

$\delta D - \delta^{18}O$ RELATIONSHIPS IN ICE FORMED BY SUBGLACIAL FREEZING: PALEOCLIMATIC IMPLICATIONS

By R. A. SOUCHEZ and J. M. DE GROOTE

(Laboratoire de Géomorphologie, Faculté des Sciences, Université Libre de Bruxelles, B-1050 Bruxelles, Belgium)

ABSTRACT. A freezing slope, distinct from that of precipitation, is displayed on a $\delta D - \delta^{18}O$ diagram by basal ice in different circumstances. However, if the subglacial reservoir allowed to freeze is mixed in the course of time with an input having a lighter isotopic composition, basal ice cannot be distinguished from glacier ice in terms of slope. Such a situation is encountered at the base of Grubengletscher and is indicated by a computer simulation using the open-system model of Souchez and Jouzel (1984). Suggested implications for the paleoclimatic interpretation of deep ice cores recovered from the bottom part of polar ice sheets are given.

RÉSUMÉ. Sur les relations $\delta D - \delta^{18}O$ dans la glace formée par regel sous-glaciaire: implications paléoclimatiques. Les échantillons de glace basale de glacier sont souvent alignés, dans un diagramme $\delta D - \delta^{18}O$, sur une pente de gel différente de celle des précipitations. Cependant, si le réservoir sous-glaciaire en cours de congélation est mélangé à un apport de composition isotopique plus négative, la glace basale ne montre plus cette différence de pente par rapport à la glace de glacier. Une telle situation

se présente à la base du Grubengletscher et est simulée par ordinateur en utilisant le modèle en système ouvert de Souchez et Jouzel (1984). Les conséquences pour l'interprétation paléoclimatique des sondages profonds des calottes glaciaires polaires sont indiquées.

ZUSAMMENFASSUNG. $\delta D - \delta^{18}O$ -Beziehungen in Eis, gebildet durch subglaziales Gefrieren: paläoklimatische Folgerungen. Eis vom Untergrund eines Gletschers weist unter verschiedenen Umständen in einem $\delta D - \delta^{18}O$ -Diagramm ein Gefriergefälle auf, das sich von dem des Niederschlages unterscheidet. Wenn jedoch das subglaziale Reservoir, das dem Gefrieren ausgesetzt ist, im Laufe der Zeit mit einem Zustrom von leichterer Isotopenzusammensetzung gemischt wird, kann Grundeis von Gletschereis nicht aus dem Gefriergefälle unterschieden werden. In dieser Lage befindet sich der Untergrund des Grubengletschers; sie wird mit einer Rechnersimulation nachgeahmt, die auf dem Modell des offenen Systems von Souchez und Jouzel (1984) beruht. Folgerungen für die paläoklimatische Interpretation tiefer Eiskerne aus dem Unterteil polarer Eisschilde werden vorgeschlagen.

INTRODUCTION

Glacier-ice temperatures near the ice-bedrock interface are very often at or near the pressure-melting point. As a consequence, phase changes are likely to occur. For instance, pressure fluctuations due to an irregular bed will induce phase changes because of the pressure dependence of the freezing temperature. In places where heat is removed, water circulating at the ice-bedrock interface will freeze and a basal ice layer will be formed at the sole of the glacier. This basal ice layer contains dirt and debris layers incorporated by the freeze-on process. Such a situation occurs for a polar glacier when water enters a zone of subglacial permafrost and cold ice is at the base. In the Alps, where permafrost is not generally present beneath a glacier, the required open thermal system exists if cold air reaches the bed through crevasses or subglacial cavities.

Freezing of water is accompanied by an isotopic fractionation. Therefore, basal ice has been studied for its isotopic composition in order to gain information on processes occurring at the glacier sole. Gow and others (1979) described an oxygen-isotope profile of the basal ice from the Byrd Station deep ice core in Antarctica. Lawson and Kulla (1978) conducted an oxygen-isotope investigation of the origin of the basal zone of Matanuska Glacier in Alaska, while Hooke and Clausen (1982) studied the bottom layers of the marginal zone of Barnes Ice Cap in Baffin Island. However, more information can be obtained if, instead of focusing on a single isotopic ratio, both D/H and $^{18}O/^{16}O$ are considered. The basal ice was only recently studied in that respect by Jouzel and Souchez (1982). The stable-isotopes fractionation process by freezing was developed theoretically for closed and open systems and experimentally tested (Souchez and Jouzel, 1984). Indeed, samples obtained by freezing melted ice cores from an Antarctic site, a Canadian Arctic glacier, and an Alpine glacier are aligned, on a $\delta D - \delta^{18}O$ diagram, along a slope that agrees fairly well with the calculated one from the model. The experimental slopes are respectively 4.37 ± 0.11 ,

5.99 ± 0.10 , and 6.63 ± 0.17 with a correlation coefficient always greater than 0.996, while the calculated slopes are respectively 4.32, 5.99, and 6.27 (Souchez and Jouzel, 1984). The aim of this paper is to describe and interpret the unusual patterns displayed by basal ice samples on a $\delta D - \delta^{18}O$ diagram in the light of the previously published papers. Consequences for the paleoclimatic interpretation of deep ice cores recovered from the bottom part of polar ice sheets are stressed.

SAMPLING PROCEDURE AND SAMPLE ANALYSIS

Samples were taken either with a Teflon-coated CRREL ice corer or with a stainless steel device hammered into the ice. Only the central core of the sample was used and this was allowed to melt entirely. Melted ice was then transferred into 30 ml glass bottles. The bottles fitted with a screw-top self-sealing cap were then sealed with paraffin wax to prevent evaporation. Glass bottles were used to avoid possible slight diffusion through the walls in the course of time.

In order to demonstrate precise $\delta D - \delta^{18}O$ relationships in basal ice, the isotopic ratios must be measured with great accuracy on the same drop. A method has been designed for simultaneous analysis on the same aliquot by twin mass spectrometers at the Centre d'Études Nucléaires de Saclay in France where our samples were treated (Hagemann and Lohez, 1978). The accuracy of the measurements is $0.5^0/00$ on δD and $0.1^0/00$ on $\delta^{18}O$, δD and $\delta^{18}O$ being expressed versus SMOW, the standard mean ocean water. D/H and $^{18}O/^{16}O$ are equal in SMOW to 155.76×10^{-6} and 2005.2×10^{-6} , respectively.

THE $\delta D - \delta^{18}O$ RELATIONSHIP

The plotting of δD against $\delta^{18}O$ opens up the possibility of following the processes in which the two heavy components behave in different ways. For instance,

detailed studies have shown a precipitation effect in which the isotopic δ values are linearly correlated over the range of variation in natural fresh water and snow, so that $\delta D = 8\delta^{18}O + 10$ (Craig and others, 1963). The independent term of this linear equation is called the deuterium excess, d , which can be calculated for each sample from the formula $d = \delta D - 8\delta^{18}O$. Deuterium excess values in precipitation samples are not always equal to 10, and Jouzel and others (1982) suggested that such values in an East Antarctic ice core were related to the relative humidity at the ocean surface at the time of the solid precipitation. The linear trend observed in precipitation is also valid for glacier ice which has not undergone isotopic changes since its formation; it is called the precipitation effect.

If, instead of being concerned with the isotopic fractionation of water during condensation or sublimation, we pay attention to the freezing process, a linear relationship between δD and $\delta^{18}O$ can also be shown to occur. However, the slope has no greater value than 8 but is given, in a closed system, by the equation

$$S = \frac{(\alpha - 1)(1 + \delta_i D)}{(\beta - 1)(1 + \delta_i^{18}O)} \quad (1)$$

in which α and β are the equilibrium-fractionation coefficients respectively for deuterium and oxygen 18; $\delta_i D$ and $\delta_i^{18}O$ are the δ values corresponding to initial water at the beginning of freezing (Jouzel and Souchez, 1982).

More recently, Souchez and Jouzel (1984) developed an open-system model that has been experimentally tested. The reservoir is supposed to remain isotopically homogeneous and this seems realistic, since the diffusion coefficients of HDO and $H_2^{18}O$ molecules in liquid water are relatively high (c. $10^{-5} \text{ cm}^2 \text{ s}^{-1}$). In this model, which considers a constant input, a constant freezing rate, and an output proportional to the remaining liquid, the variation of the δ value for the liquid is given by the equation

$$d\delta_L = \frac{(\alpha_{SL} - 1)(1 + \delta_L) - \frac{A}{S}(\delta_A - \delta_L)}{k(1 + \frac{F}{S}k - \frac{A}{S})} dk \quad (2)$$

where A , S and F are the respective input, freezing, and output-rate coefficients; α_{SL} is the equilibrium-fractionation coefficient between solid and liquid; δ_A is the δ value of the input and $k = N_L/N_0$, the ratio of the number of moles at time t in the liquid by the number of moles in the reservoir at time $t = 0$. The slope S for the solid is given by

$$S = \frac{\alpha \left[(\alpha - 1)(1 + \delta_i) - \frac{A}{S}(\delta_A - \delta_i) \right]}{\beta \left[(\beta - 1)(1 + \Delta_i) - \frac{A}{S}(\Delta_A - \Delta_i) \right]} \quad (3)$$

with α and β the equilibrium-fractionation coefficients for deuterium and oxygen 18, respectively; $(\delta_A - \delta_i)$ and $(\Delta_A - \Delta_i)$ are the differences between the δ value of the input and that of the reservoir for deuterium and oxygen 18, respectively. The slope is the same for an open system as for a closed one when the input is not significantly different in its isotopic composition from that of the initial reservoir. However, the case study below exhibits a δD - $\delta^{18}O$ relationship that can only be understood if a significantly different input is taken into account.

THE GRUBENGLETSCHER CASE STUDY

Grubengletscher is located in Wallis in western Switzerland and flows from the crest of Fletschorn (3493 m a.s.l.) in a north-west direction to an altitude of about 2800 m at its snout. It is flanked in its lower part by a rock glacier and dams a lake at an altitude of 2950 m. Part of the glacier tongue and the rock glacier are in a permafrost zone

(Haerberli, 1975). Temperature measurements made by Haerberli indicate that the ice at this point is clearly below the pressure-melting point. To control the level of the ice-dammed lake, a tunnel has been dug at the base of the Grubengletscher. It has been excavated partly in the frozen ground moraine and partly in the cold ice itself, and intersects a natural subglacial channel. A typical basal sequence consisting of dirt, debris, and bubble-free ice layers is developed at the sole of the glacier just above the frozen ground moraine. This basal ice layer has been demonstrated, on chemical grounds, to be the result of the freezing of melt water due to pressure fluctuations at the interface (Souchez and Lorrain, 1978). The situation is thus similar to that of a polar glacier where subglacial water enters a permafrost zone in the marginal area and freezes at the glacier sole.

Glacier-ice, basal ice, and water samples are indicated on the δD - $\delta^{18}O$ diagram of Figure 1. Some of the glacier-ice samples were taken from the exposure in the tunnel; others resulted from drilling at the glacier surface at 30 m, 60 m, and 90 m up-glacier from the tunnel. Basal ice samples consisted of thin bubble-free ice layers interbedded with debris and dirt layers, of interstitial ice in the upper part of the frozen ground moraine, and of ice on the floor of the subglacial channel intersected by the tunnel. Water samples were taken from the ice-dammed lake at different periods.

All the sample presented in Figure 1 show a linear relationship with a slope of 8.23 and a correlation coefficient of 0.993. However, a more careful study of the ice samples leads to the recognition of two populations with different values of deuterium excess. The mean value of deuterium excess for glacier ice is 13.0, while it is 10.5 for basal ice. Distribution of the number of samples versus deuterium excess classes for glacier ice and basal ice respectively is indicated on Figure 2. Separate slope computations for glacier-ice and for basal ice samples give similar values of

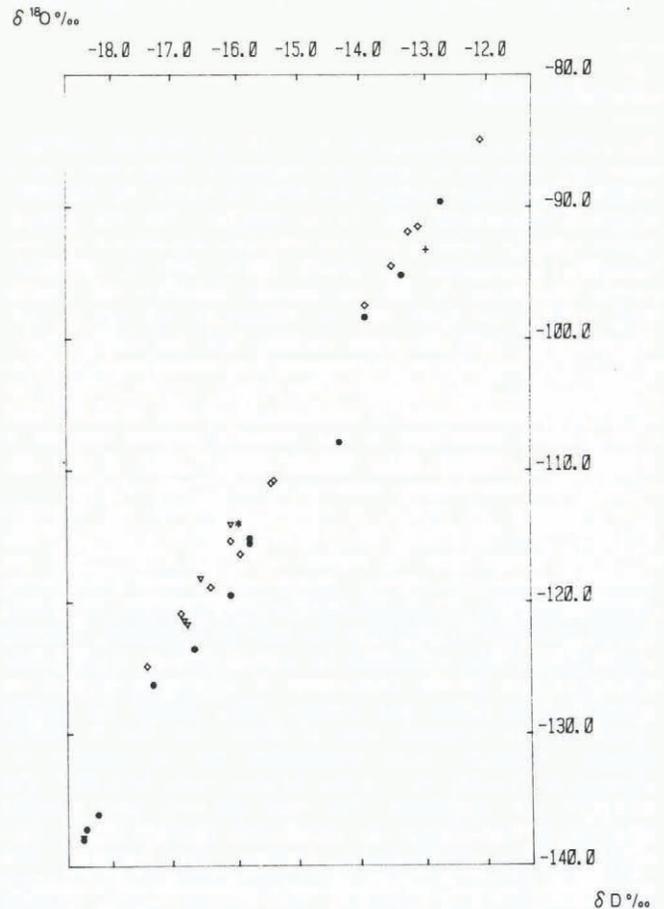


Fig. 1. δD - $\delta^{18}O$ diagram for Grubengletscher ice and water samples. Black dots for basal ice samples, open squares for glacier-ice samples, and open triangles for water samples from the ice-dammed lake.

7.96 and 8.19 respectively with a correlation coefficient always greater than 0.995. No distinction can be made between these two groups in terms of slope and only slight differences in deuterium-excess values exist. A closed-system freezing slope is not displayed in this case. Can this situation be understood by using the open-system model?

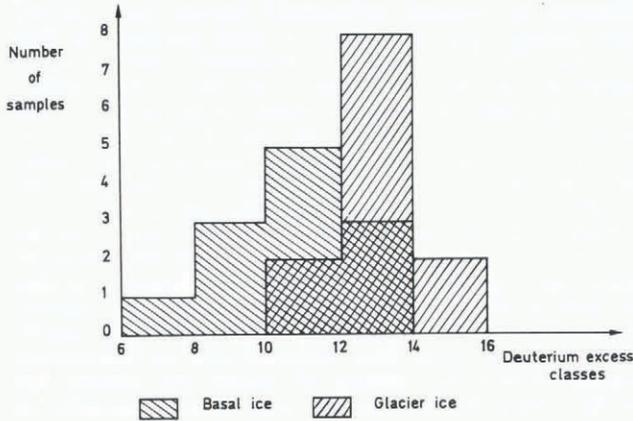


Fig. 2. Distribution of deuterium excess values in glacier-ice and basal ice samples from Grubengletscher.

COMPUTER SIMULATION

The freezing slopes in open and closed systems are practically the same if the isotopic composition of the input in the open system is not significantly different from that of the initial reservoir. A computer program has been devised to simulate the evolution in δD and $\delta^{18}O$ of ice samples if the reservoir allowed to freeze is mixed in the course of time with an input having a lighter isotopic composition than the initial liquid. This has been made by a step-by-step procedure using Equation (2). In this program, the freezing factor $K = 1 - k = 1 - (N_L/N_0)$ varies from 0.01 to 0.99 in 99 steps and the ratio between input-rate coefficient A and freezing-rate coefficient S , from 0.1 to 0.9. For each value of A/S , a line joining 99 points is obtained. The isotopic composition of the initial reservoir has been fixed at $\delta D = -118\text{‰}$ and $\delta^{18}O = -16\text{‰}$. These values are related to each other by the equation $\delta D = 8\delta^{18}O + 10$, and are within the range of variations of values from Grubengletscher. With an input having the same isotopic composition, results of the simulation give, for different values of A/S , superimposed lines forming a freezing slope that corresponds exactly to the one calculated from Equation (1). Figure 3 gives the results of the simulation with an input having $\delta D = -138\text{‰}$ and $\delta^{18}O = -18.5\text{‰}$. These values have been chosen because they are the values on the precipitation slope with $d = 10$ closest to those of the lighter water from the ice-dammed lake. No output has been considered. In Figure 3 (and in Figure 4 too), the diagonal joining the upper right-hand corner to the lower left-hand one has the equation $\delta D = 8\delta^{18}O + 10$. Results indicate a progressive change of slope around a pin-point at $\delta D = -97.2\text{‰}$ and $\delta^{18}O = -13\text{‰}$. If A/S increases, the slope becomes steeper until it approaches the value of 8 but with a lower deuterium excess. Figure 4 shows a similar pattern for a situation with the same input and with an output $F = 0.9S$ having an isotopic composition identical to that of the reservoir. If, instead of the previous range of variation, A/S varies from 1.1 to 10.1, the same trend is also observed. Thus, the computer simulation indicates that the open-system model with an input poorer in heavy isotopes than the initial reservoir will lead to a progressive change of slope around a pin-point that can be calculated from the equations

$$\delta D = \delta_i D + 20.8 \tag{4}$$

and

$$\delta^{18}O = \delta_i^{18}O + 3 \tag{5}$$

if $\alpha = 1.0208$ and $\beta = 1.5003$. Basal ice samples can thus

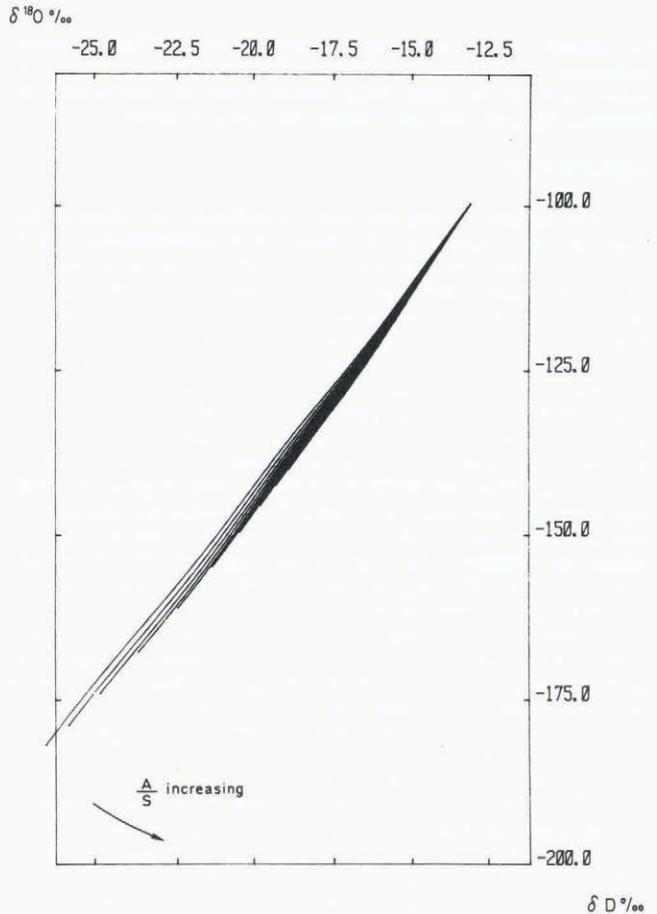


Fig. 3. Computer simulation of the evolution in δD and $\delta^{18}O$ of ice during freezing if an initial reservoir is mixed with an input having a lighter isotopic composition.

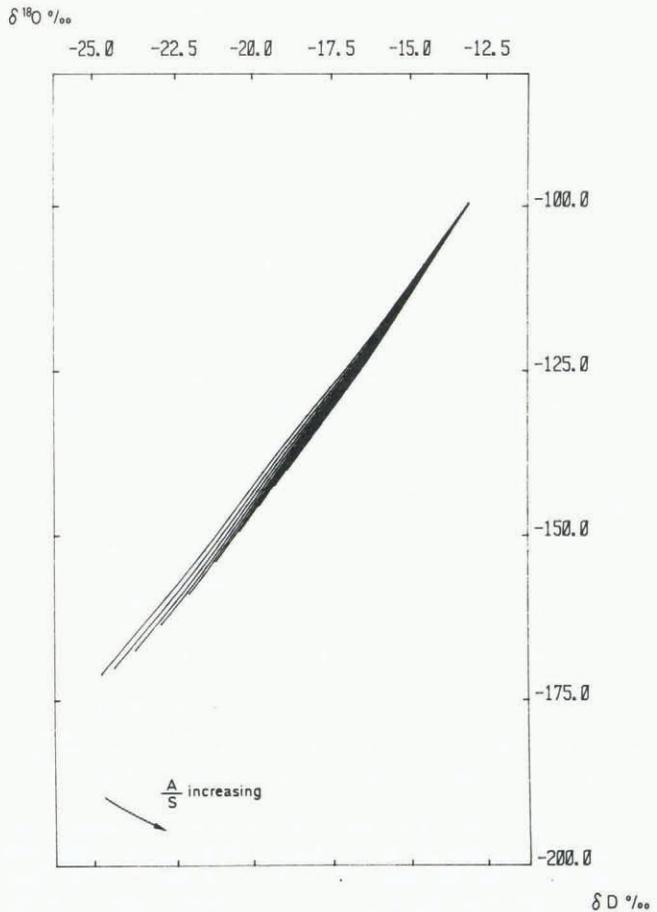


Fig. 4. Computer simulation with the same conditions as in Figure 3 but with an output.

be aligned on a precipitation slope with a slightly lower deuterium excess if an input of water impoverished in heavy isotopes is mixed with initial water in the course of freezing. Output will not change the general trend.

APPLICATION

The results of the computer simulation can explain the situation encountered at the base of Grubengletscher, if a source of more negative water than initial water is present. The ice-dammed lake can be the source of water required as an input to the subglacial freezing process. Mixing of water from different origins gives the ice-dammed lake its variable isotopic composition in the course of time. Contributions by melting of snow, melting of ice from Grubengletscher, summer rain, and run-off from the catchment basin are the variable sources of water. For example, a sample of summer rain gave surprisingly high δ values ($\delta D = -32.10/00$ and $\delta^{18}O = -5.9/00$). The highest δ value indicated for the lake on Figure 1 was obtained during the summer after heavy rain, while the lowest δ value was obtained in autumn when the upper part of the lake was already frozen. Freezing of the lake will of course make the residual water more negative.

Water from the lake currently finds its way under the glacier and seeps through the ground moraine (personal communication from H. R othlisberger). Thus it is quite probable that in winter this water contributes to the subglacial water that is allowed to freeze in an open system at the glacier sole.

Let us consider that initial water has $\delta D = -114/00$ and $\delta^{18}O = -16/00$ (point represented by a star on Figure 1) and that the input is water from the ice-dammed lake at the lowest isotopic values measured. The calculated pin-point (represented by a cross on Figure 1) from Equations (4) and (5) will have $\delta D = -93.2/00$ and $\delta^{18}O = -13/00$, close to the most positive values of basal ice encountered. On the other hand, the difference in deuterium excess in that case is 3.2 as compared to 2.5, which is the difference between the mean deuterium-excess value for glacier ice and the mean deuterium-excess value for basal ice. Thus the situation suggested by computer simulation is likely to occur at Grubengletscher.

PATTERNS DEVELOPED IN BASAL ICE

Different situations at the ice-bedrock interface are responsible for different patterns in basal ice:

1. Melt water circulating at the base from the central part of a glacier or ice sheet towards the marginal area may freeze entirely at the sole. This is the case for Aktineq Glacier in the Canadian Arctic (Jouzel and Souchez, 1982). The closed-system model applies and the basal ice samples are aligned on a freezing slope. The last frozen fractions are impoverished in heavy isotopes compared to the initial liquid represented by the intersection point between the precipitation slope and the freezing slope.

2. The freezing slope displayed for Tsanfleuron Glacier basal ice samples (Jouzel and Souchez, 1982) is the result of subglacial freezing in an open system. Water with an isotopic composition similar to that of the sheet of water circulating at the base enters a subglacial cavity where partial freezing occurs on the bedrock as a result of cold air penetration. The ice layers formed are further incorporated at the glacier sole by change of form of the cavity. These ice layers have an isotopic composition in stable isotopes in accordance with the open-system model (Souchez and Jouzel, 1984). A freezing slope is displayed on a δD - $\delta^{18}O$ diagram but only the part of it corresponding to ice samples richer in heavy isotopes than the initial liquid.

3. The Grubengletscher case study reflects a situation where water impoverished in heavy isotopes is mixed as input with initial water in the course of freezing. In such a case, basal ice samples may be aligned on a steeper slope than the freezing slope and, eventually, no distinction can be made in terms of slope from glacier-ice samples.

PALEOCLIMATIC IMPLICATIONS

As shown by Dansgaard and others (1982), polar ice sheets are proving to be a rich source of information on paleoclimates, if studies of their oxygen-isotopic profiles are conducted on deep ice cores. Close to the bed, where a larger time span is concentrated, the isotopic profile can be influenced by complex deformation features and also by phase changes, and eventually by basal freezing. If both D/H and $^{18}O/^{16}O$ ratios are considered, the δD - $\delta^{18}O$ diagram of the basal part close to the bed (a few meters) will in favorable circumstances enable us to reconstruct the original isotopic composition of the glacier ice or to evaluate the closed- or open-system character of the change that occurred. If a freezing slope is displayed, the intersection point between it and the precipitation slope obtained from the local glacier-ice samples will give the initial isotopic value. If the situation is such that basal ice samples are aligned on the same slope as glacier-ice samples but with a slightly lower deuterium excess, the isotopic values of the initial water and of the input can also be estimated. Since it has been indicated that no fractionation generally occurs by melting of glacier ice (Moser and Stichler, 1980), the probable existence of more negative ice up-glacier from the site of deep drilling can be assumed. This may be of importance for paleoclimate reconstructions made from deep ice cores that are recovered from the bottom part of polar ice sheets. It would be interesting to obtain in the future detailed δD - $\delta^{18}O$ profiles of the basal part of ice sheets.

REFERENCES

- Craig, H., and others. 1963. Isotopic exchange effects in the evaporation of water, by H. Craig, L.I. Gordon, and Y. Horibe. *Journal of Geophysical Research*, Vol. 68, No. 17, p. 5079-87.
- Dansgaard, W., and 6 others. 1982. A new Greenland deep ice core. *Science*, Vol. 218, No. 4579, p. 1273-77.
- Gow, A.J., and others. 1979. On the origin of stratified debris in ice cores from the bottom of the Antarctic ice sheet, by A.J. Gow, S. Epstein, and W. Sheehy. *Journal of Glaciology*, Vol. 23, No. 89, p. 185-92.
- Haeberli, W. 1975. Eistemperaturen in den Alpen. *Zeitschrift f ur Gletscherkunde und Glazialgeologie*, Bd. 11, Ht. 2, p. 203-20.
- Hagemann, R., and Lohez, P. 1978. Twin mass spectrometers for simultaneous isotopic analysis of hydrogen and oxygen in water. *Advances in Mass Spectrometry*, Vol. 7, p. 504-08.
- Hooke, R.L., and Clausen, H.B. 1982. Wisconsin and Holocene $\delta^{18}O$ variations, Barnes Ice Cap, Canada. *Geological Society of America. Bulletin*, Vol. 93, No. 8, p. 784-89.
- Jouzel, J., and Souchez, R.A. 1982. Melting-refreezing at the glacier sole and the isotopic composition of the ice. *Journal of Glaciology*, Vol. 28, No. 98, p. 35-42.
- Jouzel, J., and others. 1982. Deuterium excess in an East Antarctic ice core suggests higher relative humidity at the oceanic surface during the last glacial maximum, by J. Jouzel, L. Merlivat, and C. Lorius. *Nature*, Vol. 299, No. 5885, p. 688-91.
- Lawson, D.E., and Kulla, J.B. 1978. An oxygen isotope investigation of the origin of the basal zone of the Matanuska Glacier, Alaska. *Journal of Geology*, Vol. 86, No. 6, p. 673-85.
- Moser, H., and Stichler, W. 1980. Environmental isotopes in ice and snow. (In Fritz, P., and Fontes, J.C., ed. *Handbook of environmental isotope geochemistry*. Vol. 1. New York, Elsevier, p. 141-78.)
- Souchez, R.A., and Jouzel, J. 1984. On the isotopic composition in δD and $\delta^{18}O$ of water and ice during freezing. *Journal of Glaciology*, Vol. 30, No. 106, p. 369-72.
- Souchez, R.A., and Lorrain, R.D. 1978. Origin of the basal ice layer from Alpine glaciers indicated by its chemistry. *Journal of Glaciology*, Vol. 20, No. 83, p. 319-28.

MS. received 15 November 1984 and in revised form 5 February 1985