Termination V in the Vostok (Antarctica) ice core

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ABSTRACT. The age–depth relationship of the Vostok (Antarctica) ice core has been reconstructed in the depth interval 3300–3347 m, by comparing three gas properties in ice (CO_2, CH_4 and $\delta^{18}O_{atm}$) with those in the EPICA Dome C (Antarctica) core. Fourteen Vostok depths were examined in this interval, and it was found that nine samples are uniquely dated if candidate ages are restricted to the interval between 400 and 650 kyr. One of these samples is uniquely dated without restriction. The analysis supports previous reports that this section contains ice from Termination V, but that the stratigraphic order of ice is reversed. The top of the overturned layer lies between 3316 and 3319 m. At least one other stratigraphic disturbance was found between 3340 and 3343 m, as indicated by another reversal of the age–depth relationship. Finally, the oldest ice in this section is dated at ≥440 kyr, confirming the existence of ice from the cold marine isotope stage (MIS) 12 interval.

1. INTRODUCTION

The 3623 m long Vostok 5G core was drilled in the East Antarctic plateau between 1991 and 1997. The Vostok core contains a record of climate over at least the past ~400 kyr (Petit and others, 1999). However, the stratigraphic integrity of the section below ~3310 m has been questioned (Petit and others, 1999). In fact, stratigraphic disturbance of the bottom part of the ice sheet has been observed in some of the other long ice cores from polar regions, such as the GRIP and GISP2 ice cores from Summit, Greenland (Chappellaz and others 1997; Landais and others, 2003; Suwa and others, 2006). More recently, Raynaud and others (2005) suggested that the section of the Vostok 5G core between 3321.0 and 3344.9 m might contain ice from Termination V, but in reversed stratigraphic order. They reached the conclusion by visually comparing CH_4 and CO_2 measurements of samples from this section of the Vostok core with those of the EPICA Dome C (Antarctica) core, which now extends back to >650 kyr (Siegenthaler and others, 2005; Spahni and others, 2005).

Considering that glacial terminations are periods of intense scientific interest, and the precious nature of ice samples this old (to date, only the EPICA Dome C and Dome Fuji cores include Termination V ice), it is important to reconstruct the stratigraphy of this section of the Vostok core. Therefore, this paper aims to constrain the age–depth relationship of the Vostok ice core for the section between 3300 and 3347 m using gas properties. In addition to the CH_4 and CO_2 records considered by Raynaud and others (2005), we incorporate measurements of $\delta^{18}O$ of atmospheric O_2 ($\delta^{18}O_{atm}$) into the age reconstruction. We use the recently published ~800 kyr long $\delta^{18}O_{atm}$ record of the EPICA Dome C core for the reference (Dreyfus and others, 2007) and new $\delta^{18}O_{atm}$ measurements of samples from Vostok for our analysis. We note that there is no indication that the three gas properties considered in this study had been significantly modified or contaminated during ice-core extraction, core transport and gas extraction. In fact, CO_2 and CH_4 are within the expected range (Petit and others, 1999) and so are $\delta^{18}O$ and total gas content (Suwa, 2007).

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2. RECONSTRUCTING THE CHRONOLOGY USING CH_4–$\delta^{18}O_{atm}$–CO_2

The method used in this study is similar to that reported by Suwa and others (2006), who reconstructed the chronology for the bottom sections of the GISP2 and GRIP ice cores. The basis of their method is that individual samples from the stratigraphically disturbed section are dated based on their gas concentrations, which can be compared with concentration–time profiles of a stratigraphically intact ice core (i.e. Dome C). The difference between their method and the method developed here is that, in addition to the two gas properties they used, $\delta^{18}O_{atm}$ and CH_4, we use CO_2 as a third constraint. CO_2 was not useful in reconstructing the GISP2/GRIP chronologies because it cannot be measured reliably in those cores (Anklin and others, 1997; Smith and others, 1997).

2.1. CH_4–$\delta^{18}O_{atm}$–CO_2 records of the Vostok and EPICA Dome C ice cores

For the Vostok CH_4 and CO_2 records, we use values reported by Petit and others (1999). For $\delta^{18}O_{atm}$ we combine measurements by Petit and others (1999) and the new set of $\delta^{18}O_{atm}$ measurements. The method for determining $\delta^{18}O_{atm}$ for the new dataset is similar to the method described in Sowers and others (1989). We use a ~15 g sample of ice for each measurement, and apply the double melt refreeze method to extract air trapped in bubbles and clathrate hydrates in an ice sample. We then correct for the gravitational enrichment by subtracting $2 \times \delta^{15}N$ from $\delta^{18}O$ of the same sample to give $\delta^{18}O_{atm}$ (Craig and others, 1988; Schwander, 1989). Unfortunately, $\delta^{18}O_{atm}$ (and in some cases CO_2) is not measured in exactly the same sample as CH_4. Therefore, we first choose 14 samples where CH_4 and CO_2 are measured at the same depths. Values for $\delta^{18}O_{atm}$ are then interpolated for these depths. We note that $\delta^{18}O_{atm}$ changes gradually in this section, which indicates that small-scale mixing is not dominant here. Figure 1 shows CH_4, CO_2, $\delta^{18}O_{atm}$ and δD_{ice} of the Vostok ice core for the section

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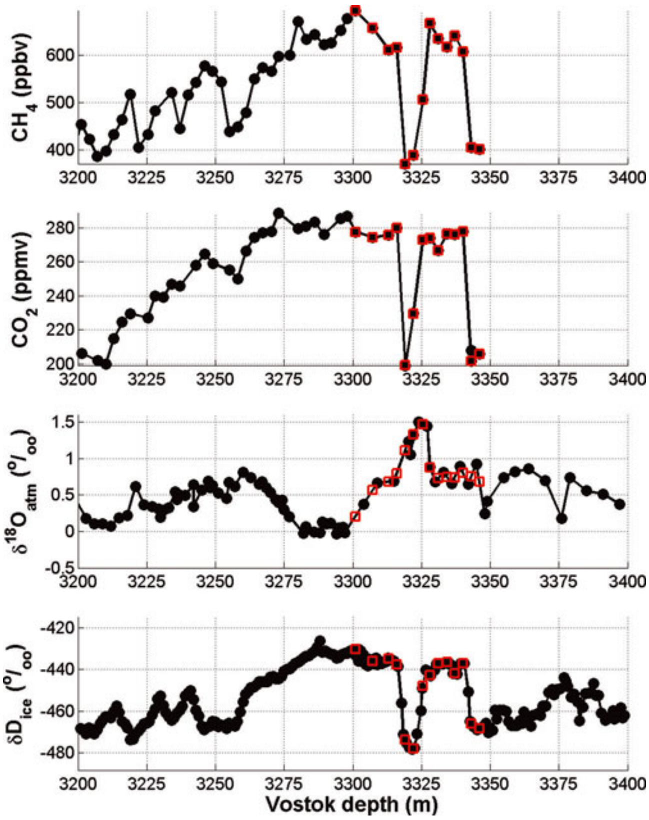

Fig. 1. The CH_4, CO_2, $\delta^{18}O_{atm}$ and δD_{ice} records for the section between 3200 and 3400 m of the Vostok ice core. Black solid circles indicate where original measurements are located. Red squares indicate values at interpolated depths used for the analysis.

between 3200 and 3400 m. Black solid circles indicate where original measurements are located. Red squares indicate 'interpolated' depths that we use for the following analysis. δD_{ice} is the temperature proxy for Vostok and Dome C.

Next, we derive the 'reference' line, which we assume is the true atmospheric history, based on the undisturbed record of EPICA Dome C. The 'reference line' in Figure 2 refers to the trajectory of $\delta^{18}O_{atm}$ vs CH_4 vs CO_2 concentration between 400 and 650 kyr on the EPICA Dome C EDC2 timescale (EPICA Community Members, 2004). We use the published CO_2 (Siegenthaler and others, 2005), CH_4 (Spahni and others, 2007) and $\delta^{18}O_{atm}$ (Dreyfus and others, 2007) records to define the reference line.

The pooled standard deviations for EPICA Dome C and Vostok are: ±0.028‰ (1σ) (Dreyfus and others, 2007) and ±0.05‰ (1σ), respectively, for $\delta^{18}O_{atm}$; ±15 ppb (1σ) (Spahni and others, 2007) and ±20 ppb (1σ) (Petit and others, 1999), respectively, for CH_4; and ±1.5 ppm (1σ) (Siegenthaler and others, 2005) and ±3 ppm (1σ) (Petit and others, 1999), respectively, for CO_2. These errors are added quadratically for each gas property. We adopt 2σ uncertainties, so that errors associated with $\delta^{18}O_{atm}$, CH_4 and CO_2 are ±0.11‰, ±50 ppb and ±6.7 ppm, respectively, in the following analysis.

2.2. Method

We first identify all compatible ages for each sample, which are our estimation of age uncertainties. This is done by seeking values for time t on the EPICA EDC2 timescale that meet the condition,

$$\frac{[CH_{4\,EDC}(t) - CH_{4\,Vtk}(z)]^2}{[2\sigma(CH_4)]^2} + \frac{[\delta^{18}O_{atm\,EDC}(t) - \delta^{18}O_{atm\,Vtk}(z)]^2}{[2\sigma(\delta^{18}O_{atm})]^2} + \frac{[CO_{2\,EDC}(t) - CO_{2\,Vtk}(z)]^2}{[2\sigma(CO_2)]^2} \leq 1, \quad (1)$$

where $CH_{4\,EDC}(t)$ is the CH_4 concentration, $\delta^{18}O_{atm\,EDC}(t)$ is the $\delta^{18}O_{atm}$ value and $CO_{2\,EDC}(t)$ is the CO_2 concentration in EPICA Dome C at time t. Likewise, $CH_{4\,Vtk}(z)$, $\delta^{18}O_{atm\,Vtk}(z)$ and $CO_{2\,Vtk}(z)$ are CH_4 concentration, $\delta^{18}O_{atm}$ value and CO_2 concentration at depth z in a sample from the section between 3300 and 3347 m of the Vostok core, and $\sigma(CH_4)$, $\sigma(\delta^{18}O_{atm})$ and $\sigma(CO_2)$ are one standard deviation for CH_4, $\delta^{18}O_{atm}$ and CO_2, respectively, as described in section 2.1.

Second, we derive the 'best-estimate age' within all compatible age ranges derived according to Equation (1). The best-estimate age is defined as t which minimizes d, the distance between a sample and the reference line, calculated as

$$d = \left([{}_nCH_{4\,EDC}(t) - {}_nCH_{4\,Vtk}(z)]^2 + [{}_n\delta^{18}O_{atm\,EDC}(t) - {}_n\delta^{18}O_{atm\,Vtk}(z)]^2 + [{}_nCO_{2\,EDC}(t) - {}_nCO_{2\,Vtk}(z)]^2 \right)^{\frac{1}{2}} \quad (2)$$

where the subscript n indicates that the term is normalized to a mean of 0 and standard deviation of 1. Normalization weights each of the three properties equally.

We first derive gas ages of samples, based on Equations (1) and (2), which are several thousand years younger than ages of ice at the same depths. This gas-age/ice-age difference (Δ_{age}) arises from the fact that the air is trapped in ice at ~100 m below the surface of the ice sheet, and thus Δ_{age} should be taken into account when plotting proxy signals recorded in ice vs time. We compute Δ_{age} using the empirical model of Herron and Langway (1980), which requires temperature and accumulation rate as input parameters. We estimate temperature from a simple linear regression of ΔT (deviation from modern Vostok temperature of –57.4°C) on δD_{ice} using values reported in Petit and others (1999), and we estimate accumulation rate from the equation used in Petit and others (1999). We understand that there are relatively large uncertainties associated with this model, especially for low-accumulation sites, but these uncertainties do not have a large impact on our results.

3. RESULTS AND DISCUSSION

The derived ages for 14 samples examined in this study produce an excellent fit between the two ice-core records, for all four geochemical parameters. The age–depth relationship so derived (Fig. 3) allows us to draw the following five conclusions. First, 9 of 14 samples have only one compatible age range which is consistent with EPICA Dome C ages between 400 and 650 kyr. Samples from 3328, 3331 and 3334 m have multiple compatible age ranges, but all ages fall between 416 and 424 kyr. The bottommost two samples of our analysis, the samples from 3343 and 3346 m, also have two compatible age ranges. One is ~440 kyr and the

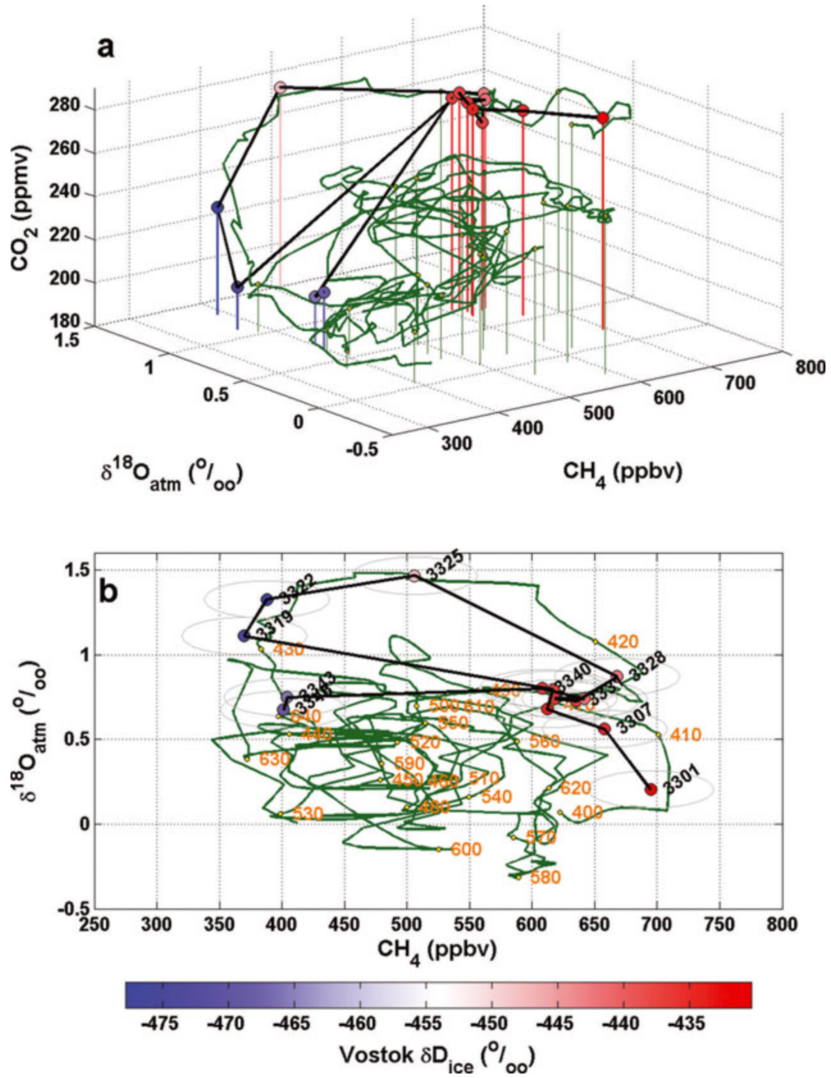

Fig. 2. (a) An x-y-z plot of CO_2 vs $\delta^{18}O_{atm}$ vs CH_4. The green curve traces the trajectory of CO_2, CH_4 and $\delta^{18}O_{atm}$ points between 400 and 650 kyr in the EPICA Dome C core. Closed circles colored in shades of red and blue are Vostok data from the disturbed section of the core; the color represents δD_{ice} at the depth of sampling. The black curve connects Vostok samples in order of increasing depth. (b) As for (a) but shown only for CH_4 and $\delta^{18}O_{atm}$. Gray ellipses surrounding each data point are uncertainty ranges. Black letters next to closed circles indicate the depths (m) of the Vostok sample. Orange labels next to yellow dots indicate ages (kyr) of Dome C samples.

other is ~460 and ~450 kyr, respectively. Second, our age reconstruction indicates that the stratigraphic disturbance starts somewhere between 3316 and 3319 m. Third, four or five samples between 3319 and ~3330 m are in reversed order. In this depth interval, one finds younger age as one goes deeper in the ice core. Fourth, it appears that there is a second stratigraphic disturbance between 3340 and 3343 m. Although the exact mechanism of development of these folds remains to be examined, layered rheological contrasts across the interglacial–glacial ice might have contributed to the process. Such folds are similar to the ones observed in the horizontal ice core retrieved from the Pâkitsoq ice-sheet margin site in Greenland (Petrenko and others, 2006). Lastly, the oldest sample in the section between 3300 and 3347 m is dated to at least ~440 kyr on the EPICA Dome C EDC2 timescale.

Figure 4 shows the comparison of CO_2, CH_4, $\delta^{18}O_{atm}$ and δD_{ice} records between EPICA Dome C and Vostok between 400 and 650 kyr. Black curves show the EPICA Dome C records, and blue circles are Vostok values plotted on their best-estimate ages. Our analysis supports the earlier

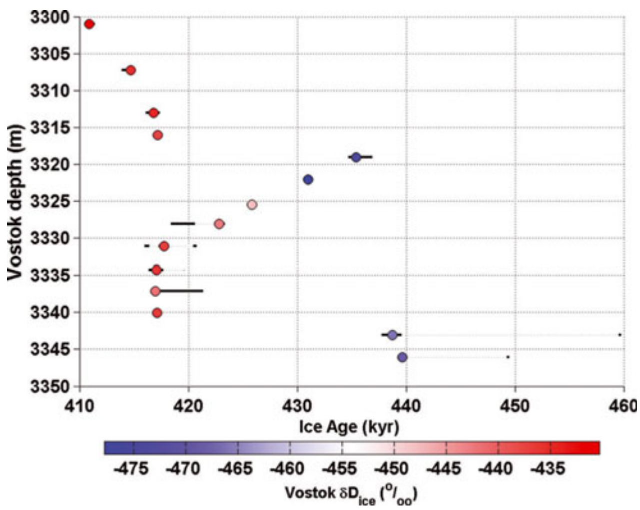

Fig. 3. The age–depth relationship reconstructed in this study. Horizontal black bars indicate all compatible age ranges. The 'best-estimate ages' are plotted as solid circles. Shades of red and blue indicate δD of ice at the same depth.

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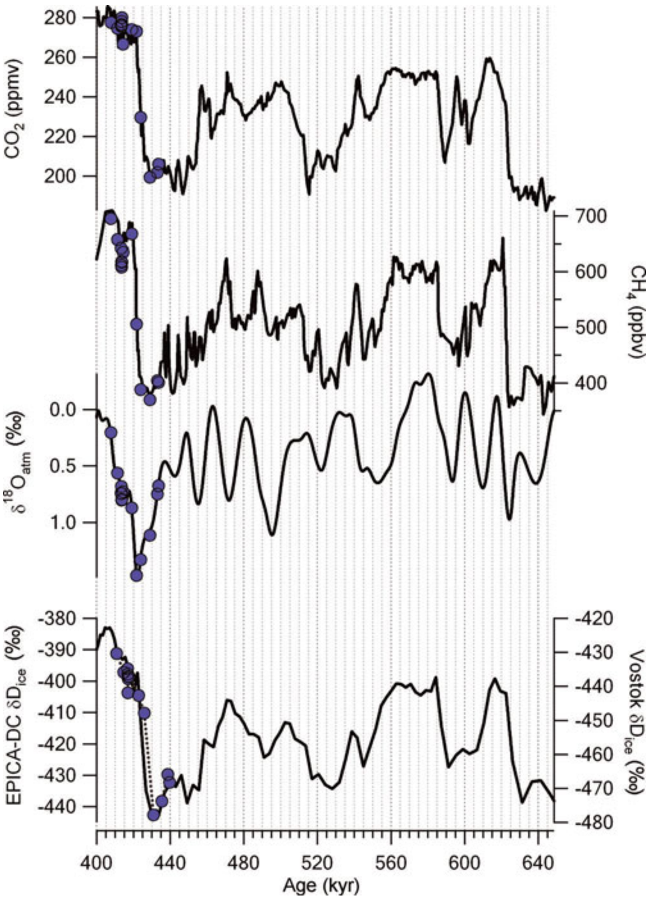

Fig. 4. CO_2, CH_4, $\delta^{18}O_{atm}$ and δD records between 400 and 650 kyr. Black curves show EPICA Dome C. Blue circles indicate Vostok samples plotted on the best-estimate ages. Note that the y axis for $\delta^{18}O_{atm}$ is reversed, and δD_{ice} is plotted on offset scales for EPICA Dome C and Vostok.

suggestion by Raynaud and others (2005) that the temperature history during Termination V is similar at the two sites.

As stated above, we limited our age search between 400 and 650 kyr. Therefore, we cannot completely dismiss the possibility that these samples are from much older age intervals. However, we note that the EPICA Dome C record shows $\delta^{18}O_{atm}$ of ~1.5‰ during Termination V. This heavy $\delta^{18}O_{atm}$ value is noteworthy as it is not reached for the rest of the published record which goes back to ~800 kyr (Dreyfus and others, 2007). Therefore, the heaviest $\delta^{18}O_{atm}$ value we observed in the Vostok samples, which is ~1.5‰, indicates that this sample is uniquely dated over the whole 800 kyr range.

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