichment is observed over the course of the winter for small tributaries draining discontinuous-permafrost wetlands, and is attributed to shifts in the isotopic composition of source water. Recommendations for further study required to verify the underlying physical processes associated with this response are outlined. Copyright © 1999 John Wiley & Sons, Ltd.

KEY WORDS stable isotopes; oxygen-18; deuterium; isotope fractionation; river ice

### INTRODUCTION

Little is known about sources and variability of winter streamflow in large northern rivers of Canada. In general, winter streamflow is thought to consist mainly of groundwater, and outflow from large lakes with outlets that do not freeze to bottom in winter. Lesser contributions, which presumably diminish over the course of freeze-back, are expected from interflow, fall snowmelt runoff, and outflow from shallow lakes and wetlands.

To gain a better understanding of these processes, and to examine the potential for use of isotopic methods in studying winter flow characteristics, a baseline river-ice and water sampling program was conducted in the Liard River Basin (Figure 1) during late March 1997. Primarily, the study was designed to test isotope river-ice stratigraphy as a strategic method for determining the isotopic composition of winter streamflow, and for examining potential changes in source-water contributions from the time of freeze-up (mid-October) until late winter. Similar methods have been applied to study formation of permafrost (Michel, 1982), frost blisters (Michel, 1986), winter groundwater exchange in lakes (Bowser and Gat, 1995), under-ice spreading rates of Mackenzie River water in the nearshore Arctic Ocean (Macdonald *et al.*, 1995) and for examining sea, lake, and river-ice processes in general (Eichen, 1998; Ferrick *et al.*, 1998).

The Liard River is the largest tributary of the Mackenzie River downstream of Great Slave Lake, draining an total area of 277 000 km<sup>2</sup> consisting of upland-alpine areas of Western Cordillera, and wetland-

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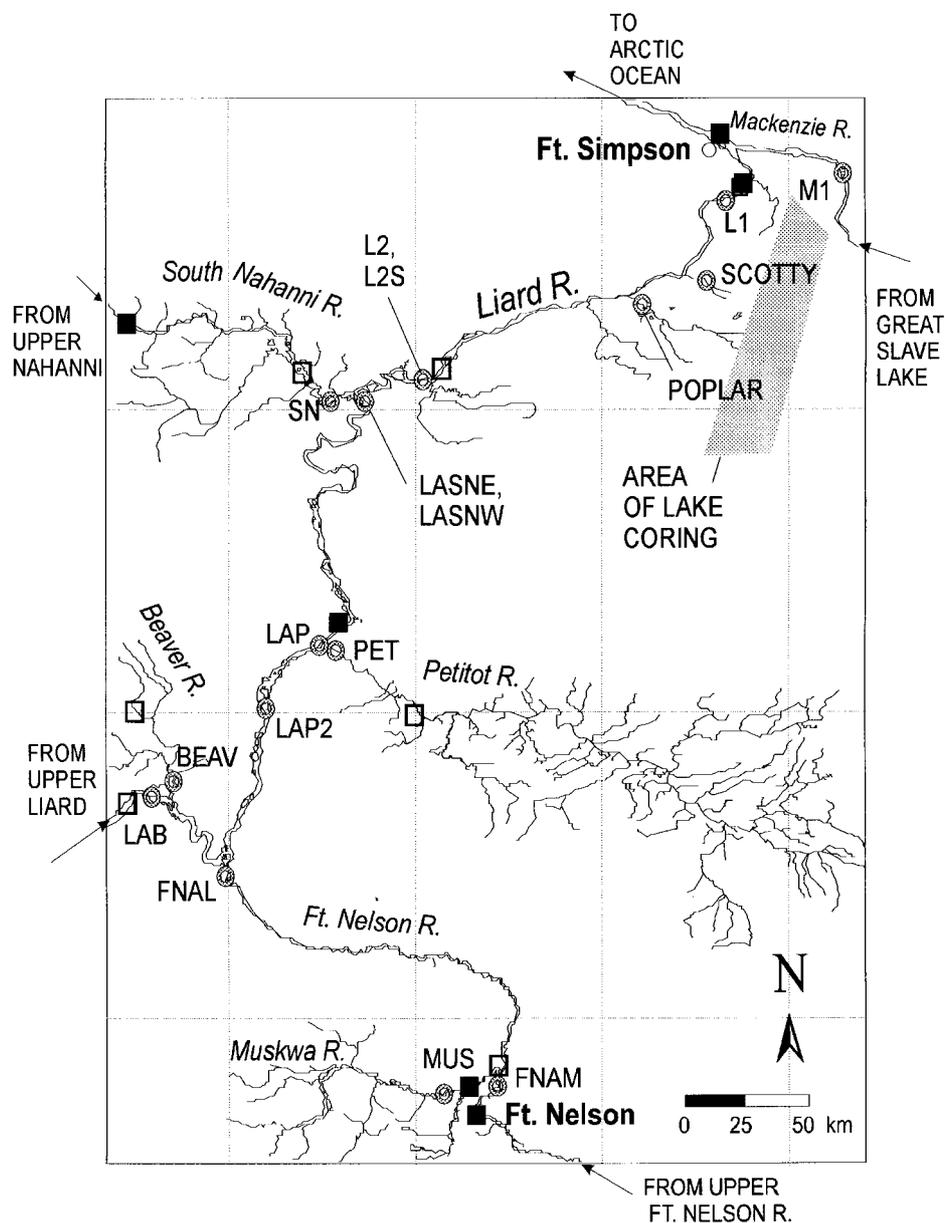


Figure 1. Map of lower Liard River, Canada showing coring locations (circles). Also shown are Water Survey of Canada stream gauging stations in operation during the winter of 1997 (solid boxes), and previously discontinued stations (open boxes)

dominated areas of northeastern British Columbia, Alberta and the Northwest Territories (see Prowse, 1986). Due to a mixture of alpine and wetland sources, the flow regime of the Liard River is complex, although tributaries are often distinctly labelled by their isotopic composition (Hitchon and Krouse, 1972). For these reasons, the Liard Basin was considered a good target for evaluating the utility of isotopic methods for analysing winter streamflow. A summary of the primary results of the program, including promising applications are presented.

The paper begins with a review of relevant theory which provides a basis for discussion. Isotopic results are reported as values which express isotopic ratios as deviations in per mille (‰) from Vienna-SMOW (Standard Mean Ocean Water), such that

$$\delta_{\text{SAMPLE}} = 1000((R_{\text{SAMPLE}}/R_{\text{SMOW}}) - 1) \quad (1)$$

where  $R$  is  $^{18}\text{O}/^{16}\text{O}$  or  $^2\text{H}/^1\text{H}$ .

## THEORY

### *Isotopic fractionation during freezing*

Isotopic fractionation occurs in the ice-water system during freezing as the rare, heavy isotopic species of water ( $^1\text{H}^1\text{H}^{18}\text{O}$  and  $^1\text{H}^2\text{H}^{16}\text{O}$ ) are preferentially incorporated into the ice phase relative to the common light species ( $^1\text{H}^1\text{H}^{16}\text{O}$ ). In the case of thermodynamic equilibrium between phases, this exchange can be expressed by a reaction rate constant also known as the equilibrium isotopic fractionation  $\alpha$  given by

$$\alpha_{\text{ice-water}} = \frac{R_{\text{ice}}}{R_{\text{water}}} \quad (2)$$

such that  $\alpha = 1$  for zero fractionation and  $\alpha > 1$  for natural freezing conditions. For convenience, equilibrium fractionation is commonly expressed using the isotopic separation factor  $\varepsilon$  defined by

$$\varepsilon_{\text{ice-water}} = 1000(\alpha - 1) \approx \delta_{\text{ice}} - \delta_{\text{water}} \quad (3)$$

in per mille (‰). Experimentally determined  $\varepsilon_{\text{ice-water}}$  near 0 °C at natural freezing rates (<2 mm/hr), in freshwater systems is about 2.8 to 3.1‰ for oxygen (Suzuoki and Kimura, 1973, O'Neill, 1968) and 17.0‰ to 20.6‰ for hydrogen (Kuhn and Thürkau, 1958, Arnason, 1969, see also Moser and Stichler, 1980). Isotopic fractionation has been shown to decrease by up to 50% in the case of very rapid freezing (>50 mm/hr, Arnason 1969), when liquid-phase mixing is inhibited (e.g. incorporation of expelled water, Suzuoki and Kimura 1973), or due to increased salinity (Macdonald *et al.*, 1995).

For freezing in an ideal open-system, where ice is formed *in situ* at slow, natural rates from source water which is rapidly flowing and well-mixed, (i.e. without a reservoir effect), it follows that isotopic composition of ice will remain constant with depth and enriched by the equilibrium separation relative to the feedwater source (open circles, Figure 2). In natural lakes and rivers, the average winter ice cover is typically found to be isotopically enriched by a value slightly less than the equilibrium separation as controlled by the ice-water boundary layer thickness (a measure of advection/diffusion in the liquid), and ice growth velocity (Ferrick *et al.*, 1998), but also due to formation of snow ice in the upper layers (Bowser and Gat, 1995).

For well-mixed, closed systems, where a water body is isolated from input and output, the isotopic composition of ice and water can become progressively enriched with time as the water body is frozen according to a Rayleigh-type fractional crystallization process (closed circles, Figure 2). In this situation, the instantaneous isotopic composition of new ice ( $\delta_R$ ) is given by

$$\delta_R = (\delta_0 + 1000)f^{(\alpha-1)} - 1000 \quad (4)$$

where  $f = V/V_0$  is the fraction of water remaining,  $V$  and  $V_0$  are the volume of the liquid at the time of ice formation and the initial volume, respectively, and  $\delta_0$  is the isotopic composition of the original liquid. As observed in frost-blister ice (Michel, 1986), and ice covers on shallow tundra lakes (Gibson, 1996), closed-system freezing can produce isotopic gradients in ice that are significantly larger than 3‰ and 20‰ in oxygen and hydrogen, respectively due to this reservoir effect.

An intermediate scenario is also depicted, as for the case of restricted circulation in a semi-closed system. In this example (shaded circles, Figure 2), isotopic changes are predicted to be intermediate between that of

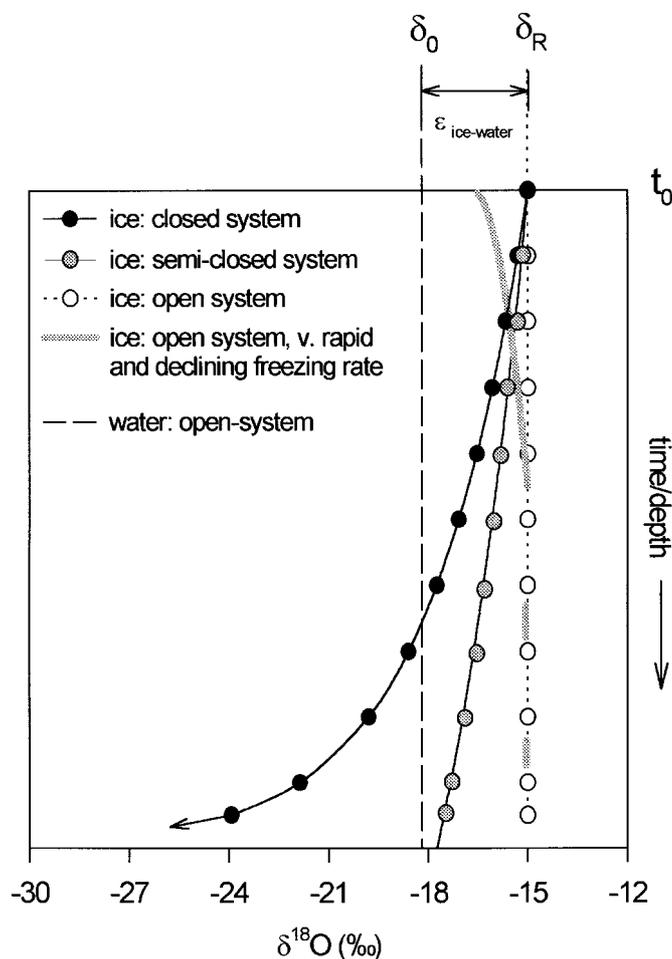


Figure 2. Theoretical development of vertical isotopic profiles in ice cover due to ice-water fractionation effects at 0 °C for the following scenarios: (1) closed-system fractionation (closed circles) where ice is progressively enriched under a Rayleigh-type condition; (2) semi-closed system fractionation (grey circles) where residual water is subject to restricted throughflow, and the isotopic composition of ice is enriched to levels intermediate between (1) and (2); (3) open system fractionation (open circles) where water with constant  $\delta^{18}\text{O}$  circulates freely beneath the ice cover, and ice composition remains constant with time/depth; and, (4) very rapid early freezing (i.e. 50 mm/hr) followed by gradual decline in freezing rates to 1 mm/d producing a slight enrichment in isotopic composition with time/depth.  $\delta_0$  and  $\delta_R$  are the isotopic compositions of water and ice, respectively, at time  $t_0$

the open and closed systems. In all the above cases, where freezing rates are maintained at slow natural rates, isotopic fractionation effects will result in either constant or progressive isotopic enrichment of an ice cover with depth. One complicating factor in natural systems is that isotopic fractionation is predicted to vary with the rate of freezing, which generally decreases with time  $t$  or depth at close to  $\sqrt{t}$  (Prowse, 1995). As such, freezing-rate effects may potentially result in a net depth increase in isotopic composition of an ice cover of about 1.5‰ and 10‰ in  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ , respectively under extreme conditions, given a constant source water composition (heavy grey line, Figure 2). In this case, extreme conditions are depicted as a surface-to-depth transition from very rapid freezing (Arnason, 1969) to slow freezing, with a corresponding increase in the isotopic fractionation factors from about 0.5  $\epsilon$  to 1  $\epsilon$ . Freezing-rate and reservoir effects may combine to produce more complicated patterns in natural ice covers (not shown).

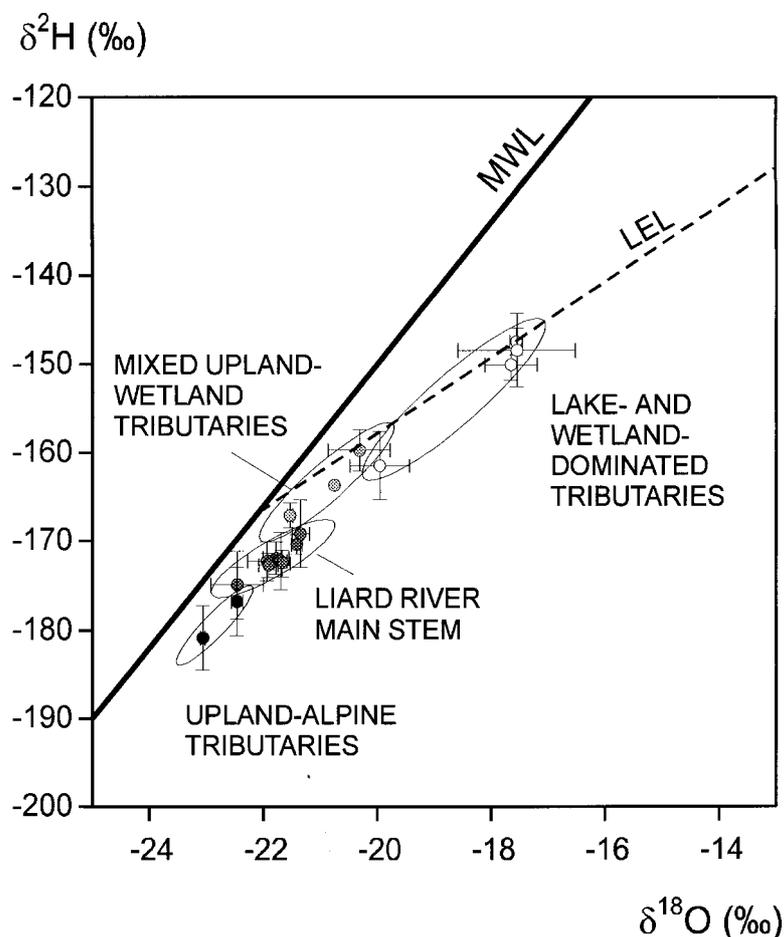


Figure 3. Plot of  $\delta^{18}\text{O}$  versus  $\delta^2\text{H}$  showing mean water compositions reconstructed from congelation ice (see source fingerprints and macro-scale partitioning). Error bars denote 1 s of observed variability. Note that lake and wetland-dominated tributaries plot close to the local evaporation line (LEL) previously established for the area (Gibson *et al.*, 1993a). Other waters lie near but slightly below the meteoric water line (MWL). See text for discussion

#### Source signals and mixing

Additional vertical isotopic variations in ice cover can result from changes in source water during the course of freezing, and these are generally more interesting from a hydrologic perspective. In natural systems, source waters are often distinctly labelled by their isotopic composition as a product of their origin, mixing, and evaporation history. On a plot of  $\delta^{18}\text{O}$  vs.  $\delta^2\text{H}$  (Figure 3), precipitation samples generally fall close to the meteoric water line (MWL) defined by  $\delta^2\text{H} = 8 \cdot \delta^{18}\text{O} + 10$  (Craig, 1961) while evaporated waters (i.e. waters exposed to open-water evaporation during residency in the basin) plot distinctly below the MWL along local evaporation lines (LEL) with slopes ranging from about 4 to 6. As shown for data collected during this study (Figure 3), tributary isotopic signatures vary systematically according to type, primarily reflecting differences in sub-basin water balance regime, but also, to a lesser degree, as a result of spatial variations in precipitation input (see also Hitchon and Krouse, 1972). Less temporal variability is observed at locations along the main river stem where waters are predominantly comprised of a mixture of several source areas.

Seasonal and event-related changes in the isotopic composition of tributary discharge have also been observed in response to snowmelt and summer rainfall episodes in the lower Liard Basin (Gibson *et al.*,

1993b). Although flow and isotopic variability in cold-regions is commonly subdued or absent during the winter months, potential changes are likely to be more readily observed in small, uniform tributaries with isotopically distinct source waters.

Overall, it is significant to note that potential changes in the isotopic composition of ice cover may result from variations in source water which may comprise groundwater, snowmelt, or surface water. A more general discussion of isotopic labelling of individual water sources is given in Gat and Gonfiantini (1981).

#### *Other effects*

Other river-ice processes such as frazil accumulation, overflow, snow incorporation, and thermal ice erosion can lead to perturbations in the expected stratigraphic trends discussed above. In general, the best archive of isotopic changes occurring in source water is obtained from congelation ice (black ice that is crystallized *in situ* from water) which can be distinguished from other ice types by morphology and texture (Ashton, 1986). For obvious reasons, white ice which may contain frazil or snow and/or air bubbles) is found to be a less reliable archive of isotopic changes in the liquid.

## FIELD WORK AND METHODS

### *Location*

Ice surveys were conducted by helicopter in late March 1997. Coring targets were selected based on proximity to hydrometric gauging stations, knowledge of river morphology, and the likely presence of congelation ice as determined from the aircraft prior to landing (i.e. smooth ice reaches). Areas where tributary runoff had not fully mixed with the main stem flow were avoided. Coring locations were determined precisely using a GPS (Global Positioning System).

### *Sampling*

Cores were extracted using a gas-powered 70.8 mm-diameter ice coring device, capable of extracting continuous cores of up to 750 cm. Extensions were available so that cores could be obtained on ice covers up to 150 cm-thick. Once extracted, cores were extruded from the core barrel onto a clean polyethylene tarp using a manual piston, photographed, and logged for ice type and thickness. Cores were split into between 5 and 10 sub-samples which were subsequently transferred to thick-walled HDPE (high density polyethylene) bags, sealed and returned to base camp. Depth-integrated on-ice snow samples were also collected, using a standard snow tube and transferred to thick-walled HDPE plastic bags. At base camp, ice and snow samples were allowed to melt entirely at room temperature and then transferred to 125 mL HDPE bottles. Water samples were collected at mid-depth between the base of river ice and bed using a drop sampler and transferred directly to 1 L HDPE bottles.

### *Isotopic analysis*

A total of 161 samples including water (23), ice (117) and snow (21) were collected for laboratory analysis of oxygen and hydrogen stable isotopes using standard methods.  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values cited herein are reported relative to Vienna-SMOW (Standard Mean Ocean Water) and normalized to  $-55.5\text{‰}$  and  $-428\text{‰}$ , respectively, for SLAP (Standard Light Antarctic Precipitation) (see Coplen, 1996). Analytical uncertainty is  $\pm 0.1\text{‰}$  for  $\delta^{18}\text{O}$  and  $\pm 2\text{‰}$  for  $\delta^2\text{H}$ .

## RESULTS AND DISCUSSION

### *Apparent ice-water fractionations*

To test the magnitude and uniformity of  $\epsilon_{\text{ice-water}}$  under natural conditions, sampling and isotopic analysis of basal congelation ice and sub-ice water was conducted at each coring location. In Figure 4, basal ice is shown to be enriched in both heavy isotopic species as compared to river water by near-constant  $\delta$  values,

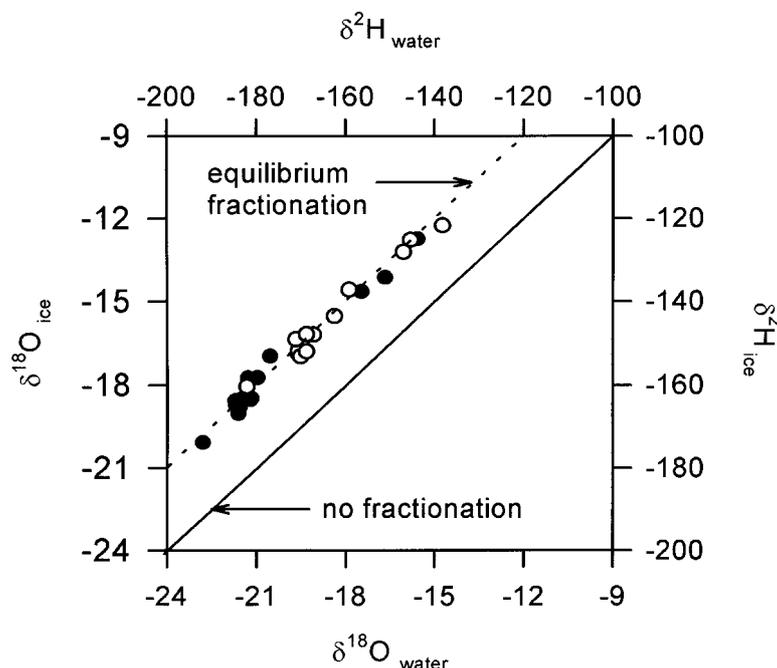


Figure 4. Crossplot of the isotopic composition of water versus ice for individual ice cores. Filled circles denote  $\delta^{18}\text{O}$  and hollow circles denote  $\delta^2\text{H}$  as read on their respective scales. Near-constant isotopic enrichment is observed for ice of 2.94‰ and 19.5‰ in  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ , respectively

close to those predicted for the case of ice-water isotopic equilibrium. Based on congelation ice/water pairs ( $n = 14$ ), the apparent  $\epsilon_{ice-water}$  ( $\pm 1\sigma$ ) was found to be  $2.94 \pm 0.33\text{‰}$  for  $\delta^{18}\text{O}$  and  $19.5 \pm 1.6\text{‰}$  for  $\delta^2\text{H}$ , which is well within the range observed in laboratory freezing experiments of freshwater (see theory section, isotopic fractionation during freezing).

This apparent ice-water fractionation verifies that ice is a reliable indicator of the isotopic composition of source water in late winter when ice growth is generally slowest. Confirmation that near-constant fractionation is maintained throughout the winter was not directly checked but is likely given the vertical isotopic distributions observed in ice cores collected in virtually open systems with constant source water (discussed later). Boundary layer effects (Ferrick *et al.*, 1998) are evidently not a major source of error in the use of ice stratigraphy methods in the current setting. Near-constant offset in sea ice/water pairs was also reported by MacDonald *et al.* (1995) for  $\delta^{18}\text{O}$  although observed  $\epsilon_{ice-water}$  was found to be smaller ( $2.57 \pm 0.10\text{‰}$ ) due primarily to salinity effects.

In contrast, the apparent  $\epsilon_{ice-water}$  for white-ice/water pairs ( $n = 8$ ) was found to be only slightly lower on average but highly variable ( $2.91 \pm 1.52\text{‰}$  for  $\delta^{18}\text{O}$  and  $16.8 \pm 8.1\text{‰}$  for  $\delta^2\text{H}$ ) suggesting that this ice type is not as reliable for reconstructing the isotopic composition of source water.

#### Vertical distributions

Three basic types of vertical isotopic distributions were observed in the survey (Figure 5). Ice cores extracted along the main stem of the Liard (L1, L2, L2S, LASNE, LASNW, LAP, LAP2, LAB, FNAL, Figure 1) and on the Mackenzie River above the Liard River confluence (M1) were found to have near-constant isotopic compositions with depth, suggesting a near-constant feedwater source, open-system conditions, and negligible freezing-rate effects. The best example of a near-constant vertical profile is shown for Mackenzie River at M1 (Figure 5a), which experiences average winter flows of about  $3500\text{ m}^3/\text{s}$ , mainly derived from Great Slave Lake (Canada, Environment Canada 1996).

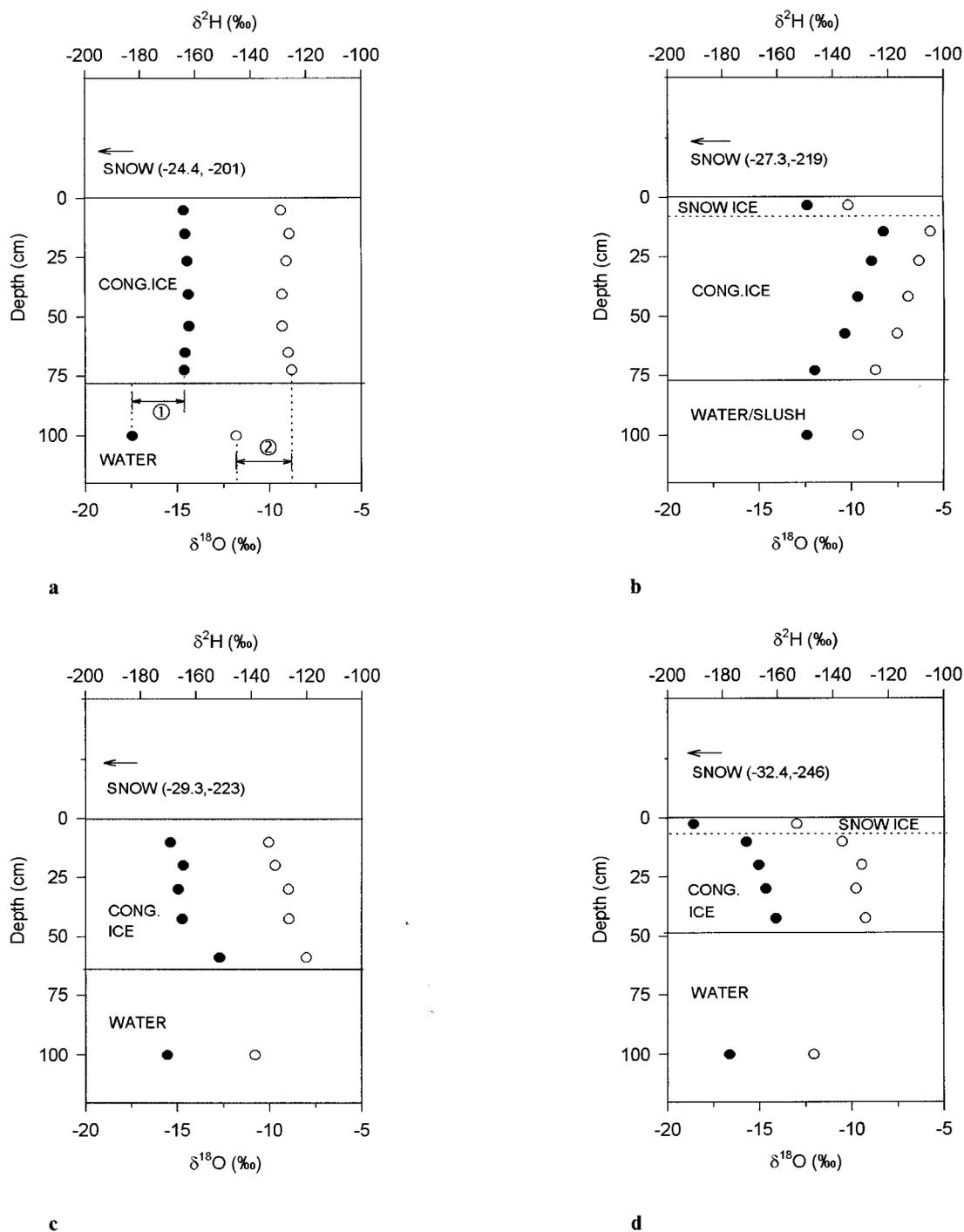


Figure 5. Vertical distributions of  $\delta^{18}\text{O}$  (closed circles) and  $\delta^2\text{H}$  (open circles) in four selected ice cores. (a) Mackenzie River above Liard River (M1) displaying near-constant vertical profiles indicative of open-system fractionation (1 and 2 are apparent  $\epsilon_{\text{ice-water}}$  for oxygen and hydrogen, respectively); (b) Goose Lake, a shallow lake displaying a Rayleigh-type depletion with depth typical of restricted water input and output (overlain by snow ice); (c) Petitot River and (d) Poplar River showing progressive enrichment in  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  with depth, attributed to changes in source water isotopic composition

Ice cores were also extracted from small, shallow lakes which are known from previous studies to be closed or restricted inflow and outflow reservoirs (Gibson *et al.*, 1993a). Below the surficial snow-ice layer, these ice covers display isotopic compositions which generally decrease with depth (Figure 5b) as predicted by equation (4) for ice formation in closed or semi-closed systems.

In contrast, cores collected from two wetlands streams (Figures 5c and 5d) display consistent and progressive isotopic enrichment with depth, beyond levels that can be explained by freezing-rate effects alone (see Figure 2). Lack of a discernible freezing-rate effect in core M1, and in nine additional cores collected in the Liard Basin, strongly suggests that this trend is more likely the result of changes in the isotopic composition of source water. One possible reason for progressive over-winter enrichment in source water of wetland streams is a decline in contributions from deep groundwater vs. interflow/surface water derived from wetlands and lakes, although this hypothesis remains to be verified.

#### *Time-scale for ice accumulation*

Previous isotope stratigraphy studies (MacDonald *et al.*, 1995) have demonstrated the application of climate-driven ice-growth models for establishing general time-scales for ice accumulation, an important step to constraining  $\delta$  vs. time variations and for correlating records among cores. Although a full review of the results is beyond the scope of this article, a simple temperature-based model was used to develop an approximate time-scale for ice growth at the various coring locations by the method described by Prowse (1995). Despite the limited number of samples collected and analysed from each ice core, the  $\delta$  versus time trends (as shown for L1, Liard R. near the mouth, Figure 6) do provide some useful information about the changing isotopic composition of winter streamflow — invaluable data for such remote and inaccessible sites where normal time-series sampling is impractical. Intercomparison of the core data at a time step suitable for understanding regional patterns in flow conditions, however, requires finer temporal resolution in the isotopic records. Although beyond the scope of this initial study, it could be achieved through finer vertical sectioning of the ice cores.

#### *Source fingerprints and macro-scale partitioning*

The isotopic composition of water was reconstructed from ice profiles at the various coring locations (Figure 1), applying a constant ice-water correction factor of 2.94‰ and 19.5‰ for oxygen and hydrogen, respectively based on field observations of  $\epsilon_{ice-water}$  (see section on apparent ice-water fractionations). On a plot of  $\delta^{18}O$  versus  $\delta^2H$  (Figure 3), reconstructed water is shown to plot along trends consistent with isotopic measurements of water made previously in the area. This broadly confirms that this simple approach is performing satisfactorily. Tributaries dominated by lakes and wetlands are notably enriched in  $\delta^{18}O$  and  $\delta^2H$  along a local evaporation line, which effectively distinguishes them from upland-alpine tributaries (S. Nahanni R., Beaver R.) and mixed tributaries of the Ft. Nelson River system. Flow at nodes along the main stem of the Liard River is clearly dominated by upland-alpine and mixed tributary sources based on the similarity in their isotopic signatures. This assertion is in good agreement with available discharge records (Canada, Environment Canada 1996). Observed over-winter variability is also shown to be greatest in wetland-dominated systems (Figure 3).

Isotopic evolution of Liard river water, as reconstructed from station LAB to L1 (Figure 7), is consistent with a gradual increase in flow contributions from wetland and mixed tributaries which dominate the lower reaches of the river. The most obvious exception to this trend is between LASNE and L2 due to substantial input of upland-alpine water from the South Nahanni River system. Although some temporal isotopic variability is recorded in the ice profiles, the same basic trends are maintained throughout the winter period, which confirms the presence of a very stable and deep- deep-seated groundwater flow regime.

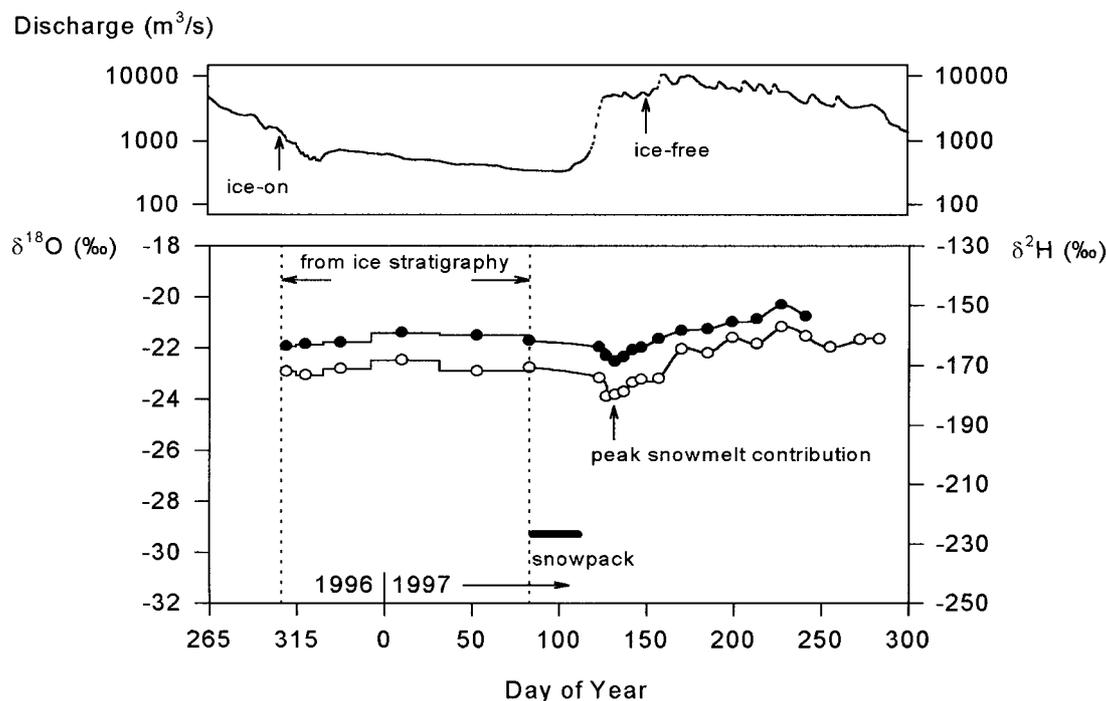


Figure 6. Time-series of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  for the Liard River near the mouth based on water sampling in 1997 and reconstructed from stratigraphy of late March 1997 ice cover. Note that over-winter variations reconstructed from the ice stratigraphy are less than 10% of variability measured in water samples collected during the subsequent melt season

One potential application of isotope stratigraphy in the study of large river systems is quantitative partitioning of winter discharge by source areas. By simple two-point mixing, the instantaneous fraction of streamflow contributed from a given tributary may be estimated as

$$I/Q_2 = (\delta_{Q_2} - \delta_{Q_1}) / (\delta_I - \delta_{Q_1}) \quad (5)$$

where  $I$  is the volume of discharge from the tributary,  $Q_2$  is the volume of discharge measured below the tributary, ( $Q_1$  being the volume of flow measured above the tributary), and  $\delta_I$ ,  $\delta_{Q_1}$  and  $\delta_{Q_2}$  are the isotopic compositions (either  $\delta^{18}\text{O}$  or  $\delta^2\text{H}$ ) of streamflow in the tributary, and river water above and below the tributary, respectively. As summarized in Figure 5 (mass balance scenario), the observed isotopic changes above and below the South Nahanni River, suggest that this tributary accounts for roughly 24% (by  $\delta^{18}\text{O}$ ) or 26% (by  $\delta^2\text{H}$ ) of winter flow to the Liard River at the downstream station (L2, L2S). Although more detailed work will be required to constrain potential errors in the use of ice stratigraphy in mass balance calculations, it is encouraging that comparable results were obtained for both oxygen and hydrogen, which are similar to average values obtained from conventional under-ice streamflow gauging (18–19%).

## CONCLUSIONS

In general, the use of river ice stratigraphy for reconstructing the isotopic composition of winter flow requires careful attention to the physical properties of the ice. As in previous studies, congelation ice (formed *in situ*) is found to be the most reliable archive. Basal congelation ice/water pairs ( $n = 14$ ) yielded fairly constant  $\varepsilon_{ice-water}$  values of  $2.94 \pm 0.33$  for oxygen and  $19.5 \pm 1.6$  for hydrogen. Due to the current uncertainty associated with freezing-rate effects, and potential interference due to frazil accumulation, snow incorporation etc., accuracy of estimates for the current setting should conservatively be set at about  $2\sigma$  or 0.66 and 3.2

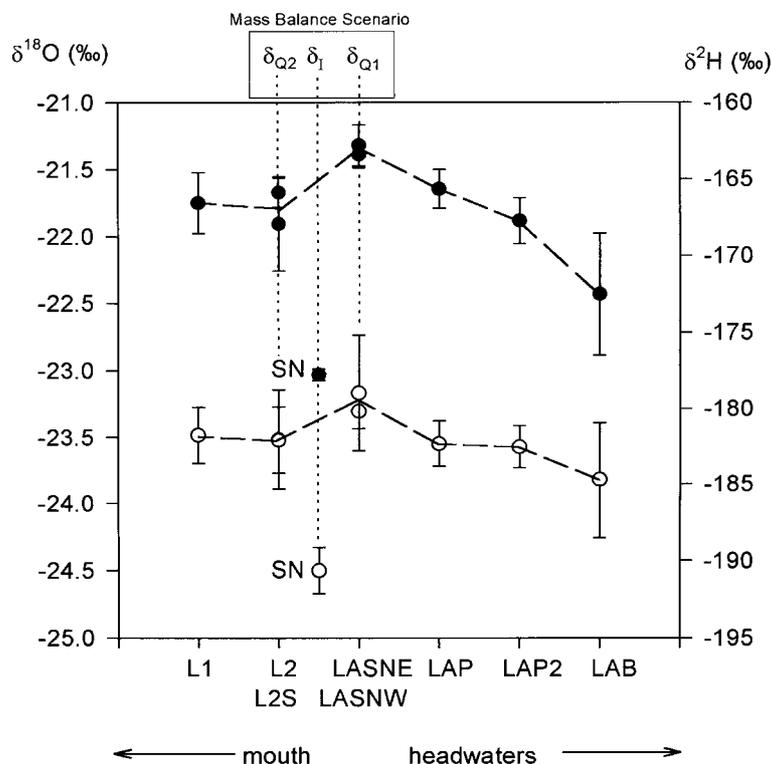


Figure 7. Trends in mean  $\delta^{18}\text{O}$  (closed circles) and  $\delta^2\text{H}$  (open circles) of river water reconstructed from ice profiles, Liard River main stem. Error bars denote 1 s of observed variations. Station-to-station isotopic shifts result from addition of distinctly labelled water from tributaries. Note the gradual increase in  $\delta$  values towards the mouth (due to progressive addition of flow from wetland and mixed tributaries), with exception of the reach between LASNE and L2. Here,  $\delta$  values are modified by abundant flow from the S. Nahanni River. The terms  $\delta_{Q1}$ ,  $\delta_{Q2}$  and  $\delta_I$  specify values used the Nahanni River mass balance scenario given by equation (5) as discussed in the text

for oxygen and hydrogen, respectively. While this limits usefulness in tracing shifts in large rivers, it still offers considerable potential for constraining winter streamflow signatures, and in particular, for tracing over-winter shifts in smaller tributaries. Further work will be required to assess uncertainties in use of ice archives in mass balance analysis.

Future studies should focus on the use of high-resolution isotope stratigraphy to examine over-winter isotopic enrichment in wetland streams in more detail. Special emphasis should be placed on the potential over-winter decline in groundwater vs surface water contributions which may account for this effect.

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