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Chronology of the Vostok ice core constrained by O_2/N_2 ratios of occluded air, and its implication for the Vostok climate records

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ABSTRACT

We present a timescale for the Vostok ice core that is derived by orbitally tuning to O_2/N_2 ratios in occluded air for depths deeper than 1550 m (>112 ka), and by gas correlation to the GISP2 chronology for the section shallower than 1422 m (<102 ka). Our chronology of the deeper section rests on the assumption that, during the bubble close off process, local summer insolation indirectly controls the extent of O_2 exclusion and hence the O_2/N_2 ratio in trapped gases. The newly derived O_2/N_2 chronology is consistent with absolutely dated speleothem records. The O_2/N_2 chronology differs from previously published orbital tuning chronologies (CH_4 and $\delta^{18}O_{atm}$) by up to $\sim\pm6$ kyr, and from the original GT4 chronology by up to $\sim$15 kyr. The difference between the O_2/N_2 chronology and the $\delta^{18}O_{atm}$ chronology varies in time with strong signals centered at 1/100 and 1/41 kyr^{-1}. The ages for the last four glacial terminations in Vostok correspond to high obliquity (>23.7° at terminations' midpoints). They also correspond with decreasing precession index, corresponding to increasing boreal summer insolation. The Vostok temperature record, boreal summer insolation, and the rate of change of the SPECMAP property (reflecting planktonic foram $\delta^{18}O$) with respect to time are highly coherent at precession and obliquity periods. These three properties vary almost synchronously, with the possibility that Vostok temperature lags behind the other two. Our new timescale supports the widespread view that boreal summer insolation played an important role in glacial–interglacial cycles.

1. Introduction

Ice cores retrieved from polar regions have provided a wealth of climate information. Ice cores from the East Antarctic Plateau are noteworthy because they have low accumulation rates and therefore give particularly long records (Petit et al., 1999; Watanabe et al., 2003; EPICA Community Members, 2004). We can reconstruct a range of climate properties from these and other ice cores. For example, the isotopic composition of hydrogen and oxygen in falling snow, which subsequently becomes ice, provides us with information on local temperature at the time of precipitation (Jouzel et al., 1987; Dansgaard et al., 1993). Deuterium excess, which is defined as the departure of the deuterium/hydrogen fractionation of water from eight times $^{18}O/^{16}O$ fractionation of the same ice, gives information about the moisture source region, such as the isotope composition of the surface water, sea surface temperature, and relative humidity (Vimeux et al., 2002; Masson-Delmotte et al., 2005). Dust concentrations in ice cores reflect the aridity of the region supplying dust and the strength of the atmospheric circulation (Petit et al., 1999). Other glaciochemical species, such as Na^+, NH_4^+, Ca^{2+} and NO_3^- concentrations, are also interpreted, in part, as indicators of the strength of atmospheric circulation (Mayewski et al., 1997). Finally, ice cores are unique in that gas trapped in air bubbles and clathrate hydrates allows us to reconstruct past changes in atmospheric chemistry, including concentrations of climatically important greenhouse gases, notably CO_2, CH_4 and N_2O (Petit et al., 1999; Siegenthaler et al., 2005; Spahni et al., 2005).

In order to understand the temporal evolution of climate, it is essential to have a good chronology. We need to constrain two properties when constructing an ice core chronology: the age–depth relationship and the gas age–ice age difference (Δage). Six methods have been used to constrain the age–depth relationships; layer counting, orbital tuning, glaciological modeling, tephrochronology, correlation with other dated climatic records, and gas synchronization between ice cores. Annual layer counting gives a reliable chronology. For instance, the chronology for the upper part of GISP2, to ~40 ka, is constructed by layer counting. Errors are estimated to be ~2% for this interval (Meese et al., 1994), and the chronology is validated by comparison with other well-dated records (Wang et al., 2001; Svensson et al., 2006).

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Layer counting, however, is not applicable to low accumulation sites on the East Antarctic Plateau, where annual cycles cannot be resolved. For cores from such sites, orbital tuning is an alternative method for constructing the timescale (Petit et al., 1999; Shackleton, 2000; Bender, 2002; Ruddiman and Raymo, 2003). Orbital tuning usually assumes a constant phase lag between a target Milankovitch curve (either an insolation curve for a specific latitude and time of year, or a curve synthesized from precession and obliquity) and a climate parameter such as the $\delta^{18}O$ of paleoatmospheric O_2 ($\delta^{18}O_{atm}$) or CH_4. In most orbital tuning chronologies, it is expected that errors do not exceed a quarter of a precession cycle, ca ± 6 kyr. Therefore, the absolute error does not grow progressively with age. Since an orbital chronology might be derived without applying any glaciological constraints, there might be inconsistencies in the resulting curve of accumulation rate. Glaciological modeling minimizes this problem, as it is strictly based on the physics of ice sheets. A glaciological model is expected to work well at a dome site, where fewer assumptions need to be invoked in calculating a timescale, but even here there are problems (e.g. Dome F Members, 2006; Dreyfus et al., 2007). At a site located on a slope, such as Vostok, complexity in the glaciological model increases, and incorporation of less well constrained parameters, such as accumulation rate at upstream sites, contributes additional error (Parrenin et al., 2001, 2004). Tephrochronology and gas synchronization are useful for correlating cores from different locations (Zielinski et al., 1997; Blunier and Brook, 2001; EPICA Community Members, 2006). If enough volcanic fragments are present, then they can be radiometrically dated (Popp et al., 2004).

The second property that must be constrained is Δage. Since gas is trapped 50–120 m below the surface of an ice sheet, the age of trapped gas is always younger than the age of ice at the same depth. The difference in age is known as the gas age–ice age difference, or Δage. ΔAge is usually constrained by a firn densification model, and its uncertainty is estimated to be as large as ± 1000 years at Vostok and other slow accumulation sites (Goujon et al., 2003; Bender et al., 2006).

This paper focuses on improving the age–depth relationship of the Vostok ice core by using O_2/N_2 ratios in occluded air. O_2/N_2 is fractionated during the close-process, with slightly smaller O_2 molecules escaping preferentially as air is trapped in isolated bubbles. The extent of O_2 fractionation most likely depends on properties of ice grains surrounding air bubbles. These ice properties are fixed at or near the surface as ice is metamorphosed by summer insolation (Bender, 2002). In this paper, we first extend the O_2/N_2 record of Bender (2002) to younger ages. We then derive a new chronology that, prior to 100 ka, is constrained by the relationship between local summer insolation and O_2/N_2 in occluded air, and during the last 100 ka is constrained by correlation with the GISP2 ice core. Using this chronology, we discuss climate records in the Vostok ice core and their relations to other climatic records and orbital parameters. Our work is very similar to the parallel study of Kawamura et al. (2007), and the timescale we derive is likewise nearly identical to theirs.

2. Constructing the chronology of the Vostok ice core using its gas records

2.1. New measurements of Vostok gas records

We have measured O_2/N_2 ratios and their isotope ratios in 931 samples from 271 depths between 1595 and 3400 m. The method used to determine gas and isotope ratios of O_2/N_2 (Suwa, 2007) is similar to that described in Sowers et al. (1989). We extracted trapped gas from ice cores by melting samples, refreezing the melt water, and collecting non-condensable gases in a stainless steel tube at liquid helium temperature. The refrozen melt water was then melted a second time, refrozen, and the trapped gases collected in liquid helium. All $\delta^{18}O_{atm}$ and O_2/N_2 values reported in this paper are corrected for gravitational enrichment based on the $\delta^{15}N$ of N_2. The paleoatmospheric $\delta^{18}O$ ($\delta^{18}O_{atm}$) is calculated by subtracting $2 \times \delta^{15}N$ of N_2 from the measured $\delta^{18}O$ value, and gravitationally corrected O_2/N_2 is calculated by subtracting $4 \times \delta^{15}N$ of N_2 from the measured O_2/N_2 value (Craig et al., 1988; Schwander, 1989).

In our data set, we observe abnormally high $\delta^{15}N$ values in a large number of samples. The source is probably high values of water in the extracted sample gas. Here, we assume that $\delta^{15}N$ values in the data set of Petit et al. (1999) are reliable, and we reject samples whose $\delta^{15}N$ values that are $\geqslant 3\sigma$ above or below the 10 point moving average. After this sample selection, we have 702 samples from 262 depths. $\delta^{18}O$ and $\delta^{15}N$ values are then used to compute $\delta^{18}O_{atm}$.

The new $\delta^{18}O_{atm}$ measurements from the depth intervals between 2650–3000 m and 3160–3260 m are ~0.1–0.2‰ heavier than the previous measurements. In these intervals, O_2/N_2 ratios are highly depleted compared to those of Bender (2002). We observe a trend of -0.01‰/‰ between pair differences in O_2/N_2 and $\delta^{18}O_{atm}$. We regard this trend as reflecting 'gas loss fractionation' during storage, with $^{16}O^{16}O$ escaping preferentially to $^{18}O^{16}O$. This gas loss fractionation is also observed for Siple Dome samples, and its magnitude is similar (Severinghaus et al., 2006). We corrected for this gas loss fractionation before combining our new $\delta^{18}O_{atm}$ data set with that of Petit et al. (1999). The mean difference between the new $\delta^{18}O_{atm}$ data set and that of Petit et al. (1999), interpolated at 1 kyr intervals, is 0.04‰, decreasing to 0.01‰ after applying the gas loss fractionation correction. The standard deviation from the mean of paired (old and new) analyses is ± 0.05‰. The combined data sets include $\delta^{18}O_{atm}$ data from a total of 557 depths, yielding a mean resolution of ~750 years.

For $\delta O_2/N_2$, we analyzed samples in two groups. $\delta O_2/N_2$ values for the first group (685 samples) are lower than those for the second group (246 samples) by ~5‰. The observed difference is probably due to insufficient removal of the surface from ice samples for the first group (2–3 mm). Therefore, we only consider the second group for $\delta O_2/N_2$. Before combing the new measurements with the original data set of Bender (2002), we further applied the following three sample selection criteria. First, we select samples which meet the $\delta^{15}N$ criterion described above (246 samples → 152 samples). Second, we reject samples whose duplicate measurements do not fall with a range of 5‰, but retain samples having no replicate measurements (152 samples → 146 samples). And third, we reject samples from depths below 2617 m for reasons described below. As a result, we have 79 samples from 70 depths from the new measurements.

Fig. 1 shows the new measurements of $\delta O_2/N_2$ (gravitationally corrected) along with the data set reported by Bender (2002). Most samples between 2617 and 2758 m (bounded by gray lines) show higher $\delta O_2/N_2$ than those of the original data set, which is unexpected because oxygen diffuses out of ice cores faster than nitrogen, thus lowering $\delta O_2/N_2$ for samples stored longer in the freezer (Ikeda-Fukazawa et al., 2005). In this depth interval, we even observe some positive $\delta O_2/N_2$ values with respect to modern air. Normally positive values are observed only within the depth interval associated with partial dissolution of air in clathrate hydrates (Suwa and Bender, 2008). We have repeated measurements at least three times for each sample of this interval (these measurements not shown in Fig. 1), reproducing the anomalous O_2/N_2 ratios. At depths >2758 m, $\delta O_2/N_2$ values are within the expected range and conform to the previously observed trend, but