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# Seasonal variations of $^{17}\text{O}$ -excess and d-excess in snow precipitation at Vostok station, East Antarctica

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**ABSTRACT.** The use of water isotopes in polar regions is essential for reconstructing past climate over glacial–interglacial cycles. In addition to  $\delta\text{D}$  or  $\delta^{18}\text{O}$ , linearly related to condensation temperature, the second-order parameters, d-excess and  $^{17}\text{O}$ -excess, provide important information on the climatic conditions of the source of precipitations. In order to best interpret the glacial–interglacial records of d-excess and  $^{17}\text{O}$ -excess in polar ice cores, it is important to document their present variability, especially in remote and cold regions of East Antarctica. Indeed, the current climatic conditions encountered in these regions provide a good analogy with glacial climatic conditions in a large part of Antarctica. Here we present the first seasonal variations of  $^{17}\text{O}$ -excess and d-excess at Vostok station on an event basis (i.e. samples were collected immediately after each precipitation event) over 1 year. These records show strong correlation between  $^{17}\text{O}$ -excess and  $\delta^{18}\text{O}$  over the course of the year, with an amplitude 40 per meg ( $10^{-3}\%$ ) in the  $^{17}\text{O}$ -excess seasonal cycle, and strong anticorrelation between d-excess and  $\delta^{18}\text{O}$ , with d-excess variations up to 20%. The d-excess and  $^{17}\text{O}$ -excess variations can be explained by the influence of kinetic fractionation at very low temperatures. The comparison with simple isotopic models confirms this explanation, but cannot explain the link between  $^{17}\text{O}$ -excess, d-excess and temperature without (1) a particular relationship between condensation and surface temperature and/or (2) seasonal changes in the climatic conditions of the source regions.

## 1. INTRODUCTION

Water isotopic ratios in polar ice cores are a major tool for temperature reconstructions over the late Quaternary (NorthGRIP members, 2004; Jouzel and others, 2007). The variations of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  in polar regions result from equilibrium and kinetic isotopic fractionations of water at each step of the hydrological cycle, extending from the oceanic source to the polar condensation point. Because equilibrium and kinetic isotopic fractionations have slightly different effects on the hydrogen and oxygen isotopic ratios of water, combining two isotopic ratios makes it possible to derive second-order information such as climatic conditions of the oceanic source regions. Polar snow d-excess (d-excess =  $\delta\text{D} - 8\delta^{18}\text{O}$  (Dansgaard, 1964)) has thus been used for 30 years to infer changes in temperature and relative humidity in the source oceanic regions (e.g. Jouzel and others, 1982; Petit and others, 1991; Vimeux and others, 1999; Stenni and others, 2001).

More recently, a method for high-precision measurements of  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  on the same water sample has permitted the development of a new tracer of the hydrological cycle:  $^{17}\text{O}$ -excess =  $\ln(\delta^{17}\text{O} + 1) - 0.528 \times \ln(\delta^{18}\text{O} + 1)$  (Barkan and Luz, 2007). In contrast to d-excess, which is sensitive to both temperature and relative humidity,  $^{17}\text{O}$ -excess is independent of the temperature at the evaporation site (Barkan and Luz, 2007; Luz and Barkan, 2010; Uemura and others, 2010). Moreover, measurements of  $^{17}\text{O}$ -excess along an Antarctic transect from the coast to the remote station of Dome C on the eastern plateau (Landais and others, 2008a) have revealed that  $^{17}\text{O}$ -excess does not show any trend associated with the  $\delta^{18}\text{O}$  decrease (between  $-28\%$  and  $-53\%$ ), mainly due to the temperature decrease over the

transect. This constant  $^{17}\text{O}$ -excess level contrasts with the d-excess increase toward central Antarctica (e.g. Petit and others, 1991; Masson-Delmotte and others, 2008) and suggests that the  $^{17}\text{O}$ -excess in precipitation remains unmodified during the air-mass trajectory. Since the  $^{17}\text{O}$ -excess in the first vapor is linearly related to relative humidity as evidenced by Uemura and others (2010), polar snow  $^{17}\text{O}$ -excess should directly reflect surface relative humidity at the oceanic source region, which makes it a more direct indicator of climatic conditions than d-excess in polar snow.

While d-excess measurements over the last deglaciation at Vostok ( $78^{\circ}27'\text{S}$ ,  $106^{\circ}50'\text{E}$ ; Fig. 1) display only a relatively small signal (1%), measurements of  $^{17}\text{O}$ -excess display a significant increase by 20 per meg (Landais and others, 2008a) that has initially been interpreted as a 20% change in relative humidity of the oceanic source region. This interpretation is, however, subject to discussion. First, a change of relative humidity by 20% in the oceanic source region contradicts modeling studies that simulate constant relative humidity over the ocean through time. Second, the seasonality of precipitation has not been considered by Landais and others (2008a), while Risi and others (2010a) have shown that seasonality may contribute significantly to the observed change in  $^{17}\text{O}$ -excess. Unfortunately, this latter study was based only on a modeling approach. Finally, even if the  $^{17}\text{O}$ -excess is stable over an Antarctic transect between Terra Nova Bay (mean  $\delta^{18}\text{O} \sim -30\%$ ) and Dome C (mean  $\delta^{18}\text{O} \sim -53\%$ ), this transect does not cover the  $\delta^{18}\text{O}$  range over the last deglaciation at Vostok ( $-60\%$  to  $-54\%$ ), and it does not exclude that  $^{17}\text{O}$ -excess in surface snow may decrease with temperature when  $\delta^{18}\text{O}$  is lower than  $-53\%$

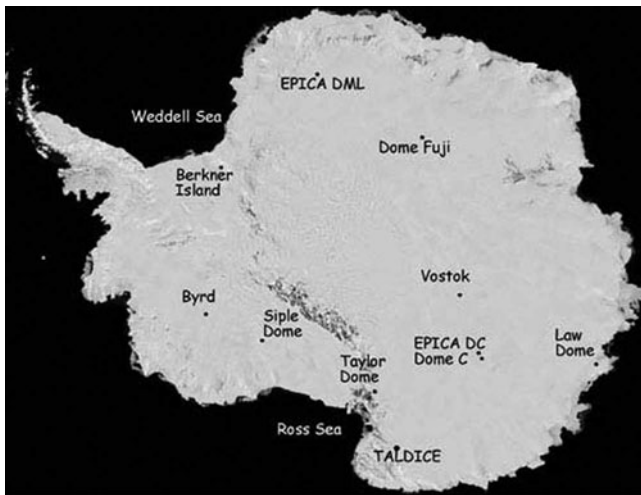


Fig. 1. Map of Antarctica showing the location of Vostok station.

(Miller, 2008). Actually, measurements of  $^{17}\text{O}$ -excess in melted snow of Antarctic origin with very low  $\delta^{18}\text{O}$  (Standard Light Antarctic Precipitation (SLAP) with  $\delta^{18}\text{O} = -55\text{‰}$ ; Dome F with  $\delta^{18}\text{O} = -58\text{‰}$ ) show values  $\sim 30\text{--}40$  per meg lower (Luz and Barkan, 2010) than the trend of the Antarctic transect of Landais and others (2008a).

In this paper, we explore the variability of the  $d$ -excess and  $^{17}\text{O}$ -excess in very remote regions where  $\delta^{18}\text{O}$  and  $\delta D$  are strongly negative. With this purpose we measured, for the first time,  $d$ -excess and  $^{17}\text{O}$ -excess from precipitation sampled over a whole year at Vostok station. Based on the comparison of  $^{17}\text{O}$ -excess,  $d$ -excess and  $\delta^{18}\text{O}$  measured values and model calculation results, we show that kinetic fractionation for condensation at very low temperatures can explain low  $^{17}\text{O}$ -excess values as well as strong seasonal variations of both parameters. Finally, we discuss the possible implications of our findings for the interpretation of  $d$ -excess and  $^{17}\text{O}$ -excess in profiles from central East Antarctica in terms of climatic conditions of oceanic source regions.

## 2. METHOD

### 2.1. Sampling

Precipitation samples were collected at Vostok by the wintering party of the 44th Russian Antarctic Expedition from December 1999 to December 2000. The precipitation trap was installed  $\sim 50\text{ m}$  windward from the station buildings  $1.5\text{ m}$  above the snow surface in order to avoid the influence of blowing snow. The trap was visited after each precipitation event (snow from clouds, diamond dust or rime). The collected precipitation was melted, poured into special plastic bottles and frozen again. We believe that this procedure prevented the alteration of the initial isotopic composition of precipitation due to sublimation, exchange with the air or water-vapor diffusion in surface snow occurring at solid–vapor isotopic equilibrium which strongly modifies  $d$ -excess and  $^{17}\text{O}$ -excess with time in the polar firm (Johnsen and others, 2000; Landais and others, 2012). In total, 56 samples were collected and further analyzed for  $\delta^{18}\text{O}$  and  $\delta D$  (performed at the Geophysics Department of the Niels Bohr Institute (NBI), University of Copenhagen), but because we lacked sufficient material, only 16 samples were used for  $^{17}\text{O}$ -excess analyses.

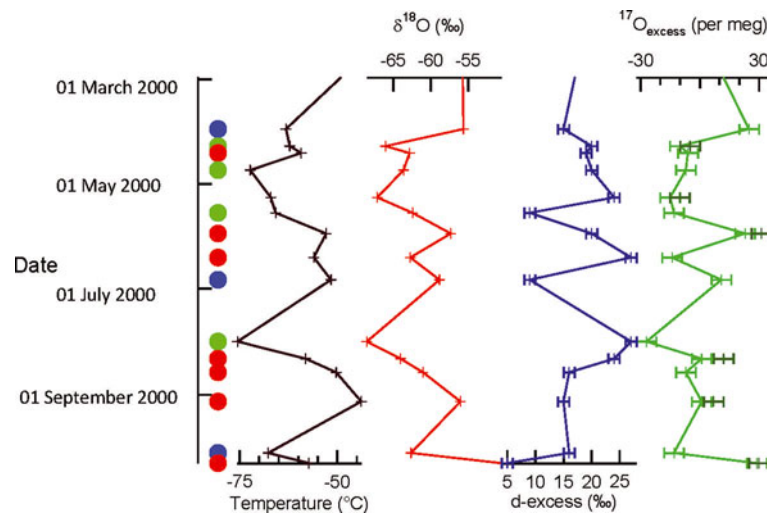
### 2.2. Measurements

The  $^{17}\text{O}$ -excess measurements presented here were obtained following the experimental set-up described by Barkan and Luz (2005). Water is converted to oxygen by fluorination with  $\text{CoF}_3$  reagent, and the produced oxygen is trapped in a tube manifold immersed in liquid helium. Each oxygen tube is then analyzed by dual inlet for  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$ . Each water sample has been converted and measured two to four times.

One flask of working water standard was analyzed daily to check the performance of both the fluorination line and the mass spectrometer. The  $\delta^{17}\text{O}$ ,  $\delta^{18}\text{O}$  and  $^{17}\text{O}$ -excess values were expressed with respect to Vienna Standard Mean Ocean Water (VSMOW). The resulting uncertainty on  $^{17}\text{O}$ -excess was 5 per meg (data are given in Table 1).

In order to check for any bias that could be introduced by the fluorination method or mass spectrometer analysis, water conversion and dual inlet analysis of precipitation samples were performed in two different laboratories. The sixteen precipitation samples were analyzed at the Institute of Earth Sciences (IES), Jerusalem, and six of them were also measured at the Laboratoire des Sciences du Climat et de l'Environnement (LSCE) in Gif-sur-Yvette. In both laboratories the same working standard, Dome F, was used during the measurement period. A difference of 17 per meg was found between the two laboratories in measured  $^{17}\text{O}$ -excess of the working standard Dome F vs VSMOW: 1 per meg at IES and 18 per meg at LSCE. Possible explanations of this difference will be published elsewhere: they are mainly due to differences in mass spectrometers used in the different institutes (e.g. different background procedures and different heating capacity of the source of the mass spectrometers that may influence the peak of mass 33). In the present study, in the absence of any absolute determination of  $^{17}\text{O}$ -excess of two water standards to calibrate mass spectrometer measurements, we have corrected the results obtained at LSCE relative to the Dome F value measured at IES because the fractionation coefficients associated with  $^{17}\text{O}$ -excess and the  $^{17}\text{O}$ -excess profile of the Vostok ice core have been measured at IES. After correction, the agreement in  $^{17}\text{O}$ -excess between the two laboratories was excellent, confirming the high reliability of the set of measurements presented here (Fig. 2).

The  $\delta^{18}\text{O}$  values of the samples were determined at NBI in August 2002 using a standard technique of water exchange with reference  $\text{CO}_2$  gas. The mean monthly isotopic values of snow precipitation content were presented by Ekaykin and others (2004), while isotope composition of individual snowfalls was never shown or discussed.  $\delta^{18}\text{O}$  values obtained by the fluorination methods at IES and LSCE are higher by  $1.9 \pm 0.8\text{‰}$  and  $0.8 \pm 0.8\text{‰}$ , respectively, than the  $\delta^{18}\text{O}$  values measured at NBI. This is mainly due to storage of flasks for 8 years at  $-20^\circ\text{C}$  at LSCE and for 6 years at  $-20^\circ\text{C}$ , then for 2 years at  $5^\circ\text{C}$  at IES. However, the variations of  $^{17}\text{O}$ -excess over the seasonal cycle at Vostok are not significantly affected by this effect. Indeed, storage of small flasks of home standard samples of low  $\delta^{18}\text{O}$  ( $-50\text{‰}$ ) at room temperature for several years has shown systematic increases of  $\delta^{18}\text{O}$  by about  $1\text{--}3\text{‰}$  (depending on the storage period), but  $^{17}\text{O}$ -excess was not modified by  $>8$  per meg. Moreover, the fact that we found comparable  $^{17}\text{O}$ -excess at LSCE and IES despite different storage histories confirms the robustness of  $^{17}\text{O}$ -excess values.



**Fig. 2.** Variations of  $^{17}\text{O}$ -excess (light green: measurements performed at IES; dark green: measurements performed at LSCE), d-excess (blue),  $\delta^{18}\text{O}$  (red) and temperature at 2 m during the precipitation event (black). At the bottom, the circles indicate the precipitation types (red: snow; blue: ice needles; green: rime). No obvious relationship is found between the isotopic composition  $^{17}\text{O}$ -excess and the type of precipitation.

### 3. RESULTS

The results displayed in Figure 2 show that over the course of the year, Vostok  $\delta^{18}\text{O}$  is significantly correlated with temperature ( $\Delta(\delta^{18}\text{O})/\Delta T = 0.35\text{‰}\text{°C}^{-1}$ ; Fig. 3a). This seasonal slope is less than that observed at the remote station at Dome F (Fig. 1) for a similar range of surface temperature and  $\delta^{18}\text{O}$  ( $0.78\text{‰}\text{°C}^{-1}$ ; Fujita and Abe, 2006) and  $0.47\text{‰}\text{°C}^{-1}$ ; Motoyama and others, 2005). It is also half the observed spatial slope over Antarctica ( $\Delta(\delta^{18}\text{O})/\Delta T = 0.75\text{--}0.80\text{‰}\text{°C}^{-1}$  (Lorius and others, 1979; Masson-Delmotte and others, 2008)). In turn, such a low value for

the temporal slope at Vostok is consistent with the temporal slope ( $\sim 0.3\text{‰}\text{°C}^{-1}$ ) observed in Greenland over the Holocene, the deglaciation and the last glacial period (Cuffey and others, 1995; Vinther and others, 2009; Capron and others, 2010). It is also consistent with the modeled slope at Vostok for a warmer climate simulated through  $\text{CO}_2$  doubling (Sime and others, 2009). In these latter cases, the low values of the temporal slope are mostly due to a change of the seasonality of the precipitation with time (more precipitation in summer during the coldest periods). As observed at Vostok, stations closer to coastal Antarctica also

**Table 1.** Data displayed in Figure 2

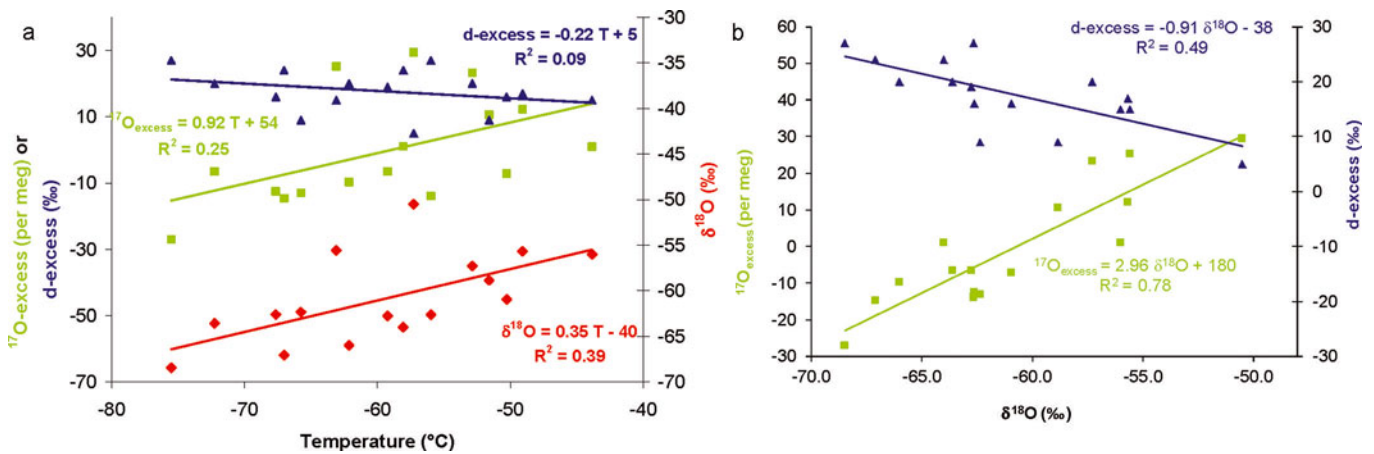
Date (2000)	Temperature 2 m (°C)	Precipitation type	NBI*		$\delta^{18}\text{O}$ (‰)	IES†		$\delta^{18}\text{O}$ (‰)	LSCE‡	
			$\delta^{18}\text{O}$ (‰)	d-excess (‰)		$\delta^{17}\text{O}$ (‰)	$^{17}\text{O}$ -excess (per meg)		$\delta^{17}\text{O}$ (‰)	$^{17}\text{O}$ -excess (per meg)
29 Feb.	-49	blowing snow?	-55.67	17	-53.904	-28.822	12			
30 Mar.	-63.1	ice needles, rime	-55.68	15	-54.532	-29.149	25			
9 Apr.	-62.1	rime	-66.02	20	-65.812	-35.316	-10	-65.511	-35.152	-5
13 Apr.	-59.2	blowing snow?	-62.76	19	-60.928	-32.653	-6			
23 Apr.	-72.2	rime	-63.59	20	-61.973	-33.222	-7			
9 May	-67	ice needles, rime	-67.08	24	-64.984	-34.870	-15	-66.219	-35.543	-10
18 May	-65.7	snow, rime	-62.36	9	-60.203	-32.265	-13			
30 May	-52	snow (+ blowing snow?)	-57.29	20	-55.352	-29.596	23	-56.152	-30.022	31
13 Jun.	-56	blowing snow?	-62.65	27	-61.035	-32.719	-14			
26 Jun.	-51.6	ice needles, rime	-58.84	9	-55.969	-29.943	11			
1 Aug.	-75.5	rime	-68.47	27	-66.368	-35.636	-27			
11 Aug.	-58.1	blowing snow?	-64	24	-62.745	-33.635	1	-63.34	-33.948	12
19 Aug.	-50.3	blowing snow?	-60.95	16	-57.887	-31.001	-7			
5 Sept.	-43.8	snow (+ blowing snow?)	-56.01	15	-53.519	-28.624	1	-54.945	-29.391	7
5 Oct.	-67.6	ice needles, rime	-62.62	16	-59.822	-32.058	-13			
11 Oct.	-57.3	snow	-50.51	5	-50.019	-26.701	29	-49.924	-26.649	30

\*Geophysical Department, Niels Bohr Institute.

†Institute of Earth Sciences, Jerusalem University.

‡Laboratoire des Sciences du Climat et de l'Environnement.

Notes: All d values are expressed versus VSMOW. The precision at NBI is 0.05‰ for  $\delta^{18}\text{O}$  and 1‰ for d-excess. The overall precision at LSCE and IES is better than 0.03‰ for both  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  and 5 per meg for  $^{17}\text{O}$ -excess obtained with two or four replicates for each sample.



**Fig. 3.** (a) Evolution of  $^{17}\text{O}_{\text{excess}}$ , d-excess and  $\delta^{18}\text{O}$  vs air temperature at 2 m height over the seasonal cycle at Vostok. (b) Evolution of  $^{17}\text{O}$ -excess and d-excess vs  $\delta^{18}\text{O}$  over the seasonal cycle at Vostok.

exhibit lower temporal slopes than the spatial slope at the seasonal scale (e.g. Van Ommen and Morgan, 1997). This is most likely explained by the relatively large amount of snowfall occurring when temperature is above average (Peel, 1992).

The explanations given above cannot be applied to explain the low  $\Delta(\delta^{18}\text{O})/\Delta T$  slope observed at the seasonal scale at Vostok since we measure temperature and isotopic composition of snow on an event basis. We thus suggest that the observed low slope can be partly explained by (1) a strong gradient between condensation and surface temperature (Ekaykin, 2003) and/or (2) changes in the source climatic conditions for moisture feeding Vostok precipitation. More information on the meteorological conditions associated with each precipitation event and use of back-trajectory analyses are needed to decipher between these different hypotheses.

As already observed at the remote Dome F site (Fujita and Abe, 2006), as well as in monthly Vostok data on temperature and isotope content (Ekaykin and others, 2004), Vostok d-excess is anticorrelated with both  $\delta^{18}\text{O}$  and temperature at the seasonal scale (Figs 2 and 3a and b). The highest values (>25‰) were obtained during the coldest periods of precipitation (April and September), and the lowest value (5‰) during a warm period in October. Still, the anticorrelation between d-excess and temperature is not significant over this seasonal cycle at Vostok ( $R^2 = 0.09$ ; Fig. 3a). The anticorrelation is actually significant only between  $\delta^{18}\text{O}$  and d-excess ( $R^2 = 0.49$ ; Fig. 3b), suggesting that parameters other than local precipitation temperature also control the isotopic composition of surface snow at Vostok.

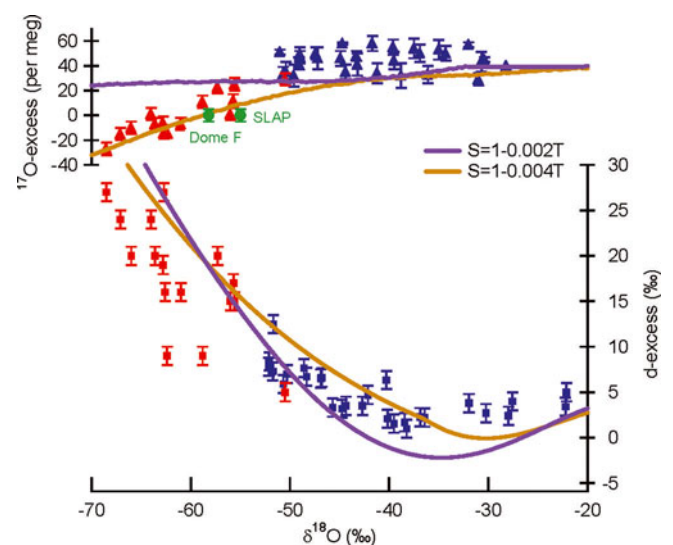
$^{17}\text{O}$ -excess depicts clear variations of the order of 40 per meg over the year, with maximal values in austral summer (>20 per meg) and minimal values in austral winter (<-20 per meg). As for the relationships between  $^{17}\text{O}$ -excess, surface temperature and  $\delta^{18}\text{O}$ , strong correlation is observed between  $^{17}\text{O}$ -excess and  $\delta^{18}\text{O}$  ( $\Delta(^{17}\text{O}\text{-excess})/\Delta(\delta^{18}\text{O}) = 2.96$  per meg ‰ $^{-1}$ ;  $R^2 = 0.78$ ; Fig. 3b), while correlation is much weaker between  $^{17}\text{O}$ -excess and surface temperature ( $\Delta(^{17}\text{O}\text{-excess})/\Delta T = 0.92$  per meg °C $^{-1}$ ;  $R^2 = 0.24$ ; Fig. 3a).

Miller (2008) suggested that part of the  $^{17}\text{O}$ -excess signal at Vostok could be induced by significant intrusion of stratospheric water vapor with associated high  $^{17}\text{O}$ -excess because of mass-independent fractionation. However, our

calculations, based on available values of  $^{17}\text{O}$ -excess at the tropopause and estimated stratospheric–tropospheric fluxes have shown that this effect should not have significant influence even at the remote Vostok station (Landais and others, 2008b). Thus, in the following discussion we do not consider the stratospheric influence.

#### 4. DISCUSSION

The seasonal variations of  $^{17}\text{O}$ -excess and the significant correlation between  $^{17}\text{O}$ -excess and  $\delta^{18}\text{O}$  observed at Vostok strongly contrast with the stable behavior of  $^{17}\text{O}$ -excess observed on an Antarctic transect between the coast and the inland Dome C station (Landais and others, 2008a) (Fig. 4). In parallel, the anticorrelation between d-excess and  $\delta^{18}\text{O}$  at the very cold Vostok site is much stronger than what was observed over the Antarctic transect (Fig. 4).



**Fig. 4.** Repartition of  $^{17}\text{O}$ -excess vs  $\delta^{18}\text{O}$  (top) and d-excess vs  $\delta^{18}\text{O}$  (bottom) for an Antarctic transect between Terra Nova Bay and Dome C (blue; Landais and others, 2008a) and for the seasonal cycle at Vostok (red). Two water standards, SLAP and Dome F (Luz and Barkan, 2010), are indicated in green.

With the purpose of explaining the different behaviors of  $^{17}\text{O}$ -excess over the seasonal cycle and over the transect, as well as understanding the influence of different climatic or cloud physics parameters on  $^{17}\text{O}$ -excess and d-excess, we used a simple modeling approach to provide a context for interpreting our data.

#### 4.1. Simple modeling approach

The  $^{17}\text{O}$ -excess correlation with  $\delta^{18}\text{O}$  observed at low temperature can be explained by the increasing importance of the kinetic effect (due to higher supersaturation) in the very cold polar regions. The fractionation coefficient associated with solid precipitation is classically expressed as (Jouzel and Merlivat, 1984)

$$^*\alpha_k = \frac{[(\text{H}_2^*\text{O})/(\text{H}_2^{16}\text{O})]_{\text{liq}}}{[(\text{H}_2^*\text{O})/(\text{H}_2^{16}\text{O})]_{\text{vap}}} = \frac{S}{(D/^*D)(S-1) + (1/^*\alpha_{\text{eq}})} \quad (1)$$

where  $S$  is the supersaturation of water vapor over ice, which increases with decreasing temperature,  $D$  and  $^*D$  are the diffusion coefficients of  $\text{H}_2^{16}\text{O}$  and  $\text{H}_2^*\text{O}$  in air,  $^*\alpha_{\text{eq}}$  is the fractionation coefficient associated with solid–vapor equilibrium for  $\text{H}_2^*\text{O}$  vs  $\text{H}_2^{16}\text{O}$ , and  $^*$  stands for 17 or 18.  $S$  is generally assumed to be a linear function of temperature (Ciais and Jouzel, 1994), so that  $S = 1 - aT$  with  $a > 0$  ( $T$  in  $^{\circ}\text{C}$ ). The main importance of the parameter  $S$  is that it controls the balance between kinetic (given by the relationship between the values of  $D/D^{18}$  and  $D/D^{17}$  for  $^{17}\text{O}$ -excess; Barkan and Luz, 2007) and equilibrium (given by the relationship between  $^{18}\alpha_{\text{eq}}$  and  $^{17}\alpha_{\text{eq}}$  for  $^{17}\text{O}$ -excess; Barkan and Luz, 2005) effects. Thus, an increase of  $S$  leads to an increase of the slope ( $\Delta^{17}\text{O-excess}/\Delta(\delta^{18}\text{O})$ ) at very low temperatures (Fig. 4). Indeed, the ratio of the equilibrium fractionation factors  $\ln(^{17}\alpha_{\text{eq}})/\ln(^{18}\alpha_{\text{eq}})$ , associated with  $\delta^{17}\text{O}$  ( $^{17}\alpha_{\text{eq}}$ ) and  $\delta^{18}\text{O}$  ( $^{18}\alpha_{\text{eq}}$ ), at temperatures below  $0^{\circ}\text{C}$  is close to 0.528 (Van Hook, 1968) and is not different from the value 0.529 obtained at temperatures of  $10$ – $40^{\circ}\text{C}$  (Barkan and Luz, 2005). As a consequence, a significant contribution of kinetic fractionation, and thus an increase of  $S$ , is needed to explain a  $^{17}\text{O}$ -excess increase with  $\delta^{18}\text{O}$ .

The balance between kinetic and equilibrium effects for solid precipitation also strongly affects d-excess. Jouzel and Merlivat (1984) first showed that pure equilibrium fractionation between vapor and solid (i.e. supersaturation of 1) leads to a strong anticorrelation between d-excess and  $\delta^{18}\text{O}$  with very high d-excess (60‰) in remote regions like Vostok. This is because the ratio of the equilibrium fractionation factors  $(^{17}\alpha_{\text{eq}} - 1)/(^{18}\alpha_{\text{eq}} - 1)$ , associated with  $\delta^{17}\text{O}$  ( $^{17}\alpha_{\text{eq}}$ ) and  $\delta^{18}\text{O}$  ( $^{18}\alpha_{\text{eq}}$ ), is significantly different from 8 at low temperatures. To explain the mean annual value of  $\sim 18\%$  at Vostok, a contribution of kinetic fractionation to the process of solid precipitation formation (i.e.  $S > 1$ ) is needed, but the anticorrelation between d-excess and  $\delta^{18}\text{O}$  remains. It is indeed observed in Figure 4 that increasing  $S$  leads to a decrease of the slope  $\Delta(\text{d-excess})/\Delta(\delta^{18}\text{O})$ .

To reproduce the evolution of the snow isotopic composition over the Antarctic transect and on the seasonal cycle at Vostok, we have used the same mixed cloud isotopic model (MCIM; Ciais and Jouzel, 1994) based on a Rayleigh distillation (Jouzel and Merlivat, 1984) and adapted to  $^{17}\text{O}$ -excess, as in Landais and others (2008a). The MCIM describes the isotopic processes at each phase transition, and thus the isotopic composition of both the condensed phase (liquid water or solid ice) and the water vapor at each

step from the oceanic source region to the precipitation site on the ice sheet. Only one trajectory with a single source and a single precipitation site can be taken into account in this model. During liquid precipitation, only equilibrium fractionation occurs. Kinetic fractionation is taken into account for snowflake formation and is controlled by supersaturation as in Eqn (1). The model receives as main inputs (1) the temperature, relative humidity, wind speed and surface atmospheric pressure of the source region as well as the isotopic composition of the surface ocean, and (2) the condensation temperature and atmospheric pressure at the precipitation site.

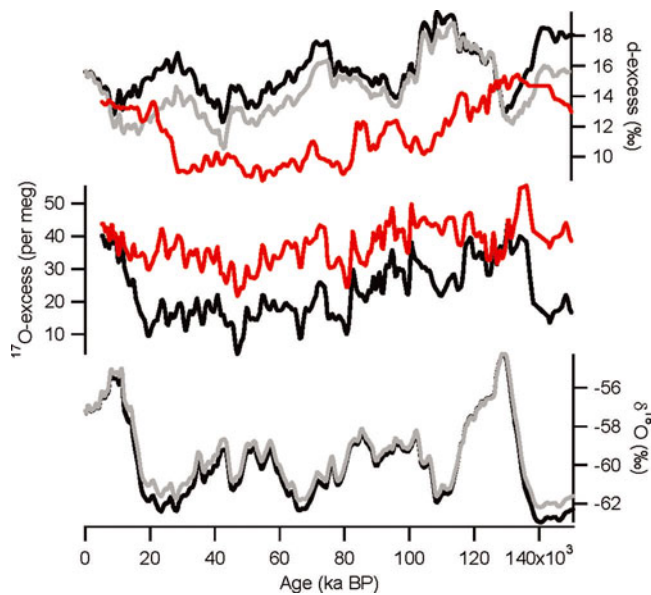
The model is first initialized through the isotopic composition of water vapor in the boundary layer above the ocean. This can be done either by imposing the isotopic composition of this water vapor or using the so-called closure assumption detailed by Merlivat and Jouzel (1979), which relies on the hypothesis that the only source of vapor in the boundary layer is from the surface evaporation. Then the transport path of the water mass is calculated in terms of temperature and pressure. The air parcel is transported in saturated (or supersaturated in polar regions) conditions from the source region to the precipitation site, hence implying continuous fractionation. The MCIM includes several tunable parameters (Ciais and Jouzel, 1994) such as the dependence of supersaturation on temperature and the fraction of condensate remaining in clouds. We performed numerous sensitivity experiments to tune these parameters (Winkler and others, 2011). For our study, the main differences between the simulated d-excess and  $^{17}\text{O}$ -excess are due to the change of the supersaturation dependency to temperature whose effect is displayed in Figure 4.

#### 4.2. Model–data comparison

The relationships between  $^{17}\text{O}$ -excess (d-excess) and  $\delta^{18}\text{O}$  over the Antarctic transect and over one seasonal cycle at Vostok can be satisfyingly reproduced with a simple isotopic model assuming a supersaturation function of  $S = 1 - 0.004T$  (Fig. 4). Yet, as we show below, such parameterization of the ratio between equilibrium and kinetic fractionation at solid precipitation is not enough to explain the relationship between surface temperature and the isotopic composition of snow at Vostok as shown in Figure 3a.

Using the parameterization of the function  $S(T)$  given above and running the MCIM with different condensation temperatures,  $T_{\text{cond}}$ , between  $-30^{\circ}\text{C}$  and  $-50^{\circ}\text{C}$ , we obtained values of  $1.7\%$   $^{\circ}\text{C}^{-1}$ ,  $3.6$  per meg  $^{\circ}\text{C}^{-1}$  and  $-2.9\%$   $^{\circ}\text{C}^{-1}$  for the gradients  $\Delta(\delta^{18}\text{O})/\Delta T_{\text{cond}}$ ,  $\Delta(^{17}\text{O-excess})/\Delta T_{\text{cond}}$  and  $\Delta(\text{d-excess})/\Delta T_{\text{cond}}$ , respectively. We note that  $T_{\text{cond}}$  is not equal to surface temperature, and the relationship between the two is strongly influenced by the atmospheric inversion layer. Classically, a slope of  $0.6$ – $0.67$  (Jouzel and Merlivat, 1984; Ekaykin and Lipenkov, 2009) is always assumed between variations of near-surface and condensation (or inversion) temperatures based on available temperature measurements performed in several places in Antarctica (Jouzel and Merlivat, 1984 and references therein). Using such a relationship between condensation temperature and surface temperature leads to a difference of a factor of two, at least, between the modeled and the measured gradients  $\Delta(\delta^{18}\text{O})/\Delta T$ ,  $\Delta(^{17}\text{O-excess})/\Delta T$  and  $\Delta(\text{d-excess})/\Delta T$ , where  $T$  is the surface temperature.

Many factors can explain the differences between model and observations. First, based on balloon sounding



**Fig. 5.** Water isotopic measurements over the last 150 ka on the Vostok ice core. The bold grey lines show the measured profiles after a five-point average (raw data for  $\delta^{18}\text{O}$  and d-excess are from Vimeux and others, 1999; raw data for  $^{17}\text{O}$ -excess are from Landais and others, 2008a). The bold black lines display the  $\delta^{18}\text{O}$  and d-excess profiles after correction for the change in  $\delta^{18}\text{O}$  of the global ocean of 1‰ over glacial–interglacial periods, but no correction is needed for  $^{17}\text{O}$ -excess. The bold red lines account for the d-excess and  $^{17}\text{O}$ -excess after they were corrected by the observed seasonal tendencies  $\Delta(^{17}\text{O}\text{-excess})/\Delta(\delta^{18}\text{O})$  (2.96 per meg‰ $^{-1}$ ) and  $\Delta(\text{d-excess})/\Delta(\delta^{18}\text{O})$  (−0.91‰‰ $^{-1}$ ).

measurements of the temperature of the inversion layer at the seasonal scale over almost 30 years (1963–91), Ekaykin (2003) estimated that at Vostok the slope of the seasonal relationship between near-surface and condensation temperatures may be only  $\sim 0.32$ . From this relationship, the modeled gradients  $\Delta(\delta^{18}\text{O})/\Delta T$ ,  $\Delta(^{17}\text{O}\text{-excess})/\Delta T$  and  $\Delta(\text{d-excess})/\Delta T$  can be calculated as 0.54‰ $^{\circ}\text{C}^{-1}$ , 1.1 per meg  $^{\circ}\text{C}^{-1}$  and  $-0.93$ ‰ $^{\circ}\text{C}^{-1}$ , respectively. In this case, the first two values are the same order as the measured values ( $\Delta(\delta^{18}\text{O})/dT = 0.35$ ‰ $^{\circ}\text{C}^{-1}$ ,  $\Delta(^{17}\text{O}\text{-excess})/\Delta T = 0.92$  per meg  $^{\circ}\text{C}^{-1}$ ; Fig. 3a), and only the calculated and observed  $\Delta(\text{d-excess})/\Delta T$  slopes differ strongly:  $-0.22$  and  $-0.93$ ‰ $^{\circ}\text{C}^{-1}$ , respectively.

The second potential problem is that our model considered constant climatic conditions (relative humidity, temperature, etc.) for the oceanic source regions. This is obviously not correct, since relative humidity and temperature are not constant at the ocean surface throughout the year. This effect has a strong influence on polar snow  $^{17}\text{O}$ -excess and d-excess. Indeed, at Vostok, Risi and others (2010a) and Winkler and others (2011) estimated variations of  $^{17}\text{O}$ -excess in polar snow with relative humidity at the source of  $\sim 1$  per meg‰ $^{-1}$ , and variations of d-excess in polar snow with  $T_{\text{source}}$  of  $\sim 1.5$ ‰ $^{\circ}\text{C}^{-1}$ . Moreover, the location of Vostok's oceanic source regions changes over the year, as was shown by retrotrajectory analyses (Sodemann and others, 2008; Sodemann and Stohl, 2009). First, the sources of water vapor precipitating at Vostok are mainly from the austral ocean in winter, while there is a possible contribution of recycling over Antarctica in summer (Winkler and others, 2011). Second, Ekaykin and Lipenkov

(2009) noted that the observed seasonal cycle of d-excess at Vostok can be explained if we suggest that the weighted source temperature is 1.5°C lower in summer than in winter, likely due to reduced sea-ice coverage around Antarctica, so that the region of evaporation is extended to higher latitudes. The significance of these additional effects is that it is not possible to quantitatively predict the seasonal variations of  $\delta^{18}\text{O}$ ,  $^{17}\text{O}$ -excess and d-excess with the MCIM considering only one trajectory and one constant moisture source. Thus, the next step should be to use water-isotope tagging in Atmospheric General Circulation Models (AGCMs) to quantify the different influences on  $\delta^{18}\text{O}$ , d-excess and  $^{17}\text{O}$ -excess seasonal variations. There have been some attempts to incorporate  $\delta^{18}\text{O}$  and  $\delta\text{D}$  in such models (e.g. Hoffmann and Heimann, 1993; Risi and others, 2010b). However, until now, while these models are able to reproduce the relative evolution of d-excess with respect to  $\delta^{18}\text{O}$  in polar regions as the MCIM does (e.g. Schmidt and others, 2005; Risi and others, 2010b), they are still not able to simulate the extremely cold conditions of central East Antarctica, nor the observed d-excess changes over time.

#### 4.3. Implications for interpretation of water isotopic records from Antarctic ice cores

The results obtained for  $^{17}\text{O}$ -excess variations over the seasonal cycle are instructive with respect to the  $^{17}\text{O}$ -excess change of  $\sim 20$  per meg at Vostok between the Last Glacial Maximum and the early Holocene. As shown in Figure 5, the relative change in  $^{17}\text{O}$ -excess vs  $\delta^{18}\text{O}$  observed over the last deglaciation in Vostok (3.8 per meg‰ $^{-1}$ ) is of the same order of magnitude as the relative change in  $^{17}\text{O}$ -excess vs  $\delta^{18}\text{O}$  over the Vostok seasonal cycle (2.96 per meg‰ $^{-1}$ ). From this similarity, it is tempting (as suggested by Miller, 2008) to conclude that the observed change in  $^{17}\text{O}$ -excess over the last deglaciation in Vostok could be interpreted as a local temperature effect, and not as a climatic signal from the source region.

In Figure 5 together with the measured  $\delta^{18}\text{O}$  and d-excess values, we present the corresponding values corrected (using the formulas given in Jouzel and others, 2003) for the observed change in  $\delta^{18}\text{O}$  of the global ocean ( $\delta^{18}\text{O}_{\text{sw}}$ ) of 1‰ over glacial–interglacial periods (Waelbroeck and others, 2002). No corrections for  $\delta^{18}\text{O}_{\text{sw}}$  are needed for  $^{17}\text{O}$ -excess (Luz and Barkan 2010; Risi and others, 2010a). Then,  $^{17}\text{O}$ -excess and d-excess values were corrected for the observed trends over the seasonal cycle:  $\Delta(^{17}\text{O}\text{-excess})/\Delta(\delta^{18}\text{O}) = 2.96$  per meg‰ $^{-1}$  and  $\Delta(\text{d-excess})/\Delta(\delta^{18}\text{O}) = -0.91$ ‰‰ $^{-1}$ .

The residual signal (red line in Fig. 5) does not show a significant increase of  $^{17}\text{O}$ -excess over the deglaciation, but clearly evidences a minimum at  $\sim 50$  ka BP. Such a flat  $^{17}\text{O}$ -excess signal over the deglaciation is in good agreement with the small or non-existent increasing  $^{17}\text{O}$ -excess trends observed over the same climatic transition in more coastal ice cores over Antarctica (Winkler and others, 2011). This confirms the interpretation proposed by Winkler and others (2011) that the Vostok site has a too remote location in East Antarctica, preventing the confident use of  $^{17}\text{O}$ -excess for reconstructing past relative humidity. For such sites, the influence of local temperature on  $^{17}\text{O}$ -excess should be taken into account. This can best be done by combining surface measurements and isotopic modeling as presented in this paper.

The same comparison between seasonal and glacial–interglacial changes can be drawn for d-excess. The residual

d-excess signal after the two corrections (red line in Fig. 5) is very different from the original one. We note particularly that after corrections the 41 ka obliquity cycles, generally observed on d-excess long records from ice cores from East Antarctica and Greenland (Vimeux and others, 1999; Uemura and others, 2004; Masson-Delmotte and others, 2005; Stenni and others, 2010), disappear. We also observe a strong increase of d-excess by  $>4\%$  leading the last deglaciation by 10 ka. This trend cannot be explained simply by a change in the temperature of the oceanic source region unless we suggest that the source regions move northward at that period. However, at present we have no evidence for such a change in the location of the oceanic source region.

Finally, we should be cautious when comparing changes in  $^{17}\text{O}$ -excess and d-excess at the seasonal cycle with those over the last climatic cycle. Possible limits of this analogy are (1) a change of seasonality of the precipitation over the last climatic cycle and/or (2) a change in the source regions or of the trajectory of the water mass over the seasonal cycle. To go further on the use of the seasonal cycle data for interpretation of ice-core profiles, more complete studies, including meteorological datasets and back-trajectory analysis, should be drawn on the seasonal scale, and modeling experiments on past periods should be launched using an AGCM including water isotopes.

## 5. CONCLUSION AND PERSPECTIVES

The first measurements of  $^{17}\text{O}$ -excess on an event basis over 1 year at the remote East Antarctic station of Vostok showed a strong correlation between  $^{17}\text{O}$ -excess and  $\delta^{18}\text{O}$ , with seasonal variations of  $^{17}\text{O}$ -excess larger than 40 per meg. In contrast, a clear anticorrelation is observed between d-excess and  $\delta^{18}\text{O}$  at the same timescale, with seasonal variations of d-excess of the order of 20‰. The correlation of  $^{17}\text{O}$ -excess and anticorrelation of d-excess with  $\delta^{18}\text{O}$  could easily be explained by taking into account the relative proportion of kinetic to equilibrium fractionation at solid precipitation in a MCIM. In a classical approach their proportion is regulated using the supersaturation function,  $S$ , related to the condensation temperature  $T_{\text{cond}}$ . Our results are best fitted with  $S = 1 - 0.004T_{\text{cond}}$ . However, while this approach successfully explains the relationships between  $^{17}\text{O}$ -excess, d-excess and  $\delta^{18}\text{O}$ , it fails to simulate correctly the link between the surface temperature and the isotopic composition of water. In this case, the model predicts too strong an influence of temperature on  $\delta^{18}\text{O}$ , d-excess and  $^{17}\text{O}$ -excess. At least two effects can explain this discrepancy: (1) a particular link between inversion and surface temperature at Vostok and/or (2) seasonal changes in the source (i.e. evaporative regions) climatic conditions.

Our first results of  $^{17}\text{O}$ -excess of precipitation over a whole year at Vostok station have important applications for paleoclimate reconstruction from deep ice cores, especially the Vostok core:

1. The  $^{17}\text{O}$ -excess increase observed over the deglaciation on the Vostok ice core can be explained by a balance of kinetic to equilibrium fractionation at solid precipitation in very cold sites in Antarctica. The tuning of supersaturation dependency to temperature is critical for interpreting the  $^{17}\text{O}$ -excess changes with  $\delta^{18}\text{O}$  in these regions. The  $^{17}\text{O}$ -excess of polar ice cores should not be used to reconstruct source relative humidity in remote

locations, but rather in coastal regions, where the influence of supersaturation on  $^{17}\text{O}$ -excess local variations is weak.

2. The large variations of  $^{17}\text{O}$ -excess and d-excess during a year suggest that a change of the seasonality of the precipitation with time (e.g. over the deglaciation) strongly influences the mean level of  $^{17}\text{O}$ -excess and d-excess archived in the ice core. Thus, it is essential to consider the seasonality issue when interpreting water isotopic composition in polar ice cores.

At present, we have no clear quantitative explanation for the link between local temperature and water isotopic composition at Vostok, and this calls for the following future studies:

1. Fractionation coefficients associated with  $\delta^{18}\text{O}$ ,  $\delta^{17}\text{O}$  and  $\delta\text{D}$  should be measured at very low temperature. Indeed, strong discrepancies exist between the few available estimates for  $\delta^{18}\text{O}$  and  $\delta\text{D}$  (Merlivat and Nief, 1967; Matsuo and Matsubaya, 1969; Jansco and others, 1970; Majoube, 1971; Jakli and Staschewski, 1977; Ellehøj, 2011), and no direct measurements have been performed so far for  $\delta^{17}\text{O}$ .
2. Meteorological studies are required to enable us (1) to quantify the relationship between condensation, inversion and surface temperatures and (2) to trace the origin of the precipitation through back-trajectories at the event, seasonal and interannual scale.
3. Mean annual levels of  $^{17}\text{O}$ -excess should be measured at very remote sites in East Antarctica (e.g. Dome A, Dome F) in order to check if the correlation observed between  $^{17}\text{O}$ -excess and  $\delta^{18}\text{O}$  at the seasonal scale is also seen spatially.

In conclusion, there is no doubt that combining  $^{17}\text{O}$ -excess and d-excess measurements in East Antarctica is essential to document climate and paleoclimate through model–data approaches. This first study should be used as a benchmark for AGCM experiments including water isotopes.

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