Interactive comment on “Acquisition of isotopic composition for surface snow in East Antarctica and the links to climatic parameters” by A.Touzeau et al.

Anonymous Referee #1

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Review

General comments: The topic of this manuscript is up-to-date. Interpreting the climate signal from water isotope records of low accumulation rate site has a lot of difficulties. To understand how the climatic and environmental signature is imprinted in the water isotopic composition of the surface snow is an important step in the process of understanding. My impression is that this study is thoroughly done and can provide new insights into the understanding of water isotope signal. The manuscript has a clear overall structure and good readability. However, the figures and method description need some improvements. The topic fits the scope of “The Cryosphere” and should be published after some minor revisions.

Specific comments: A more detailed description of the sampling method is needed.

P 6283 L17 surface samples of 10-30 cm pits- what is the annual resolution? Is the mean value an average over depth or over time? What about changes in the accumulation rate along the different transects?

The sampling strategy was different for the three transects:
- For the Zhongshang-Dome A profile, the first 10 centimeters of snow were collected for all the sites, regardless of the accumulation rate (Pang et al., 2015). They correspond to 102 % of the year at Dome A and to 21-38 % of the year for the coastal regions (Pang et al., 2015).
-In the case of the Terra-Nova Bay-Dome C traverse, the samples for the isotopic analysis correspond to 1 m of snow (Proposito et al., 2002; Magand et al., 2004) and thus represent an average value for 2 years (coastal sites) to 12 years (inland sites).
-For the Syowa-Dome F transect, the sampling depth for the surface snow varies depending on the position. Larger samples (from surface to 30 centimeters depth) were taken at coastal sites, where accumulation rates are higher, whereas samples at inland sites were shallower (from surface to ten centimeters of depth). The chosen depth allows, for each pit, to have one complete year recorded. This limits the seasonal bias. At Dome Fuji, the accumulation rate is about 25-29 kg/m^2/y (Fujita et al., 2011), and the density of the snow in the first decimeters is on average 340 kg/m^3 (Igarashi et al., 2011). Thus 7-8 centimeters of snow are deposited every year (and 10 centimeters were sampled). At EPICA DML, the accumulation rate is 73 kg/m^2/y (Fujita et al., 2011). The snow density in the first decimeters at Dronning Maud Land varies between 360 and 440 kg/m^3 (Vihma et al., 2011). Thus a year corresponds to about 20 cm of snow there.

We propose the following correction:
p. 6283 l. 17: **“The surface snow samples were obtained from shallow pits on which the average water isotopic composition was measured. These pits had a depth of 1 m for the Terra-Nova Bay-Dome C traverse (Proposito et al., 2002; Magand et al., 2004), 10 cm for the Zhongshang-Dome A traverse (Pang et al., 2015) and 10 to 30 centimeters for the Syowa-Dome F traverse. Because the accumulation decreases from the coast towards the inland sites, the period recorded, for the first transect, varies from 2 years near the coast**

to 12 years at Dome C. For the Chinese traverse, the recorded period varies from one year in inland areas to 3 months in coastal areas. For the Syowa-Dome F traverse, the pits were shallower at inland sites (10 centimeters) and deeper at coastal sites in order to record at least one year in each sample."

Vostok p 6287 : The description of the sampling strategy at Vostok needs more details. What is the sample volume? How long is a precipitation event? Is there sublimation expected?

The sampling at Vostok was described in greater details in Landais et al., 2012:
"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 about 50 m windward from the station buildings 1.5 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 and exchange with the atmospheric water vapor."
We will add the reference to this work in this section (see below).

Sample volume was really different, varying from 1 ml or less in case of diamond dust to maybe 10-20 ml in case of "heavy" snowfall (this is an estimate, because the sample volumes was not measured).
The duration of precipitation event was from few hours to few days (the latter is typical for diamond dust). For lengthy events (diamond dust), we took sample once a day, whereas for short events, the sampling was made after the precipitation event was over.

No, sublimation is not expected for these samples for 2 reasons:
- the trap to collect the precipitation had rather high walls, so the snow was in a shadow;
- most of the samples discussed in our paper were taken in winter with low or no Sun.

Thus we do not expect any influence of sublimation on the isotopic content of the samples.

We have modified the text to provide more information on the sampling to the reader:
P. 6287, l. 12: "**At Vostok, precipitation occur under three forms: snow from clouds, diamond dust, and rime. The duration of precipitation event vary from a few hours to a few days (the latter is typical for diamond dust).** The Vostok precipitation sampling has been performed immediately after each precipitation event from December 1999 to December 2000 and can be separated in two datasets. The first one (series A) corresponds to sampling from precipitation trap placed at 1.5 m above the snow surface and at ~50 m windward from the station (**Landais et al., 2012a**). Samples collected in this trap consist of pure precipitation as ascertained by the calm weather conditions and absence of blowing snow at the time of collection. **Sublimation in the trap is unlikely for two reasons. First, the high walls of the trap shaded the precipitation within it. Second, most of the samples were collected in winter, when insolation is minimal.** The second one (series B) corresponds to sampling from a lower precipitation trap buried with its upper edge at the snow surface. Thus the flow of blowing snow around the trap was unimpeded and the snow collected consists of a mixture of precipitation and blowing snow. **After the collection, the samples from the two series were melted, poured into special plastic bottles and frozen again. This procedure was followed to avoid alteration of the initial isotopic composition of precipitation due to sublimation and exchange with the atmospheric water vapor. Sample volume varied between 1 mL (diamond dust) and 10-20 mL ("heavy" precipitation)"**

Dome C P 6288 L 25: Soft surface snow was scraped and sampled- Which distance is between the sampling area(s), is there information about drift? What about the topography of the snow surface? Were there any changes during the year eg dunes?

The total sampling zone covers ca. 1 000 m^2. Approximately 5 to 10 spots few m^2 apart are sampled for every collect within this 1 000 m^2, depending on the hardness of the surface. To collect enough snow for the studies (including isotope chemistry not included in the present manuscript), an area of roughly 5 m^2 is sampled for a given sample, thereby averaging the various types of snow that can be present during the sampling. This surface ensures that the sampling is not biased by the operator. The only criterion is to sample no more than few mm of surface snow. The operator thus adopts special cares when a soft snow is encountered. If the sampling tool (a 20 cm stainless steel blade) goes too deep in the snow layer, then this snow is disregarded and the operator moves to a next spot. For security reasons, the sampling site is located ca. 100 m away of the atmospheric shelter, in the direction of the clean area. Therefore, drifted, wind crust, soft, hard, hoar snow can be sampled indiscriminately. In fact the idea is to sample all types of snow present during the day of sampling but in direct contact of the atmosphere to access the average composition of the surface snow.

The time of snow collection was variable, but in majority they were sampled at the end of the morning.

Regarding the topography of the surface, sastrugis (small dunes) are present all year round. They have a height ranging between 5 cm and 10 cm. However the sampling was limited to flat areas, so the sastrugis flanks were not sampled.

To clarify these points in the manuscript, we propose the following correction:

p. 6288, l. 25: "The sampling of surface snow at Dome C has been performed **between December 2010 and December 2011, in the clean area, about 1km away from Concordia Station, according to the following procedure : each day of collection an area of approximatively 5 m^2 is chosen (different from the previous one) and snow is scrapped on 5 to 10 spots (ca 0.04 m^2) within this area. This variability is due to the necessity to collect enough snow for later analysis. Only the first 1-2 mm of snow are collected, using a metal blade. The snow collected is homogenized and melted, and a fraction destined for isotopic analysis** is transferred into a 20mL vial and then kept frozen until analysis. **In every 5 m^2 area, sastrugis are avoided, but otherwise (i.e. on flat areas) the sampling is performed randomly and no distinction is made between snow types: drifted snow, wind crust, soft, hard, and hoar snow are sampled indiscriminately. The aim is to sample all types of snow present during the day of sampling to access the average composition of the surface snow in direct contact of the atmosphere.** On this set…"

Fig. 4: What about the correlation between $\delta^{18}O$ and temperature or d excess and precipitation? What happens June/July 2011 that there is a peak in temperature but not in the $\delta^{18}O$ samples? Is there any information about wind and drift at Dome C?

R	T	$\delta^{18}O$	d-excess	^{17}O-excess
$\delta^{18}O$	0.54	1.00	-0.40	0.32

d-excess	-0.46	-0.40	1.00	0.06
^{17}O-excess	0.25	0.32	0.06	1.00
P (daily)	0.25	0.27	0.03	0.24
P (av. 6 days)	0.25	0.34	-0.16	0.46
P (av. 10 days)	0.07	0.30	-0.05	0.47

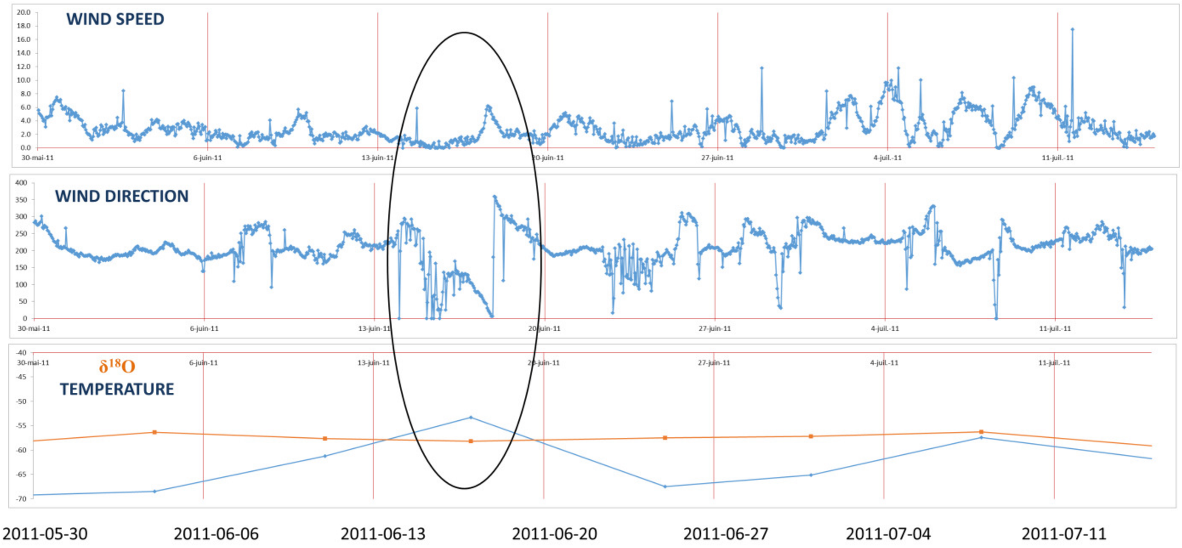
There are strong correlations with temperature for δ^{18}O (positive) and d-excess (negative).
There is also a correlation between temperature and ^{17}O-excess, but smaller.
We did not present the correlation with the precipitation amount in the paper, because

1) We do not expect causal relationships between precipitation amount and isotopic compositions;
2) The correlation with the precipitation is never strong (even when considering average values instead of the value of the day).

Discrepancies between δ^{18}O and temperature are expected because we are measuring natural samples, and because temperature is not the only parameter controlling the δ^{18}O values. The sampling may be responsible for a value of δ^{18}O higher/lower than what could be expected for a given temperature (a cut too deep for example → old snow). To better discuss the different effects of temperature at condensation and of post-deposition processes (snow/air exchanges) it would be useful to have the isotopic compositions in the precipitation for the same day. However, only the data for the year 2010 are available now for the precipitation at Dome C.

Regarding the event in temperature June/July, that does not correspond to a peak in δ^{18}O, several explanations can be considered. Because sublimation is unlikely in winter, the most plausible scenario is that the snow deposited was blown away.

We note that the peak in temperature is associated with relatively strong wind (6 m/s) and with a strong change of the wind direction which turns to north. Such a change of wind direction could be responsible of erosion of the surface hoar layer (after Champollion et al., 2013).



To answer these questions in the text, we propose the following modification in the manuscript:

p. 6290, l. 14: " Second, **several** short warming events during winter 2011 are also clearly imprinted in the δ^{18}O signal. Because warm events are often associated with precipitation events (Fig. 4), the temperature–δ^{18}O link during these events can result from fresh snow deposition. **Note that the warm event of mid-June (June 17th) is not reflected in the δ^{18}O signal. This may be due to wind erosion and re-deposition of the snow. "**

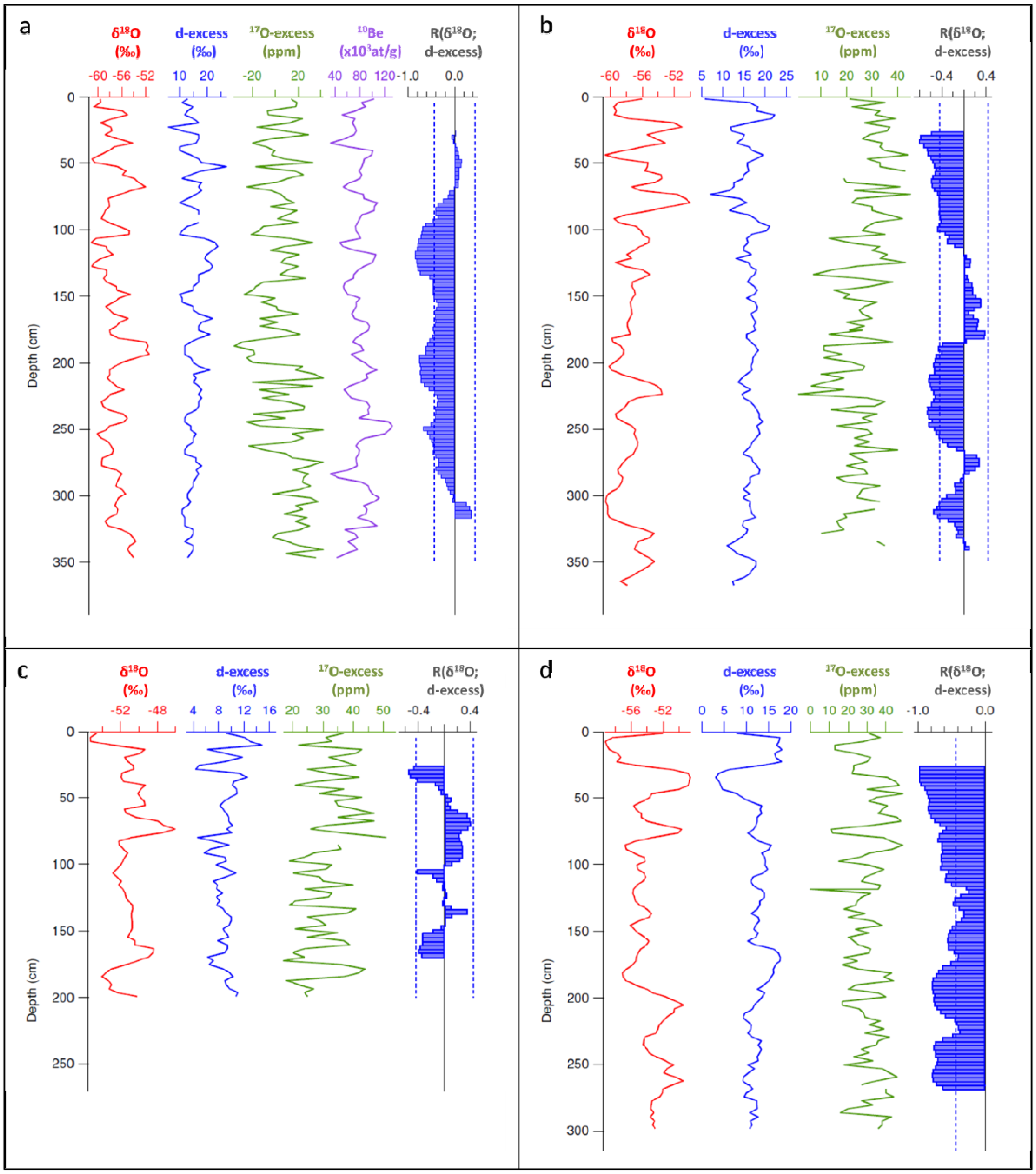
Fig. 5: Why is there no correlation given at the top or bottom of the pit? What does the dotted line mean? If it is the confidence interval write it in the figure caption. What about the correlation changes for δ^{18}O and dexcess?

The correlation was calculated with a 20-point running window, so there are necessarily 19 missing values for the correlation points (R) relative to the original series of isotopic values (**δ^{18}**O, d-excess, ^{17}O-excess). We have chosen to put the first correlation point (corresponding to the first 20-points window of **δ^{18}**O values) in front of the 9th **δ^{18}**O point (middle of the interval for the correlation).

The dotted line corresponds to the limit of significance of the correlation coefficients. The correlation coefficients are significant ($p<0.05$) if they are larger in absolute value than 0.443 (see text, p. 6293, l21).

Addition to the figure caption:
"**Each correlation coefficient R between δ^{18}O and ^{17}O-excess corresponds to a correlation realized over 20 points (see Sect. 4.3). The correlation coefficients are significant when they are larger than 0.443 in absolute values. The limit of significance is displayed as a green dotted line.**"

The correlation coefficients between δ^{18}O and d-excess were computed but not presented on the Figure 5, which was already very dense. We could add them in this figure (but it is already quite small). However we can provide another figure in the supplement (Supp. Fig. 1) with these correlations (see below). For Vostok_winkler (a), Vostok(b), and S2 (d), the correlation coefficients are generally negative. They are particularly strong in absolute value at S2. For Dome C, there is no clear correlation between these two parameters.



Supplementary Figure 1:
Same as Figure 5 except that the correlation coefficients that are displayed (blue bars) are the correlation coefficients between δ^{18}O and d-excess values.

P 6284 L5 If the increase of d excess for decreasing δ^{18}O is linked to distillation is there a possible reason why at -40 the relationship between δ^{18}O and 17O excess changes?

The different reasons behind the different comportments of these two tracers are highlighted in the paragraph 2.3. The increase in d-excess at low δ^{18}O values is due to a combination of kinetic and equilibrium fractionation processes, whereas only the kinetic fractionation affects the ^{17}O-excess. Kinetic fractionation tends to reduce the ^{17}O-excess. This kinetic fractionation becomes stronger when the temperature decreases, since supersaturation increases toward low temperature. As a result, ^{17}O-excess values are more and more depleted toward low temperature. This effect becomes significant in cold environment and particularly when δ^{18}O is below ~-40‰.

We propose the following modification to the text:
p. 6284 l. 25: "… as explained in Jouzel and Merlivat (1984), the anti-correlation between d-excess and δ^{18}O is muted by the existence of the kinetic effect. Indeed, when considering also kinetic effect in addition to equilibrium during solid precipitation, $(\alpha^{D}_{V\text{-}S}–1)/(\alpha^{18}_{V\text{-}S}–1)$ equals 11.4 at –40℃. **Still, the distillation effect dominates over the effect of both equilibrium and kinetic fractionation (0.6x11.4 still remains smaller than 8) and the d-excess tends to increase toward low temperature.**

The decrease of ^{17}O-excess with decreasing temperature is not linked to distillation effect. **Pure equilibrium fractionation in a Rayleigh fractionation with similar dependencies of** α^{17}_{V-S} **and** α^{18}_{V-S} **to temperature (with** $\ln\left(\frac{\alpha^{17}_{V-S}}{\alpha^{18}_{V-S}}\right)=0.528$**) would lead to an increase of ^{17}O-excess toward low temperatures (Landais et al., 2012b; Van Hook, 1968). Actually, the decrease of the ^{17}O-excess toward low temperature is due** to the kinetic effect at condensation. **Indeed, the ratio** $\ln\left(\frac{D}{D^{17}}\right)\Big/\ln\left(\frac{D}{D^{18}}\right)$ **is significantly lower (0.518) than the corresponding ratio between equilibrium fractionation factors and it results in a decrease of the ^{17}O-excess in a Rayleigh distillation system when kinetic effect at condensation is significant.**

When the temperature decreases, the supersaturation in the air mass increases. This enhances the kinetic effect at condensation and leads to a decrease of both ^{17}O-excess and d-excess compared to their evolutions at pure equilibrium.

Technical corrections: I would appreciate a description of the general climatic conditions like mean temperature or wind speed for the study sites Vostok and Dome C. This could either be part of the methods chapter where the different sampling strategies are described or earlier in the introduction. Table 1 gives a good overview but is located too late in the text (p. 6292). It would be helpful to have this information earlier/ before the sampling methods description.

It is true that the description of the climatic conditions at Vostok and Dome C should be presented before the 4th section, since precipitation and surface snow samples were also taken at these sites. Thus we propose to move a part of the "Description of the sampling sites" (Sub-section 4.1) to the "Method" of section 3 ("Temporal variation").

p.6287 l.11: "3.2 Method

Precipitation and surface snow samples come from two stations located on the East Antarctica plateau: Vostok and Dome C (Fig. 1). Climatological characteristics for these stations are listed in Table 1. Vostok and Dome C are both located on top on the east Antarctica plateau in low-accumulation regions (2–3 cm ice eq. yr−1, Table 1). Vostok station is the most remote and highest station. In terms of temperature, Vostok experiences the coldest conditions, and the wind speed is greater at Vostok relative to Dome C (Table 1).

At Vostok, precipitation occur under three forms: snow from clouds, diamond dust, and rime. The duration of precipitation event varies from a few hours to a few days (the latter is typical for diamond dust). The Vostok precipitation sampling has been performed immediately after each precipitation event from December 1999 to December 2000 and can be separated in two datasets. The first"

In the "description of sampling sites", we will reduce the text to avoid repetition:

"Here, we compare the results obtained from snow pits from three localities: Vostok, S2 and Dome C (Fig. 1). **The main characteristics of the sampling sites are described in Table 1. From Dome C to S2, and then to Vostok, the temperature decreases while the altitude increases. Thus the combination of the continental effect and** of the altitudinal effect should lead to decreasing $\delta^{18}O$ values, because of a more advanced distillation at the most remote sites. Interestingly, results from modelling of air parcel trajectories (Reijmer et al., 2002) indicate that air parcels moving toward Vostok pass over Dome C, thus confirming the pathway of the distillation."

Finally, we complete the Table 1 to include more meteorological data (wind speed, air temperature).

	VOSTOK	**S2**	**DOME C**
Latitude	-78.5 °S	-76.3 °S	-75.1 °S
Elevation	3488 m	3229 m	3233 m
Mean annual air T (2 m) air	**-55.2 °C**	**NA**	**-51.7 °C**
Air T coldest month	**-68.0 °C (Aug.)**	**NA**	**-63.5 °C (Jul.)**
Air T hottest month	**-31.8 °C (Dec.)**	**NA**	**-31.3 °C (Jan.)**
10 m borehole T	**-57 °C**	**-55.1 °C**	**-54.9 °C**
Acc. rate (ice eq.)	2.4 cm/y	2.1 cm/y	2.7 cm/y
Wind speed	**5.1 m/s**	**NA**	**3.3 m/s**
Average $\delta^{18}O$	-57.13 ‰* ; -57.06 ‰	-53.81 ‰	-51.14 ‰
Average d-excess	15.3‰*; 16.1‰	12.3 ‰	9.1 ‰
Average ^{17}O-excess	10 ppm* ; 26 ppm	32 ppm	31 ppm

Table 1: Main characteristics of the sites snow pits drilled in East Antarctica on 3 different stations. **Meteorological data for Vostok from** www.aari.ru**.** Data indicated by a * correspond to the snow pit Vostok_winkler **(Winkler et al., 2013).** Accumulation rate (S2) from E. Le Meur et al. 2015/16, the Cryosphere (submitted). Temperature at S2: L. Arnaud, pers. comm. **10 m temperature at Dome C: J. Schwander, unpublished data, 2001. Wind speed at Dome C**

from IPEV/PNRA Project "Routine Meteorological Observation at Station Concordia - www.climantartide.it**.**

Fig. 2: Reference for MCIM factors as on p. 6285 is not given in the figure caption.

The curves on Figure 2 are the same as the curves in Figure 4 of Landais et al., 2012 (S=1-0.002T and S=1-0.004T).

Thus we propose the following modification to the figure caption:
"Terra Nova Bay-Dome C transect) and comparison with modeling outputs (black and grey line: MCIM with **$S = 1-0.004T$ and $S = 1-0.002T$, respectively, from Landais et al., 2012;** dotted line: LMDZ-iso with $S = 1-0.004T$, Risi et al., 2013)"

We also modify slightly the main text:
"Figure 2 shows that a good agreement can be obtained between isotopic data and modeling results when using a simple model of water trajectory (**MCIM**, Ciais and Jouzel, 1994; Landais et al., 2008, 2012) with an appropriate tuning of the supersaturation function (**S = 1–0.0033T or S=1-0.004T according to the tuning of other parameters such as the temperature of solid condensation) (Landais et al., 2012a; Pang et al., 2015; Winkler et al., 2012).** Winkler et al. (2012) discussed in details the tuning of the different parameters of the MCIM to be able to fit together δ^{18}O, d-excess and ^{17}O-excess in central Antarctica and showed that supersaturation is indeed the key parameter to fit the relative evolution of ^{17}O-excess vs. δ^{18}O and d-excess vs. δ^{18}O. When supersaturation is too low (e.g. $S = 1-0.002T$), equilibrium fractionation dominates and modeled ^{17}O-excess and d-excess are too high at low temperature (Fig. 2)."

Fig. 3: This figure is too small. The "a)" and "b)" for the left and right subfigure is not given, however it might be clear that the left one should be "a)". I also would recommend to write "Vostok" and "Dome C" at the top of the figures. In figure 3a) the A (yellow) and B (blue) letters are too small and difficult to find.

Thank you for these remarks, I will provide a new figure, accordingly.

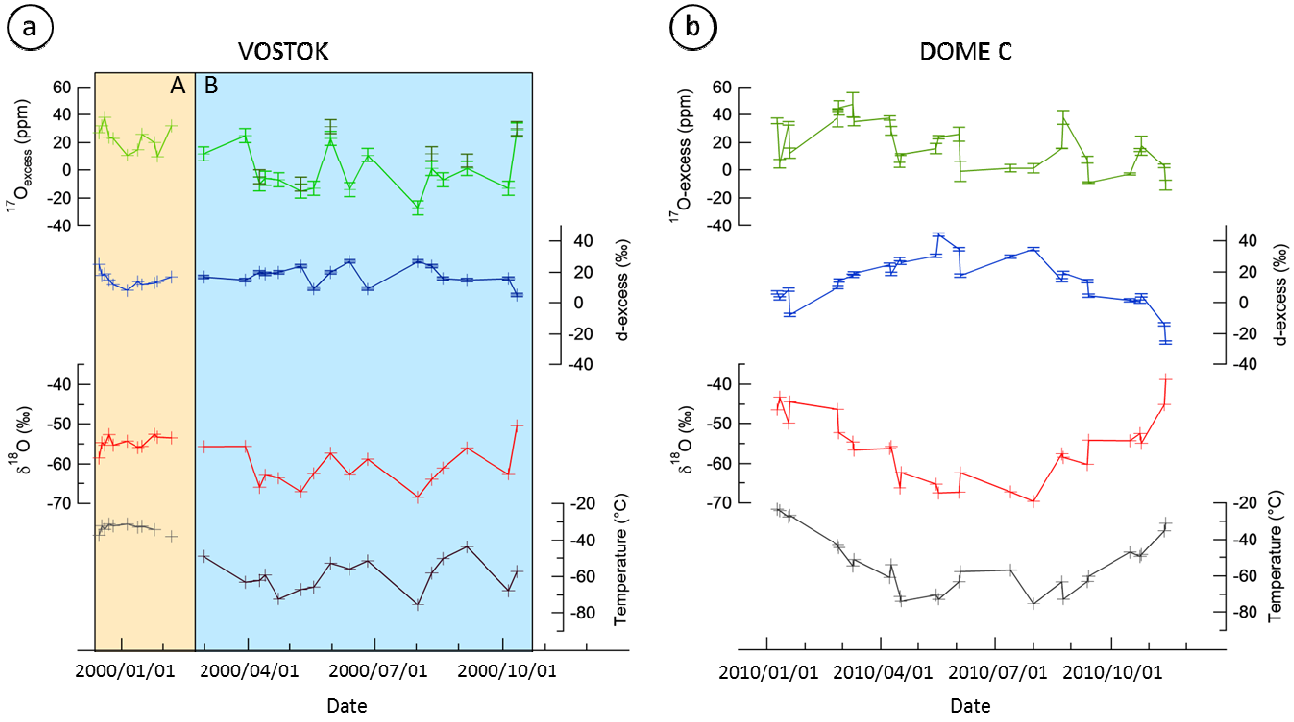


Fig 5: Too small. Reference for Vostok_winkler is not given.

OK, I will add the reference.

Referee 2 S. Li

General comments:

This is a timely and excellent paper compiling a remarkable data set for stable isotopic measurements in high latitude. It is an important contribution to the growing literature on ^{17}O-excess signatures of the hydrologic cycle, past and present. The authors speculate qualitatively on some of the climatic information extracted from the observed isotopic variations in East Antarctica. It should definitely be published following minor revisions.

My main suggestion for the authors is to make their arguments about the data more quantitative. In particular, because some complexity processes such as postdeposition of snow, by their nature, I understand the authors desire not to over-interpret the data. Note that one of the active debates in the cryosphere science is what information does the ice core record. A large dataset like this in snow precipitation, 'upstream' of the where this debate is centered, should be a more comprehensive angle for future research.

The effect of post-deposition processes on the final isotopic compositions in the ice cannot yet be quantitatively assessed. Taking together the various snow samples that we have allows us to show that in some cases, the isotopic compositions (and the links between isotopic parameters) are different from what would be expected under a climatic control. We suggest alternative processes that may be at play. But we do not go as far to assess how much of the original climatic signal remains after the action of post-deposition processes.

The following points can be stressed for the benefit of the ice-core community:

1) From the traverses, we note that the **δ^{18}O** decreases, that the **d-excess** increases and that the **^{17}O-excess** decreases when going toward the center of Antarctica, i.e. toward low temperatures. These evolutions are well explained by the effect of **distillation, associated with equilibrium and (at low temperature) kinetic fractionation**. This pattern serves as reference for the normal behavior of these parameters under a distillation process.
2) The same relationships are observed **in the precipitation** at Vostok (and partly at Dome C) over a season, indicating that the effect of **the distillation at low temperature is also the main control** then.
3) However the **temporal slope δ^{18}O/T in the precipitation is lower than the geographical slope** (and even lower when looking at surface snow). If the smaller (temporal) slope is the true one, then using the geographical slope can lead to an **underestimation of past temperature change from ice cores**.
4) The study of surface snow suggests that **exchanges with atmospheric vapor** in-between precipitation events can modify the isotopic composition in the snow. This modification seems to follow air temperature variations (so it tends to reinforce climatic signal). However, the amplitude of variation of δ^{18}O is also reduced in the surface snow, indicating that post-deposition processes (maybe through mixing) decrease the signal to noise ratio in the snow after deposition. Clearly, **more observations** are needed to understand how the surface snow composition varies. **Numerical models** are also a good option to test **how the composition in the precipitation, or in the vapor, is transmitted to the surface snow and preserved**.
5) In the snow pits, the relationships between isotopic parameters change strongly compared to what is expected from the distillation process. The anti-correlation between

$\delta^{18}O$ and ^{17}O-excess can result **from stratospheric influence** or **post-deposition processes** in the snowpack. The first hypothesis can be tested by looking at other markers of stratospheric influence (^{10}Be, tritium). Regarding post-deposition, modelling what is happening in the snow after deposition is the key to understand and quantify the effect of these processes, and their possible impact for climatic reconstructions from ice-cores.

We have modified the 'Conclusions' section, to better highlight how the isotopic compositions can be modified in the surface snow and in the snowpack, and what are the suggested processes. We also stress the need for more data, and for models of post-deposition processes.

p.6297, l. 6: "From the different types of snow in East Antarctica, we always observe a positive relationship between changes in surface temperature and change in $\delta^{18}O$ of snow, even in the absence of precipitation. **If confirmed by future studies, the correlation between $\delta^{18}O$ of surface snow and temperature in the absence of precipitation in East Antarctica has strong importance for the interpretation of water isotopes in deep ice cores. Indeed, East Antarctica is characterized by very small accumulation rate (even smaller during glacial periods) so that post-deposition effects are expected to have a significant effect. Our findings suggest that post-deposition effects in the surface snow lead to a correlation between $\delta^{18}O$ and temperature. To better understand the exchanges between surface snow and atmospheric vapor, and assess their impact on the isotopic compositions, detailed models focusing on these interactions are needed. In the future, the development of models of post-deposition processes equipped with water isotopes may become the key to the quantitative interpretation of isotopes in ice-cores.**"

Specific comments:
P6279 L3: Here the authors define the two important parameters d-excess and ^{17}O-excess. I suggest putting the definition into context of global meteoric water line, as a better preparation when the authors mention the slopes 8 and 0.528 in P6284 L21 and P6285 L10, respectively.

Thanks for this remark. Please find below the edited text.

p. 6279, l. 1: "In addition to δD and $\delta^{18}O$ records bringing information on temperature at first order, additional climatic information can be retrieved from second order parameters like d-excess (d-excess= δD -8* $\delta^{18}O$) and ^{17}O-excess (^{17}O-excess=ln($\delta^{17}O$+1)-0.528*ln($\delta^{18}O$+1)) (Dansgaard 1964, Barkan & Luz, 2007; Landais et al., 2008). **These parameters represent the y-intercepts of two straight lines, one relating δD and $\delta^{18}O$ with a slope of 8, and the other relating ln($\delta^{17}O$+1) and ln($\delta^{18}O$+1) with a slope of 0.528. Most meteoric and surface waters over the globe fall on a line with a slope of 8 and a y-intercept of 10 in the δD / $\delta^{18}O$ diagram, called the Global Meteoric Water Line (Craig, 1961). However, variations of d-excess values have been observed in waters from various regions around the globe, and have been attributed, in the mid to low latitudes, to regional hydrological conditions (importance of evaporation and precipitation amount). When plotting the isotopic compositions of meteoric waters in a ln($\delta^{17}O$+1)/ln($\delta^{18}O$+1) diagram, they fall on a straight line with a slope of 0.528 (Barkan and Luz, 2007; Landais et al., 2008; Luz and Barkan, 2010; Meijer and Li, 1998). Following the model of the d-excess definition, Barkan and Luz**

(2007) defined the ^{17}O-excess in this diagram, and proposed that it was a tracer of kinetic processes. The fact that δ^{18}O, d-excess and ^{17}O-excess"

P6280 L5: Reference is needed for the information "30ppmv at Vostok, ranging from ~ 1ppmv in winter to ~100 ppmv in summer".

The original value was ~0 mbar in winter, ~0.07 mbar for the annual average and about 0.29 mbar in summer, in the thesis of A. Ekaykin (2003). This vapor pressure corresponds to a relative humidity of 70% (relative to liquid water, with the equation of Goff and Gratch, 1945), relatively constant throughout the year (Ekaykin, 2003). In the manuscript, there was an error in the conversion of these values to water vapor densities. Using the vapor pressure and the temperatures provided by A. Ekaykin (-55.4°C annually and -32.6°C in summer; Ekaykin, 2003), the density of vapor can be calculated as:

The vapor densities obtained are 70 $\cdot 10^{-6}$ kg/m^3 for the annual average and 261$\cdot$ 10^{-6} kg/m^3 for the summer.
They correspond to specific humidity of 464 ppmv and 112 ppmv respectively (using the average annual atmospheric pressure of 625 mbar, Ekaykin et al., 2003).
These values are lower than those observed at Dome C (200-900 ppmv in summer, Casado et al., submitted).

We propose the following modification to the text:

P6280 L2: "**This effect is generally marginal since the amount of water vapor in the stratosphere is very small (a few ppm only). However, it can become significant in East Antarctica where surface humidity is very low (i.e. at Vostok, average specific humidity value is ~112 ppmv and decrease to almost 0 ppmv in winter (Ekaykin, 2003)).**

P6281 L16-19: I suggest putting "(MCIM)" and "(AGCM, LMDZ-iso)" behind the two types of models as preparation for your follow-up discussion.

Thank you for your remark. This is the modified text:
"**For quantitative interpretations, the isotopic measurements are also classically combined to simple isotopic models (such as Mixed Cloud isotopic Model, i.e. MCIM: Ciais and Jouzel, 1994) or more sophisticated general circulation models equipped with water isotopes (AGCM model such as LMDZ-iso: Risi et al., 2010 ; Risi et al., 2013).**"

P6282 L7: Regarding the calculation of supersaturation function: S = 1-aT, people realize that the a value is still not well constrained by observations. But you could mention a common range of "a" values observed in experiments or modeling.

Thanks for this remark.

The 'a' value is obtained by testing various equations for the supersaturation and comparing the model outputs to the data. Depending on the model used the value of 'a' can change markedly.

We can consider three classes of models:
First if we look at **simple parcel models** (models following one air parcel from the source to the precipitation site), the 'a' value can vary greatly depending on the model used and on the

site of origin of the moisture. For example, Petit et al. (1991) propose two different supersaturation functions for sources at 30°S (Si=1.02-0.0038*Tinv) and at 40°S (Si=1.03-0.0025*Tinv). Then for sources at latitudes of 50°C and 60°C (below 15°C), they could not reproduce correctly the observed d-excess distribution with a supersaturation related to temperature by a linear function. Greater values have also been found: Jouzel & Merlivat (1984) propose 'a' value of 0.006, for a source at 20°C and 80% relative humidity. Steen-Larsen et al. (2011) use a very high 'a' for fitting the present-day Greenland δ^{18}O and d-excess values with a simple parcel isotopic model (up to 0.008) (Johnsen et al., 1989).

Second, we consider **more sophisticated parcel models that include a mixed phase (liquid/solid) in the cloud**. The Mixed Cloud Isotope Model by Ciais and Jouzel (1994) has been applied to simulate evolution of air masses by various authors (Vimeux et al., 2002; Masson-Delmotte et al., 2005 ; Winkler et al., 2012). Using this model, fitted on d-excess and δ^{18}O values of the transects (not on ^{17}O-excess), the variability in 'a' values is much more restricted: S= 1-0.002T to 1-0.004T. The function at Vostok using this model remains the same as the one described before (1.02-0.0038 T).

Third, in **General Circulation Models**, the values tested are often on the range 0.003-0.005 (1-0.003T or 1-0.004T : Jouzel et al., 1991; 1-0.004T: Lee et al., 2007; 1-0.004T: Risi et al., 2010; 1-0.004T: Schmidt et al., 2005; 1-0.005T: Tindall et al., 2009; 1.01-0.0045T: Werner et al., 2011).

We propose the following modification:
"where α_{eq} is the fractionation coefficient at equilibrium between vapor and solid, *D* and *D** are the diffusion coefficients of the light and heavy water isotopes in air. In the classical approach, *S* is related to inversion temperature, *T* in °C, at which precipitation is assumed to form, so that $S = 1-aT$ (Ciais and Jouzel, 1994; Jouzel and Merlivat, 1984). The relationship between supersaturation and temperature is not well constrained from atmospheric data. The classical way to adjust the slope a in the different models is to compare water isotopes data and model outputs in polar regions. More precisely, because d-excess is very sensitive to kinetic effects at condensation in cold polar regions, the tuning of the supersaturation relationship to temperature is performed so that the observed relationship between δ^{18}O and d-excess in Antarctica can be reproduced by the model (Ciais and Jouzel, 1994; Risi et al., 2013; Schmidt et al., 2007). **In GCM models, this tuning leads to values for 'a' between 0.003 and 0.005, with recent models (Risi et al., 2010, Lee et al., 2007; Schmidt et al., 2005; Tindall et al., 2009; Werner et al., 2011) favoring values equal or superior to 0.004.** Using the link between ^{17}O-excess and δ^{18}O on polar transects is an additional constraint (Landais et al., 2008; **Winkler et al., 2012;** Pang et al., 2015). **The best fit of an MCIM model to the isotopic compositions (d-excess and ^{17}O-excess) measured on the Terra Nova Bay-Dome C traverse, is obtained with a value for 'a' of 0.0033 (Winkler et al., 2012). Pang et al. (2015) used the same value to fit to the Zhongshan-Dome A traverse. Adequate tuning of** supersaturation is the key to quantitatively interpret the influence of temperature and moisture origin on"

P6283 L28: The authors should be more specific when reporting the standard deviation (1sigma). This may be difficult as this paper compiles a large dataset that includes data from other publications, with different ways of reporting the analytical precision (e.g., pooled standard deviation, Students t-test with certain confidence limits, etc). Even just for the standard deviation, readers will want to know whether it is calculated based on the lab working references or for replicates of each samples (n≥?). Alternatively, you could

re-calculate the precision in a chosen way and describe clearly how you did it, or list all the manners of precision calculation and summarize an upper limit of error.

All the precisions reported are pooled standard deviations. They are computed from duplicate injection, fluorination and IRMS measurements of the same sample. The standard deviation (1σ) for ^{17}O-excess is often 5-6 ppm.

We propose the following modification to the text:
p. 6283, l. 26: “The measurements were calibrated vs. VSMOW and SLAP taking reference values for δ^{18}O and ^{17}O-excess of respectively 0‰ and 0 ppm (or per meg) and −55.5‰ and 0 ppm (Pang et al., 2015; Schoenemann et al., 2013; Winkler et al., 2012). **The pooled standard deviation (1σ) was computed from duplicate injection, fluorination and IRMS measurements of the same sample, and is on average of 5-6 ppm for ^{17}O-excess.”**

P6284 L15 and P6285 L9: The authors should be careful here to “head off careless readers at the pass” by making a distinction between what exponent is intrinsic to a process vs. what exponent is measured. For example, in the case of purely unidirectional kinetic flow, e.g., a Rayleigh fractionation process, the measured slope would express itself in the residue as an array in δ^{17}O vs. δ ^{18}O space with the slope of the line equal to (α^{17} – 1) / (α^{18} – 1) whereas pure diffusion process, the intrinsic slope is calculated as ln(D/D^{17}) / ln(D/D^{18}).

We have rewritten this section to render it more intelligible to the reader:

p. 6284 l. 25: “… as explained in Jouzel and Merlivat (1984), the anti-correlation between d-excess and δ^{18}O is muted by the existence of the kinetic effect. Indeed, when considering also kinetic effect in addition to equilibrium during solid precipitation, $(\alpha^{D}_{V\text{-}S}-1)/(\alpha^{18}_{V\text{-}S}-1)$ equals 11.4 at −40 ℃. **Still, the distillation effect dominates over the effect of both equilibrium and kinetic fractionation (0.6x11.4 still remains smaller than 8) and the d-excess tends to increase toward low temperature.**

The decrease of ^{17}O-excess with decreasing temperature is not linked to distillation effect. **Pure equilibrium fractionation in a Rayleigh distillation with similar dependencies of** α^{17}_{V-S} **and** α^{18}_{V-S} **to temperature (with** $\ln\left(\frac{\alpha^{17}_{V-S}}{\alpha^{18}_{V-S}}\right)=0.528$**) would lead to an increase of ^{17}O-excess toward low temperatures (Landais et al., 2012b; Van Hook, 1968). Actually, the decrease of the ^{17}O-excess toward low temperature is due** to the kinetic effect at condensation. **Indeed, the ratio** $\ln\left(\frac{D}{D^{17}}\right)\Big/\ln\left(\frac{D}{D^{18}}\right)$ **is significantly lower (0.518) than the corresponding ratio between equilibrium fractionation factors and it results in a decrease of the ^{17}O-excess in a Rayleigh distillation system when kinetic effect at condensation is significant.**

When the temperature decreases, the supersaturation in the air mass increases. This enhances the kinetic effect at condensation and leads to a decrease of both ^{17}O-excess and d-excess compared to their evolutions at pure equilibrium.”

P6285 L10: The authors should cite Luz and Barkan (2010), as they pioneered the definition of the slope of meteoric water line as 0.528.

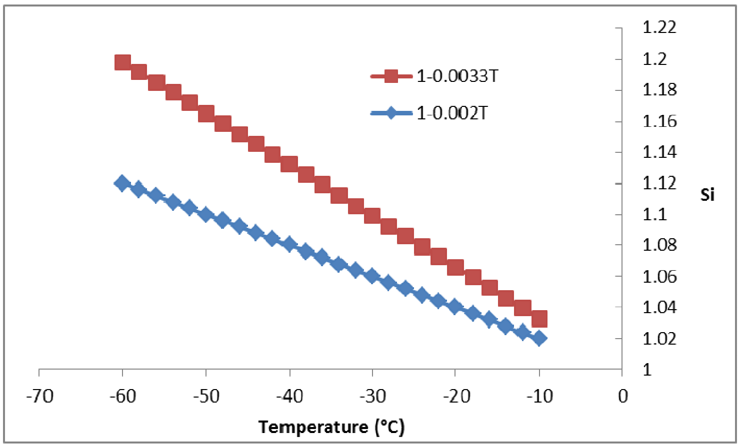
We have added the original references (Meijer and Li, 1998; Barkan and Luz, 2007), but earlier in the text, in the Introduction section.

p. 6279, l. 4: **“When plotting the isotopic compositions of meteoric waters in a ln(δ^{17}O+1)/ln(δ^{18}O+1) diagram, they fall on a straight line with a slope of 0.528 (Barkan and Luz, 2007; Landais et al., 2008; Luz and Barkan, 2010; Meijer and Li, 1998). Following the model of the d-excess definition, Barkan and Luz (2007) defined the ^{17}O-excess in this diagram, and proposed that it was a tracer of climatic conditions at evaporation.** The fact that δ^{18}O, d-excess and ^{17}O-excess”

P6285 L28: Why is S=1-0.002T “too low”? It should represent a stronger supersaturation than S=1-0.0033T does.

First it should be noted that here, the temperature are in Celsius degrees, so T is negative. When T decreases, S increases.

Second, the equation S=1-0.002T has a smaller slope (in absolute value) than the slope for S=1-0.0033T. Thus the increase in supersaturation when temperatures are decreasing is slower. For a same temperature, the supersaturation will be smaller.



P6286 L18: At the end of this line, what does “1” represent? Is there a slope unit missing there?

You are right the unit is missing.
We have modified the text:
“stations of East Antarctica (Dome A, Vostok, Dome C): **1 ‰.°C^{-1}, -1.8 ‰.°C^{-1}** and 0.3 ppm.°C^{-1}.”

P6288 L1: I suggest changing “than” into “as”.

OK.

P6288 L5: In "analyzed in δD and δ^{18}O", I suggest change "in" into "for".
OK.

P6288 L6: Cut off "s" in "samples collection".
OK.

P6288, the last paragraph starting from L25: I would provide the time scheme of the collection of surface snow at Dome C, just as you did in descriptions of precipitation collections. From Fig. 4, is it between Dec 2010 and Dec 2011?

Yes. The sampling took place between Dec. 2010 and Dec. 2011. This is the edited sentence.

"The sampling of surface snow at Dome C has been performed **between December 2010 and December 2011 in the clean area, about 1 km away from Concordia Station, according to the following procedure: each day of collection an area of approximatively 5 m^2 is chosen (different from the previous one) and snow…**"

P6290 L7-21: For the two time slots, what are the R and p values for δ^{18}O-T correlation for each scenario, respectively?
That's a very good question.

- For the first slot (December to March) the correlation was calculated on 10 points (from 2010/12/03 to 2011/03/18, without 2010/12/10 and 2010/02/25 that correspond to precipitation events). The resulting correlation is R=0.77 and the p-value=0.008. Of course this should be confirmed with a larger number of points (daily sampling…).
- For the second slot, the correlation was realized between the 2011/03/18 and the 2011/10/21 (32 points) and the resulting values are: R=0.319 and p-value=0.07. Thus the correlation is not significant for this slot. Even if several warm events are clearly imprinted in the δ^{18}O signal, there are also discrepancies (in particular during the warm event of June/July 2011), and there are not enough points to conclude about the relationship between temperature and δ^{18}O at such short timescales (the annual relationship remains!).

We have modified the text to stress that for these two time slots, the relationships are only suggested for now, and that higher resolution studies are necessary to verify these relationships (and the processes behind).

"As for the surface snow at Dome C, there is a rather good correlation between δ^{18}O and 2m air temperature (Fig. 4) with a global slope of 0.14‰℃$^{-1}$ ($R = 0.54$, $p < 0.05$). This slope is lower than the annual slope in the precipitation at Dome C (0.46‰℃$^{-1}$, $R = 0.88$, $p < 0.05$) and hence much lower than the spatial slope. The fact that temporal slopes are smaller than the spatial ones has to be kept in mind when applying these slopes to past temperature reconstructions. When looking in more detail at the evolution of δ^{18}O over one year, two observations can be made. First, between December 2010 and March 2011, we **observe a long term decreasing** trend of both temperature and surface snow δ^{18}O, in a period associated with only rare precipitations events. **Here the number of points is limited and this correlation should be checked by a higher resolution study. A possible explanation for the joint evolution of these two parameters (between precipitation events) would be surface snow metamorphism and exchange with the atmospheric water vapor as already evidenced in Greenland** (Steen-Larsen et al., 2013). This mechanism is supported by the synchronous prolonged period of hoar formation (Fig. 4), "surface hoar" crystals being the product of water vapor condensation (Champollion et al., 2013). Besides, the porous "surface hoar" could also act as a trap for the rare snow particles and diamond dust (Champollion et al., 2013), therefore facilitating the evolution of the isotopic composition of the snow in the absence of precipitation events. Second, **several short warming events** during winter 2011 are also clearly imprinted in the δ^{18}O signal. Because warm events are often associated with precipitation events (Fig. 4), the temperature–δ^{18}O link during these events can result from fresh snow deposition. **Note that the warm event of mid-June (June 17th) is not reflected in the δ^{18}O signal. This may be due to wind erosion and re-deposition of the snow."**

P6290-6291, for Section 3.3: Figure 3b hints a negative correlation between ^{17}O-excess and d-excess for precipitation at Dome C, which is not observed for either precipitation at Vostok or for surface snow at Dome C.

The labels 'a' and 'b' for Figure 3 were not visible on the pdf, sorry for that!
'a' should correspond to the figure on the left, which is Vostok
'b' should correspond to the figure on the right, which is Dome C
Depending on how which part of the figure you were referring to, we must answer your question differently.

If you were referring to the left figure as Dome C (false):
In fact this figure corresponds to Vostok. We agree that there is a clear anti-correlation at this station between d-excess and ^{17}O-excess. This is coherent with the fact that **δ^{18}**O is anti-correlated to d-excess (R=-0.64) and positively correlated to ^{17}O-excess (R=0.88). While we attribute the first anti-correlation to distillation (kinetic effects being negligible for d-excess), we attribute the second to kinetic effects (only apparent because equilibrium fractionation does not affect ^{17}O-excess). The variations of ^{17}O-excess testify that supersaturation exists, but it is never strong enough to over-compensate the equilibrium fractionation for d-excess.

If you were referring to the right figure as Dome C (which is the truth):
This figure does not show a clear correlation between ^{17}O-excess and d-excess. At the best, what I see is a positive correlation from **jan to mar** and from **oct to nov**, and maybe a negative correlation between **apr and aug**.

- With the same arguments as for Vostok, the possible/proposed negative correlation **in winter** should result from distillation with negligible kinetic effect for d-excess and with sizeable kinetic effect on ^{17}O-excess.
- During **summer**, the positive correlation between d-excess and ^{17}O-excess could theoretically result from very strong supersaturation (leading to low ^{17}O-excess values and low d-excess values). But meteorological data indicates that supersaturation is stronger in winter relative to summer at Vostok, and never reaches values high enough to over-compensate the variations of d-excess caused by equilibrium fractionation. Another explanation for this positive correlation could be a source effect, with conjunct low excesses reflecting evaporation under relatively humid conditions.

Because this is very speculative, we choose not to modify the text.

As the authors discussed in Section 2.3, variation of the slope in δD-δ^{18}O space, and thus d-excess, reflects both equilibrium fractionation during distillation and kinetic effect during supersaturation. Variation in ^{17}O-excess is dominantly controlled by kinetic effects. Then, a combination of ^{17}O-excess and d-excess should help tear apart distillation process from supersaturation condensation.

In an ideal case this is true, but we have still a long way to go before applying this idea. A first thing to do would be to experiment in the lab under very controlled conditions. Then we could for example measure the supersaturation instead of deducing it *a posteriori*. The temperature of condensation would also be measured, instead of estimated from the 2m air temperature.

In the field, the moisture source can change from day to day, as well as the air mass trajectory, and the latter strongly controls the distillation and therefore the final isotopic compositions. Solving the equations for the supersaturation would be easier if the whole trajectory of the air mass was known (each point) instead of only the point of arrival (and a few points in-between that may or may not be under the influence of the same air mass).

Correlation between ^{17}O-excess and d-excess (Fig.3b) should reflect that kinetic effect (supersaturation) in colder conditions is the major control of the isotopic fractionation. Otherwise, the lack of such correlation (Fig.3a and Fig. 4) indicates a less stable/warmer condition, which is consistent with the discussion in P6291 L15- 20, just from another aspect.

While we agree in general with this idea, we prefer not to include this discussion here. Indeed the effect of kinetic fractionation on d-excess at low temperature is often obliterated by the distillation effect.

P6297 L9: I suggest the information in Table 2 to be mentioned earlier in each method sections. This table should be cited along with the figures when any correlation among parameters are discussed throughout the text, so that the readers could have a clearer sense of these relationships.

We agree with this suggestion. We will add the reference to this table throughout the text :

P. 6284 L. 3-9. "All three transects show similar evolutions for the relationships between d-excess and δ^{18}O on the one hand and ^{17}O-excess vs. δ^{18}O on the other hand (Fig. 2, **Table 2**). For δ^{18}O level lower than −40‰, d-excess decreases for increasing δ^{18}O with a slope of −0.95‰‰$^{-1}$. ^{17}O-excess does not exhibit any significant trend if we restrict the data in the range of δ^{18}O > −50‰ as in the Terra Nova Bay – Dome C transect (Fig. 2, **Table 2**). For δ^{18}O values lower than −40 ‰, ^{17}O-excess increases with δ^{18}O with a slope of 0.91 ppm‰$^{-1}$ (Table 2)."

P. 6289 L9-12: "As already observed for other Antarctic sites where δ^{18}O measurements on precipitation samples have been performed, δ^{18}O of falling snow is strongly related to temperature both at Dome C ($R = 0.88$, $p < 0.05$, **Table 2**) and at Vostok ($R = 0.77$, $p < 0.05$, **Table 2**). The annual slope of δ^{18}O vs. temperature is respectively of 0.46 and 0.26‰℃$^{-1}$ at Dome C and Vostok, **Table 2**).

P. 6290 L1-4: “As for the surface snow at Dome C, there is a rather good correlation between δ^{18}O and 2m air temperature (Fig. 4) with a global slope of 0.14‰ ℃$^{-1}$ ($R = 0.54$, $p < 0.05$, **Table 2**).

This slope is lower than the annual slope in the precipitation at Dome C (0.46‰ ℃$^{-1}$, $R = 0.88$, $p < 0.05$, **Table 2**) and hence much lower than the spatial slope.”

P. 6290 L22-25: “ The relationship between d-excess or ^{17}O-excess and δ^{18}O can also help understanding the annual variation of the isotopic composition of the snow. Both for Vostok and Dome C precipitation, d-excess and δ^{18}O are anti-correlated with a slope of −1.61 ($R = -0.88$, $p < 0.05$, **Table 2**) at Dome C and −0.7 at Vostok ($R = -0.64$, $p < 0.05$, **Table 2**).”

P. 6291 L1-2: “is also globally anti-correlated with δ^{18}O over the whole year 2011 with a slope of −0.47‰‰$^{-1}$ ($R = -0.4$, $p < 0.05$, **Table 2**),”

P. 6291 L3-6: “^{17}O-excess of precipitation is significantly correlated with δ^{18}O at Vostok (2.95 ppm‰$^{-1}$, $R = 0.88$, $p < 0.05$, **Table 2**) with a higher slope and correlation coefficient compared to the transect dataset with δ^{18}O < −40‰ (0.91 ppm‰$^{-1}$, $R = 0.36$, $p < 0.05$, **Table 2**).

Interactive comment on “Acquisition of isotopic composition for surface snow in East Antarctica and the links to climatic parameters”

by A. Touzeau et al.

Anonymous Referee #3

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This paper attempts to integrate isotopic variations in Antarctica from a few sets of intensive observations, covering spatial and temporal (seasonal and longer term) trends in surface samples, precipitation, and snow pits. The most novel part of the paper is that ^{17}O-excess is measured along with δ^{18}O and δD for the same samples. Compared to most previous studies, ^{17}O-excess potentially provides additional degrees freedom by which the data can be used to infer and constrain processes related to the moisture evolution. Unfortunately, the integration and interpretation are not as insightful as I expected. There is also at least one fundamental error (General Comment 3) that must be corrected before publication of this manuscript.

General Comments:

1) The framework of interpretation is largely based on simple one source Rayleigh distillation. This implies that the source moisture is constant, although this is not stated explicitly. In recent years, large quantities of data and analysis have demonstrated significant isotopic variations in the marine boundary layer vapor that serves as the beginning of the Rayleigh trajectory. For example, the source can contribute up to 10‰ variations in d-excess (Steen-Larsen et al., 2014). Related to this issue, the source region also influences moisture transport and distillation. Compared to coastal precipitation sites, inland sites tend to get condensed moisture from greater heights, where the moisture has transported (and thus lifted) for a longer distance. While I do not disagree that snow formation may change d-excess and ^{17}O-excess, these additional processes (particularly the variability of the source) should not be ignored. The observed result is a combination of these processes - as well as others. Acknowledgements and discussions about the moisture isotopic property variations at the source as a potential mechanism of their observed isotopic variations should be made in the revised manuscript, and the size of the error attributable to neglect of this mechanism should be evaluated.

We agree with the reviewer that the source has a large effect on the various isotopic parameters studied here, and in particular, on d-excess and ^{17}O-excess.

The sensitivity of the snow and ice isotopic composition (δ^{18}O, d-excess, ^{17}O-excess) to the temperature and relative humidity at the source as well as to the site temperature has been extensively studied in the last decade.

Sensitivity of ΔδD				
Dome C, Stenni et al., 2001:	$\Delta\delta D =$	$7.6\,\Delta T_{site}$	$-3.5\,\Delta T_{source}$	$+5.0\,\Delta\delta^{18}O_{ocean}$
Vostok, Vimeux et al., 2002:	$\Delta\delta D =$	$7.1\,\Delta T_{site}$	$-3.7\,\Delta T_{source}$	$+4.8\,\Delta\delta^{18}O_{ocean}$
Dome F, Uemura et al., 2012:	$\Delta\delta D_{corr} =$	$7.7\,\Delta T_{site}$	$-3.2\,\Delta T_{source}$	

The main control over the δD value is the temperature of the site, but the source temperature has also an impact.

Sensitivity of Δd					
Vostok, Stenni et al., 2001	$\Delta d =$	$-0.5\,\Delta T_{site}$	$+1.3\,\Delta T_{source}$	$-2.6\,\Delta\delta^{18}O_{ocean}$	
Vostok, Vimeux et al., 2002	$\Delta d =$	$-0.5\,\Delta T_{site}$	$+1.3\,\Delta T_{source}$	$-2.8\,\Delta\delta^{18}O_{ocean}$	
Vostok, Landais et al., 2009	$\Delta d =$	$-1.0\,\Delta T_{site}$	$+1.4\,\Delta T_{source}$	$-2.8\,\Delta\delta^{18}O_{ocean}$	$-0.12\Delta RH_{source}$
Vostok, Risi et al., 2010	$\Delta d_{corr} =$	$-1.1\,\Delta T_{site}$	$+1.5\,\Delta T_{source}$		$-0.38\Delta RH_{source}$
East Antarctica, **Winkler et al., 2012**	$\Delta d =$	$-\begin{pmatrix} 1.29 \\ to\ 2.04 \end{pmatrix}\Delta T_{site}$	$+\begin{pmatrix} 1.31 \\ to\ 1.5 \end{pmatrix}\Delta T_{source}$	$-3\Delta\delta^{18}O_{ocean}$	$-\begin{pmatrix} 0.045 \\ to\ 0.095 \end{pmatrix}\Delta RH_{n}$
Dome F, Uemura et al., 2012	$\Delta d_{corr} =$	$-1.3\,\Delta T_{site}$	$+1.6\,\Delta T_{source}$		
Dome A, Pang et al., 2015	$\Delta d =$	$-1.8\,\Delta T_{site}$	$+1.6\,\Delta T_{source}$		$-0.18\Delta RH_{source}$

Regarding the d-excess, a change of a few Celsius degrees at the source can lead to a change of a few ‰ in d-excess values (with sensitivities of ~1.4‰·°C^{-1}). When we compare this amplitude of variation to the amplitude of variations observed, it seems evident that they are not the main factor behind the variability in the snow.

In Figure 1, the source effect is probably responsible for the scattering of the data points, for values of $\delta^{18}O$ between -20‰ and -40‰; but it cannot explain the higher values obtained for $\delta^{18}O$ values below -50‰. In Figure 3-5, the variability at seasonal and interannual scale is of 10-20‰, largely higher than the few ‰ expected from the variability of the source temperature.

The d-excess sensitivity to the variations of the site temperature is of the same order than the sensitivity to source temperature (1.1‰·°C^{-1} instead of 1.3‰·°C^{-1}). But because the site temperature can vary more widely than the source temperature, the effect of the site temperature on d-excess is generally dominant. Moreover, if you consider a high supersaturation (corresponding to very low temperatures), the sensitivity of d-excess to the site temperature can reach values up to -2.9‰·°C^{-1} (Winkler et al., 2013), almost three times the sensitivity to the source temperature.

The sensitivity to the relative humidity at the source is about -0.1‰%$^{-1}$ (Winkler et al., 2013). Thus seasonal/interannual variations in the humidity at the source of about 10% are not large enough to account for more than one per mil of variation in d-excess.

Sensitivity of Δ^{17}O-excess				
Vostok, Landais et al., 2009	$\Delta^{17}O_{excess} =$			$-0.9\Delta RH_{source}(\%)$
East Antarctica, **Winkler et al., 2012**	$\Delta^{17}O_{excess} =$	$-\begin{pmatrix} -0.2 \\ to\ 0.5 \end{pmatrix}\Delta T_{site}$	$+\begin{pmatrix} 0.34 \\ to\ 0.61 \end{pmatrix}\Delta T_{source}$	$-\begin{pmatrix} 0.86 \\ to\ 1.1 \end{pmatrix}\Delta RH_{n}(\%)$
Dome A, **Pang et al., 2015**	$\Delta^{17}O_{excess} =$	$-(-0.33)\Delta T_{site}$		$-(1.1)\Delta RH(\%)$

The ^{17}O-excess is particularly sensitive to the relative humidity at the source (1 ppm·%$^{-1}$). A change of 10% of the relative humidity can lead to a change of ~10 ppm in the snow. A change of a few Celsius degree of the source temperature will lead to only a few ppm of variation and therefore is negligible compared to the variability associated with relative humidity. The sensitivity to the site temperature is also relatively small, but becomes higher at low temperatures, when the supersaturation increases. Winkler et al. (2013) propose an upper estimate of this sensitivity at Vostok of 3.6 ppm·°C^{-1}. Then a change of a few Celsius degrees of

T_{site} could lead to a change of ~10 ppm of ^{17}O-excess values, equivalent to the change expected from humidity variations.

In Figure 2, the relative stability of the ^{17}O-excess values (and their scattering) between δ^{18}O values of -20 and -40‰, probably indicate that the original signature of relative humidity remains well preserved as long as the temperature is not too low. Between δ^{18}O values of -40 and -60‰, there is also a large scattering, but in average the ^{17}O-excess changes from +30 ppm to +10 ppm. This shift of 20 ppm can only by explained by the effect of supersaturation, because it exceeds the variability expected from variations in the source relative humidity or temperature.

In Figures 3-5, weekly/seasonal/interannual variability of ^{17}O-excess reaches 30 to 40‰, and again, this range of variation can only result from the effect of the supersaturation at very low temperatures.

To better acknowledge and quantify the source contribution to the variability of the isotopic parameters in polar snow, we propose the following modifications to the text:

In the Introduction:
p. 6279, l. 20: "Presence of sea ice at the oceanic water evaporative regions may also contribute to the d-excess and ^{17}O-excess signal (Gao et al., 2011; Schoenemann et al., 2014). **However, at very low temperatures, and therefore in the central regions of Antarctica, the d-excess and ^{17}O-excess in the precipitation become much more sensitive to the temperature of condensation than in the coastal regions. By using two parameters (for instance δ^{18}O and d-excess) it remains possible to separate the influence of the source temperature from the influence of the local temperature, as was done in central Greenland (Masson-Delmotte et al., 2005; Jouzel et al., 2005) and more recently in East Antarctica (Uemura et al., 2012) with a sensitivity of polar d-excess to source temperature of 1.5‰·°C^{-1} (Risi et al., 2010) and a sensitivity of polar ^{17}O-excess to source relative humidity of -0.9 ppm·%$^{-1}$ (Landais et al., 2009).** Because ^{17}O-excess is less sensitive to temperature than d-excess, **the site** temperature influence on ^{17}O-excess is only perceptible in very remote sites of East Antarctica (Winkler et al., 2012). Finally, ^{17}O-excess may also bear the signature…"

In the Discussion of the transects (Section 2.3):

p. 6284, l. 11:
"**For δ^{18}O values between -20 and -40‰, there is a large scattering of the d-excess values, with no clear trend. This can be due to a variability of the climatic conditions (temperature and relative humidity) at the source. For δ^{18}O values below -40‰, d-excess values are clearly anti-correlated with the δ^{18}O values and change from ~4‰ to about 25‰. Such a change cannot be due to a change of the relative humidity of the source nor to a change of the source temperature that could explain only a few per mil changes. Thus, the increase of d-excess for decreasing δ^{18}O values is probably caused by the fractionation at condensation during the distillation. This increase of d-excess is directly related to a decrease of the slope (dδD/dδ^{18}O) of the distillation line towards low δ18O values (i.e. low temperatures).** Indeed, in the"

p. 6285, l. 13: "In turn, the evolution of d-excess and ^{17}O-excess at low temperature can help tuning the kinetic effect (Eq. 1) and especially the dependency of supersaturation to temperature. **A change in the source region of the water vapor also influences ^{17}O-excess and d-excess at low temperature, but cannot by itself explain the decrease in ^{17}O-excess**

from about 30 ppm to about 10 ppm between $\delta^{18}O$ values of -50 and -60‰ (Figure 2). Following Winkler et al. (2012), we estimate that the effect of relative humidity would not be more than 10 ppm and the effect of a change of temperature, not more than 3 ppm.

In the discussion of the precipitation:

p. 6290, l. 24: The relationship between d-excess or ^{17}O-excess and $\delta^{18}O$ can also help understanding the annual variation of the isotopic composition of the snow. **Here the annual amplitude of variation (10-20 ‰ for d-excess and 30-40 ppm for ^{17}O-excess) suggests that the main control is the site temperature, because other parameters such as source temperature and relative humidity would not account for more than a few per mil for d-excess or more than 10 ppm for ^{17}O-excess (Winkler et al., 2012).**

In the discussion of the snow pits:

p. 6294, l. 18: "Global Spearman's correlations led to significant negative correlations between $d^{18}O$ and d-excess for S2, Vostok and Vostok_winkler. These negative correlations are consistent with those already detected in the snow from transects and in the precipitation, and therefore with a distillation process. **An effect of the source is also possible, but not sufficient to explain the large amplitude of variations in d-excess and ^{17}O-excess (10-20 ‰ for d-excess and 30-40 ppm for ^{17}O-excess).**"

2) **One reviewer was disappointed that the data interpretation was not more quantitative. I agree. Ideally, a simple Rayleigh model (since they really emphasize Rayleigh processes) including both d-excess and ^{17}O-excess, should be used to interpret the data, which would have made the paper more interesting, more informative and more original. I do recognize that this task may lead to its own independent contribution. Therefore, I support publication of this paper if all the data are included in the supplementary material (it seems to me). Other investigators may use the data for additional interpretation and modeling.**

It is true that modelling is useful to understand the mechanisms behind the natural variations of isotopic ratios. We are aware of this and we incidentally say so in the paper. However, some modelling had already been done on this data, and it was not useful to duplicate these studies and their conclusions.

For example, the MCIM model outputs that we present are from Landais et al. (2012) and were already compared in the original publication to the seasonal variations in the precipitation at Vostok. Their conclusions were that: 1) At Vostok, the MCIM, with a tuning of $S=1-0.004T$, correctly reproduces the annual relationships between $\delta^{18}O$, d-excess and ^{17}O-excess. 2) However, the relation between isotopic parameters and surface temperature is not well reproduced, either because of an error in the relationship between surface temperature and condensation temperature, or because of a change of the moisture source between seasons.

Pang et al. (2015) and Winkler et al. (2012) have compared the results of MCIM simulations to the Terra Nova Bay-Dome C transect and the Zhongshang–Dome A transect. They found the same tuning of the supersaturation function (S=1-0.0033). Pang et al. (2015) stressed that the source used for their tuning is not the same as the source obtained from retro-trajectories and discussed the limits of MCIM modelling.

Regarding the modelling of the seasonal variations in the precipitation at Dome C, since our dataset is only a small subset of a 3-year measurement campaign, it seems more relevant to compare modelling outputs to the entire dataset (even if it means waiting a bit longer for the conclusions…) in order to have more robust conclusions. The paper on the entire dataset, by Barbara Stenni and others, is on preparation.

And for the surface snow, processes other than the Rayleigh distillation are expected (in particular post-deposition processes). They require a detailed model of the interactions between the surface snow and the atmosphere and are beyond the scope of this paper.

Note that all the data used for the various figures is available in the supplementary tables.

3) **One mistake has to be corrected before publication. Equation 2 is the basis for discussions of d-excess through a Rayleigh process, in which condensation occurs upon cooling. However, this equation is not appropriate for the discussion. Equation 2 is derived from the integrated Rayleigh equation for delta values of liquid based on the unstated assumption that the isotopic fractionation factor between liquid and vapor is constant. Therefore, this relationship is not applicable to an explanation of changing slope with temperature along a single Rayleigh trajectory, which is exactly what they did. Obviously there is a logical contradiction, i.e., assuming no temperature change to obtain the equation and then using the equation to discuss the effect of temperature change. What Equation 2 does allow is a comparison of slopes for CONSTANT-fractionation Rayleigh distillation processes at two different temperatures. This comparison would be pointless, however. A valid argument has to be based on a Rayleigh process with cooling. In this case, the cooling history would have to be provided. The slope change during simple cooling scenarios, such as adiabatic or isobaric cooling, was discussed by Dansgaard (1964), a half-century ago. Therefore, Equation 2 and related discussions have to be removed or redone based on correct Rayleigh curves. (It is also unacceptable that neither they gave the source of the equation, nor did they state the assumption for its derivation.)**

It is true that we did not justify enough where Equation 2 comes from. In the following we have tried to clarify how we arrive at this equation. We have also modified the text (see below) to better explain the origin of this equation to the reader.

The Equation 2 was not derived from the integrated Rayleigh equation. However it is based on the Rayleigh model, and therefore on two hypotheses:
“**the condensed phase is formed at isotopic equilibrium with the surrounding vapor** and **is immediately removed from the air mass after its formation**.” (after Jouzel & Merlivat, 1984)

Using these hypotheses it is possible to compute the isotopic composition of the remaining vapor as:

$$\frac{d\delta_v}{1+\delta_v} = (\alpha - 1)\frac{dm_v}{m_v}$$

(Equation 1 in Jouzel & Merlivat, 1984)

This is the differentiated form of the Rayleigh equation, not the integrated one. It is an equation to determine the local slope at a given moment, with no assumption on the previous or subsequent distillation trajectory. In fact, this equation is deduced from a simple mass balance, and applying the hypotheses that fractionation occurs at equilibrium and that the condensed form is immediately removed.

Locally, when a small quantity of snow is produced, it is produced at equilibrium so its composition is:

$$R_{sn}^{18} = R_v^{18} \cdot \alpha_{eq}^{18}$$

The mass balance indicates that following this production of a small amount of snow, the ratio in the vapor is modified:

$$R_{v,end}^{18} \cdot m_{v,end} = R_v^{18} \cdot m_v + R_{sn}^{18} \cdot dm_v$$

(Note that here $dm_v<0$, since vapor is precipitated and extracted from the air mass; R_{sn}^{18} is the ratio in the snow that is precipitated)

$$R_{v,end}^{18} \cdot m_{v,end} = R_v^{18} \cdot m_v + R_v^{18} \cdot \alpha_{eq}^{18} \cdot dm_v$$

$$R_{v,end}^{18} \cdot m_{v,end} = R_v^{18} \cdot \left(m_v + \alpha_{eq}^{18} \cdot dm_v\right)$$

$$R_{v,end}^{18} = \frac{R_v^{18} \cdot \left(m_v + \alpha_{eq}^{18} \cdot dm_v\right)}{m_{v,end}}$$

The change in the ratio in the vapor due to the precipitation is:

$$dR_v^{18} = R_{v,end}^{18} - R_v^{18} = \frac{R_v^{18} \cdot \left(m_v + \alpha_{eq}^{18} \cdot dm_v - m_v - dm_v\right)}{m_v + dm_v} = \frac{R_v^{18} \cdot \left(\alpha_{eq}^{18} - 1\right) \cdot dm_v}{m_v + dm_v}$$

This is almost the same equation as the equation by Jouzel and Merlivat (1984) except for the dm_v at the denominator (which is negligible relative to m_v). However the denominators cancel out when we compute the slope $\frac{d\delta D}{d\delta^{18}O}$ (see below) so this is of little consequence.

Similarly for the deuterium ratio:

$$dR_v^D = \frac{R_v^D \cdot \left(\alpha_{eq}^D - 1\right) \cdot dm_v}{m_v + dm_v}$$

Then we have:

$$\frac{dR_v^D}{dR_v^{18}} = \frac{R_v^D \cdot \left(1 - \alpha_{eq}^D\right)}{R_v^{18} \cdot \left(1 - \alpha_{eq}^{18}\right)}$$

And then:

$$\frac{d\delta D}{d\delta^{18}O} = \frac{(\delta D + 1)\cdot(1 - \alpha_{eq}^{D})}{(\delta^{18}O + 1)\cdot(1 - \alpha_{eq}^{18})}$$

During this precipitation of a very small quantity of snow, very locally, the temperature does not change (so the two fractionation coefficients are constant).
We then apply this local differential equation at 2 points (0℃ and -40℃). The fractionation coefficients in that case depend only on the chosen temperature (no hypothesis on the trajectory). The delta values depend of course of the distillation history, but here we do not use precise values. The only important issue for our calculation is to compare 1+δ to 1. Close to the coast 1+δ is not significantly different from 1 (δ^{18}O~-20‰ and δD~-140‰ at Zhongshang) whereas far in the interior we consider that it is no longer the case (δ^{18}O~-60‰ and δD~-450‰ i.e. 1+δD~0.65 at Dome A).

Since Equation 2 is valid at any point during the distillation process, it does not seem necessary to modify our conclusions that are based on this equation.

To clarify the origin of the equation, we propose the following modification to the text:

"Indeed, in the case of simple Rayleigh distillation**, when the snow precipitated is immediately removed from the air mass and when only equilibrium fractionation occurs,** we can express **the local slope** of the **Rayleigh's distillation** line **at a given point as**:

$$\frac{d\delta D}{d\delta^{18}O} = \frac{(\alpha_{V-S}^{D} - 1)}{(\alpha_{V-S}^{18} - 1)} \times \frac{(1 + \delta D)}{(1 + \delta^{18}O)}$$

This slope expression comes from a simple mass balance associated with a condensation step, with a small amount of snow precipitated at equilibrium and thus removed from the vapor. No assumption is made on the previous distillation path."

Specific Comments:
P6281, last paragraph through P6282 first paragraph: The idea of tuning is to assume that ALL the changes in d-excess from coast to inland is caused by kinetic fractionation during snow formation. This assumption has to be stated explicitly. With that I do not understanding how, after tuning, the information about the source can be extracted without circular reasoning. Also see my General Comment 1 about contribution of isotopic variations at the moisture source region.

It is a fact that, in simple models, only one source is defined, and there is a continuous distillation towards the defined point of arrival. So, of course, the effect of various sources of moisture is not taken into account (except if your repeat the experiment with another point of origin). However, in GCMs, multiple moisture sources may exist for a single site of precipitation, because the dynamics of the atmosphere exists in the model and air masses can be mixed. Thus, if the tuning with a simple parcel model neglects the effect of varying moistures sources, the tuning using GCMs include this effect.

When we use simple models (and in particular the MCIM model) and compare the model outputs to transect data to tune the supersaturation dependency on temperature, we are aware that the effect of source variability is included in the data, but is absent from the model. In order to

reduce the bias the tuning the supersaturation is realized mostly on the last part of the traverse (δ^{18}O values below -40‰). For this part of the traverse, the effect of the supersaturation dominates and the source effect is reduced.
Between interior sites located 4° apart in latitude (i.e. Dome C ~75°S and Vostok~79°S), the change in temperature at the source deduced from the relative contributions of the various source regions (from Delaygue et al., 2000) is very limited (Dome C: 8.3°C in summer and 12.1°C in winter; Vostok: 7.4°C in summer and 12.4°C in winter). It seems that the intra-annual variability at a site is much higher (~5°C) than the variability between sites (~1°C). Using a value of 1.4‰·°C^{-1} (Winkler et al., 2012) for the sensitivity of d-excess to source temperature, a change of 1°C would only lead to an increase of 1.4‰ of d-excess due to the change in source temperature between the two sites.
For the Zhongshang-Dome A traverse, keeping only the values of δ^{18}O below -40‰ corresponds to keeping the latitudes between 73°S and 80°S. This corresponds to a change of 7° in latitude and potentially to a change of 2°C of the annual temperature of the source. Thus again the change in d-excess expected from the source contribution is small (a few ‰) and negligible compared to the geographical variation of d-excess observed on the traverses (from 5 to 20‰).

Locally, however, at a given site, the source effects are much more important, in particular if you look at intra-annual or even intra-seasonal scales. The variability in the ratios at this time scale is controlled by the changes in air masses and the variations in the local temperature of condensation (both through equilibrium and kinetic fractionation). Using the estimated dependency of the supersaturation to the temperature (from model-data comparison), the temperature effects can be known (since the temperature itself is deduced from δ^{18}O), and the rest of the variation attributed to other causes, for example moisture sources. This is what we were meaning with our last sentence.
p.6282, l. 16: This tuning of supersaturation is the key to quantitatively interpret the influence of temperature and moisture origin on δ^{18}O, d-excess and ^{17}O-excess, especially in deep ice core records (Masson-Delmotte et al., 2005; Stenni et al., 2010; Winkler et al., 2012).

P6284, line 14: Please distinguish the "meteoric water line" (MWL) from "Rayleigh line" (you should definite latter term). These two are fundamentally different. At best, the Rayleigh line is an interpretation of the MWL.

You are right, this sentence was a little confusing, because the Rayleigh line result from a model and the meteoric water line from observations, and also because we said “THE meteoric water line”, which could be understood as a reference to “THE Global Meteoric Water Line”. To better convey our meaning we propose the following modification:

“Indeed, in the case of simple Rayleigh distillation**, when the snow precipitated is immediately removed from the air mass and when only equilibrium fractionation occurs,** we can express **the local slope** of the **Rayleigh’s distillation line at a given point as**:

$$\frac{d\delta D}{d\delta^{18}O} = \frac{(\alpha^{D}_{V-S} - 1)}{(\alpha^{18}_{V-S} - 1)} \times \frac{(1 + \delta D)}{(1 + \delta^{18}O)}$$

This slope expression comes from a simple mass balance at a given point of the line, with a small amount of snow precipitated at equilibrium and thus removed from the vapor. No assumption is made on the previous distillation path.”

P6284, Equation 2. See my General Comment 3. Please fix all the discussions and conclusions based on this equation.

We have explained above that our discussion is based on a differentiated equation, and clarified this aspect in the text.

P6288, line 18: "interpolated". Do you mean "extrapolated"?

Yes, we have modified the text.

"These dilutions and associated measurements have shown that the SMOW-SLAP calibration for δ^{18}O on our instrument can be **extrapolated** down to –90 ‰."

Acquisition of isotopic composition for surface snow in East Antarctica and the links to climatic parameters.

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Abstract

The isotopic composition of oxygen and hydrogen in ice cores are invaluable tools for the reconstruction of past climate variations. Used alone, they give insights into the variations of the local temperature, whereas taken together they can provide information on the climatic conditions at the point of origin of the moisture. However, recent analyses of snow from shallow pits indicate that the climatic signal can become erased in very low accumulation regions, due to local processes of snow reworking. The signal to noise ratio decreases and the climatic signal can then only be retrieved using stacks of several snow pits. Obviously, the signal is not completely lost at this stage, otherwise it would be impossible to extract valuable climate information from ice cores as has been done, for instance, for the last glaciation. To better understand how the climatic signal is passed from the precipitation to the snow, we present here results from varied snow samples from East Antarctica. First, we look at the relationship between isotopes and temperature from a geographical point of view, using results from three traverses across Antarctica, to see how the relationship is built up through the distillation process. We also take advantage of these measures to see how second order parameters (d-excess and ^{17}O-excess) are related to δ^{18}O and how they are controlled. d-excess increases in the interior of the continent (i.e. when δ^{18}O decreases), due to the distillation process, whereas ^{17}O-excess decreases in remote areas, due to kinetic fractionation at low temperature. In both cases, these changes are associated with the loss

of original information regarding the source. Then, we look at the same relationships in precipitation samples collected over one year at Dome C and Vostok, as well as in surface snow at Dome C. We note that the slope of the δ^{18}O **vs temperature (*T*)** relationship decreases in these samples compared to those from the traverses, and thus advocate caution when using spatial slopes for past climate reconstruction. The second-order parameters behave in the same way in the precipitation as in the surface snow from traverses, indicating that similar processes are active **and that their interpretation in terms of source climatic parameters is strongly complicated by local temperature effects in East Antarctica**. Finally we check if the same relationships between δ^{18}O and second-order parameters are also found in the snow from four snow pits. While the d-excess remains opposed to δ^{18}O in most snow pits, the ^{17}O-excess is no longer positively correlated to δ^{18}O and even shows anti-correlation to δ^{18}O at Vostok. This may be due to a stratospheric influence at this site and/or to post-deposition processes.

1. Introduction

Water isotopic composition of shallow and deep ice cores has long been used for reconstructing past climatic conditions in polar regions (Jouzel et al., 2007; Küttel et al., 2012; Schneider et al., 2006). The correlation between temperature and $\delta^{18}O$ in polar regions is explained by the progressive relative loss of heavy isotopes with respect to the light ones during distillation of the water mass along its trajectory from warm to cold regions. However, more and more recent studies are evidencing that the water isotopic composition ($\delta^{18}O$ or δD) in shallow snow pits in Antarctica does not follow the recent (last 50 years) temporal evolution of temperature, especially in regions of very low accumulation like the East Antarctic plateau (Ekaykin et al., 2002; Ekaykin et al., 2004; Hoshina et al., 2014; Winkler et al., 2013). Post-depositional effects at the snow surface (Sokratov and Golubev, 2009) are responsible for a large noise, i.e. a non-climatic signal, in water isotopic records. This non-climatic signal can be shaped by many local effects such as surface relief, accumulation rate (Ekaykin et al., 2004) or temperature gradient in surface snow (Town et al., 2008). The situation is however improved when working on stacks of several shallow pits from which a climatic signal can be extracted (Altnau et al., 2015; Ekaykin et al., 2014; Schneider et al., 2006). In addition, the fact that $\delta^{18}O$ or δD records in deep ice cores are providing robust and high resolution records of past temperature over the last glacial period clearly confirms the direct link between temperature and water isotopic composition of surface snow. Accordingly, either the post-depositional noise is not strong enough to entirely erase the original climatic signal, or some of the post-deposition processes are under the control of local temperature and thus reinstate a link between $\delta^{18}O$ and temperature.

In addition to δD and $\delta^{18}O$ records bringing information on temperature at first order, additional climatic information can be retrieved from second order parameters like d-excess (d-excess = $\delta D - 8* \delta^{18}O$) and ^{17}O-excess ($^{17}O\text{-excess}=\ln(\delta^{17}O+1)-0.528*\ln(\delta^{18}O+1)$) (Dansgaard, 1964; Barkan and Luz, 2007; Landais et al., 2008). **These parameters represent the y-intercepts of two straight lines, one relating δD and $\delta^{18}O$ with a slope of 8, and the other relating $\ln(\delta^{17}O+1)$ and $\ln(\delta^{18}O+1)$ with a slope of 0.528. Most meteoric and surface waters over the globe fall on a line with a slope of 8 and a y-intercept of 10 in the δD / $\delta^{18}O$ diagram, called the Global Meteoric Water Line (Craig, 1961). However, variations of d-excess values have been observed in waters from various regions around the globe, and have been attributed, in the mid to low latitudes, to regional hydrological conditions (importance of evaporation and precipitation amount). When plotting the isotopic compositions of meteoric waters in a $\ln(\delta^{17}O+1)/\ln(\delta^{18}O+1)$ diagram, they fall on a straight line with a slope of 0.528 (Barkan and Luz, 2007; Landais et al., 2008; Luz and Barkan, 2010; Meijer and Li, 1998). Following the model of the d-excess definition, Barkan and Luz (2007) defined the ^{17}O-excess in this diagram, and proposed that it was a tracer of climatic conditions at evaporation. The fact that $\delta^{18}O$, d-excess and ^{17}O-excess** bear slightly different climatic information is due to influences of both equilibrium and kinetic fractionation processes on the water isotopic composition. **Equilibrium and kinetic fractionation** effects are induced by differences in saturation vapor pressure and diffusivities among isotopes, respectively. The different water isotopes exhibit different sensitivities to equilibrium and kinetic fractionation leading to variations in d-excess and ^{17}O-excess. At low latitudes, both d-excess and ^{17}O-excess will be sensitive to relative humidity during evaporation because of large variations in kinetic fractionation (Gat, 1996; Uemura et al., 2010; Uemura et al., 2008). However, along the distillation process, the influence of relative humidity on d-excess is fading away to the benefit of the temperature gradient between the source and the precipitation site through equilibrium fractionation (Petit et al., 1991; Vimeux et al., 1999).

For coastal stations of Antarctica, ^{17}O-excess and d-excess are markers of water origin, mainly temperature for d-excess (Delmotte et al., 2000; Kurita, 2011; Schlosser et al., 2008) and relative humidity for ^{17}O-excess (Winkler et al., 2012). Presence of sea ice at the oceanic water evaporative regions may also contribute to the d-excess and ^{17}O-excess signal (Gao et al., 2011; Schoenemann et al., 2014). **However, at very low temperatures, and therefore in the central regions of Antarctica, the d-excess and ^{17}O-excess in the precipitation become much more sensitive to the temperature of condensation than in the coastal regions. By using the different isotopic parameters, it remains possible to separate the influence of the source temperature from the influence of the local temperature, as was done in central Greenland (Masson-Delmotte et al., 2005; Jouzel et al., 2005) and more recently in East Antarctica (Uemura et al., 2012) with a sensitivity of polar d-excess to source temperature of 1.5‰.°C^{-1} (Risi et al., 2010) and a sensitivity of polar ^{17}O-excess to source relative humidity of -0.9 ppm.%$^{-1}$ (Landais et al., 2009).** Because ^{17}O-excess is less sensitive to temperature than d-excess, **the site** temperature influence on ^{17}O-excess is only perceptible in very remote sites of East Antarctica (Winkler et al., 2012). Finally, ^{17}O-excess may also bear the signature of stratospheric input since photochemical reactions involving ozone can affect the triple isotopic composition of oxygen in water in the stratosphere (Franz and Röckmann, 2005; Lin et al., 2013; Winkler et al., 2013; Zahn et al., 2006). This effect is generally marginal since the amount of water vapor in the stratosphere is very small (a few ppm only). However, it can become significant in East Antarctica where surface humidity is very low (**i.e. at Vostok, average specific humidity value is ~112 ppmv and decrease to almost 0 ppmv in winter (Ekaykin, 2003)).**

The goal of this study is to understand how a climatic and environmental signature can be imprinted in the water isotopic composition of surface snow in remote East Antarctica. Our strategy is to make an optimal use of the combination of all water stable isotopes (δD, $\delta^{17}O$, $\delta^{18}O$) in different types of snow on the Antarctic plateau (precipitation, surface snow, buried snow) to disentangle temperature, water cycle and stratospheric influences.

The outline of our study is the following. In Sect. 2, we present the spatial distribution of water isotopic composition averaged in the top 30 cm of surface snow in East Antarctica with a focus on the remote East Antarctic plateau. In Sect. 3, we present variations of isotopic composition of precipitation and surface snow on two drilling sites in East Antarctica (Dome C, Vostok). Section 4 is a multi-isotope compilation of new data on several snow pits in East Antarctica. Each section is organized in three sub-sections: an introductive state of the art, a description of new measurements and results, and a discussion. The final discussion shows that the multi-isotopes approach at different sites with similar temperature and accumulation rate characteristics is a useful tool to identify the main drivers for the water isotopic variations observed on shallow ice cores and to test the origin of the $\delta^{18}O$ variations classically interpreted in term of past temperature changes.

2. Spatial variations of d-excess vs $\delta^{18}O$ and ^{17}O-excess vs $\delta^{18}O$ in Antarctic transects

2.1. State of the art

The measurements of water isotopic composition in Antarctic transects have first provided a spatial relationship of 0.8 ‰.°C^{-1} between surface temperature and $\delta^{18}O$ in snow (Lorius and

Merlivat, 1977; Masson-Delmotte et al., 2008). Applications of this relationship for reconstructing past temperature from records of $\delta^{18}O$ in ice cores have however revealed some limitations because of combined influences of the seasonality of precipitations, origin of moisture, variations in elevation or post-deposition effects (e.g. Charles et al., 1994; Fawcett et al., 1997; Hoshina et al., 2014; Jouzel et al., 2003; Krinner et al., 1997; Masson-Delmotte et al., 2012; Neumann et al., 2005). Changes in moisture source, post-deposition effects and ice condensation are associated with kinetic fractionation effects. As a consequence, ^{17}O-excess and d-excess are useful tools to disentangle the different influences on water isotopic composition in ice cores and hence improve our knowledge of the $\delta^{18}O$ vs temperature relationship.

For quantitative interpretations, the isotopic measurements are also classically combined to simple isotopic models (**such as Mixed Cloud Isotope Model**, i.e. MCIM, Ciais and Jouzel, 1994) or more sophisticated general circulation models equipped with water isotopes (**AGCM model such as LMDZ-iso: Risi** et al., 2010; Risi et al., 2013). The aim of such model – data approach is twofold. First, the comparison of data and model on the present-day spatial repartition of water isotopic composition in Antarctica is essential for the validation of the implementation of water isotopes in the model. Second, the use of isotopic models is essential to quantitatively interpret the water isotopic records in deep ice cores and translate them in records of climatic parameters (e.g. local temperature).

The model-data comparison over polar transects enables the correct implementation of the relative influences of kinetic vs equilibrium fractionation processes during snow formation. These different influences are balanced through the expression of the supersaturation function, *S*, in the formulation of the fractionation coefficient ($\alpha_{v\text{-}s}$) during snow formation so that:

$$\alpha_{V-S} = \frac{S}{(S-1)\,D/D^{*} + 1/\alpha_{eq}} \qquad (1)$$

where α_{eq} is the fractionation coefficient at equilibrium between vapor and solid, D and D^* are the diffusion coefficients of the light and heavy water isotopes in air. In the classical approach, S is related to inversion temperature, T in °C, at which precipitation is assumed to form, so that S=1-aT (Ciais and Jouzel, 1994; Jouzel and Merlivat, 1984). The relationship between supersaturation and temperature is not well constrained from atmospheric data. The classical way to adjust the slope a in the different models is to compare water isotopes data and model outputs in polar regions. More precisely, because d-excess is very sensitive to kinetic effects at condensation in cold polar regions, the tuning of the supersaturation relationship to temperature is performed so that the observed relationship between δ^{18}O and d-excess in Antarctica can be reproduced by the model (Ciais and Jouzel, 1994; Risi et al., 2013; Schmidt et al., 2007). **In GCM models, this tuning leads to values for *a* between 0.003 and 0.005, with recent models (Risi et al., 2010, Lee et al., 2007; Schmidt et al., 2005; Tindall et al., 2009; Werner et al., 2011) favoring values equal or superior to 0.004.** Using the link between ^{17}O-excess and δ^{18}O on polar transects is an additional constraint (Landais et al., 2008; Pang et al., 2015). **The best fit of an MCIM model to the isotopic compositions (d-excess and ^{17}O-excess) measured on the Terra Nova Bay-Dome C traverse, is obtained with a value for *a* of 0.0033 (Winkler et al., 2012). Pang et al. (2015) used the same value to fit to the Zhongshan-Dome A traverse. Adequate tuning of** supersaturation is the key to quantitatively interpret the influence of temperature and moisture origin on δ^{18}O, d-excess and ^{17}O-excess, especially in deep ice core records (Masson-Delmotte et al., 2005; Stenni et al., 2010; Winkler et al., 2012).

The longest ice core records (Dome C, Dome F, and Vostok) are located in the cold and dry regions of East Antarctica (EPICA comm. members, 2004; Kawamura et al., 2007; Petit et al., 1999). In these cold regions, the kinetic fractionation is very strong because of high supersaturation level. The influence of kinetic fractionation on water isotopic composition is even stronger in glacial climatic conditions. In order to quantitatively interpret these glacial isotopic records, the expression of kinetic fractionation during snow formation should be known precisely at very low temperature. Unfortunately, there are barely any present-day analog for the glacial conditions encountered at Dome F, Vostok and Dome C. To better document the water isotopic composition of snow in extremely cold regions of Antarctica, and to improve the tuning of the supersaturation function, recent transects have been performed toward remote regions of the East Antarctic plateau (e.g. Becagli et al., 2004; Fujita et al., 2011; Masson-Delmotte et al., 2008; Mayewski and Goodwin, 1999; Pang et al., 2015).

2.2.Measurements and results

We present here a compilation of existing and new transect data combining the measurements of all water stable isotopes (δ^{18}O, d-excess and ^{17}O-excess). The first transect combining these surface measurements was obtained within the ITASE project (Magand et al., 2004; Mayewski and Goodwin, 1999; Mayewski et al., 2005) between Terra Nova Bay and Dome C (***Fig. 1***) and water isotopic data were already published (Landais et al., 2008; Proposito et al., 2002). The second transect was performed between Zhongshan station and Dome A (***Fig. 1***) during the CHINARE expedition and water isotopic data were published in Pang et al. (2015). Finally, we present new water isotopic records from a transect obtained between Syowa, Dome Fuji, and EPICA DML (***Fig. 1***) through a Swedish-Japanese project (Fujita et al., 2011).

The surface snow samples were obtained from shallow pits on which the average water isotopic composition was measured. These pits had a depth of 1 m for the Terra-Nova Bay-Dome C traverse (Proposito et al., 2002; Magand et al., 2004), 10 cm for the

Zhongshang-Dome A traverse (Pang et al., 2015) and 10 to 30 centimeters for the Syowa-Dome F traverse. Because the accumulation decreases from the coast towards the inland sites, the period recorded, for the first transect, varies from 2 years near the coast to 12 years at Dome C. For the Chinese traverse, the recorded period varies from one year in inland areas to 3 months in coastal areas. For the Syowa-Dome F traverse, the pits were shallower at inland sites (10 centimeters) and deeper at coastal sites in order to record at least one year in each sample. For the 3 transects presented here, ^{17}O-excess measurements were obtained by fluorination method of water to oxygen (Barkan and Luz, 2005) followed by dual inlet measurements of produced oxygen vs a reference oxygen standard. Measurements of the Terra Nova Bay-Dome C transect were performed at the Hebrew University of Jerusalem Israël (HUJI) using a Delta V mass spectrometer. Measurements of the two other transects were performed in France at the Climate and Environment Sciences Laboratory (LSCE) on a MAT 253 instrument. The measurements were calibrated vs VSMOW and SLAP taking reference values for δ^{18}O and ^{17}O-excess of respectively 0 ‰ and 0 ppm (or per meg) and -55.5 ‰ and 0 ppm (Pang et al., 2015; Schoenemann et al., 2013; Winkler et al., 2012). **The pooled standard deviation (1σ) was computed from duplicate injection, fluorination and IRMS measurements of the same sample, and is on average of 5-6 ppm for ^{17}O-excess.** The δ^{18}O and d-excess measurements for Syowa-Dome Fuji transect were performed using an equilibration method (Uemura et al., 2007) at National Institute of Polar Research, Japan.

All three transects show similar evolutions for the relationships between d-excess and δ^{18}O on the one hand and ^{17}O-excess vs δ^{18}O on the other hand (***Fig. 2, Table 2***). For δ^{18}O level lower than -40 ‰, d-excess decreases for increasing δ^{18}O with a slope of -0.95‰.‰$^{-1}$. ^{17}O-excess does not exhibit any significant trend if we restrict the data in the range of δ^{18}O > -50 ‰ as in the Terra

Nova Bay – Dome C transect (***Fig. 2, Table 2***). For δ^{18}O values lower than -40 ‰, ^{17}O-excess increases with δ^{18}O with a slope of 0.91 ppm.‰$^{-1}$ (***Table 2***).

2.3.Discussion

For δ^{18}O values between -20 and -40‰, there is a large scattering of the d-excess values, with no clear trend. This can be due to a variability of the climatic conditions (temperature and relative humidity) at the source. For δ^{18}O values below -40‰, d-excess values are clearly anti-correlated with the δ^{18}O values and change from ~4‰ to about 25‰. Such a change cannot be due to a change of the relative humidity of the source nor to a change of the source temperature that could explain only a few per mil changes. Thus, the increase of d-excess for decreasing δ^{18}O values is probably caused by the fractionation at condensation during the distillation. This increase of d-excess is directly related to a decrease of the slope (dδD/dδ^{18}O) of the distillation line towards low δ^{18}O values (i.e. low temperatures). Indeed, in the case of simple Rayleigh distillation, **when the snow precipitated is immediately removed from the air mass and when only equilibrium fractionation occurs**, we can express the **local slope** of the **Rayleigh's distillation line at a given point** as:

$$\frac{d\delta D}{d\delta^{18}O} = \frac{(\alpha^{D}_{V-S} - 1)}{(\alpha^{18}_{V-S} - 1)} \times \frac{(1+\delta D)}{(1+\delta^{18}O)} \qquad (2)$$

This slope expression comes from a simple mass balance associated with a condensation step, with a small amount of snow precipitated at equilibrium and thus removed from the vapor. No assumption is made on the previous distillation path. When considering only equilibrium, $(\alpha^{D}_{V-S} - 1)/(\alpha^{18}_{V-S} - 1)$ equals 8.7 at 0 °C and then increases for lower temperature (it equals 10.1 at -40 °C). However, when distillation increases, the ratio

$(1+\delta D)/(1+\delta^{18}O)$ does no longer equal 1 and 1+δD reaches values lower than 0.6 (corresponding to δD lower than -400 ‰) in East Antarctica. The combined effect of distillation and equilibrium fractionation at low temperature leads to a slope of the meteoric water line smaller than 8 at about -40 °C (i.e. 0.6 × 10.1 is smaller than 8). The distillation effect is thus responsible for the decrease of the slope of the meteoric water line and hence the increase of d-excess for cold regions. Still, as explained in Jouzel and Merlivat (1984), the anti-correlation between d-excess and $\delta^{18}O$ is muted by the existence of the kinetic effect. Indeed, when considering also kinetic effect in addition to equilibrium during solid precipitation, $(\alpha^{D}_{V-S}-1)/(\alpha^{18}_{V-S}-1)$ equals 11.4 at -40 °C. **Still, the distillation effect dominates over the effect of both equilibrium and kinetic fractionation (0.6 × 11.4 still remains smaller than 8) and the d-excess tends to increase toward low temperature.**

The decrease of ^{17}O-excess with decreasing temperature is not linked to distillation effect. **Pure equilibrium fractionation in a Rayleigh distillation with similar dependencies of** α^{17}_{V-S} **and** α^{18}_{V-S} **to temperature (with** $\ln\left(\alpha^{17}_{V-S}/\alpha^{18}_{V-S}\right)=0.528$**) would lead to an increase of** ^{17}**O-excess toward low temperatures (Landais et al., 2012b; Van Hook, 1968). Actually, the decrease of the** ^{17}**O-excess toward low temperature is due** to the kinetic effect at condensation. **Indeed, the ratio** $\ln\left(D/D^{17}\right)/\ln\left(D/D^{18}\right)$ **is significantly lower (0.518) than the corresponding ratio between equilibrium fractionation factors and it results in a decrease of the** ^{17}**O-excess in a Rayleigh distillation system when kinetic effect at condensation is significant.**

When the temperature decreases, the supersaturation in the air mass increases. This enhances the kinetic effect at condensation and leads to a decrease of both ^{17}O-excess and d-excess compared to their evolutions at pure equilibrium. In turn, the evolution of d-excess and ^{17}O-excess at low temperature can help tuning the kinetic effect (equation 1) and especially the dependency of supersaturation to temperature. **A change in the source region of the water vapor also influences ^{17}O-excess and d-excess at low temperature, but cannot by itself explain the observed decrease in ^{17}O-excess from about 30 ppm to about 10 ppm between δ^{18}O values of -50 and -60‰ (Fig. 2). Following Winkler et al. (2012) we estimate that the effect of relative humidity would not be more than 10 ppm and the effect of a change of temperature, not more than 3 ppm.**

The three transect datasets are of primary interest to constrain the fractionation formulation between vapor and snow in remote regions of Antarctica as has already be done in previous publications (Landais et al., 2008; Pang et al., 2015; Winkler et al., 2012). We give here two examples for this tuning using published modeling experiments incorporating all stable water isotopes. ***Fig. 2*** shows that a good agreement can be obtained between isotopic data and modeling results when using a simple model of water trajectory (**MCIM**, Ciais and Jouzel, 1994; Landais et al., 2008) with an appropriate tuning of the supersaturation function (**S=1-0.0033T or S=1-0.004T according to the tuning of other parameters such as the temperature of solid condensation) (Landais et al., 2012a; Pang et al., 2015; Winkler et al., 2012**). Winkler et al. (2012) discussed in details the tuning of the different parameters of the MCIM to be able to fit together δ^{18}O, d-excess and ^{17}O-excess in central Antarctica and showed that supersaturation is indeed the key parameter to fit the relative evolution of ^{17}O-excess vs δ^{18}O and d-excess vs δ^{18}O. When supersaturation is too low (e.g. S=1-0.002T), equilibrium fractionation dominates and modeled ^{17}O-excess and d-excess are too high at low temperature (***Fig. 2***).

Things are more complicated when using AGCM equipped with water isotopes. ***Figure 2*** shows that a d-excess increase and ^{17}O-excess decrease for decreasing δ^{18}O are also predicted by the LMDZ-iso model with an appropriate supersaturation function (S=1-0.004T, Risi et al., 2013). However, the modeled δ^{18}O values are not low enough in Antarctica thus leading to a strong discrepancy between the East Antarctica datasets and the modeling outputs. One of the main reasons for this disagreement is that temperatures in Antarctica are not cold enough in the LMDZ model. The overestimation of polar temperature is a common bias of CMIP5-PMIP3 simulations (e.g. Cauquoin et al., 2015b; Risi et al., 2010; Werner, 2011). This problem might be linked to the general poor representation of the polar atmospheric boundary layer and related atmospheric inversion temperatures in GCMs (e.g. Krinner et al., 1997). Future improvements in the incorporation of the water isotopes in AGCM should take advantage of the transect data presented here.

Finally, the combined measurements of water isotopes along the three transects are essential to quantify the temperature influence on $\delta^{18}O$, d-excess and ^{17}O-excess. Using the supersaturation tuning on the transect data, Winkler et al. (2012) and Pang et al. (2015) found the following influences of temperature on $\delta^{18}O$, d-excess and ^{17}O-excess in the remote drilling stations of East Antarctica (Dome A, Vostok, Dome C): 1 ‰.°C^{-1}, -1.8 ‰.°C^{-1} and 0.3 ppm.°C^{-1}. These determinations are in agreement with the recent estimates by Uemura et al. (2012) for the Dome F d-excess and $\delta^{18}O$ sensitivity to temperature.

3. Temporal variation of the water isotopic composition on the East Antarctic plateau.

3.1.Introduction

While the spatial relationship between $\delta^{18}O$ and temperature has long been the reference to link $\delta^{18}O$ records in ice cores to past temperature variations (Jouzel et al., 2013), numerous studies have shown the limitations of such approach because climate influences $\delta^{18}O$ in a complex way (see 2.1). One way to capture the uncertainty associated with such reconstruction is to evaluate the temporal dependency of $\delta^{18}O$ to temperature. In this section, we thus estimate the relationship between temperature and water isotopes in precipitating snow over one year and the relationship between temperature and water isotopes in the surface snow on the same site. Because isotopic composition archived in ice core probably results both from the isotopic composition of the precipitation and from post-deposition effect, we study the annual relationship between the isotopic composition of snow and the temperature, both on precipitation samples and on surface snow sampled every week.

3.2.Method

Precipitation and surface snow samples come from two stations located on the East Antarctica plateau: Vostok and Dome C (Fig. 1). Climatological characteristics for these stations are listed in Table 1. Vostok and Dome C are both located on top on the east Antarctica plateau in low-accumulation regions (2–3 cm ice eq. yr−1, Table 1). Vostok station is the most remote and highest station. In terms of temperature, Vostok experiences the coldest conditions, and the wind speed is greater at Vostok relative to Dome C (Table 1).

At Vostok, precipitation occur under three forms: snow from clouds, diamond dust, and rime. The duration of precipitation event vary from a few hours to a few days (the latter is typical for diamond dust). The Vostok precipitation sampling has been performed immediately after each precipitation event from December 1999 to December 2000 and can be separated in two datasets. The first one (series A) corresponds to sampling from precipitation trap placed at 1.5 m above the snow surface and at ~50 m windward from the station (**Landais et al., 2012a**). Samples collected in this trap consist of pure precipitation as ascertained by the calm weather conditions and absence of blowing snow at the time of collection. **Sublimation in the trap is unlikely for two reasons. First, the high walls of the trap shaded the precipitation within it. Second, most of the samples were collected in winter, when insolation is minimal.** The second series (B) corresponds to sampling from a lower precipitation trap buried with its upper edge at the snow surface. Thus the flow of blowing snow around the trap was unimpeded and the snow collected consists of a mixture of precipitation and blowing snow. **After the collection, the samples from the two series were melted, poured into special plastic bottles and frozen again. This procedure was followed to avoid alteration of the initial isotopic composition of precipitation due to sublimation and exchange with the atmospheric water vapor. Sample volume varied between 1 mL (diamond dust) and 10-20 mL ("heavy" precipitation).**

The δD, δ^{8}O and ^{17}O-excess measurements for the 16 samples of series A (**Fig. 3a, blue panel: Feb. 2000-Sept. 2000**) have been published in Landais et al. (**2012a**). δ^{18}O and d-excess measurements were performed at Geophysics Department, Niels Bohr Institute, University of Copenhagen, while ^{17}O-excess was measured at HUJI using a Delta V instrument (duplicate measurements of ^{17}O-excess were also realized at LSCE for 6 samples). The 11 samples of series B were measured in the same institutions **as** the samples of series A (**Fig. 3a, yellow panel: Dec. 1999-Feb. 2000**).

The Dome C precipitation sampling is performed continuously since December 2007 in the frame **of the Italian glaciology program at Concordia station**. Almost 100 samples are collected every year and analyzed **for** δD and δ^{18}O. Here, we present only a subset of this **sample** collection from January to December 2010 (***Fig. 3b***). Unfortunately, samples from the year 2011 (period when the surface snow was sampled, see the last paragraph of this section) were not available. The ^{17}O-excess has been measured at LSCE using the fluorination method followed by dual inlet analysis on a MAT 253 as for the transect samples of previous section (Sect. 2) and Vostok precipitation samples.

It should be noted that some δ^{18}O values presented on ***Fig. 3*** are significantly lower than the δ^{18}O value of the SLAP (-55.5‰). The classical two point calibration SMOW-SLAP is thus possibly not valid here. We have addressed the δ^{18}O calibration issue for very low δ^{18}O values by diluting well characterized standards with almost pure $H_2{}^{16}O$ (Isotec Water-16O from Sigma-Aldrich; Casado et al., submitted). These dilutions and associated measurements have shown that the SMOW-SLAP calibration for δ^{18}O on our instrument can be **extrapolated** down to -90‰. It was not possible to make the same exercise with ^{17}O-excess because the water with almost pure $H_2{}^{16}O$ (99.98%, Casado et al., submitted) was not characterized in $H_2{}^{17}O$ content. Still, measurements of much depleted δ^{18}O samples on different mass spectrometers suggest that we may create biases of up to 10 ppm in the ^{17}O-excess values expressed in a SMOW-SLAP scale. Mean ^{17}O-excess values associated with $\delta^{18}O<-55.5$‰ and performed on different mass spectrometers may therefore not be directly comparable.

The sampling of surface snow at Dome C has been performed between December 2010 and December 2011, in the clean area, about 1 km away from Concordia Station, according to the following procedure: each day of collection an area of approximatively 5 m^2 is chosen (different from the previous one) and snow is scrapped on 5 to 10 spots (ca 0.04 m^2) within this area. This variability is due to the necessity to collect enough snow for later analysis. Only the first 1-2 mm of snow are collected, using a metal blade. The snow collected is homogenized and melted, and a fraction destined for isotopic analysis is transferred into a 20mL vial and then kept frozen until analysis. In every 5 m^2 area, sastrugis are avoided, but otherwise (i.e. on flat areas) the sampling is performed randomly

and no distinction is made between snow types: drifted snow, wind crust, soft, hard, and hoar snow are sampled indiscriminately. The aim is to sample all types of snow present during the day of sampling to access the average composition of the surface snow in direct contact of the atmosphere. On this set of samples, $\delta^{18}O$ and δD have been measured by a wavelength scanned cavity ring-down spectroscopy instrument (Picarro L2130i) with a resulting uncertainty of $1\sigma = 0.05‰$ for $\delta^{18}O$ and 0.5‰ for δD. As for the other new ^{17}O-excess data presented in this manuscript, we used here the fluorination method coupled with dual inlet mass spectrometry (MAT 253) with a resulting uncertainty $1\sigma = 5$ ppm.

3.3.Discussion

As already observed for other Antarctic sites where $\delta^{18}O$ measurements on precipitation samples have been performed, $\delta^{18}O$ of falling snow is strongly related to temperature both at Dome C (R=0.88, $p<0.05$, ***Table 2***) and at Vostok (R=0.77, $p<0.05$, ***Table 2***). The annual slope of $\delta^{18}O$ vs temperature is respectively of 0.46 ‰.°C^{-1} and 0.26 ‰.°C^{-1} at Dome C and Vostok (***Table 2***). The annual slope at Dome C is comparable to the one observed at Dome F for a similar temperature level (0.47 to 0.78 ‰.°C^{-1}, Fujita and Abe, 2006; Motoyama et al., 2005) while the Vostok seasonal $\delta^{18}O$ vs temperature slope is significantly lower. Using only the samples of series A (instead of A+B) increases slightly the annual slope at Vostok (0.35 ‰.°C^{-1}) suggesting that this low slope can result from post-deposition noise (i.e. blowing snow with an isotopic composition different from the one of the falling snow). Several other possible explanations have already been evoked to explain this low slope (Ekaykin, 2003; Landais et al., **2012a**) such as a strong gradient between condensation and surface temperature at Vostok when precipitation occurred, or a change in the type of precipitation at Vostok (possible high contribution of diamond dust in precipitation). However, we should also note that at Vostok, we have only a small number of water samples corresponding to precipitation events associated with the largest amount of snow. These large precipitation events are associated with relatively high temperature in winter. Such selection of particular precipitation events may also have an influence on the final $\delta^{18}O$ vs temperature slope so that we avoid speculating on this particular value with so few data points (26 at Vostok).

As for the surface snow at Dome C, there is a rather good correlation between $\delta^{18}O$ and 2 m air temperature (***Fig. 4***) with a global slope of 0.14 ‰.°C^{-1} (R=0.54, p<0.05, ***Table 2***). This slope is lower than the annual slope in the precipitation at Dome C (0.46‰.°C^{-1}, R=0.88, p<0.05, ***Table 2***) and hence much lower than the spatial slope. The fact that temporal slopes are smaller than the spatial ones has to be kept in mind when applying these slopes to past temperature reconstructions. When looking in more detail at the evolution of $\delta^{18}O$ over one year, two observations can be made. First, between December 2010 and March 2011, we **observe a long term decreasing trend** of both temperature and surface snow $\delta^{18}O$, in a period associated with only rare precipitations events. **Here the number of points is limited and this correlation should be checked by a higher resolution study. A possible explanation for the joint evolution of these two parameters (between precipitation events) would be surface snow metamorphism and exchange with the atmospheric water vapor as already evidenced in Greenland** (**Casado et al., submitted; Ritter et al., 2016;** Steen-Larsen et al., 2013). This mechanism is supported by the synchronous prolonged period of hoar formation ***(Fig. 4)***, 'surface hoar' crystals being the product of water vapor condensation (Champollion et al., 2013). Besides, the porous 'surface hoar' could also act as a trap for the rare snow particles and diamond dust (Champollion et al., 2013), therefore facilitating the evolution of the isotopic composition of the snow in the absence of precipitation events. Second, **several short warming events** during winter 2011 are also clearly imprinted in the $\delta^{18}O$ signal. Because warm events are often associated with precipitation events (***Fig. 4***), the temperature-$\delta^{18}O$ link during these events can result from fresh snow deposition. **Note that the warm event of mid-June (June 17th) is not reflected in the $\delta^{18}O$ signal. This may be due to wind erosion and re-deposition of the snow.**

The relationship between d-excess or ^{17}O-excess and $\delta^{18}O$ can also help understanding the annual variation of the isotopic composition of the snow. **Here the annual amplitude of variation (10-20 ‰ for d-excess and 30-40 ppm for ^{17}O-excess) suggests that the main control is the site temperature, because other parameters such as source temperature and relative humidity would not account for more than a few per mil for d-excess or more than 10 ppm for ^{17}O-excess (Winkler et al., 2012).** Both for Vostok and Dome C precipitation, d-excess and $\delta^{18}O$ are anti-correlated with a slope of **-1.61 ‰.‰$^{-1}$** (R=-0.88, p<0.05, ***Table 2***) at Dome C and -0.7 at Vostok (R=-0.64, p<0.05, ***Table 2***). Even if there is a large difference between the two slopes, this anti-correlation is expected and has already been observed with similar values (1 to 2 ‰.‰$^{-1}$) on the transect data: for $\delta^{18}O$ level below -40 ‰, we observe a clear an anti-correlation between $\delta^{18}O$ and d-excess linked to the effect of distillation. In the surface snow at Dome C, d-excess is also globally anti-correlated with $\delta^{18}O$ over the whole year 2011 with a slope of -0.47 ‰.‰$^{-1}$ (R=-0.4, p<0.05, ***Table 2***), indicating that the effect of the distillation process is still perceptible in the surface snow but somehow obscured by another process.

^{17}O-excess of precipitation is significantly correlated with $\delta^{18}O$ at Vostok (2.95 ppm.‰$^{-1}$, R=0.88, p<0.05, ***Table 2***) with a higher slope and correlation coefficient compared to the transect dataset with $\delta^{18}O$ < -40‰ (0.91 ppm.‰$^{-1}$, R=0.36, p<0.05, ***Table 2***). On the opposite, no clear relationship can be drawn from the ^{17}O-excess vs $\delta^{18}O$ values in the precipitation at Dome C even if sampling at both sites encompasses the same range of $\delta^{18}O$ values down to -70 ‰ and surface temperature down to -75 °C. Such result suggests that the kinetic effect during condensation is not the only driver for ^{17}O-excess variations in East Antarctica. The analysis of the surface snow at Dome C, however, shows a small (but significant) correlation between ^{17}O-excess and $\delta^{18}O$. How can this correlation exist in the surface snow and not (significantly) in the precipitation at the same site? We propose two hypotheses to this phenomenon. First, at Dome C the annual cycle of temperature in 2010 is very well defined and do not show the frequent warming events (up to -50 °C) observed during the winter in 2011 at Dome C and in 2000 at Vostok. In other words, natural variability may be the cause of these differences, with a winter 2010 experiencing more stable (and therefore colder) conditions than the winter 2000 and 2011 and thus reduced correlation between ^{17}O-excess and $\delta^{18}O$. Alternatively, the post-deposition processes within the snow could be responsible for a renewed correlation between ^{17}O-excess and $\delta^{18}O$.

4. Variability of water isotopic composition in snow pits

4.1.Description of the sampling sites

The next step to understand the archiving of the water isotopic composition is to look at the combined water isotopes on short snow pits at different places in Antarctica. The isotopic composition on snow pits will indeed be influenced by the isotopic composition of snow precipitation, diamond dust deposition and post-deposition effects involving exchanges with the atmospheric water vapor. Many isotopic measurements have been performed on snow pits in Antarctica (e.g. Altnau et al., 2015; Ekaykin et al., 2014) but except the study from Winkler et al.

(2013) focusing on one shallow pit only in Vostok, none of the previous studies have combined measurements of all stable water isotopes.

Here, we compare the results obtained from snow pits from three localities: Vostok, S2 and Dome C (***Fig. 1***). **The main characteristics of the sampling sites are described in Table 1. From Dome C to S2, and then to Vostok, the temperature decreases while the altitude increases. Thus the combination of the continental effect** and of the altitudinal effect should lead to decreasing $\delta^{18}O$ values, because of a more advanced distillation at the most remote sites. Interestingly, results from modelling of air parcel trajectories (Reijmer et al., 2002) indicate that air parcels moving toward Vostok pass over Dome C, thus confirming the pathway of the distillation.

To see if the distillation is indeed the main process controlling the isotopic composition in the snow pits, we first compare the average values between the pits, and then look at the evolution of isotopic parameters. Given the accumulation rate, several decades are probably recorded (about 60 years). However, we avoid discussing any precise age scale for these shallow pits drilled in East Antarctica. Indeed, because of the low accumulation rate and re-deposition effects in this region, the precise chronology is uncertain (possibility of gaps or snow layer repetition). This prevents a proper interpretation of isotopic variations in term of interannual variability and we only discuss in the following the average isotopic values and correlation between the different isotopic parameters. If distillation is the main driver, we expect low $\delta^{18}O$ values to be associated with high d-excess values, because they would be symptomatic of a more pronounced distillation, and with lower ^{17}O-excess values, because of the kinetic effect at very low temperature.

4.2. Isotopic measurements

Here, we have analyzed the isotopic composition of the first (2 to 4) meters of snow at three localities: Vostok, S2 and Dome C (***Fig. 1***). At Vostok, we can compare new data from the snow pit obtained for this study to a snow pit previously analyzed in δD, δ^{18}O and δ^{17}O (Winkler et al., 2013) that was dated to 1951 at 3.46 m. In the following, this snow pit will be called Vostok_winkler. For the different snow pits, the snow was sampled every three centimeters from the top to the bottom. The new δ^{18}O, δD and ^{17}O-excess measurements presented here were performed following the analytical methods of Sect. 2.2 with a MAT253, while the data from Vostok_winkler were measured on a Delta V.

4.3. Results

The average values for δ^{18}O (***Table 1***) are decreasing from Dome C to Vostok. The average d-excess values have an opposite trend relative to the δ^{18}O values (they increase from 9.1‰ at Dome C to 12.3‰ at S2 and to 16.1‰ at Vostok). Finally, the average ^{17}O-excess values measured on the same instrument are similar at Dome C, S2 and Vostok (~30 ppm). Correlations between variations of δ^{18}O, d-excess and ^{17}O-excess were inferred first for the whole isotopic series of the snow pits and then, for the couple δ^{18}O/^{17}O-excess for sub-sections of 20 points, corresponding to 60 cm, or about 10 years. The Spearman's correlations performed over 20 points shifting window are significant (with α=0.05) if the absolute value of the correlation coefficient ρ is higher than 0.443.

The results of Spearman's correlations for the whole series are presented in ***Table 2***. For the d-excess/δ^{18}O couple of parameters, the correlation is negative in all the pits, and strongest at S2. We note that the correlation at Dome C is also negative but not significant at the 0.05 level.

Regarding the ^{17}O-excess/δ^{18}O couple of parameters, the correlation is significant only in the Vostok_winkler snow pit. At this site, the correlation is negative.

The shifting window correlation coefficients between ^{17}O-excess and δ^{18}O are overall negative at Vostok and S2 (***Fig. 5a-c***). They are significant in most of the core (70% of cases) for Vostok_winkler, and also in a large part of the core for the second snow pit at Vostok (30% of cases) and at S2 (40% of cases). At Dome C, the correlation coefficients are small, and oscillate between positive and negative values (***Fig. 5d***). They only reach significant values in 4% of cases.

4.4.Interpretation of the results and discussion of processes

The comparison of the average values between sites is coherent with the distillation process, with δ^{18}O values decreasing and d-excess values increasing from Dome C to Vostok. However, the kinetic effect at condensation is not clearly apparent, as the ^{17}O-excess values remain more or less the same between the sites.

Global Spearman's correlations led to significant negative correlations between δ^{18}O and d-excess for S2, Vostok and Vostok_winkler. These negative correlations are consistent with those already detected in the snow from transects and in the precipitation, and therefore with a distillation process. **An effect of the source is also possible, but not sufficient to explain the large amplitude of variations in d-excess and ^{17}O-excess (10-20 ‰ for d-excess and 30-40 ppm for ^{17}O-excess).** At Dome C, the absence of significant correlation in the snow pit is unexpected, considering the anti-correlation observed at this site both in the precipitation and in the surface snow. Thus the distillation process at this site appears somehow obliterated by post-deposition processes (erosion, transport and redepositing of snow, diffusion of isotopes within the firn) affecting the isotopic compositions and their relationships.

The overall negative relationship between $\delta^{18}O$ and ^{17}O-excess at Vostok and S2 (considering not only the whole series values but also the sub-sections values) is rather intriguing. In effect, this is opposed to what has been observed on transects and at the seasonal scale for precipitation samples. The anti-correlation between ^{17}O-excess and $\delta^{18}O$ in these two sites definitively shows that distillation is not the driver of the ^{17}O-excess variations in the East Antarctica snow pits. Other mechanisms must then be considered to account for such negative correlation. Winkler et al. (2013) have explored different possible explanations for the relationships between ^{17}O-excess, $\delta^{18}O$ and δD. Using additional ^{10}Be measurement in the same pit at Vostok and the good correlation between ^{10}Be and ^{17}O-excess, they have concluded that stratospheric input may be a good candidate for explaining the high ^{17}O-excess values concomitant with high ^{10}Be and low $\delta^{18}O$. Indeed, mass independent fractionation associated with reaction with ozone in the stratosphere may lead to strong ^{17}O-excess in the stratosphere (Zahn et al., 2006). Even if the amount of water vapor is very small there (2 ppm), East Antarctica is very dry (30 ppm at Vostok) and located under the influence of the polar vortex hence with significant stratospheric input (e.g. Cauquoin et al., 2015a; Stohl and Sodemann, 2010). We propose here that the more frequent anti-correlation between ^{17}O-excess and $\delta^{18}O$ observed at Vostok relative to S2, and also at Vostok and S2 with respect to Dome C is linked to a stronger influence of stratospheric input in areas that are more remote (i.e. Vostok and S2). This is supported by the highest level of natural tritium observed at Vostok (100 TU) compared to Dome C (30 TU) (Becagli et al., 2004; Fourré et al., 2006; Proposito et al., 2002). Natural tritium is indeed mainly produced by the interaction of cosmic radiations with the upper atmosphere (Craig and Lal, 1961; Masarik and Beer, 2009) and is thus a good marker of stratospheric water input when measured in surface snow. Unfortunately, no tritium measurement is available at S2 now.

Finally, note that post-deposition could also have an effect on the relationship between $\delta^{18}O$, d-excess and ^{17}O-excess. This effect has been studied in Winkler et al. (2013) who showed by simple calculations at steady state that this effect could be important. Still, this calculation could not explain the observed relationship at Vostok_winkler and particularly how the seasonal correlation between $\delta^{18}O$ and ^{17}O-excess observed in precipitation at Vostok can be changed in an anti-correlation in the snow. As a perspective, to better quantify this effect in East Antarctica, modeling of post-deposition effect should be improved using a dynamic model as in Town et al. (2008) and using field measurements and experiments to tune it on the East Antarctic plateau.

5. Conclusion

We presented a compilation of new water stable isotopic data in East Antarctica on surface snow, precipitation, and snow pits. The comparison of the different stable isotope parameters $\delta^{18}O$, d-excess and ^{17}O-excess are very useful to decipher the various influences on the water isotopic composition in ice cores that is further archived in deep ice cores. We selected sites in East Antarctica with extreme climatic and isotopic values ($\delta^{18}O$ down to -70 ‰ in winter) in order to have present-day equivalent to glacial period archived in deep ice cores. These sites are located at the very end of the distillation trajectory with possible significant input of stratospheric water vapor that has an influence on water isotopic ratios.

Table 2 presents the compilation of the relationships between the different isotopic parameters and temperature for the different types of snow and different locations. Measurements of water isotopes in average surface snow and precipitations show a systematic anti-correlation between d-excess and $\delta^{18}O$ for $\delta^{18}O$ lower than -40 ‰ and, except at Dome C, a systematic correlation between ^{17}O-excess and $\delta^{18}O$ for $\delta^{18}O$ lower than -40 ‰. Even if the low $\delta^{18}O$ values encountered in East Antarctica cannot yet be reproduced by AGCM equipped with water isotopes, the (anti-)correlation between water isotopic parameters can well be explained. The anti-correlation between d-excess and $\delta^{18}O$ results from the distillation and the correlation between ^{17}O-excess and $\delta^{18}O$ at very low temperature is the result of kinetic effects at condensation in strongly supersaturated environment.

The links between isotopic parameters are however different in snow pits of East Antarctica. Especially, the positive relationship between $\delta^{18}O$ and ^{17}O-excess, associated with kinetic effects at low temperatures, is not visible, and an anti-correlation between $\delta^{18}O$ and ^{17}O-excess appears at Vostok and S2 that could be explained by a stratospheric input of water vapor. ^{10}Be values, measured in the same snow pit at S2, show a positive correlation to ^{17}O-excess values (M. Baroni, pers. comm.), and thus give weight to this explanation. Such an effect is not visible at Dome C where no particular relationship between ^{17}O-excess and $\delta^{18}O$ is visible.

From the different types of snow in East Antarctica, we always observe a positive relationship between changes in surface temperature and change in $\delta^{18}O$ of snow, even in the absence of precipitation. **If confirmed by future studies, the correlation between $\delta^{18}O$ of surface snow and temperature in the absence of precipitation in East Antarctica has strong importance for the interpretation of water isotopes in deep ice cores. Indeed, East Antarctica is characterized by very small accumulation rate (even smaller during glacial periods) so that post-deposition effects are expected to have a significant effect. Our findings suggest that post-deposition effects lead to a correlation between $\delta^{18}O$ and temperature. To better understand the exchanges between surface snow and atmospheric vapor, and assess their impact on the isotopic compositions, detailed models focusing on these interactions are needed. In the future, the development of models of post-deposition**

processes equipped with water isotopes may become the key to the quantitative interpretation of isotopes in ice-cores.

Finally, from our data, we calculated a wide range of temporal slopes between δ^{18}O and temperature (0.14 to 0.46 ‰.°C^{-1}, ***Table 2***). They are in general significantly lower than the spatial slope of the δ^{18}O vs temperature relationship over Antarctica (0.8‰, Lorius and Merlivat, 1977; Masson-Delmotte et al., 2008). Such results have important implications for the temperature reconstructions from deep ice cores in central Antarctica. Indeed, with a smaller δ^{18}O vs temperature slope, the δ^{18}O-infered amplitude of past temperature changes is larger. This is in agreement with outputs of experiments performed with AGCM equipped with water isotopes. Indeed, the modeled temporal slopes between δ^{18}O vs temperature over the East Antarctic plateau both at the annual and glacial-interglacial scales are generally smaller by up to a factor of two compared to the present-day spatial slope over Antarctica (Cauquoin et al., 2015b; Lee et al., 2008; Risi et al., 2010; Schmidt et al., 2007; Sime et al., 2008; Sime et al., 2009).

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TABLES

	VOSTOK	**S2**	**DOME C**
Latitude	-78.5 °S	-76.3 °S	-75.1 °S
Elevation	3488 m	3229 m	3233 m
Mean annual air T (2 m)	**-55.2°C**	**NA**	**-51.7 °C**
Air T coldest month	**-68.0 °C (Aug.)**	**NA**	**-63.5 °C (Jul.)**
Air T hottest month	**-31.8 °C (Dec.)**	**NA**	**-31.3 °C (Jan.)**
10 m borehole T	**-57 °C**	**-55.1 °C**	**-54.9 °C**
Acc. rate (ice eq.)	2.4 cm/y	2.1 cm/y	2.7 cm/y
Wind speed	**5.1 m/s**	**NA**	**3.3 m/s**
Average δ^{18}O	-57.13 ‰* ; -57.06 ‰	-53.81 ‰	-51.14 ‰
Average d-excess	15.3‰*; 16.1‰	12.3 ‰	9.1 ‰
Average ^{17}O-excess	10 ppm* ; 26 ppm	32 ppm	31 ppm

Table 1: Main characteristics of the snow pits drilled in East Antarctica on 3 different stations. **Meteorological data for Vostok from** www.aari.ru**.** Data indicated by a * correspond to the snow pit Vostok_winkler **(Winkler et al., 2013).** Accumulation rate (S2) from E. Le Meur et al. 2015/16, the Cryosphere (submitted). Temperature at S2: L. Arnaud, pers. comm. **10 m temperature at Dome C: J. Schwander, unpublished data, 2001. Wind speed at Dome C from IPEV/PNRA Project "Routine Meteorological Observation at Station Concordia -** www.climantartide.it**.**

	δ^{18}O/Temp					**d-excess/δ^{18}O**					**^{17}O-excess/δ^{18}O**				
	N	R	p-value	slope	SD	N	R	p-value	slope	SD	N	R	p-value	slope	SD
Traverses															
All points															
Dome A	42	0.897	8.9E-16	**0.92**	**0.07**	42	-0.406	7.6E-03	**-0.24**	**0.08**	31	0.456	9.9E-3	**0.40**	**0.15**
Dome F	13	0.950	7.1E-07	**0.91**	**0.09**	29	-0.809	1.1E-07	**-0.45**	**0.06**	29	0.575	1.1E-3	**0.67**	**0.18**
Dome C	29	0.833	2.1E-03	**1.20**	**0.15**	29	-0.609	4.6E-04	**-0.18**	**0.04**	29	0.056	0.775	**na**	**na**
$\delta^{18}O<-40$‰															
Dome A	11	0.911	9.3E-05	**0.75**	**0.11**	11	-0.868	5.2E-04	**-1.41**	**0.27**	17	-0.018	0.946	**na**	**na**
Dome F	8	0.799	1.7E-02	**0.64**	**0.20**	23	-0.834	7.5E-07	**-0.64**	**0.09**	23	0.396	0.061	**na**	**na**
Dome C	16	0.951	1.5E-08	**0.77**	**0.07**	18	-0.711	9.4E-04	**-0.43**	**0.11**	16	0.219	0.416	**na**	**na**
All transects	35	0.858	4.2E-11	**0.71**	**0.07**	52	-0.777	1.3E-11	**-0.95**	**0.11**	56	0.355	7.2E-03	**0.91**	**0.01**
Precipitation															
DOME C	28	0.877	9.2E-10	**0.46**	**0.05**	28	-0.884	4.7E-10	**-1.61**	**0.16**	28	0.105	0.596	**na**	**na**
VOSTOK (A)	16	0.625	9.6E-06	**0.35**	**0.12**	16	-0.698	2.6E-03	**-0.91**	**0.25**	16	0.884	5.7E-06	**2.95**	**0.42**
VOSTOK (A&B)	26	0.765	5.4E-06	**0.26**	**0.04**	27	-0.635	3.8E-04	**-0.73**	**0.17**	27	0.854	1.5E-08	**3.12**	**0.38**
Surf. snow															
DOME C	50	0.542	4.8E-05	**0.14**	**0.03**	50	-0.398	4.3E-3	**-0.47**	**0.16**	50	0.320	2.3E-02	**0.76**	**0.32**
Snow pits															
DOME C	na	na	na	**na**	**na**	67	-0.157	0.205	**na**	**na**	66	0.026	0.834	**na**	**na**
S2	na	na	na	**na**	**na**	102	-0.804	<5E-16	**-1.03**	**0.07**	101	0.002	0.986	**na**	**na**
VOSTOK	na	na	na	**na**	**na**	123	-0.436	4.5E-07	**-0.46**	**0.09**	112	-0.079	0.412	**na**	**na**
VOSTOK	na	na	na	**na**	**na**	115	-0.335	2.5E-04	**-0.49**	**0.14**	116	-0.396	1.1E-05	**-3.95**	**0.73**

<u>Table 2:</u> Correlation coefficients and slopes of the linear regression between: δ^{18}O and temperature, deuterium excess and δ^{18}O, and ^{17}O-excess and δ^{18}O, for various sample types (Traverse: see Sect. 2; Precipitation and Surface snow: see Sect. 3; Snow pits: see Sect. 4). The slopes between parameters are only indicated when the correlation coefficient are significant at the 95% level (p-value <0.05). (NB: Correlation coefficients: Pearson's R for traverse, precipitation, surf. snow; Spearman's R for the snow pits)

Figure captions:

Figure 1: Map of the sites discussed in this manuscript.

Figure 2: Water isotopic composition along Antarctic transects (blue: Zhongshan-Dome A transect; green: Syowa-Dome F transect; red: Terra Nova Bay-Dome C transect) and comparison with modeling outputs (black and grey line: MCIM with **S=1-0.004T** and S=1-0.002T respectively, **from Landais et al., 2012a**; dotted line: LMDZ-iso with S=1-0.004T (Risi et al., 2013))

Figure 3: (a) Isotopic composition of the precipitation at Vostok over one year. A: samples from the upper trap (pure precipitation); B: samples from the lower trap (precipitation mixed with blowing snow). For the ^{17}O-excess, dark green points were measured at LSCE whereas light green points were measured at HUJI. (b) Isotopic composition of the precipitation at Dome C over one year.

Figure 4: Isotopic composition of surface snow sampled every 1-2 weeks at Dome C.

Figure 5: Water isotopic data from snow pits and correlation between δ^{18}O and ^{17}O-excess for Vostok_winkler (a**; Winkler et al., 2013**), Vostok (b), Dome C (c) and S2 (d). **Each correlation coefficient R between δ^{18}O and ^{17}O-excess corresponds to a correlation realized over 20 points (see Sect. 4.3). The correlation coefficients are significant when they are larger than 0.443 in absolute values. The limit of significance is displayed as a green dotted line.**

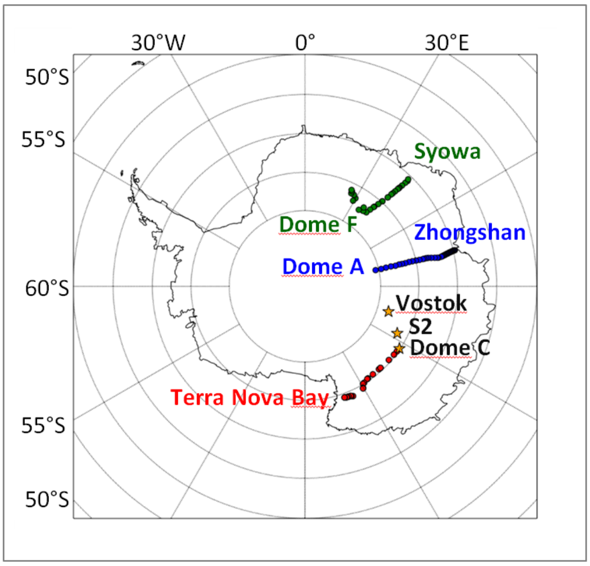


Figure 1

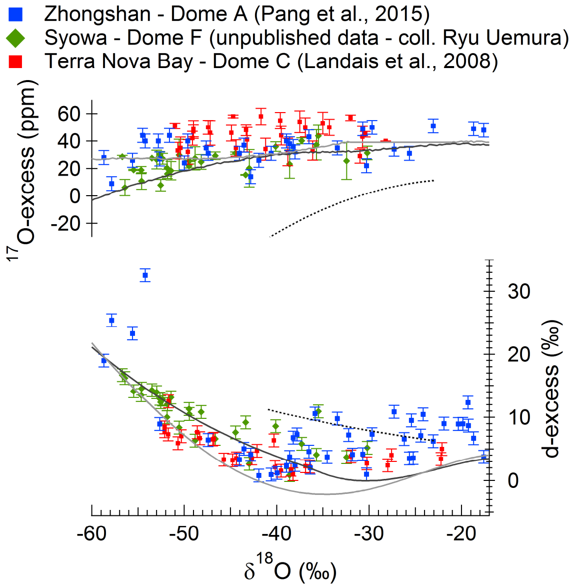


Figure 2

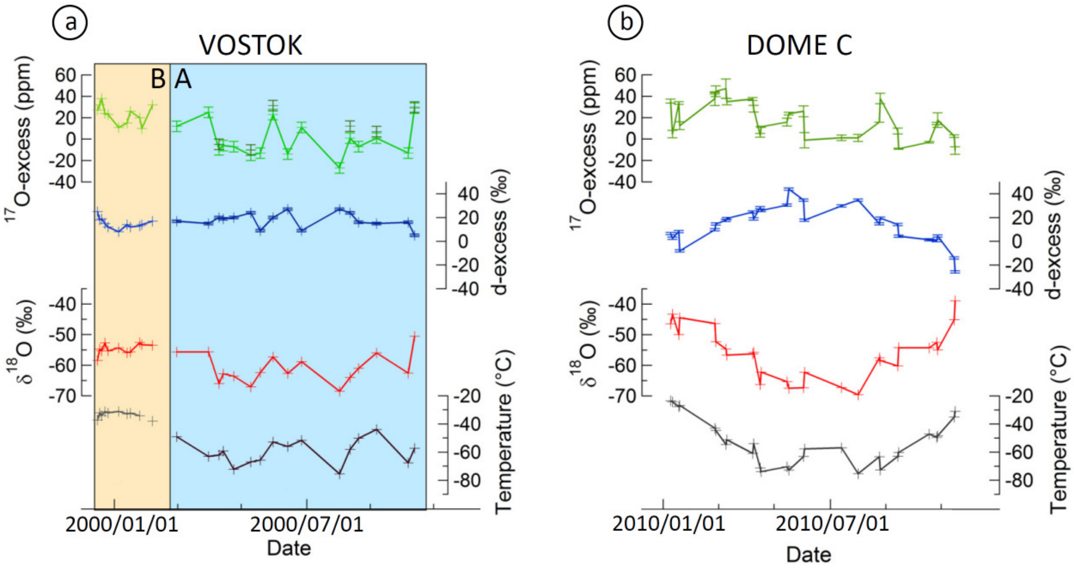


Figure 3

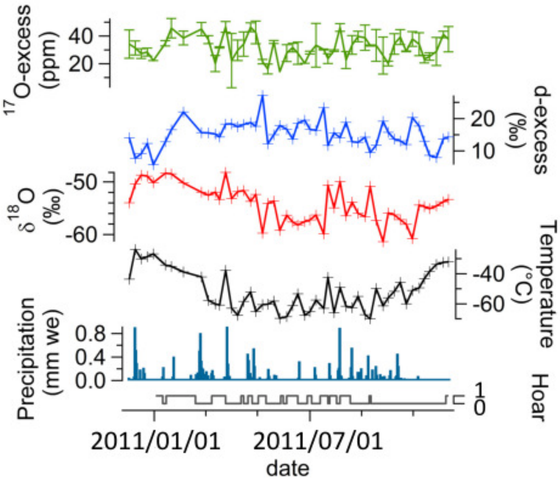


Figure 4

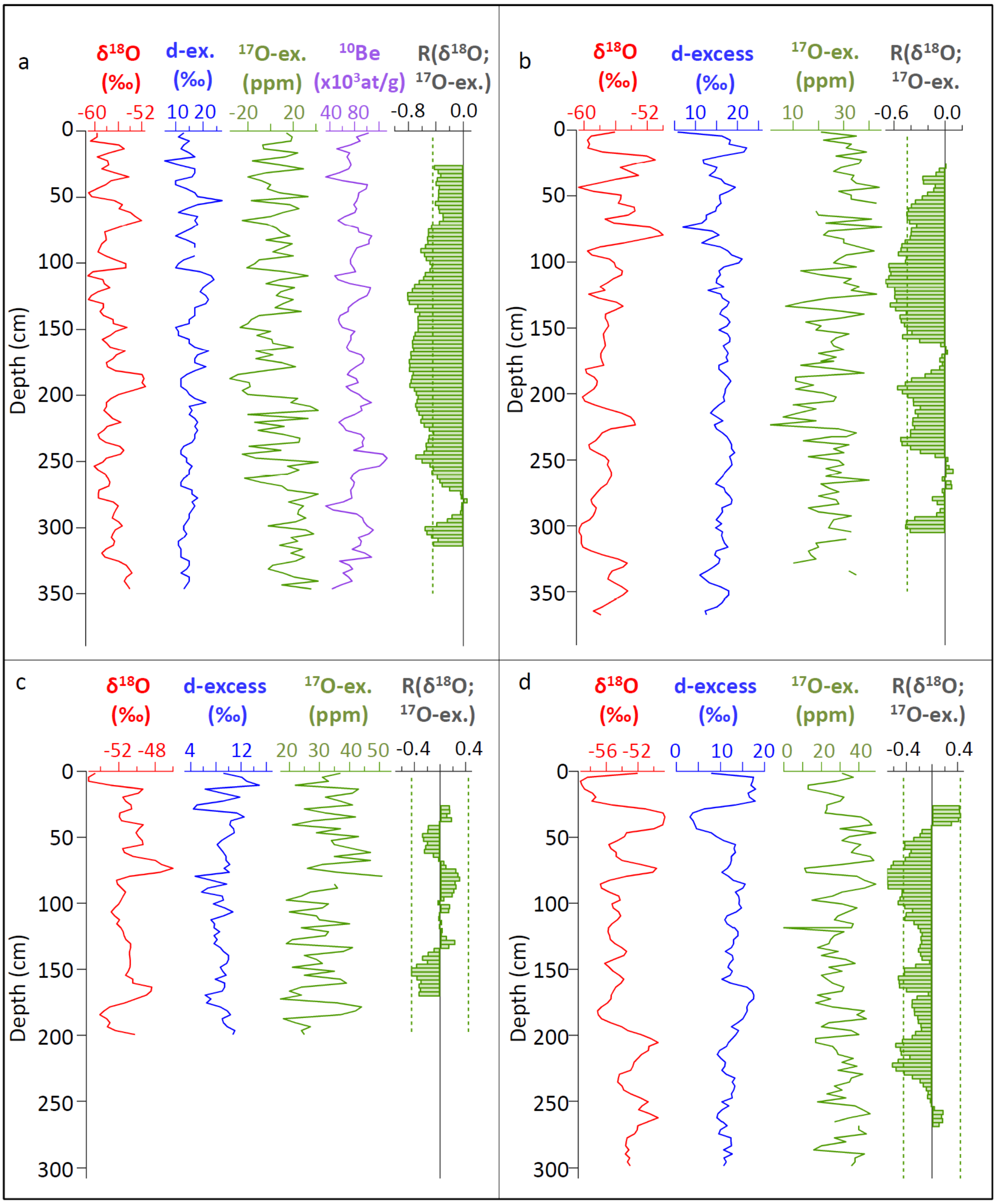
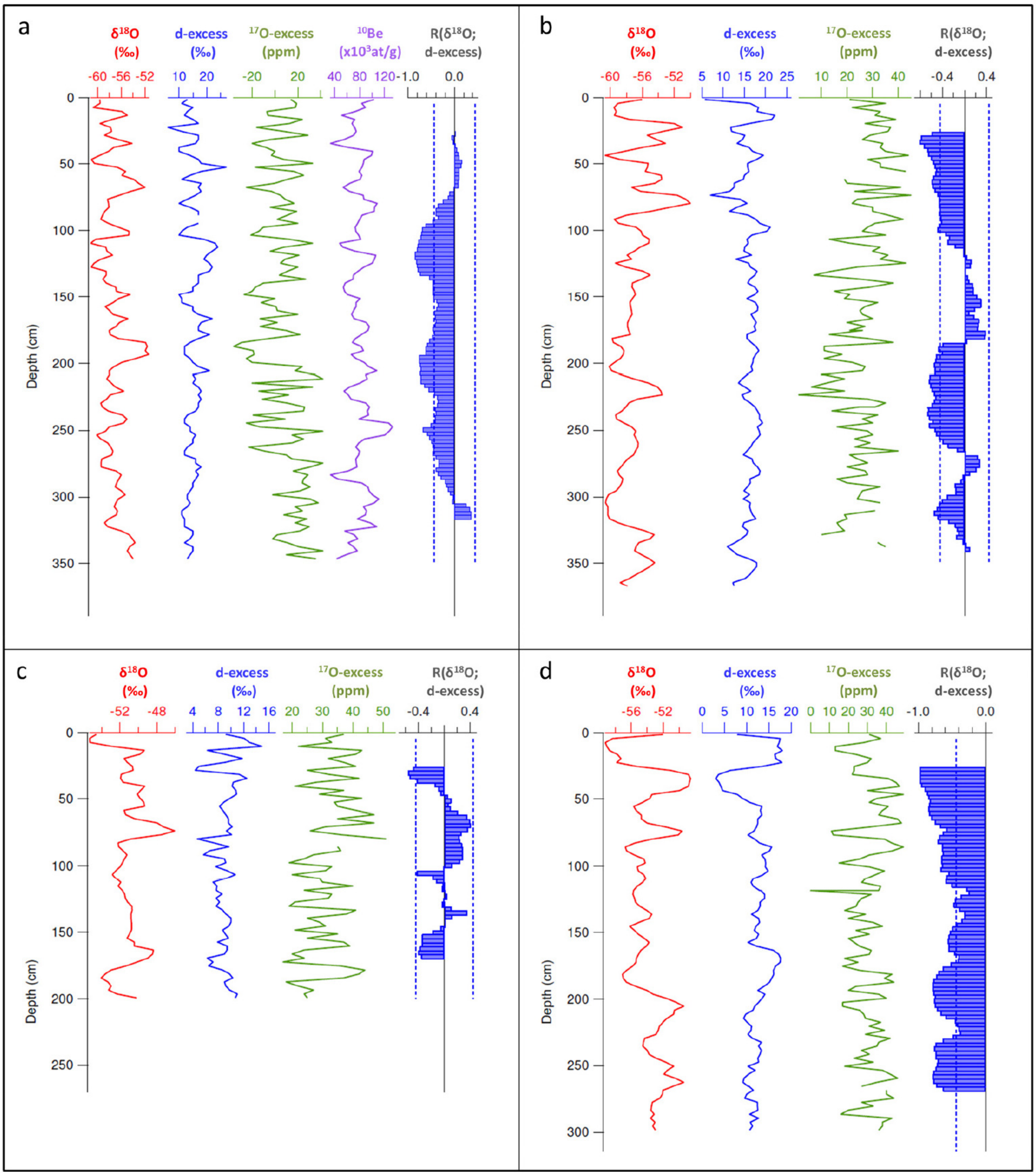

a
δ18O (‰)
d-ex. (‰)
17O-ex. (ppm)
10Be (x10³at/g)
R(δ18O; 17O-ex.)
-60 -52
10 20
-20 20
40 80
-0.8 0.0
Depth (cm)
0
50
100
150
200
250
300
350
b
δ18O (‰)
d-excess (‰)
17O-ex. (ppm)
R(δ18O; 17O-ex.
-60 -52
10 20
10 30
-0.6 0.0
Depth (cm)
0
50
100
150
200
250
300
350
c
δ18O (‰)
d-excess (‰)
17O-ex. (ppm)
R(δ18O; 17O-ex.)
-52 -48
4 12
20 30 40 50
-0.4 0.4
Depth (cm)
0
50
100
150
200
250
300
d
δ18O (‰)
d-excess (‰)
17O-ex. (ppm)
R(δ18O; 17O-ex.)
-56 -52
0 10 20
0 20 40
-0.4 0.4
Depth (cm)
0
50
100
150
200
250
300

Figure 5


a
δ18O (‰)
d-excess (‰)
17O-excess (ppm)
10Be (x10³at/g)
R(δ18O; d-excess)
-60 -56 -52
10 20
-20 20
40 80 120
-1.0 0.0
Depth (cm)
0 50 100 150 200 250 300 350
b
δ18O (‰)
d-excess (‰)
17O-excess (ppm)
R(δ18O; d-excess)
-60 -56 -52
5 10 15 20 25
10 20 30 40
-0.4 0.4
Depth (cm)
0 50 100 150 200 250 300 350
c
δ18O (‰)
d-excess (‰)
17O-excess (ppm)
R(δ18O; d-excess)
-52 -48
4 8 12 16
20 30 40 50
-0.4 0.4
Depth (cm)
0 50 100 150 200 250
d
δ18O (‰)
d-excess (‰)
17O-excess (ppm)
R(δ18O; d-excess)
-56 -52
0 5 10 15 20
0 10 20 30 40
-1.0 0.0
Depth (cm)
0 50 100 150 200 250 300

Supp. Fig. 1