

## ISOTOPE STUDIES OF HYDROGEN AND OXYGEN IN GROUND ICE – EXPERIENCES WITH THE EQUILIBRATION TECHNIQUE

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Equilibration technique suitable for a large amount of samples is described for hydrogen and oxygen isotope analyses of ground ice, especially ice wedges, including the sampling strategy and the analytical procedure as well as the calibration of the Finnigan MAT Delta-S mass spectrometer in June, 1999. Since for future analyses of ice wedges, a higher sampling resolution with limited sample volume is required, the limit of the equilibration technique for small water sample sizes of between 0.05 and 5 ml was checked. For water samples smaller than 1 ml, corresponding to a molar ratio  $[H_2O]/[H_2]$  of smaller than 0.994, a balance correction has to be applied. The experimental errors due to partial evaporation during evacuation, the balance calculation of the isotope equilibration process, the linearity as well as memory effects of the mass spectrometer for samples with large differences in  $\delta^{18}O$  and  $\delta D$  are tackled in this paper. In the polar regions of Northern Siberia without Late Pleistocene and Holocene glaciation, ground ice is used as an archive for paleoclimate studies. First results of stable isotope measurements on ice wedges clearly show a shift towards heavier isotopes and thus warmer winter temperatures as well as a change in the source of the precipitation between Late Pleistocene and Holocene. These results indicate the high potential of ground ice for paleoclimate studies.

**Keywords:** Calibration; Equilibration technique; Ground ice; Hydrogen-2; Ice wedges; Oxygen-18; Natural abundance; Paleoclimate; Siberia; Small sample size; Stable isotopes

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## INTRODUCTION

In former times, hydrogen isotopes of water samples were measured by Zn, U or Cr reduction method. Automated equilibration technique is used since 1953 [1] for oxygen isotope analysis, but can only be applied for hydrogen isotopes since a few years [2]. There are some major advantages of this technique:

- a. the whole procedure is fully automatic and both elements can be measured in one run,
- b. oxygen isotope analysis by equilibration is less time consuming than converting the oxygen of the water into either O<sub>2</sub> by the fluorination or into carbon monoxide by high temperature conversion, which are both difficult to be automated besides possible memory effects,
- c. hydrogen isotope determination by reducing the water to hydrogen with either zinc, chromium or uranium involves the possibility of considerable memory effects [3].

Hydrogen and oxygen isotopes are well known as useful tools for paleoclimate studies in ice bodies, especially for paleotemperature reconstruction and for the identification of the source of the precipitation [4]. During the last 30 years, many efforts have been made in isotope analysis of the ice caps of Greenland and Antarctica in order to provide information on climate changes through time [5, 6]. In polar regions without actual glaciation, such as most of the Eurasian Arctic, glacier ice cores are not available and, therefore, other climatic archives have to be considered for paleoclimate reconstruction. The equilibration technique of hydrogen and oxygen isotopes was applied by the authors to a high number of Siberian ground ice samples. In our studies, carried out at the Bykovsky Peninsula in the Lena Delta area, NE Siberia, we mainly used ice-rich sediments with huge polygonal ice wedge systems [7]. These ice wedges consist of thin subvertical annual ice veins, which have been formed since the Weichselian period. An annual sampling resolution with limited sample volume is desired for future analyses. Therefore, we checked the equilibration technique to small water sample sizes.

## ANALYTICAL PROCEDURE

Our measurements were carried out with a Finnigan MAT Delta-S mass spectrometer endowed with two equilibration units (MS Analysentechnik, Berlin). Each unit has a capacity of 24 sample bottles. Both oxygen and hydrogen isotopes of ground ice have been analysed using common equilibration technique.

For isotopic analysis, an aliquot of ca. 5 ml of the water sample is filled into a ~25 ml glass bottle, attached to a rack and then immersed to two thirds of its height into a water bath (Gesellschaft für Labortechnik, Burgwedel, type GFL 1086 modified). The water baths are stirred at a frequency of  $90 \text{ min}^{-1}$  for temperature homogenisation. In order to avoid condensation in the upper part of the reaction bottle, the temperature of the water baths is kept well below room temperature [8]. Both water baths are temperature constant at  $18.00 \pm 0.01^\circ\text{C}$  within measuring time. Figure 1 shows a 10 hour plot of the temperature in the water bath.

Since the fractionation factor for deuterium ( $\text{H}_2\text{O}/\text{H}_2$ ) has a temperature coefficient of  $-5.4\%/^\circ\text{C}$  [9], the temperature of the water shaking bath (actually the surface of the catalyst sticks where equilibration happens) has to be constant within  $\pm 0.05^\circ\text{C}$  or better.

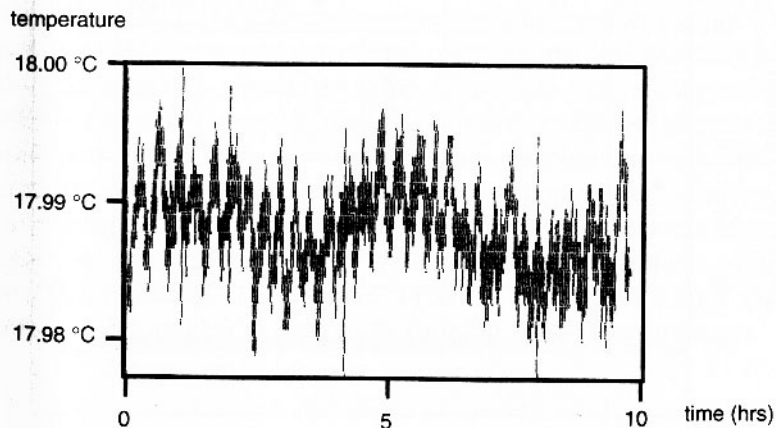


FIGURE 1 10 hour temperature plot of a water bath (type GFL 1086, modified) mean value:  $17.988^\circ\text{C}$ ; standard deviation:  $0.003^\circ\text{C}$ ; maximum:  $18.002^\circ\text{C}$ ; minimum:  $17.976^\circ\text{C}$ .

A two stage rotary pump (type E2M1.5, Edwards Vacuum Products) evacuates the bottles. As a first step, hydrogen isotope measurements are carried out. Hydrogen isotopes are equilibrated between the water and the H<sub>2</sub> gas for 120 min. Activated platinum condensed on a hydrophobic stick (MS Analysentechnik, Berlin) is used as catalyst for the hydrogen isotope exchange. After finishing the complete hydrogen measuring sequence, the same sample aliquots are equilibrated with CO<sub>2</sub> for  $\delta^{18}\text{O}$  measurement. For the determination of the time necessary for complete equilibration of oxygen isotopes in the water–CO<sub>2</sub> system, test measurements were carried out for different equilibration times with our standard NGT1 until the known  $\delta^{18}\text{O}$  of  $-34.40\text{‰}$  was achieved (see Fig. 2). As can be seen from these experiments, equilibrium is complete after 200 min. For safety reasons, an equilibration time of 400 min is used in our laboratory during routine analyses with 5 ml samples.

The first bottle of each unit is equipped with our laboratory standard NGT1 (snow, North Greenland Traverse). The H<sub>2</sub> and CO<sub>2</sub> gas equilibrated with NGT1 is subsequently transferred into the standard bellow of the inlet system and used as reference standard for

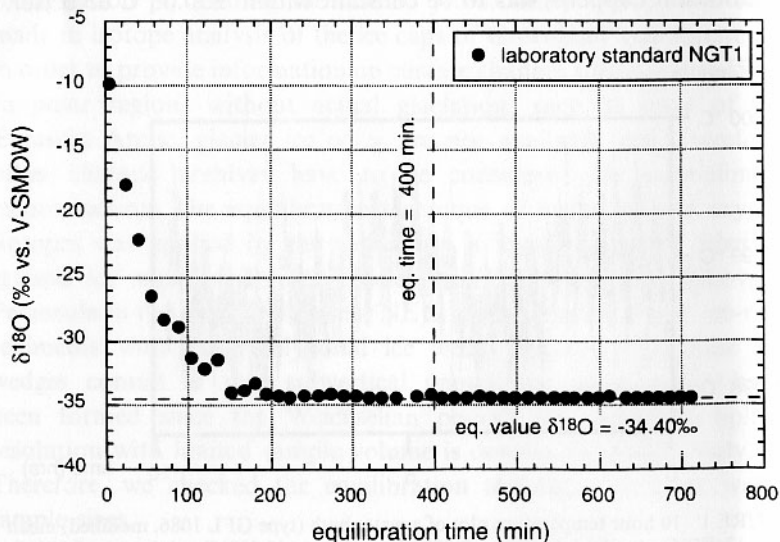


FIGURE 2 Determination of the equilibration time for  $\delta^{18}\text{O}$ .

the whole unit. We prefer this technique since normal tank gas differs considerably in its isotopic composition from natural water samples. Both possible errors in connection with measuring large isotopic differences – uncertainties of  $\delta$ -determinations and varying  $H_3^+$ -contributions – are limited. After equilibration of the water sample with  $H_2$  or  $CO_2$ , an aliquot of equilibrated gas is separated from water vapour by freezing the water in a cooling trap at  $-78^\circ C$  and then transferred into the sample bellow. With the dual inlet method, sample and reference gases are alternately introduced from the bellows through a viscous leak into the mass spectrometer. Ten measurements are carried out at 5 nA  $H_2$  signal for  $\delta D$  and at 10 nA mass 44 intensity for  $\delta^{18}O$ . In order to avoid any changes of the isotopic composition of the standard gases caused by demixing during the run of the samples, the pressure in the standard bellow was chosen higher (150 to 200 mbar) compared to the pressure in the sample bellow (30 to 50 mbar). A standard gas in the standard bellow measured against the same standard gas in the sample bellow yields a difference of  $-1\text{‰}$  for  $\delta D$ . These differences caused by the experimental set-up are linear and have to be corrected. For  $\delta^{18}O$ , no demixing of the standard gas could be observed.

$\delta D$  and  $\delta^{18}O$  values are calculated by the commercial software ISODAT (Version 5.2) and displayed as permil differences relative to V-SMOW.  $^{17}O$  and  $H_3^+$  corrections are carried out automatically. The measured  $H_3^+$  factor was determined routinely and was normally less than 5 ppm/nA  $H_2$  signal (the mean value from June to September, 1999 is  $4.44 \pm 0.11$  ppm/nA). For both isotope systems, 48 samples are measured in less than two days including preparation time. Three standard samples per unit are used for quality control, for isotopically light samples NGT1 is selected. In general, all samples are analysed twice in order to check the quality and reproducibility of the measuring process. The internal  $1\sigma$  error is generally better than 0.8‰ for  $\delta D$  and better than 0.1‰ for  $\delta^{18}O$  for all measurements.

## CALIBRATION

Our Delta-S mass spectrometer was calibrated for  $\delta^{18}O$  and  $\delta D$  in June, 1999, using IAEA standards V-SMOW, SLAP and GISP and

laboratory standards OCE2, ANST3, NGT1, PAK5 and HL1. In order to demonstrate the analytical precision of the measurements, the results of the calibration and the accepted values for IAEA standards are shown in Table I.

In Figure 3, the excellent precision for both  $\delta^{18}\text{O}$  and  $\delta\text{D}$  is displayed. V-SMOW was set zero, then scaled to SLAP ( $\delta\text{D} = -428\text{‰}$  and  $\delta^{18}\text{O} = -55.5\text{‰}$ ) and controlled by GISP ( $\delta\text{D} = -189.7\text{‰}$  and  $\delta^{18}\text{O} = -24.8\text{‰}$ ).

The  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values of GISP are within the analytical precision identical to those published by Gonfiantini *et al.* [10]. Additionally, the standard deviation of the isotopically lighter laboratory standard NGT1 ( $\delta\text{D} = -265.4 \pm 0.5\text{‰}$  and  $\delta^{18}\text{O} = -34.40 \pm 0.03\text{‰}$ ,  $N = 16$ ) is slightly better than for the isotopically heavier OCE2 ( $\delta\text{D} = -5.3 \pm 0.4\text{‰}$  and  $\delta^{18}\text{O} = -0.73 \pm 0.07\text{‰}$ ,  $N = 15$ ). Thus, we conclude that the calibration is accurate, especially for isotopically light samples such as ground ice.  $\delta^{18}\text{O}$  measurements of NGT1 carried out at the UFZ Leipzig-Halle (Kowski, pers. comm.) support our calibration ( $\delta^{18}\text{O} = -34.44 \pm 0.06\text{‰}$ ,  $N = 14$ ).

From June to October, 1999, NGT1 had a mean value of  $-34.39 \pm 0.06\text{‰}$  for  $\delta^{18}\text{O}$  and of  $-265.3 \pm 0.5\text{‰}$  for  $\delta\text{D}$  relative to V-SMOW corresponding well with the calibrated value (see Fig. 4).

After a careful determination of the  $\text{H}_3$ -contribution on mass 3, a  $\delta\text{D}$  of  $-427.9 \pm 0.4\text{‰}$  was measured for V-SMOW-SLAP, giving

TABLE I  $\delta\text{D}$  and  $\delta^{18}\text{O}$  of IAEA and laboratory standards (vs. V-SMOW)

Standard	$\delta\text{D}$ (‰) mean value $\pm$ S.D.	$\delta^{18}\text{O}$ (‰) mean value	$\delta^{18}\text{O}_{\text{corrected}}$ (‰) mean value $\pm$ S.D. <sup>a</sup>	N
V-SMOW	+0.1 $\pm$ 0.1	+0.01	+0.01 $\pm$ 0.00	2
OCE2	-5.3 $\pm$ 0.4	-0.71	-0.73 $\pm$ 0.07	15
GISP	-189.7 $\pm$ 0.1	-24.28	-24.81 $\pm$ 0.01	2
ANST3	-220.4 $\pm$ 0.2	-27.56	-28.16 $\pm$ 0.00	2
NGT1	-265.4 $\pm$ 0.5	-33.66	-34.40 $\pm$ 0.03	16
PAK5	-288.6 $\pm$ 0.0	-35.67	-36.46 $\pm$ 0.00	2
HL1	-363.2 $\pm$ 0.5	-45.17	-46.17 $\pm$ 0.03	5
SLAP	-428.8 $\pm$ 0.1	-54.32	-55.52 $\pm$ 0.01	2
International accepted values as given in Gonfiantini <i>et al.</i> (1995)				
V-SMOW	0.0		0.00	
GISP	-189.7		-24.78	
SLAP	-428.0		-55.50	

<sup>a</sup> a correction factor of 1.022 was applied.

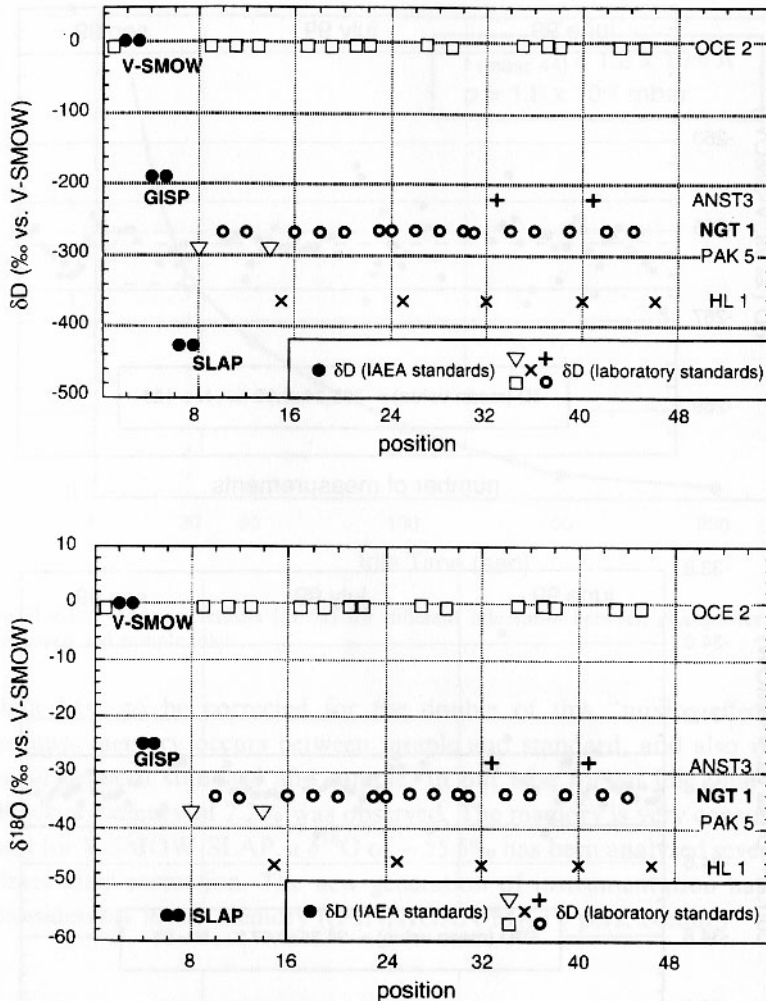


FIGURE 3 Calibration of Delta-S mass spectrometer. Above:  $\delta D$ ; below:  $\delta^{18}O$ . Error in Figure 3 below: Instead of  $\delta D$ , please read  $\delta^{18}O$ .

evidence that a “stretching-correction” had not to be applied. Within our limits of error, we have no indication for any memory effects of neither the equilibration line nor the mass spectrometer when we used samples with up to 700‰ enrichments in the  $\delta D$ -values.

For  $\delta^{18}O$ , a correction factor of 1.022 was applied to all samples due to the memory effect in the mass spectrometer. A possible memory can

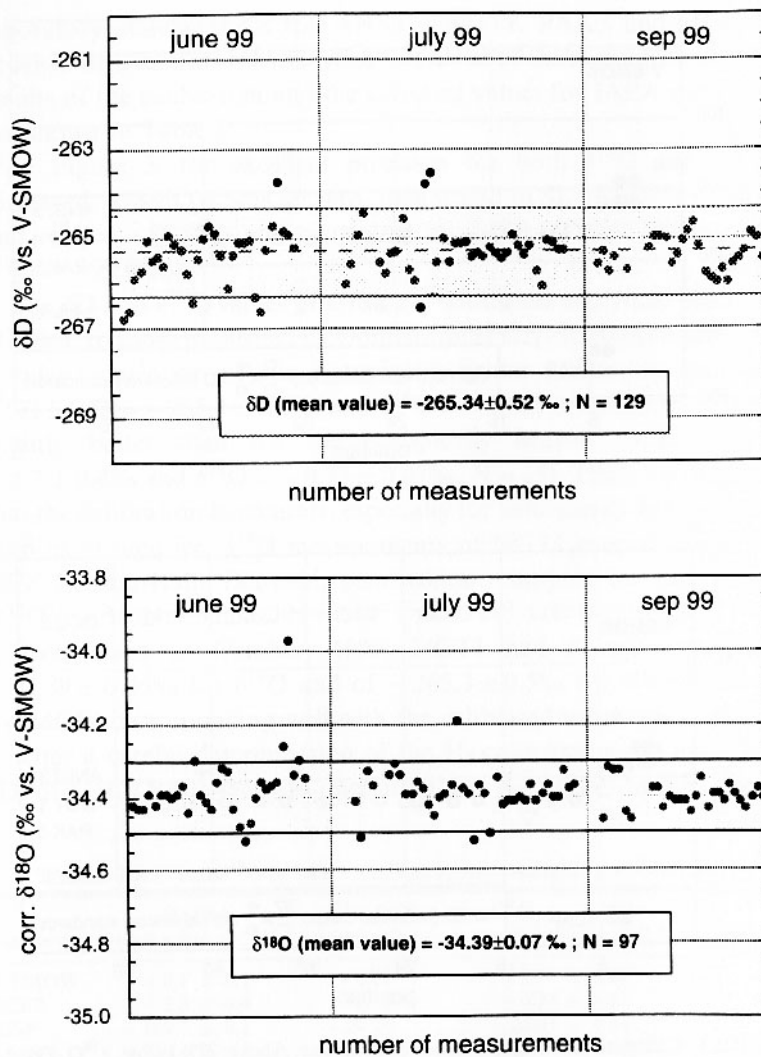


FIGURE 4 Temporal variation of  $\delta$  values for the laboratory standard NGT1. Above:  $\delta D$ ; below:  $\delta^{18}O$ . The shaded field displays the maximal accepted internal  $1\sigma$  error ( $\delta D_{int.} = 0.8\%$ ;  $\delta^{18}O_{int.} = 0.1\%$ ).

be checked easily by changing the idle time before measuring a gas after changeover.

Figure 5 displays the memory (in %) vs. idle time of between 10 and 200 sec for  $CO_2$  at an inlet rate of  $3.10^{-14}$  molecules per sec. The raw



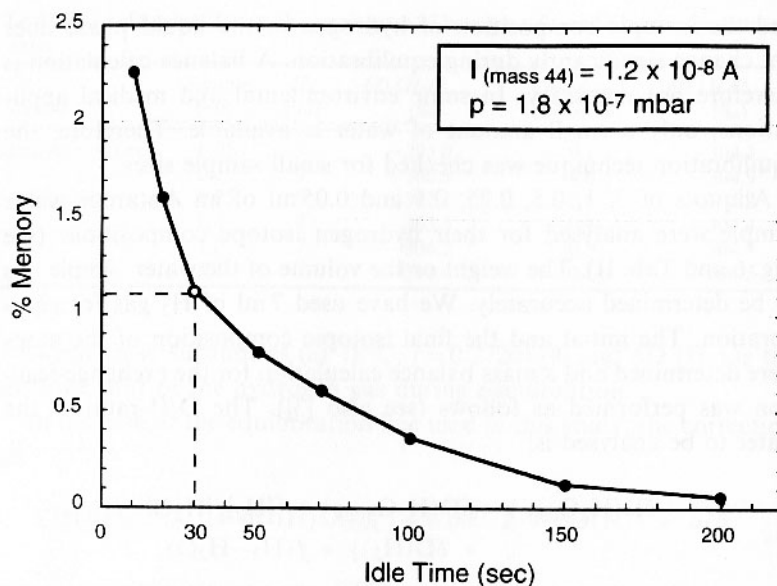


FIGURE 5 Memory effects (in %) for different idle times between changeover of standard and sample inlet.

data have to be corrected for the double of this “mixing-effect”, because memory occurs between sample and standard, and also *vice versa* between standard and sample. In our case for an idle time of 30 sec, a memory of 2.2% was observed. The memory is very constant and for V-SMOW-SLAP, a  $\delta^{18}\text{O}$  of  $-55.5\text{‰}$  has been analysed several times after correction. The new generation of instrumentation has a considerably lower memory ((FINNIGAN-MAT) pers. comm.)

### EQUILIBRATION TECHNIQUE AND SMALL SAMPLE SIZES

During equilibration between water and hydrogen, the isotopic composition of both phases, liquid water and hydrogen gas, are altered. Therefore, the isotope shift of the water during this reaction has to be calculated in order to get an information on the original D/H-ratio of the liquid. If ample liquid is available, the molar ratio of the two phases  $[\text{H}_2\text{O}]/[\text{H}_2]$  is higher than 0.998 (for 5 ml  $\text{H}_2\text{O}$  and 7 ml  $\text{H}_2$ )

and the isotopic composition of hydrogen in the liquid phase does not change significantly during equilibration. A balance calculation is therefore not necessary. In some environmental and medical applications, only a small amount of water is available. Therefore, the equilibration technique was checked for small sample sizes.

Aliquots of 5, 1, 0.5, 0.25, 0.1 and 0.05 ml of an Antarctic water sample were analysed for their hydrogen isotope compositions (see Fig. 6 and Tab. II). The weight or the volume of the water sample has to be determined accurately. We have used 7 ml of H<sub>2</sub> gas for equilibration. The initial and the final isotopic composition of the gases were determined and a mass balance calculation for the exchange reaction was performed as follows (see also [3]). The D/H-ratio of the water to be analysed is:

$$\delta D(\text{H}_2\text{O}_{\text{corr.}}) = \delta D(\text{H}_2\text{O}_{\text{meas.}}) + \left\{ \frac{[\text{H}_2]}{[\text{H}_2\text{O}]} \right\} * \delta D(\text{H}_2) * f(\text{H}_2 - \text{H}_2\text{O}),$$

where  $\delta D(\text{H}_2\text{O}_{\text{meas.}})$  is the raw delta between hydrogen gas equilibrated with the water sample and hydrogen equilibrated with the reference water (V-SMOW),  $[\text{H}_2]/[\text{H}_2\text{O}]$  is the molar ratio of these phases,  $f(\text{H}_2 - \text{H}_2\text{O})$  the isotopic fractionation of the D/H-ratio

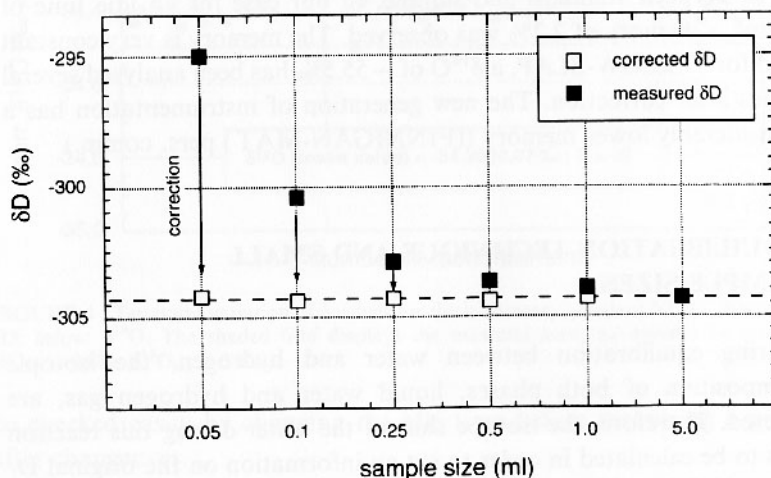


FIGURE 6 Equilibration technique applied to small sample sizes.

TABLE II  $\delta D$  values for small sample sizes of between 0.05 and 5 ml for an Antarctic water

Sample	Sample (ml)	H <sub>2</sub> (ml)	$\delta D$ (H <sub>2</sub> O <sub>meas.</sub> ) (‰)	Calculated correction	$\delta D$ (H <sub>2</sub> O <sub>corr.</sub> ) (‰)
Antarctic water	0.05	7	-295.0	-9.1	-304.1
	0.1	7	-300.3	-4.6	-304.9
	0.25	7	-302.4	-1.9	-304.2
	0.5	7	-303.5	-0.9	-304.4
	1.0	7	-304.2	-0.5	-304.7
	5.0	7	-304.4	-0.1	-304.5

between these substances (at 18°C,  $f=0.2720$ ) [9] and  $\delta D$  (H<sub>2</sub>) is the isotopic shift of the hydrogen gas during equilibration.

In the case of the equilibration line used in this study, the correction is:

$$\delta D(\text{H}_2\text{O}_{\text{corr.}}) = \delta D(\text{H}_2\text{O}_{\text{meas.}}) + 0.00022 * \delta D(\text{H}_2) * a/b,$$

where  $a$  = ml (hydrogen gas, STP) and  $b$  = ml water (liquid).

The original composition of the hydrogen can be analysed by the same line filling one of the bottles only with hydrogen and no catalyst. In Figure 6, results for the equilibration of water samples with the same isotopic composition of between 50  $\mu\text{l}$  and 5 ml are displayed. These waters have been equilibrated with a hydrogen gas enriched in its D/H-ratio by 304.2‰ in comparison to the equilibrated hydrogen. Filled dots represent the measured values, open dots the corrected values.

Thielecke *et al.* [11] recently published an algorithm for D/H isotope ratios of small sample volumes. The main difference between [11] and our approach is the fact that they did not consider the isotope fractionation factor for their balance correction.

Since at 18°C the water is enriched in deuterium (fractionation factor near 4), normally deuterium is transferred into the water phase. It is recommended to use a hydrogen gas for the equilibration with a deuterium content of one fourth of the D/H-ratio of the water to be analysed (close to equilibrium). Hydrogen of this isotopic composition can be purchased from Messer-Griesheim, Duisburg or it can be produced by a small appendix in the equilibration line. Depending on the total isotope shift of the gases, a correction of the  $\delta$ -values has to be applied for sample sizes smaller than 1 ml, corresponding to a molar

ratio  $[H_2]/[H_2O]$  of smaller than 0.994. The correction is smaller for hydrogen than for oxygen due to the low deuterium content of the equilibrated gas.

The equilibration of the oxygen isotopes  $^{18}O$  and  $^{16}O$  between  $H_2O$  and  $CO_2$  in a shaking water bath at  $18^\circ C$  is completed after more than 24 h for small amounts of water down to 0.05 ml. Since at equilibrium the fractionation factor between  $CO_2$  and  $H_2O$  is near unity (at  $18^\circ C$ ,  $f(CO_2-H_2O) = 1.0425$  [9]) and the molar ratio of oxygen between  $CO_2$  and  $H_2O$  is 2, the balance correction for the  $^{18}O/^{16}O$  ratio is higher by a factor of 8 compared to hydrogen.

$$\Delta(^{18}O-H_2O_{true}) = \Delta(^{18}O_{meas.}) + 2 * \{[CO_2]/[H_2O]\} * \Delta(^{18}O - CO_2) * f(CO_2 - H_2O),$$

where  $\Delta(^{18}O_{meas.})$  is  $\delta^{18}O(CO_{2\text{sample}}) - \delta^{18}O(CO_{2\text{standard}})$ ,  $[CO_2]/[H_2O]$  the molar ratio of these phases and  $\Delta(^{18}O - CO_2)$  is the isotopic shift of the  $CO_2$  towards equilibration.

The equations for small volumes have been checked with water and urine samples of between 1.13 g and 0.19 g (supplied by Dr. E. Forsum, Karolinska Hospital, Stockholm). The  $\delta D$  and  $\delta^{18}O$  values of

TABLE III Small sample sizes and large differences in  $\delta D$  and  $\delta^{18}O$  values

Sample	Sample (mg)	$H_2$ (ml)	$\delta D$ ( $H_2O_{meas.}$ ) (‰)	$\delta D$ ( $H_2O_{corr.}$ ) (‰)	$CO_2$ (ml)	$\Delta(^{18}O_{meas.})$ (‰)	$\Delta(^{18}O - H_2O_{true})$ (‰)
water 1	1.05	7.2	43.4	43.2	7.3	13.07	13.32
	0.55	7.2	43.7	43.4	7.3	12.86	13.33
	0.37	7.2	44.3	43.8	7.3	12.66	13.36
water 2	0.94	7.2	-49.2	-49.5	7.3	-7.12	-7.10
	0.67	7.2	-49.1	-49.6	7.3	-7.18	-7.16
	0.27	7.2	-48.6	-49.8	7.3	-7.00	-6.94
water 3	0.96	7.2	-71.1	-71.5	7.3	-7.16	-7.14
	0.53	7.2	-70.6	-71.3	7.3	-7.05	-7.02
	0.25	7.2	-69.6	-71.0	7.3	-7.06	-6.99
water 4	0.97	7.2	172.4	172.4	7.3	39.66	40.27
	0.51	7.2	173.4	173.4	7.3	39.33	40.48
	0.37	7.2	173.6	173.6	7.3	38.95	40.52
	0.42	7.2	173.9	173.8	7.3	38.97	40.35
water 5	1.13	7.2	693.2	692.5	7.3	153.51	155.26
	0.51	7.2	692.6	691.0	7.3	151.41	155.24
	0.26	7.2	693.2	690.1	7.3	148.32	155.69
	0.19	7.2	694.0	689.7	7.3	145.08	154.96

the H<sub>2</sub> and CO<sub>2</sub> gas used for equilibration are +152‰ and –8.43‰ on the V-SMOW scale. Five liquids were analysed for large differences in δ<sup>18</sup>O and δD values of up to 150‰ and 700‰, respectively, confirming the suitable application of the algorithms (see Tab. III).

After the correction, the δ-values for the D/H-ratio did not differ by more than 1.5‰ and for the <sup>18</sup>O/<sup>16</sup>O ratio by more than 0.25‰ from the values analysed with 5 ml of liquid. The equilibration time for oxygen however had to be extended to more than 24 hours for these samples sizes. We have not observed any isotopic shifts of small water samples during the analytical procedure due to partial evaporation.

### SAMPLING STRATEGY FOR GROUND ICE

The ground ice, defined as all types of ice contained in frozen or freezing ground [12], is fed by meteoric water sources, and therefore can be studied as paleoclimate archive using hydrogen and oxygen isotope methods [13], similar to those in glaciers and ice caps. In the permafrost sequences studied at the Bykovsky Peninsula, two types of ground ice are found: ice wedges and segregated ice. The most promising archives for paleoclimate reconstruction are syngenetic ice wedges, which may reach widths of 5 m and heights of 40 m or more. Ice wedges are formed principally by frost cracking in the upper part of permafrost due to very cold winter temperatures and a thin snow cover with low heat insulation. During annual snow melt in spring, meltwater of previous years' winter precipitation penetrates into the frost cracks, in general in the middle of the ice wedge, and freezes immediately due to the low permafrost temperatures (at Bykovsky Peninsula presently ca. –10°C). Thus, the stable isotope composition of the ice wedges reflects the mean annual winter temperature [14]. Isotope fractionation during the fast freezing process can be neglected [15]. Repeated annual freezing and thawing leads to a succession of vertical ice veinlets. As a consequence of this process, in the ideal case, ice wedges get continuously older from the middle towards the margins. Syngenetic ice wedges also grow vertically, because they are formed in areas with sediment accumulation. Therefore, sampling was performed both in vertical and in horizontal direction (see Fig. 7). We have observed single veinlets with widths of between 1 and 4 mm.

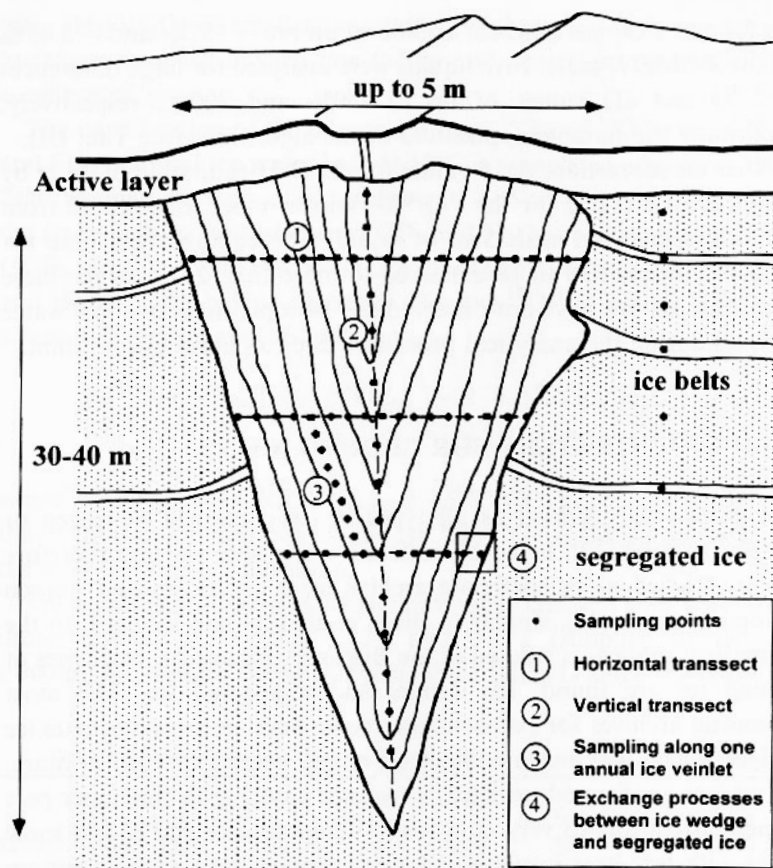


FIGURE 7 Sampling strategy for ground ice (ice wedges and segregated ice).

Thus, the sampling resolution (10 cm intervals) in our studies corresponds probably to time intervals of less than 100 years between two horizontal samples assuming frost cracking as an annual process. In order to verify the working hypothesis – one ice vein represents one year – we also have sampled along one vertical striking annual veinlet. Since for future analyses of ice wedges, an annual sampling resolution with limited sample volume is desired, we have extended the equilibration technique to water sample sizes of between 0.05 and 5 ml. In addition, the contact zone between ice and sediment was sampled carefully for the identification of exchange processes between ice wedge and frozen sediment.

Despite of fractionation processes, which may occur during freezing and despite of the participation of different water sources in its formation, segregated ice may also be used for paleoclimatic studies. This subject will be treated elsewhere.

The ground ice was sampled using an ice screw or a chain saw, and was thawed on site. 30 ml of meltwater was collected in plastic bottles for stable isotope analysis.

### FIRST RESULTS

In Figure 8, first isotopic data are presented for two Siberian ice wedges of the Bykovsky Peninsula. One Holocene ice wedge penetrates into a Late Pleistocene ice wedge of the Ice Complex.

In the  $\delta^{18}\text{O}$ - $\delta\text{D}$  diagram, we can clearly identify both generations of ice wedges by means of their absolute  $\delta$  values showing lighter isotope ratios for the Pleistocene part and heavier isotope ratios for the Holocene part. This presumably reflects lower winter temperatures for the Late Pleistocene compared to the Holocene. Additionally, the position relative to the Global Meteoric Water Line changes towards

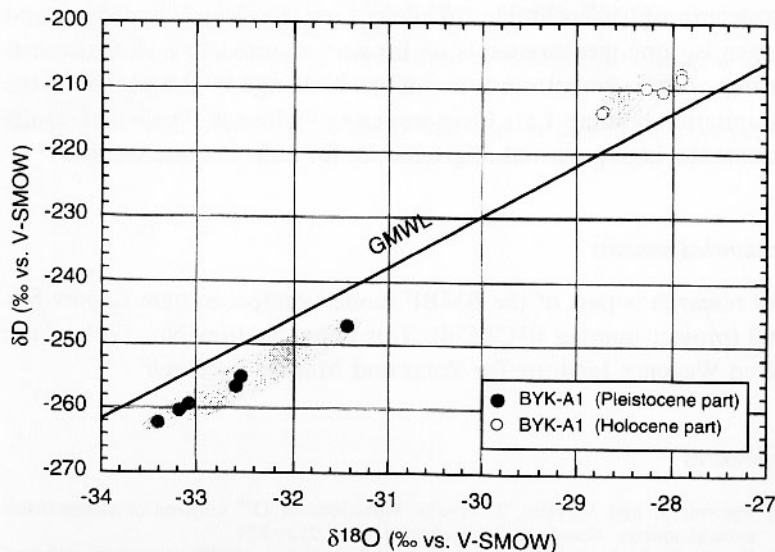


FIGURE 8 First isotopic data of two Siberian ice wedges from the Bykovsky Peninsula. One ice wedge of Holocene age penetrates into a Late Pleistocene ice wedge.

the Holocene. This increase of the deuterium excess may probably be attributed to a change in the source of the precipitation. These first results show the potential of ground ice for the paleoclimate reconstruction in non-glaciated regions, which cover extent areas in Northern Siberia. Results of stable isotope measurements for ground ice samples obtained during field campaigns in 1998 and 1999 will be published in detail elsewhere.

## CONCLUSIONS

The equilibration technique allows a sufficiently high number of isotopic analyses of approximately 24 samples per day for both  $\delta D$  and  $\delta^{18}O$ . The Delta-S mass spectrometer at the Alfred Wegener Institute in Potsdam was calibrated accurately in June, 1999. Its analytical precision is excellent, especially for isotopically light samples such as ground ice as shown by the new laboratory standard NGT1. The equilibration technique was checked for small sample sizes in order to extend the method and to enable a higher, possibly annual sampling resolution for ice wedges. A balance correction has to be applied to water samples smaller than 1 ml. Ground ice and especially ice wedges are promising paleoclimate archives. First results of hydrogen and oxygen isotope measurements on ice wedges indicate a shift towards warmer winter temperatures as well as a change in the source of the precipitation between Late Pleistocene and Holocene. These first results indicate the high potential of ground ice for paleoclimate studies.

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