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Estimation of temperature change and of gas age - ice age difference, 108 kyr B.P., at Vostok, Antarctica

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Abstract. Air trapped in ice core bubbles provides our primary source of information about past atmospheres. Air isotopic composition ($^{15}N/^{14}N$ and $^{40}Ar/^{36}Ar$) permits an estimate of the temperature shifts associated with abrupt climate changes because of isotope fractionation occurring in response to temperature gradients in the snow layer on top of polar ice sheets. A rapid surface temperature change modifies temporarily the firn temperature gradient, which causes a detectable anomaly in the isotopic composition of nitrogen and argon. The location of this anomaly in depth characterizes the gas age - ice age difference (Δ_{age}) during an abrupt event by correlation with the δD (or $\delta^{18}O$) anomaly in the ice. We focus this study on the marine isotope stage 5d/5c transition (108 kyr B.P.), a climate warming which was one of the most abrupt events in the Vostok (Antarctica) ice isotopic record [*Petit et al.*, 1999]. A step-like decrease in $\delta^{15}N$ and $\delta^{40}Ar/4$ from 0.49 to 0.47 ‰ (possibly a gravitational signal due to a change in firn thickness) is preceded by a small but detectable $\delta^{15}N$ peak (possibly a thermal diffusion signal). We obtain an estimate of 5350 ± 300 yr for Δ_{age}, close to the model estimate of 5000 years obtained using the Vostok glaciological timescale. Our results also suggest that the use of the present-day spatial isotope-temperature relationship slightly underestimates (but by no more than 20 ± 15%) the Vostok temperature change from present day at that time, which is in contrast to the temperature estimate based on borehole temperature measurements in Vostok which suggests that Antarctic temperature changes are underestimated by up to 50% [*Salamatin et al.*, 1998].

1. Introduction

The reconstruction of climate changes in polar regions traditionally relies on the interpretation of oxygen 18 ($\delta^{18}O$) or deuterium (δD) profiles recorded in polar ice cores [*Dansgaard et al.*, 1993; *Jouzel et al.*, 1987]. This approach is based on an observed linear relationship between the mean annual isotopic content ($\delta^{18}O$ or δD) of middle and high-latitude precipitation and the mean annual temperature at the precipitation site. This relation results from the fractionation processes that affect the water isotopic molecules (HDO and $H_2{}^{18}O$) at each phase change during their atmospheric cycle [*Dansgaard*, 1964]. Although this linear relationship is particularly well obeyed over Greenland [*Johnsen et al.*, 1989] and Antarctica [*Lorius and Merlivat*, 1977], this does not guarantee that it can be used as a paleothermometer. The slope of the present-day spatial relation (the "spatial slope") is not necessarily a surrogate of the slope through time (the "temporal slope") as has been sometimes assumed in paleoclimatic studies. This is because factors other than the temperature of the site affect precipitation's isotopic composition, such as the origin and the seasonality of the precipitation or the relationship between cloud and surface temperature [*Dansgaard*, 1964; *Jouzel et al.*, 1997].

Indeed, this assumption has been challenged at least for Greenland where borehole paleothermometry shows that the cooling between present day and the Last Glacial Maximum (LGM) about 21 kyr B.P. (thousands of years before present) was about twice larger than predicted from the $\delta^{18}O$ profiles using the spatial slope [*Cuffey et al.*, 1995; *Johnsen et al.*, 1995; *Dahl-Jensen et al.*, 1998]. The same method also suggests that present-day/LGM Antarctic temperature changes are underestimated by up to 50% [*Salamatin et al.*, 1998], but this estimate is subject to large uncertainties because of signal diffusion due to low precipitation rates [*Rommelaere*, 1997].

Severinghaus et al. [1998] have recently developed an independent method allowing estimates of short-term temperature changes. This method is based on the fact that during the firnification processes that lead to the trapping of air bubbles in ice, the composition of the air is slightly modified by physical processes such as gravitational and thermal fractionation. This creates anomalies in the isotopic composition of nitrogen and argon, which, as fully discussed below, allow estimates of temperature changes both from their strength and their position. However, to be easily detectable, these anomalies should correspond to rapid climatic changes. This is why this new method has until now only been applied to Greenland cores, where it has indicated that the classical isotopic interpretation not only underestimates temperature changes for the LGM but also those during abrupt climate changes [*Jouzel*, 1999; *Lang et al.*, 1999; *Leuenberger et al.*, 1999; *Severinghaus and Brook*, 1999].

The Antarctic climate is not characterized by such abrupt changes as observed in Greenland. However, a theoretical

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estimate of the isotopic anomalies at the time of maximum change in the Vostok core led us to estimate that although small, they should be detectable. With this in mind we have undertaken a detailed study of a warming event that occurred between 107 and 108 kyr BP. We have been successful in detecting a small isotopic anomaly both in nitrogen and argon that may correspond to this event. This gas phase marker of the warming provides, for the first time, a direct estimate of the depth at which air bubbles close (the close-off depth (COD)) and provides information on the gas age/ice age difference (here in after referred to as Δ_{age}) and on the temperature at that time. After describing the fractionation processes occurring in the firn, we present how we theoretically estimate the isotopic anomalies and then discuss how our isotopic measurements imply that both Δ_{age} and temperature change are slightly underestimated when using the spatial isotope/temperature slope to interpret the Vostok deuterium record.

2. Fractionation Processes in the Firn

The isotopic composition of atmospheric nitrogen ($^{15}N/^{14}N$) and argon ($^{40}Ar/^{36}Ar$) is constant over the period of interest here [*Mariotti*, 1983]. Therefore all changes in the isotope ratios (here in after referred to as δ units in per mil with respect to the atmosphere, $\delta^{15}N$ and $\delta^{40}Ar$, respectively) will reflect changes through processes occurring in the firn. This firn can schematically be divided into three zones with different properties concerning the movement of air: (1) the convective zone in which the air is well mixed, (2) the diffusive zone in which vertical transport is primarily by molecular diffusion, and (3) the nondiffusive zone in which air does not migrate vertically, and at the bottom of which the air is trapped [*Sowers et al.*, 1993]. This entrapped air is younger than the surrounding ice, which results in an age difference (Δ_{age}) between the ice and the air bubbles that it contains. Δ_{age} depends both on accumulation and on temperature, with increasing values for decreasing accumulation and temperature, and it is estimated using a firn densification model developed by *Barnola et al.* [1991].

Two effects are known to alter the isotopic composition of the air in the firn. The first one is the consequence of the gravitational field that leads to an enrichment of heavier isotopes at the bottom of the firn in the diffusive zone. This enrichment is a function of the mass difference between the considered isotopic species [*Craig et al.*, 1988; *Schwander*, 1989; *Sowers et al.*, 1989]. Use of the barometric equation allows one to relate the isotopic composition of the air to the thickness of the diffusive column and to the ambient temperature through

$$\delta\,(‰)=\left[\exp\left(\frac{\Delta mgz}{RT}\right)-1\right]1000, \qquad (1)$$

where Δm is the mass difference between the isotopic species, z is the thickness of the diffusive column, g is the gravitational acceleration, and R is the gas constant. T is the firn temperature (Kelvin), which is very close to the mean annual surface temperature at Vostok. For example, a diffusive column height of 85 m at 216 K (present condition) will lead to a $\delta^{15}N$ enrichment of 0.478‰ and to a $\delta^{40}Ar$ enrichment precisely 4 times more, as Δm is equal to 4 instead of 1 for nitrogen isotopes. The parameter $\delta^{40}Ar/4$ is thus equally affected as $\delta^{15}N$ by gravitational enrichment, and both parameters contain information about the diffusive column height (here in after DCH) in times past.

The second effect results from the phenomenon of thermal diffusion fractionation that occurs in a gas mixture when a temperature gradient exists in this gas [*Chapman and Dootson*, 1917]. This occurs in firn when the surface temperature changes either due to seasonal or to longer-term climate variation because of the thermal inertia of the underlying firn. Because gases diffuse about 10 times as fast as heat in firn, fractionated gas can penetrate throughout the firn in decades during the finite time required for the firn to equilibrate with the new surface temperature (a few hundred years). The heavier gas migrates generally toward the colder part of the firn column, which leads to a fractionation that is proportional to the temperature difference between the surface and the close-off depth ($\Delta T_{anomaly}$). The proportionality is given by the "thermal diffusion sensitivity parameter" Ω, and the isotopic anomaly is defined as

$$\delta_{anomaly} = \Omega\Delta T_{anomaly}. \qquad (2)$$

This parameter, recently accurately measured, is equal to 0.014 ‰/°C for $\delta^{15}N$ and 0.036 ‰/°C for $\delta^{40}Ar$ at 213 K and is approximately constant in the range of temperature relevant to ice core studies [*Severinghaus and Brook*, 1999; *Severinghaus et al.*, 2001].

The thermal anomaly depends both on the size and on the rate of warming (or cooling), being larger and thus more detectable if the change is rapid. The consequence of the thermal anomaly is an anomaly in the isotopic signal of $\delta^{15}N$ and $\delta^{40}Ar$ which then persists in the firn for several hundred years. For example, during an abrupt warming an increase of the isotopic composition takes place at the bottom of the firn followed by a gradual decrease as the temperature gradient between the surface and the bottom of the firn column becomes stable. Typically, a rapid warming of 10°C in a few tens of years will result in a positive anomaly of 0.14‰ in $\delta^{15}N$ (and of 0.09‰ in $\delta^{40}Ar/4$). Note that any temperature increase is generally accompanied by an accumulation increase. Warming also causes the firn to thin, because the transformation of snow to ice proceeds faster at warmer temperature due to the fact that it is a temperature-activated metamorphic process. As a result, there is a concurrent change in the depth of the close-off, and very likely in the thickness of the diffusive column, which means that observed anomalies are generally due to a combination of gravitational and thermal fractionation. The interest of measuring both nitrogen and argon isotopes is that this allows separating the thermal effect from the gravitational settling by comparing $\delta^{15}N$ with $\delta^{40}Ar/4$, because the latter is about 63% as sensitive to thermal fractionation as $\delta^{15}N$ [*Severinghaus and Brook*, 1999].

Sowers et al. [1992] have used the gravitational signal in $\delta^{15}N$ to infer information about the past thickness of the diffusive column in Antarctic cores. However, until now, studies combining both gravitational and thermal effects have been limited to Greenland cores (GISP2 and GRIP) with a focus on abrupt events for which the thermal effect is expected to be large. *Severinghaus et al.* [1998] showed that isotopic anomalies due to thermal diffusion are detectable at the time of the rapid warming occurring at the end of the Younger Dryas, 11.6 kyr B.P. ago. They separated the thermal and diffusional effects, combining nitrogen and argon measurements, but were cautious in inferring a temperature change from the strength of the anomaly ($\delta^{15}N$ = +0.15 ± 0.02‰) because of analytical uncertainties and of a lack of accurate knowledge of the thermal diffusion sensitivities. Instead, they took advantage of the possibility of an accurate determination of Δ_{age} by counting the annual layers between the level of the gas-isotopic anomaly that marks the end of the Younger Dryas and the corresponding isotopic change recorded in the ice. They then used a firn densification model to relate Δ_{age} to absolute temperature, finding that Younger Dryas in Greenland was 15±3°C colder than present. *Severinghaus and Brook* [1999] performed a similar study for the Bölling transition at ~14.6 kyr but took advantage of new determinations of the thermal diffusion sensitivity to propose an estimate of the temperature change directly from the strength of the anomaly. Unlike those two studies, the approach followed by *Leuenberger et al.* [1999] for the 8.2 kyr BP event and *Lang et al.* [1999] for Dansgaard-Oeschger event 19 (~ 71 kyr BP) was limited to measurement of nitrogen isotopes. By using the position of the anomaly and either assuming a negligible influence of the gravitational effect [*Leuenberger et al.*, 1999], or accounting for a link between accumulation and temperature [*Lang et al.*, 1999], these authors derived temperature change estimates for those two events without argon isotope data.

3. Search for Isotopic Thermal Anomalies in the Vostok Core

Providing a direct estimate of the close-off depth (COD) at low-accumulation sites from Central Antarctica is of particular interest as it would give constraints on Δ_{age} up to now estimated from densification models. This would thus improve our ability to better assess the timing of, for example, changes in greenhouse gases, CO_2 and CH_4, and changes in temperature, and would also provide indirect estimates of Antarctic surface temperature at that time. Such an estimate of the COD can be inferred by identifying the depths, Z_{ice} and Z_{gas}, at which an atmospheric event such as a temperature change is recorded in the ice on the one hand and in the air bubbles on the other hand. With this in mind we explored the possibility of using isotopic thermal anomalies and gravitational signals in the Vostok ice core. To this aim we focus on the event corresponding roughly to the marine isotope stage 5d/5c transition, dated ~ 108 kyr B.P. using the glaciological timescale GT4 [*Petit et al.*, 1999]. This change ($Z_{ice(observed)}$ = 1503 m in the 5Γ Vostok core) corresponds to one of the most rapid events recorded in this core (Figure 1), with a warming rate of 0.4°C/ 100 years as inferred from the classical interpretation of the ice deuterium record (still 50 times slower than at the end of the Younger Dryas in central Greenland). Because the duration of the event is greater than the thermal relaxation time of the firn, the close-off should have partially warmed before the surface temperature reached its maximum, so we expect the signal to be more attenuated than the signals of abrupt warming found in Greenland.

We first estimated the size and location of the expected isotopic signals ($\delta^{15}N$ and $\delta^{40}Ar$) in order to plan our sampling and measurement strategy. We combined the use of a model accounting for thermal diffusion in the firn [*Severinghaus et al*, 1998; C. Ritz, personal communication, 2000] and the firn densification models [*Barnola et al.*, 1987, 1991; *Arnaud et al.*, 2000] to calculate the close-off depth (COD). In these models the COD depends both on the temperature and on the accumulation rate with deeper COD for higher accumulation and colder temperatures. Using the temperature and accumulation estimates ΔT_{GT4} and Acc_{GT4} as defined by *Petit et al.* [1999], as well as the GT4 timescale, we obtain a COD (COD_{GT4}) of 105 to 126 m for the period between 110 and 104 kyr B.P. We then estimated the isotopic changes with two different assumptions. First, we kept a constant 95-m-deep diffusive column with no convective zone and no accumulation change. We derived a $\delta^{15}N$ anomaly of about 0.02 ‰, which here is only due to the thermal effect (Figure 2). In a second case we accounted for both the thermal and the gravitational effects by assuming a nonconstant diffusive column with a depth DCH equal to COD_{GT4} − 25 m. The physical significance of this 25 m is not clear but plausibly could be due to convective and nondiffusive zones. A shallowing of the COD results from the temperature increasing, whereas the deepening due to the associated accumulation increase is negligible. This causes a decrease of the modeled gravitational effect from ~0.49 ‰ to ~0.44 ‰ in $\delta^{15}N$ across the event with a transition between these two levels lasting about 1000 years. This gravitational effect is superimposed on the thermal effect such that going forward in time, the $\delta^{15}N$ (and $\delta^{40}Ar$) signal is stable, then increases rapidly due to the thermal effect and then decreases more gradually toward a lower stable level (Figure 2). Both the isotopic increase and the decrease occur very close in time (within 300 years) and can thus be used as markers of the warming in the gas phase (once account is taken of the fact that the isotopic decrease due to the gravitational effect is felt some time Δt_{grav} after the start of the isotopic increase due to the thermal effect).

Detecting a $\delta^{15}N$ anomaly as small as 0.02 ‰ is not an obvious task, because $\delta^{15}N$ analytical precision obtained in recent studies is of this order [*Lang et al.*, 1999; *Severinghaus and Brook*, 1999]. However, this should be possible through a very detailed and careful isotopic study of the entrapped air bubbles. Assuming that temperature and accumulation as used for deriving the GT4 timescale are correctly estimated (see discussion below), we should expect to find the thermal anomaly associated with the 5d/5c warming at a depth $Z_{gas(GT4)}$ of 1566 m, which corresponds to a $\Delta_{age(GT4)}$ of ~5000 years (Figure 2). This implies a 63-m depth difference ($\Delta_{depth(GT4)} = Z_{ice} - Z_{gas(GT4)}$) between the start of the deuterium/temperature change in the ice and the thermal isotopic anomaly in the gas. A 20% larger or 20% smaller Δ_{age} would place this anomaly at 1577 m or 1553 m (i.e., Δ_{depth} of 74 m or 50 m, respectively). An additional uncertainty in evaluating the $\Delta_{depth(GT4)}$ from COD is related to the thinning of the ice layers with depth (see below).

To avoid the risk of missing this anomaly, we chose to perform detailed isotopic measurements on a more extended depth range from 1546 to 1587 m. All measurements have been done at the Scripps Institution of Oceanography (University of California, San Diego) using ice from the more recent 5Γ core. To account for the slight deuterium depth shift previously noted between 3Γ and 5Γ cores [*Basile*, 1997; *Petit et al.*, 1999], we have measured the deuterium concentration on these 5Γ ice samples. These deuterium measurements fully confirm the shape of the warming as recorded in core 3Γ.

For $\delta^{15}N$ analysis the extraction method is the melt-refreeze method [*Severinghaus and Brook*, 1999; *Sowers et al.*, 1989], and the isotopic ratio is measured on a Finnigan MAT 252 mass spectrometer. We made at least triplicate $\delta^{15}N$ measurements on each sample (Table 1). We rejected three measurements on the basis of gross leaks, identified by a high

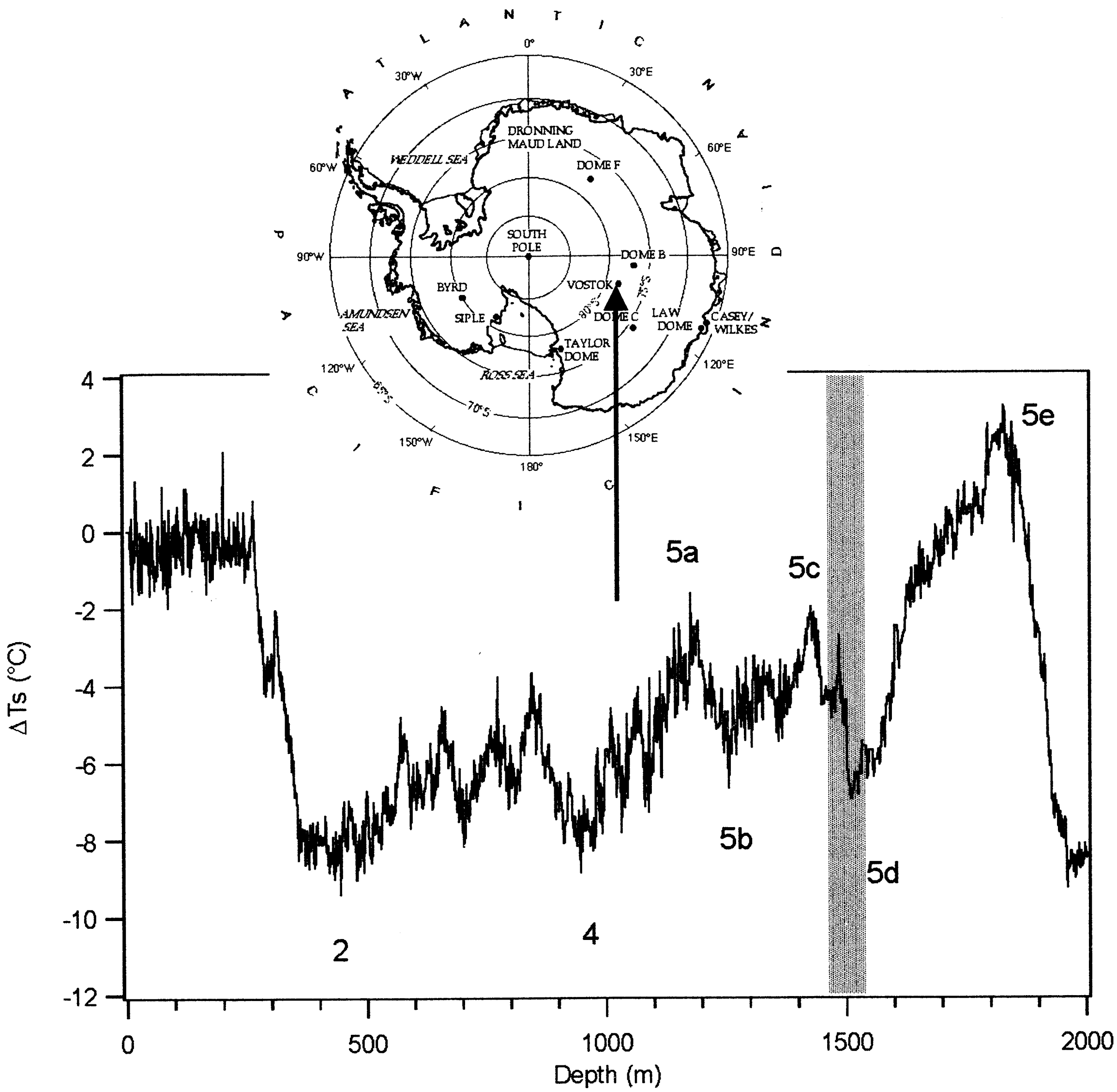

Figure 1. Variation with depth in the core of atmospheric temperature change at Vostok (3Γ ice core) as derived from the deuterium profile with the classical deuterium/temperature spatial relation. The arrow on the map gives the drilling site of Vostok. The box shows the event studied here.

residual pressure (which should be stable) or a rising residual pressure at the end of the sample transfer to cold trap. For the same reason, we also decided not to run on the mass spectrometer 4 other gas samples. From the distribution of individual measurements we estimated that the standard deviation is equal to 0.007‰. The uncertainty on the mean sample value (1σ) is thus ±0.004‰ when triplicate measurements are performed (and slightly better in case of more measurements; see Table 1). These error estimates do not, however, include any estimate of systematic bias. It is difficult to evaluate systematic error, but we subjectively estimate that it is not larger than ±0.01‰. This is based on agreement of $\delta^{15}N$ and $\delta^{40}Ar/4$ in ice formed under periods of constant climate in which the firn is presumed to have been isothermal (in the annual mean).

We also performed $\delta^{40}Ar$ measurements for most of the samples (Table 1). The $\delta^{40}Ar$ was measured using a wet extraction method [*Severinghaus and Brook*, 1999] in which the ice sample is melted and the gases transferred to a water trap through a capillary tube thus using water vapor as a carrier gas. To enhance gas exchange, the melted ice is agitated during the extraction (15 min). The dried gas is frozen in a vessel immersed in liquid helium and then gettered (Zr/Al at 900°C) for 10 min [*Severinghaus et al.*, 1998]. Except for four samples, duplicate measurements were carried out with a pooled standard deviation of 0.024‰ and an estimated 1σ uncertainty of 0.023‰.

To correct the measured values of $\delta^{15}N$ and $\delta^{40}Ar$ for zero enrichment, simulated extractions for both $\delta^{15}N$ and $\delta^{40}Ar$ measurements were performed by using a sample of dry San Diego air and following the normal extraction procedure. Results of these experiments revealed no systematic variation due to the extraction and analysis procedure. Therefore the San Diego air value versus standard remained constant over the period of analysis. To increase precision, we took special precautions concerning the inlet temperature during the sample and standard introduction in the mass spectrometer: (1) the inlet system of the mass spectrometer was insulated to

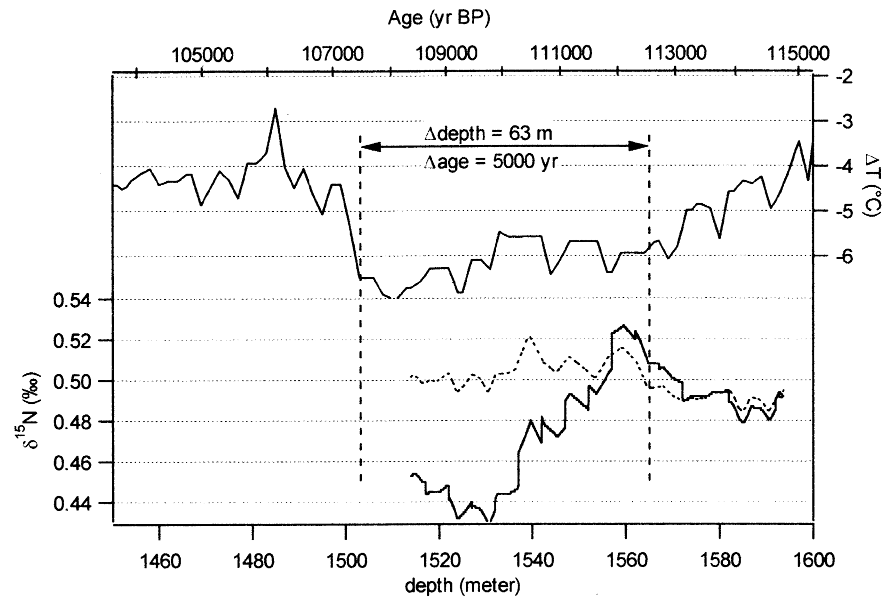

Figure 2. Model results. The solid curve (top) is the surface temperature profile deduced from the δD from the ice. The dotted curve is the $\delta^{15}N$ signal from the model obtained with a constant diffusive column height of 95 m. The solid curve (bottom) is the $\delta^{15}N$ signal with a variable diffusive column equal to the close-off depth minus 25 m.

reduce temperature fluctuations, (2) the standard cans were maintained horizontal on the inlet to prevent thermal convection and fractionation during separation of an aliquot from them. (3) The inlet temperatures during all runs were monitored for stability.

4. Results: Estimate of Δ_{depth}

Deuterium, $\delta^{15}N$, and $\delta^{40}Ar$ measurements are shown in Figure 3 with respect to depth. In this graph, ice and gas depths are shifted by 63 m, the expected $\Delta_{depth(GT4)}$ based on the assumption that the temporal deuterium/temperature slope is equal to the spatial slope [*Jouzel et al.*, 1993; *Petit et al.*, 1999]. For both $\delta^{15}N$ and $\delta^{40}Ar$ signals we have the same general pattern with two roughly stable levels separated by a step-like decrease at ~1566-m depth. Mean values below and above this depth differ by 0.017‰ and 0.019‰ for $\delta^{15}N$ and $\delta^{40}Ar/4$, respectively. These differences are small but, as shown by a Monte Carlo approach that we have performed, highly significant (the standard deviation of the difference between the mean values above and below 1566 m is lower than 0.002‰ in both cases). In the $\delta^{15}N$ record, these two levels are separated by a spike, which is not clearly visible for $\delta^{40}Ar$ possibly because of the different sampling (see discussion below). The change between roughly stable levels before and after this transition should result from the difference in the gravitational effect and reflect a modification of the DCH. Estimates of the DCH calculated from the $\delta^{15}N$ and $\delta^{40}Ar$ values and equation (1) suggest a decrease from 86 to 84 m (assuming a temperature of 210 K; note that this calculation is relatively insensitive to the absolute temperature chosen). Note, however, that the DCH estimate is less accurate after the transition because the stationary level is probably not yet reached at 1546 m, the shallowest sample we have analyzed.

In the $\delta^{15}N$ profile, the presence at 1570 m of a positive spike (~ + 0.015 ‰, which although low is 3 times the analytical uncertainty) gives this record a shape similar to what is expected from the thermal anomaly of our model results. The shape of the data matches the model well if it is assumed that the start of this spike ($Z_{gas(observed)} = 1572 \pm 0.5$ m) coincides with the start of the warming as derived from the ice deuterium record (Z_{ice} = 1503 m). The return to lower values also resembles what is expected from the thinning of the firn thickness and the associated DCH thinning, but it occurs more rapidly than expected. The observed depth difference is also about 2 m instead of 3.5 m for the model value. This could either reflect a more rapid heat transfer than modeled or be due to the lack of data points between 1570 and 1568 m, which prevents an accurate assessment of the shape of the end of the spike. We thus retain 1572 ± 0.5 m as our best estimate of the start of the warming as seen in the gas phase.

Whereas the gravitational effect is clearly imprinted in the $\delta^{40}Ar$ profile (with two clearly defined stable levels around 0.490 and 0.470 ‰ for $\delta^{40}Ar/4$), the expected positive spike of $\delta^{40}Ar$ (0.038‰ based on a $\delta^{15}N$ spike of 0.015‰) due to thermal fractionation is not seen in the profile. This may be due to the lower resolution of this profile with respect to $\delta^{15}N$. Owing to the lack of sufficiently large ice samples (a $\delta^{40}Ar$ measurement requires 40 g of ice instead of 10 g for $\delta^{15}N$), there is no $\delta^{40}Ar$ data between 1570 and 1567 m, making it very difficult to characterize the $\delta^{40}Ar$ thermal anomaly. A first $\delta^{40}Ar$ decrease is then observed at 1566 m and is followed by a rapid increase and a subsequent decrease starting at 1565 m. These latter features allow an estimate of an upper limit for the depth of the start of the warming in the gas phase. As both gases should respond simultaneously to changes in DCH, comparison with the $\delta^{15}N$ profile suggests that the first decrease is due to the gravitational effect although the possibility that it is the second decrease observed at 1565 m cannot be excluded. As for $\delta^{15}N$, we then assume that this isotopic decrease resulting from the gravitational effect occurs 2 m above the start of the warming as seen in the gas phase (due to the time for the heat to diffuse within the firn). This

Table 1. Measured Gas Isotopic Data[a]

	$\delta^{15}N$		$\delta^{40}Ar$		
Depth (m)	n	$\delta^{15}N$ Mean (‰)	n	$\delta^{40}Ar$ Mean (‰)	$\delta^{40}Ar/4$ (‰)
1546.05	3	0.464	2	1.893	0.473
1547.05	4	0.477	2	1.961	0.490
1548.10	5	0.466	2	1.867	0.467
1549.07	5	0.457	2	1.876	0.469
1551.15	3	0.458	2	1.890	0.472
1552.05	3	0.460	2	1.952	0.488
1552.87	3	0.470	2	1.888	0.472
1554.00	3	0.465			
1555.51	4	0.462	1	1.881	0.470
1557.00	7	0.478			
1558.07	3	0.462	2	1.846	0.462
1559.05	3	0.475	2	1.899	0.475
1559.85	3	0.475	2	1.927	0.482
1561.07	3	0.470	2	1.884	0.471
1563.07	3	0.462	2	1.854	0.464
1564.80	2	0.478	1	1.983	0.496
1564.90			2	1.990	0.497
1565.05	4	0.467	2	1.965	0.491
1565.30	4	0.466	1	1.906	0.477
1565.85	3	0.482	2	1.884	0.471
1566.00	3	0.471	1	1.949	0.487
1567.07	3	0.473	2	1.941	0.485
1568.02	3	0.480			
1568.10	3	0.479			
1568.20	3	0.481			
1570.07	3	0.491	2	1.949	0.487
1571.05	4	0.482	2	1.972	0.493
1571.87	4	0.477			
1572.00	3	0.476			
1573.07	3	0.478	2	1.959	0.490
1574.05	3	0.476			
1574.87	4	0.480	2	1.993	0.498
1575.00	3	0.475			
1576.05	3	0.483	2	1.976	0.494
1578.22	3	0.482			
1579.07	4	0.478			
1580.04	3	0.478			
1581.05	3	0.481	2	1.957	0.489
1582.05	3	0.472	2	1.933	0.483
1582.85	3	0.480	2	1.970	0.492
1585.05	3	0.482	2	1.981	0.495
1586.08	3	0.484	2	1.981	0.495
1586.86	3	0.483			

[a] The $\delta^{15}N$ value is a mean of at least triplicate measurements except for the sample at 1564.80 m. The $\delta^{40}Ar$ value is a mean of duplicate measurements except for three samples.

places the start at a depth Z_{gas} of 1568 m (or of 1567 m if the value of 1565 m corresponds to the start of the warming). Assuming that the depth difference is higher than 2 m, as suggested by our model, would result in deeper values of Z_{gas}. As a result, we can tentatively conclude, combining the different information we have (thermal and gravitational effects), that Z_{gas} is very likely equal to 1570 ± 3 m. We thus estimate that Δ_{depth} is between 64 and 70 m, i.e., a value 1 to 7 m (~5% on the average) larger than $\Delta_{depthGT4}$ (see Figure 3 which compares the deuterium in ice and isotopic gas records).

5. Close-Off Depth, Temperature, and Δ_{age} Estimates

Estimating the COD from Δ_{depth} is straightforward by accounting for the thinning of the ice layers with depth and for the density profile in the firn. The thinning function regularly decreases between 1503 and 1570 m from 0.742 to 0.722 (as inferred from the two-dimensional (2-D) ice flow model developed by *Ritz* [1992]. The densification model [*Barnola et al.,* 1991] indicates that the ice equivalent thickness corresponds to 0.71 times the firn thickness in the range of temperature and accumulation of interest. The COD in the firn at that time can thus be estimated as Δ_{depth}/(0.71*0.732). Thus the combined information derived from $\delta^{15}N$ and $\delta^{40}Ar$ places the COD between 123 and 135 m, slightly deeper than COD_{GT4} (121.5 m).

This places constraints both on Δ_{age} and on the relationship between deuterium and accumulation that we now discuss. To illustrate how both temperature and Δ_{age} can be inferred from Δ_{depth}, we have plotted in a temperature-accumulation diagram (Figure 4) the curves corresponding to different values of Δ_{depth} and Δ_{age} (these two parameters only depend on accumulation and temperature). We have plotted each Δ_{depth} curve, corresponding respectively to $\Delta_{depth(GT4)}$ = 63 m and to the minimum and maximum estimates (64 and 70 m). The temperature at the surface is the main factor influencing the COD (about 1.8 m per 1°C change), whereas COD is less sensitive to accumulation. We then calculated the COD for different values of the temperature change by varying the deuterium/temperature coefficient used to infer the Vostok temperature change and keeping unchanged the accumulation around the 5d/5c transition (note that Figure 4 is drawn, assuming a constant accumulation over the entire depth interval, and does not exactly correspond to these calculations). For CODs equal to 64 and 70 m, we respectively estimate a temperature difference $\Delta T_{5d/modern}$ with respect to the modern value of -6.6° and -8.6°C, which is slightly colder than the estimate of Petit et al. ($\Delta T_{5d/modern}$ = -6.5°C). This indicates that the use of the spatial slope to interpret the Vostok deuterium data underestimates $\Delta T_{5d/modern}$ by 20 ±15%, assuming accumulation was unchanged.

In a second step we propose to improve previous estimates of Δ_{age} taking into account this lower temperature. Keeping unchanged the accumulation, our temperature and COD estimates lead to Δ_{age} lower and upper values of 5100 and 5600, respectively, leading to an estimate of 5350 ± 250 years. This estimate is slightly older than the 5000 years obtained from the firn densification model with the temperature and accumulation estimates based on the present-day deuterium/temperature slope.

However, unlike on the COD, accumulation change has a large influence on Δ_{age} because, for a given COD, Δ_{age} varies inversely with accumulation (more than counterbalancing the effect of the COD change itself). This dependency of Δ_{age} on accumulation makes estimates of Δ_{age} more complex. However, the accumulation change, or at least its average value over long periods, is constrained by the fact that the Vostok timescale is accurately known. For the last 110 kyr (Z_{ice} = 1503 m), GT4 is estimated to be accurate to better than ± 5 kyr [*Petit et al.*, 1999]. As the thinning is accurately known for the upper part of the ice cap, the average accumulation over this entire period is also known within ~ ± 5%. This would increase the uncertainty on Δ_{age} from ~ 250 to ~ 300 years.

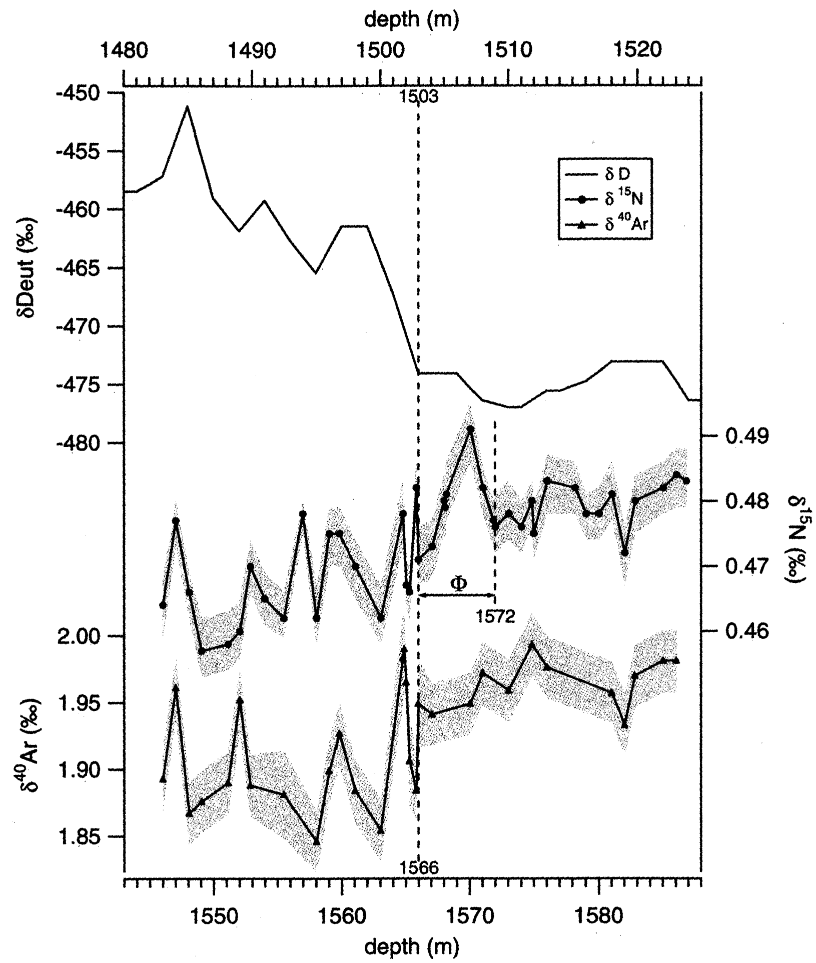

Figure 3. The $\delta^{15}N$ and $\delta^{40}Ar$ of the gas trapped in air bubbles versus depth. Means of replicate measurements of separate pieces of ice cut from the same hand sample are shown for both cases with shading showing 1σ analytical uncertainty. The start of the transition is clearly located by δD at 1503 m. Φ is the difference (6 m) between the start of the $\delta^{15}N$ spike (1572 m) and the depth (1566 m) where we expected to find the start of the thermal anomaly according to the model result.

However, there is no guarantee that accumulation changes are not larger than 5% over certain parts of the record. Again, because of dating constraints the effects of such additional changes should be limited. To illustrate this point, let us assume, as an extreme case, that Vostok temperature changes are twice larger than predicted using the spatial isotope/temperature slope. Keeping unchanged the assumption that accumulation change (with respect to its present-day value) is proportional to the derivative of the saturation vapor pressure [*Petit et al.*, 1999], implies that the accumulation at the 5c/5d transition was 47 % lower than for present day (instead of 28 % with the current GT4 model). We then impose the age at 1534 m to be 110 kyr B.P. as in GT4 [*Petit et al.*, 1999] by modifying how the present-day accumulation varies between Vostok and Ridge B (upflow from Vostok). The accumulation at the 5d/5c transition then differs by only a few percent from its GT4 value. The influence of the accumulation change on Δ_{age} is thus probably relatively limited, and we can thus retain the value of 5350 ± 300 years as the most likely estimate of Δ_{age}. This is a considerable improvement with respect to the current model estimate, the accuracy of which is probably no better than 1000 years. Still, as discussed below, the influence of accumulation changes and of other parameters has to be more carefully examined to fully assess the uncertainty attached to the estimate of Δ_{age}.

6. Discussion and Conclusion

The approach we have presented here to estimate the COD, temperature, and Δ_{age} at the 5d/5c transition is not fully satisfying. Analytical noise is large in comparison with the signals obtained, and the prominent spike in $\delta^{40}Ar$ at 1565 m remains unexplained, as does the absence of a spike in $\delta^{40}Ar$ at 1570 m. The respective influence of temperature and accumulation on Δ_{age} is difficult to assess in the more general case where the relationship between those two parameters differs from the simple assumption that has been used up to now to interpret Vostok data. Various uncertainties linked either with the different factors influencing the COD itself (density profile, temperature, and accumulation) or with the glaciological model and the timescale (thinning, accumulation) cannot explicitly be taken into account. One way to account for these various aspects is to extend the inverse approach that *Parrenin et al.* [this issue] have recently developed to date the Vostok core using a glaciological and an accumulation model,

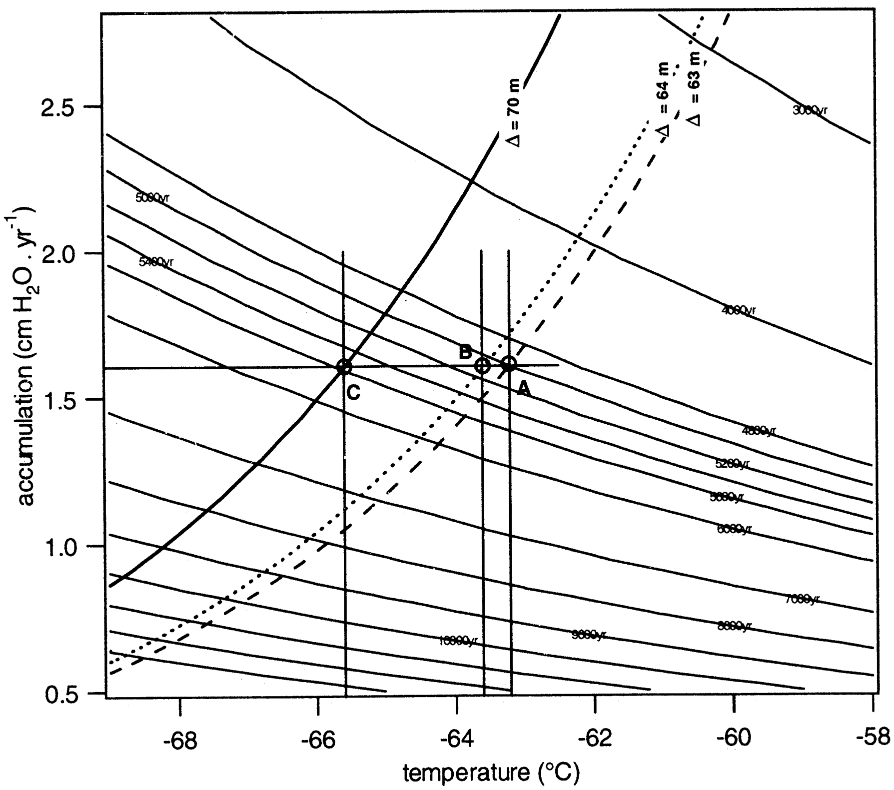

Figure 4. This figure illustrates how Δ_{age}, calculated with the steady state Barnola model, depends on the accumulation and the temperature at Vostok around the 5d/5c transition. The solid and dotted lines indicate two scenarios for the measured distance in the core (Δ_{depth}) between the signal of the warming seen in the gas ($\delta^{15}N$ and $\delta^{40}Ar$) and the signal seen in the ice (δD). The B scenario is obtained by assuming that only the step-like decrease of $\delta^{15}N$ and $\delta^{40}Ar$ records the start of the 5d/5c transition. The C scenario is the result obtained by associating the $\delta^{15}N$ spike with the warming. The dashed line (A scenario) is the predicted Δ_{depth} obtained for this transition using the Barnola model, which assumes that the spatial relationship is valid.

incorporating various sources of chronological information. This inverse approach, which allows a refining of the estimates of ΔT and Δ_{age} and estimates of associated errors, will be presented in a separate article (F. Parrenin et al., manuscript in preparation, 2001).

Despite its limitation, the current interpretation of the $\delta^{15}N$ and $\delta^{40}Ar$ data is extremely interesting. In particular, for the first time there is a clear indication that the use of the spatial slope is indistinguishable from or slightly underestimates the temporal slope. Indeed, our results suggest that the use of the isotope/temperature slope for interpreting $\delta^{18}O$ or δD in Antarctic cores may slightly underestimate temperature change but by no more than 20±15%. This is in contrast to the temperature estimate based on borehole temperature measurements in Vostok which suggests that Antarctic temperature changes are underestimated by up to 50% [*Salamatin et al.*, 1998]. Our finding that the temporal slope does not deviate greatly from the spatial slope, unlike in Greenland, is also well explained by model results. These models suggest that both changes in precipitation seasonality [*Delaygue et al.*, 2000a; *Krinner et al.*, 1997; *Werner et al.*, 2001] and precipitation origin [*Delaygue et al.*, 2000b] seem to have little influence on Antarctic temporal slopes. Also, temporal slopes calculated from Last Glacial Maximum and present–day isotopic GCM experiments are, although slightly higher, close on the average of present-day spatial slopes over Antarctica [*Hoffmann et al.*, 2000]. We also provide the first direct estimate of Δ_{age}, which is important because an uncertainty of 1000 years or more is attached to model estimates in sites with such a low accumulation.

This first example of the use of isotopic anomalies due to the thermal and gravitational effects in an Antarctic core shows the potential of the method for Antarctica as a whole, as rates of temperature and accumulation change were probably of the same order of magnitude all over Antarctica. However, it is almost certain that there is no place in Antarctica where those changes are sufficiently rapid for providing an estimate of the temperature change from the strength of the anomaly as done for Greenland cores. We are thus limited to infer information from the anomaly position which, again, is not so straightforward as in Greenland because (owing to low accumulation) dating by layer counting is not possible. The direct comparison of $\delta^{15}N$ and $\delta^{40}Ar$ with other gases such as CO_2 and CH_4 circumvents the need to establish Δ_{age} and holds potential for addressing the leads and lags of changes in these gases with changes in Antarctic temperature [*Caillon et al.*, 2000]. Despite some limitations we have shown the potential of the method for extracting information about the COD, the temperature and the Δ_{age}. A more accurate interpretation of these isotopic anomalies should result from the application of an inverse method as recently developed for establishing the Vostok timescale.

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