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## Climatology of stable isotopes in Antarctic snow and ice: Current status and prospects

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Stable isotopic composition in Antarctic snow and ice is commonly regarded as one of invaluable palaeoclimate proxies and plays a critically important role in reconstructing past climate change. In this paper we summarized the spatial distribution and the controlling factors of  $\delta D$ ,  $\delta^{18}O$ , d-excess and  $\delta^{17}O$ -excess in Antarctic snow and ice, and discussed their reliability and applicability as palaeoclimate proxies. Recent progress in the stable isotopic records from Antarctic deep ice cores was reviewed, and perspectives on bridging the current understanding gaps were suggested.

Antarctic Ice Sheet,  $\delta D$  and  $\delta^{18}O$ , d-excess, <sup>17</sup>O-excess, snow and ice, climate change

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Antarctic Ice Sheet is a highly important part of the Earth system. Thanks to its extraordinary environment of very low temperature, extremely low snow accumulation rate and thick ice layer, a wealth of high resolution and long chronology paleoclimatic information is stored, and hence Antarctic Ice Sheet is honored as archives of the Earth's climate. Because the reliability of future climate prediction is, to a great degree, dependent on our knowledge of the past climatic evolution, Antarctic ice core records play an important role in the current global change studies.

As one of most valuable and applicable climate proxies, stable isotopic composition ( $\delta D$ ,  $\delta^{18}O$ ) recorded in Antarctic ice cores is widely utilized to reconstruct the past climate change. Particularly,  $\delta D$  or  $\delta^{18}O$  in the Vostok and the EPICA Dome C ice cores have documented temperatures over the past 400 ka and 800 ka BP (before present), respectively [1–4], which well reflects the glacial-interglacial change. A drilling has successfully reached the bedrock at the Dome F

site providing an ice core which covers more than 700 ka [5]. The robust couplings of dust-climate and CO<sub>2</sub>-climate over the glacial-interglacial timescales are also revealed by a comparison between  $\delta D$  ( $\delta^{18}O$ ) and the corresponding dust and CO2 records from the same ice cores, taking account of the ice core ice-age and gas-age difference [6-8]. These results contribute significantly to our understanding of the Earth's climatic and environmental evolution during the past hundreds of thousands years. A combination of  $\delta D$ and  $\delta^{18}$ O (i.e. deuterium-excess or d-excess= $\delta$ D- $8\delta^{18}$ O [9]) provides a second-order stable isotopic information, which reflects the kinetic fractionation during evaporation. It largely depends on the sea surface temperature (SST), relative humidity and wind speed at the moisture source region [10,11]. Therefore, d-excess in Antarctic snow and ice is generally used to infer moisture source history, and to calibrate the climatic interpretation of  $\delta D$  and  $\delta^{18}O$  records. Recent development in the stable isotopic analysis technology makes it possible to measure  $\delta^{17}$ O and  $\delta^{18}$ O with a high precision [12,13]. Similar to d-excess, another second order parameter

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 $^{17}\text{O-excess}$ , expressed as  $10^6 \times (\ln(\delta^{17}\text{O}/1000+1)-0.528\ln(\delta^{18}\text{O}/1000+1))$  [14], is developed as a new tracer of the hydrological cycle.  $^{17}\text{O-excess}$  in atmospheric water vapor is strongly controlled by the relative humility [15], but insensitive to temperature and  $\delta^{18}\text{O}$  of the oceanic surface water where moisture evaporates [16]. It therefore provides potential for Antarctic ice cores to retrieve singular meteorological information over the moisture origin region. However, monitoring and modeling of the stable isotopic fractionation exhibit modulation of the stable isotopic signals caused by many processes (e.g., atmospheric circulation, firn process, ice flow), which challenge the quantification of the past climatic change by means of the stable isotopic composition in Antarctic snow and ice.

This paper firstly summarized the spatial distribution of the stable isotopic composition in Antarctic surface snow and the factors controlling this distribution based on the stable isotopic observation and simulation. In particular, we discussed the extent that the stable isotopic proxies can be used as a surrogate for climatic variables. Additionally, results of the climate change reconstruction by the stable isotopes in Antarctic deep ice cores were reviewed. In the last paragraph, perspectives on future development were offered.

## 1 Spatial distribution of $\delta D$ and $\delta^{18}O$ in Antarctic surface snow and the factors controlling their variability

#### 1.1 Spatial distribution of $\delta D$ and $\delta^{18}O$

An accurate assessment of spatial distribution of  $\delta D$  and δ<sup>18</sup>O in Antarctic surface snow is required for the interpretation of Antarctic ice core stable isotopic records. However, sufficient in situ observations are prerequisite for the assessment. Lorius and Merlivat [17] documented the relationship between both  $\delta D$  and  $\delta^{18}O$  and parameters such as the mean annual temperature and the surface elevation for sites in the sector between Dumont d'Urville and Vostok. Morgan [18] collected  $\delta^{18}$ O measurements at 189 sites and constructed the first database of stable isotopic composition in Antarctic surface snow. In 1997, Giovinetto and Zwally [19] updated this database by extending spatial coverage of  $\delta^{18}$ O measurements. In the following year, this database was updated again by Zwally et al. [20]. Most recently, Masson-Delmotte et al. [21] compiled the most complete database of Antarctic surface snow stable isotopic composition using the available measurements of snowfall, surface snow, snow pit and shallow firn cores. This database constitutes the stable isotopic observations at 1279 sites since the 1960s, including 938  $\delta$ D observations, 1125  $\delta$ <sup>18</sup>O observations, and 794 observations for both  $\delta D$  and  $\delta^{18}O$  resulting in the calculation of d-excess. Although there are still data gaps in the Antarctic coastal regions and the East Antarctic plateau, the spatial distribution is essentially presented, including

depletion of the heavy stable isotopes from mid-latitudes to high latitudes, decline of  $\delta D$  and  $\delta^{18}O$  from the coast toward Antarctic inland, and decreasing  $\delta D$  and  $\delta^{18}O$  with increasing elevation.

Early attempts to represent the spatial stable isotopic distribution in Antarctic surface snow involved a continuous trend surface generated by spatial interpolation technologies. Giovinetto and Zwally [19] and Zwally et al. [20] established a multiple linear regression model by investigating the relationship between Antarctic surface snow  $\delta^{18}$ O data vs. geographical and meteorological parameters including latitude, elevation, distance from coast and air temperature. A 100-km resolution  $\delta^{18}$ O map was generated using this linear regression model and digital elevation model (DEM). However, the accuracy of the maps was challenged by the colinearity of predictor variables. Based on the recent compilation of the stable isotopic composition in Antarctic surface snow by Masson Delmotte et al. [21], Wang et al. [22] modified the Bowen and Wilkinson (BW) model [23] and explored a quantitative relationship between  $\delta^{18}$ O in Antarctic surface snow vs. latitude and altitude. This quantitative model integrating with the other factors affecting  $\delta^{18}$ O (e.g., moisture origin, moisture transportation paths) was employed to produce a 1-km resolution gridded map of  $\delta^{18}$ O. It is convinced by cross validation that generalized additive model (GAM) is a useful tool to assess the spatial distribution of  $\delta^{18}$ O and  $\delta$ D in Antarctic surface snow [24]. A 1-km resolution gridded dataset of  $\delta^{18}$ O and  $\delta$ D were produced using high resolution DEM as an input for this model (Figure 1). The resulting stable isotopic distribution indicates the effects of latitudinal, altitudinal, and continentality on the stable isotopes in precipitation. It is highly useful for the comparison/validation with simulation of atmospheric general circulation models (AGCMs) and mixed cloud isotopic model (MCIM).

## 1.2 Factors controlling spatial distribution of $\delta D$ and $\delta^{18}O$

According to Rayleigh distillation model, Dansgaard [9] summarized the factors controlling stable isotopes in meteoric precipitation, including temperature effect, latitude effect, elevation effect, continental effect, moisture origin and so on. Previous studies have shown that air temperature is the key controlling factor in the mid and high latitudes, especially in the polar region [9,25,26]. Masson-Delmotte et al. [21] confirms that the spatial distribution of stable isotopes in Antarctica is highly associated with condensation temperature, which itself is controlled by geographical parameters (latitude, distance from the coast and elevation). Among these parameters, elevation is the first driver of the spatial distribution of stable isotopes in Antarctica [24].

Although temperature is the key factor controlling the spatial distribution of stable isotopes in Antarctic snow,

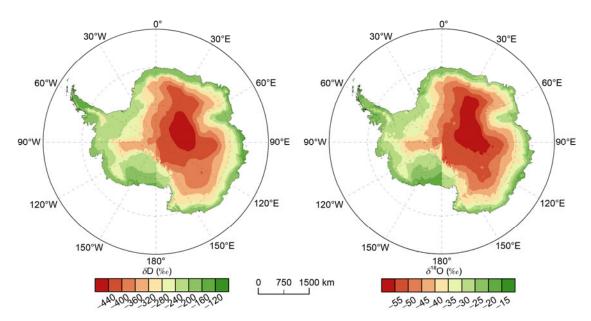


Figure 1 Spatial distribution of  $\delta^{18}$ O and  $\delta D$  in Antarctic surface snow. Data come from [24].

several other factors such as moisture origin and transport paths [27,28], precipitation seasonality/intermittency [29,30], and post depositional processes [31-33], might result in large uncertainty when reconstructing paleotemperature from ice cores. Precipitation falling in a target region over Antarctica usually receives moisture from several different oceanic source regions. Changes of vapor source conditions and air mass transport may produce stable isotopic variability, and changes of seasonality of Antarctic snowstorm intensity can precipitate a large fraction of air mass moisture, and result in <sup>2</sup>H- and <sup>18</sup>O-depleted precipitation. Modeling attempts also highlight the importance of precipitation seasonality/intermittency on stable isotopic variation [34,35]. Stable isotopic signals can be smoothed by diffusion in firn and ice during the densification process after snow deposition. In addition, spatial difference in stable isotopic composition may result from sublimation effects over Antarctic inland and wind-driven ablation on the flanks of the Antarctic Ice Sheet.

#### 1.3 Modeling the spatial distribution of $\delta^{18}$ O and $\delta$ D

A Rayleigh distillation model (RM) [11,36] has the advantage of representation of key microphysical processes and the fractionation along the water cycle path. Thus, this type of model simulates quite satisfyingly the dependence of stable isotopes in precipitation on atmospheric parameters, moisture origin diagnostic and air mass trajectories. These simulation results provide a theoretical basis for interpretation of the ice core stable isotopic records. However, the modeling air parcel trajectories are strongly simplified. AGCMs and MICM has the advantage of estimating spatial and temporal variation of stable isotopes. Jouzel et al. [37] provides the first estimate of an annual average distribution

of water isotopes over Antarctica through AGCMs. Hereafter, with the enhancement of the capability to explicitly simulate the water isotopes, a number of studies have attempted to use AGCMs and MICM to evaluate the spatial and temporal variability in Antarctic precipitation isotopes to better interpret the stable isotopic records in Antarctic ice cores [37-44]. AGCMs [37-43] and MICM [44] well reproduce the spatial distribution of stable isotopes in Antarctic precipitation, especially in West Antarctica and in the coastal areas. Stable isotopic minima are located over the East Antarctic Plateau where the lowest temperature is observed. However, the modeling  $\delta^{18}$ O values over the East Antarctic Plateau were overestimated by even 10% in relative to real observations [38,39,43]. Although development in the vertical and horizontal resolution of AGCMs largely improved their accuracy in recent years, its simulation ability remains limited for the Antarctic inland (Figure 2(a) and (b)) [42], likely due to poor representation of atmospheric boundary layer, temperature inversion, cloud microphysics, and large scale advection of water vapor [36,45]. Warm biases of AGCMs could result in the insufficient estimate of the stable isotopic depletion.

# 2 Relationship between the stable isotopic composition $(\delta)$ and temperature (T) $(\delta - T \text{ relationship})$

The basis of paleotemperature reconstruction is the strong relationship between the stable isotopic composition in Antarctic surface snow and temperature on varied temporal scales. Picciotto et al. [46] quantified a temporal relationship between  $\delta^{18}$ O in snowfall and the corresponding cloud temperature from measurements at the Roi Baudouin Station

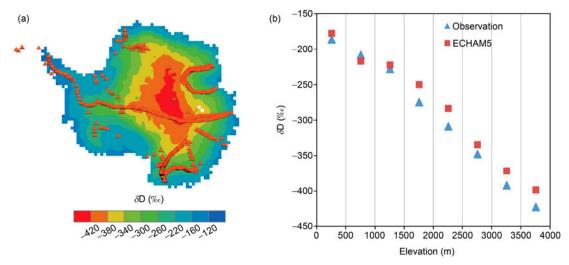


Figure 2 (a) Spatial distribution of  $\partial D$  simulated by ECHAM5 [41] and observations [22]; (b) a comparison of  $\partial D$  observations and simulation by ECHAM5.

at the coastal Antarctic Ice Sheet. On seasonal scale,  $\delta$  correlates linearly with T at Dome F [47], Vostok [48], Dronning Maud Land [49] and west Antarctic ice divide [50]. However, the  $\delta$ -T temporal slopes vary significantly from one site to another. On longer temporal scales,  $\delta$ -T relationships can be hardly explored from the short instrumental stable isotope and temperature measurements over Antarctica. Also, no good independent proxy can capture the long-term Antarctic  $\delta$ -T relationship. Jouzel et al. [51] indicated that AGCMs is regarded as a good alternative to detect the long-term  $\delta$ -T temporal relationships.

Lorius and Merlivat [17] firstly explored the  $\delta^{18}$ O-T and  $\delta$ D-T spatial relationships using surface snow  $\delta^{18}$ O,  $\delta$ D, and annual mean temperature measurements along a traverse from the Dumont d'Urville Station to Dome C. Qin et al. [52] reported changes in regional  $\delta$ -T spatial gradients by analyzing the  $\delta$ -T relationships over the different geographic sections along the International Trans-Antarctic Scientific

Expedition (Table 1). Zhang et al. [53] observed different spatial slopes over the East and West Lambert Glacier (Table 1). Regional difference in the spatial slopes is also observed over Dronning Maund Land [54], nearby Dome C [4], and along the traverse from the Zhongshan Station to Dome A [55]. Based on the most complete compile of the stable isotopic composition in Antarctic surface snow, Masson-Delmotte et al. [21] explored  $\delta$ -T relationships at continental and regional scales. For the whole continent, the spatial slopes are  $0.80\pm0.01\%$  of (n=745) for  $\delta^{18}$ O-T, and  $6.34\pm0.09\%$  or more [21], which can be simulated by MICM [44] and GCMs [56].

Stable isotopes in precipitation represent not only local conditions where precipitation occurs, but also a combination of source conditions, rainout, and post-deposition processes. Thus, local  $\delta$ -T temporal relationship is usually slowly weakened than the  $\delta$ -T spatial relationship [29,41,57].

**Table 1** Regional  $\delta$ -T gradients in Antarctica

Area	$\delta^{18}$ O-T slope (% $\sigma$ °C)	$\delta$ D- $T$ slope (% $\sigma$ )°C)	Reference
Dumont d'Urville Station-Dome C	0.76	6.00	[17]
Patrot Hills-Vostok	0.77	5.84	[52]
Komsomolskaya-Mirnyy	0.90	7.00	[52]
Amundsenisen	0.77±0.14	=	[54]
Dome C	0.75±0.15	6.04	[4]
Transect between Zhongshan Station and Dome A	0.84	=	[55]
Western Lambert Glaicer Basin	0.84	=	[53]
Eastern Lambert Glacier Basin	0.58	=	[53]
Western Vostok region	0.89±0.11	7.00	[52]
Eastern Vostok region	0.89±0.039	5.84	[52]
Antarctic Ice Sheet	$0.80 \pm 0.01$	6.34±0.09	[21]

Furthermore, significant regional anomalies in stable isotopes usually occur, resulting from atmospheric circulation variability. Though  $\delta$ -T spatial relationship is used as a surrogate of  $\delta$ -T temporal relationship to quantify the past temperature from ice cores [58], this method is questioned for the interpretation of glacial-interglacial stable isotopic variations over Greenland likely due to the glacial-interglacial change in the seasonality of precipitation [59]. Due to limited topographical and geographical changes between glacial and interglacial climates, Antarctica is less affected by such changes in seasonality; this gives arguments for the validity of temperature reconstruction on glacial-interglacial scale from the Antarctic interior ice cores, such as Vostok, Dome F and EPICA Dome C, with their uncertainties up to 20%–30% [60], which to great extents result from the regional changes in  $\delta T$  spatial slopes [21]. Additionally, changes in oceanic moisture origin conditions [27,28,60], precipitation seasonality/intermittency [35,38,39,61], Ice Sheet elevation [62,63], and atmospheric circulation may influence  $\delta$ -T relationship, especially during the abrupt climate change. Jouzel et al. [60] pointed out the necessity of making corrections for the impact of ocean stable isotopic change when interpreting the ice core stable isotopic records. Lee et al. [64] quantified the influence of changes in the moisture source conditions on  $\delta T$  correlation during the Last Glacial Maximum through AGCM. The  $\delta$ -T temporal slope at East Antarctica is about 50% of the  $\delta$ -T spatial slope because of the modulation of seawater stable isotopic content in the Southern Ocean. By making use of ERA40 (1980–2002) reanalysis data, Masson-Delmotte et al. [65] calculated the difference between temperature and precipitation-weighted temperature to investigate the effect of precipitation seasonality/intermittency on  $\delta$ -T correlation. In the East Antarctic interior, biases of stable isotopic thermometer result largely from precipitation seasonality. But in the other Antarctic regions, especially the coastal regions, the synoptic variation in precipitation contributes more to biases than precipitation seasonality. The importance of precipitation intermittency is also highlighted by modeling attempts [35,38,39,61]. Sime et al. [56] simulated the stability of  $\delta$ -T correlation in response to increase in greenhouse gas concentrations, and showed a slowly weaker  $\delta$ -T temporal slope than  $\delta$ -T spatial slope at Dome F and EDML, and a significantly weak temporal slope equivalent to 40% of the spatial slope nearby Dome C and Vostok, resulting from changes in precipitation intermittency under warmer climates. Schmidt et al. [66] used a coupled ocean-atmosphere model equipped with stable isotopic fractionation to detect the  $\delta$ -T temporal relationship during mid-Holocene, in response to changes in orbital forcing and greenhouse gas concentrations. The  $\delta$ -T temporal slope over eastern Antarctica is 0.2–0.5% of C lower than the present-day  $\delta$ -T spatial slope. Therefore, Sime et al. [67] concluded that interglacial temperature was badly underestimated by means of modern

 $\delta$ -T spatial slope as a surrogate for temporal slope.

## 3 d-excess and <sup>17</sup>O-excess in Antarctic snow and ice

### 3.1 Spatial distribution of d-excess and its controlling factors

d-excess in precipitation reflects the stable isotopic kinetic fractionation when water phase changes. Jouzel and Merlivat [11] firstly theoretically revealed the dependence of d-excess on SST controlling the saturated vapor pressure, relative humidity controlling the vapor diffusion rate and wind speed affecting the turbulent transport processes in the oceanic source regions. Armengaud et al. [68] further confirmed the control of kinetic evaporation conditions in the moisture source region on d-excess. Furthermore, there are robust correlations between d-excess in atmospheric vapor and SST and relative humidity in the mid-high altitude Southern Oceans [69]. As a result, d-excess is considered as a good tracer for moisture origin.

Spatial distribution of d-excess in Antarctic snow and ice exhibits a distinct difference between Antarctic coastal regions below 2000 m and Antarctic interior above 2000 m. d-excess values change little for the coastal regions, while increase evidently for Antarctic interior, with the highest values over the East Antarctic plateau [21,70,71]. Statistic analysis shows that d-excess correlates positively with altitude and distance from Antarctic coasts, and negatively with temperature for the whole Antarctic Ice Sheet, especially for Antarctic interior above 2000 m [21]. Results of RM [70] and AGCM [21] demonstrated that difference in moisture sources accounts for the discrepancy of d-excess spatial distribution between the Antarctic coastal and inland regions. Antarctic coastal regions receive moisture mostly from offshore waters, whereas in Antarctic interior, moisture originates mostly from open sea, which is supported by a Lagrangian moisture source diagnostic [72] and air mass trajectory tracking model [73]. Additionally, d-excess is sensitive to changes in stable isotopic equilibrium fractionation temperature. Gradual decrease in condensation temperature during the moisture transport from the Southern Oceanic regions towards Antarctica results in the increase of d-excess in vapor and reaches the highest value in Antarctic interior. Atmospheric vapor during polar snow formation is generally supersaturated due to rather low temperature, leading to kinetic fractionation for ice crystals. The kinetic fractionation is more vigorous as temperature decreases, resulting in increase of d-excess. Besides, depth hoar within snowpack growing from vapor sublimation may cause increase of d-excess [74], while material loss during firnification in regions with low accumulation rate may lead to decrement of d-excess [32,33]. d-excess in Antarctic snow and ice is also influenced by the stable isotopic diffusion after snow deposition, generally accompanying with the stable

isotopic kinetic fractionation. Therefore, it is clear that d-excess in Antarctic snow and ice depends largely on the conditions of moisture source (SST, relative humidity, stable isotopic composition of ocean water and wind speed), but importance of condensation temperature at precipitation site [75], the supersaturation of vapor [11] and post-depositional processes [32,33] cannot be ignored. Moreover, the degree of influence from these parameters varies from one site to another [21,76]. As a result, it is not easy to obtain quantitative information of meteorological conditions over moisture source by d-excess. Consequently, it is required to take into account the disturbance of non-moisture source conditions when retrieving moisture source information by means of d-excess in Antarctic snow and ice. The approaches for the calibration of interpretation of d-excess include modeling methods (e.g. the kinetic fractionation model under the supersaturation conditions during snow formation [11] and the stable isotopic diffusion model [77]), empirical formula [78] and <sup>17</sup>O-excess.

#### 3.2 <sup>17</sup>O-excess record

Triple stable isotopic composition of oxygen in atmospheric vapor collected over the Southern Oceans show that <sup>17</sup>Oexcess in vapor is mainly controlled by the relative humidity over moisture source [79]. In comparison with d-excess, <sup>17</sup>O-excess is independent of SST and water  $\delta^{18}$ O in oceanic regions [15] and depends hardly on the condensation temperature during vapor transport [16]. <sup>17</sup>O-excess is therefore not only a tracer for the relative humidity over oceanic source regions, but also can be used to make corrections for the influence of non-moisture source conditions on d-excess in precipitation. At the NEEM (North Greenland Eemian Ice Drilling) of Greenland, simultaneous measurements of  $\delta^{17}$ O and  $\delta^{18}$ O in atmospheric vapor vs. precipitation validated firstly the theoretical coefficient of meteoric water line for  $\delta^{17}$ O and  $\delta^{18}$ O, and showed that seasonal variation of <sup>17</sup>O-excess is in phase with relative humility over oceanic source regions [80]. <sup>17</sup>O-excess is therefore regarded as a potential tool for reconstructing relative humidity over moisture source. Measurements of <sup>17</sup>O-excess in surface snow along a transect from Terra Nova Bay to Dome C and Vostok [16] did not reveal an apparent trend along this transect. <sup>17</sup>O-excess of the Vostok ice core increases by 20% from the Last Glacial Maximum (LGM) to Early Holocene (EH), which could be explained by 20% decrease in the relative humidity at the oceanic source regions. However, this is not supported by AGCM simulations [81]. During the same period, <sup>7</sup>O-excess of the Dome C ice core shows a reverse trend in comparion to the Vostok ice core, and there is no significant change in <sup>17</sup>O-excess of the Talos Dome ice core [82]. The moisture origin diagnostic model, RM and MCIM, show that the spatial discrepancy of <sup>17</sup>O-excess is largely associated with relative humidity over moisture source [82]. Nevertheless, <sup>17</sup>O-excess in Antarctic snow and

ice could be also affected by mass-independent oxygen isotopic fractionation of tropospheric vapor [83] and kinetic isotopic fractionation during ice crystal formation under the supersaturation conditions [11,15]. In general, vapor in cloud in East Antarctic interior is in a supersatured environment due to extreme low temperature and it could be condensed directly into ice crystal. The condensation processes accompanying the stable isotopic kinetic fractionation have an evident impact on <sup>17</sup>O-excess in snow and ice. RM results indicate the different responses of d-excess and <sup>17</sup>O-excess to the kinetic fractionation during ice crystal formation under the supersaturation conditions, with significant d-excess increase and 17O-excess decrease with increase of the vapor supersaturation degree as temperature decreases [15]. Therefore, combination of d-excess and <sup>17</sup>O-excess is advantageous for understanding the stable isotopic kinetic fractionation processes during ice crystal formation under the supersatured environment. The above analyses suggest that the climatic information on moisture source regions could be inferred from the ice core 17O-excess records, which would provide a more direct indicator than d-excess for the climatic signature of the first vapor. However, <sup>17</sup>Oexcess in remote sites of East Antarctica may be highly sensitive to local effects and getting additional information from this parameter is probably more reliable for coastal sites [82].

## 4 Temperature reconstruction from stable isotopes in Antarctic deep ice cores

Temperature reconstruction is an essential part of past global change research [84]. Stable isotopes archived in Antarctic deep ice cores have drawn especial attention. During the past decades, several ice cores have been drilled in Antarctica (Figure 3 and Table 2). The depths of ice cores at

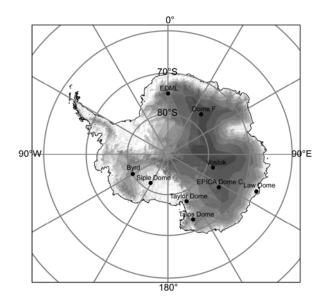


Figure 3 Locations of the deep ice cores in Antarctica.

Table 2 Basic information of the deep ice cores in Antarctica

Sites	Latitude	Longitude	Altitude (m)	Distance from coast (m)	Accumulation rate (mm a <sup>-1</sup> )	Air temperature (°C)	Ice core depth (m)	Reference
Vostok	78°28′S	106°48′E	3490	1260	23	-55.5	3623	[1]
Taylor Dome	77°48′S	158°43′E	2365	120	50 to 70	-43	554	[85]
Byrd	80°01′S	119°31′W	1530	620	100 to 120	-28	2164	[86]
Law Dome	66°46′S	112°48′E	1370	90	700	-22	1195.6	[87]
Dome F	77°19′S	39°40′E	3810	1000	23	-57	3035.2	[2]
Talos Dome	72°47′S	159°04′E	2315	250	80	-40.1	1620	[88]
EPICA Dome C	75°6′S	123°21′E	3233	912	25	-54.5	3259.7	[4]
EDML	75°00′S	00°04′E	2822	577	64	-44.6	2774	[89]
Siple Dome	81°40′S	148°49′W	621	439	124	-24.5	1003	[90]

Vostok, EPICA Dome C and Dome F are over 3000 m, with their bottom ice ages over hundreds of thousands of years. These ice cores are uniquely advantageous for the determination of climatic evolution on the millennial to orbital timescales. Ice cores recovered from the Antarctic coastal regions with relatively higher snow accumulation could provide high resolution records, which can be used to decipher details of climate change on the decadal to millennial timescales.

#### 4.1 Temperature change at orbital timescale

Four complete glacial-interglacial temperature cycles were identified by the stable isotopic records ( $\delta^{18}O$  and  $\delta D$ ) of the Vostok ice core [1]. This record is extended back to the past 800 ka by the EPICA Dome C ice core, with eight glacialinterglacial cycles [3,4]. Both ice cores decipher the 100 ka, 40 ka and 19-23 ka cycles driven by the earth orbital parameters, and the 100 ka periodicity is dominant. Nevertheless, the fluctuation magnitude and the duration of the periodicities show a little decrease during the period 800-430 ka BP compared with those during the period 0-430 ka BP. Within each glacial-interglacial cycle, the duration of the glacial condition accounts generally for more than 80% of the glacial-interglacial cycle, whereas the interglacial condition for less than 20%. The duration for the interglacial is about 10-30 ka. The stable isotopic records of the ice cores at EPICA Dome C [3], Dome F [2] and Vostok [1] show a synchronous climate change during the past 400 ka over the East Antarctica (Figure 4). Records of Loess [91] and marine [92] sediments also show a similar glacial-interglacial cycle, suggesting a synchronization of global climate change on orbital timescale, reflecting the periodic variations of the earth's orbital parameters. According to Milankovitch theory, the main driving factor for the glacial-interglacial cycle of climate is the amount of summer solar radiation received by the Earth at high northern latitude [93]. The signal of the summer solar radiation is conveyed through variations of greenhouse gas concentration and thermohaline circulation intensity. Nevertheless, the synchronous increase of CO<sub>2</sub>

concentration and air temperature over the MIS (Marine Isotope Stage) 5e recorded in the Vostok ice core could not be explained by the Milankovitch theory. Furthermore, Laepple et al. [94] argued that the temperature retrieved from the stable isotopic records of the Vostok, Dome C and Dome F ice cores tends to reflect changes of the winter temperature in the southern hemisphere because of seasonality of the Antarctic snow accumulation, and that the glacial-interglacial cycle of local changes in the solar radiation play a decisive role, regardless the summer solar radiation at high latitude in northern hemisphere.

The most prominent feature of the glacial-interglacial cycle is the shift of the dominant cycles from 40 ka to 100 ka occurring around 900 ka. This climatic shift event is called the Mid-Pleistocene climate transition (MPT), which has been found in the benthic stable oxygen isotopic records [95] and verified by the loess-paleosoil stable isotopic profiles [96]. The MPT seems to be reflected in the stable isotopic record of the EPICA Dome C ice core [4]. Although many assumptions concerning to the greenhouse effect were used to explain MPT, its intrinsic mechanism has not been clarified so far. Because of ice cores as a unique medium that can be used to retrieve directly the ancient atmospheric composition, together with its precise dating, high temporal resolution and good continuity, ice cores with an age more than one million years are extremely crucial for verifying MPT. Consequently, seeking such kind of old ice cores from Antarctica is of vital importance, which is also one of the primary goals of the International partnership Ice Core Sciences (IPICS). Dome A, the highest point of the Antarctic ice sheet, is characterized by the lowest annual average temperature (-58°C) [97], low accumulation rates (<25 mm/a water equivalent) [98,99], neglectable ice flow velocity and exceeding 3000 m ice thickness [100], meets the necessary conditions for retrieving such very old ice cores [101].

### **4.2** Temperature change at millennial to sub-millennial timescales

Because millennial to sub-millennial climate change and

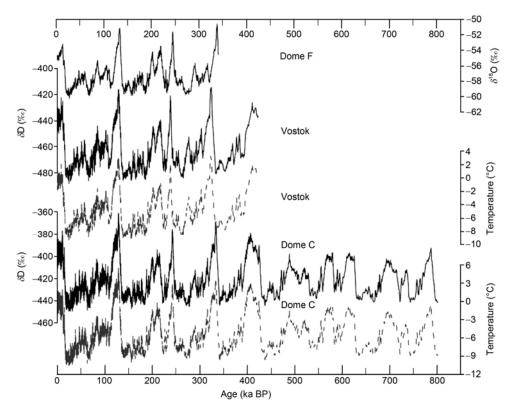


Figure 4 Records of the stable isotopic profiles of Dome F [2], Dome C [3] and Vostok [1] ice cores and their corresponding reconstructed temperature time series.

abrupt climate change events are particularly important to the prediction of future climate, they attract great concerns even beyond the earth science community, especially for the climate change during the last glacial-interglacial cycle.

A comparison of climate between the last interglacial and the Holocene was made by Massion-Delmotte et al. [65] from six deep Antarctic ice core  $\delta^{18}$ O records. They identified a similar pattern of the stable isotopic records of these ice cores during the last interglacial and the Holocene, suggesting a consistent Antarctic temperature change on millennial scale. However, there are regional magnitude differences of the stable isotopic variation, probably due to difference in moisture sources, altitude evolutionary history of the local ice sheet, seasonal changes in precipitation or intermittent precipitation. During the last deglaciation, the synthetic  $\delta^{18}$ O record [87] from the Antarctic coastal Law Dome [87], Talos Dome [88], Simple Dome [90], EDML [89] and Byrd [86] ice cores is rather accordant with the  $\delta^{18}$ O record of the EPICA Dome C ice core (Figure 5(a)), further confirming the uniformity of Antarctic temperature change on millennial scale. However, regional difference in the warming rate from the last glacial to Holocene is significant [88]. It's interesting to point out that the stable isotopic record of the Taylor ice core from the Coast of Ross Sea [85] during the last deglaciation corresponds reversely to that of the ice cores mentioned above, but Stenni et al. [88] indicated the dating lethality of the Taylor core [88].

Phase relationship of the bipolar climate events is essential for understanding the climate system coupling of the northern and southern hemispheres and its interaction mechanism. A series of abrupt climate change events lasting several centuries to several thousand years were identified by the Greenland ice cores, from which standing out the Dansgaard/Oeschger (DO) [102,103] and the Younger Dryas (YD) [104] events. On the contrary, Antarctic climate is relatively moderate, with a certain climate warming events of 1–3°C, called the Antarctic Isotope Maxima events (AIM) [2,3,105]. Although the YD event was not observed in the Antarctic ice core reocrds, the Antarctic Cold Reversal (ACR) was identified before the occurrence of the YD event [106,107]. In order to ascertain the phase relationship of these events over the bipolar regions, the age scale of the Greenland and the Antarctic ice cores were synchronized by their corresponding CH<sub>4</sub> records, demonstrating a biploar seesaw between the millennial ACR events observed in Antarctica and the DO events in Greenland during the MIS 2-4 periods [86]. During MIS 3, all the AIM events correspond one-to-one to the DO stadials of Greenland [89] (Figure 5(b)). The coldest ACR event occurred during 14.4– 12.9 ka BP, corresponding to the Bølling warm event in Greenland, and an Antarctic warming is in response to the timing of Allerød cold event in Greenland [87] (Figure 5(c)). The bipolar seesaw of climate change was suggested to be related to the ocean's Meridional Overturning Circulation

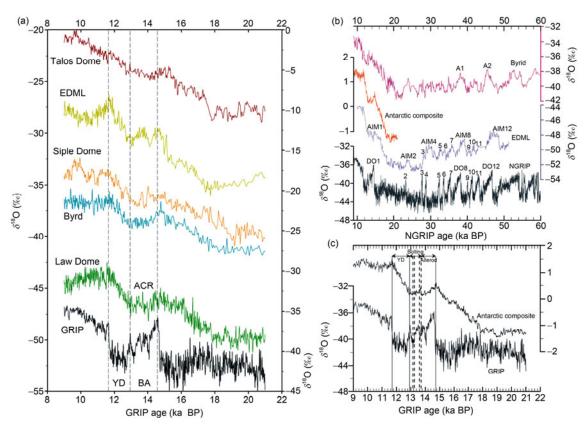


Figure 5 (a) Comparisons of the  $\delta^{18}$ O records of the GRIP, Law Dome, Siple Dome, EDML and Talos Dome ice cores since LGM. The dataset are from reference [87]. (b) A one-to-one coupling of the Antarctic warming events (AIM) vs. the Greenland DO events [89]. (c) A comparison between the Antarctic  $\delta^{18}$ O composite from the Law Dome, Siple Dome, EDML and Talos Dome ice cores and the North Greenland (NGRIP)  $\delta^{18}$ O record [87].

(MOC) [108,109].

#### 5 Summary and outlook

In summary, temperature is the main controlling factor for the spatial distribution of the stable isotopes ( $\delta D$  and  $\delta^{18}O$ ) in Antarctic surface snow and ice. However, the distribution can be influenced, to a certain degree, by precipitation seasonality, moisture source, vapor transport, and post-depositional processes, resulting in uncertainty to reconstruct past climate change by the stable isotopic records of the Antarctic ice cores. To discern the disturbance of these factors, further monitoring and modeling efforts on the modern processes of the stable isotopes are very important, especially the observation of the stable isotopic composition in atmospheric vapor and its variation during transport towards Antarctica. Evaporation from the ocean surface is the first stage for the Antarctic precipitation, with the initial stable isotopic fractionation in vapor over the moisture source. Precipitation gradually falls during vapor transport towards Antarctica under a certain conditions of temperature, pressure and humidity, together with regular stable isotopic fractionation. In-situ and real-time measurements of the stable isotopic composition in atmospheric vapor at the airsea interface and during the vapor transport would help to understand the dynamic mechanism of the stable isotopic fractionation processes in vapor at the air-sea interface, changing conditions over water vapor source and the influence of vapor transport on the stable isotopes in snow and ice. Additionally, simultaneous observations of stable isotopes ( $\delta D$  and  $\delta^{18}O$ ) in atmospheric vapor above the landatmosphere interface (near ground) and in surface snow are helpful to understand the impact of post-depositional processes on the stable isotopes.

Progress in paleoclimatology depends largely on the quality and applicability of the paleoclimate proxies. Due to the complexity of the stable isotopic fractionation, the response of the stable isotopes in Antarctic snow and ice to temperature differs spatially and temporally, resulting in uncertainties of the temperature reconstruction based on the Antarctic ice cores. Such uncertainties may be partly solved by understanding the mechanisms of spatial and temporal variabilities in  $\delta T$  relationship through in-situ observations and numerical simulations. Quantitative comparison of the  $\delta T$  relationship variabilities driven by variable forcings, such as changes in greenhouse gas concentration, orbital parameters, freshwater infiltration and changes in ice sheet elevation is beneficial. On the East Antarctic Plateau, in addition to the conventional snow precipitation, ice crystal

(diamond dust) or clear-sky precipitation is another important type of precipitation, which is related to the degree of vapor supersaturation under the very low temperature conditions. Though this type of precipitation may have an impact on  $\delta T$  relationship, this has not attracted much attention.

<sup>17</sup>O-excess and d-excess are two important tracers for identifying conditions over moisture source. In comparison with d-excess, <sup>17</sup>O-excess is mainly controlled by the relative humidity over moisture source and has different response manner to the stable isotopic kinetic fractionation under the supersaturation conditions. <sup>17</sup>O-excess in snow and ice shows great potential for quantitative recovery of single meteorological information about vapor source. It provides the possibility to distinguish the influences of relative humidity as well as SST over moisture source, vapor transport processes and local temperature from the ice core stable isotopes when combining both <sup>17</sup>O-excess and d-excess data. However, only limited <sup>17</sup>O-excess measurements were performed up to now, including the surface snow samples collected along a transect from Terra Nova Bay to Dome C [16] and at NEEM [80], as well as the ice core samples from Vostok, EPICA Dome C and Talos Dome [81]. Thus, it is necessary to obtain more <sup>17</sup>O-excess measurements from the other locations (especially the West Antarctica) to explore the spatial and temporal variations of <sup>17</sup>O-excess. Moreover, much attention should be paid on the fractionation mechanism of <sup>17</sup>O-excess during the ice crystal formation under the supersaturation conditions, the influence of mass-independent stable isotope fractionation, and the effects of the post-depositional processes on <sup>17</sup>O-excess.

Eight glacial-interglacial cycles of temperature during the past 800 ka were revealed by the stable isotopic records of the EPICA Dome C ice core, and a bipolar seesaw of temperature variation on millennial timescale was identified. Thus climate change in Greenland during the past 800 ka could be reconstructed by means of the thermal bipolar seesaw phenomenon [110]. However, the Milankovitch theory that drives the glacial-interglacial cycle of Antarctic temperature was challenged [94]. As a result, it is necessary to improve the ability of paleoclimate simulations, or to conceive new hypothese for further understanding the driving mechanism of the glacial-interglacial cycle of Antarctic temperature. It is very hopeful to discern MPT through the proposing oldest ice cores from Antarctica. Among the potential sites in the East Antarctic plateau for a bottom ice age over one million years, Dome A possesses prerequisite conditions for such a purpose [101]. Moreover, the moisture source and seasonal variation of accumulation at Dome A seem to be different from what observed at Vostok, EPICA Dome C and Dome F [99]. Thus the proposing deep ice core stable isotopic record from Dome A integrating with the existing stable isotopic records of the other Antarctic deep ice cores would provide a good chance for further identifying orbital climate change and its mechanisms.

The stable isotopic records of Antarctic ice cores reveal a homogeneity of temperature variation on millennial timescale but with regional differences in the magnitude of variations. High resolution ice core records and simulations are urgently needed to decipher the spatial discrepancy and its driving mechanism. Additionally, ice cores from both Antarctica and Greenland with sound chronology quality and enough high resolution are crucial for studying the phase relationship of bipolar climate change.

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