Record of $\delta^{18}\text{O}$ and $^{17}\text{O}$-excess in ice from Vostok Antarctica during the last 150,000 years

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[1] We measured $^{17}\text{O}$ and $^{18}\text{O}$ in recent Antarctic snow and down the Vostok ice core and calculated the excess of $^{17}\text{O}$ with respect to VSMOW. The magnitude of the $^{17}\text{O}$ excess in the Holocene and the last interglacial is $\sim$45 per meg, and it remains constant in a transect from the coast to the continental interior. Analysis of the transect data shows that the $^{17}\text{O}$-excess is not sensitive to temperature variations over the continent. There are significant shifts in $^{17}\text{O}$-excess from low values in glacial to high values in interglacial times. The observed shifts suggest higher normalized relative humidity and/or wind speeds over the source oceanic regions in glacial times. Citation: Landais, A., E. Barkan, and B. Luz (2008), Record of $^{18}\text{O}$ and $^{17}\text{O}$-excess in ice from Vostok Antarctica during the last 150,000 years, Geophys. Res. Lett., 35, L02709, doi:10.1029/2007GL032096.

1. Introduction

[2] Stable isotope ratios in H$_2$O from the Vostok ice core have been extremely useful in the interpretation of past climates. While both $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ are proxies of past temperatures [e.g., Lorius et al., 1969], it has been shown that their combination that gives the parameter d-excess ($= \delta^{18}\text{O} - 8\delta^{17}\text{O}$) [Dansgaard, 1964], adds information on variations of past temperature and evaporative conditions over the ocean [Jouzel et al., 1982; Vimeux et al., 1999]. This is so because the isotope fractionations in vapor-condensed phase equilibria and in water vapor diffusion in air are different. The magnitude of d-excess in ice is affected by the relative humidity of the oceanic source region as well as by sea surface and polar temperatures [e.g., Vimeux et al., 2002]. Therefore, d-excess alone cannot be used as a sole indicator of any of these important climatic variables.

[3] Based on theoretical considerations, it has been suggested that the combination of $^{18}\text{O}$ and $^{17}\text{O}$ in ice might provide additional independent information on past variations in oceanic humidity [Angert et al., 2004]. These authors pointed out however, that realization of this potential requires very high precision in measurements of the isotopic ratios that was not attainable at the time of their publication. Recent analytical developments have made it possible to measure both $^{17}\text{O}$ and $^{18}\text{O}$ with very high precision [Barkan and Luz, 2005, 2007] and to test the hypothesis of Angert et al. [2004].

[4] In this paper, we present results of measurements of $^{17}\text{O}$ and $^{18}\text{O}$ with high resolution in the Vostok ice core and along a transect from the edge to the interior of the Antarctic continent. Based on these data and the current understanding of the processes affecting the triple oxygen isotope composition of Antarctic precipitation, we suggest a paleoclimatic interpretation of the Vostok record.

2. Triple Oxygen Isotope Composition in Meteoric Water

[5] Variations in the ratios H$_2^{17}$O/H$_2^{16}$O, H$_2^{18}$O/H$_2^{16}$O and HD$_2$O/H$_2^{16}$O in studies of water isotopes are generally expressed in the standard $\delta$ notation with respect to the VSMOW standard as:

$$\delta = \frac{R_{\text{sample}}}{R_{\text{VSMOW}}} - 1$$

where R stands for the ratio between water containing heavy isotopes (H$_2^{17}$O, H$_2^{18}$O or HDO) and H$_2$O (note, we omit the factor of 10$^3$, but the $\delta$O results are reported in %).

[6] In studying relationships among all three oxygen isotopes we use a modified $\delta$, hereafter designated $\delta'$ [Hulston and Thode, 1965]:

$$\delta' \ln(\delta + 1) = \ln \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} \right)$$

Using the modified $\delta$ is advantageous because fractionation lines are straight in $^{17}\text{O}$ versus $^{18}\text{O}$ plots, but in $^{17}\text{O}$ versus $^{18}\text{O}$ plots, fractionation lines slightly curve [Luz and Barkan, 2005].

[7] Meijer and Li [1998] measured $^{17}\text{O}$ and $^{18}\text{O}$ in a wide range of meteoric waters. When their measurements are displayed in a $^{17}\text{O}$ - $^{18}\text{O}$ plot they fall on a line whose slope is 0.528. Because this slope appears universal in all meteoric water, we chose to use it as a reference slope.

[8] In our previous study [Landais et al., 2006] we measured $^{17}\text{O}$ and $^{18}\text{O}$ of meteoric water from different climate regions. These samples fall above a line with a slope of 0.528 that passes through VSMOW in a $^{17}\text{O}$ versus $^{18}\text{O}$ plot. Meteoric waters, therefore, have an excess of $^{17}\text{O}$ with respect to ocean water. Accordingly, we define the $^{17}\text{O}$ excess as:

$$^{17}\text{O} \text{ excess} = \delta^{17}\text{O} - 0.528 \delta^{18}\text{O}$$

Because the magnitudes of the $^{17}\text{O}$ excess are very small, they are multiplied by 10$^6$ and reported in per meg with
humidity and 18 Thiemens account both vapor-liquid equilibrium and vapor diffusion with the ocean surface. The free atmosphere divided by the same ratio in air in (b) 17O excess in the Antarctic transect.

18 [2005, 2007]; hn is normalized relative Barkan and Luz diffusion fractionations are based on the experiments of 17O that was reported in stratospheric gases such as O3 and 18 [2005]. Summarizing, 2 O2 gas by fluorination using CoF3. The produced O2 is warmed up to room temperature and connected to a Fin-nigan Deltaplus mass spectrometer. δ17O and δ18O of O2 are measured simultaneously in dual inlet mode by multi-collector mass spectrometry. Each mass spectrometric measurement consists of three separate runs during which the ratio of sample to reference is determined 30 times. The reported δ-values are averages of the three runs. The analytical errors (standard error of the mean (n = 90) multiplied by Student’s t-factor for a 95% confidence limits) in δ18O and δ17O are 0.004 and 0.008%, respectively [Barkan and Luz, 2003]. All the measurements were run against a working O2 standard calibrated against VSMOW (all the data are given in the auxiliary material).1

3. Results

[12] It is important to note that liquid precipitation occurs close to equilibrium [Craig and Horibe, 1967; Jacob and Sonntag, 1991], and in this case, 17O-excess in liquid precipitation should not vary with temperature (this is the direct consequence of the ratio ln 17Oeq/ln 18Oeq being independent of temperature). However, solid precipitation is more complicated because it involves both equilibrium and diffusion fractionation [Jouzel and Merlivat, 1984]. In order to find out how these two processes affect 17O-excess, we performed measurements of 17O-excess in surface snow along a transect from the coast to the Antarctic interior.

3.1. Spatial Variations in δ17O and 17O Excess Over East Antarctica

[14] In Figure 1 we show the variations of δ17O versus δ18O and 17O-excess in samples of surface snow taken along a transect between Terra Nova Bay (74.7°S 159.7°E) and Dome C (75.1°S 123.4°E). From regression of δ17O against δ18O we obtain a slope of 0.528, which is identical to the slope measured by Meijer and Li [1998] and Barkan and Luz [2005]. This confirms the universality of the 0.528 slope for all meteoric water.

[15] All the points in Figure 1 have distinct 17O-excess and there is no trend in 17O-excess with respect to either temperature, δ18O or the distance from the coast line. It is important to note, that the scatter of the data along the transect is larger than the analytical precision (error bars in

**Figure 1.** (a) The relationship among δ17O and δ18O and (b) 17O excess in the Antarctic transect.
Figure 2. The 150,000 years records of (a) $\delta^{18}O$, (b) $^{17}O$-excess, and (c) d-excess in Vostok. G and IG designate average values of $^{17}O$-excess for glacial and interglacial, respectively.

Figure 1). Such scattering is not unexpected because each surface snow sample may correspond to a particular snowfall event with probable different trajectory and different oceanic source region. Indeed, such variations are observed also in the measurements of $\delta^{18}O$, $\delta D$ and d-excess in surface snow [Ekaykin et al., 2004].

3.2. Temporal Variations of $^{17}O$ Excess in Vostok Ice

[16] Figure 2 shows the records of $^{17}O$-excess and $\delta^{18}O$ obtained in the present study together with the record of d-excess [after Vimeux et al., 1999]. The curves shown have been smoothed (5-point moving average). We note that our $\delta^{18}O$ values agree well with the corresponding values of Vimeux et al. [1999]. As can be seen, major shifts in $^{17}O$-excess are observed over the two major deglaciations (20 to 9 kyrs BP and 145 to 128 kyrs BP) with an increase in $^{17}O$-excess of about 20 per meg. Over the glacial inception (120 to 109 kyrs BP) $^{17}O$-excess remained roughly constant, and then decreased gradually over the glacial period and reached a minimum between 20 and 40 kyrs BP. This deglaciation shift is probably a general phenomenon, at least over East Antarctica, because our preliminary measurements show a similar shift in the Dome C ice core.

[17] Comparison of the $^{17}O$-excess and d-excess records shows considerable differences, and suggests that they registered different paleoclimatic information.

4. Discussion

[18] From the results above, the average $^{17}O$-excess along the Antarctic transect is about 45 per meg and it does not show any trend from the coast to the remote East Antarctic plateau. This suggests that despite large changes in temperature and surface elevation, $^{17}O$-excess of air moisture is conserved during the precipitation process over Antarctica.

[19] In order to evaluate the effects of vapor transport on Antarctic $^{17}O$-excess, we used a model to simulate different precipitation scenarios (Appendix). These simulations showed that, for today, the $^{17}O$-excess of oceanic vapor is the major factor affecting $^{17}O$-excess of Antarctic snow. Assuming that the situation was the same during the last glacial (i.e. no effect of polar temperature on $^{17}O$-excess), we conclude that the glacial to post glacial shift in $^{17}O$-excess results from a change in the hydrology of the source oceanic regions.

[20] In an attempt to quantify the glacial to post glacial shift in terms of changes in humidity, we used equation 4. We first calculated the $^{17}O$-excess for the post glacial. This required us to assume a value for $^{18}O_{air}$, which depends on wind speeds and the roughness of the sea surface [Merlivat and Jouzel, 1979]. According to Eriksson and Bolin [1964], 95% of the ocean is characterized by a smooth regime so that $^{18}O_{air}$ of 1.006-1.007 seems reasonable [Johnsen et al., 1989]. Using $^{18}O_{air}$ of 1.0065, normalized relative humidity ($h_r$) of 0.6 and any temperature in the range 9 to 19°C, we calculated $^{17}O$-excess as 18 per meg. The value of 0.6 for $h_r$ seems a reasonable minimum but the obtained $^{17}O$-excess is smaller than the measured post glacial value (~40 per meg versus VSMOW). A possible explanation of this difference is that the $^{17}O$-excess of surface seawater in the S. Ocean is higher than in VSMOW, but more study is needed in order to test this possibility.

[21] Assuming $^{18}O_{air}$ of 1.0065, a 20 per meg increase of the $^{17}O$-excess during glacial-post glacial transitions corresponds to a change in $h_r$ from 0.88 to 0.6. Even if we choose the lowest value for $^{18}O_{air}$ from Merlivat and Jouzel [1979] of 1.003, we calculate a decrease of $h_r$ from 0.7 to 0.6. These simple calculations show that during the last glacial, $h_r$ over the S. Ocean should have been at least 10% higher than today. This conclusion is in agreement with Jouzel et al. [1982], who, based on the first d-excess profile in the old Dome C ice core, suggested a decrease of relative humidity over the deglaciation.

[22] Implicit in the above conclusion is the assumption that polar temperature did not affect ice $^{17}O$-excess during glacial. We cannot prove this assumption but it will be interesting to test it by reconstruction of the $^{17}O$-excess transect of the last glacial. As shown by a simple modeling approach (Appendix), it would be possible to explain the shift in $^{17}O$-excess if the supersaturation effect in Antarctica decreased over the deglaciation. Such a decrease may be possible by an increased dust load. However, ice core records show the opposite with dust load decreasing over the deglaciation [Legrand et al., 1988], so we consider our above assumption robust.

[23] In the above analysis we ignored vapor inputs other than from evaporation at the source sites. However, if one considers the global atmospheric circulation, it is clear that part of the moisture above such sites is advected from elsewhere. Taking the example of the polar cell, Salamatin et al. [2004] suggested that in addition to evaporation at the starting point of storm trajectories, there is vapor input by recirculation of cold Antarctic air. The input of Antarctic moisture by air flowing from the continent must be small due to the low specific humidity of this very cold air. Yet, the inflow of such dry air over the ocean has the potential to modify the isotopic composition of the vapor at the source sites. Taking this effect into account in GCM simulations is expected to help in understanding the temporal $^{17}O$-excess changes.
Appendix A: $^{17}$O-Excess Modeling of Antarctic Precipitation

In order to evaluate the effects of vapor transport on Antarctic $^{17}$O-excess, we chose the simple Mixed Cloud Isotope Model (MCIM) of Ciais and Jouzel [1994] that was used for simulating d-excess. The only needed modification for modeling $^{17}$O-excess was a replacement of the fractionation factors for HD$^{18}$O/H$^{16}$O by the corresponding ones for H$^{17}$O/H$^{16}$O.

In the MCIM, the closure assumption (equation 4) is used for simulating the isotopic composition of the first vapor over the ocean. Then, liquid precipitation is considered as an equilibrium process between vapor and liquid water, and the isotopic fractionation is calculated with a fractionation factor $\alpha_{eq}$ for vapor-ice transition, both equilibrium and kinetic processes are involved, and the total fractionation factor is expressed as $\alpha = \alpha_{eq} \times \alpha_k$, where $\alpha_k$ depends on the degree of supersaturation ($S$) within the clouds [Jouzel and Merlivat, 1984]:

$$\alpha_k = \frac{S}{1 + \alpha_{eq} \frac{D}{D'}(S-1)}$$  \hspace{1cm} (A1)

Here, $\alpha_{eq}$ is the equilibrium fractionation factor for solid/vapor and $D/D'$ is the diffusivity ratio of H$^{16}$O and water containing heavy isotopes. The equilibrium fractionation factor $17\alpha_{eq}$ was calculated as: $17\alpha_{eq} = (18 \alpha_{eq})^{0.529}$ [Barkan and Luz, 2005], where $18\alpha_{eq}$ for liquid-vapor equilibrium were taken from Horita and Wesolowski [1994] and for ice–vapor equilibrium from Majoube [1971]. The values of $16D/17D$ and $16D/18D$ have been recently determined by Barkan and Luz [2007].

As in previous studies [e.g., Petit et al., 1991], we assume $S$ to be linearly related to cloud temperature $T_c$ such that $S = p + qT_c$, where $T_c$ is expressed in degrees Celsius. We obtained $p$ and $q$ from best fitting of snow isotopic composition calculated by the MCIM with our observations (Figure A1): $S = 1 - 0.002T_c$. Our tuning of supersaturation dependence on cloud temperature is comparable to previous studies based on $\delta^{18}O$ and d-excess [e.g., Petit et al., 1991].

We ran numerous sensitivity tests with the MCIM model to determine the main influences on ice $^{17}$O-excess. Here, we restrict the discussion to supersaturation effects on ice $^{17}$O-excess. For present-day, $S = 1 - 0.003T_c$ is the highest limit for supersaturation (Figure A1), but even in this case, we can calculate that Vostok ice $^{17}$O-excess changes by less than 0.8 permeg for a 1°C change in polar temperature while for the best fit ($S = 1 - 0.002T_c$) there is no temperature influence at all. Together with the other sensitivity tests, this suggests that $^{17}$O-excess is mainly sensitive to normalized relative humidity and diffusivity fractionation at the oceanic source of vapor, in accordance with equation 4.

For simplicity we assumed a single moisture source for all the precipitation along the transect: south Indo-Pacific (temperature $\sim$17°C; relative humidity $\sim$0.8 [Werner et al., 2001]). In fact the coastal regions of east Antarctica receive more moisture from the nearby ocean while the inland regions receive moisture from further north [Werner et al., 2001]. We note however, that the main relevant difference between these regions is in temperature ($\sim$3°C). Because $^{17}$O-excess is not sensitive to sea-surface temperature, the assumption of a single source region is of no consequence for our modeling.

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Figure A1. Comparison of (a) simulated d-excess and (b) $^{17}$O-excess with observed values in the Antarctic transect.
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