



## Article

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# Spatial and temporal variations of fractionation of stable isotopes in East-Antarctic snow

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**Abstract**

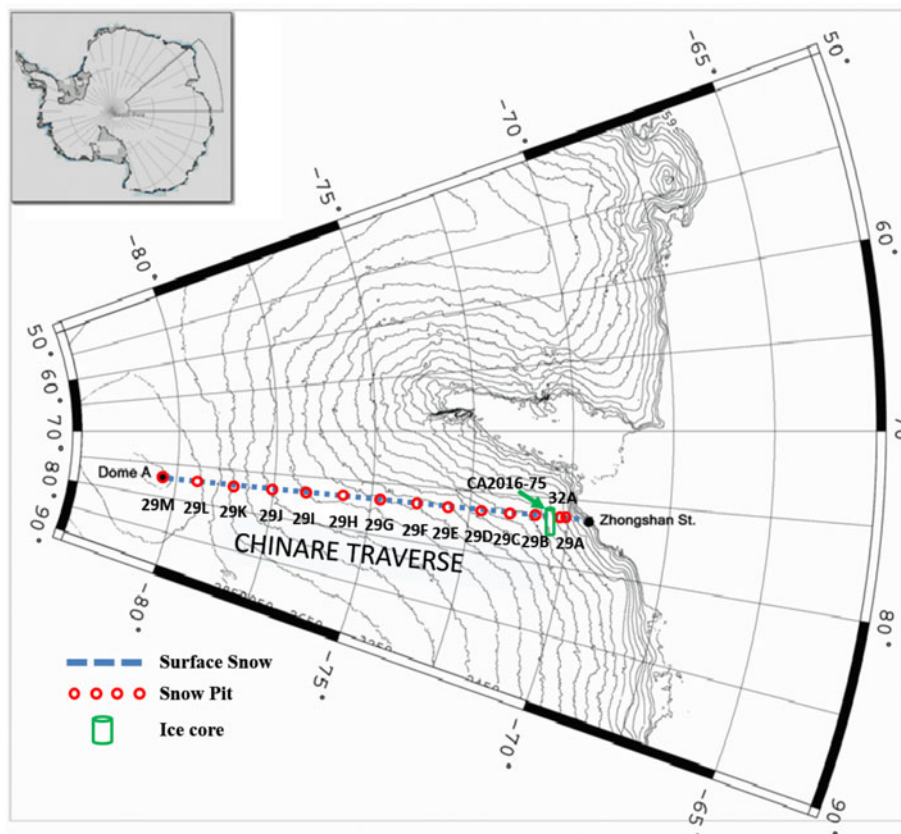
Stable isotope ratios ( $\delta^{18}\text{O}$  and  $\delta\text{D}$ ) in Antarctic snow and ice are basic proxy indices of climate in ice core studies. The relation between the ratios has important indicative significance for moisture sources. In general, the fractionation characteristics of the two isotopes vary with different meteorological and topographical conditions. This paper presents the spatial and temporal distribution of meteoric water line (MWL) slopes along a traverse from the Zhongshan Station (ZSS) to Dome A in East Antarctica. It is found that the slopes decrease with the increasing distance inland from the coast and the lowest slope occurred at Dome A, where the long-range transported moisture dominates and clear sky snowing have an influence. The slopes in different layers of the snowpack showed a decreasing trend with depth and this is attributed to the fractionation during the interstitial sublimation and re-condensation processes of the water vapor. Frost flower development on the interior plateau surface can greatly alter the depth evolution of the MWL slope. The coastal snow pits also go through the post-depositional smoothing effect, but their influences are not so significant as the inland regions.

**Introduction**

Stable isotope records of snow and ice cores in Antarctica were widely used to infer past local temperature variations and moisture origin (Dansgaard, 1964; Landais and others, 2008; Steen-Larsen and others, 2011; Xiao and others, 2013). The isotopic composition in snow, namely the ratio between its heavy and light water molecules, is expressed as  $\delta\text{D}$  or  $\delta^{18}\text{O}$  relative to the Vienna Standard Mean Ocean Water (V-SMOW) reference ( $\delta\text{D}$  and  $\delta^{18}\text{O}$ , defined as  $\delta\text{D} = (([\text{HD}^{16}\text{O}]/[\text{H}_2^{16}\text{O}])_{\text{sample}} / ([\text{HD}^{16}\text{O}]/[\text{H}_2^{16}\text{O}])_{\text{V-SMOW}} - 1) \times 1000$ ;  $\delta^{18}\text{O} = (([\text{H}_2^{18}\text{O}]/[\text{H}_2^{16}\text{O}])_{\text{sample}} / ([\text{H}_2^{18}\text{O}]/[\text{H}_2^{16}\text{O}])_{\text{V-SMOW}} - 1) \times 1000$ ) (Craig, 1961; Dansgaard, 1964; Masson-Delmotte and others, 2008; Steen-Larsen and others, 2011). More recent ice core studies in Antarctica have been dedicated to obtaining the longest possible climate records in the Polar Regions (e.g., Jouzel and others, 2007), or characterizing at high-resolution structure of climate variability during glacial (Masson-Delmotte and others, 2003; EPICA Community Members, 2006; Stenni and others, 2010) or interglacial periods (Pol and others, 2011). Ongoing efforts are directed at documenting the regional variability of climate in various sectors of Antarctica and the related trajectories of air mass transportation and moisture origin. Triple oxygen isotopes ( $^{16}\text{O}$ ,  $^{17}\text{O}$  and  $^{18}\text{O}$ ) and double hydrogen isotopes ( $^1\text{H}$  and  $^2\text{H}$ ) and the second-order parameters (d-excess and  $^{17}\text{O}$ -excess, calculations follow the equations  $\text{d-excess} = \delta\text{D} - 8 \times \delta^{18}\text{O}$  and  $^{17}\text{O}\text{-excess} = 10^6 (\ln(\delta^{17}\text{O}/1000 + 1) - 0.528 \times \ln(\delta^{18}\text{O}/1000 + 1))$ ), respectively) were widely involved to study the temporal and spatial variations of water isotopes (Dansgaard, 1964; Masson-Delmotte and others, 2003; Barkan and Luz, 2007; Hou and others, 2007, 2013; Landais and others, 2008; Xiao and others, 2013; Benetti and others, 2014; Pang and others, 2015, 2019). The isotopic content is strongly influenced by fractionation processes encountered by the air mass throughout its history, such as evaporation conditions, mixture of moisture sources and distillation of the air mass (Dansgaard, 1964; Masson-Delmotte and others, 2003, 2008; Steen-Larsen and others, 2015). The variations of the relationship between stable isotopes and the temperature arise from changes in ocean evaporation conditions such as sea surface temperatures (SST), relative humidity and ocean surface water isotopic composition (Bonne and others, 2019). When only the equilibrium isotopic fractionation occurs, a mean slope of 8.0 for  $\delta\text{D}/\delta^{18}\text{O}$  of the precipitation will be presented. However, during non-equilibrium phase occurs, such as ocean surface evaporation processes, a kinetic fractionation effect is added to the equilibrium fractionation (Craig and Gordon, 1965), which causes a

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**Fig. 1.** Surface sampling sites along the CHINARE inland traverse between Zhongshan Station and Dome A. Red dots show the snow pit locations, the blue dotting line shows the surface sample sampling sites and the green column shows the location of the coastal ice core (CA2016-75).

larger kinetic fractionation for  $\text{H}_2^{18}\text{O}$  than for HDO due to their different molecular diffusivities. As a result, d-excess is strongly imprinted by the kinetic effect. Therefore, the calculation of the d-excess will provide independent isotopic information related to the initial air mass evaporation conditions at the ocean surface (mainly SST and relative humidity) (Merlivat and Jouzel, 1979; Bonne and others, 2019).

The mean slope between  $\delta\text{D}$  and  $\delta^{18}\text{O}$  during the equilibrium fractionation (8.0) also known as the mean meteoric water line (MWL) was widely used to study the fractionation of the water isotopes in the worldwide precipitation (Dansgaard and others, 1964). However, a lower mean MWL slope (7.75) was detected on Antarctica ice sheet (Masson-Delmotte and others, 2008) and showed great spatial variations (Xiao and others, 2013; Li and others, 2016). The evaporation, transportation, condensation and the post-depositional processes on water vapor have influences on both the evolution of the water stable isotopes and MWL slopes (both for the equilibrium fractionation and kinetic fractionation) in Antarctic snowpack (Masson-Delmotte and others, 2008). The influencing factors at the deposition site mainly include the meteorological and topographical conditions (Xiao and others, 2013), precipitation type and intermittency (Cuffey and Steig, 1998; Helsen and others, 2006; Laepple and others, 2018), redistribution of snow (Ekaykin and others, 2002; Ekaykin and Lipenkov, 2009; Laepple and others, 2016; Münch and others, 2016), cyclones and cyclone paths (Qin and others, 1994), surface and interstitial sublimation and re-condensation processes (Ding and others, 2010, 2011; Steen-Larsen and others, 2013; Xiao and others, 2013; Madsen and others, 2019), etc. Calculations of the d-excess based on the routine MWL slope would result in great discrepancies in different sites. By now, few systematic studies on the spatial variations on MWL slopes were executed in Antarctica (Masson-Delmotte and others, 2008). In order to accurately interpret the stable water isotope records from deep ice cores, it is critical to evaluate the spatial

and temporal distribution of MWL slopes, which needs to be documented from modern measurements and processes studies (Xiao and others, 2013).

In addition, the influences of the fractionation on the initial deposition signals of the water isotopes and the alteration of climatic information were another research topic for inland Antarctic regions (Hoshina and others, 2014, 2016; Casado and others, 2016, Casado, 2018; Ritter and others, 2016). During the past decades, there existed some opposing views on what drives that deposition of water isotopes were due to climate variations or post-deposition noise. Some sites seemed to be greatly influenced by the signal (e.g., Dome F, Dome C and Vostok) while other sites were not (e.g. DML and South Pole) (Steen-Larsen and others, 2014; Münch and others, 2016). To make these controversial debates clear, more inland and coastal sites should be included and detailed studies on fractionation effects on temporal isotopic evolution process should be executed.

Here we present a modern process study on spatial and temporal variations of water stable isotopes ( $\delta^{18}\text{O}$  and  $\delta\text{D}$ ) in the snow along a traverse from coast to interior plateau in eastern Antarctica, and two topics are mainly involved: (1) spatial distribution of the MWL slopes at different sites with varied environmental and geographical conditions along the traverse and (2) the temporal variations of the MWL slopes in different depth of the snow pits and ice core and the possible causes for their spatial and temporal variations.

## Samples and data

### Samples and analysis

Dome A is located at the highest point of Eastern Antarctica ice sheet (4093 m) and 1248 km from the nearest coast (Fig. 1) (Hou and others, 2007; 2013; Xiao and others, 2008; 2013). According to in-situ measurement at the Dome A station (Hou

and others, 2007; Xiao and others, 2008; Ma and others, 2010), the mean annual temperature at Dome A is  $-58.5^{\circ}\text{C}$ , the accumulation rate is  $0.023\text{ m a}^{-1}$  w.e. and the mean wind velocity is  $2.2\text{ m s}^{-1}$ . These values are the lowest among the stations in Antarctica. During the 29th Chinese National Antarctica Research Expedition (CHINARE) inland expedition from coastal Zhongshan Station (ZSS,  $69^{\circ}37'31''\text{S}$ ,  $76^{\circ}37'22''\text{E}$ ) to inland Dome A ( $80^{\circ}25'01''\text{S}$ ,  $77^{\circ}06'58''\text{E}$ ) in the austral summer in 2012/13, 13 snow pits and 115 surface samples were approximately evenly captured along the transect (Fig. 1 and Table 1) (Li and others, 2016). The depth of the snow pits varied from 2 to 3 m and the period covered changed from  $\sim 4$  years at the coastal region to  $\sim 36$  years at the interior regions. For the inland two snow pits (29-M and 29-L, Table 1), the mean sampling resolution was 3 cm, amounted to 0.3–0.4 year per sample depending on the density. The sampling depth for the surface samples along the traverse was 3–5 cm and the time covered varied from  $\sim 1$  year in the interior regions to only the summer precipitation episodes at the coast. During the 32nd CHINARE inland expedition in 2015/16, another coastal snow pit (32-A) with larger depth (3 m) and higher sampling resolution ( $\sim 4$  cm per sample) was dug. During the same expedition, an ice core (CA2016-75) with the length 33.24 m were drilled (75 km from the coast) in a dry hole with a mechanical drill. The length, weight and diameter of each piece of ice core were measured just after its extraction.

All the samples were transported frozen to Lanzhou and all the analyzing procedures were executed at the State Key Laboratory of the Cryospheric Science (SKLCS) in Lanzhou China under 100–1000 class clean environment. Cations were analyzed on a Dionex ISC 3000 ion chromatograph (Dionex ISC 3000, Thermo Scientific, USA) using an Ion Pac CS12A column, 20  $\text{m mol L}^{-1}$  MSA eluent and a cation electrolytically regenerated suppressor (CERS). The anions were analyzed on a Dionex ISC3000 ion chromatograph (Dionex ISC3000, Thermo Scientific, USA) using an Ion Pac AS11-HC column, 25  $\text{m mol L}^{-1}$  KOH eluent, and an anion electrolytically regenerated suppressor (ASRS). The detection limit, defined as 3 times the standard deviation of the baseline noise, is  $\sim 1\text{ ng g}^{-1}$  for all major ions. The stable isotope (D and  $^{18}\text{O}$ ) compositions of all samples were analyzed by a liquid-water isotope analyzer (DLT 100, Los Gatos, USA) based on off-axis integrated cavity output spectroscopy (OA-ICOS) at the SKLCS. The isotopic ratios are expressed in per mil (‰) units relative to Vienna Standard Mean Ocean Water (V-SMOW) (Xiao and others, 2013; Li and others, 2016). The accuracies of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  measurements are  $\pm 0.6$  and  $\pm 0.2\text{‰}$ , respectively.

The linear second-order parameters on water isotopes of d-excess and the logarithmic d-excess (d-ln) are both adopted in this study to show their spatial and temporal variations and the related influencing factors and the calculation of d-ln is based on the equation:  $\text{d-ln} = \ln(1 + \delta\text{D}) + 0.0285 (\ln(1 + \delta^{18}\text{O}))^2 - 8.47 \ln(1 + \delta^{18}\text{O})$  (Uemura and others, 2012; Markle and others, 2017).

### Ancillary data

The coastal ice core (CA2016-75) was dated by the annual layer counting from the seasonal variation profiles of marine ions ( $\text{Na}^+$ ,  $\text{SO}_4^{2-}$ ) and black carbon (BC). The separated dating results on  $\text{Na}^+$  and BC are well consistent with the uncertainty of  $\pm 2$  years for 102 years (1915–2016 A.D.). The calculated annual mean accumulation rates on the ice core is  $\sim 0.180\text{ m a}^{-1}$  w.e., met well with the previous results (Ding and others, 2011). The two inland snow pits (29-M and 29-L) were dated according to the volcanic deposit signals (Li and others, 2014) and the accumulation rate data. Because of the relative calm wind condition, the

influence of the drifting snow was negligible at Dome A. The calculated accumulation rates for the whole duration (37 years for 29-M and 36 years for 29-L) are consistent with the measurements by the automatic weather station (AWS) (Ma and others, 2010).

## Results and Discussions

### Spatial distribution of slopes along the transect

$\delta\text{D}$  and  $\delta^{18}\text{O}$  both show decreasing trends while d-excess increases with the distance from the coast along the ZSS to Dome A traverse (Xiao and others, 2013; Pang and others, 2015, 2019; Li and others, 2016). The mean slope of  $\delta\text{D}$  with the surface temperature was  $6.4 \pm 0.2\text{‰ per }^{\circ}\text{C}$ , like the average for East Antarctica (Masson-Delmotte and others, 2008; Xiao and others, 2013). The mean MWL slope in surface snow samples in this study ( $7.78 \pm 0.04$ ,  $R^2 = 0.99$ ) is little larger compared with the values measured before ( $7.5 \pm 0.1$ ,  $R^2 = 0.99$ ) along the same traverse (Xiao and others, 2013). We speculate the different sampling depth is responsible for the discrepancy. Our sampling depth (3–5 cm) is less compared with Xiao's study (5 cm) (Xiao and others, 2013).

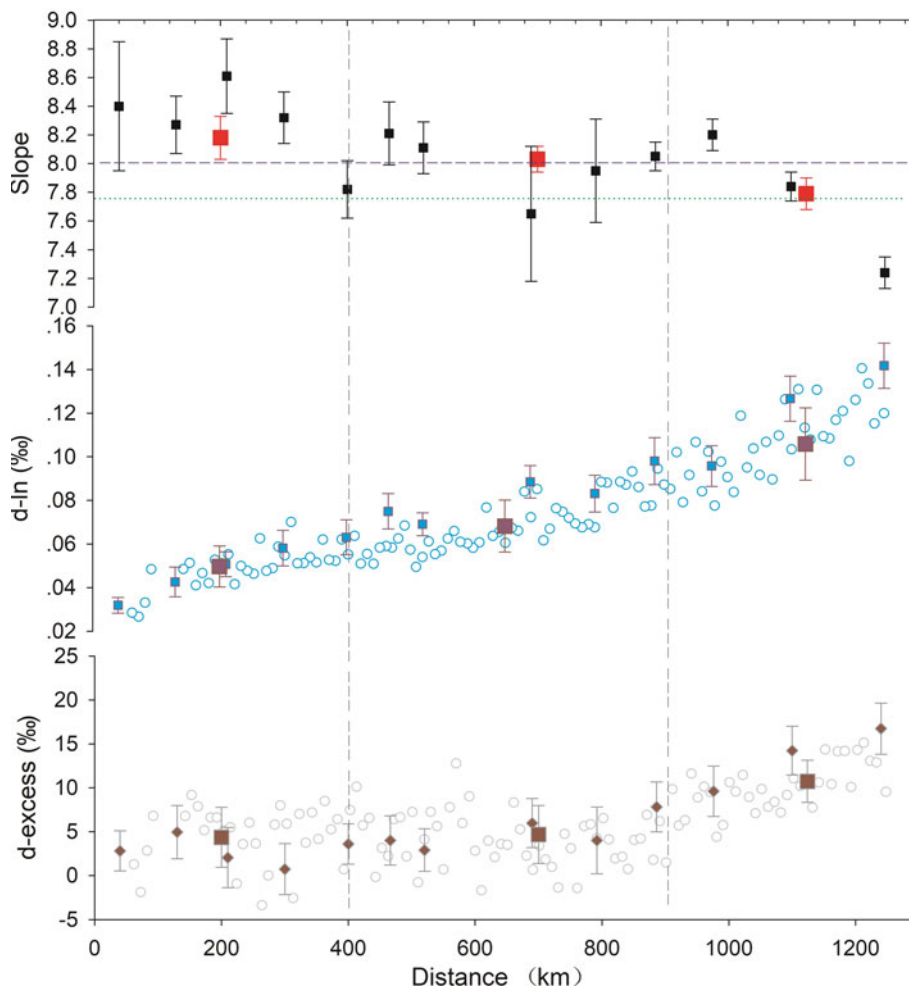
According to the spatial variations of the accumulation rates and the impurities in snow (Ma and others, 2010; Ding and others, 2011; Xiao and others, 2013; Li and others, 2014, 2016; Shi and others, 2019; Ma and others, 2020), the ZSS-Dome A traverse can be divided into three different sections, the coastal section (0–400 km), the intermediate section (400–900 km) and the interior section (900–1248 km). The mean slopes between  $\delta\text{D}$  and  $\delta^{18}\text{O}$  in the coastal, intermediate and interior sections are  $8.18 \pm 0.15$  ( $R^2 = 0.99$ ,  $n = 30$ ),  $8.03 \pm 0.09$  ( $R^2 = 0.99$ ,  $n = 50$ ) and  $7.79 \pm 0.10$  ( $R^2 = 0.99$ ,  $n = 35$ ), respectively. The general decreasing trend of the MWL slopes in three sections may be caused by the increasing distance from the source regions and intensified fractionation effects (Masson-Delmotte and others, 2008; Xiao and others, 2013; Pang and others, 2015, 2019).

To get a detailed spatial distribution pattern of the slopes along the traverse, the MWL slopes in the 13 snow pits were calculated (Fig. 2). In general, the slopes have a decreasing trend with the increasing distance inland. The snow pits located near the coast always show relatively higher slopes (Table 1) and the highest slope occurs in snow pit 29-C ( $8.61 \pm 0.26$ ,  $R^2 = 0.98$ ,  $n = 20$ ) and this value was significantly larger than the global mean MWL (8.0) (Dansgaard and others, 1964) and also larger than the mean slope of the Antarctic snow ( $7.75 \pm 0.02$ ,  $R^2 = 0.998$ ) (Masson-Delmotte and others, 2008) (Fig. 2). Coastal regions of Antarctic ice sheet usually receive moisture from adjacent offshore water while the interior regions get sources from the distant open sea (Reijmer and others, 2002; Masson-Delmotte and others, 2008; Sodemann and Stohl, 2009). The higher MWL slopes at the coastal section may indicate less fractionation during the evaporation and the transportation processes (Hou and others, 2013; Xiao and others, 2013). In addition, the high accumulation at coastal section can cause a quick bury of the deposited snow, which is of benefit to stop (or reduce) the surface sublimation and condensation processes (Ding and others, 2010). The slopes in the intermediate section (400–900 km) generally show a 'V' spatial pattern and the slopes decrease at the initial part potentially implies a decrease of water vapor sources from the adjacent coastal ocean. However, after  $\sim 700$  km, the slope shows an increasing trend till the  $\sim 900$  km inland. We speculate that the intensified wind speed, special surface topography and the post-depositional effects may have influences to some extent (Xiao and others, 2013; Münch and others, 2016). The most interior snow pit at Dome A (29-M) has the lowest slope ( $7.24 \pm 0.11$ ,

**Table 1.** Statistics of the slopes of  $\delta D$  and  $\delta^{18}O$  in snow samples along the ZSS-Dome A traverse<sup>a</sup>

Sample information	Serial number	Location	Distance (km)	Elevation (m)	Depth (cm)	$\delta^{18}O$ (‰)	$\delta D$ (‰)	Slope	Sample amount
Snow pits along the transect	29-M	80°22'00"S, 77°21'11"E	1248	4093	300	-58.46 ± 2.22	-450.93 ± 16.25	$\delta D = (7.24 \pm 0.11) \times \delta^{18}O - 27.61$ ( $R^2 = 0.98$ )	100
	29-L	79°05'57.1"S, 76°59'42.9"E	1100	3757	250	-55.02 ± 2.69	-425.97 ± 21.26	$\delta D = (7.84 \pm 0.10) \times \delta^{18}O + 5.88$ ( $R^2 = 0.98$ )	100
	29-K	77°59'51.1"S, 77°06'42.2"E	976	3169	200	-47.25 ± 3.02	-368.40 ± 24.90	$\delta D = (8.20 \pm 0.11) \times \delta^{18}O + 19.28$ ( $R^2 = 0.99$ )	80
	29-J	77°12'2.7"S, 76°58'3.7"E	886	2967	200	-48.52 ± 3.28	-380.33 ± 26.54	$\delta D = (8.05 \pm 0.10) \times \delta^{18}O + 10.23$ ( $R^2 = 0.99$ )	80
	29-I	76°20'45.2"S, 77°02'14.4"E	792	2830	200	-45.01 ± 2.48	-356.09 ± 20.09	$\delta D = (7.95 \pm 0.36) \times \delta^{18}O + 1.68$ ( $R^2 = 0.96$ )	20
	29-H	75°27'0.7"S, 76°53'42.6"E	690	2799	100	-46.15 ± 2.04	-363.22 ± 15.82	$\delta D = (7.65 \pm 0.47) \times \delta^{18}O - 10.22$ ( $R^2 = 0.97$ )	10
	29-G	73°54'52.7"S, 76°59'15.6"E	520	2631	300	-40.60 ± 1.74	-321.91 ± 14.31	$\delta D = (8.11 \pm 0.18) \times \delta^{18}O + 7.24$ ( $R^2 = 0.97$ )	60
	29-F	73°26'7.1"S, 76°59'20.7"E	466	2551	200	-42.25 ± 2.91	-333.98 ± 24.08	$\delta D = (8.21 \pm 0.22) \times \delta^{18}O + 12.99$ ( $R^2 = 0.99$ )	20
	29-E	72°51'27.2"S, 77°22'31.9"E	400	2514	200	-38.09 ± 2.70	-301.16 ± 21.23	$\delta D = (7.82 \pm 0.20) \times \delta^{18}O - 3.18$ ( $R^2 = 0.99$ )	20
	29-D	71°58'42.8"S, 77°56'45.3"E	300	2351	200	-37.23 ± 3.52	-297.10 ± 29.37	$\delta D = (8.32 \pm 0.18) \times \delta^{18}O + 12.59$ ( $R^2 = 0.99$ )	20
	29-C	71°11'12.7"S, 77°21'52.2"E	210	2074	150	-33.81 ± 2.68	-268.41 ± 23.23	$\delta D = (8.61 \pm 0.26) \times \delta^{18}O + 22.55$ ( $R^2 = 0.98$ )	20
	29-B	70°30'11.9"S, 76°49'36.5"E	130	1697	200	-28.87 ± 3.40	-226.04 ± 28.22	$\delta D = (8.27 \pm 0.20) \times \delta^{18}O + 12.60$ ( $R^2 = 0.99$ )	20
	29-A	69°42'39.5"S, 76°28'43"E	40	832	200	-24.70 ± 1.93	-194.79 ± 16.35	$\delta D = (8.40 \pm 0.45) \times \delta^{18}O + 12.65$ ( $R^2 = 0.98$ )	8
	32-A	71°47'18.3"S, 76°29'30"E	49	932	300	-25.42 ± 2.62	-197.91 ± 21.77	$\delta D = (8.27 \pm 0.09) \times \delta^{18}O + 12.35$ ( $R^2 = 0.99$ )	78
	Surface snow samples	Total	-	30-1248	622-4093	5	-40.95 ± 8.13	-321.69 ± 63.38	$\delta D = (7.78 \pm 0.04) \times \delta^{18}O - 3.10$ ( $R^2 = 0.99$ )
Interior		-	900-1248	3264-4093	-	-50.23 ± 4.51	-392.08 ± 34.87	$\delta D = (7.71 \pm 0.10) \times \delta^{18}O - 4.94$ ( $R^2 = 0.99$ )	35
middle		-	400-900	2516-3264	-	-39.66 ± 4.49	-313.19 ± 37.07	$\delta D = (8.23 \pm 0.09) \times \delta^{18}O + 13.16$ ( $R^2 = 0.99$ )	50
Coastal		-	30-400	622-2516	-	-32.26 ± 4.15	-253.75 ± 34.12	$\delta D = (8.18 \pm 0.15) \times \delta^{18}O + 10.11$ ( $R^2 = 0.99$ )	30
29-M	Upper	80°22'00"S, 77°21'11"E	1248	4093	0-100	-58.71 ± 2.84	-451.65 ± 21.49	$\delta D = (6.99 \pm 0.30) \times \delta^{18}O - 44.11$ ( $R^2 = 0.95$ )	33
	Middle	-	-	-	100-200	-58.62 ± 2.34	-451.24 ± 16.76	$\delta D = (7.14 \pm 0.14) \times \delta^{18}O - 32.75$ ( $R^2 = 0.99$ )	34
	Lower	-	-	-	200-300	-58.04 ± 1.11	-449.87 ± 7.96	$\delta D = (7.51 \pm 0.11) \times \delta^{18}O - 10.74$ ( $R^2 = 0.99$ )	33
29-L	Upper	79°05'57.1"S, 76°59'42.9"E	1100	3757	0-83	-55.48 ± 2.74	-430.22 ± 22.10	$\delta D = (8.01 \pm 0.18) \times \delta^{18}O + 14.32$ ( $R^2 = 0.98$ )	33
	Middle	-	-	-	84-167	-54.63 ± 2.83	-421.65 ± 22.47	$\delta D = (7.91 \pm 0.15) \times \delta^{18}O + 10.35$ ( $R^2 = 0.99$ )	34
	Lower	-	-	-	167-250	-55.05 ± 2.49	-426.82 ± 18.72	$\delta D = (7.44 \pm 0.18) \times \delta^{18}O - 17.05$ ( $R^2 = 0.98$ )	33
CA2016-75	Total	70°04'30"S, 77°07'03"E	75	1220	0-3324	-27.33 ± 1.85	-216.37 ± 14.14	$\delta D = (8.54 \pm 0.11) \times \delta^{18}O + 20.23$ ( $R^2 = 0.98$ )	799
	Upper	-	-	-	0-1000	-26.29 ± 2.04	-211.41 ± 15.81	$\delta D = (8.56 \pm 0.08) \times \delta^{18}O + 21.74$ ( $R^2 = 0.99$ )	236
	Lower	-	-	-	1000-3324	-27.77 ± 1.56	-218.45 ± 12.84	$\delta D = (8.37 \pm 0.09) \times \delta^{18}O + 15.81$ ( $R^2 = 0.96$ )	563

<sup>a</sup>For the detailed data and information, please refer to Fig. S1 and Table S1 to S16 in the supplementary materials.



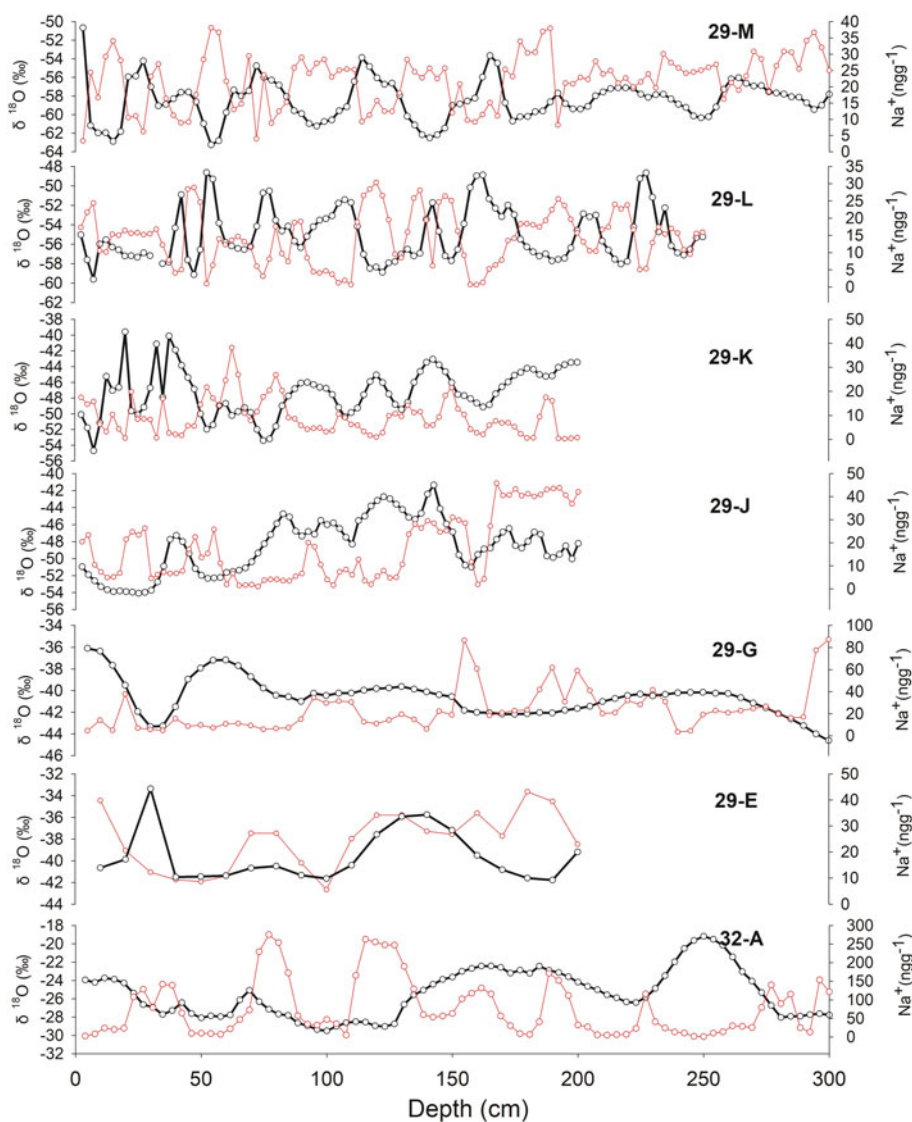
**Fig. 2.** Spatial distribution of the MWL (meteoric water line) between  $\delta D$  and  $\delta^{18}O$  in 13 snow pits (29-M to 29-A, black square) and surface snow (red square) along the traverse from Zhongshan Station to Dome A together with the d-excess (bottom) and d-ln (middle). Different sections of the traverse are divided by the vertical dashed lines and the mean values of the parameters in different sections are shown in squares. The horizontal dotted lines show the global mean meteoritic water line (8.0, Dansgaard, 1964) and the mean slope in Antarctic snow (7.75, Masson-Delmotte and others, 2008).

$R^2 = 0.98$ ,  $n = 100$ ), much lower than the global mean MWL and the Antarctic snow samples. Another interior snow pit 29-L also shows a low slope value ( $7.84 \pm 0.10$ ,  $R^2 = 0.98$ ,  $n = 100$ ). The distance between the two sites is 148 km and they share similar environmental conditions (Ren and others, 1995, 2010).

In the previous studies, most interior snow samples usually show the lowest water isotope ratios (Masson-Delmotte and others, 2008; Xiao and others, 2013; Li and others, 2016). The water isotope ratios at the snow pit 29-M vary between  $-394.80$  and  $-485.96\text{‰}$  with the mean  $-450.93 \pm 16.25\text{‰}$  for  $\delta D$  and between  $-63.25$  and  $-50.67\text{‰}$  with the mean  $-58.46 \pm 2.22\text{‰}$  for  $\delta^{18}O$ . These values are the lowest in Antarctica up to date. Two potential reasons can be put forward to be mainly accountable for the lowest slope at the Dome A region. The first is the moisture source. The moisture arriving in the interior region is mainly from the low to mid-latitudes open oceans and has experienced long-distance transportation in the upper troposphere or lower stratosphere, and thus more intensive fractionation effects may occur during the long pathway (Xiao and others, 2013). The second is that at Dome A, low temperature together with the special precipitation form and accumulation have an intensifying effect on the surface evaporation and re-condensation of the water vapor at this highest location of Eastern Antarctica (Fujita and others, 2006; Ding and others, 2015). Clear sky precipitation (diamond dust) is particular in interior regions on the Antarctic ice sheet and can occupy a large fraction of the total accumulation (Hou and others, 2007). During the days with weak wind and higher temperature at the snow surface compared to the air, the vapor pressure of the air mass close to the snow surface can reach or even exceed saturation, resulting in frost flower growth

at the snow surface (Hou and others, 2007; Xiao and others, 2013). According to Hou and others (2007), the frost flower can comprise  $\sim 7\%$  of the whole accumulation at Dome A. The diamond dust and frost flowers both present a large specific surface area ( $300\text{--}590\text{ cm}^2\text{ g}^{-1}$ ) and hence are favorable to intensify the surface sublimation and re-condensation processes of water vapor. During the sublimation of ice grains and re-condensation of water vapor onto ice grains under extremely low temperatures, the isotopic fractionations will occur in the porous snow layers (Town and others, 2008; Wang and others, 2012; Hoshina and others, 2016; Casado and others, 2016, Casado, 2018; Madsen and others, 2019).

Comparison between the slopes and the mean d-excess values in the 13 snow pits shows that they have a generally opposite spatial variability ( $R = -0.71$ ,  $P < 0.01$ ,  $N = 13$ ), the slopes decrease with the distance inland while the d-excess increase simultaneously (Fig. 2). They also show some different variation patterns at the coastal and the intermediate sections. The d-excess value in Antarctic snow is mainly controlled by the relative humidity, sea surface temperature and wind velocities at the moisture source regions (Hou and others, 2013; Bonne and others, 2019) and also influenced by the condensation conditions at the deposition site (Markle and others, 2017). The slope between  $\delta D$  and  $\delta^{18}O$  is mainly controlled by the climatic and meteorological conditions of snowfall (air temperature, relative humidity, wind velocity, etc.) (Masson-Delmotte and others, 2008). Therefore, the difference between the slope and the d-excess may indicate that the local climatic and meteorological conditions had significant influences on the fractionation processes of the water isotopes. One point should be pointed out that the relation between the slopes



**Fig. 3.** Temporal variations of the  $\delta^{18}\text{O}$  (black) and  $\text{Na}^+$  (red) in different snow pits along the traverse between ZZS and Dome A.

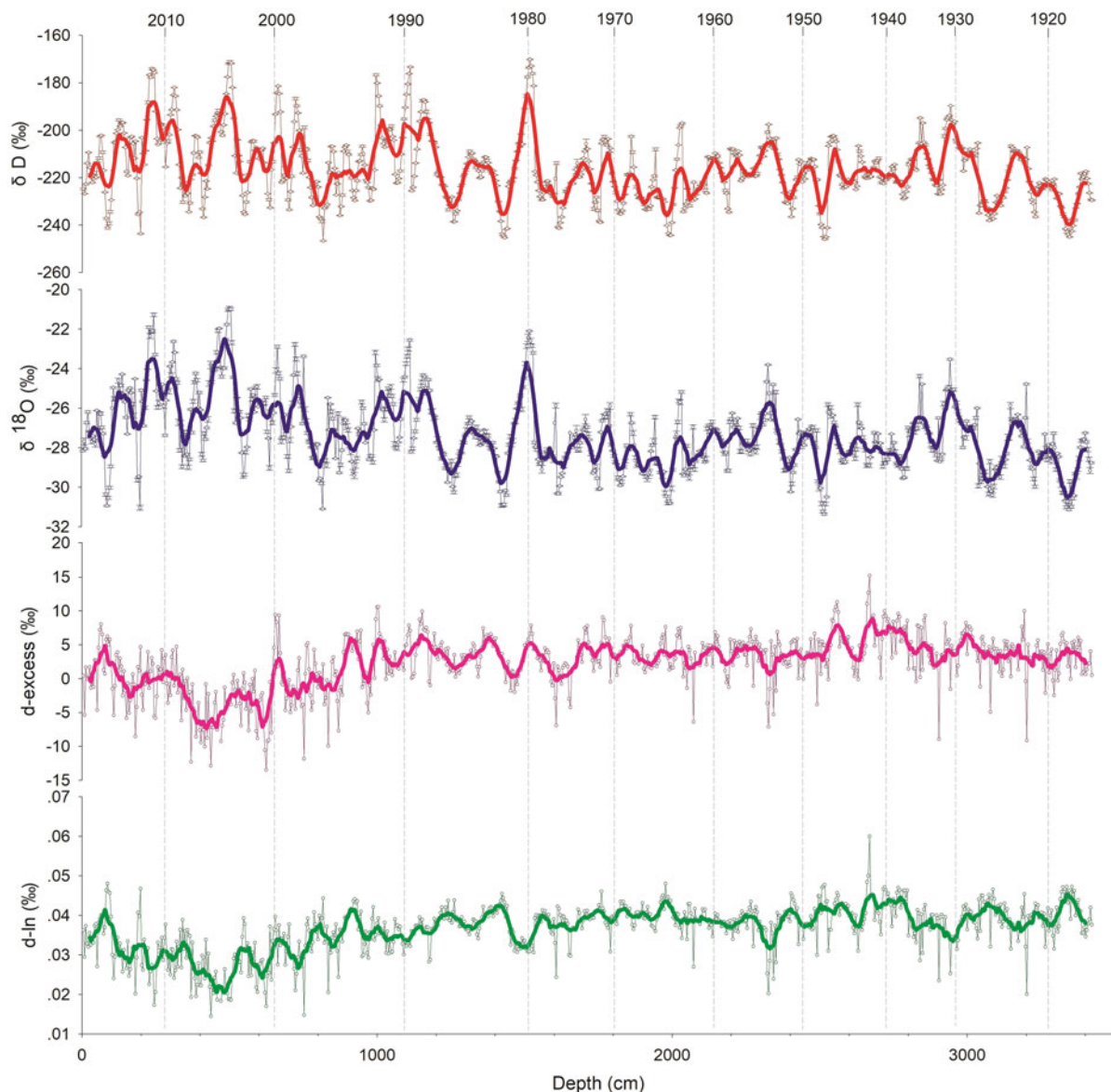
and the source region conditions is mainly based on distillation modeling and future observations are in great demand to testify that (Masson-Delmotte and others, 2008).

The lognormal statistical on deuterium excess ( $d\text{-ln}$ ) can effectively reduce the influences from the non-source factors and is regarded as an optimal index to study the climatic variations at the moisture source regions (Uemura and others, 2012; Markle and others, 2017). We made some comparisons among the slopes,  $d\text{-excess}$  and the  $d\text{-ln}$  values along the traverse (Fig. 2). The  $d\text{-ln}$  clearly indicates a consistently increasing trend inland, implying a constant shift of different source regions and this is consistent with previous results (Masson-Delmotte and others, 2008; Xiao and others, 2013). The difference between the  $d\text{-ln}$  and the slopes may be mainly caused by the influences from the local environment, especially on the intermediate section.

#### Temporal variations of water isotopes

The mean water isotopes ( $\delta\text{D}$  and  $\delta^{18}\text{O}$ ) values in the 13 snow pits are systematically lower than the surface snow in the same areas, implying depleted isotope signals exist in the snow pits (Xiao and others, 2013; Li and others, 2016). We further investigate the temporal variations of the fractionation between  $\delta\text{D}$  and  $\delta^{18}\text{O}$  in the snow pits and ice core. The temporal variations of the slopes in the two inland snow pits (29-M and 29-L) are firstly

investigated. The two pits are vertically divided into three parts (1 m resolution for 29-M and 0.83 m for 29-L). It shows a distinct increase ( $K=0.26$ ,  $P=0.15$ ) of the slope with depth in the 29-M ( $6.99 \pm 0.30$ ,  $7.14 \pm 0.14$  and  $7.51 \pm 0.11$  for the top, middle and bottom sections, respectively), but 29-L shows an opposite variation pattern ( $K=-0.29$ ,  $P=0.23$ ) ( $8.01 \pm 0.18$ ,  $7.91 \pm 0.15$  and  $7.44 \pm 0.18$  for the top, middle and bottom sections, respectively). This difference between the two snow pits should reflect the different fractionation processes at the two sites. During expeditions inland by the CHINARE, surface frost flower has been only seen at the 1150–1248 km on the traverse and no frost flower layer had been detected at 29-L. The fractionations of the water isotopes will sustain in the snow layer during the snow metamorphism and cause an increase of the isotopic composition in the upper layer. Isotope exchange and diffusion within the porous matrix of the snowpack affect snow isotopic composition (Langway, 1970; Johnsen, 1977; Ebner and others, 2017; Casado and others, 2018) and this procedure will be sustained until the firm transformation into ice. The different fractionation procedures between  $\text{HDO}$  and  $\text{H}_2^{18}\text{O}$  in the snowpack may be the causes for the increase of the slopes at the upper layers at 29-L (Masson-Delmotte and others, 2003). The inverse variations of the slopes at 29-M should be caused by the intensified fractionation effects on the frost flower with much lower slopes. The mixing effects within the surface snow will decrease the mean slope in



**Fig. 4.** Temporal variations of the  $\delta D$  (red),  $\delta^{18}O$  (blue), d-excess (pink), d-ln (green) in the CA2016-75 ice core. The vertical dotted lines show the dating results of the ice core and the thick solid lines show the 10-point smoothing results (red for  $\delta D$ , blue for  $\delta^{18}O$ , pink for d-excess and green for d-ln, respectively).

the upper snow layers and the mixing effect decrease with depth can cause the slope increase. Because no surface frost flower is developed, no specific fractionation mechanism exists at the surface of 29-L, so the slope vertical variation shows an opposite pattern to 29-M, i.e. the slope decreases with depth at 29-L.

The vertical temperature gradients in different layers of the snow pits may be another important factor for the fractionation. The temperature gradient can cause the convection of the water vapor in the firn layers. Especially during the autumn and winter seasons, when the surface is significantly cooled down while the deeper layer still kept a relatively higher temperature, the water vapor sublimates at the lower depth can move upward and re-condenses at the shallower layers accompanied by the kinetic fractionation (Masson-Delmotte and others, 2008). The formation of depth hoar in the snow layers also has a great influence on the fractionation of water isotopes, especially at the sites in the inland with low accumulations (Satake and Kawada, 1997; Neumann and Waddington, 2004; Neumann and others, 2005). The widespread depth hoar in East Antarctic snow layers during the winter is a good proof for the interstitial sublimation and re-condensation processes (Qin and others, 1992, 1993; Ekaykin

and others, 2009). However, no depth hoar layers were observed in our snow pits since all the snow pits were dug in the summer season.

Previous studies on the variations of water isotopes with depth in the inland Antarctic snow pits (e.g. Vostok, Dome F, Dome C) showed a mean 20 cm cycle, and these intervals were ascribed to accumulation adjusting, wind erosion and post-depositional redistribution, which can significantly alter the initial seasonal depositional signals and climatic information (Hoshina and others, 2014, 2016; Casado and others, 2016; Laepple and others, 2016; Casado, 2018). We check the deposition signals of  $\delta^{18}O$  in the snow pits along the traverse and find a similar variation pattern (Fig. 3). The two interior snow pits display the cycle periodicity varied between 16 and 51 cm with the mean value  $32.38 \pm 11.36$  cm at 29-M and between 10 and 34 cm with the mean value of  $23.89 \pm 8.95$  cm at 29-L. Moreover, both the snow pits show enlarged cycle periodicity with the depth accompanied by the decreasing variation amplitudes, implying that the smoothing effects of the isotopes is intensified with depth. The smoothing effects on the water stable isotopes with the depth can also be seen at the coastal and intermediate sections (Fig. 3). 29-G

shows an extreme smoothing trend in the bottom part, suggesting that besides the interstitial sublimation and re-condensation effects, the intensified wind erosion and mixing effects on the snow have great influences on the variations of the isotopes at this site. Sodium ( $\text{Na}^+$ ) is usually regarded as a good indicator of the seasonal variations of the marine incursion, but its seasonal signals seem to be smoothed at the inland snow layers with similar depth intervals to the water isotopes (Fig. 3). Opposite variation patterns between the  $\text{Na}^+$  and the water isotopes always exist generally in our inland snow pits and this phenomenon seems widespread among the eastern Antarctica (Hoshina and others, 2016). However, at the coastal snow pits, such as 32-A,  $\text{Na}^+$  has clear seasonal variations but the water isotopes do not.

Because of the smoothing influences on the water isotopes in the inland snow pits, we select the ice core (CA2016-75) at the coastal region to study the annual variations of the water isotopes and the potential influencing factors (Fig. 4). The CA2016-75 ice core drilling site has a relatively high accumulation rate ( $\sim 0.18 \text{ m a}^{-1}$  w.e.) and thickness of annual layers vary between 30 and 40 cm, so the annual mean depth usually has seven–ten samples and is sufficient to study the seasonal variations. Based on the dating results, the annual mean water isotopes and the second-order proxies (d-excess and d-ln) are calculated (Fig. 4). The seasonal variations of the  $\delta^{18}\text{O}$  and  $\delta\text{D}$  can be detected for the top 10 m depth (since  $\sim 1990\text{s}$ ). The smoothing effect is significantly below 10 m depth, eliminating the annual and seasonal signals. From this phenomenon, we can find the post-depositional sublimation and re-condensation of the water vapor is also significant in the coastal region, even for the sites with the high accumulation rates.

The MWL slope for the whole ice core ( $8.54 \pm 0.11$ ) is similar with the coastal 29-A and 32-A snow pits and a decrease of the slopes with depth is also detected ( $8.56 \pm 0.08$  for the upper 10 m and  $8.37 \pm 0.09$  for the lower 23.24 m, Table 1). The temporal variability of water isotopes at CA2016-75 ice core is different from the Law Dome ice core (DE08-2) which shows significant seasonal cycles till 150 m depth (Masson-Delmotte and others, 2003). Higher accumulation for DE08-2 ice core site (between 1.00 and  $1.50 \text{ m a}^{-1}$  w.e.) and lower wind speed may be the dominant factors for the good preservation of the seasonal cycles of water isotopes in the ice core (Masson-Delmotte and others, 2003).

Variations of water isotope ratios ( $\delta\text{D}$ ,  $\delta^{18}\text{O}$ , Fig. 4) show a general flat pattern between 1910s and mid-1980s, after that significant increases during 1980s–90s ( $K = 2.89$ ,  $P < 0.0001$ ,  $N = 92$  for  $\delta\text{D}$  and  $K = 0.36$ ,  $P < 0.0001$ ,  $N = 92$  for  $\delta^{18}\text{O}$ , respectively) and the ratios stay at a relatively higher level till the sampling time. The d-excess and d-ln show similar temporal variations for the whole duration (mid-1910s–2015A.D.) (Fig. 4). They both show relatively flat variations between 1910s and 1990s, and significant decreasing trends are followed till the mid-2000s and then a quick increasing trend till the sampling time. The reasons for the variations and variability of the isotopes and the second-order parameters (d-excess and d-ln) are beyond the scope of this paper and more detailed discussions will be included in the following studies.

## Conclusions

Spatial and temporal distributions of fractionation slopes between  $\delta\text{D}$  and  $\delta^{18}\text{O}$  in the surface snow, snow pits and ice core samples along the traverse from ZSS to Dome A were calculated. Three spatial sections were divided along the traverse, the low slope existed at the interior section and high values at the coastal region, the intermediate section showed large variations implying that complex mechanisms were involved in the fractionation processes

and more efforts are needed in the future. The lowest slope existed at Dome A and was much lower than the mean MWL, it was speculated that the long-range transportation of moisture to this interior plateau and the particular precipitation and accumulation styles at Dome A are the dominant influencing factors. Inland snow pits showed significant smoothing effects on the water isotopes as ever been found in other inland sites (Vostok, Dome C, Dome F, etc.) in eastern Antarctica and the original deposition signals of the water isotopes has been significantly altered. Moreover, not only the inland snow pits, the coastal snow pits in our study were also found for the post-depositional smoothing effects. The persistent sublimation, migration, and re-condensation of the water vapor in the snow (firn) layers caused by the deviations of the temperature in different depths and the wind sweeping effects may be the main influencing factors. The slopes of the isotopes in different depth changed significantly. Variations of the slopes with depth at Dome A snow pit (29-M) showed opposite distribution pattern to 29-L and the existence of the frost flower or not may be mainly accountable for the discrepancy. Coastal snow pits and ice cores showed different smoothing effects on the snow impurities which presented significant seasonal variations and multi-year oscillation. More efforts on other water isotopes tracers (e.g.  $\delta^{17}\text{O}$  and tritium) in the near future are in demand to study the sources of the moisture along the traverse between ZSS and Dome A and their fractionation procedures under different environmental conditions and also for their relationships with the climatic variations.

**Supplementary material.** The supplementary material for this article can be found at <https://doi.org/10.1017/jog.2021.5>

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