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Influence of Summer Sublimation on δD , $\delta^{18}O$, and $\delta^{17}O$ in Precipitation, East Antarctica, and Implications for Climate Reconstruction From Ice Cores

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RESEARCH ARTICLE

10.1029/2018JD030218

Key Points:

- Isotopic composition in summer precipitation on inland East Antarctica is more depleted than expected from the range of surface air temperatures during precipitation
- The strong depletion of isotopic composition in summer precipitation is caused by the combined effects of weak or nonexistent temperature inversion and moisture recycling associated with snow sublimation
- Isotopic fractionation occurs during the moisture recycling process

Supporting Information:

- Supporting Information S1

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Influence of Summer Sublimation on δD , $\delta^{18}O$, and $\delta^{17}O$ in Precipitation, East Antarctica, and Implications for Climate Reconstruction From Ice Cores

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Abstract In central Antarctica, where accumulation rates are very low, summer sublimation of surface snow is a key element of the surface mass balance, but its fingerprint in isotopic composition of water (δD , $\delta^{18}O$, and $\delta^{17}O$) remains unclear. In this study, we examined the influence of summer sublimation on δD , $\delta^{18}O$, and $\delta^{17}O$ in precipitation using data sets of isotopic composition of precipitation at various sites on the inland East Antarctica. We found unexpectedly low $\delta^{18}O$ values in the summer precipitation, decoupled from surface air temperatures. This feature can be explained by the combined effects of weak or nonexistent temperature inversion and moisture recycling associated with sublimation-condensation processes in summer. Isotopic fractionation during the moisture-recycling process also explains the observed high values of d-excess and ^{17}O -excess in summer precipitation. Our results suggest that the local cycle of sublimation-condensation in summer is an important process for the isotopic composition of surface snow, water vapor, and consequently precipitation on inland East Antarctica.

1. Introduction

Measurements of $\delta^{18}O$ and δD in polar ice cores have long been used to reconstruct past changes in local surface air temperature (Jouzel et al., 1987; EPICA, 2004; NEEM community members, 2013; WAIS Divide Project Members, 2013). This was initially based on the assumption that the slope of the present-day spatial linear relationship between isotopic composition in surface snow and temperatures— δ/T (δ stands for either $\delta^{18}O$ or δD and T for the surface air temperature)—is equal to the temporal δ/T and remains constant over time. However, the spatial δ/T may differ from the temporal δ/T because many factors other than the condensation temperature during precipitation may modify isotopic values of precipitation. To avoid possible confusion with postdepositional processes, the terminology “condensation” rather than “deposition” is used in this paper to represent the water phase change from vapor to solid. In Greenland, where alternative paleothermometry methods are available, several studies demonstrate that the temporal δ/T varies in time and space, and is significantly lower than the spatial δ/T over Greenland due to the seasonality of precipitation and possibly postdepositional processes (Buizert et al., 2014; Guillevic et al., 2013; Jouzel et al., 1997; Masson-Delmotte et al., 2011; Steen-Larsen, Masson-Delmotte, et al., 2014; White et al., 1997). In Antarctica, most observations indicate that the temporal slopes of δ/T in precipitation at seasonal or subseasonal timescales are significantly lower (0.24–0.57‰/°C) (Ekaykin et al., 2004; Fernandoy et al., 2012; Motoyama et al., 2005; Schlosser et al., 2004; Schoenemann & Steig, 2016; Stenni et al., 2016; Touzeau et al., 2016; van Ommen & Morgan, 1997) than the spatial slope of 0.8‰/°C of Antarctic surface snow obtained by Masson-Delmotte et al. (2008), with one the exception of one study showing relatively high value (0.78‰/°C; Fujita & Abe, 2006). It was suggested that the observed low temporal δ/T may reflect a

strong gradient between condensation and surface temperature in winter (Ekaykin et al., 2004; Landais, Ekaykin, et al., 2012) and/or the vanishing inversion layer in summer (Landais et al., 2017). In the central Antarctic Plateau with very low snow accumulation rates (0.016–0.038 m/w.e.a; Ekaykin et al., 2004; Hou et al., 2007; Jouzel et al., 2001; Masson et al., 2000; Watanabe et al., 2003), postdepositional processes could significantly modify the isotopic composition of surface snow (Casado et al., 2018; Laepple et al., 2018; Münch et al., 2017; Ritter et al., 2016). Recent observations in the summer have revealed that the isotopic composition of surface snow in the absence of precipitation varies with changes of the surface vapor isotopic composition (Casado et al., 2016, 2018; Ritter et al., 2016; Steen-Larsen, Masson-Delmotte, et al., 2014; Touzeau et al., 2016), suggesting possible isotopic exchange between surface snow and atmospheric water vapor in the polar regions. However, the potential impact of the local vapor/snow interaction on the temporal slopes of δ/T in precipitation on the East Antarctic Plateau has not yet been assessed.

The second-order parameters of δD , $\delta^{18}O$, and $\delta^{17}O$, d-excess and ^{17}O -excess, defined as $d\text{-excess} = \delta D - 8 \times \delta^{18}O$ (Dansgaard, 1964) and $^{17}O\text{-excess} = \ln(\delta^{17}O + 1) - 0.528 \times \ln(\delta^{18}O + 1)$ (Barkan & Luz, 2007; Landais et al., 2008; Luz & Barkan, 2010), can preserve a climatic signal from the moisture source region (Angert et al., 2004; Johnsen et al., 1989; Jouzel et al., 1982; Jouzel et al., 2013; Landais et al., 2008; Masson-Delmotte et al., 2005; Markle et al., 2017; Merlivat & Jouzel, 1979; Uemura et al., 2012; Vimeux et al., 1999, 2001), imprinted by kinetic fractionation of water stable isotopes during evaporation. The d-excess is mainly controlled by the sea surface temperature (SST) and/or relative humidity (RH) at the moisture source region (Merlivat & Jouzel, 1979; Steen-Larsen, Sveinbjörnsdottir, et al., 2014; Uemura et al., 2008), though the effect of SST has been questioned by direct observations of water stable isotopes in water vapor in the marine boundary layer (Steen-Larsen et al., 2015, 2017). The ^{17}O -excess in marine vapor is mainly determined by the normalized RH at the moisture source region (Landais et al., 2008; Landais, Steen-Larsen, et al., 2012; Risi et al., 2013; Schoenemann & Steig, 2016; Uemura et al., 2010; Winkler et al., 2012). The d-excess records in polar ice cores have previously been used to infer past SST and potential RH in the moisture source region (Jouzel et al., 1982; Petit et al., 1991; Stenni et al., 2003; Uemura et al., 2012; Vimeux et al., 1999), and the ^{17}O -excess records are considered to potentially indicate the normalized RH at the moisture source region (Landais et al., 2008; Winkler et al., 2012). However, in addition to the evaporative conditions at the moisture source region, other factors, such as distillation along the air mass trajectory, can also influence the d-excess and ^{17}O -excess of polar precipitation. Moreover, Steen-Larsen, Masson-Delmotte, et al. (2014) found parallel changes of d-excess and ^{17}O -excess in surface snow and near-surface vapor in-between precipitation events at NEEM (Greenland), suggesting that the isotopic exchange between the surface snow and atmospheric water vapor also influences d-excess and ^{17}O -excess. As a result, understanding the local effects on the d-excess and ^{17}O -excess is necessary for using water stable isotopes in ice cores to reconstruct climate characteristics at the moisture source region.

Previous studies have indicated that summer sublimation of surface snow is significant in the interior of Antarctica due to the greater solar radiation (Ding et al., 2016; Ekaykin et al., 2004; Frezzotti et al., 2004; Kameda et al., 1997). Simulations from the Melbourne University atmospheric general circulation model (GCM) indicated that over 50% of the moisture condensing above the Antarctica during the summer months (DJF) comes from the Antarctica itself, with ~42% from inland sublimation (Noone & Simmonds, 2002). This result is comparable with the values of 35–40% derived from the ECHAM GCM (Werner et al., 2001). Although the GCM models only incorporated a simplified representation of surface snow, without accounting for metamorphism, these simulations suggest that moisture recycling may be an important process for summer precipitation over the central Antarctic plateau, which is characterized by very low snow accumulation rates. Laboratory experiments, field observations, and simple isotopic simulations have demonstrated that isotopic fractionation occurs during surface snow sublimation (Lechler & Niemi, 2011; Neumann et al., 2008; Ritter et al., 2016). However, the effects of summer sublimation on δD , $\delta^{18}O$, and $\delta^{17}O$ as well as their second-order parameters (d-excess and ^{17}O -excess) in inland Antarctica remain unclear.

Observations of isotopic composition in precipitation at synoptic or diurnal timescales are essential for understanding the isotopic fractionation processes at play, and for studying the influence of local post-depositional processes. However, up to now, only a few studies have been conducted on stable isotopes in daily precipitation over the central East Antarctica, specifically at Dome F (Fujita & Abe, 2006), Vostok (Landais, Ekaykin, et al., 2012; Touzeau et al., 2016), and Dome C (Stenni et al., 2016). So far, there have

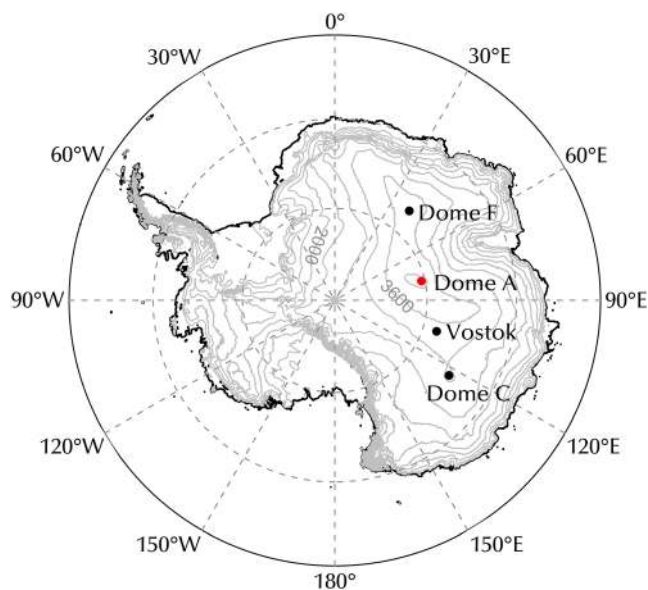


Figure 1. The topographic map of Antarctica, showing Dome A and other deep ice core drilling sites discussed in the text. The topographic data were extracted from ETOPO1 global elevations data set (<https://www.ngdc.noaa.gov/mgg/global/global.html>).

been no reported measurements on stable isotope ratios in precipitation at Dome Argus (Dome A) of East Antarctica, the highest point of Antarctic ice sheet and a place with the potential for recovering the oldest ice core on Earth (Xiao et al., 2008; Zhang et al., 2007). In addition, measurements of $\delta^{17}\text{O}$ (hence ^{17}O -excess) in precipitation over central East Antarctica are even more sparse than δD and $\delta^{18}\text{O}$. The lack of reported measurements of δD , $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ in precipitation on inland East Antarctica limits our understanding of the isotopic fractionation processes at play and the potential effects of the postdepositional processes. Here, we present δD , $\delta^{18}\text{O}$, and $\delta^{17}\text{O}$ measurements of summer precipitation and surface frost sampled from individual precipitation events at Dome A (Figure 1). The new isotopic data (especially the ^{17}O -excess) are a useful supplement to the sparse data of precipitation stable isotopes on the East Antarctic Plateau. In addition to the new isotopic data at Dome A, we also compiled isotopic data of precipitation and water vapor at other sites in East Antarctica (Figure 1). Using the data sets, we examine the effects of summer sublimation on δD , $\delta^{18}\text{O}$, and $\delta^{17}\text{O}$ in precipitation in East Antarctica, and implications for climate reconstruction from ice cores.

2. Materials and Methods

Samples of precipitation and surface frost were collected at the Chinese Kunlun Station of Dome A ($80^{\circ}22'51''\text{S}$, $77^{\circ}27'23''\text{E}$), East Antarctica, in January 2010 during the 26th Chinese National Antarctic Research Expedition (CHINARE-26). Eight precipitation samples (namely, D1, D2, ..., D8) were collected on the surface of a box covered by clean plastic film (90-cm length \times 55-cm width). The surface of the box was set at 2 m above the snow surface. Seven frost samples (namely, F1, F2, ..., F7) were collected from the steel cable used for securing field materials on the sledge. The height of the steel cable was ~ 0.5 m above the snow surface. In addition, two ice needle samples (namely S1 and S2) were collected from surface snow (sampling depth less than 0.5 cm). Details of the samples are listed in Table 1.

The measurements of δD , $\delta^{18}\text{O}$, and $\delta^{17}\text{O}$ were performed at the Laboratoire des Sciences du Climat et de l'Environnement, France. The chromium reduction method (Pang et al., 2015) was used to prepare hydrogen from the water samples, for measurements of δD with an associated precision of 0.7‰. For oxygen isotopes, water samples were converted to oxygen by a water fluorination technique, and the produced oxygen was then analyzed by the dual inlet mass spectrometer (MAT 253) for $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ (Barkan & Luz, 2005; Landais et al., 2008). The measurements were calibrated using Vienna Standard Mean Ocean Water and Standard Light Antarctic Precipitation. The reference values are 0‰ and -55.5 ‰ for $\delta^{18}\text{O}$ and 0 ppm for ^{17}O -excess (Schoenemann et al., 2013; Touzeau et al., 2016; Winkler et al., 2012). The analytical uncertainty is 0.05‰ for both $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ and 5 ppm for ^{17}O -excess. The quadratic error for d-excess is 0.8‰, estimated by the uncertainties of $\delta^{18}\text{O}$ and δD .

In addition, several previously published precipitation isotopic data sets at various sites in inland East Antarctica were included for comparison and analysis. Specifically, $\delta^{18}\text{O}$ and d-excess in daily precipitation sampled at Dome F in 2003 (Fujita & Abe, 2006) and at Dome C from late 2007 to 2010 (Stenni et al., 2016), and a subset of $\delta^{18}\text{O}$, d-excess, and ^{17}O -excess in precipitation collected at Vostok from December 1999 to December 2000 (Landais, Ekaykin, et al., 2012; Touzeau et al., 2016). It should be noted that the various sampling techniques were used in these studies. At Dome F, daily precipitation samples were collected in two plastic containers (0.53×0.35 m²) placed on the roof of the Dome Fuji station about 4 m from surface. In many cases the snow accumulated on the roof was also added to the samples because the amount of snow in the containers was insufficient for analysis (Fujita & Abe, 2006). At Dome C, daily precipitation samples were collected on an 80 \times 120-cm wooden platform covered by a polystyrene/Teflon plate at 1 m above the snow surface (Stenni et al., 2016). At Vostok, precipitation samples were collected by a precipitation trap at 1.5 m above the snow surface (Landais, Ekaykin, et al., 2012). It is possible that some precipitation samples were impacted by blowing snow at Dome C and

Table 1

Isotopic Ratios (δD , $\delta^{18}O$, and $\delta^{17}O$) and Their Second-Order Parameters (d-excess and ^{17}O -excess) in the Summer Precipitation, Surface Frost, and Surface Ice Needle Collected at Dome A During 2010, East Antarctica

Sampling ID	Precipitation type	Sampling time (hh:hh, dd/mm)	AirT1 (°C)	AirT4 (°C)	AirT4-AirT1 (°C)	δD (‰)	$\delta^{18}O$ (‰)	$\delta^{17}O$ (‰)	d-excess (‰)	^{17}O -excess (ppm)
D1	precipitation	UTC07:00–18:00, 06/01	−28.29	−25.55	2.74	−385.0	−49.610	−26.469	11.9	40
D2	precipitation	UTC07:00, 09/01 to UTC03:00, 10/01	−30.88	−27.16	3.72	−391.4	−51.592	−27.538	21.4	44
D3	precipitation	UTC07:00, 10/01 to UTC03:00, 11/01; UTC15:00, 11/01 to UTC03:00, 12/01; UTC05:00–08:00, 12/01	−28.88	−28.48	0.39	−384.7	−49.990	−26.690	15.2	24
D4	precipitation	UTC14:00, 18/01 to UTC03:00, 19/01	−30.37	−31.09	−0.72	−332.6	−42.397	−22.577	6.6	38
D5a	precipitation	UTC15:00–19:00, 20/01	−32.50	−32.90	−0.39	−380.4	−49.012	−26.137	11.7	50
D5b	precipitation	UTC15:00–19:00, 20/01	−32.50	−32.90	−0.39	−377.6	−48.870	−26.050	13.4	59
D6	precipitation	UTC19:00, 20/01 to UTC01:00, 21/01	−34.90	−34.93	−0.03	−359.8	−45.383	−24.177	3.2	49
D7	precipitation	UTC19:00, 21/01 to UTC02:00, 22/01	−35.54	−36.76	−1.22	−370.3	−47.886	−25.526	12.8	52
D8	precipitation	UTC19:00, 22/01 to UTC03:00, 23/01	−34.99	−34.71	0.29	−375.0	−48.893	−26.066	16.1	56
F1	surface frost	UTC03:00, 12/01	—	—	—	−405.1	−54.488	−29.107	30.8	44
F2	surface frost	UTC03:00, 18/01; UTC03:00, 19/01;	—	—	—	−398.1	−52.806	−28.200	24.4	40
F3	surface frost	UTC03:00, 19/01 to UTC03:00, 20/01	−29.72	−29.75	−0.03	−365.4	−47.620	−25.398	15.5	35
F4	surface frost	UTC03:00, 20/01 to UTC03:00, 21/01	−30.33	−30.75	−0.42	−367.8	−48.168	−25.675	17.5	55
F5	surface frost	UTC03:00, 21/01 to UTC03:00, 22/01	−32.06	−33.33	−1.27	−378.7	−49.802	−26.578	19.8	36
F6	surface frost	UTC03:00, 22/01 to UTC03:00, 24/01	−32.79	−32.79	0.00	−384.3	−50.229	−26.813	17.5	32
F7	surface frost	UTC03:00, 24/01 to UTC03:00, 25/01	−33.55	−34.89	−1.34	−394.3	−51.128	−27.307	14.8	23
S1	surface ice needle	16/01				−397.3	−53.009	−28.304	26.7	46
S2	surface ice needle	25/01				−387.5	−51.220	−27.333	22.3	48

Note. AirT1 (AirT4) stands for the mean air temperature at 1 m (4 m) above the snow surface during the sampling period, measured by an automatic weather station installed at Dome A since 2005. For sample D5, we collected two samples (D5a and D5b) simultaneously at two places (with a distance ~50 m) for comparison. The air temperatures for F1 and F2 were not available because the sampling time intervals were not recorded.

Vostok due to the lower sampling heights, and that some precipitation samples at Dome F were influenced by wind erosion or sublimation due to the mixing of the snow accumulated on the roof. The relatively low $\delta^{18}O$ values and high d-excess values in summer precipitation at Dome A seem to suggest that the effects of blowing snow and/or sublimation during the collection periods were not substantial. Nevertheless, the precipitation isotopic data at Dome A, Dome F, Dome C, and Vostok are comparable due to their short sampling periods (daily or less). Additional data sets used for comparison include the ^{17}O -excess data of a subset of the 2010 precipitation samples collected at Dome C (Touzeau et al., 2016) and the isotopic data ($\delta^{18}O$ and d-excess) in water vapor measured by the cavity-enhanced spectroscopic technique at the Kohnen Station from December 2013 to January 2014 (Ritter et al., 2016) and at Dome C from December 2014 to January 2015 (Casado et al., 2016).

In the interior of Antarctica, summer months (December and January) are the warmest of the year and snow sublimation primarily occurs during the warmest season (Ding et al., 2016; Ekaykin et al., 2004; Frezzotti et al., 2004; Kameda et al., 1997). As a result, we focus our analysis on isotopic composition in summer precipitation and compare our data with results from surface snow at other sites of Antarctica (Masson-Delmotte et al., 2008) and nonsummer season precipitation (February to November) on the East Antarctic Plateau.

3. Results

The isotopic values in summer precipitation at Dome A range from $-42.4‰$ to $-51.6‰$ with a mean value of $-48.2 \pm 2.7‰$ for $\delta^{18}O$, from $3.2‰$ to $16.1‰$ with a mean value of $12.5 \pm 5.3‰$ for d-excess, and from 24 to 59 ppm with a mean value of 46 ± 11 ppm for ^{17}O -excess. The isotopic values in frost vary from $-47.6‰$ to $-54.5‰$ with a mean value of $-50.6 \pm 2.4‰$ for $\delta^{18}O$, from $14.7‰$ to $30.8‰$ with a mean value of $20.0 \pm 5.7‰$ for d-excess, and from 23 to 55 ppm with a mean value of 38 ± 10 ppm for ^{17}O -excess. For all the samples (including the two surface ice needle samples S1 and S2), the mean values of $\delta^{18}O$, d-excess, and ^{17}O -

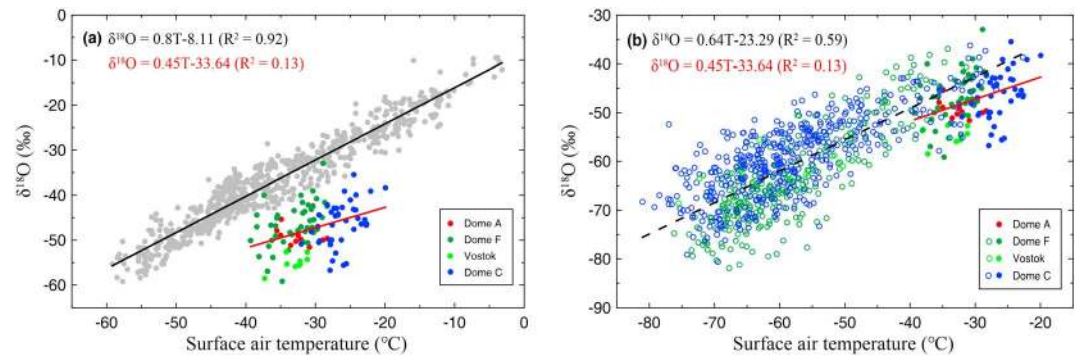


Figure 2. (a) A comparison between the $\delta^{18}\text{O}/T$ relationship for summer precipitation (December and January) in central East Antarctica (Dome A, Dome F, Vostok, and Dome C, colored dots and the red line) and the $\delta^{18}\text{O}/T$ relationship for surface snow at other sites of Antarctica (gray dots and the black line; data from Masson-Delmotte et al., 2008). Analysis of covariance indicates that the linear slopes of $\delta^{18}\text{O}/T$ in summer precipitation and in surface snow are significantly different at the 99% confidence level. (b) A comparison of the $\delta^{18}\text{O}/T$ relationship between summer (December and January, solid dots and the red line) and nonsummer (all other months, open dots and the black dashed line) precipitation in central East Antarctica (Dome A, Dome F, Vostok, and Dome C). Analysis of covariance indicates that the linear slopes of $\delta^{18}\text{O}/T$ in precipitation during summer and nonsummer seasons are significantly different at the 99% confidence level.

excess are $-49.6 \pm 2.8\%$, $16.8 \pm 6.8\%$, and 43 ± 10 ppm, respectively. Here, the symbol \pm indicates one standard deviation.

For further analysis, we combined our data with other precipitation isotope data sets collected at Dome C, Dome F, and Vostok and separated them into summer and nonsummer precipitation data. Compared with the $\delta^{18}\text{O}$ values in surface snow of Antarctica (Figure 2a) and nonsummer precipitation (Figure 2b), the $\delta^{18}\text{O}$ values in summer precipitation are lower at similar surface air temperatures. In addition, the temporal $\delta^{18}\text{O}/T$ slope in summer precipitation is significantly lower than both the spatial $\delta^{18}\text{O}/T$ slope in surface snow of Antarctica (Figure 2a and Table 2) and the temporal $\delta^{18}\text{O}/T$ slope in nonsummer precipitation (Figure 2b and Table 2).

In general, the d-excess increases when $\delta^{18}\text{O}$ or δD decreases due to the distillation process. However, the linear slope (absolute value) between d-excess and $\delta^{18}\text{O}$ in summer precipitation is significantly higher than both spatial slope of d-excess/ $\delta^{18}\text{O}$ in surface snow of Antarctica (Figure 3a and Table 2) and the temporal slope of d-excess/ $\delta^{18}\text{O}$ in nonsummer precipitation (Figure 3b and Table 2). We also calculated the logarithmic definition of deuterium excess, $d_{\ln} = \ln(1 + \delta\text{D}) + 0.0285 \times (\ln(1 + \delta^{18}\text{O}))^2 - 8.47 \times \ln(1 + \delta^{18}\text{O})$, proposed by Uemura et al. (2012). The d_{\ln} is considered a more faithful proxy for moisture source conditions because it eliminates both the equilibrium effect and the kinetic fractionation (like snow formation effect; Markle et al., 2017; Schoenemann et al., 2014; Schoenemann & Steig, 2016; Uemura et al., 2012). The results show very weak correlations between d_{\ln} and $\delta^{18}\text{O}$ in surface snow of Antarctica (Figure 3c and Table 2) and nonsummer precipitation (Figure 3d and Table 2), but significantly stronger d_{\ln} - $\delta^{18}\text{O}$ correlations in summer precipitation (Figure 3c and Table 2). In addition, based on the d-excess and d_{\ln} values, the summer precipitation samples could be divided into two categories: most of the Dome A samples and some Dome C and Dome F samples have relatively high d-excess and d_{\ln} values, whereas some samples at Dome F and Dome C have very low d-excess and d_{\ln} values.

In inland East Antarctica, generally there exists a positive correlation between ^{17}O -excess and $\delta^{18}\text{O}$ in precipitation, probably due to the influence of kinetic fractionation at very low temperature (Angert et al., 2004; Pang et al., 2015; Risi et al., 2013) or the kinetic fractionation during diamond dust nucleation and growth that results in ^{17}O depletion relative to synoptic precipitation at the same $\delta^{18}\text{O}$ value (Miller, 2018). However, no significant correlation is observed between ^{17}O -excess and $\delta^{18}\text{O}$ in summer precipitation (Figure 4 and Table 2). Moreover, most of the ^{17}O -excess values in summer precipitation at Dome A lie above the regression lines between ^{17}O -excess and $\delta^{18}\text{O}$ in surface snow along the Antarctic Syowa-Dome F and Zhongshan-Dome A traverses (Figure 4a), indicating a relatively high ^{17}O -excess in summer precipitation at Dome A relative to surface snow of the Antarctic traverses at the same $\delta^{18}\text{O}$ values.

Table 2
Linear Slopes of $\delta^{18}\text{O}/T$, $d\text{-excess}/\delta^{18}\text{O}$, $d_{\text{IN}}/\delta^{18}\text{O}$, $^{17}\text{O-excess}/\delta^{18}\text{O}$, and $\delta D/\delta^{18}\text{O}$ of Summer and Nonsummer Precipitation at Various Sites on the East Antarctic Plateau

Site name	Season	$\delta^{18}\text{O}/T$ ($\%/\text{C}$)	$d\text{-excess}/\delta^{18}\text{O}$	$d_{\text{IN}}/\delta^{18}\text{O}$	$^{17}\text{O-excess}/\delta^{18}\text{O}$	$\delta D/\delta^{18}\text{O}$	References
Dome A	Summer	-0.05 ± 0.30 ($R^2 = 0.08, N = 14$)	-2.12 ± 0.29 ($R^2 = 0.76, N = 18$)	-2.52 ± 0.46 ($R^2 = 0.63, N = 18$)	0.46 ± 0.91 ($R^2 = 0.05, N = 18$)	5.88 ± 0.29 ($R^2 = 0.96, N = 18$)	This study
Vostok	Summer	0.59 ± 0.27 ($R^2 = 0.32, N = 9$)	-1.55 ± 0.77 ($R^2 = 0.25, N = 10$)	-1.20 ± 1.33 ($R^2 = 0.02, N = 10$)	-1.62 ± 1.70 ($R^2 = 0.01, N = 10$)	6.45 ± 0.77 ($R^2 = 0.89, N = 10$)	Landais, Ekaykin, et al., 2012;
	Nonsummer	0.35 ± 0.10 ($R^2 = 0.43, N = 17$)	-0.81 ± 0.24 ($R^2 = 0.40, N = 17$)	-0.63 ± 0.44 ($R^2 = 0.06, N = 17$)	3.14 ± 0.40 ($R^2 = 0.79, N = 17$)	7.19 ± 0.24 ($R^2 = 0.98, N = 17$)	Touzeau et al., 2016
Dome C	Summer	0.89 ± 0.29 ($R^2 = 0.18, N = 40$)	-3.49 ± 0.33 ($R^2 = 0.74, N = 40$)	-4.61 ± 0.52 ($R^2 = 0.67, N = 40$)	-4.42 ± 2.91 ($R^2 = 0.39, N = 3$)	4.51 ± 0.33 ($R^2 = 0.83, N = 40$)	Stenni et al., 2016;
	Nonsummer	0.55 ± 0.02 ($R^2 = 0.59, N = 460$)	-1.43 ± 0.04 ($R^2 = 0.69, N = 459$)	-0.65 ± 0.08 ($R^2 = 0.13, N = 459$)	1.23 ± 0.50 ($R^2 = 0.19, N = 22$)	6.57 ± 0.04 ($R^2 = 0.98, N = 459$)	Touzeau et al., 2016; Casado et al., 2016
Dome F	Summer, vapor	0.65 ± 0.23 ($R^2 = 0.23, N = 23$)	-2.81 ± 0.43 ($R^2 = 0.66, N = 23$)	-3.27 ± 0.85 ($R^2 = 0.39, N = 23$)		5.19 ± 0.43 ($R^2 = 0.87, N = 23$)	
	Summer	0.77 ± 0.21 ($R^2 = 0.22, N = 46$)	-2.39 ± 0.38 ($R^2 = 0.46, N = 46$)	-2.80 ± 0.61 ($R^2 = 0.31, N = 46$)		5.61 ± 0.38 ($R^2 = 0.83, N = 46$)	Landais, Ekaykin, et al., 2012; Touzeau et al., 2016
Kohnen station,	Nonsummer	0.86 ± 0.03 ($R^2 = 0.72, N = 290$)	-1.69 ± 0.05 ($R^2 = 0.80, N = 290$)	-0.89 ± 0.09 ($R^2 = 0.25, N = 290$)		6.31 ± 0.05 ($R^2 = 0.98, N = 290$)	
	Summer, vapor	0.74 ± 0.15 ($R^2 = 0.45, N = 29$)	-1.97 ± 0.26 ($R^2 = 0.67, N = 29$)	-2.17 ± 0.44 ($R^2 = 0.45, N = 29$)		6.03 ± 0.26 ($R^2 = 0.95, N = 29$)	Ritter et al., 2016
East Antarctica Plateau, precipitation	Summer	0.45 ± 0.11 ($R^2 = 0.13, N = 109$)	-2.75 ± 0.21 ($R^2 = 0.61, N = 114$)	-3.37 ± 0.33 ($R^2 = 0.47, N = 114$)	0.68 ± 0.67 ($R^2 = 0.00, N = 32$)	5.25 ± 0.21 ($R^2 = 0.85, N = 114$)	This study
	Nonsummer	0.64 ± 0.02 ($R^2 = 0.59, N = 767$)	-1.47 ± 0.03 ($R^2 = 0.71, N = 766$)	-0.59 ± 0.06 ($R^2 = 0.11, N = 766$)	1.12 ± 0.40 ($R^2 = 0.14, N = 41$)	6.53 ± 0.03 ($R^2 = 0.98, N = 766$)	
Antarctica, surface snow		0.80 ± 0.01 ($R^2 = 0.92, N = 754$)	-0.37 ± 0.02 ($R^2 = 0.43, N = 602$)	0.06 ± 0.02 ($R^2 = 0.01, N = 602$)		7.75 ± 0.01 ($R^2 = 0.99, N = 794$)	Masson-Delmotte et al., 2008

Note. In addition, the slopes from observations of summer water vapor stable isotopes at Dome C and Kohnen station as well as observations of surface snow stable isotopes at the sites of Antarctica are also presented for comparisons. The three outliers (see Figure 4b) were not included when calculating the linear slopes of $^{17}\text{O-excess}/\delta^{18}\text{O}$ of summer and nonsummer precipitation at Dome C, and the symbol \pm indicates standard error.

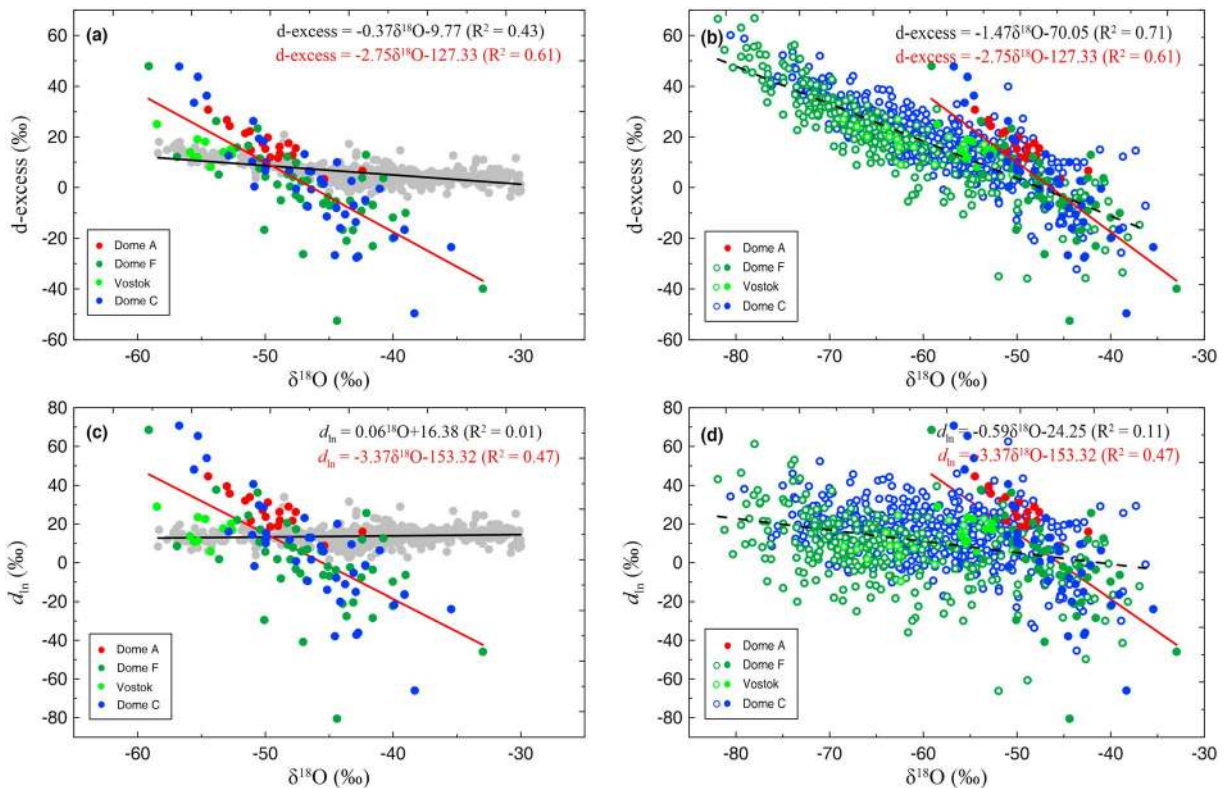


Figure 3. (a) A comparison between the d-excess/ $\delta^{18}\text{O}$ relationship for summer precipitation (December and January) in central Antarctica (Dome A, Dome F, Vostok, and Dome C, colored dots and the red line) and the d-excess/ $\delta^{18}\text{O}$ relationship for surface snow at other sites of Antarctica (gray dots and the black line, data from Masson-Delmotte et al., 2008). Sites with surface snow $\delta^{18}\text{O}$ values greater than -30‰ (indicating coastal regions of Antarctica) are excluded. Analysis of covariance indicates that the linear slopes of d-excess/ $\delta^{18}\text{O}$ in summer precipitation and in surface snow are significantly different at the 99% confidence level. (b) A comparison of the d-excess/ $\delta^{18}\text{O}$ relationship between summer (December and January, solid dots and the red line) and nonsummer (all other months, open dots and the black dashed line) precipitation in central East Antarctica (Dome A, Dome F, Vostok, and Dome C). Analysis of covariance indicates that the linear slopes of d-excess/ $\delta^{18}\text{O}$ in precipitation during summer and nonsummer seasons are significantly different at the 99% confidence level. (c and d) Same as (a) and (b) but for the $d_{in}/\delta^{18}\text{O}$ relationship.

4. Discussion

4.1. Factors Controlling δD , $\delta^{18}\text{O}$, and $\delta^{17}\text{O}$ of Summer Precipitation in Central East Antarctica

There are many factors that can influence the isotopic composition in precipitation on the East Antarctic Plateau, including condensation temperature of precipitation, variations of marine moisture sources, and possible local processes such as blowing snow and moisture recycling associated with sublimation-condensation processes. In the following, we discuss which factor can account for the observed unexpectedly low $\delta^{18}\text{O}$ values as well as high values of d-excess and ^{17}O -excess in summer precipitation on the East Antarctic Plateau.

4.1.1. Condensation Temperature

The isotopic composition of precipitation is mainly affected by the temperature of the atmosphere at the level of condensation, rather than the surface air temperature. In general, there exists a temperature inversion layer with warmer air up to several hundred meters thick over polar ice sheets due to the radiative loss of heat by the surface (Ohtake, 1978; Phillpot & Zillman, 1970). It is usually believed that precipitation is formed close to the upper boundary of the temperature inversion layer where the largest moisture amount is found due to the highest air temperature (Jouzel & Merlivat, 1984; Robin, 1977). However, previous studies indicated that the temperature inversion is weak or even nonexistent over the East Antarctic Plateau during summer (Hudson & Brandt, 2005; Pietroni et al., 2014), which may cause relatively cool condensation temperature of precipitation, leading to the observed lower $\delta^{18}\text{O}$ in summer precipitation. At Dome A, the condensation temperature data are unavailable due to the lack of radiosonde measurements. However, the existence of a temperature inversion layer may be recognized by the difference between the air

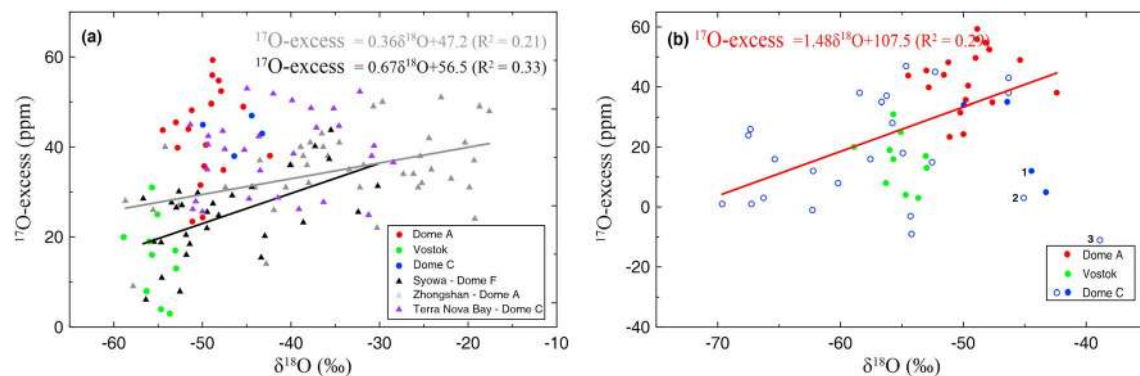


Figure 4. (a) A comparison of the ^{17}O -excess/ $\delta^{18}\text{O}$ relationship between summer precipitation (December and January) in central Antarctica (Dome A, Vostok, and Dome C, colored dots) and the surface snow along the traverses from Zhongshan station to Dome A (light gray triangles and the light gray line), Syowa station to Dome F (black triangles and the black line), and Terra Nova Bay to Dome C (purple triangles). It is noted that the shallow surface snow sampling depth (10 cm) of the traverse from Zhongshan station to Dome A may bias the seasonality of precipitation (Pang et al., 2015). (b) The ^{17}O -excess/ $\delta^{18}\text{O}$ relationship in precipitation at Dome A, Vostok, and Dome C (colored dots for summer precipitation and open dots for nonsummer precipitation). The 16 clear-sky precipitation samples at Vostok collected during nonsummer season (between 29 February and 11 October 2000) were not included in Figure 4b because the oxygen triple-isotope distribution of clear-sky precipitation is distinctly different from that of synoptic precipitation (Miller, 2018). The red line is the linear regression line of all the data except for the three outliers of Dome C (indicated by numbers 1, 2, and 3). The d-excess values of the three outliers are -8.0‰ , -14.1‰ , and -25.7‰ , respectively, indicating that the three samples contained much blowing snow and suffered strong sublimation. The ^{17}O -excess data in precipitation at Vostok and in surface snow along the traverses from Terra Nova Bay to Dome C have been Vienna Standard Mean Ocean Water-Standard Light Antarctic Precipitation calibrated (Tables S2 and S3 in the supporting information).

temperature measurements at the heights of 4 and 1 m above the snow surface. In Table 1, the existence of temperature inversion is detected for samples D1–D3 and D8, and is nonexistent for samples D4–D7. In addition, we observed a higher mean value of surface air temperature at 1m for samples D1–D3 and D8 (-30.8 °C) than that for samples D4–D7 (-33.2 °C). Thus, we speculate that the mean condensation temperature for samples D1–D3 and D8 is higher than that for samples D4–D7. However, the average value of $\delta^{18}\text{O}$ of D1–D3 and D8 (-50.0‰) is lower than the average value of D4–D7 (-46.7‰), which seems to suggest that the weak or nonexistent temperature inversion is not the key factor driving the observed strong depletion of $\delta^{18}\text{O}$ in summer precipitation at Dome A. At Dome C, the temperature at the upper limit of the inversion layer (which is assumed to be equal to the condensation temperature as a first approximation) was retrieved from radiosonde data measured since 2005 (<http://www.climantartide.it>; Stenni et al., 2016). There is a weak positive correlation between this “condensation” temperature and $\delta^{18}\text{O}$ in summer daily precipitation at Dome C (figure not shown). Nevertheless, it is difficult to determine the actual condensation temperature at which the precipitation forms when the temperature inversion is weak or even nonexistent during the summer. Moreover, it was suggested that only roughly half of the humidity inversions are associated with temperature inversions and a typical humidity profile contains several separate inversion layers (Nygard et al., 2013). As a result, we cannot preclude the contribution of the weak or nonexistent temperature inversion to our observed strong depletion of isotopic ratios in summer precipitation on the East Antarctic Plateau.

To further analyze the effect of condensation temperature on the isotopic composition in summer precipitation at Dome A, we used the Mixed Cloud Isotopic Model (MCIM; Ciais & Jouzel, 1994) to simulate the $\delta^{18}\text{O}$, d-excess, and ^{17}O -excess in summer precipitation at Dome A. The MCIM has been widely used in simulating the isotopic composition of precipitation in polar regions (Casado et al., 2016; Landais, Ekaykin, et al., 2012; Masson-Delmotte et al., 2004; Pang et al., 2015; Uemura et al., 2012; Vimeux et al., 1999; Winkler et al., 2013). Although the MCIM has been parameterized based on the isotopic composition of surface snow along a traverse from the Zhongshan Station to Dome A (Pang et al., 2015), the parameterization may require further tuning because the shallow surface snow sampling depth (10 cm) may bias the seasonality of precipitation. In addition, the equilibrium and kinetic fractionation factors of water stable isotopes have been updated (Ellehøj et al., 2013; Luz & Barkan, 2010). As a result, the MCIM was updated with the new equilibrium and kinetic fractionation factors and retune the model with the isotopic data of surface snow along a traverse from the Syowa Station to Dome F, because the surface snow samples cover at least a full year (Touzeau et al., 2016). Details of updates and parameterizations of the MCIM are presented in Appendix

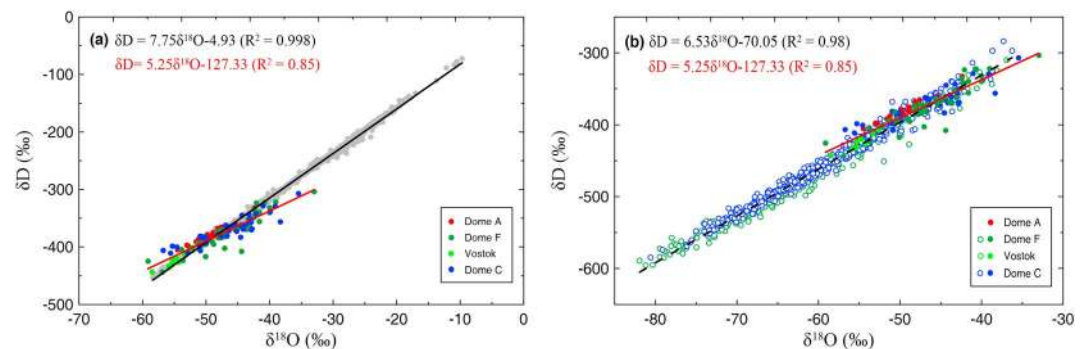


Figure 5. (a) A comparison of the $\delta D/\delta^{18}O$ slope between summer precipitation (December and January) at Dome A, Dome F, Vostok, and Dome C (colored dots and the red line) and surface snow at other sites of Antarctica (gray dots and the black line, data from Masson-Delmotte et al., 2008). Analysis of covariance indicates that the linear slopes of $\delta D/\delta^{18}O$ in summer precipitation and in surface snow at other sites of Antarctica are significantly different at the 99% confidence level. Panel 5b shows a comparison of the $\delta D/\delta^{18}O$ slope between summer (December and January, solid dots and the red line) and nonsummer (all other months, open dots and the black dashed line) precipitation at Dome A, Dome F, Vostok, and Dome C. Analysis of covariance indicates that the linear slopes of $\delta D/\delta^{18}O$ in precipitation during summer and nonsummer seasons are significantly different at the 99% confidence level.

A. We use the same parameterizations of the MCIM as in Appendix A except for the moisture source temperature (SST) and the condensation temperature (T_c) at the precipitation site to simulate $\delta^{18}O$, d-excess, and ^{17}O -excess in summer precipitation at Dome A. Details of the isotopic simulations of summer precipitation at Dome A are presented in Appendix B. The simulated values are shown in Table A1. The simulated $\delta^{18}O$ (-41.0‰) is much higher than the observed value ($-49.6\text{‰} \pm 2.8$) and the simulated d-excess (5.8‰) and ^{17}O -excess (28 ppm) are lower than the observed values ($16.8 \pm 6.8\text{‰}$ for d-excess and 43 ± 10 ppm for ^{17}O -excess). These discrepancies suggest that the isotopic composition in summer precipitation at Dome A could not be satisfactorily explained by the Rayleigh distillation process, which is mainly determined by condensation temperature of precipitation.

In addition, we observed lower $\delta D/\delta^{18}O$ slopes in summer precipitation compared surface snow of Antarctica (Figure 5a) and nonsummer precipitation (Figure 5b). The observed summer $\delta D/\delta^{18}O$ slope at Dome A (5.88) is much lower than the simulated value (7.62) by the MCIM for the temperature range during the sampling period. Moreover, Casado et al. (2016) found that the observed $\delta D/\delta^{18}O$ slope of summer water vapor at Dome C is also much lower than the MCIM simulated value. These results suggest that the observed lower $\delta D/\delta^{18}O$ slopes (Figure 5 and Table 2) of summer precipitation on the East Antarctic Plateau could not be satisfactorily explained solely by a distillation process.

4.1.2. Variations of Marine Moisture Sources

In order to analyze the possible contribution of variations of marine moisture sources to the observed lower $\delta^{18}O$ values as well as high values of d-excess and ^{17}O -excess in summer precipitation at Dome A, we use the Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPPLIT) to trace the moisture sources for summer precipitation and frost events at Dome A. In general, water vapor transport is usually concentrated in the middle and lower troposphere (Bershaw et al., 2012). Moreover, Sodemann and Stohl (2009) demonstrated that only when allowing for a transport time of 15 days can 90% of the precipitation in the high-latitude region of Antarctica be assigned to source regions. As a result, vapor trajectories back to 15 days at 500, 1,000, and 2,000 m above ground level for summer precipitation and frost events at Dome A were simulated by the HYSPPLIT, as shown in Figure 6. It is clear that most vapor trajectories of summer precipitation and frost events at Dome A are derived from the high latitudes of the Southern Oceans, a result of the poleward migration of subtropical highs in summer, which moves moisture sources to higher latitudes (Feng et al., 2009). SST is relatively low and the RH is relatively high in the high latitudes of the Southern Oceans. These conditions would lead to higher $\delta^{18}O$ values as well as lower values of d-excess and ^{17}O -excess in precipitation. Therefore, we think that variations of marine moisture sources cannot account for the observed lower $\delta^{18}O$ values as well as high values of d-excess and ^{17}O -excess in summer precipitation at Dome A.

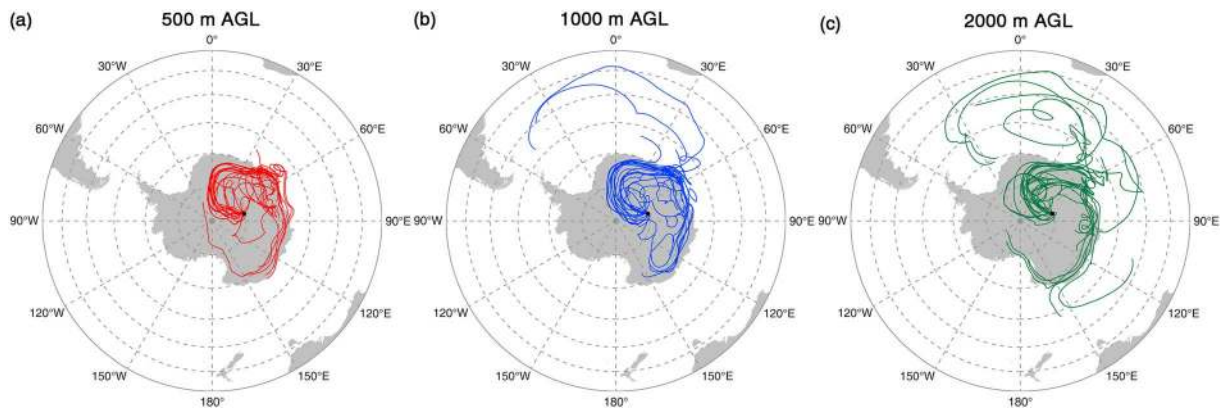


Figure 6. The air mass trajectories back to 15 days at 500 (a), 1,000 (b), and 2,000 (c) m above ground level (AGL) for precipitation and frost events during summer of 2010 at Dome A simulated by the Hybrid Single-Particle Lagrangian Integrated Trajectory model. The simulations start from the end of each precipitation or frost event.

4.1.3. Possible Influence of Blowing Snow

It has been indicated that isotopic composition in surface snow at Vostok can be modified significantly by blowing snow (Ekaykin et al., 2002). At Dome A, the annual precipitation amount is very low and the very shallow annual snow layer could be blown up by wind. As a result, the deposition or adding of the blowing snow from the annual snow layer at Dome A (with lower $\delta^{18}\text{O}$ values and higher d-excess values) into our samples could explain the observed lower $\delta^{18}\text{O}$ values and higher d-excess values in summer precipitation at Dome A. However, the ^{17}O -excess values of the blowing snow should be lower due to the influence of kinetic fractionation at very low temperature (Angert et al., 2004; Pang et al., 2015; Risi et al., 2013), which cannot account for the observed high values of ^{17}O -excess in summer precipitation at Dome A. Moreover, the wind speed at Dome A during summer is usually <3 m/s (Ding et al., 2016), which limits the blowing snow process. Therefore, we think that the blowing snow process should not be the reason for the observed lower $\delta^{18}\text{O}$ values as well as high values of d-excess and ^{17}O -excess in summer precipitation at Dome A.

4.1.4. Moisture Recycling on the East Antarctic Plateau

During the summer on the East Antarctic Plateau, the sublimation of snow is significant because of the greater solar radiation (Ding et al., 2016; Ekaykin et al., 2004; Frezzotti et al., 2004; Kameda et al., 1997). The relatively high air temperature during the day can cause the development of a convective boundary layer (Mastrantonio et al., 1999). The vapor sublimated from the surface snow in the day is rapidly mixed with the drier overlying air during the convection. The air becomes saturated or supersaturated in the night due to the decrease of air temperature, which may facilitate precipitation or surface frost. In this section, we discuss the possible influence of the moisture recycling process associated with snow sublimation on the isotopic composition in summer precipitation on the East Antarctic Plateau.

In order to evaluate the influence of sublimation-condensation processes on the isotopic composition of summer precipitation at Dome A, we calculate the isotopic ratios of the condensate derived only from the local sublimate using the simple Rayleigh distillation model, assuming a closed system. That is, we consider local sublimation and condensation without taking into account the advection of water vapor from other places or mixing with previous water vapor at the same place. It is reasonable to assume that the surface snow sublimation occurs during the warming phase (UTC: 02:00–16:00) and condensation of the sublimate happens during the cooling phase (UTC: 0:00–2:00 and 16:00–0:00) of the day. According to the meteorological observations in January 2010 when all precipitation samples were collected, the average surface air temperature at 2 m of the warming phase (the cooling phase) was -29.3 °C (-34.5 °C). Thus, we simply assume that sublimation (condensation) occurs at a constant temperature -29.3 °C (-34.5 °C). The remaining fraction of the sublimate after condensation is estimated to be 0.59 based on the ratio of the saturated vapor density at -34.5 and -29.3 °C.

Observations in a cold laboratory indicated that several centimeters of surface snow can be a source of sublimation (Sokratov & Golubev, 2009), because of interconnection of pores and the temperature gradient resulted from sublimation cooling (Golubev & Sokratov, 1991). On the East Antarctic Plateau, the annual

Table 3

Comparison of the Observed $\delta^{18}\text{O}$, d-excess, and ^{17}O -excess of Summer Precipitation at Dome A and the Simulated Values of the Condensate Deriving from the Sublimate

Scenarios	$\delta^{18}\text{O}$ (‰)	d-excess (‰)	^{17}O -excess (ppm)
The observed values at Dome A	-49.6 ± 2.8	16.8 ± 6.8	43 ± 10
The simulated values by the MCIM	-41.0	5.8	28
Initial isotopic values of surface snow for sublimation	-58.69	19.0	28
No fractionation, scenario (i)	-42.2 (-44.4)	-16.2 (-9.5)	60 (70)
Equilibrium fractionation, scenario (ii)	-62.3 (-64.4)	25.7 (34.1)	39 (48)
Kinetic fractionation, scenario (iii)	-64.1 (-66.2)	39.2 (47.6)	60 (69)

Note. The isotopic composition of the condensate is calculated under two conditions of equilibrium fractionation (RH = 1.0) and kinetic fractionation (RH = 1.1; numbers in brackets). For comparison, the initial isotopic values of surface snow for sublimation and the MCIM simulated isotopic values in summer precipitation at Dome A are also presented. MCIM = Mixed Cloud Isotopic Model.

precipitation amount is very low. Each precipitation event during summer does not form a complete layer of snow and is possibly mixed with earlier winter snowfall (Genthon et al., 2016). Therefore, the surface snow layer where sublimation occurs may include summer precipitation and the underneath nonsummer snowfall. As a result, the initial isotopic values of surface snow for sublimation are roughly assumed to be the isotopic values (-58.69‰ for $\delta^{18}\text{O}$, 19.0‰ for d-excess, and 28 ppm for ^{17}O -excess) of the surface snow (10-cm depth) at Dome A collected before precipitation sampling during the CHINARE-26 (Pang et al., 2015).

It has been proposed that no fractionation occurs during the snow sublimation (Friedman et al., 1991), but this is limited only to whole-grain, ice-vapor transitions, and layer-by-layer mass loss from the snowpack (Lechler & Niemi, 2011). Experimental and observational studies indicate that isotopic fractionation occurs during snow sublimation when exchanges of water molecules between atmosphere and snow are driven by the sublimation-condensation processes (Casado et al., 2018; Ritter et al., 2016; Sokratov & Golubev, 2009). To test the possible influence of the moisture recycling process associated with snow sublimation on the isotopic composition in summer precipitation at Dome A, the isotopic composition of the sublimate is estimated under three different scenarios: (i) no fractionation; (ii) the sublimate being isotopically in equilibrium with the surface snow; and (iii) with equilibrium and kinetic fractionation during sublimation if the air is undersaturated. For the last scenario, we use the closure assumption from Merlivat and Jouzel (1979) to calculate the isotopic composition of the sublimate ($\delta_{\text{sublimate}}$) in the scenario (iii) as follows:

$$\delta_{\text{sublimate}} = \frac{(1 + \delta_{\text{snow}})(1 - k)}{\alpha_{\text{eq}}(1 - \text{RH} \times k)} - 1,$$

where δ_{snow} is the isotopic composition of surface snow and we set the RH as 0.8. According to Pfahl and Wernli (2009) and Uemura et al. (2010), the kinetic fraction factor k corresponds to $1 - 1/\alpha_{\text{diff}}^*$, where α_{diff}^* is the effective molecular diffusion fractionation factor (see Appendix A). Here we use the following k values: $k_{\delta^{18}\text{O}} = 9.5\%$, $k_{\text{d-excess}} = 8.4\%$, and $k_{\delta^{17}\text{O}} = 4.9\%$.

The isotopic composition of the condensate deriving from the sublimate is calculated under two different conditions: equilibrium fractionation (RH = 1.0) and kinetic fractionation (RH = 1.1) under supersaturation conditions, as shown in Table 3. In scenario (i), the simulated $\delta^{18}\text{O}$ of the condensate is much higher than the observed value of summer precipitation at Dome A, suggesting that the observed strong depletion of $\delta^{18}\text{O}$ in summer precipitation at Dome A cannot be caused by the admixture of condensate deriving from sublimate with no isotopic fractionation during sublimation. In scenarios (ii) and (iii), the simulated $\delta^{18}\text{O}$ (d-excess and ^{17}O -excess) is much lower (higher) than the observed values of summer precipitation at Dome A, suggesting that the observed strong depletion of $\delta^{18}\text{O}$ and relatively high d-excess and ^{17}O -excess of summer precipitation at Dome A could be, at least partly, due to admixture of the condensate deriving from the sublimate with isotopic fractionation during sublimation. It is noted that the simulated d-excess and ^{17}O -excess of the condensate are higher when the sublimate condensates under the supersaturation condition (RH = 1.1) than under the equilibrium condition (RH = 1.0), suggesting that the condensation of the sublimate under supersaturation condition may be important for the observed relatively high d-excess and ^{17}O -excess in summer precipitation at Dome A.

The results in Table 3 are in agreement with isotopic fractionation occurring during surface snow sublimation (Casado et al., 2018; Moser & Stichler, 1974; Ritter et al., 2016; Sokratov & Golubev, 2009; Stichler et al., 2001). The moisture sublimated from surface snow would be depleted in heavy isotopes due to the lighter water isotopologues diffusing faster than the heavier ones during sublimation. Indeed, the average value of vapor $\delta^{18}\text{O}$ (-68.9‰) measured at Dome C during December 2014 to January 2015 is much lower than the prediction of vapor $\delta^{18}\text{O}$ (-51.6‰) by the MCIM (Casado et al., 2016). However, it is consistent with the simulated vapor $\delta^{18}\text{O}$ (-68.2‰) if taking account of the atmospheric vapor that is equilibrated with the surface snow (Casado et al., 2016). In addition, the average value of vapor $\delta^{18}\text{O}$ (-54.4‰) observed at the Kohnen Station during the surface snow diurnal cycle experiment (8 to 10 January 2014) is also consistent with the simulated vapor $\delta^{18}\text{O}$ (-55.8‰) if assuming isotopic equilibrium between the atmospheric vapor and the surface snow (Ritter et al., 2016).

In addition to equilibrium fractionation at sublimation, kinetic fractionation could also occur as suggested in our case (iii). The d-excess of the sublimated moisture would increase due to HDO diffusing faster than H_2^{18}O during sublimation. The average value of d-excess (55‰) in vapor measured at Dome C during December 2014 to January 2015 was very high (Casado et al., 2016). Moreover, high summer d-excess values in near-surface water vapor were also observed on the Greenland ice sheet (Bonne et al., 2014, 2015; Steen-Larsen et al., 2013; Steen-Larsen, Masson-Delmotte, et al., 2014). This could be explained by an important contribution of sublimated moisture with kinetic fractionation. Additionally, the significant negative correlation between d_{in} and $\delta^{18}\text{O}$ in summer precipitation on the East Antarctic Plateau (Figure 3c) should indicate the effect of kinetic fractionation during sublimation because the influences of equilibrium fractionation and kinetic fractionation during snow formation on deuterium excess are eliminated by the logarithmic definition (Markle et al., 2017; Schoenemann et al., 2014; Schoenemann & Steig, 2016; Uemura et al., 2012). When the $\delta^{18}\text{O}$ is lower (corresponding to lower temperature and RH), stronger kinetic fractionation during sublimation is expected, and vice versa. If the sublimated moisture contributes significantly to summer precipitation (i.e., sublimated moisture recycling), this can explain the observed relatively high values of d-excess in summer precipitation on the East Antarctic Plateau. Observations of water vapor isotopes at Summit (Greenland) carried out by Berkelhammer et al. (2016) suggest that moisture sublimated from the ice sheet surface can recondense on fog particles, and ultimately returns to the ice surface under stable conditions associated with temperature inversion during summertime nights. More recently, high values of d-excess in summer precipitation and low values in winter precipitation at Summit (Greenland) were observed by Kopec et al. (2019), a pattern opposite to that found at most high-latitude locations. They propose that the observed summer d-excess maximum at Summit is due to the contribution of high d-excess moisture from sublimation of surface snow on the Greenland Ice Sheet. We also note some very low values of d-excess (below zero) of some summer precipitation samples at Dome F and Dome C (Figure 3a), which might be due to the presence of some blowing snow in these samples. The blowing snow would have a very low value of d-excess due to sublimation.

4.2. Implications for Interpreting Isotopic Surface Data From Inland Antarctica

4.2.1. Influence of the Observed Low $\delta^{18}\text{O}$ Values in Summer Precipitation on Temporal δ/T at Seasonal Scale

Low temporal slopes of the $\delta^{18}\text{O}$ versus surface air temperature at the seasonal or subseasonal timescales observed in Antarctica could be partly explained by the enhanced depletion of H_2^{18}O in summer precipitation, which is probably caused by the combined effects of weak or nonexistent temperature inversion and moisture recycling over the interior of Antarctica due to surface snow sublimation. Several studies have pointed out that the temporal δ/T over Antarctica can be significantly influenced by the strength of temperature inversion (Jouzel et al., 1997; Peel et al., 1988; Van Lipzig et al., 2002). Our results suggest that the post-depositional process of moisture recycling associated with the sublimation-condensation processes has the potential to significantly modify the temporal δ/T , too. Previous studies also indicated that isotopic exchange in near-surface snow can influence the temporal δ/T (Town et al., 2008; Waddington et al., 2002). This suggests that postdepositional modification of water stable isotopes is also an important factor for the temporal δ/T . However, above factors are difficult to quantify due to limited observations of condensation temperature and inversion strength (Jouzel et al., 1983; Motoyama et al., 2005; Stenni et al., 2016) as well as poor understanding of postdepositional processes in the interior of Antarctica. Therefore, we stress the

importance of further investigations on condensation temperature and postdepositional processes in the interior of Antarctica, given the importance of the temporal δ/T for paleotemperature reconstructions from the isotopic records of Antarctic ice cores.

4.2.2. Correction for Local Temperature Effect on d-excess and ^{17}O -excess

In order to establish from the d-excess records in polar ice cores a climatic history of vapor source regions, the d-excess record should be corrected for the site temperature effect (i.e., the dependency of the d-excess on the $\delta^{18}\text{O}$ or δD in the inland of polar ice sheets). This is commonly done through the use of isotopic models (Stenni et al., 2001; Vimeux et al., 2001). Nevertheless, the uncertainty may be large due to different in the models and the tuning of poorly constrained parameters. Uemura et al. (2004) proposed an alternative observation-based method, which corrects the site temperature effect on d-excess with the observed spatial relationship between δD and d-excess in present surface snow of Antarctica, based on the assumption that the present spatial slope between δD and d-excess has not changed through time. However, the linear slope between d-excess and $\delta^{18}\text{O}$ of surface snow over inland Antarctica (-0.37 ± 0.02) is significantly lower than the values for nonsummer precipitation (-1.47 ± 0.03) and summer precipitation (-2.65 ± 0.21) over the East Antarctic Plateau (Table 2 and Figure 3). This seems to suggest that post-depositional processes significantly decrease the slope between d-excess and $\delta^{18}\text{O}$ or δD in precipitation on the East Antarctic Plateau. This should be taken into account when correcting the site temperature effect on d-excess.

Although the ^{17}O -excess has the potential for reconstructing normalized RH in the moisture source region, recent theoretical simulations and observations have suggested that it is also affected by the kinetic isotopic fractionation associated with condensation of vapor over ice crystals under supersaturation condition at very low temperature in inland Antarctica (Landais, Ekaykin, et al., 2012; Pang et al., 2015; Risi et al., 2013; Schoenemann et al., 2014). This leads to a positive correlation between ^{17}O -excess and $\delta^{18}\text{O}$ or δD (dependence of temperature); we refer to this as the local temperature effect on ^{17}O -excess. In addition, Miller (2018) found that H_2^{17}O is usually abundant in the clear-sky precipitation (“diamond dust”), which also leads to a positive correlation between ^{17}O -excess and $\delta^{18}\text{O}$ or δD (dependence of the kinetic fractionation during clear-sky precipitation and irrespective of water vapor supersaturation); we refer to this as the local clear-sky precipitation effect on ^{17}O -excess. Because diamond dust nucleation and growth gives a constant slope ($\lambda = 0.531$) between $\ln(1 + \delta^{17}\text{O})$ and $\ln(1 + \delta^{18}\text{O})$ irrespective of temperature (Miller, 2018), the local clear-sky precipitation effect can be removed by calculating the deviations of $\ln(1 + \delta^{17}\text{O})$ from the $\lambda = 0.531$ regression line. On the other hand, similar to the method for correcting the local temperature effect on d-excess, the slope of ^{17}O -excess vs. $\delta^{18}\text{O}$ can be used for correcting the local temperature effect on ^{17}O -excess. Using the limited ^{17}O -excess data available in polar synoptic precipitation (excluding the 16 clear-sky precipitation samples collected at Vostok between 29 February and 11 October 2000), we established a linear regression relationship between ^{17}O -excess and $\delta^{18}\text{O}$ at the seasonal scale in the interior of Antarctica (Figure 4b). The ^{17}O -excess- $\delta^{18}\text{O}$ slope (1.48 ± 0.33 ppm/‰) could be used to correct the site temperature on ^{17}O -excess in ice cores with negligible mass contribution from clear-sky precipitation, before they are used to estimate past changes in humidity at the moisture source region. Nevertheless, more measurements of ^{17}O -excess in precipitation in the inland of Antarctica are needed for establishing more reliable regression relationship between ^{17}O -excess and $\delta^{18}\text{O}$.

4.2.3. Potential Influence of Summer Sublimation on the Isotopic Composition of Surface Snow

Our results support previous studies suggesting that fractionation occurs during surface snow sublimation (Casado et al., 2018; Moser & Stichler, 1974; Ritter et al., 2016; Sokratov & Golubev, 2009; Stichler et al., 2001). Some investigations have indicated that the mass loss by surface snow sublimation during summer in the inland of Antarctica is significant (Ding et al., 2016; Ekaykin et al., 2004; Frezzotti et al., 2004; Kameda et al., 1997). Thus, the mass loss due to surface snow sublimation certainly leads to enrichment of H_2^{18}O , H_2^{17}O , and HDO abundances and lower d-excess and ^{17}O -excess in the surface snow (Sokratov & Golubev, 2009). Taking Dome A as an example, the effects of sublimation on the stable isotopic composition of surface snow may be evaluated by the simple Rayleigh distillation model based on the following assumptions: (1) take annual accumulation snow at Dome A as an isolated layer, and there is no mass exchange with the underneath annual snow layer and above the atmosphere except for sublimation; (2) the whole annual snow layer is sublimated at a constant temperature and the sublimate leaves the snow layer immediately; and (3) equilibrium fractionation occurs during snow sublimation. Based on the estimation of 5-year (2005–2010) averages of daily mean sublimation, the mass loss by sublimation during summer

at Dome A is $2.22 \pm 0.02 \text{ kg} \cdot \text{m}^{-2} \cdot \text{year}^{-1}$, $\sim 9\%$ of its annual precipitation amount (Ding et al., 2016). We take the initial isotopic values for sublimation as the observed surface snow isotopic values (-58.69% for $\delta^{18}\text{O}$, 19.0% for d-excess and 28 ppm for ^{17}O -excess, see section 4.1.4) at Dome A. The equilibrium fractionation coefficients are calculated for -33.6°C (the average of air temperature at 2 m during December to January at Dome A) using the equations of Ellehøj et al. (2013). Using the simple Rayleigh distillation model, we estimate the isotopic values of the surface snow after potential sublimation to be -56.70% for $\delta^{18}\text{O}$, 13.3% for d-excess, and 13 ppm for ^{17}O -excess. Obviously, the enrichment of H_2^{18}O , H_2^{17}O and HDO abundances as well as the decrease of d-excess and ^{17}O -excess of surface snow due to sublimation are possible in comparison to their initial values. Although the effect of sublimation on surface snow isotopes could be partly compensated by the moisture recycling process associated with snow sublimation as discussed in section 4.1.4, the snow sublimation in the interior of Antarctica is an important process that can modify the isotopic composition of surface snow because of mass loss and isotopic fractionation during sublimation. However, concurrent observations of stable isotopes in atmospheric water vapor, precipitation, and surface snow are necessary to quantify net changes in the isotopic composition of surface snow due to sublimation over the course of the summer.

5. Conclusions

H_2^{18}O , H_2^{17}O , and HDO abundances are more depleted in summer precipitation on the East Antarctic Plateau than what would be expected from surface air temperatures during precipitation. It is probably caused by the summer weak or nonexistent temperature inversion and the contribution of moisture recycling from sublimation of surface snow to summer precipitation over inland Antarctica. We suggest that these two processes may partly explain the observed low temporal slopes of δ/T in precipitation at the seasonal scale in inland Antarctica.

We observe more depleted H_2^{18}O , H_2^{17}O , and HDO abundances and higher d-excess and ^{17}O -excess values in summer precipitation on the East Antarctic Plateau than expected from theoretical simulations performed with a MCIM. The isotopic simulations of the condensate deriving from the sublimate by the simple Rayleigh distillation model suggest that the mismatches between the MCIM simulations and observations could be caused by the local moisture recycling process due to summer sublimation. Moreover, isotopic fractionation occurs during the moisture recycling process.

Our results indicate that the local moisture recycling due to sublimation is potentially an important process for the isotopic composition of surface snow, water vapor, and consequently precipitation on the East Antarctic Plateau. This effect, however, is still poorly documented and understood quantitatively due to lack of simultaneous isotopic measurements of atmospheric water vapor, precipitation, and surface snow at short timescales, and lack of accurate representation of snow metamorphism, as well as interplay between sublimation, boundary layer and condensation processes in state of the art isotopic models. In the future, it is essential to study the continuum between atmosphere, precipitation and surface snow for quantitatively interpreting the isotopic records in ice cores from inland of Antarctica.

Appendix A: Updates and Parameterizations of the MCIM

A.1 MCIM Updates

The liquid-vapor equilibrium fractionation factors for deuterium (${}^2\alpha_{l-v}^{eq} = (\text{HD}^{16}\text{O})_l/(\text{H}_2^{16}\text{O})_v$) and oxygen-18 (${}^{18}\alpha_{l-v}^{eq} = (\text{H}_2^{18}\text{O})_l/(\text{H}_2^{16}\text{O})_v$) are calculated using the temperature-dependent values from Horita and Wesolowski (1994) for $T > 273 \text{ K}$, which are considered to be more accurate based on the greater temperature range and precision, where $l = \text{liquid}$ and $v = \text{vapor}$:

$${}^2\alpha_{l-v}^{eq} = \exp(1.1588(T^3/10^9) - 1.6201(T^2/10^6) + 0.79484(T/10^3) - 0.16104 + 2.992(10^6/T^3)) \quad (1)$$

$${}^{18}\alpha_{l-v}^{eq} = \exp(-7.685 \times 10^{-3} + 6.7123/T - 1.6664(10^3/T^2) + 0.35041(10^6/T^3)) \quad (2)$$

We use the update of ice-vapor equilibrium fractionation factors for deuterium (${}^2\alpha_{i-v}^{eq}$) and oxygen-18 (${}^{18}\alpha_{i-v}^{eq}$) for temperatures between 233 K and 273 K from Ellehøj et al. (2013):

$${}^2\alpha_{i-v}^{eq} = \exp(0.2133 - 203.10/T + 48888/T^2) \quad (3)$$

$${}^{18}\alpha_{i-v}^{eq} = \exp(0.0831 - 49.192/T + 8312.5/T^2) \quad (4)$$

The equilibrium fractionation factors of oxygen-17 are calculated as ${}^{17}\alpha_{eq} = ({}^{18}\alpha_{eq})^{0.529}$ for temperatures both above and below 273K (Barkan & Luz, 2005).

For the kinetic diffusion of H_2^{18}O and H_2^{17}O over the ocean during evaporation, we use the effective molecular diffusion fractionation factors as ${}^{18}\alpha_{diff}^* = 1.0096$ and ${}^{17}\alpha_{diff}^* = ({}^{18}\alpha_{diff}^*)^{0.518}$ (Barkan & Luz, 2007; Luz & Barkan, 2010). The value of ${}^{18}\alpha_{diff}^*$ was determined from water vapor samples collected over the South Indian and the Southern Oceans, incorporating the influences of pure molecular diffusion and turbulence diffusion. The effective molecular diffusion fractionation factor of HDO is calculated as ${}^2\alpha_{diff}^* = ({}^{18}\alpha_{diff}^*)^{0.88}$ (Luz et al., 2009).

Following Jouzel and Merlivat (1984), the kinetic fractionation during snow formation is calculated as

$$\alpha_{kin} = \frac{S}{1 + \alpha_{eq} \cdot \alpha_{diff}^* \cdot (S-1)} \quad (5)$$

where S is the supersaturation parameter, which is assumed to be linearly related to condensation temperature, defined by $S = 1 - qt$, where t is in degrees Celsius. The effective fractionation factor is then given by $\alpha_{eff} = \alpha_{eq} \cdot \alpha_{kin}$. Because the effective diffusion fractionation factors (α_{diff}^*) during snow formation are not constrained (see Schoenemann & Steig, 2016), we use the same values of effective diffusion fractionation factors over the ocean during evaporation.

A.2 MCIM Parameterizations

In the MCIM, three types of important parameters can be adjusted, including the initial parameters (SST and RH) at the moisture source region, the supersaturation parameter (S) in the cloud during snow formation, and the condensation temperature parameter at the precipitation site.

Lagrangian moisture source diagnostics indicate that moisture for precipitation at Dome F originates mainly from the mid-latitude southern oceans (about 37–47°S, 110°W to 60°E) (Sodemann & Stohl, 2009; Wang et al., 2013). Thus, for the climatic parameters at the moisture source region, we vary SST between 7.7 and 16.7 °C and RH between 0.81 and 0.86, which are calculated based on the reanalysis data of monthly long term means of SST and RH over the moisture source region of Dome F.

The supersaturation parameter ($S = 1 - qt$) is a most important tuning parameter. Previous work indicated that tuning of q is strongly dependent on the choice of equilibrium and kinetic fractionation factors that are being used in the model, and higher values of q can better capture the Antarctic spatial isotope gradients and temporal change from LGM to Early Holocene (Schoenemann et al., 2014). Thus, we tune q ranging between 0.002 and 0.008.

In Antarctica, due to thermal inversion, it is usually assumed that condensation temperature (T_c) is approximately equal to the air temperature at the upper boundary of the inversion layer (Robin, 1977). The equation $T_c = 0.67 \times T_{site} - 1.2$ (Jouzel & Merlivat, 1984) is widely used in the isotopic models for estimating condensation temperature, where T_{site} is the surface air temperature at the site of precipitation. The mean annual surface air temperature -57.7 °C at Dome F (Motoyama et al., 2005) corresponds to the mean annual condensation temperature -39.9 °C calculated based on the above equation. However, the estimated T_c -39.9 °C at Dome F may be higher than the actual value because precipitation forms throughout the surface-based temperature inversion. According to Ekaykin (2003), the predictive mean weighted condensation temperature at the Vostok Station equals -43 °C, ~ 5 °C lower than the air temperature on the top of inversion layer. Thus, we set condensation temperature -42.9 °C (3 °C lower than the air temperature on the top of inversion layer) in the MCIM for isotopic simulations, which is compromised and may be reasonable.

Through the model tuning, the MCIM can well simulate the spatial distribution of ${}^{17}\text{O}$ -excess and d -excess along a traverse from Syowa to Dome F with setting $SST = 15$ °C, $RH = 0.81$, and $S = 1 - 0.005T_c$ (Figure A1). Although the moisture source temperature 15 °C is within the SST ranges 7.7–16.7 °C in the midlatitude

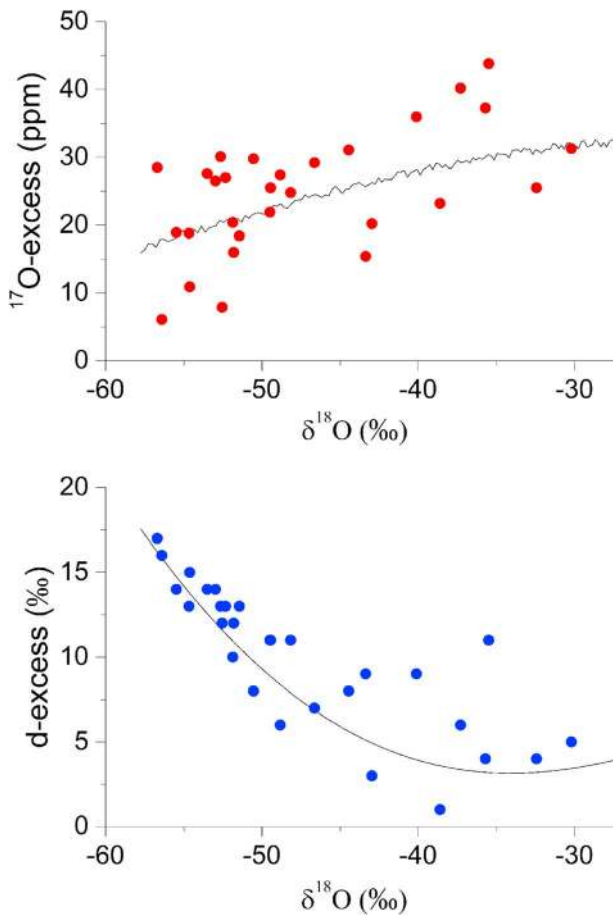


Figure A1. Comparison of the observed ^{17}O -excess (upper panel, the red dots) and d-excess (lower panel, the blue dots) as a function of $\delta^{18}\text{O}$ in surface snow along a traverse from Syowa to Dome F and the simulated values by Mixed Cloud Isotopic Model (the black curves).

moisture source region of Dome F, it seems that the described SST is still a little high. Nevertheless, the described moisture source temperature is lower than SST in the subtropical region that was generally used in previous MCIM simulations (Landais, Steen-Larsen, et al., 2012; Pang et al., 2015; Steen-Larsen et al., 2011; Uemura et al., 2012). The linear dependence of S with T_c is tuned with $q = 0.005$, which is higher than most q values in previous isotopic simulations (Landais et al., 2008; Pang et al., 2015; Risi et al., 2013; Uemura et al., 2012; Winkler et al., 2012).

Appendix B: Isotopic Simulations of Summer Precipitation at Dome A

We use the same parameterizations of the MCIM (Appendix A) except for the moisture source temperature (SST) and the condensation temperature (T_c) at precipitation site to simulate $\delta^{18}\text{O}$, d-excess, and ^{17}O -excess in summer precipitation at Dome A.

To test if the parameterizations of the MCIM (Appendix A) are suitable for isotopic simulations at Dome A, we first simulate mean annual isotopic values at Dome A for validation. Although the isotopic composition of surface snow along a traverse from Syowa to Dome F can be simulated well with the updated MCIM, as mentioned above, the source temperature 15°C set in the MCIM may be still higher than the actual value of the moisture source temperature at Dome F. According to Wang et al. (2013), Dome A has a more southerly moisture origin. As a result, setting a cooler source temperature in the MCIM for simulating the isotopic composition in precipitation at Dome A is inadvisable. For this reason, we roughly assume that the mean annual moisture source temperature at Dome A in the model is also 15°C as Dome F. Following the same method for calculating condensation temperature as Dome F, the mean annual surface temperature of -58.3°C at Dome A (Xiao et al., 2008) corresponds to the mean annual condensation temperature of -43.3°C . Based on the parameterizations, the simulated values of mean annual of $\delta^{18}\text{O}$, d-excess, and ^{17}O -excess at Dome A are -58.4‰ , 18.4‰ , and 16 ppm, respectively.

The simulated values are well consistent with the observed multiyear averaged values (-58.2‰ for $\delta^{18}\text{O}$, 18.6‰ for d-excess, and 15 ppm for ^{17}O -excess; Table S1 in the supporting information) of a 3.0-m snow pit excavated at Dome A during the CHINARE-26. This suggests that parameterizations of the MCIM in Appendix A are suitable for isotopic simulations at Dome A.

For similarity, we assume that the moisture source region in summer is the same as the mean annual moisture source region at Dome A. According to the calculations, the mean annual SST in the southern oceans ($32.5\text{--}45^\circ\text{S}$, $0\text{--}360^\circ\text{E}$) is $\sim 15^\circ\text{C}$ (same as the described SST at moisture source region in the MCIM) and the mean SST of this region in January is 17.4°C . Therefore, we set the source temperature to 17.4°C in the MCIM for simulating isotopic composition in summer precipitation at Dome A.

The meteorological data show that the multiple-year mean surface air temperature at 2 m in November and December at Dome C is approximately equal to the January mean surface air temperature at Dome A. According to the radiosonde data measured at Dome C since 2005, the multiple-year mean air temperature of -30.5°C at the top of inversion layer is slightly higher than the multiple-year mean surface air temperature of -32.1°C in November and December, suggesting a weak temperature inversion. We assume that summer precipitation at Dome A forms throughout the weak surface-based temperature inversion. In addition, the summer frost at Dome A forms near the snow surface. As a result, we set the mean value of daily surface air temperature of -31.8°C in

Table A1
Comparison of the Observed $\delta^{18}\text{O}$, d-excess and ^{17}O -excess in Precipitation at Dome A in January 2010 and the Simulated Values by MCIM

Observation or simulation	$\delta^{18}\text{O}$ (‰)	d-excess (‰)	^{17}O -excess (ppm)
The simulated values	-41.0	5.8	28
The observed values	-49.6 ± 2.8	16.8 ± 6.8	43 ± 10

Note. MCIM = Mixed Cloud Isotopic Model.

January 2010 at Dome A as the condensation temperature in the MCIM. In January at Dome A, we think the actual condensation temperature of our precipitation samples is not less than its surface air temperature.

Based on above parameterizations of the MCIM, the isotopic values of $\delta^{18}\text{O}$, d-excess, and ^{17}O -excess are simulated for precipitation at Dome A in January 2010, as shown in Table A1.

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