



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

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[1] We measured $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ in recent Antarctic snow and down the Vostok ice core and calculated the excess of ^{17}O with respect to VSMOW. The magnitude of the ^{17}O excess in the Holocene and the last interglacial is ~ 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}O -excess is not sensitive to temperature variations over the continent. There are significant shifts in ^{17}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 $\delta^{18}\text{O}$ and ^{17}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_2O from the Vostok ice core have been extremely useful in the interpretation of past climates. While both δD and $\delta^{18}\text{O}$ are proxies of past temperatures [e.g., *Lorius et al.*, 1969], it has been shown that their combination that gives the parameter d-excess ($= \delta\text{D} - 8\delta^{18}\text{O}$) [*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 $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ 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 $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ 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 $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ 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 $\text{H}_2^{17}\text{O}/\text{H}_2^{16}\text{O}$, $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$ and $\text{HD}^{16}\text{O}/\text{H}_2^{16}\text{O}$ in studies of water isotopes are generally expressed in the standard δ notation with respect to the VSMOW standard as:

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

where R stands for the ratio between water containing heavy isotopes (H_2^{17}O , H_2^{18}O or HDO) and H_2^{16}O (note, we omit the factor of 10^3 , but the $\delta^*\text{O}$ results are reported in ‰).

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

$$\delta' \ln(\delta + 1) = \ln\left(\frac{R_{\text{sample}}}{R_{\text{standard}}}\right) \quad (2)$$

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

[7] *Meijer and Li* [1998] measured $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ in a wide range of meteoric waters. When their measurements are displayed in a $\delta^{17}\text{O} - \delta^{18}\text{O}$ 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 $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ 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 $\delta^{17}\text{O}$ versus $\delta^{18}\text{O}$ plot. Meteoric waters, therefore, have an excess of ^{17}O with respect to ocean water. Accordingly, we define the ^{17}O excess as:

$$^{17}\text{O excess} = \delta^{17}\text{O} - 0.528 \delta^{18}\text{O} \quad (3)$$

Because the magnitudes of the ^{17}O excess are very small, they are multiplied by 10^6 and reported in per meg with

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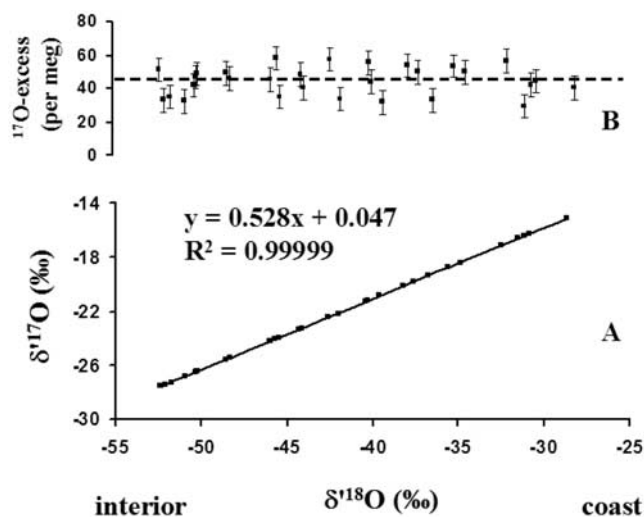


Figure 1. (a) The relationship among $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ and (b) ^{17}O excess in the Antarctic transect.

respect to VSMOW. Note that, the ^{17}O -excess definition is analogous to the one for deuterium excess of meteoric water.

[9] As discussed by *Barkan and Luz* [2007], an important cause of the ^{17}O -excess in meteoric water is the different ratios among the fractionation factors (α) in vapor-liquid equilibrium ($\ln^{17}\alpha_{\text{eq}}/\ln^{18}\alpha_{\text{eq}} = 0.529$) and in vapor diffusion in air ($\ln^{17}\alpha_{\text{diff}}/\ln^{18}\alpha_{\text{diff}} = 0.518$). We emphasize that the origin of ^{17}O -excess is not related to an excess in ^{17}O that was reported in stratospheric gases such as O_3 and CO_2 due to anomalous mass-independent fractionation [e.g., *Thiemens*, 1999].

[10] During evaporation, the isotopic composition of marine vapor can only be explained when taking into account both vapor-liquid equilibrium and vapor diffusion in air [*Craig et al.*, 1963]. Similarly to d excess, the ^{17}O -excess of water vapor is increased when the relative proportion of the diffusion induced fractionation is increased. Then, following the approach of *Merlivat and Jouzel* [1979] for d excess, *Barkan and Luz* [2007] explained the ^{17}O -excess of marine vapor as a function of humidity and $^{18}\alpha_{\text{diff}}$. In a situation where there is local balance such that all the water lost by evaporation returns to the ocean as rain (i.e. the “closure assumption”), ^{17}O -excess can be calculated from the following equation:

$$^{17}\text{O excess} = -\ln\left(^{18}\alpha_{\text{eq}}^{0.529}\left(^{18}\alpha_{\text{diff}}^{0.518}(1-h_n)+h_n\right)\right) + 0.528 \cdot \ln\left(^{18}\alpha_{\text{eq}}\left(^{18}\alpha_{\text{diff}}(1-h_n)+h_n\right)\right) \quad (4)$$

where the exponents 0.529 and 0.518 for equilibrium and diffusion fractionations are based on the experiments of *Barkan and Luz* [2005, 2007]; h_n is normalized relative humidity [e.g., *Gat et al.*, 2000] – water-air mixing ratio in the free atmosphere divided by the same ratio in air in equilibrium with the ocean surface.

[11] The magnitude of ^{17}O -excess changes with h_n and $^{18}\alpha_{\text{diff}}$ (a function of wind speed [*Merlivat and Jouzel*, 1979]). In contrast, it is insensitive to $^{18}\alpha_{\text{eq}}$ (a function of ocean surface temperature). For example, at 25°C , for given h_n and $^{18}\alpha_{\text{diff}}$ of 0.6 and 1.007 respectively, ^{17}O -excess

equals 19 per meg. At 10°C , for the same h_n and $^{18}\alpha_{\text{diff}}$, ^{17}O -excess equals 18 per meg. The difference is smaller than the measurement error. The main reason for this low sensitivity is that $\ln^{17}\alpha_{\text{eq}}/\ln^{18}\alpha_{\text{eq}}$ ratio remains constant regardless of temperature [*Barkan and Luz*, 2005]. Therefore, we expected that measurements of ^{17}O -excess in ice cores would yield important information on past evaporation conditions such as humidity and wind speed. In order to take advantage of this potential, we performed measurements of ^{17}O -excess down the Vostok ice core in East Antarctica.

[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, ^{17}O -excess in liquid precipitation should not vary with temperature (this is the direct consequence of the ratio $\ln^{17}\alpha_{\text{eq}}/\ln^{18}\alpha_{\text{eq}}$ 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 ^{17}O -excess, we performed measurements of ^{17}O -excess in surface snow along a transect from the coast to the Antarctic interior.

3. Results

[13] The analytical method for the determination of oxygen isotope ratios in water is detailed by *Barkan and Luz* [2005]. Summarizing, $2\ \mu\text{L}$ of water are converted to O_2 gas by fluorination using CoF_3 . The produced O_2 is transferred to a stainless steel tube on a collection manifold immersed in liquid helium. After processing, the manifold is warmed up to room temperature and connected to a Finnigan Delta^{plus} mass spectrometer. $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ of O_2 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 $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ are 0.004 and 0.008‰, respectively [*Barkan and Luz*, 2003]. All the measurements were run against a working O_2 standard calibrated against VSMOW (all the data are given in the auxiliary material).¹

3.1. Spatial Variations in $\delta^{18}\text{O}$ and ^{17}O Excess Over East Antarctica

[14] In Figure 1 we show the variations of $\delta^{17}\text{O}$ versus $\delta^{18}\text{O}$ and ^{17}O -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 $\delta^{17}\text{O}$ against $\delta^{18}\text{O}$ 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 ^{17}O -excess and there is no trend in ^{17}O -excess with respect to either temperature, $\delta^{18}\text{O}$ 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

¹Auxiliary materials are available in the HTML. doi:10.1029/2007GL032096.

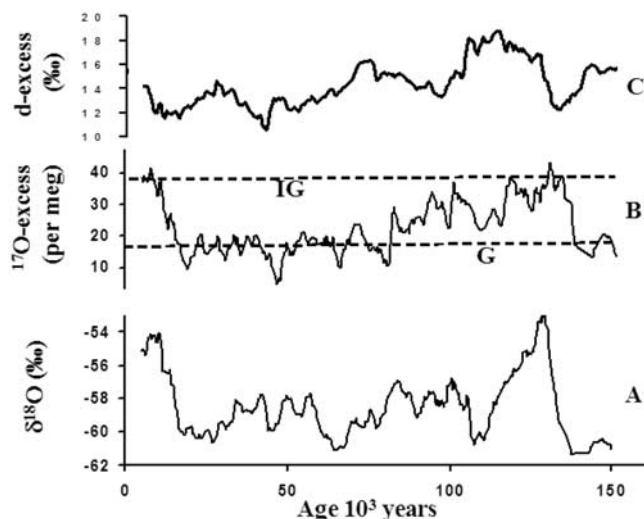


Figure 2. The 150,000 years records of (a) $\delta^{18}\text{O}$, (b) ^{17}O -excess, and (c) d-excess in Vostok. G and IG designate average values of ^{17}O -excess for glacial and interglacial, respectively.

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 $\delta^{18}\text{O}$, δD 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 $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ 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 $^{18}\alpha_{\text{diff}}$, 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 $^{18}\alpha_{\text{diff}}$ of 1.006–1.007 seems reasonable [Johnsen *et al.*, 1989]. Using $^{18}\alpha_{\text{diff}}$ of 1.0065, normalized relative humidity (h_n) 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_n 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 $^{18}\alpha_{\text{diff}}$ of 1.0065, a 20 per meg increase of the ^{17}O -excess during glacial-post glacial transitions corresponds to a change in h_n from 0.88 to 0.6. Even if we choose the lowest value for $^{18}\alpha_{\text{diff}}$ from Merlivat and Jouzel [1979] of 1.003, we calculate a decrease of h_n from 0.7 to 0.6. These simple calculations show that during the last glacial, h_n 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 glacials. 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.

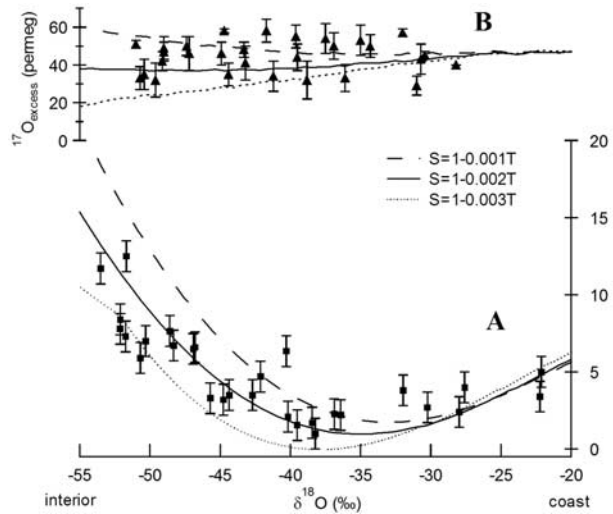


Figure A1. Comparison of (a) simulated d-excess and (b) ^{17}O -excess with observed values in the Antarctic transect.

[24] Another possible source of vapor is the tropical ocean. We do not know the ^{17}O -excess of this vapor, but it is likely to be relatively high because partial re-evaporation of rain drops [e.g., Worden *et al.*, 2007] will increase the ^{17}O -excess of atmospheric vapor. If this process decreased during the glacial due to changes in tropical air circulation, the ^{17}O -excess of the marine air-moisture could have decreased and perhaps affected ^{17}O -excess of polar precipitation. Modeling studies may help in assessing the influence of such changes in the tropics on polar precipitation.

[25] Finally, we note that the records of d-excess and ^{17}O -excess are very different despite many similarities in the origins of these two parameters. The main reason for the different trends is the relatively large effect of temperature on d excess and its negligible effect on ^{17}O -excess. In future studies, it will be interesting to combine both d-excess and ^{17}O -excess in an attempt to untangle possible paleo-temperature information.

5. Conclusions

[26] We have shown that ^{17}O -excess of recent snow in East Antarctica do not change from the coast to the continental interior and remains around 45 per meg with respect to VSMOW. Such measurements indicate that ice ^{17}O -excess is a robust indicator of diffusive fractionation over the ocean and does not depend on temperature at the deposition site. Thus, the significant increases in ^{17}O -excess between glacial to interglacials in the Vostok ice core most likely indicate smaller effect of diffusion fractionation and hence higher normalized relative humidity and wind speeds over the source oceanic regions in glacial times.

Appendix A: ^{17}O -Excess Modeling of Antarctic Precipitation

[27] 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 $\text{HD}^{16}\text{O}/\text{H}_2^{16}\text{O}$ by the corresponding ones for $\text{H}_2^{17}\text{O}/\text{H}_2^{16}\text{O}$.

[28] 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 α_{eq} . For vapor-ice transition, both equilibrium and kinetic processes are involved, and the total fractionation factor is expressed as $\alpha = \alpha_{\text{eq}} \times \alpha_{\text{k}}$, where α_{k} depends on the degree of supersaturation (S) within the clouds [Jouzel and Merlivat, 1984]:

$$\alpha_{\text{k}} = \frac{S}{1 + \alpha_{\text{eq}} \cdot D/D'(S - 1)} \quad (\text{A1})$$

Here, α_{eq} is the equilibrium fractionation factor for solid/vapor and D/D' is the diffusivity ratio of H_2^{16}O and water containing heavy isotopes. The equilibrium fractionation factor $^{17}\alpha_{\text{eq}}$ was calculated as: $^{17}\alpha_{\text{eq}} = (^{18}\alpha_{\text{eq}})^{0.529}$ [Barkan and Luz, 2005], where $^{18}\alpha_{\text{eq}}$ for liquid-vapor equilibrium were taken from Horita and Wesolowski [1994] and for ice-vapor equilibrium from Majoube [1971]. The values of $^{16}\text{D}/^{17}\text{D}$ and $^{16}\text{D}/^{18}\text{D}$ have been recently determined by Barkan and Luz [2007].

[29] As in previous studies [e.g., Petit *et al.*, 1991], we assume S to be linearly related to cloud temperature T_{c} such that $S = p + qT_{\text{c}}$, 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): $S = 1 - 0.002T_{\text{c}}$. Our tuning of supersaturation dependence on cloud temperature is comparable to previous studies based on $\delta^{18}\text{O}$ and d-excess [e.g., Petit *et al.*, 1991].

[30] 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, $S = 1 - 0.003T_{\text{c}}$ 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 ($S = 1 - 0.002T_{\text{c}}$) 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.

[31] For simplicity we assumed a single moisture source for all the precipitation along the transect: south Indo-Pacific (temperature $\sim 17^\circ\text{C}$; relative humidity ~ 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 ($\sim 3^\circ\text{C}$). 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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