Interannual variation of water isotopologues at Vostok indicates a contribution from stratospheric water vapor

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Combined measurements of water isotopologues of a snow pit at Vostok over the past 60 y reveal a unique signature that cannot be explained only by climatic features as usually done. Comparisons of the data using a general circulation model and a simpler isotopic distillation model reveal a stratospheric signature in the 17O-excess record at Vostok. Our data and theoretical considerations indicate that mass-independent fractionation imprints the isotopic signature of stratospheric water vapor, which may allow for a distinction between stratospheric and tropospheric influences at remote East Antarctic sites.

Table water isotopic ratios (δ18O and δ2H) have been used for many years as a proxy for local temperature T, reconstruction in East Antarctica (1, 2). The link with temperature results from mass-dependent isotopic fractionation of water at each phase transition along the water mass trajectory from the evaporative zone to the polar precipitation site. Two different kinds of mass-dependent fractionation effects lead to the depletion in heavy isotopologues of the water vapor. First, equilibrium fractionation is caused by the lower vapor pressure for the heavy isotopologues compared with the one for the abundant light (H2O) water molecules. Second, kinetic fractionation leads to isotopic fractionation due to different molecular diffusivity constants of the light and heavy water isotopologues (light molecules diffuse faster in air than the heavy ones) (3). The observed spatial slope of δ18O vs. ΔT, lies between 0.75‰ and 0.8‰ °C−1 [±20% at glacial timescales (4–6)] and builds the basis for past temperature reconstruction from δ18O in ice cores. It should be noted that this relationship can be associated with larger uncertainties of factor 2 for warmer than present-day climates (7). Biases to a constant temporal δ18O vs. temperature slope may arise from changes of moisture origin for the polar precipitation, precipitation intermittency at the seasonal or interannual scale, postdeposition effects, and changes of moisture trajectories. Tools exist to quantify such biases. First, the second-order parameters deuterium (d)-excess (8) and 17O-excess (9), defined as

\[ \text{d-excess} = \delta^2H - 8 \times \delta^{18}O \]

and

\[ 17\text{O-excess} = \ln(\delta^{17}O + 1) - 0.528 \ln(\delta^{18}O + 1), \]

are significantly imprinted by the climatic conditions (temperature and relative humidity) of the moisture origin. Second, the development of atmospheric general circulation models (AGCM) with implemented water isotopologues and water tagging is a strong added value to test the existence of temporal variations of precipitation intermittency or changes of moisture trajectories. These AGCM simulations reproduce indeed very well the seasonal cycles of all water isotopologues in polar regions (10), even if they still fail to represent polar d-excess variations at the glacial-interglacial transition. This makes the use of simpler water isotopic models [mixed-cloud isotopic model (MCIM) (11)] of distillation paths also useful to interpret the d-excess and 17O-excess.

Vostok is a remote region in East Antarctica, characterized by extreme climatic and environmental conditions (78°S,106°E, 3,488 m above sea level, annual mean temperature −55 °C, accumulation rate 21.5 kg m−2·y−1 water equivalent). In addition, Vostok is located within the Antarctic vortex, which makes it sensitive to stratospheric input (up to 5%) (12). Only one-quarter of the precipitation originates from tropospheric snowfall, whereas 75% is due to frost deposition and needle fallout (diamond dust), which may originate from the stratosphere (13, 14). The influence of such stratospheric water vapor input has been only marginally investigated even if the existence of mass independent fractionation (MIF) in the stratosphere is expected to strongly affect 17O-excess (15). This is because other effects become also prominent in these regions. First, at the observed very low temperature range (−50 °C), the second-order parameters d-excess and 17O-excess are expected to show strong variations with condensation temperature (16). Second, the interpretation of water isotopic profiles is complicated by postdeposition effects at these very low accumulation sites.

The aim of this article is to identify the main drivers of water isotopologues changes at remote sites in East Antarctica. To achieve this, we present a fully integrated method, (i) combining measurements of δ18O, d-excess, and 17O-excess on (ii) the seasonal, interannual, and glacial-interglacial timescales and (iii) comparing the data with AGCM and MCIM model outputs.

For interannual variations we present δ18O, d-excess, and 17O-excess results of a snow pit, situated at the remote East Antarctic research facility of Vostok station covering the period from 1949 to 2008 (instrumental period), and compare them with the already available δ18O, d-excess, and 17O-excess data of...
seasonal and glacial–interglacial timescales (17–19). To examine a possible stratospheric influence in tandem with MIF effects, we present a budget calculation of the oxygen $^{17}$O-anomaly of water from the stratosphere at the site of Vostok. These calculations together with considerations about postdeposition effects allow us to identify the important determinants of $\delta^{18}$O, d-excess, and $^{17}$O-excess on the interannual timescale.

**Methodology**

To disentangle the different influences (climate, postdeposition, and stratospheric influences) we focus on relative variations of the isotopologues rather than on their absolute values. The absolute values are indeed a complex result of many different influences whereas the relative variations should bring to light the driving processes of each isotopic change. To identify the climatic drivers (local temperature, moisture source relative humidity, and temperature) we also compare the observed relative variation with those simulated by an AGCM simulating intermittency at remote sites is a crucial factor for the interpretation of the interannual isotopic records of shallow ice cores, the AGCM is nudged to reanalyse over the instrumental period. Climate models do not take into account removal processes in the surface snow layers as well as diffusion of the water molecules in the firm. All these effects have been shown to be important on the interannual scale (20, 21). To investigate snow removal effects we store event-based seasonal precipitation data with the interannual variations of the snow pit data. Postdeposition effects on the snow are studied by an isotopic box model, accounting for postdeposition sublimation and recondensation effects and the diffusion theory of water isotopologues within the firn layer (22). Finally, the possibility of a stratospheric input is assessed by MIF signatures in the oxygen isotopic composition of the snow.

**Snow Pit Analyses.** Several series of adjacent snow samples were collected from the same pit wall, from the surface down to 3.65 m for every 3 cm (23). Isotopic analyses were performed on 116 samples. $\delta^{18}$O and $\delta^{17}$O measurements were performed using the method of water fluorination, as described in ref. 9, followed by isotope ratio mass spectrometry using a Delta V mass spectrometer from ThermoFisher. The overall uncertainty for the $^{17}$O-excess data is ±0.6 ppm. The d-excess measurements were performed on a Picarro instrument (1σ of 1.4%). In an earlier work (23) 124 samples from the same depth were analyzed for beryllium-10 ($^{10}$Be) and ion chemistry [Na$, Mg^{2+}$, Ca$^{2+}$, K$^+$, (SO$_4$)$_2$$^{-}$, Cl$^{-}$, and (NO$_3$)$_2$]. The snow pit chronology was based on the identification of non-sea-salt sulfate spikes associated with the volcanic eruptions of Agung (Indonesia, March 1963, snow imprint in January 1964 ±1 y) and Pinatubo (Philippines, June 1991, snow imprint in January 1992 ±1 y). The gross $\beta$-radioactivity indicated the maximum fallout of the nuclear bomb tests in 1955 and 1965, respectively. Purple arrows: volcanic eruptions in 1963 (recorded 1964, Agung, Indonesia) and 1991 (recorded 1992, Pinatubo, Philippines).

**Interannual Simulations with a General Circulation Model.** To help interpret the results, we use simulations of the Laboratoire de Meteorologie Dynamique Atmospheric General Circulation Model (LMDZ, 51 points) and a Rayleigh distillation-type model. As precipitation intermittency at remote sites is a crucial factor for the interpretation of the interannual isotopic records of shallow ice cores, the AGCM is nudged to reanalyse over the instrumental period. Climate models do not take into account removal processes in the surface snow layers as well as diffusion of the water molecules in the firm. All these effects have been shown to be important on the interannual scale (20, 21). To investigate snow removal effects we store event-based seasonal precipitation data with the interannual variations of the snow pit data. Postdeposition effects on the snow are studied by an isotopic box model, accounting for postdeposition sublimation and recondensation effects and the diffusion theory of water isotopologues within the firn layer (22). Finally, the possibility of a stratospheric input is assessed by MIF signatures in the oxygen isotopic composition of the snow.

**Results**

**Interannual Variability of $\delta^{18}$O, d-Excess, and $^{17}$O-Excess.** In the Vostok snow pit, over the period from 1949 to 2008, $\delta^{18}$O, d-excess, and $^{17}$O-excess data show strong variations of, respectively, 10‰, 20‰, and 40 ppm (Fig. 1 and Dataset S1), which are much larger than the glacial–interglacial variations (respectively, 6‰, 3‰, and 20 ppm between the Last Glacial Maximum and the Early Holocene) (1, 19, 28). The seasonal variations are of the same amplitude as the interannual ones (17).

An anticorrelation between $\delta^{18}$O and d-excess ($R = -0.32$) and between $\delta^{18}$O and $^{17}$O-excess ($R = -0.45$) can be observed (Fig. 1). To help interpret the results, we use simulations of the Laboratoire de Meteorologie Dynamique Atmospheric General Circulation Model (LMDZ, 51 points) and a Rayleigh distillation-type model. As precipitation intermittency at remote sites is a crucial factor for the interpretation of the interannual isotopic records of shallow ice cores, the AGCM is nudged to reanalyse over the instrumental period. Climate models do not take into account removal processes in the surface snow layers as well as diffusion of the water molecules in the firm. All these effects have been shown to be important on the interannual scale (20, 21). To investigate snow removal effects we store event-based seasonal precipitation data with the interannual variations of the snow pit data. Postdeposition effects on the snow are studied by an isotopic box model, accounting for postdeposition sublimation and recondensation effects and the diffusion theory of water isotopologues within the firn layer (22). Finally, the possibility of a stratospheric input is assessed by MIF signatures in the oxygen isotopic composition of the snow.

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a site temperature. Also, opposite to the seasonal record, the large interannual variability of $\delta^{18}$O and d-excess cannot be reproduced by the model. The LMDZ output shows a strong correlation between $\delta^{18}$O and $^{17}$O-excess (10) and a strong anticorrelation between d-excess and $T_{\text{site}}$ ($R = -0.56$), which corresponds well to the seasonal and glacial–interglacial observations. This strong link between $\delta^{18}$O and the site temperature ($R = 0.88$) is easily predicted by the equilibrium and kinetic fractionation during the Rayleigh distillation toward low temperatures, as observed in any isotopic distillation model.

To identify the causes of the large isotopic variations observed on the snow pit that are not included in the AGCM, a systematic isotopic distillation model. Rayleigh distillation toward low temperatures, as observed in any isotopic distillation model.

Climatic Effects. We have shown that the LMDZ nudged to reanalyses is able to simulate the interannual temperature variations, but fails in properly simulating interannual variations of $\delta^{18}$O and d-excess. Even if the model properly reproduces $\delta^{18}$O vs. $^{17}$O-excess correlation on a seasonal scale, data–model comparisons have evidenced weaknesses for properly describing $\delta^{18}$O and especially d-excess and $^{17}$O-excess in remote regions of Antarctica (10). Indeed, the LMDZ does not take into account mechanisms like the Bergeron–Findesine process (11), overestimates the temperature at Vostok, and underestimates the relative humidity influence on $^{17}$O-excess and d-excess at evaporation (32). As a consequence, to quantify the climatic determinants of $\delta^{18}$O, d-excess, and $^{17}$O-excess with correct temperature and source climatic inputs, we use a Rayleigh-type model (mixed-cloud isotopic model (refs. 11 and 18 and SI Text)). In the MCIM, like in all AGCM equipped with water isotopeologues, the supersaturation ($S$) of air is the main tuning parameter of simulated d-excess and $^{17}$O-excess. This is especially important for remote regions with extremely low temperature, because $S$ is classically parameterized to increase with decreasing temperature. Model simulations revealed a much larger sensitivity to $S$ for $^{17}$O-excess than for $\delta^{18}$O and d-excess (Table 1, rows $S_{\text{low}}$ and $S_{\text{high}}$). For example, a concomitant decrease of $\delta^{18}$O and $^{17}$O-excess combined with an increase of d-excess can be simply explained by a decrease of local temperature in the case of a relatively high supersaturation (17, 18). Although this local temperature effect is satisfying to explain a large part of the water isotopic variations on the seasonal scale at Vostok, it fails to explain the large and anticorrelated variations of $\delta^{18}$O and $^{17}$O-excess on an interannual scale. Our

**Table 1. Sensitivity of $\delta^{18}$O, d-excess, and $^{17}$O-excess on climatic factors, postdeposit, and stratospheric impact**

<table>
<thead>
<tr>
<th>Variability</th>
<th>$\Delta \delta^{18}$O, %</th>
<th>$\Delta$ d-excess, %</th>
<th>$\Delta^{17}$O-excess, ppm</th>
<th>$\Delta d$ – excess/$\Delta \delta^{18}$O</th>
<th>$\Delta^{17}$O – excess/$\Delta \delta^{18}$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seasonal</td>
<td>10</td>
<td>20</td>
<td>40</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>Interannual</td>
<td>10</td>
<td>20</td>
<td>40</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>Glacial</td>
<td>6</td>
<td>3</td>
<td>20</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Climatic factors</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Relative humidity</td>
<td>0.15%$^{+1}$</td>
<td>-0.1%$^{-1}$</td>
<td>-1 ppm$^{-1}$</td>
<td>-0.67</td>
<td>-6.7 ppm$^{-1}$</td>
</tr>
<tr>
<td>SST</td>
<td>-1.5%$^{-1}$</td>
<td>1.5%$^{+1}$</td>
<td>0.45 ppm$^{-1}$</td>
<td>2.8</td>
<td>-1.33</td>
</tr>
<tr>
<td>$\delta^{18}$O$_{\text{ocean}}$</td>
<td>0.95</td>
<td>3</td>
<td>0</td>
<td>3.16</td>
<td>0</td>
</tr>
<tr>
<td>$S_{\text{low}}$</td>
<td>1.5%$^{-1}$</td>
<td>1.5%$^{-1}$</td>
<td>-0.15 ppm$^{-1}$</td>
<td>-0.13 ppm$^{-1}$</td>
<td>0</td>
</tr>
<tr>
<td>$S_{\text{high}}$</td>
<td>1.7%$^{-1}$</td>
<td>2.9%$^{+1}$</td>
<td>3.6 ppm$^{-1}$</td>
<td>2.12 ppm$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Postdeposit</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20% sublimation</td>
<td>-2.1%</td>
<td>-2.8%</td>
<td>-43 ppm</td>
<td>-1.33</td>
<td>-20.2 ppm$^{-1}$</td>
</tr>
<tr>
<td>20% recondensation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No isotopic fractionation</td>
<td>-2.1%</td>
<td>-2.8%</td>
<td>-43 ppm</td>
<td>-1.33</td>
<td>-20.2 ppm$^{-1}$</td>
</tr>
<tr>
<td>Strato-impact</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.014% STE</td>
<td>-0.013%</td>
<td>+0.07%</td>
<td>+0.2 ppm</td>
<td>-5.2</td>
<td>-16.87 ppm$^{-1}$</td>
</tr>
<tr>
<td>2% STE</td>
<td>-1.9%</td>
<td>+9.7%</td>
<td>+32 ppm</td>
<td>-5.2</td>
<td>-17.15 ppm$^{-1}$</td>
</tr>
</tbody>
</table>

For variability, columns 2–4 show absolute variations of $\delta^{18}$O, d-excess, and $^{17}$O-excess for three different timescales. Columns 5 and 6 show slope $\delta^{18}$O vs. second-order parameters. Positive (negative) sign of slope indicates (anti)correlation. For climatic factors, postdeposit, and strato-impact, main determinants of the $\delta^{18}$O, d-excess, and $^{17}$O-excess, $S_{\text{low}}$ and $S_{\text{high}}$ are the supersaturation of the air of 8% and 16%, respectively. For strato-impact, 2% of Vostok’s moisture stems from the stratosphere. STE, stratosphere-troposphere exchange.
The snow isotopic composition evolved with an increase in both the Vostok snow when it is exposed to relatively dry conditions. An experiment was performed to look at the isotopic evolution of temperatures and moderate wind speed (13). In addition, an excess. Furthermore, strong sublimation effects have been reported for sites with strong katabatic winds and for relatively high accumulation rate. In this section we examine the possible influence of stratospheric water vapor under the consideration of the stratosphere to troposphere exchange (STE) due to the Brewer–Dobson circulation (38, 39) and the isotopic composition of stratospheric H2O.

About half of the stratospheric water content has a tropospheric origin, whereas the other half is produced via H-abstraction from methane (and other H-bearing species, HO2 and HNO3) through the OH radical (40, 41):

\[ CH4 + OH → CH3 + H2O. \]

Due to large H2O recycling via HO2 and NO3 that exceeds the net H2O production, the newly formed H2O and the recycled tropospheric H2O carry the same isotopic signature (15). Furthermore, model studies have shown that stratospheric H2O carries a large 17O-anomaly of up to 30‰ (15) that stems from MIF that originates from the O3 molecule (42, 43). Zahn et al. (15) have shown that the 17O-anomaly depends on their model specifications and on altitude, and for our estimations we take 17O-anomaly = 3‰, which corresponds to their most robust model output and tropical tropopause layer (TTL) of ≈15km. The above 17O-anomaly of 3‰ is in fairly good agreement with the stratospheric water vapor 17O-excess measurements of Franz and Röckmann (44).

The annual gross flux of stratospheric vapor into the troposphere (STE) was estimated at 1.73 × 1014 kg s⁻¹ on a global average, accounting for only 0.014% of Vostok’s precipitation (ref. 36 and SI Text). However, this number may be much larger at Vostok because most of the descending flux from the stratosphere occurs at high latitudes between 40° and 90° and also because large seasonal to interannual variations of the STE were proposed (45). For an estimation of the stratospheric contribution we have used the model study of Stohl and Sodemann (37), with 2% of the air near the surface of the Antarctic plateau having a stratospheric origin. This is a conservative assumption, because studies have shown that 5% of the precipitation in Antarctica during winter stems from the stratosphere (12).

Table 1 displays the stratospheric influence on 17O-excess (+32 ppm), δ18O (−1.9‰), and δ-d-excess (+9.7‰), under the assumption of 2% of Vostok’s precipitation having a stratospheric origin. Associated influences of δ18O and δ-d-excess are due to the very strong Rayleigh distillation effects within the cold TTL. An aircraft-based measurement campaign across the TTL revealed very depleted values of δ18O of −150‰ in tandem with very high values of d-excess of ≈500‰ (46). Stratospheric influence could at least partly explain the observed anticorrelations between δ18O and 17O-excess and d-excess (Table 1 and SI Text).

To summarize, there are several ways to explain the interannual water isotopologue variations within a period of 2.5–5 y. Even if we cannot make a strong argument from this periodicity, close to the stratigraphic noise in such a low accumulation rate. In this site, we note that it is close to the Southern Annual Mode (SAM) or Antarctic circumpolar wave (ACW) periodicity (47). The SAM influences local temperature of Antarctica and source-to-site tropospheric transport (e.g., refs. 23, 48, 49). As explained above (Table 1), these mechanisms cannot explain the anticorrelation between δ18O and 17O-excess, which is our most robust observation. We have shown that seasonal or interannual variations of STE within the presented range (0.014% and 2%) can explain a large part of the 17O-excess interannual variations (Table 1) and, most important, they may explain the anti-correlation between δ18O and 17O-excess, if the stratospheric influence happens mainly during the cold periods. Stratospheric
inputs may also be seen in 10Be variability, as suggested by the coherence of 17O-excess with 10Be (Figs. 1C and 2). Indeed, variations in 10Be concentration at Vostok were shown to result from the combined influences of 10Be production, modulated by solar activity; modulation of tropospheric air mass transportation (linked to SAM and ACW); and stratospheric input (23). Because of these numerous influences on 10Be, we do not expect a perfect correlation between 10Be and 17O-excess. Moreover, we note that the correlation between 10Be and 17O-excess is not significant before 1970. This may be due to the effect of diffusion increasing with depth in the firn. As for the deposition that is not the same for 10Be (dry deposition) and 17O-excess (wet deposition), the diffusion in the firn is different for both tracers, i.e., much smaller for 10Be compared with water isotopic diffusion.

The question arises why the MIF signature of 17O-excess is observed at interannual but not at seasonal and glacial scales. It should be noted that the seasonal record (17) contains only the measurements of 16 precipitation events, 9 of them being associated with snowfall and only 4 of them containing ice needles (in addition to hoar frost). Thus, the 16 seasonal samples do not represent an average precipitation composition of 1 y (up to 91% clear sky precipitation) and are underestimating clear sky precipitation with possible stratospheric origin and much larger 17O-excess due to MIF effects in the stratosphere. Therefore, we do not expect an anticorrelation between δ18O and 17O-excess in the seasonal record.

The correlation between δ18O and 17O-excess on glacial-interglacial transition is difficult to explain with the stratospheric input as observed on the interannual scale. Still, it is not easy to predict the 17O-excess signature due to stratospheric input on this long timescale because of numerous modifications that may occur: First, the strength of the polar vortex and thus the input of water from the stratosphere may be influenced not only by temperature at this timescale but also by greenhouse gas (including ozone, methane and water vapor) concentrations that control the vertical temperature gradient. Second, due to possible changes in the ozone concentration, the stratospheric chemistry and therefore also the 17O-anomaly may differ from the Last Glacial Maximum (LGM) to the present day.

**Summary and Conclusions**

We measured the triple oxygen isotopic composition of a snow pit from the vicinity of Vostok (East Antarctica) on the interannual timescale. We observed large variations in the records of δ18O (10%), d-excess (20%), and 17O-excess (40 ppm), during the period of 1949–2008. We compared the water isotopic data with the output of an AGCM (LMDZ) and a simpler Rayleigh-type model (MCIM). The AGCM was able to reconstruct the seasonal water isotopic variations, as well as the variability of the site temperature on the interannual scale, but failed to capture the anticorrelation between δ18O and 17O-excess on the interannual scale. These findings were confirmed by the MCIM and lead us to the conclusion that interannual isotopic variance at Vostok is not solely determined by changing surface climatic conditions.

We presented the possible influence of intermittency of precipitation and postdeposition processes and showed that such effects cannot explain the significant anticorrelation between δ18O and 17O-excess. Stratospheric water intrusions would mainly increase 17O-excess and d-excess, whereas δ18O would undergo a slight decrease. The observed anticorrelations between δ18O on the one hand and d-excess and 17O-excess on the other hand could be the consequence of stratospheric influences. In addition, the observed correlation between 17O-excess and 10Be may be a consequence of stratospheric air intrusion that modulates both parameters.

Finally our work has two important implications:

1. The comparison between our data and the models clearly shows that interannual isotopic variations at very low accumulation sites in Antarctica should not be interpreted as a proxy for a change in surface climatic conditions. Other mechanisms can superimpose the surface climatic determinants on this timescale. However, at this stage this conclusion does not preclude the use of water isotopologues as proxies of climatic conditions (e.g., local temperature) on longer timescales.

**Outlook**

One way to further investigate the stratospheric water input in remote East Antarctica would be to lead to observations in a more coastal site. It would also be of great interest to compare real-time triple oxygen isotopic measurements of Antarctic water vapor and to compare these data with regional meteorological models. Also, more precise measurements of the stratospheric water vapor isotopic signature (especially of 17O-excess) are needed to further quantify their influence on tropospheric water isotopologues.

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Supporting Information

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SI Text

Mixed-Cloud Isotopic Model

The mixed-cloud isotopic model (MCIM) (1) is, among other models (2–4), one of the most efficient in simulating the fractionation of isotopes at the snow surface. The MCIM is based on a Rayleigh distillation (5, 6). It describes the isotopic composition of the condensed phase (liquid water or ice) and the water vapor at each step between the oceanic source region and the precipitation site on the ice sheet. To determine the isotopic composition of the first water vapor over the ocean surface, the assumption that all of the evaporated water will return to the ocean as rain (Merlivat’s closure assumption) is made.

During the formation of liquid, only equilibrium fractionation occurs. Depending on temperature, the MCIM allows in the zone of “mixed cloud” the coexistence of liquid droplets and ice crystals. In this zone, the Bergeron–Findeisen process associated with kinetic fractionation effects is taken into account (1). The formation of snow crystals is a nonequilibrium process and the fractionation factor is a function of $\alpha_{eq}$ and $\alpha_{kin}$:

$$\alpha = \alpha_{eq}\alpha_{kin}. \hspace{1cm} [S1]$$

The relative proportion of kinetic fractionation is governed by the supersaturation function in the cloud, which is (5)

$$\alpha_{kin} = \frac{S}{1 + \alpha_{eq} \left( \frac{D}{D^*} \right) (S - 1)}. \hspace{1cm} [S2]$$

$D$ and $D^*$ correspond to the diffusion constants for the light and the heavy isotopologues, respectively. As in previous studies (7–10) we described $S$ as a linear function of temperature: $S = p + qT_c$, where $T_c$ is the temperature in the cloud in degrees centigrade for every step of the distillation process, $p$ and $q$ are tunable parameters.

Forcing and Tuning of the MCIM

The model is prescribed by initial parameters such as the temperature ($T_{source}$), relative humidity ($RH_s$), wind speed, and pressure of the source region as well as the isotopic composition of the ocean and the condensation temperature ($T_c$; assumed to be linearly related to the surface temperature) (11) and pressure at the precipitation site. There are several tuning parameters (1) such as the dependence of supersaturation on temperature ($S = p + qT_c$); the fraction of condensate remaining in the cloud; the temperature range where liquid and solid water can coexist; a coefficient that determines the proportion of the reevaporation of liquid phase; and the parameter, which controls at what temperature the first ice forms. For the tuning of the model, we used the same method as in previous studies with $\delta^{18}O$, $\delta^{16}O$, and $\delta^2H$ (7–9).

Sensitivity to Initial Conditions. Table 1 in the main text displays the results of the sensitivity study of the MCIM. Two different supersaturation functions were chosen. First, $S_{low}$ refers to $S = 1 - 0.002 T_c$. Second, $S_{high}$ refers to $S = 1 - 0.004 T_c$, as it was used for the model study of the seasonal isotopic data (7). At a condensation temperature of $-40^\circ C$, this leads to a supersaturation of, respectively, 8% and 16%. $S_{low}$ was also used to simulate the stable behavior of $\delta^{18}O$ excess over an Antarctic transect (Terra Nova Bay to Dome C), covering a large $\delta^{18}O$ range from $-30\%e$ to $-53\%e$ (9), and $S_{high}$ has been used for the Last Glacial Maximum (LGM) to the present simulations of Laboratoire de Meteorologie Dynamique-Zoom (LMDZ).iso (12).

Postdeposition

The process of sublimation leads to consecutive evaporation of the snow layers, starting with the very top layer of the snow surface. The water molecules in the snow are sublimated following the stratigraphy (layer by layer) and independent of their isotopes. Therefore, for the process of sublimation no isotopic fractionation has been assessed (13). In contrast, for the condensation process, the isotopic fractionation during the vapor to solid phase change has been taken into account.

The fractionation from the vapor to the solid phase during the condensation onto the snowpack has been calculated with the use of the equilibrium fractionation factors for $\delta^{18}O$ (14), $\delta^2H$ (15), and $\delta^{17}O$ (16). The fractionation factors are a function of temperature and the condensation process happens mainly during the cold season, as indicated by observations at Vostok station. For a temperature of $-55^\circ C$, the fractionation factors $\alpha_{ob}$ between solid and red vapor for $\delta^{18}O$, $\delta^2H$, and $\delta^{17}O$ are 1.0264, 1.2826, and 1.0139, respectively. The fractionation leads to a depletion of the remaining water vapor compared with its condensate of, respectively, $-24.42\%e$, $-135.36\%e$, and $-13.3\%e$. For the snow isotopic composition, this leads to an increase $\delta^{18}O$ (+2.1%), a d-excess decrease ($-2.8\%e$), and a $\delta^{17}O$-excess decrease ($-43$ ppm) (Table 1, main text). If we take into account kinetic fractionation during the condensation process (assuming $S = 1 - 0.004 T_c$), this would lead to a smaller $\delta^{18}O$ increase ($+0.25\%e$), a large d-excess increase ($+5.66\%e$) instead of a decrease without kinetic fractionation, and a much smaller decrease ($-19$ ppm) in $\delta^{17}O$-excess. Thus, taking into account kinetic fractionation effects during the condensation process does not provide a better explanation for the observed anticorrelation between $\delta^{18}O$ and d-excess and $\delta^{17}O$-excess.

$\delta^{17}O$-Excess Interlaboratory Differences

As discussed already (7, 8), differences in $\delta^{17}O$-excess, between the Institute of Earth Science in Jerusalem (IESJ) and the Laboratoire des Sciences du Climat et de l’Environnement (LSCE), of some water standards have been observed. The largest difference of 17 ppm has been observed for the very depleted standard of Dome F ($\delta^{18}O = -58.2\%e$). These differences are mainly due to peculiarities of the mass spectrometers (e.g., source heating efficiency, background signals) and contamination with trace gases affecting mass 33 is. Because there is no internationally accepted $\delta^{18}O$-excess reference that would allow us to calibrate the mass spectrometric measurements and because the fractionation coefficients associated with $\delta^{17}O$ were determined at the IESJ, we have decided to correct our measurements with respect to those of the IESJ. This means that we assess a $\delta^{17}O$-excess value of 1 ppm to the Dome F water standard instead of 18 ppm, as it has been measured at LSCE. This correction decreases the absolute value vs. Vienna Standard Mean Ocean Water of our snow pit $\delta^{17}O$-excess data. However, because we are discussing only the relative interannual variability, this correction has no significant influence on our conclusions. That approach is analogous to the corrections that were applied to the seasonal record at Vostok (7) and also to the glacial-interglacial record of European Project for Ice Coring in Antarctica Dome C and Talos Dome (8). So, the dataset of this work is coherent compared with the datasets of the seasonal and glacial-interglacial records.
Calculation of the Stratospheric Input
Following Stohl and Sodemann (17), we assumed 2% of the precipitation having a stratospheric origin. We used the study of Sayres et al. (18) with $\delta^{18}$O$_{str}$ = -150‰, $\delta^{17}$H$_{str}$ = -70‰, and thus a d-excess$_{str}$ of 500‰. We also used the modeled $\delta^{18}$O-excess$_{str}$ of 3,000 ppm, following the work of Zahn et al. (19). Thus, 98% of the precipitation has a $\delta^{18}$O$_{mix} = -57.13‰$, $\delta^{17}$H$_{ trop}$ = -441.74‰, and thus a d-excess$_{ trop}$ of 15.3‰ and $\delta^{18}$O-excess$_{ trop}$ = 6.74 ppm (mean values over the interannual record). Note that $\delta^{18}$O-O-excess$_{mix}$ is the result of $\delta^{18}$O$_{str}$ and $\delta^{18}$O$_{ trop}$ put into the logarithmic definition of $\delta^{18}$O-excess and not the average of all $\delta^{18}$O-excess values (0.6 ppm lower than the arithmetic mean). The resulting $\delta^{18}$O and d-excess are the weighted average of both values; thus

$$\delta^{18}O_{mix} = 0.02 \cdot \delta^{18}O_{str} + 0.98 \cdot \delta^{18}O_{ trop}$$

$$d\text{-excess}_{mix} = 0.02 \cdot d\text{-excess}_{str} + 0.98 \cdot d\text{-excess}_{ trop}.$$

This leads to $\delta^{18}O_{str} = -58.99‰$ and d-excess$_{str} = 25‰$. So, stratospheric input decreases $\delta^{18}$O by 1.9‰ and increases d-excess by 9.7‰. For $\delta^{18}$O-excess$_{mix}$, first $\delta^{18}$O$_{str}$ under the assumption of $\delta^{18}$O-excess$_{str}$ = 3,000 ppm has to be calculated and then $\delta^{18}$O$_{ trop} = -31.55‰$ is calculated analogously to $\delta^{18}$O$_{mix}$:

$$\delta^{18}O_{str} = \exp\left(\delta^{18}O_{excess_{str}} + 0.528 \ln\left(\delta^{18}O_{ trop} + 1\right)\right) - 1.$$  

The $\delta^{18}$O-excess$_{mix}$ that results from the mixing of 98% tropospheric with 2% stratospheric air can now be calculated through

$$\delta^{18}O_{excess_{mix}} = \ln\left(\delta^{18}O_{max} + 1\right) - 0.528 \ln\left(\delta^{18}O_{ trop} + 1\right).$$

The above calculation of $\delta^{18}$O-excess$_{mix}$ yields 38.6 ppm and thus is 31.85 ppm larger than the average of $\delta^{18}$O-excess over the Vostok record.

Stratospheric Moisture Descending at Vostok
Following the approach of Yang and Tung (20) we calculated an annual global downward flux of water vapor from the stratosphere into the troposphere of 5.45573 10$^{11}$ kg. The main subsiding areas are between 40° and 90° on both hemispheres during most of the year. Using this information one can calculate an annual mean stratospheric water input per square kilometer in the descending areas. We have calculated the surface A of the spherical cap that covers the region between 40° and 90° on the globe. This is done by the formula

$$A = 2 \pi r h,$$

where $r$ is Earth’s radius (6,371 km) and $h$ is the distance from the pole to the intersection of Earth’s axis with the circle at 40° latitude.

The calculated subsiding area is 2 $A = 182.2174 \times 10^6$ km$^2$ (Northern and Southern spherical cap). Using that and the above result of the water vapor downward flux, the annual mean downward flux at the subsiding area is 2.994 kg km$^{-2}$. Comparing this number with the annual precipitation at Vostok of 21.5 10$^6$ kg km$^{-2}$ leads to a stratospheric contribution to the total precipitation at Vostok of 0.014%. Because stratosphere–troposphere exchange may be subject to large seasonal and interannual variations (main text), we assumed that, during some periods (months, years), 2% (instead of only 0.014%) of Vostok’s moisture is of stratospheric origin. Larger stratosphere to troposphere exchange (STE) (up to 5%) is also in agreement with the studies of Stohl and Sodemann (17) and Roscoe (21).