

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

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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

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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 I. 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 description of the : The sampling strategy at Vosmore details. What the volume? tok needs is sample How long is precipitation event? ls there sublimation expected? а

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).

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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 \sim 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.

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

p. 6288, I. 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 18O and temperature or d excess and precipitation? What happens June/July 2011 that there is a peak in temperature but not in the δ 18O samples? Is there any information about wind and drift at Dome C?

R T δ 18O d-excess 17O-excess δ 18O 0.54 1.00 -0.40 0.32 d-excess -0.46 -0.40 1.00 0.06 17O-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 18O (positive) and d-excess (negative). There is also a correlation between temperature and 17O-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 18O and temperature are expected because we are measuring natural samples, and because temperature is not the only parameter controlling the δ 18O values. The sampling may be responsible for a value of δ 18O 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 18O, 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, I. 14: "Second, several short warming events during winter 2011 are also clearly imprinted in the δ 18O signal. Because warm events are often associated with precipitation events (Fig. 4), the temperature– δ 18O 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 18O signal. This may be due to wind erosion and re-deposition of the snow. "

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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 18O 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 180, d-excess, 170-excess). We have chosen to put the first correlation point (corresponding to the first 20-points window of δ 180 values) in front of the 9th δ 180 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 18O and 17Oexcess 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 18O 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 18O and d-excess values.

P 6284 L5 If the increase of d excess for decreasing δ 18O is linked to distillation is there a possible reason why at -40 the relationship between δ 18O 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 18O 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 17Oexcess. 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 18O is below \sim -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 18O 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 and to temperature (with) 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 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

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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 help-ful 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 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 180 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 T -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 18O -57.13 ‰; -57.06 ‰ -53.81 ‰ -51.14 ‰ Average d-excess 15.3‰; 16.1‰ 12.3 ‰ 9.1 ‰ Average 17O-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.

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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 180, d-excess and 170-excess in central Antarctica and showed that supersaturation is indeed the key parameter to fit the relative evolution of 170-excess vs. δ 180 and d-excess vs. δ 180. When supersaturation is too low (e.g. S = 1-0.002T), equilibrium fractionation dominates and modeled 170-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.

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

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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 18O 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 180/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 180 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 18O 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 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, 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 18O of snow, even in the absence of precipitation. If confirmed by future studies, the correlation between δ 18O 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 18O 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 $\delta 180$ records bringing information on temperature at first order, additional climatic information can be retrieved from sec-

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ond order parameters like d-excess (d-excess= $\delta D - 8^* \delta 180$) and 17O-excess (17O-excess=ln($\delta 17O+1$)-0.528*ln($\delta 18O+1$)) (Dansgaard 1964, Barkan & Luz, 2007; Landais et al., 2008). These parameters represent the y-intercepts of two straight lines, one relating δD and $\delta 180$ with a slope of 8, and the other relating ln($\delta 17O+1$) and ln($\delta 18O+1$) 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 $\delta D / \delta 180$ 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($\delta 17O+1$)/ln($\delta 18O+1$) 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 $\delta 180$, d-excess and 17O-excess"

P6280 L5: Reference is needed for the information "30ppmv at Vostok, ranging from \sim 1ppmv in winter to ${\sim}100$ 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 IG10-6 kg/m3 for the annual average and 261IG 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 \sim 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 com-C2988

paring 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 18O 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 18O 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 tem-

perature, 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 18O 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 18O 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 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.

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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 17O-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 18O 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 170 vs. δ 180 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/D17) / ln(D/D18).

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 18O is muted by the existence of the kinetic effect. Indeed, when considering also kinetic effect in addition to equilibrium during solid precipitation, (α D V-S-1)/(α 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 and to temperature (with) 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 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."

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, I. 4: "When plotting the isotopic compositions of meteoric waters in a $ln(\delta 17O+1)/ln(\delta 18O+1)$ 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 $\delta 18O$, d-excess and 17O-excess"

P6285	L28:	Why is	S=1-0.002T "too	low"?	It should	rep-
resent	а	stronger	supersaturation	than	S=1-0.0033T	does.

First it should be noted that here, the temperature are in Celsius degrees, so T is

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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 "1"	L18: represent?	At Is			this slope	line, unit	what missing	does 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	cha	inging	"than"	into	"as".		
		"analyzed in				est chang	 je "in" int	o "for".		
OK P6288		Cut	off	"S"		"sample	es coll	ection".		
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 slots, what the R and two time are δ18O-T values for correlation for each scenario, respectively? p

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 18O 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 18O 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).

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■ ■, ■■ ■ .

 δ = = = -=% = = δ = = -=.=% \blacksquare 1.170-excess does not exhibit any significant trend if we restrict the data in the range of δ 1(Table 2).''9.22, 23 2 2 - 9.22, 2 2.22, 2 2. 22 δ **₩** δ**₩₩** ₩₩₩₩ ₩ −₩.₩ − −₩.₩, ₩ ₩.₩, ₩ ₩ ₩ ₩ ₩ −₩.₩ − −₩.₩, ₩ ₩.₩, ₩ ₩.₩, ₩ ₩.₩, C2996 \blacksquare (R = 0.4, p < 0.05, Table 2),"= 0.88, p< 0.05, Table 2) with a higher slope and correlation coefficient compared to the transect data set with the transect data set wit \bullet $\Delta \delta \bullet$, $\bullet \bullet$., $\bullet \bullet \bullet$, \bullet \bullet ., $\bullet \bullet \bullet \bullet$., $\bullet \bullet \bullet \bullet$. \blacksquare Δ , \blacksquare \blacksquare , \blacksquare

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∎ 🖬 🖬 🖩 🗸 🖬 🖬 🖬 🛲 🐜 🖬 페‰ butitcannotexplainthehighervaluesobt
 ■‰ n Figure 3-5, the variability at seasonal and interannual scale is of 10-20‰
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Fig. 1. Supplementary Figure 1: Same as Figure 5 except that the correlation coefficients that are displayed (blue bars) are the correlation coefficients between δ 180 and d-excess values.



Fig. 2. Corrected figure 3

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