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On-Line Determination of Oxygen Isotope Ratios of Water or Ice by Mass Spectrometry

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Oxygen isotope ratio determination on any of the water phases (water vapor, water, ice) is of great relevance in different research fields such as climate and paleoclimate studies, geological surveys, and hydrological studies. The conventional technique for oxygen isotope measurement involves equilibration with carbon dioxide gas for a given time with a subsequent isotope determination. The equilibration technique is available in different layouts, but all of them are rather time-consuming. Here we report a new on-line technique that processes water samples as well as ice samples. The same principal, CO_2 hydration, is used but speeded up by (i) a direct injection and full dissolution of CO_2 in the water, (ii) an increased isotope exchange temperature at 50 °C, and (iii) a rapid gas extraction by means of an air-permeable membrane into a continuous helium flux supplying the isotope ratio mass spectrometer with the sample gas. The precision is better than 0.1‰ which is only slightly larger than with the conventional equilibration technique. This on-line technique allows analysis of 1 m of ice with a resolution of 1−3 cm, depending on the meltwater flux, within 1 h. Similarly, continuous and fast analysis can be performed for aqueous samples for hydrological, geological, and perhaps medical applications.

Measurement of the oxygen isotopic composition of water is a key parameter in many research fields such as hydrology, limnology, geology, and paleoclimatology. $\delta^{18}O$ obtained from Greenland and Antarctic ice cores is a proxy for regional temperature at the time of the snow/ice formation and hence is a central measurement to detect past changes of climate. For a rapid advancement of the science in all areas of climate reconstruction based on ice cores, a field-based analysis method along with the coring operation would be of tremendous value.

The general method for analyzing water isotopes is based on equilibrating isotopes of gaseous carbon dioxide with those of the water at a given temperature in a vacuum-tight sample container. During this equilibration, oxygen isotopes of the water and CO_2 exchange via HCO_3^- and CO_3^{2-}. The equilibration process may be accelerated by shaking these containers.[1] The precision of these measurements is 0.05‰.

Using this conventional method in paleoclimatology is time-consuming: the ice core has to be cut in small sections, which are separately packed. Preparation and measurement is done on each sample later in the laboratory. For the more than 3000-m-long ice core from the Greenland Ice Core Project (GRIP), this corresponds to more than 100 000 single samples. With the increasing demand to produce high-resolution records, we have developed an on-line technique that is capable of processing 1 m of ice within ∼1 h with a precision similar to that obtained by a conventional system. Here we describe this new rapid method for oxygen isotope analysis on aqueous solutions.

METHOD AND MATERIALS

The new on-line technique (Figure 1) is based on our continuous flow analysis (CFA) experience.[2,3] For ice samples, we use a melting device similar to that developed for the chemical components (it is bypassed for water sample analysis). This melting device has undergone several improvements and was very successfully used during many field seasons in Greenland and in the Antarctic as well as in different laboratories.[3,4] An ice bar of 10−100 cm in length with a square area of 2 × 2 cm is slightly forced onto a heated device, where the ice continuously melts. The meltwater is pumped off through a borehole (1 cm^2) in the center of the melting device. Therefore, only ∼25% of the meltwater is used for the actually measurement; the rest is used to seal the melted air−water mixture from ambient air. This is, however, more important for measurement on the air components than for the water isotope determination.[5] The water, both sample and standard, is pumped off by a multichannel tubing pump (Ismatec SA) that has an adjustable pumping speed. A four-way rotary valve (Rheodyne Inc.) is used to change between sample and standard water. In a bubble generator, CO_2 gas is injected either into the sample water or into the standard water stream, depending on the valve position. To obtain a rapid dissolution of the admixed CO_2 in the water, we used a short and thin capillary (15 cm in length with 35 μm in diameter applying a pressure of 3 bar) to produce tiny CO_2 bubbles. The CO_2−water mixture then entered a thin, 0.75-mm-diameter, 2-m-long PEEK ($^1/_{16}$-in. tubing,

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(1) Epstein, S.; Mayeda, T. *Geochim. Cosmochim. Acta* **1953**, *4*, 213−224.
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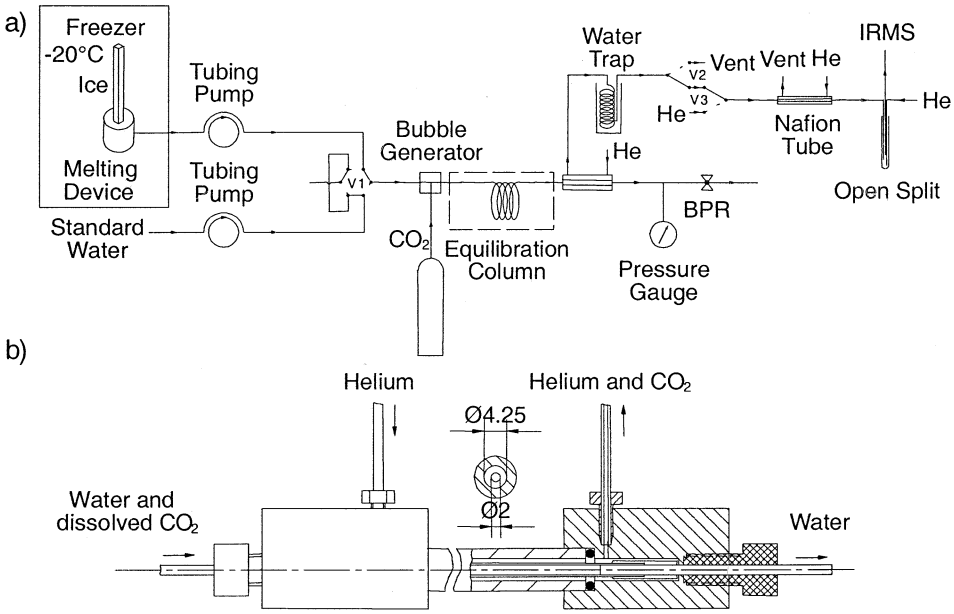

Figure 1. (a) System layout of the on-line determination of oxygen isotope ratio for water samples and (b) the degassing unit, as described in the Method and Materials section.

Omnilab AG) column where CO_2-H_2O isotope exchange for equilibration immediately starts. This column is immersed into a water bath held at 50 °C. This allows a quick equilibration between the CO_2 and water oxygen isotopes. The residence time in this column is dependent on the pumping rate (melting velocity) defining the pressure gradient applied to the system (in our case, the flux is 1 mL/min corresponding to ~60-s transfer time). The degassing unit (Figure 1b) consists of a gas-permeable membrane (Accurel, Microdyn Techn. Inc.), of 5−10 cm in length and a diameter of 2 mm, that is placed into a plexiglass tube of the same length. Both are fixed on aluminum bodies to seal it from ambient air. The volume between the membrane and the plexiglass tube is flushed with helium, which carries the CO_2 diffusing out of the water flux through the membrane due to the partial pressure difference (pressure of the water is ~0.5 atm above the helium pressure). Seals consists of Teflon tubing and Delrin connectors ($^1/_{16}$-in. Delrin nut, Omnilab AG). The helium flux is sealed with small Viton O-rings pressed onto an aluminum body. The helium−CO_2 mixture (20 mL/min) passes through a water trap (see Figure 1a) held at dry ice temperature (−78 °C) for drying. With a two-position switching valve (V2 and V3 in Figure 1a), one can change between bypass helium and the system helium flux; this allows us to determine the background signals in the isotope ratio mass spectrometer (IRMS) and to remove the degassing unit and the water trap for maintenance without breaking the helium flux of the interface, which connects our measuring system with the IRMS. Into this interface (a GP-Interface, Finnigan MAT) is placed a second drying column (Nafion tubing, Perma Pure Inc.) in front of the open split where the helium−CO_2 mixture enters the IRMS capillary. Only a small percentage of the main flux enters the IRMS capillary. The open split also allows us to dilute the sample gas in order to match the specific requirements of the IRMS. An important unit is the back-pressure regulator (BPR) at the end of the water flux (Jour Backpressure Regulator 0−7 bar, OmniLab AG). It guarantees an adjustable overpressure in the degassing unit. We usually set it to ~0.5 atm above the helium pressure. A manometer (Mano Gauge 1−10 bar range, Keller AG) is used to continuously monitor the pressure and its fluctuations. Our experience has shown that large pressure fluctuations can lead to a leak in the degassing unit, compromising the measurements.

RESULTS

Hydration Dynamics. A prerequisite for on-line determination of oxygen isotopes of water samples is a fast isotopic exchange between water and added carbon dioxide. However, a complete equilibration between water and carbon dioxide is not required as shown by several test runs. The measured difference with the on-line device, $\Delta\delta^{18}O_{on-line}$, between two water samples did not linearly increase with increasing isotope exchange time. But for a fixed isotope exchange time the ratio of the conventionally to the on-line measured differences is constant. This corresponds to a linear dependence of the on-line to the conventional obtained values. The measurements can therefore be corrected by applying a scaling factor γ according to the eq 1, where $\Delta\delta^{18}O_{on-line}$ and

$$\gamma = \Delta\delta^{18}O/\Delta\delta^{18}O_{on-line} \quad (1)$$

$\Delta\delta^{18}O$ correspond to the difference between two water samples of oxygen δ-values for the on-line and the conventional system, respectively.

This linear dependence is demonstrated in Figure 2 for three different isotope exchange times, 106, 300, and 1215 s. The slope of the linear dependence corresponds to the inverse scaling factor with which the measured values have to be corrected. The dynamics of the hydration process determines these slopes, i.e., the dependence of those slopes on the isotope exchange time between water and CO_2 isotopes. Dissolved CO_2 is hydrated

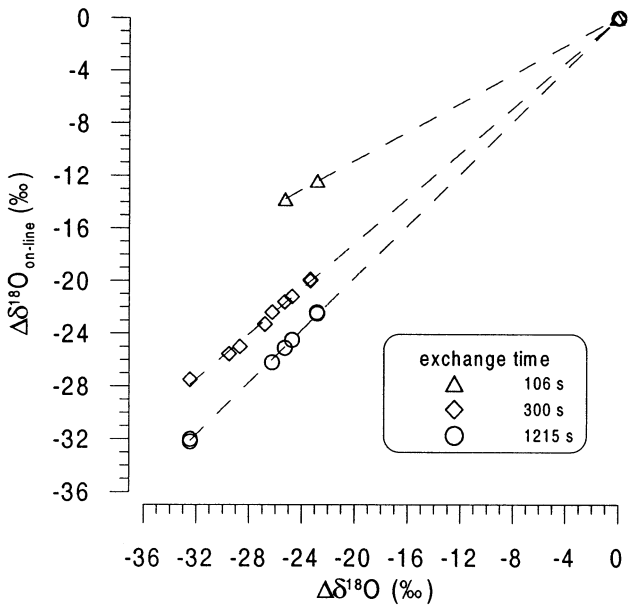

Figure 2. Linear dependence between on-line and conventionally measured differences for three chosen isotope exchange times (106, 300, and 1215 s). The slopes correspond to the inverse scaling factor, γ from eq 1, with which the measured values have to be adjusted to obtain the conventionally measured values.

Table 1. Kinematics of the Hydration of CO_2[a]

T (°C)	k_{CO_2}	$t_{1/2}$ (s) pH = 5	pH = 6	pH = 6.5	pH = 7
0	0.002^{pim}	8.9	72	158	251
10	0.007^{pim}	3.4	26	52	77
15	0.012^{pim}	2.1	16	32	46
20	0.019^{pim}	1.5	11	21	29
25	0.030^{pim}	0.9	6.5	13	18.5
30	0.055^{i}	0.6	4.0	7.5	10.5
30	0.040^{m}	0.8	5.5	10.5	14.5
40	0.105^{i}	0.3	2.2	4.1	5.5
40	0.070^{m}	0.5	3.3	6.1	8.3
50	0.270^{i}	0.1	0.9	1.6	2.2
50	0.110^{m}	0.3	2.2	3.9	5.3

[a] k_{CO_2} and $t_{1/2}$ are given as functions of the temperature and pH. The multiple values for a given temperature corresponds to the different data fitting procedure as described in Kern[6] and in this study (see also Figure 4). Indexes p, i, and m correspond to photometric, isotopic, and manometric techniques, respectively.

through two paths. Below a pH of 8, the direct hydration is dominant:[6,7]

$$CO_2 + H_2O \rightarrow H_2CO_3 \quad (2)$$

$$H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O \quad \text{(immediate)} \quad (3)$$

The rate of hydration is

$$-\frac{d[CO_2]}{dt} = k_{CO_2}[CO_2], \quad k_{CO_2} = 0.019\ s^{-1}\ (T = 20\ °C)$$

The corresponding dehydration processes is

$$H_2CO_3 \rightarrow H_2O + CO_2,$$
$$k_{H_2CO_3} = k_{CO_2}K \cong 13\ s^{-1}\ (T = 20\ °C) \quad (4)$$

For full equilibration, $H_2CO_3 \Leftrightarrow CO_2 + H_2O$, $K = [CO_2]/[H_2CO_3] = k_{H_2CO_3}/k_{CO_2}$ is ~700.

Table 1 comprises values for k_{CO_2} as a function of temperature obtained by a variety of techniques for the hydration dynamics that are described in Kern.[6]

For a pH above 10, the direct reaction with OH^- is dominant:

$$CO_2 + OH^- \rightarrow HCO_3^- \quad (5)$$

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \quad \text{(immediate)} \quad (6)$$

The rate of this reaction is

$$-\frac{d[CO_2]}{dt} = k_{OH}[OH^-][CO_2], \quad k_{OH} = 6300\ s^{-1}(mol/L)^{-1}$$
$$(T = 20\ °C)$$

The second path is not important for most of our samples (water samples as well as ice core samples) since they have a pH value of less than 8. Therefore, we investigate in the following the isotopic equilibration processes through the direct hydration according to the eqs 2 and 3. For each hydrated CO_2 molecule according to (2) a new CO_2 molecule is produced by eq 4 as soon as the chemical equilibrium for these two reactions is reached. This newly formed molecule now carries a mixed oxygen isotope signal (one-third from the water signal and two-thirds from the CO_2 signal). This means that the isotopic exchange rate, $k_{isotope}$, is only a third of the CO_2 hydration rate, k_{CO_2}.

With the isotopic exchange rate we can investigate the dynamics of the isotope equilibration process:

$$-\frac{d(\delta^{18}O_{CO_2} - \delta^{18}O_{H_2O} - \epsilon_q)}{dt} =$$
$$k_{isotope}(\delta^{18}O_{CO_2} - \delta^{18}O_{H_2O} - \epsilon_q) \quad (7)$$

where $\delta^{18}O_{CO_2}$ and $\delta^{18}O_{H_2O}$ are the isotopic compositions of CO_2 and H_2O and ϵ_q is the equilibrium fractionation between CO_2 and H_2O.

Assuming that $\delta^{18}O_{H_2O}(t) = \delta^{18}O_{H_2O}$ is constant, we obtain

$$\delta^{18}O_{CO_2}(t) = \delta^{18}O_{H_2O} + \epsilon_q + (\delta^{18}O_{CO_2} -$$
$$\delta^{18}O_{H_2O} - \epsilon_q)\exp(-k_{isotope}t) \quad (8)$$

The measured difference between two samples then corresponds to

$$\Delta\delta^{18}O_{on-line} = \Delta\delta^{18}O(1 - \exp(-k_{isotope}t)) \quad (9)$$

Based on these considerations, we obtain the scaling factor defined by eq 1:

(6) Kern, D. *J. Chem. Educ.* **1960**, *37*, 14−23.
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$$\gamma = \frac{\Delta\delta^{18}\mathrm{O}}{\Delta\delta^{18}\mathrm{O}_{\mathrm{on-line}}} = \frac{1}{1 - \exp(-k_{\mathrm{isotope}}t)} \qquad (10)$$

This means that this factor is only dependent on the isotopic exchange rate. For a temperature of 20 ± 1 °C, k_{isotope} yields (6.3 ± 1.0) × 10^{-3} s^{-1}, since k_{CO_2} is (0.019 ± 0.003) s^{-1}.[6] By fitting our measured values for five different water samples according to eq 9, we obtain a mean value for k_{isotope} of (6.3 ± 0.2) × 10^{-3} s^{-1}. For this determination, we reanalyzed samples that previously were measured by a conventional water equilibration system. They cover a δ^{18}O range of 10‰, when including the reference (−11‰ on the V-SMOW scale), the range widens up to 34‰. Figure 3 shows the isotope exchange as a function of time for these water samples. By normalizing the measured on-line δ^{18}O values to the previously measured δ^{18}O values, an additional estimate for k_{isotope} can be derived by fitting the scaling factor (see eq 10) against the applied isotope exchange time. The best fit is obtained for k_{isotope} = (6.37 ± 0.11) × 10^{-3} s^{-1} rejecting four values; three of them are values for an isotope exchange time of 1200 s. Both estimates are in very good agreement with the mean literature value for a temperature of 20 °C as given above.[6] In an additional experiment, we extended the isotopic exchange rate value to 40 and 50 °C, as seen in Figure 4, to check which of the two sets of values (photometric and manometric techniques [8]) mentioned by Kern[6] corresponds better with our measured values. From Figure 4, our values depend linearly on the inverse temperature in the logarithmic plot in agreement with measurements of Mills and Urey[9] using the isotope exchange method.

Signal Dispersion. From Figure 3, it is also obvious that for precise measurements a long isotope exchange time is required, ensuring a rather complete isotopic equilibrium. If this is not the case, small variations in the isotope exchange time (occurring through variations in the pumping force and alteration in dissolution velocity of CO_2 in water) or variations in the exchange rate (dependent on pH or temperature variations) will lead to significant changes in the measured signal. On the other hand, the larger the isotope exchange time is the higher the signal dispersion becomes, which has a direct influence on the resolution of the system. In our system, the water passes through a pipe with radius, *R*. For our settings, we can assume that the flux is laminar. After Navier−Stokes, a parabolic velocity profile is expected with the central fluid parcel having twice the mean velocity and is sticking at the edges. Based on these large velocity gradients within the pipe, a dispersion builds up that increases with the isotope exchange time. However, the Navier−Stokes approach leads to far too high dispersion times compared to values obtained from our measurements. This can be understood by the fact that molecular diffusion in a radial direction dampens the developing dispersion. Molecular diffusion forces the dissolved CO_2 molecule to diffuse toward the edges of the pipe, where the velocity is lower than in the center. Taylor[10,11] and Aris[12] investigated the dispersion of a dissolved material in a fluid, which is now referred to as the Taylor−Aris dispersion. After Taylor, the mean concentration

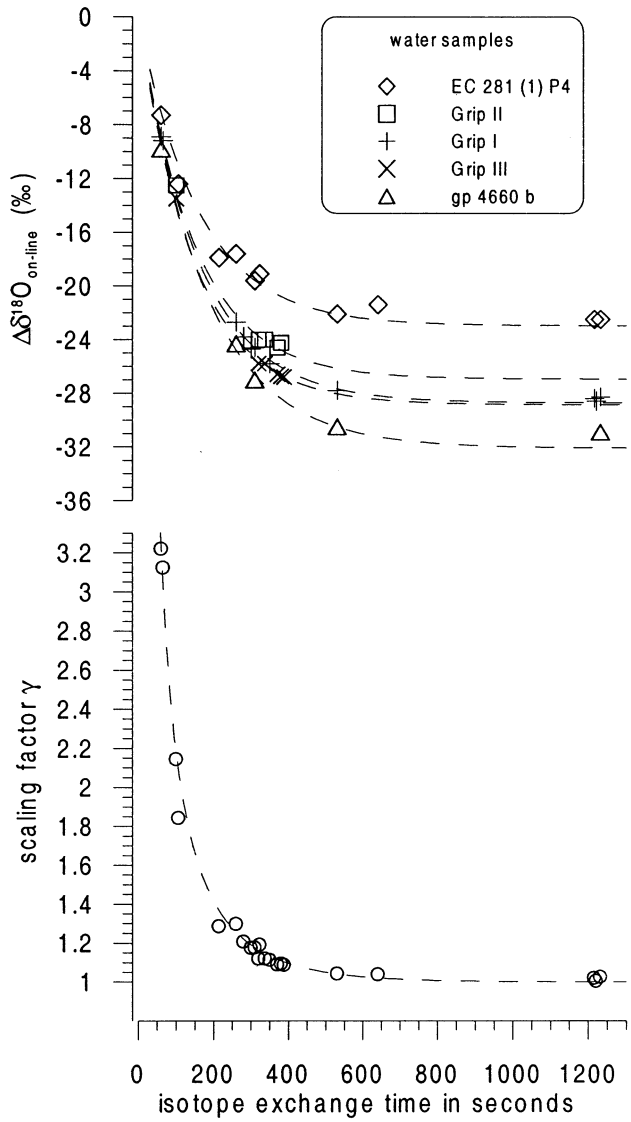

Figure 3. (Top) On-line δ^{18}O measurements plotted against the isotope exchange time for five different water samples. The curves are calculated after eq 9 by adjusting k_{isotope}. (Bottom) Normalized measurements of the top panel according to eq 10 versus the isotope exchange time. This normalized values correspond to the scaling factors. The curve is fitted to the values through eq 10 by varying k_{isotope}.

c(z, t) of the dissolved material over the square area of the pipe can be given by a diffusion equation such as

$$\frac{\partial c}{\partial t} + u\,\frac{\partial c}{\partial z} = D\,\frac{\partial^2 c}{\partial z^2} \quad \text{where} \quad D = D_{CO_2}\left(1 + \frac{1}{48}\,\frac{u^2R^2}{D_{CO_2}{}^2}\right) \qquad (11)$$

where *R*, *z*, and D_{CO_2} denote the pipe radius, the coordinate along the pipe, and the diffusion coefficient of CO_2 in water. The mean velocity of the dissolved matter is *u* with a Gaussian distribution that becomes larger with $(Dt)^{0.5}$. The main contribution to the dispersion is given by the term $1/48(u^2R^2/D_{CO_2})$ that is inversely proportional to the diffusion constant of CO_2. For a constant water flux, *F*, the mean velocity $u(R, F)$ becomes $F/\pi R^2$. The dispersion time, *T*, is $4[D(R)t]^{0.5}/u(R, F)$. According to eq 11, the increase

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(9) Mills, G.; Urey, H. *J. Am. Chem. Soc.* **1940**, *62*, 1019−1026.
(10) Taylor, G. *Proc. R. Soc. London* **1953**, *A219*, 186−203.
(11) Taylor, G. *Proc. R. Soc. London* **1954**, *225*, 473−477.
(12) Aris, R. *Proc. R. Soc. London* **1956**, *235*, 67−77.

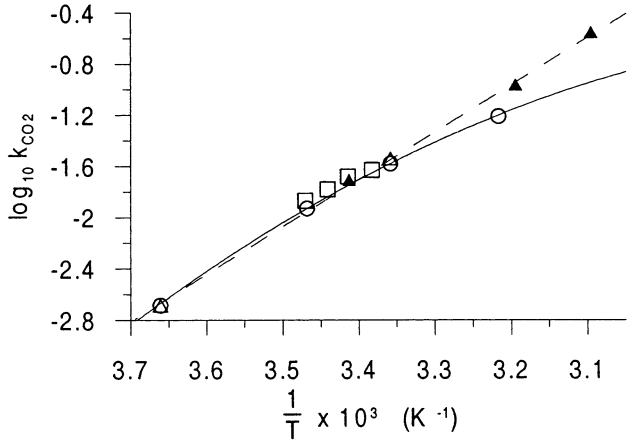

Figure 4. Logarithmic plot for k_{CO_2} versus the inverse temperature. Squares and circles correspond to previously published values obtained by the photometric and manometric hydration techniques, respectively.[8] Triangles corresponds to values obtained by the isotope exchange technique (filled triangles refer to our values for three different temperatures, open triangles is from Mills and Urey[9]). The solid line follows the manometric data. The dotted line is obtained by a linear fit through our data completed by the two isotopic data points from Mills and Urey,[9] which are in good agreement.

becomes proportional to R and $t^{0.5}$ when the product uR is large compared to D_{CO_2}. Hence, for a minimal dispersion influence, one requires not only a short isotope exchange time but also a small pipe radius. However, the pipe cannot be too small in diameter because the pumping resistance will grow as $\propto R^{-4}$. This optimization problem has to be solved according to the specific needs of the applications, either an excellent precision (long isotope exchange times, mean pipe diameter) or high resolution in time (short isotope exchange time, small pipe diameter).

Our measured dispersion values can be understood with Taylor's theory. However, besides the Taylor dispersion in a pipe, there are other mechanisms leading to an enhanced widening of our signal. In particular, the length of the Accurel membrane and the direction of the helium carrier flux are important. In Figure 5b, two estimates of dispersion times of our system for a steplike signal are shown, for a 10-cm Accurel membrane with a backflush helium carrier and a 5-cm Accurel membrane with an unidirectional helium carrier flux. The dispersion is, as expected, smaller for the second case by 5 s. About 70% of this reduction comes from the shorter Accurel membrane and about 30% is due to the equal direction helium carrier flux since the carrier gas moves the same direction as the signal. However, a disadvantage of shorter membrane is a lower degassing efficiency, implying a higher admission of CO_2 gas, which could lead to a longer dissolution of CO_2. This could finally lead to a lower reproducibility.

Resolution of Ice Core Measurements. Resolution of the conventional equilibration method used for discrete samples must be chosen prior to sampling. For the GRIP samples were targeted to a 2-cm resolution. This corresponds to an enormous amount of samples to be measured (~100 000). The resolution of our system depends mainly on (i) the melting velocity of the ice, (ii) the dispersion in the equilibration column as described above, (iii) the dispersion associated with gas extraction membrane and the direction of carrier flux, and (iv) the open split characteristic. The melting velocity of the ice is commonly set to ~3 cm/min

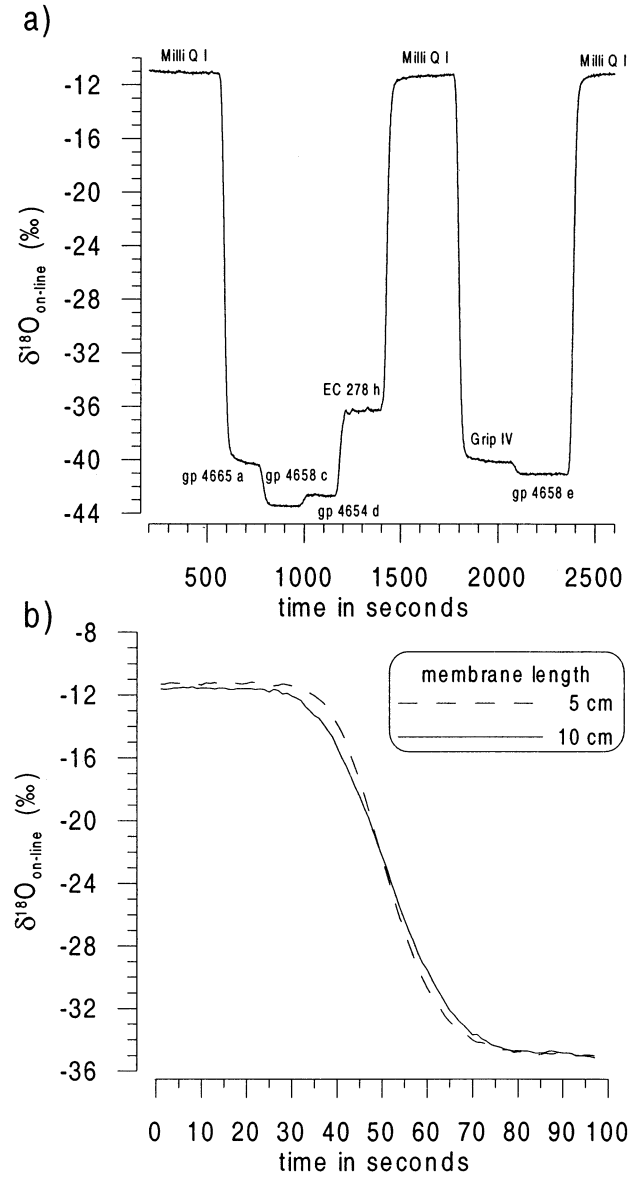

Figure 5. (a) Continuous measurement of oxygen isotope ratio for a sequence of Greenland ice core water samples. Our standard (Milli-Q I) is purified tap water with a δ-value of −11.10‰ against V-SMOW. Sample description is given for each signal level. (b) Dispersion of our measuring system for a steplike signal, for a 10-cm-long Accurel membrane combined with a backflush helium carrier (flux directions are opposite, solid line) and for a 5-cm-long Accurel membrane combined with a helium carrier set to the same flux direction (dashed line).

(temperature of the melting device 25 °C). However, it would be possible to lower this velocity by lowering the melting device temperature. A water flux of 1 mL/min, corresponding to 1 cm/min for our melting device with an area of 1 cm^2, is sufficient. Therefore, the melting velocity allows us to adjust the resolution such that it meets the application needs. For a fixed water flux, the resolution is actually determined by the dispersions either in the equilibration column, in the degassing unit, or in the open split. The main contribution comes from the dispersion in the equilibration column since a compromise between dispersion time and equilibration percentage must be found. Full equilibration leads to longer tubes and therefore higher dispersion times (see also below). The dispersions associated with the open split and

Table 2. Compilation of Seven On-Line Measuring Sequences (A−H) of Overall 13 Different Greenland Ice−Water Samples Previously Measured with the Conventional Equilibration Technique[a]

ice−water sample	conventional measured $\delta^{18}O$(‰)	difference between on-line and conventional measurements ($\delta^{18}O_{on-line} - \delta^{18}O$(‰))									
		A	B	C	D	E	F	G	H	mean	std dev
Eiswasser I/2	−35.50	0.15	0.10							0.13	0.04
EC 278 f	−35.76								0.36	0.36	
EC 278 h	−36.25			−0.05	0.15					0.05	0.10
EC 278 k	−36.28					0.08	0.08	−0.02		0.05	0.05
gp 4666 a	−38.92	0.02	0.22							0.12	0.10
gp 4658 b	−40.26	0.16								0.16	
gp 4665 a	−40.39			0.09						0.09	
Grip IV	−40.58			0.38						0.38	
gp 4658 e	−41.36			0.26	0.06		0.36			0.23	0.12
gp 4654 d	−42.67			0.02			−0.03	−0.13	0.07	−0.02	0.07
gp 4658 c	−43.48			0.08	−0.02	0.08				0.05	0.05
gp 4662 b	−43.63		0.08							0.08	
gp 4659 e	−43.89	0.04								0.04	

[a]As standard we used purified tap water (Milli-Q) with a $\delta^{18}O$ of −11.10‰ on the V-SMOW scale.

the degassing unit are mainly dependent on the geometrical dimensions that can be adjusted. They are in our case lower than the dispersion in the equilibration column. Our system gives us a dispersion of ∼30 s defined as the time between 8 and 92% of the isotope signal change (Figure 5b). Therefore, an ice melting velocity of 3 cm/min corresponds to a core resolution of ∼1.5−2 cm dependent on the $\delta^{18}O$ range of the sample. This can be improved by lowering the melting device temperature and therefore the melting velocity. With the present melting device, a maximum core resolution slightly larger than 0.5 cm is possible.

Precision of Measurements. As mentioned above, precision depends on several variables of the system. One important parameter is the percentage of equilibration. From Figure 3 it is obvious that a nearly complete equilibration leads to a better precision due to minimal changes in the scaling factor. To improve precision without having counteracting influences on the dispersion, we increased the equilibration temperature to 50 °C. This leads to a more than 14.5-fold shorter time for complete equilibration compared to ambient temperature of 20 °C. An example of such a measurement is given in Figure 5a (corresponds to sequence C in Table 2). It is a continuous measurement of oxygen isotope ratios for a sequence of Greenland ice core water samples over a measuring time of ∼45 min. The δ-value range of those samples is more than 9‰, when including the standard (Milli-Q I), it extents to more than 30‰, which is much larger than actual changes in ice cores. Therefore, this plot underestimates the precision but allows us to determine the dispersion (defined as 8−92% signal time) rather well. Table 2 shows a compilation of seven measuring sequences (capital letters A−H on the top of the columns) of different Greenland ice−water samples that were previously measured with the conventional equilibration technique. As standard we used purified (Milli-Q system) tap water with a $\delta^{18}O$ = −11.10‰ on the V-SMOW scale. For each measuring sequence, at least one standard water check was performed prior and after the sample sequence (see Figure 5a). The Greenland samples vary between −34 and −44‰ V-SMOW. The values obtained by the conventional method are given in column two. The differences between on-line and conventional determinations of oxygen isotope ratios for are given in columns A−H. They vary in the range of −0.13 to +0.38‰. The values are on average 0.1‰ too high. This can be explained by a slightly incomplete equilibration (99.6%) of the order of a few per mil (scaling factor 1.004 ± 0.001). The means and standard deviations of replicates of those water samples are given in the last columns. The standard deviation for a single sample difference is 0.13‰. The standard deviation of replicates is lower, namely, 0.08‰. Since the former number includes the uncertainty of the conventional method of 0.05‰, the precision as well as the accuracy are similar, i.e., 0.1‰ (Figure 6).

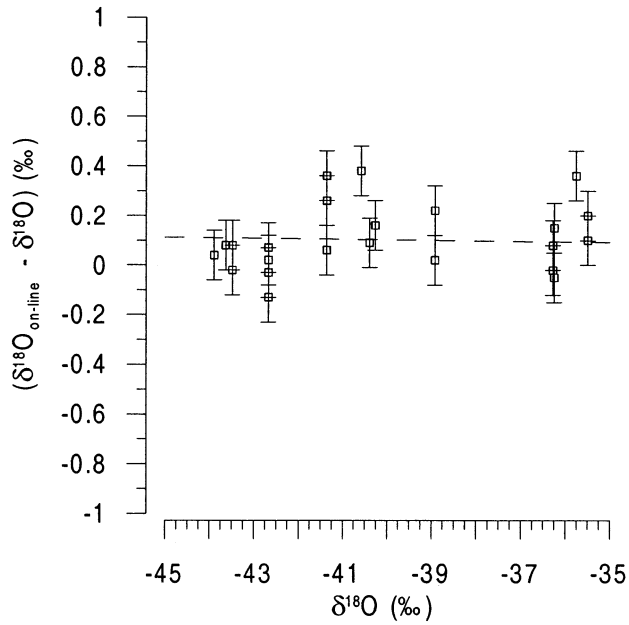

Figure 6. Measurement precision of on-line oxygen isotope determination as derived from 14 different water samples (squares). The precision of the measurements as obtained from replicate determinations is ∼0.1‰ (error bars). An indication of the accuracy of those values is given by the standard deviation of the differences between on-line and conventional determinations, which is 0.13‰. The small offset from zero can be explained by a slightly incomplete equilibration (see text).

Complications with Impurities in the Ice. Ice water samples are not as clean as our standard, purified tap water. In particular,

ice from glacial times carries more impurities than ice from interglacial times. Furthermore, Greenland ice contains many more impurities than Antarctic ice.[13] Chemical impurities have to be checked in this respect since they have the potential of altering the pH value of the melted ice. In the worst case, a buffering of the expected pH drop during the addition of CO_2 may lead to a different path of hydration which could influence our isotope determination. However, our experience with Greenland ice–water samples (Table 2) does not support this view. The kinematics of the CO_2 hydration is very fast (<2.5 s) for pH 5–7 at a temperature of 50 °C (Table 1.). Therefore, no major problems should be expected from chemical impurities. Perhaps more important could be major impurities with particles (dust), which could affect the permeability of the Accurel membrane. However, we did not experience this problem during our test measurements.

CONCLUSIONS AND OUTLOOK

The presented on-line measuring system is capable of handling a wide range of aqueous solutions for precise and rapid oxygen isotope ratio determinations (patent pending). The authors can foreseen several applications in the fields of glaciology, hydrology, geology, pharmacy, and medicine, since the new method allows a simple and fast analysis procedure in a fully continuous or semicontinuous mode (switching between single samples). In glaciology, we see the following advantages: (i) continuous measurements on ice sections and thus high-resolution isotope profiles along the ice core can be obtained; (ii) isotope field measurements may become possible soon; (iii) can be coupled to a CFA melting device. Such a system combined with a benchtop mass spectrometer may allow one to continuously measure the water isotopes in the field shortly after the ice core retrieval. This would be a major step forward in establishing an age scale already in the field.

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