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 Received and published: 22 December 2015

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/m²/y (Fujita et al., 2011), and the density of the snow in the first decimeters is on average 340 kg/m³ (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/m²/y (Fujita et al., 2011). The snow density in the first decimeters at Dronning Maud Land varies between 360 and 440 kg/m³ (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, I. 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 m². Approximately 5 to 10 spots few m² apart are sampled for every collect within this 1 000 m², 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 m² 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 m² is chosen (different from the previous one) and snow is scrapped on 5 to 10 spots (ca 0.04 m²) 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 m² 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 δ^{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 δ^{18} O samples? Is there any information about wind and drift at Dome C?

R	Т	δ^{18} O	d-excess	¹⁷ O-excess
δ ¹⁸ Ο	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 $\delta^{18}O$ (positive) and d-excess (negative). There is also a correlation between temperature and ^{17}O -excess, but smaller.

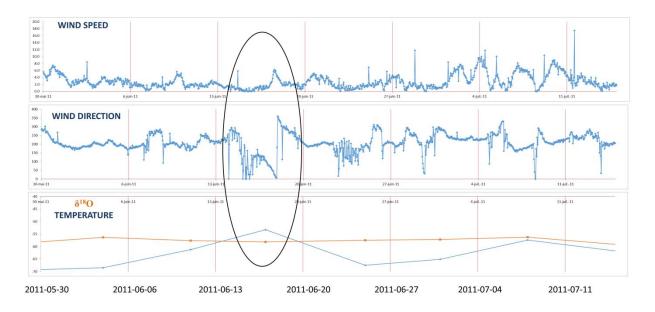
We did not present the correlation with the precipitation amount in the paper, because

- 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 \rightarrow 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, ¹⁷O-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).

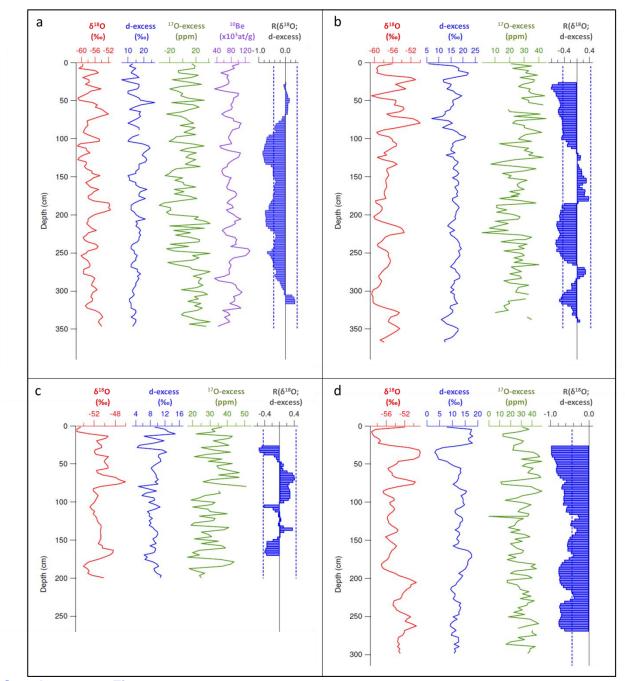
The dotted line corresponds to the limit of significance of the correlation coefficients. The correlation coefficients are significant (p<0.05) if they are larger in absolute value than 0.443 (see text, p. 6293, I21).

Addition to the figure caption:

"Each correlation coefficient R between δ^{18} O and ¹⁷O-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 ¹⁷O-excess. Kinetic fractionation tends to reduce the ¹⁷O-excess. This kinetic fractionation becomes stronger when the temperature decreases, since supersaturation increases toward low temperature. As a result, ¹⁷O-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 I. 25: "... as explained in Jouzel and Merlivat (1984), the anti-correlation between dexcess 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, $(\alpha^{D}_{V-S}-1)/(\alpha^{18}_{V-S}-1)$ equals 11.4 at -40°C. Still, the distillation effect dominates over the effect of both equilibrium and kinetic fractionation (0.6x11.4 still remains smaller than 8) and the d-excess tends to increase toward low temperature.

The decrease of ¹⁷O-excess with decreasing temperature is not linked to distillation effect. **Pure equilibrium fractionation in a Rayleigh fractionation with similar dependencies of**

 α_{V-S}^{17} and α_{V-S}^{18} to temperature (with $\ln\left(\frac{\alpha_{V-S}^{17}}{\alpha_{V-S}^{18}}\right) = 0.528$) would lead to an increase of ¹⁷O-

excess toward low temperatures (Landais et al., 2012b; Van Hook, 1968). Actually, the decrease of the ¹⁷O-excess toward low temperature is due to the kinetic effect at condensation. Indeed, the ratio $\ln\left(\frac{D}{D^{17}}\right) / \ln\left(\frac{D}{D^{18}}\right)$ is significantly lower (0.518) than the

corresponding ratio between equilibrium fractionation factors and it results in a decrease of the ¹⁷O-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 ¹⁷O-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" (Subsection 4.1) to the "Method" of section 3 ("Temporal variation").

p.6287 I.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 δ^{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."

	VOSTOK	S 2	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 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

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

<u>Table 1</u>: Main characteristics of the sites snow pits drilled in East Antarctica on 3 different stations. **Meteorological data for Vostok from** <u>www.aari.ru</u>. 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 - <u>www.climantartide.it</u>.

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 ¹⁷O-excess in central Antarctica and showed that supersaturation is indeed the key parameter to fit the relative evolution of ¹⁷O-excess vs. δ^{18} O and d-excess vs. δ^{18} O. When supersaturation is too low (e.g. S = 1-0.0027), equilibrium fractionation dominates and modeled ¹⁷O-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.

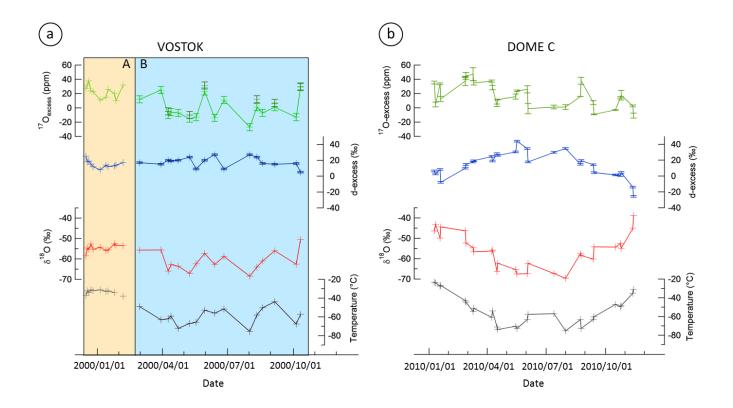


Fig 5: Too small. Reference for Vostok_winkler is not given.

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 ¹⁷O-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 ¹⁷O-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 inbetween 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

 δ^{18} O and ¹⁷O-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 (¹⁰Be, 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 icecores.

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, I. 6: "From the different types of snow in East Antarctica, we always observe a positive relationship between changes in surface temperature and change in δ^{18} O of snow, even in the absence of precipitation. If confirmed by future studies, the correlation between δ^{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 δ^{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 ¹⁷O-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= $\delta D - 8^* \delta^{18}O$) and ¹⁷O-excess (¹⁷O-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 $\delta D / \delta^{18}O$ 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 (Meijer and Li, 1998; Landais et al., 2008; Luz and Barkan, 2010). Following the model of the d-excess definition, Landais et al. (2008) defined the ¹⁷O-

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 ·10⁻⁶ kg/m³ for the annual average and 261 · 10⁻⁶ kg/m³ 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 $\overline{\delta}^{18}$ 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 ¹⁷O-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 ¹⁷O-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 (dexcess and ¹⁷O-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 ($n \ge ?$). 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 (1 σ) for ¹⁷O-excess is often 5-6 ppm.

We propose the following modification to the text:

p. 6283, I. 26: "The measurements were calibrated vs. VSMOW and SLAP taking reference values for δ^{18} O and ¹⁷O-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 (1 σ) was computed from duplicate injection, fluorination and IRMS measurements of the same sample, and is on average of 5-6 ppm for ¹⁷O-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 $(\alpha^{17} - 1) / (\alpha^{18} - 1)$ 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 dexcess 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, $(\alpha^{D}_{V-S}-1)/(\alpha^{18}_{V-S}-1)$ equals 11.4 at -40°C. Still, the distillation effect dominates over the effect of both equilibrium and kinetic fractionation (0.6x11.4 still remains smaller than 8) and the d-excess tends to increase toward low temperature.

The decrease of ¹⁷O-excess with decreasing temperature is not linked to distillation effect. **Pure equilibrium fractionation in a Rayleigh distillation with similar dependencies of** α_{ν}^{17} .

and α_{V-S}^{18} to temperature (with $\ln\left(\frac{\alpha_{V-S}^{17}}{\alpha_{V-S}^{18}}\right) = 0.528$) would lead to an increase of ¹⁷O-excess

toward low temperatures (Landais et al., 2012b; Van Hook, 1968). Actually, the decrease of the ¹⁷O-excess toward low temperature is due to the kinetic effect at condensation.

Indeed, the ratio $\ln\left(\frac{D}{D^{17}}\right) / \ln\left(\frac{D}{D^{18}}\right)$ is significantly lower (0.518) than the corresponding

ratio between equilibrium fractionation factors and it results in a decrease of the ¹⁷Oexcess 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 ¹⁷O-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.

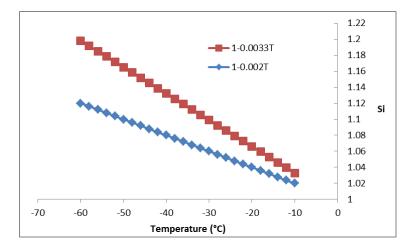
We have added the original references (Meijer and Li, 1998; Barkan and Luz, 2007), but earlier in the text, in the Introduction section.

p. 6279, l. 4: "When plotting the isotopic compositions of meteoric waters in a $In(\delta^{17}O+1)/In(\delta^{18}O+1)$ 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 ¹⁷O-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 ¹⁷O-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 $\delta^{18}O$ ", 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 m² 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 δ¹⁸O 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 δ¹⁸O 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 $0.14\%^{\circ}C^{-1}$ (R = 0.54, p < 0.05). This slope is lower than the annual slope in the precipitation at Dome C ($0.46\%^{\circ}C^{-1}$, 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 ¹⁷O-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 ¹⁷O-excess. This is coherent with the fact that δ^{18} O is anti-correlated to d-excess (R=-0.64) and positively correlated to ¹⁷O-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 ¹⁷O-excess). The variations of ¹⁷O-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 ¹⁷O-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 ¹⁷O-excess.
- During summer, the positive correlation between d-excess and ¹⁷O-excess could theoretically result from very strong supersaturation (leading to low ¹⁷O-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 - $\delta^{18}O$ space, and thus d-excess, reflects both equilibrium fractionation during distillation and kinetic effect during supersaturation. Variation in ¹⁷O-excess is dominantly controlled by kinetic effects. Then, a combination of ¹⁷O-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 ¹⁷O-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 dexcess and δ^{18} O on the one hand and ¹⁷O-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. ¹⁷O-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 ‰, ¹⁷O-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‰°C⁻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‰°C⁻¹ (*R* = 0.54, *p* < 0.05, **Table 2**).

This slope is lower than the annual slope in the precipitation at Dome C ($0.46\%^{\circ}C^{-1}$, 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 ¹⁷O-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: "¹⁷O-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 Received and published: 4 January 2016

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 ¹⁷O-excess is measured along with δ^{18} O and δ D for the same samples. Compared to most previous studies, ¹⁷O-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 ¹⁷O-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 ¹⁷O-excess.

The sensitivity of the snow and ice isotopic composition (δ^{18} O, d-excess, ¹⁷O-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, $\Delta\delta D = 7.6 \Delta T_{site} -3.5 \Delta T_{source} +5.0 \Delta \delta^{18} O_{ocean}$							
Stenni et al., 2001:							
Vostok,	$\Delta \delta D =$	$7.1 \Delta T_{site}$	$-3.7 \Delta T_{source}$	$+4.8 \Delta \delta^{18} O_{ocean}$			
Vimeux et al., 2002:							
Dome F,	$\Delta \delta D_{corr} =$	7.7 ΔT_{site}	$-3.2 \Delta T_{source}$				
Uemura et al., 2012:							

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

Sensitivity of ∆d					
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	$\Delta d =$	$-\binom{1.29}{to\ 2.04}\Delta T_{site}$	$+ \begin{pmatrix} 1.31\\ to \ 1.5 \end{pmatrix} \Delta T_{source}$	$-3\Delta\delta^{18}O_{ocean}$	$-\left(\frac{0.045}{to\ 0.095}\right)\Delta RH_n$
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 δ^{18} O between -20‰ and -40‰; but it cannot explain the higher values obtained for δ^{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 $(1.1\% \cdot °C^{-1})$ instead of $1.3\% \cdot °C^{-1}$). 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 $-2.9\% \cdot °C^{-1}$ (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 $\Delta^{17}O_{excess} = -0.9\Delta R H_{source}$						
East Antarctica, Winkler et al., 2012	$\Delta^{17}O_{excess} =$	$-\left(\begin{array}{c}-0.2\\to\ 0.5\end{array}\right)\Delta T_{site}$	$+ \begin{pmatrix} 0.34\\ to \ 0.61 \end{pmatrix} \Delta T_{source}$	$-\left(\begin{array}{c}0.86\\to\ 1.1\end{array}\right)\Delta RH_n(\%)$		
Dome A, Pang et al., 2015	$\Delta^{17}O_{excess} =$	$-(-0.33)\Delta T_{site}$		$-(1.1)\Delta RH(\%)$		

The ¹⁷O-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 ¹⁷O-excess values, equivalent to the change expected from humidity variations.

In Figure 2, the relative stability of the ¹⁷O-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 ¹⁷O-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 ¹⁷O-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, I. 20: "Presence of sea ice at the oceanic water evaporative regions may also contribute to the d-excess and ¹⁷O-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 ¹⁷O-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 ¹⁷O-excess is less sensitive to temperature than d-excess, the site temperature influence on ¹⁷O-excess is only perceptible in very remote sites of East Antarctica (Winkler et al., 2012). Finally, ¹⁷O-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 (d δ D/d δ^{18} O) of the distillation line towards low δ 18O values (i.e. low temperatures). Indeed, in the"

p. 6285, l. 13: "In turn, the evolution of d-excess and ¹⁷O-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 ¹⁷O-excess and d-excess at low temperature, but cannot by itself explain the decrease in ¹⁷O-excess

from about 30 ppm to about 10 ppm between δ^{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 ¹⁷O-excess and δ^{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 ¹⁷O-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 dexcess or more than 10 ppm for ¹⁷O-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 d¹⁸O 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 ¹⁷O-excess (10-20 ‰ for d-excess and 30-40 ppm for ¹⁷O-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 ¹⁷O-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 δ^{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:

$$dR_{\nu}^{D} = \frac{R_{\nu}^{D} \cdot \left(\alpha_{eq}^{D} - 1\right) \cdot dm_{\nu}}{m_{\nu} + dm_{\nu}}$$

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:

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

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°C and -40°C). 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 δ D~-140‰ at Zhongshang) whereas far in the interior we consider that it is no longer the case (δ^{18} O~-60‰ and δ D~-450‰ i.e. 1+ δ D~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:

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

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 ¹⁷O-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 <u>Rayleigh's distillation line</u> at a given point as:

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

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 ‰."