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Surface studies of water isotopes in Antarctica for quantitative interpretation of deep ice core data



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ABSTRACT

Polar ice cores are unique climate archives. Indeed, most of them have a continuous stratigraphy and present high temporal resolution of many climate variables in a single archive. While water isotopic records (δD or $\delta^{18}O$) in ice cores are often taken as references for past atmospheric temperature variations, their relationship to temperature is associated with a large uncertainty. Several reasons are invoked to explain the limitation of such an approach; in particular, post-deposition effects are important in East Antarctica because of the low accumulation rates. The strong influence of post-deposition processes highlights the need for surface polar research programs in addition to deep drilling programs. We present here new results on water isotopes from several recent surface programs, mostly over East Antarctica. Together with previously published data, the new data presented in this study have several implications for the climatic reconstructions based on ice core isotopic data: (1) The spatial relationship between surface mean temperature and mean snow isotopic composition over the first meters in depth can be explained quite straightforwardly using simple isotopic models tuned to d-excess vs. $\delta^{18}O$ evolution in transects on the East Antarctic sector. The observed spatial slopes are significantly higher ($\sim 0.7\text{--}0.8\text{‰}\cdot^{\circ}\text{C}^{-1}$ for $\delta^{18}O$ vs. temperature) than seasonal slopes inferred from precipitation data at Vostok and Dome C (0.35 to $0.46\text{‰}\cdot^{\circ}\text{C}^{-1}$). We explain these differences by changes in condensation versus surface temperature between summer and winter in the central East Antarctic plateau, where the inversion layer vanishes in summer. (2) Post-deposition effects linked to exchanges between the snow surface and the atmospheric water vapor lead to an evolution of $\delta^{18}O$ in the surface snow, even in the absence of any precipitation event. This evolution preserves the positive correlation between the $\delta^{18}O$ of snow and surface temperature, but is associated with a much slower $\delta^{18}O$ -vs-temperature slope than the slope observed in the seasonal precipitation. (3) Post-deposition effects clearly limit the archiving of high-resolution (seasonal) climatic variability in the polar snow, but we suggest that sites with an accumulation rate of the order of $40\text{ kg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ may record a seasonal cycle at shallow depths.

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1. Introduction

Polar ice cores are unique archives of multiple sources of information on past changes in climate and environment. Indeed, most polar ice cores have a continuous stratigraphy, and allow extracting highly resolved records, reaching seasonal resolution in Greenland and coastal Antarctica. Today, the ice core spanning continuously the longest period is the EPICA Dome C ice core, drilled on the East Antarctic plateau and covering the last 800 ka, hence eight climatic cycles (EPICA Community Members, 2004). Earlier discontinuous records have been extracted from blue ice fields (Higgins et al., 2015). The International Partnership for Ice Core Science is searching drilling sites where records spanning the last 1.5 million years could be extracted (Fischer et al., 2013). In central Greenland, where accumulation rates are at least 10 times larger than in the East Antarctic plateau, the longest continuous climatic record from NorthGRIP is limited to the last 120 ka (NorthGRIP-community-members, 2004), but information back to 130 ka has been extracted from an undisturbed section of the NEEM ice core (NEEM community members, 2013).

Various proxies are measured in ice cores enabling the reconstruction of climatic and environmental variables. While concentration of greenhouse gases (CO_2 , CH_4 , NO_2) is directly measured by the extraction of the air trapped in the ice, other proxies are more indirect, such as chemical proxies to infer changes in distal climatic conditions, atmospheric circulation, atmospheric chemistry, sea ice extent or fire records (e.g., Legrand et al., 2016; Wolff et al., 2010). Similarly, while high-resolution water isotopic records (δD or $\delta^{18}\text{O}$) in ice cores are often taken as references for past atmospheric temperature variations, their quantitative interpretation is not straightforward and may be associated with large uncertainties. The initial method of temperature reconstruction from water isotopes is based on the present-day spatial relationship between δD or $\delta^{18}\text{O}$ and surface temperature on polar transects. This spatial slope is then used as a surrogate for the relationship between changes in water isotopic composition and temperature from past to present (“temporal slope”). In East Antarctica, the amplitude of temperature change over glacial–interglacial transitions was mainly estimated based on water isotopes with an associated error of -10 to $+30\%$. In West Antarctica, the amplitude of the last deglaciation has been estimated to $+11.3^\circ\text{C}$ based on measurements of isotopic composition of air isotopes, i.e. 2 to 4°C larger than the water isotopes estimated amplitude of the last deglaciation in East Antarctica (Cuffey et al., 2016). At the glacial–interglacial scale, most atmospheric General Circulation Models equipped with water isotopes suggest that temporal slopes are close to spatial slopes (Jouzel et al., 2007; Risi et al., 2010; Stenni et al., 2010) with one exception (Lee et al., 2008) producing smaller slopes attributed to evaporative recharge over the Southern Ocean. For inter-annual variations under present-day climate or for simulated climates warmer than today due to increased greenhouse gas concentration, several studies produce temporal slopes up to twice smaller than the spatial ones,

mostly because of precipitation–temperature covariance effects through precipitation intermittency (Schmidt et al., 2007; Sime et al., 2009). Temporal slopes lower than spatial slopes for climates warmer than pre-industrial ones (early Holocene, earlier interglacial periods) are also supported independently by investigations of isotope–temperature–accumulation relationships (Cauquoin et al., 2015).

Sources of uncertainties in the use of the spatial slope as a surrogate for temporal slopes emerge from (1) past changes in moisture source regions and the corresponding climatic variations, affecting the isotopic composition of the water vapor that will finally precipitate in polar regions (e.g., Lee et al., 2008), (2) past changes in the trajectories of water masses toward the polar regions affecting water isotopes in precipitation independently of changes in local condensation temperature (Helsen et al., 2006), (3) past changes in precipitation intermittency including seasonal effects (Krinner and Werner, 2003; Laepple et al., 2011; Masson-Delmotte et al., 2006; Sime et al., 2009) causing a distortion between the ice core signal (precipitation-weighted) and annual mean temperature; and finally (4) post-deposition effects leading to a modification of the isotopic composition of the surface snow after its deposition and before it is buried (Johnsen et al., 2000; Neumann and Waddington, 2004; Town et al., 2008).

In Greenland, the diffusion of the $\delta^{18}\text{O}$ seasonal signal can be corrected (e.g., Steen-Larsen et al., 2011) and other post-deposition effects have long been estimated to be of second order because of the high accumulation rate. However, recent studies claim that post-deposition processes could represent a significant contribution to the isotopic signal (Steen-Larsen et al., 2014). Still, alternative temperature measurements have been developed such as borehole temperature measurements (Dahl-Jensen, 1998) or direct quantification of the amplitude of temperature changes through air isotopic measurements (Landais et al., 2004a, b; Orsi et al., 2014; Severinghaus and Brook, 1999). These methods allow estimating temperature changes with an accuracy estimated at $\pm 3^\circ\text{C}$ for Dansgaard–Oeschger abrupt events (Buizert et al., 2014; Kindler et al., 2014). These analyses reveal that, in Greenland, temporal isotope–temperature slopes are systematically lower than spatial slopes, with marked regional characteristics (e.g., Guillevic et al., 2013).

In the central East-Antarctic plateau, low accumulation rate and slow past temperature make borehole temperature reconstructions more difficult to interpret (Salamatin et al., 1998) and preclude the use of air isotopic measurements for quantitative temperature reconstructions (Landais, 2011). In this region, there is thus a strong need to better understand and quantify the processes potentially affecting the relationship between water isotopes and temperature, and specifically post-deposition processes that may have a strong influence when surface snow is exposed to exchanges with air during long time periods.

These facts have motivated the development of two types of surface polar programs in addition to deep drilling programs. The first type of surface program is focused on investigating the surface characteristics of a deep drilling

site through the deployment of numerous instruments to monitor the variability of weathering conditions and/or surface snow characteristics, as implemented at Concordia Station for the EPICA Dome C (Champollion et al., 2013; Genthon et al., 2013; Libois et al., 2015). Other programs explore the variability of surface characteristics (accumulation rate, layer structure, isotopic and chemistry composition...) through traverse expeditions, and information retrieved from the network of pits and shallow ice cores (Goursaud et al., 2016; Mayewski and Al, 2006).

Here, we review the importance of surface programs for the climatic interpretation of ice core water isotopic records. For this purpose, we report new results on water isotopes from several recent surface programs, mostly over East Antarctica. These new results are confronted to previous data and used to update guidelines for interpretation of water isotopic records in ice core.

2. Methods

Various datasets from several campaigns are used in this manuscript. We first describe the sample collection, then the measurements techniques and the calibration protocol.

2.1. Sample collection

2.1.1. Transects

Several transects have been performed in the recent years with sampling of surface snow down to a depth sufficient to characterize the average isotopic composition at the site. On each sampling site, a metallic tube (titanium) is used to penetrate into the first 30–100 cm of the snow and extract a snow sample, which is then

mixed for homogenization. In low accumulation sites, this simple method enables the collection of a sample of the average snow isotopic composition over several years.

We present here water isotopic datasets from two new transects in Antarctica (Fig. 1): the French–Russian Taste-Idea Explore campaign performed in 2011–2012 in the central East Antarctic Plateau (hereafter referred to as TI11) and the Spanish expedition Expedición Acciona Windpowered Antarctica, performed in 2011–2012 in the inland Atlantic sector of East Antarctica. The TI11 campaign provided samples in very cold and low-accumulation regions of East Antarctica, between Dome C and Vostok, hence completing a previous transect between the coastal site of Terra Nova Bay and Dome C where δD , $\delta^{18}O$ and $\delta^{17}O$ were already documented (Landais et al., 2008). The Spanish expedition provided samples from the edge of the East Antarctic plateau south of the coastal Novolazarskaja station to South Pole Station. These transects are compared to previously published datasets: one Swedish–Japanese transect from Syowa to Dome F and one Chinese transect from Zongshan to Dome A (Fig. 1).

2.1.2. Precipitation and surface snow

Surface studies have been developed thanks to the establishment of the permanent overwintering stations in East Antarctica, for instance at Dome C and Vostok (Fig. 1). Sampling of precipitation is being performed routinely since 2008 at Dome C (Stenni et al., 2016). Precipitation is sampled on a wood table covered by a polystyrene/Teflon plate and standing 1 m above the snow surface. The precipitated snow layer is removed ideally every day at 1 am UTC (Coordinated Universal Time). Few snow samples were collected annually as precipitation events are rare at Dome C. Moreover, even if the wood table is

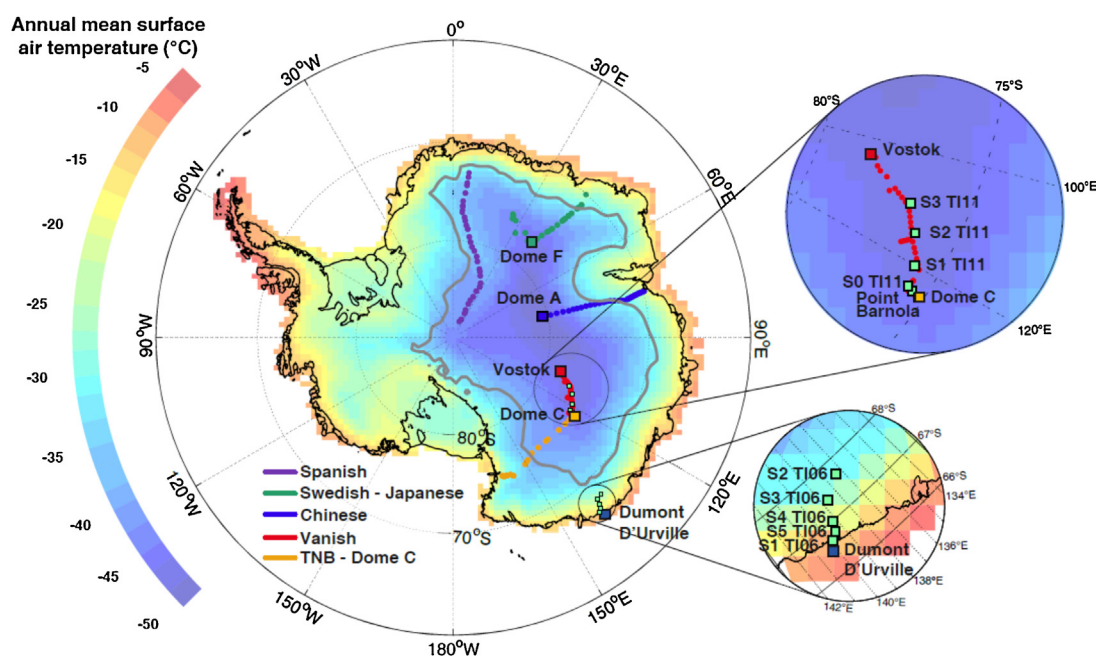


Fig. 1. Recent surface transects performed in East Antarctica and location of the different snow-pit sampling sites mentioned in this study, with indication of the mean surface air temperature (Nicolas and Bromwich, 2014).

Table 1

Summary of the different snow pits used in this study.

Sites	Latitude S	Longitude E	Resolution (cm)	Accumulation (kg·m ⁻² ·yr ⁻¹)	10 m depth Temperature (°C)	Altitude (m)	Year of sampling
S1 TI06	66°42'25	139°49'53	5	219	−13.1	279	2007 ³
S2 TI06	67°39'35	137°31'26	5	360	−29.5	1808	2007 ³
S3 TI06	67°24'39	138°37'53	5	260	−25.8	1578	2007 ³
S4 TI06	67°02'29	139°08'12	5	280	−22.4	1170	2007 ³
S5 TI06	66°46'30	139°33'25	5	310	NA	653	2007 ³
S0 TI11	75°42'44	123°16'49	3	25.7	−55.1	3197	2012 ³
S1 TI11	75°42'97	120°13'54	10	22.4	−56.0	3206	2012 ³
S2 TI11	76°17'37	117° 16'56.3	3	21	−55.1	3229	2012 ²
S3 TI11	76°50'	113° 01'46	10	22.2	−54.5	3324	2012 ³
Point Barnola	75°42'55	123°15.50'	5	26	NA	3236	2012 ³
Vostok	78°27'52	106°50'14	3	21	−57	3488	2008 ² and 2014 ²
Dome C	75°06'	123°19'48	1.5 to 3	27–35	−54.3	3233	1978 ¹ and 2007 ² and 2012 ¹

Superscript numbers indicate the reference for the subset of records recently published by: (1) Casado et al. (2016b) and (2) Touzeau et al. (2016); (3) indicate new unpublished datasets (this study).

placed 1 m above the surface, it is not always simple to distinguish between blowing snow and precipitation events. Finally, the distance between the main building and the wood table (800 m) makes manual sampling sometimes impossible under very cold weather conditions.

In parallel, other polar programs have implemented routine sampling of surface snow (Casado et al., 2016a; Touzeau et al., 2016). For the data presented here, surface snow was sampled on random spots of a clean area about 1 km from the Concordia station on a weekly basis. Samples from the surface were gathered from the surface skin layer (the few upper millimeters).

2.1.3. Snowpits collection

We present depth profiles of isotopic composition from snow pits realized over different locations of the Antarctic Plateau (Table 1 and Fig. 1). The samples were taken in plastic flasks and shipped frozen to France where they were analyzed. First, in the Austral summer 2006–2007, five 1–2-meter-deep snow pits have been sampled during the Taste Idea campaign (hereafter TI06) with a vertical resolution of 5 cm. These snow pits were taken on the slope of the Antarctic plateau with an accumulation rate varying between 200 and 400 kg·m⁻²·yr⁻¹, i.e. approximately 90 cm of snow each year. In 2011/12, another series of snow pits was realized in the framework of the TI11 campaign between Dome C and Vostok. Four 1–3-meter-deep snow pits were realized with a resolution from 3 to 10 cm in an area with accumulation rates around 20 to 30 mm kg·m⁻²·yr⁻¹. A 110 m core has also been sampled at Point Barnola during this campaign.

In addition to the pits and cores realized during transect, three snow pits from Dome C and two from Vostok are included in this study. They were sampled from 2008 to 2015.

2.2. Snow isotopes analysis

After collection, the snow samples were placed in closed corning tubes or sealed bags and kept frozen all the way back from Antarctica to France. They were melted only prior to measurement to ensure correct conservation of the water isotopic composition.

Two methods for $\delta^{18}\text{O}$ measurements were used in this study. The samples from the TI06 campaign were measured at the “Laboratoire des sciences du climat et de l’environnement” (LSCE) by water–CO₂ equilibration using a calibration performed vs V-SMOW and V-SLAP. The most recent measurements of $\delta^{18}\text{O}$ (after 2011) and δD measurements presented here were also performed at LSCE, but using a laser cavity ring-down spectroscopy (CRDS) analyzer PICARRO. A special care has been dedicated to the calibration of this instrument since many data displayed here have a $\delta^{18}\text{O}$ lower than −55.5‰. This means that the usual V-SMOW vs V-SLAP calibration on the range −55.5‰ to 0‰ cannot be applied directly. To address this issue, a calibration study has been performed during the measurement period through the realization of water samples with $\delta^{18}\text{O}$ as low as −80‰ (Casado et al., 2016a). Finally, the accuracy for $\delta^{18}\text{O}$ and δD measurements displayed here is about 0.1 and 1‰, respectively.

3. Results

3.1. Isotopic composition of surface snow along transects

3.1.1. Motivation

Transects are key to document the spatial distribution of the multi-annual average isotopic composition, and, together with average temperature measurements, estimate the spatial relationships between $\delta^{18}\text{O}$ and temperature (Lorius and Merlivat, 1977; Lorius et al., 1969; Masson-Delmotte et al., 2008; Touzeau et al., 2016). They are of primary importance to benchmark atmospheric general circulation models equipped with water isotopes (e.g., Risi et al., 2010; Werner et al., 2015), especially in central East Antarctica, where modeling uncertainties also arise from poorly characterized fractionation coefficients at low temperature.

Over the last decades, numerous analytical and theoretical studies have been devoted to constrain the fractionation coefficients associated with water isotopes (e.g., Cappa et al., 2003; Ellehoj et al., 2013; Horita et al., 2008; Luz et al., 2009; Majoube, 1971a, b; Merlivat and Nief, 1967; Pinilla et al., 2014; Van Hook, 1968).

Nevertheless, uncertainties remain associated with the quantification of isotopic fractionation between water vapor and snow during condensation in polar regions, where several specific effects should be taken into account. First, unlike for condensation of rainwater in clouds, snowflakes formation does not occur at equilibrium between the vapor and the condensed phase. The air is generally oversaturated with water vapor and strong kinetic fractionation (i.e. linked with diffusivity) occurs in addition to equilibrium fractionation between water vapor and snow. This kinetic effect is enhanced when supersaturation increases, which is the case when air temperature decreases. The parameterization of the vapor–snow fractionation proposed by Jouzel and Merlivat (1984) expresses the fractionation coefficient (α_{v-s}) during snow formation by the formula:

$$\alpha_{v-s} = \frac{S}{(S-1)D/D^* + 1/\alpha_{eq}} \quad (1)$$

where α_{eq} is the fractionation coefficient at equilibrium between vapor and solid, D and D^* are the diffusion coefficients of the light and heavy water isotopes in air. In the classical approach, supersaturation S is related to inversion temperature, T in °C, at which precipitation is assumed to form, so that $S = 1 - aT$, with a varying between 0.002 and 0.007 (Ciais and Jouzel, 1994; Jouzel and Merlivat, 1984). This relationship is constrained by atmospheric measurements and the “ a ” coefficient is adjusted to reduce model-data mismatches for polar precipitation. The second-order parameter d-excess, defined as $d\text{-excess} = \delta D - 8 \times \delta^{18}O$ (Dansgaard, 1964), is indeed very sensitive to kinetic effects at condensation in cold polar regions. As a consequence, the tuning of the supersaturation relationship to temperature is performed so that the observed relationship between $\delta^{18}O$ and d-excess in Antarctica can be reproduced by GCMs (Risi et al., 2010; Schmidt et al., 2007). Adequate tuning of supersaturation in mixed-cloud distillation models is essential for quantitative reconstructions of climate variables (site temperature, evaporation conditions at moisture sources) based on $\delta^{18}O$ and d-excess from deep ice core records (Ciais and Jouzel, 1994; Masson-Delmotte et al., 2005; Stenni et al., 2010; Winkler et al., 2012).

3.1.2. Results

The new data from the TI11 and Spanish expeditions provide water isotopic data in very cold regions. Snow in these regions is particularly depleted in both $H_2^{18}O$ and $HD^{18}O$, and we focus here on snow with $\delta^{18}O$ lower than -40‰ . This snow is also associated with an increase in the second-order parameter d-excess, which is a result of the strong distillation of the moist air mass when it arrives at the end point of its trajectory; the amplitude of this d-excess increase is attenuated by kinetic effects at condensation that decrease d-excess in precipitation. The increase in snow d-excess when $\delta^{18}O$ is decreasing is evidenced by TI11 data, showing much smaller isotopic scattering than in the Chinese transect near Dome A (Pang et al., 2015). This new set of data will therefore help better tuning of models implemented with water isotopes for Antarctica.

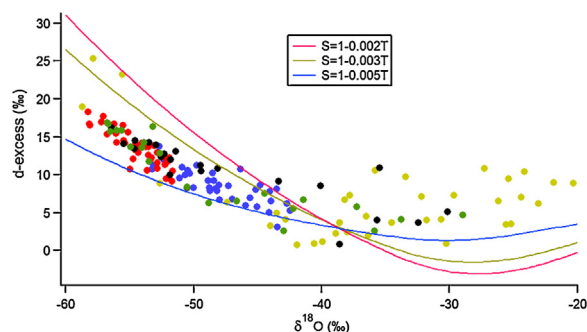


Fig. 2. Evolution of the d-excess vs $\delta^{18}O$ for the samples obtained on transects from Fig. 1, using the same color code (red, blue, yellow, green and black circles correspond respectively to the French–Russian TI11, Spanish, Chinese, Swedish–Japanese and Italian–French transects) together with MCIM simulations of d-excess calculated along a cooling trajectory for different parameterizations of the supersaturation function (thin lines). Note that it is not expected that one single distillation trajectory should encompass all traverse data, given the fact that different locations receive moisture from different sources and through different cooling trajectories.

Fig. 2 displays a comparison between the new transect data and outputs of the Mixed Cloud Isotopic Model (MCIM) (Ciais and Jouzel, 1994), which computes the evolution of the isotopic composition of water vapor and condensed liquid and snow along a moist air trajectory, allowing for a proportion of the condensed water to remain in the cloud and the coexistence of liquid water and ice in intermediate temperature ranges. This model is commonly used for a first-order quantitative interpretation of water stable isotope records from Antarctic deep ice cores (e.g., Landais et al., 2008; Stenni et al., 2003; Vimeux et al., 2001; Winkler et al., 2012). Fig. 2 shows the sensitivity of d-excess simulated by MCIM to the supersaturation parameterization, especially for low $\delta^{18}O$ (for $\delta^{18}O > -40\text{‰}$, temperature is not low enough for the supersaturation influence to be significant). The best fit between the model outputs and all datasets (Fig. 2) is obtained for a parameterization of S in the range from $S = 1 - 0.003 T$ to $S = 1 - 0.005 T$, which is also the range commonly used in general circulation models equipped with water stable isotopes (e.g., Risi et al., 2010; Schmidt et al., 2005; Werner et al., 2011). The new data presented here lead to a tuning of the supersaturation as $S = 1 - 0.004 T$ over the two transects (Fig. 2). Note that the isotopic data with $\delta^{18}O > -40\text{‰}$ are of no use to tune supersaturation, and the scattering of the data reflects the different moisture source and trajectories of the water mass toward Antarctica (influences of temperature, humidity of the evaporative region as well as presence of sea ice).

3.2. Precipitation vs surface snow at Dome C

Fig. 3 displays daily variations in surface air temperature, precipitation, $\delta^{18}O$ of precipitation events and $\delta^{18}O$ of weekly sampled surface snow during year 2011. Stenni et al. (2016) already stressed the close day-to-day correlation between temperature and the $\delta^{18}O$ of the precipitation. First, seasonal variations are marked by higher precipitation $\delta^{18}O$ in austral summer (with a

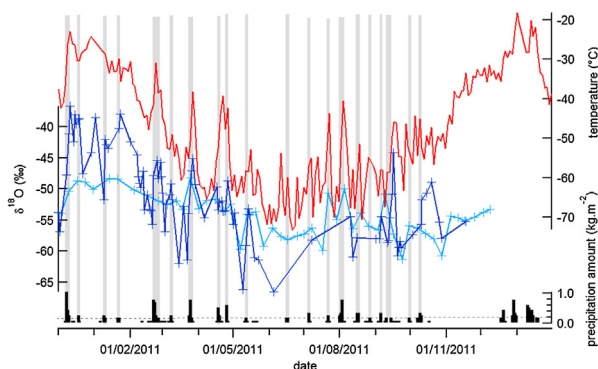


Fig. 3. Variations of 2m surface air temperature measured by an automatic weather station (red, Genthon et al., 2013), $\delta^{18}\text{O}$ of precipitation (dark blue crosses) and $\delta^{18}\text{O}$ of surface snow (light blue crosses) for the year 2011 at Dome C. The amount of precipitation is a product of ERA-interim reanalyses (Dee et al., 2011). The grey bars indicate precipitation amounts larger than 0.2 kg m^{-2} .

maximum value of -37‰) and lower values in austral winter (with a minimum value of -67‰). Second, short-lived warm events associated with significant precipitation events are also associated with $\delta^{18}\text{O}$ peaks (e.g., 21–22 February 2011, 25 March 2011). Such a correlation between temperature and the $\delta^{18}\text{O}$ of precipitation is not unexpected; it results from the distillation of the water mass from the low to high latitudes associated with the gradual decrease of $\delta^{18}\text{O}$ in water vapor and precipitation. The relationship obtained between $\delta^{18}\text{O}$ and temperature for the annual distribution of precipitation at Dome C is on average $0.49 \pm 0.01\text{‰} \cdot ^\circ\text{C}^{-1}$ (Stenni et al., 2016); for the year 2011 displayed in Figs. 3 and 4, the slope is of $0.48 \pm 0.035\text{‰} \cdot ^\circ\text{C}^{-1}$ ($R^2 = 0.29$, $N = 80$). This slope is significantly lower than the spatial $\delta^{18}\text{O}$ -vs-temperature relationship of $0.8 \pm 0.01\text{‰} \cdot ^\circ\text{C}^{-1}$ given by Masson-Delmotte et al. (2008).

More surprisingly, despite the very small cumulative snow accumulation over one year at Dome C and strong blowing snow events that regularly remove the recently deposited snow, the surface snow $\delta^{18}\text{O}$ also follows the temperature evolution at the annual scale, even in the absence of abundant precipitation (e.g., from January to March). Still, the amplitude is much smaller ($0.14 \pm 0.01\text{‰} \cdot ^\circ\text{C}^{-1}$, Fig. 4) than the amplitude of the

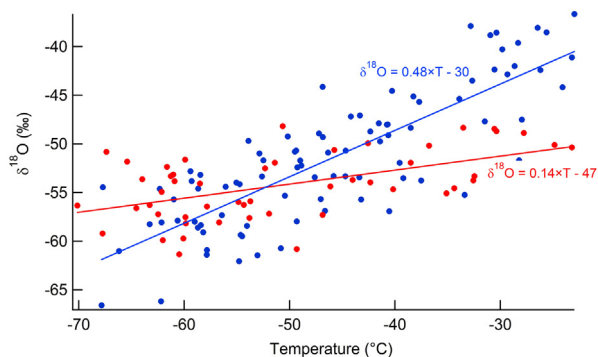


Fig. 4. Relationship between $\delta^{18}\text{O}$ and temperature for surface snow (red) and precipitation (blue) at Dome C for the year 2011.

precipitation $\delta^{18}\text{O}$ -vs-temperature evolution. The correlation between $\delta^{18}\text{O}$ and temperature in the absence of precipitation events necessarily reflects post-deposition processes of exchange between water vapor and surface snow, as observed in Greenland (Steen-Larsen et al., 2014). In addition, some warming events often associated with precipitation during the austral winter are also clearly imprinted in the surface snow $\delta^{18}\text{O}$ (e.g., 22 July and 3 August). These results suggest that even if important deposition and post-deposition processes affect surface snow isotopic composition, the co-variations of $\delta^{18}\text{O}$ with temperature are preserved in the surface snow. Still, quantifying the link between temperature and the $\delta^{18}\text{O}$ of precipitation as currently performed with models equipped with isotopes is not sufficient; surface exchanges should be implemented, which strengthens the need for surface studies as the one presented here.

3.3. Snow pits

Deposition and post-deposition processes may not only affect the surface layer as documented in the previous section, but also deeper snow layers. At shallow depth, snow porosity is large and wind ventilation favors water vapor circulation and hence exchange with snow crystals (Neumann and Waddington, 2004). Surface snow also undergoes sublimation and wind blowing effects, leading to complex accumulation patterns affecting the whole snow stratigraphy (Groot Zwaftink et al., 2013; Libois et al., 2014). Wind speeds are remarkably high on the margin of the Antarctic plateau due to katabatic winds (gravity-driven downslope descent of cold surface air towards the coastal areas), leading to large blowing snow events (Scarchilli et al., 2010). In order to assess how the initial seasonal or inter-annual variability of precipitation isotopic signal is preserved down into the firn, numerous shallow snow pits have been sampled and analyzed for water stable isotopes.

Earlier studies have demonstrated that annual layer counting is possible using water isotopes records, but often more equivocal than through seasonally resolved records of major ions on the Antarctic plateau (probably continental erosion and sea ice for Ca^{2+} and Na^+), or seasonal signals evidenced through electrical conductivity or dielectric continuous measurements (e.g., Rasmussen et al., 2006). This mismatch is particularly true for sites with relatively low accumulation rate where diffusion of water vapor will affect more strongly the isotopic composition of snow than the concentration of chemical species (Hoshina et al., 2016).

Despite limitations by diffusion, water isotopes in snow pits and shallow ice cores are still largely used for the reconstruction of recent climate variations (Altnau et al., 2014; Goursaud et al., 2016; Jouzel et al., 1983; Küttel et al., 2012; Schneider et al., 2006). For sites characterized by low accumulation rate, stacking several pits enables one to increase the ratio between signal and noise, hence improving the climatic reconstruction (Ekaykin et al., 2014; Münch et al., 2015).

We present here a compilation of new water isotopic records obtained over the recent years from Taste-Idea transects (Fig. 1, Table 1). These data are also complemented by snow pits from Dome C sampled at a resolution

down to 1.5 cm in depth. Our analysis of these records is devoted to the cause of the observed variability through depth: under which conditions and until which depth can an annual cycle be recorded? What is the significance of centimetric variations in surface snow water stable isotope records?

3.3.1. Taste Idea snow pits

At the coastal site S1 TI06, where the highest temperature was recorded at a depth of 10 m (-13°C), we can compare isotopic profiles from one snow pit with one 22.4 m shallow core drilled at a distance of about 5 m (Goursaud et al., 2016). The parallel $\delta^{18}\text{O}$ variations (Fig. 5) suggest limited noise associated with spatial variability at a site where the accumulation rate is high and corresponds to an annual mean deposition of $190 \pm 60 \text{ kg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ (Goursaud et al., 2016). The maximum of $\delta^{18}\text{O}$ observed at about 1 m depth in the pit most likely corresponds to the snow layer of the previous summer, as expected from the range of snow accumulation. For the S2 TI06 pit, the depth difference of about 130 cm between the two $\delta^{18}\text{O}$ minima also corresponds to the average accumulation rate obtained from nearby stakes ($\sim 320 \text{ kg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$).

The detection of an annual cycle is more complicated at other sites, because the snow pits are too shallow. The top layer does not systematically correspond to high $\delta^{18}\text{O}$

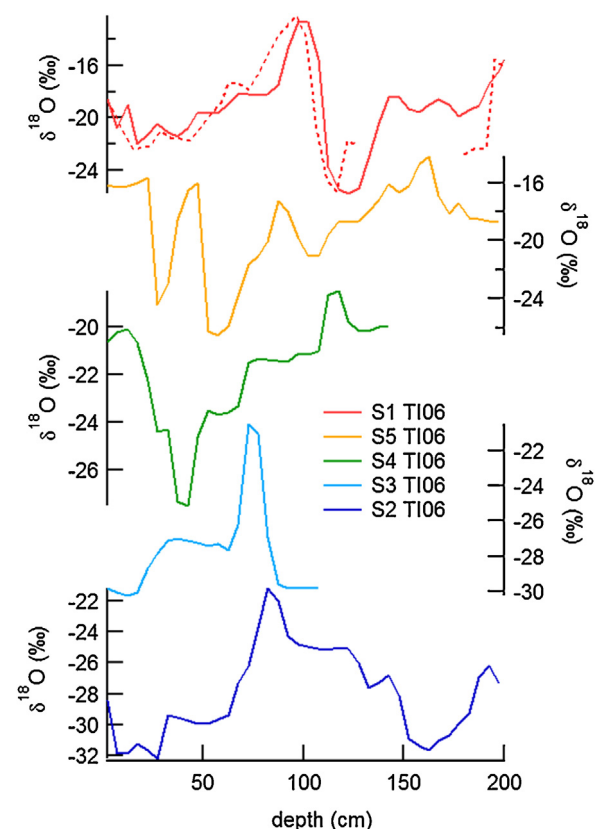


Fig. 5. Depth evolution of $\delta^{18}\text{O}$ in the five snow pits from the Taste Idea campaign 2006–07 (TI06) (see Fig. 1 for locations). For S1 TI06, we represent the records from the snow pit (red solid line) and 22 m shallow core (red dotted line, Goursaud et al., 2016).

values (especially at S306) despite the fact that sampling was performed during the warmest summer months. This suggests that, even at sites with relatively high accumulation rates, deposition and post-deposition effects (including snow blowing and intermittency of precipitation) complicate the identification of summer layers in shallow ice cores and hence limit the resolution of the associated climate reconstructions. Duplicate and longer records from deeper pits or shallow cores are needed to deconvolve post-deposition from climatic signals.

3.3.2. Snow pits on the East Antarctic plateau

Fig. 6 displays $\delta^{18}\text{O}$ variations over the top 1 m of snow on several snow pits sampled in 2011–2012 during the TI11 campaign. Altogether, $\delta^{18}\text{O}$ values range between -58 and -46 ‰; this 8‰ amplitude is twice smaller than that observed in precipitation samples from Dome C and Vostok (Ekaykin et al., 2004; Stenni et al., 2016), and similar to the seasonal amplitude observed in surface snow samples at Dome C (Fig. 3). Comprehensive statistical analyses cannot be applied on such short records, but we may identify 2–3 cycles of $\delta^{18}\text{O}$ variations within 1 m (Fig. 6), corresponding to a depth periodicity of 20 to 50 cm in the $\delta^{18}\text{O}$ signal. Because the annual accumulation rate is in general

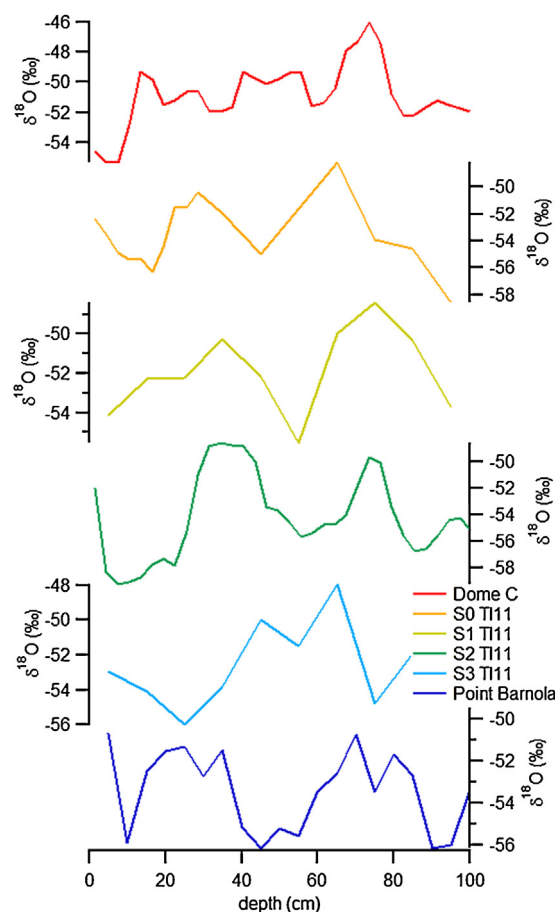


Fig. 6. $\delta^{18}\text{O}$ evolution on the first meter of East Antarctic snow pits at low-accumulation sites from the Vanish-Explore campaign (2011–2012). The data from Dome C and S2 TI11 were published in Touzeau et al. (2016).

lower than $100 \text{ kg} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ on the Antarctic plateau, these $\delta^{18}\text{O}$ “cycles” cannot be understood as reflecting seasonal variations, as discussed previously for the coastal site S1 TI06.

The periodicity of the signal can be investigated in more details using the $\delta^{18}\text{O}$ records obtained from 3-m-deep snow pits in the same region (Fig. 7). The records confirm the previous observation of much longer periodicity than the annual accumulation rate for the different sites as also detailed in Casado et al. (2016a, b). There is only one exception for this behavior from the Dome C $\delta^{18}\text{O}$ record, obtained on the snow pit dug in 2007. On this snow pit, the scattering of $\delta^{18}\text{O}$ data obtained on a 3-cm resolution observed over the first meter can be related to a high-frequency variability of $\delta^{18}\text{O}$ ($\sim 6\text{--}9 \text{ cm}$). Deeper in the firn, the record is smoother, possibly due to diffusion. Diffusion is indeed expected to increase strongly on the first meters of snow as shown by calculations of diffusion given in Johnsen et al. (2000). The diffusion length increases rapidly from the surface, reaching 2 cm at 1 m depth and more than 6 cm at 4 m at Dome C. This means that a signal associated with a 10 cm periodicity will be attenuated by a factor of 2 at 1 m and by a factor of 10 at 4 m. An annual cycle should hence be visible at 1 m at Dome C, but vanishes deeper as observed for the snow pit drilled in 2007.

We finally stress here the large dispersion between $\delta^{18}\text{O}$ records from the same site (e.g., for Vostok and Dome C). This confirms the strong spatial variability already observed on records of impurities, densities and isotopes from different snow pits drilled the same year, but at distances of several tenths of meters (Ekaykin et al., 2014; Gautier et al., 2016; Hoshina et al., 2016; Laepple et al., 2016; Libois et al., 2014; Münch et al., 2015).

Intermittency of precipitation, sublimation of snow, deposition and post-deposition effects (e.g., firn

ventilation, diffusion and blowing snow) are good candidates for explaining the lack of seasonal record archived in snow pits. Several studies have also highlighted the discontinuous accumulation process at sites like Dome C linked to wind events (Groot Zwaaftink et al., 2013; Libois et al., 2014). Still, the fact that the 2007 Dome C $\delta^{18}\text{O}$ record displays high-frequency variability over the first meter raises the question of a possible missing seasonal signal in the other records. Indeed, Dome C is the site with the highest accumulation rate beyond the different sites presented in Fig. 7 and the sampling resolution of 3 cm may not be enough to capture the high-frequency (seasonal) variability present in the other records.

3.3.3. Focus on Dome C

The previous results suggest that seasonal cycles might be identified at Dome C with a higher-resolution sampling. We thus performed high-resolution (1.5 cm) $\delta^{18}\text{O}$ measurements on two snow pits drilled during the summer season 2014–2015 at Dome C (Fig. 8). It is possible to identify three maxima (indicated by arrows) and two minima over the top 20 cm, as expected from the average accumulation rate of $\sim 8\text{--}10 \text{ cm}$ of snow per year ($27\text{--}35 \text{ kg} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$) at Dome C. These results confirm that seasonal cycles may be recorded in the upper 20 cm of the snow layers at Dome C. At deeper depths, a longer periodicity (at least 20 cm) appears more prominent, similar to that evidenced from the 3 m snow pits described in the previous section.

Finally, we investigate $\delta^{18}\text{O}$ profiles over the upper 50 cm of snow performed every 4 hours at Dome C between 21 and 23 December 2015 (Fig. 9). All eight profiles exhibit relatively low $\delta^{18}\text{O}$ values near the surface and a strong $\delta^{18}\text{O}$ increase up to -42‰ at depths between 6 and 10 cm. Such coherency between the $\delta^{18}\text{O}$ profiles is

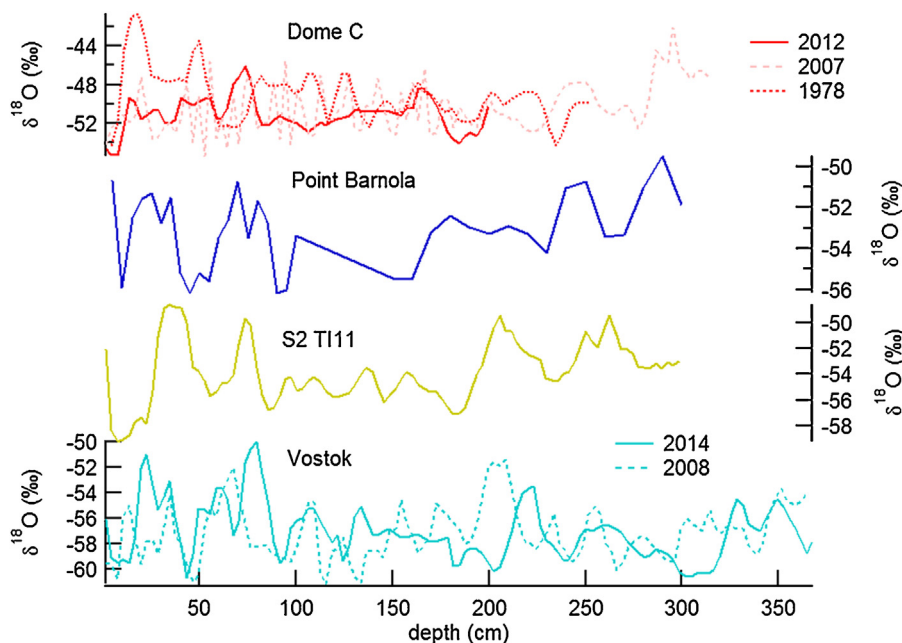


Fig. 7. A compilation of $\delta^{18}\text{O}$ records from 3–4 m deep snow pits in low accumulation sites from East Antarctica (see Fig. 1 for the location of these sites).

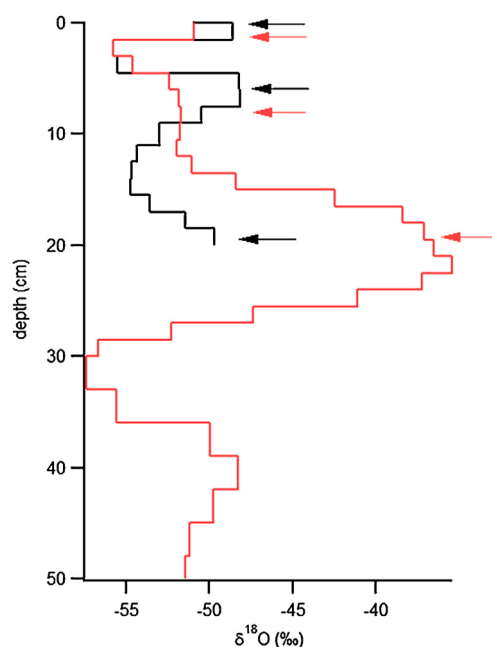


Fig. 8. $\delta^{18}\text{O}$ records from two snow pits (black and red) drilled at Dome C in summer 2014–2015 and sampled at a depth of 1.5 cm. The arrows show the location of the three first $\delta^{18}\text{O}$ maxima (or inflexion point for the second red arrow).

supported by a principal components (PC) analysis, with PC1 capturing 67% of the variance, showing the strong $\delta^{18}\text{O}$ peak depths of 6–10 cm as well as two oscillations of smaller amplitude at higher depths. This suggests that a common signal can be extracted from high-resolution $\delta^{18}\text{O}$ snow pit profiles. This common signal may either be produced by deposition (snowfall $\delta^{18}\text{O}$ signal linked to atmospheric processes along transport and at condensation) or produced

by post-deposition processes and snow–air isotopic exchanges with a spatial coherence at the scale of a few meters at least.

The eight $\delta^{18}\text{O}$ profiles exhibit significant differences, such as the amplitude of the peak observed at depths between 6 and 10 cm. There is no link between the variations of amplitude of this sub-surface $\delta^{18}\text{O}$ peak and the surface temperature, hence with the temperature gradient at the very surface of the snow. Even if the pits are rather close (1 m distance between successive pits), variations in $\delta^{18}\text{O}$ from one snow pit to the next one may be affected by wind blowing or wind scouring effects (Libois et al., 2014). Some small surface inhomogeneity or snow dunes at Dome C are indeed observed at the meter scale (Picard et al., 2014), reflecting erosion and enhanced deposition on different sites of the snow dunes. Such snow redistribution processes probably explains stratigraphic noise and/or hiatus observed in the different snow pits at very low accumulation rates (e.g., Kameda et al., 2008).

4. Conclusions and perspectives

Together with previously published data, the new data presented in this study have several implications for the climatic reconstruction based on ice core isotopic data.

The spatial relationship between surface temperature and isotopic composition of precipitation can be explained quite straightforwardly using simple isotopic models tuned on d-excess vs $\delta^{18}\text{O}$ evolution in transects on the East Antarctic sector. The spatial slopes deduced from the transects are however systematically higher (~ 0.7 – $0.8\text{‰}\cdot\text{°C}^{-1}$ for $\delta^{18}\text{O}$ vs temperature, Masson-Delmotte et al., 2008; Touzeau et al., 2016) than temporal slopes calculated from seasonal variations in precipitation $\delta^{18}\text{O}$ at sites from East Antarctica like Vostok and Dome C (0.35 to $0.46\text{‰}\cdot\text{°C}^{-1}$ (Landais et al., 2012; Stenni et al., 2016). These

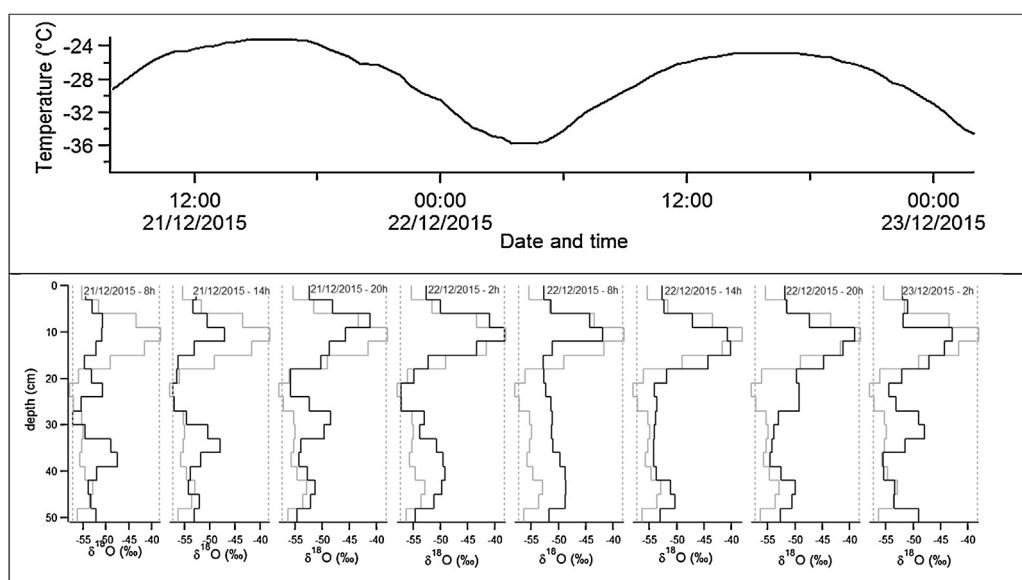


Fig. 9. Top: 2 m surface air temperature measurements at Dome C. Bottom: 8 $\delta^{18}\text{O}$ records (black) from eight snow pits located at 1 m distance drilled every 6 h between 21 and 23 December 2015 at Dome C. The grey curve displays the first component (PC1) of a principal component analysis and captures 67% of the common variance of the eight $\delta^{18}\text{O}$ records.

differences may be explained by the vanishing inversion layer in summer (Casado et al., 2016a, b; Landais et al., 2012), and therefore different relationships between condensation and surface temperature.

Post-deposition effects linked to exchanges between the snow surface and the atmospheric water vapor lead to an evolution of $\delta^{18}\text{O}$ in the surface snow in the absence of any precipitation event in Antarctica, as previously evidenced for Greenland. This process preserves the positive correlation between the $\delta^{18}\text{O}$ of snow and surface temperature at the seasonal scale, but with a much slower $\delta^{18}\text{O}$ -vs-temperature slope than observed with seasonal precipitation data (Casado et al., 2016b; Touzeau et al., 2016). Such relationship likely involves equilibrium and kinetic fractionation at the interface between snow and atmosphere at sublimation and hoar condensation (Casado et al., 2016b; Ritter et al., 2016; Steen-Larsen et al., 2014). It is now a priority to quantify the importance of these processes for different deep-drilling sites, as it is highly important both for the comparison of ice core data with atmospheric model outputs and for assessing uncertainties attached to past temperature reconstructions from ice cores. Implementing isotopes in snow models is a crucial step forward.

Post-deposition effects clearly limit the possible archiving of high-resolution (seasonal) climatic variability in the polar snow. Earlier studies suggested that seasonal cycles could not be recorded in snow water isotopes from low accumulation rate sites of East Antarctica (Ekaykin et al., 2014). Using new isotopic records from snow pits drilled in high-accumulation and low-accumulation sites of East Antarctica, we are able to adjust/refine this statement. Sites with an accumulation rate larger than $70\text{--}80\text{ kg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ such as Kohnen (Münch et al., 2015) record a seasonal cycle in the absence of large wind effects. It is challenging to identify seasonal cycles on sites from the East Antarctic plateau: in the different snow pits recovered associated with the T111 campaign and at Vostok, no variations are identified at depths corresponding to the average annual accumulation rate. The only exception is for one snow pit drilled at Dome C in 2007, where the water isotopic record depicts high-frequency variations over the first meter, which may correspond to seasonal signals. This finding is further supported by water isotopic records from two snow pits from Dome C, analyzed at 1.5 cm resolution. Our results also depict a smoothing of these signals below one meter in depth, probably due to diffusion.

An important result of our study is that seasonal climate variability may affect the surface snow isotopic composition at the surface and possibly over the top 50 cm, at least at Dome C. We are still lacking high-resolution (1 cm) deep snow pits and associated snow modeling to study how the seasonal cycle is preserved or not in the snow when diffusion and wind ventilation induce important water vapor transport in the zone where porosity is still important.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.crte.2017.05.003>.

References

- Altnau, S., Schlosser, E., Isaksson, E., Divine, D., 2014. Climatic signals from 76 shallow firn cores in Dronning Maud Land, East Antarctica. *Cryosph. Discuss.* 8, 5961–6005, <http://dx.doi.org/10.5194/tcd-8-5961-2014>.
- Buizert, C., Gkinis, V., Severinghaus, J.P., He, F., Lecavalier, B.S., Kindler, P., Leuenberger, M., Carlson, A.E., Vinther, B., Masson-Delmotte, V., White, J.W.C., Liu, Z., Otto-Bliesner, B., Brook, E.J., 2014. Greenland temperature response to climate forcing during the last deglaciation. *Science* 345 (6201), 1177–1180, <http://dx.doi.org/10.1126/science.1254961>.
- Cappa, C.D., Hendricks, M.B., DePaolo, D.J., Cohen, R.C., 2003. Isotopic fractionation of water during evaporation. *J. Geophys. Res.* 108 (D16), 4525, <http://dx.doi.org/10.1029/2003JD003597>.
- Casado, M., Landais, A., Masson-Delmotte, V., Genthon, C., Kerstel, E., Kassi, S., Arnaud, L., Picard, G., Prie, F., Cattani, O., Steen-Larsen, H.-C., Vignon, E., Cermak, P., 2016a. Continuous measurements of isotopic composition of water vapour on the East Antarctic Plateau. *Atmos. Chem. Phys.* 16, 8521–8538, <http://dx.doi.org/10.5194/acp-16-8521-2016>.
- Casado, M., Landais, A., Picard, G., Münch, T., Laepple, T., Stenni, B., Dreossi, G., Ekaykin, A., Arnaud, L., Genthon, C., Touzeau, A., Masson-Delmotte, V., Jouzel, J., 2016b. Archival of the water stable isotope signal in East Antarctic ice cores. *Cryosph. Discuss.* 2016, 1–33, <http://dx.doi.org/10.5194/tc-2016-263>.
- Cauquoin, A., Landais, A., Raisbeck, G.M., Jouzel, J., Bazin, L., Kageyama, M., Peterschmitt, J.-Y., Werner, M., Bard, E., Team, A., 2015. Comparing past accumulation rate in the East Antarctic ice cores using ^{10}Be , water isotopes and CMIP5-PMIP3 models. *Clim. Past* 11, 355–367, <http://dx.doi.org/10.5194/cp-11-355-2015>.
- Champollion, N., Picard, G., Arnaud, L., Lefebvre, E., Fily, M., 2013. Hoar crystal development and disappearance at Dome C, Antarctica: observation by near-infrared photography and passive microwave satellite. *Cryosphere* 7 (4), 1247–1262, <http://dx.doi.org/10.5194/tc-7-1247-2013>.
- Ciais, P., Jouzel, J., 1994. Deuterium and oxygen 18 in precipitation: isotopic model, including mixed cloud processes. *J. Geophys. Res. Atmos.* 99 (D8), 16793–16803.
- Cuffey, K.M., Clow, G.D., Steig, E.J., Buizert, C., Fudge, T.J., Koutnik, M., Waddington, E.D., 2016. Deglacial temperature history of West Antarctica. *PNAS* 113 (50), 14249–14254, <http://dx.doi.org/10.1073/pnas.1609132113>.
- Dahl-Jensen, D., 1998. Past Temperatures Directly from the Greenland Ice Sheet. *Science* 282 (5387), 268–271, <http://dx.doi.org/10.1126/science.282.5387.268>.
- Dansgaard, W., 1964. Stable isotopes in precipitation. *Tellus* 16, 436–468.
- Dee, D.P., Uppala, S.-m., Simmons, A.J., Berrisford, P., Poli, P., Kobayashi, S., Andrae, U., Balmaseda, M.A., Balsamo, G., Bauer, P., Bechtold, P., Beljaars, A.C.M., van de Berg, L., Bidlot, J., Bormann, N., Delsol, C., Dragani, R., Fuentes, M., Geer, A.J., Malmberger, L., Healy, S.B., Hersbach, H., Hólm, E.V., Isaksen, I., Källberg, P., Köhler, M., Matricardi, M., McNally, A.P., Monge-Sanz, B.M., Morcrette, J.-J., Park, B.-K., Peubey, C., de Rosnay, P., Tavolato, C., Thépaut, J.N., Vitart, F., 2011. The ERA-Interim: configuration and performance of the data assimilation system. *Q. J. R. Meteorol. Soc.* 137, 553–597, <http://dx.doi.org/10.1002/qj.828>.

- Ekaykin, A.A., Kozachek, A.V., Lipenkov, V.Y., Shibaev, Y.A., 2014. Multiple climate shifts in the Southern Hemisphere over the past three centuries based on central Antarctic snow pits and core studies. *Ann. Glaciol.* 55 (66), 259–266, <http://dx.doi.org/10.3189/2014AoG66A189>.
- Ekaykin, A.A., Lipenkov, V.Y., Kuzmina, I.N., Petit, J.R., Masson-Delmotte, V., Johnsen, S.J., 2004. The changes in isotope composition and accumulation of snow at Vostok station, East Antarctica, over the past 200 years. *Ann. Glaciol.* 39 (1), 569–575.
- Ellehoj, M.D., Steen-Larsen, H.C., Johnsen, S.J., Madsen, M.B., 2013. Ice-vapor equilibrium fractionation factor of hydrogen and oxygen isotopes: experimental investigations and implications for stable water isotope studies. *Rapid Commun. Mass Spectrom.* 27 (19), 2149–2158, <http://dx.doi.org/10.1002/rcm.6668>.
- Epica Community Members, 2004. Eight glacial cycles from an Antarctic ice core. *Nature* 429 (6992), 623–628, http://www.nature.com/nature/journal/v429/n6992/supinfo/nature02599_S1.html.
- Fischer, H., Severinghaus, J., Brook, E., Wolff, E., Albert, M., Alemany, O., Arthern, R., Bentley, C., Blankenship, D., Chappellaz, J., Creys, T., Dahl-Jensen, D., Dinn, M., Frezzotti, M., Fujita, S., Gallee, H., Hindmarsh, R., Hudspeth, D., Jügle, G., Kawamura, K., Lipenkov, V., Miller, H., Mulvaney, R., Parrenin, F., Pattyn, F., Ritz, C., Schwander, J., Steinhage, D., Van Ommen, T., Wilhelms, F., 2013. Where to find 1.5 million yr old ice for the IPICS “Oldest-Ice” ice core. *Clim. Past* 9 (6), 2489–2505, <http://dx.doi.org/10.5194/cp-9-2489-2013>.
- Gautier, E., Savarino, J., Erblant, J., Lanciki, A., Possenti, P., 2016. Variability of sulfate signal in ice core records based on five replicate cores. *Clim. Past* 12 (1), 103–113, <http://dx.doi.org/10.5194/cp-12-103-2016>.
- Genthon, C., Six, D., Gallée, H., Grigioni, P., Pellegrini, A., 2013. Two years of atmospheric boundary layer observations on a 45-m tower at Dome C on the Antarctic plateau. *J. Geophys. Res. Atmos.* 118 (8), 3218–3232, <http://dx.doi.org/10.1002/jgrd.50128>.
- Goursaud, S., Masson-Delmotte, V., Favier, V., Preunkert, S., Fily, M., Gallée, H., Jourdain, B., Legrand, M., Magand, O., Minster, B., Werner, M., 2016. A sixty year ice-core record of regional climate from Adélie Land, coastal Antarctica. *Cryosph. Discuss.* 2016, 1–36, <http://dx.doi.org/10.5194/cp-2016-179>.
- Groot Zwaartink, C.D., Cagnati, A., Crepez, A., Fierz, C., MacElloni, G., Valt, M., Lehning, M., 2013. Event-driven deposition of snow on the Antarctic Plateau: analyzing field measurements with SNOVPACK. *Cryosphere* 7 (1), 333–347, <http://dx.doi.org/10.5194/cp-7-333-2013>.
- Guillevic, M., Bazin, L., Landais, A., Kindler, P., Orsi, A., Masson-Delmotte, V., Blunier, T., Buchardt, S.L., Capron, E., Leuenberger, M., Martinier, P., Prié, F., Vinther, B.M., 2013. Spatial gradients of temperature, accumulation and $\delta^{18}\text{O}$ -ice in Greenland over a series of Dansgaard-Oeschger events. *Clim. Past* 9 (3), 1029–1051, <http://dx.doi.org/10.5194/cp-9-1029-2013>.
- Helsen, M.M., van de Wal, R.S.W., van den Broeke, M.R., Masson-Delmotte, V., Meijer, H.A.J., Scheele, M.P., Werner, M., 2006. Modeling the isotopic composition of Antarctic snow using backward trajectories: simulation of snow pit records. *J. Geophys. Res. Atmos.* 111 (15), 1–19, <http://dx.doi.org/10.1029/2005JD006524>.
- Higgins, J.A., Kurbatov, A.V., Spaulding, N.E., Brook, E., Introne, D.S., Chimiak, L.M., Yan, Y., Mayewski, P., Bender, M.L., 2015. Atmospheric composition 1 million years ago from blue ice in the Allan Hills, Antarctica. *Proc. Natl. Acad. Sci. USA* 112 (22), 6887–6891, <http://dx.doi.org/10.1073/pnas.1420232112>.
- Horita, J., Rozanski, K., Cohen, S., 2008. Isotope effects in the evaporation of water: a status report of the Craig-Gordon model. *Isotop. Environ. Health Stud.* 44 (1), 23–49, <http://dx.doi.org/10.1080/10256010801887174>.
- Hoshina, Y., Fujita, K., Iizuka, Y., Motoyama, H., 2016. Inconsistent relationships between major ions and water stable isotopes in Antarctic snow under different accumulation environments. *Polar Sci.* 10 (1), 1–10, <http://dx.doi.org/10.1016/j.polar.2015.12.003>.
- Johnsen, S.J., Clausen, H.B., Cuffey, K.M., Hoffmann, G., Schwander, J., Creys, T., 2000. Diffusion of stable isotopes in polar firn and ice: the isotope effect in firn diffusion. *Phys. Ice Core Rec.* 159, 121–140.
- Jouzel, J., Merlivat, L., 1984. Deuterium and oxygen 18 in precipitation: modeling of the isotopic effects during snow formation. *J. Geophys. Res. Atmos.* 89 (D7), 11749–11757.
- Jouzel, J., Merlivat, L., Petit, J.-R., Lorius, C., 1983. Isotopic Record in the South Pole Snow. *J. Geophys. Res.* 88 (2), 2693–2703.
- Jouzel, J., Masson-Delmotte, V., Cattani, O., Dreyfus, G., Falourd, S., Hoffmann, G., Minster, B., Nouet, J., Barnola, J.-M., Chappellaz, J., Fischer, H., Gallet, J.C., Johnsen, S., Leuenberger, M., Loulergue, L., Luethi, D., Oerter, H., Parrenin, F., Raisbeck, G., Raynaud, D., Schilt, A., Schwander, J., Selmo, E., Souchez, R., Spahni, R., Sauffer, B., Steffensen, J.P., Stenni, B., Stocker, T.F., Tison, J.L., Werner, M., Wolff, E.W., 2007. Orbital and millennial Antarctic climate variability over the past 800,000 years. *Science* 317 (5839), 793–796.
- Kindler, P., Guillevic, M., Baumgartner, M., Schwander, J., Landais, A., Leuenberger, M., 2014. Temperature reconstruction from 10 to 120 kyr b2k from the NGRIP ice core. *Clim. Past* 10 (2), 887–902, <http://dx.doi.org/10.5194/cp-10-887-2014>.
- Krinner, G., Werner, M., 2003. Impact of precipitation seasonality changes on isotopic signals in polar ice cores: A multi-model analysis. *Earth Planet. Sci. Lett.* 216 (4), 525–538, [http://dx.doi.org/10.1016/S0012-821X\(03\)00550-8](http://dx.doi.org/10.1016/S0012-821X(03)00550-8).
- Küttel, M., Steig, E.J., Ding, Q., Monaghan, A.J., Battisti, D.S., 2012. Seasonal climate information preserved in West Antarctic ice core water isotopes: relationships to temperature, large-scale circulation, and sea ice. *Clim. Dynam.* 39 (7), 1841–1857, <http://dx.doi.org/10.1007/s00382-012-1460-7>.
- Laepplé, T., Hörhold, M., Münch, T., Freitag, J., Wegner, A., Kipfstuhl, S., 2016. Layering of surface snow and firn at Kohnen Station, Antarctica – noise or seasonal signal? *J. Geophys. Res. Earth Surf.*, <http://dx.doi.org/10.1002/2016JF003919>.
- Laepplé, T., Werner, M., Lohmann, G., 2011. Synchronicity of Antarctic temperatures and local solar insolation on orbital timescales. *Nature* 471 (7336), 91–94.
- Landais, A., 2011. Utility of stable isotopes of N and Ar as tracers to retrieve past air temperature from air trapped in ice cores. In: *Handbook of Environmental Isotope Geochemistry*, 865–886.
- Landais, A., Barkan, E., Luz, B., 2008. Record of $\delta^{18}\text{O}$ and ^{17}O -excess in ice from Vostok Antarctica during the last 150,000 years. *Geophys. Res. Lett.* 35 (2), L02709.
- Landais, A., Caillon, N., Severinghaus, J., Barnola, J.M., Goujon, C., Jouzel, J., Masson-Delmotte, V., 2004a. Analyse isotopique de l'air piégé dans la glace pour quantifier les variations de température. *C. R. Geoscience* 336 (11), 963–970.
- Landais, A., Jouzel, J., Masson-Delmotte, V., Caillon, N., 2004b. Large temperature variations over rapid climatic events in Greenland: a method based on air isotopic measurements. *C. R. Geoscience* 337 (10–11), 947–956.
- Landais, A., Ekaykin, A., Barkan, E., Winkler, R., Luz, B., 2012. Seasonal variations of ^{17}O -excess and d-excess in snow precipitation at Vostok station. *East Antarctica. J. Glaciol.* 58 (210), 725–733, <http://dx.doi.org/10.3189/2012JoG11J237>.
- Lee, J., Fung, I., Depaolo, D.J., Otto-bliesner, B., 2008. Water isotopes during the last glacial maximum: new general circulation model calculations. *J. Geophys. Res.* 113, <http://dx.doi.org/10.1029/2008JD009859>.
- Legrand, M., McConnell, J., Fischer, H., Wolff, E.W., Preunkert, S., Chellman, N., Leuenberger, D., Maselli, O., Sigl, M., Schüpbach, S., Flannigan, M., 2016. Boreal fire records in Northern Hemisphere ice cores: a review. *Clim. Past Disc.* 1–43, <http://dx.doi.org/10.5194/cp-2016-70>.
- Libois, Q., Picard, G., Arnaud, L., Dumont, M., Lafaysse, M., Morin, S., Lefebvre, E., 2015. Summertime evolution of snow specific surface area close to the surface on the Antarctic Plateau. *Cryosphere* 9 (6), 2383–2398, <http://dx.doi.org/10.5194/cp-9-2383-2015>.
- Libois, Q., Picard, G., Arnaud, L., Morin, S., Brun, E., 2014. Modeling the impact of snow drift on the decimeter-scale variability of snow properties on the Antarctic Plateau. *J. Geophys. Res. Atmos.* 119 (20), 11662–11681, <http://dx.doi.org/10.1002/2014JD022361>.
- Lorius, C., Merlivat, L., 1977. Distribution of mean surface stable isotope values in East Antarctica: observed changes with depth in coastal area. In: *Isotopes and impurities in snow and ice. IAHS Grenoble, France* 127–137.
- Lorius, C., Merlivat, L., Hagemann, R., 1969. Variation in the mean deuterium content of precipitations in Antarctica. *J. Geophys. Res.* 74 (28), 7027–7031.
- Luz, B., Barkan, E., Yam, R., Shemesh, A., 2009. Fractionation of oxygen and hydrogen isotopes in evaporating water. *Geochim. Cosmochim. Acta* 73 (22), 6697–6703, <http://dx.doi.org/10.1016/j.gca.2009.08.008>.
- Majoube, M., 1971a. Fractionnement en oxygène 18 entre la glace et la vapeur d'eau. *J. Chim. Phys.* 68 (4), 625–636.
- Majoube, M., 1971b. Fractionnement en oxygène 18 et en deutérium entre l'eau et sa vapeur. *J. Chim. Phys.* 68 (7–8), 1423–1436.
- Masson-Delmotte, V., Jouzel, J., Landais, A., Stievenard, M., Johnsen, S.J., White, J.W.C., Werner, M., Sveinbjornsdottir, A., Fuhrer, K., 2005. GRIP deuterium excess reveals rapid and orbital-scale changes in Greenland moisture origin. *Science* 309 (5731), 118–121.
- Masson-Delmotte, V., Dreyfus, G., Braconnot, P., Johnsen, S., Jouzel, J., Kageyama, M., Landais, A., Loutre, M.F., Nouet, J., Parrenin, F., Raynaud, D., Stenni, B., Tüenter, E., 2006. Past temperatures reconstructions from deep ice cores: relevance for future climate changes. *Clim. Past* 2, 145–165.
- Masson-Delmotte, V., Hou, S., Ekaykin, A., Jouzel, J., Aristarain, A., Bernardo, R.T., Bromwich, D., Cattani, O., Delmotte, M.M., Falourd, S.,

- Frezzotti, M., Gallée, H., Genoni, L., Isaksson, E., Landais, A., Helsen, M.M., Hoffmann, G., Lopez, J., Morgan, V., Motoyama, H., Noone, D., Oerter, H., Petit, J.R., Royer, A., Uemura, R., Schmidt, G.A., Schlosser, E., Simoes, J.C., Steig, E.J., Stenni, B., Stievenard, M., Van Den Broeke, M.R., Van De Wal, R.S.W., Van De Berg, W.J., Vimeux, F., White, J.W.C., 2008. A review of Antarctic surface snow isotopic composition: observations, atmospheric circulation, and isotopic modeling. *J. Climate* 21 (13), 3359–3387. <http://dx.doi.org/10.1175/2007JCLI2139.1>.
- Mayewski, P., Al, E., 2006. The International Trans-Antarctic Scientific Expedition (ITASE): An overview. *Ann. Glaciol.* 41, 180–185.
- Merlivat, L., Nief, G., 1967. Fractionnement isotopique lors des changements d'état solide-vapeur et liquide-vapeur de l'eau à des températures inférieures à 0 °C. *Tellus* 19 (1), 122–127.
- Münch, T., Kipfstuhl, S., Freitag, J., Meyer, H., Laepple, T., 2015. Regional climate signal vs. local noise: a two-dimensional view of water isotopes in Antarctic firn at Kohnen station. *Clim. Past Discuss.* 5605–5649. <http://dx.doi.org/10.5194/cpd-11-5605-2015>.
- NEEM Community members, 2013. Eemian interglacial reconstructed from a Greenland folded ice core. *Nature* 493 (7433), 489–494. <http://dx.doi.org/10.1038/nature11789>.
- Neumann, T., Waddington, E.D., 2004. Effects of firn ventilation on isotopic exchange. *J. Glaciol.* 50 (169), 183–194.
- Nicolas, J.P., Bromwich, D.H., 2014. New reconstruction of Antarctic near-surface temperatures: multidecadal trends and reliability of global reanalyses. *J. Climate* 27, 8070–8093. <http://dx.doi.org/10.1175/JCLI-D-13-00733.1>.
- NorthGRIP-community-members, 2004. High resolution climate record of the northern hemisphere reaching into last interglacial period. *Nature* 431, 147–151.
- Orsi, A.J., Cornuelle, B.D., Severinghaus, J.P., 2014. Magnitude and temporal evolution of Dansgaard-Oeschger event 8 abrupt temperature change inferred from nitrogen and argon isotopes in GISP2 ice using a new least-squares inversion. *Earth Planet. Sci. Lett.* 395, <http://dx.doi.org/10.1016/j.epsl.2014.03.030>.
- Pang, H., Hou, S., Landais, A., Masson-Delmotte, V., Prie, F., Steen-Larsen, H.C., Risi, C., Li, Y., Jouzel, J., Wang, Y., He, J., Minster, B., Falourd, S., 2015. Spatial distribution of ^{17}O -excess in surface snow along a traverse from Zhongshan station to Dome A, East Antarctica. *Earth Planet. Sci. Lett.* 414, 126–133. <http://dx.doi.org/10.1016/j.epsl.2015.01.014>.
- Picard, G., Royer, A., Arnaud, L., Fily, M., 2014. Influence of meter-scale wind-formed features on the variability of the microwave brightness temperature around Dome C in Antarctica. *Cryosphere* 8 (3), 1105–1119. <http://dx.doi.org/10.5194/tc-8-1105-2014>.
- Pinilla, C., Blanchard, M., Balan, E., Ferlat, G., Vuilleumier, R., Mauri, F., 2014. Equilibrium fractionation of H and O isotopes in water from path integral molecular dynamics. *Geochim. Cosmochim. Acta* 135, 203–216. <http://dx.doi.org/10.1016/j.gca.2014.03.027>.
- Rasmussen, S.O., Andersen, K.K., Svensson, A.M., Steffensen, J.P., Vinther, B.M., Clausen, H.B., Siggaard-Andersen, M.L., Johnsen, S.J., Larsen, L.B., Dahl-Jensen, D., Bigler, M., Röthlisberger, R., Fischer, H., Goto-Azuma, K., Hansson, M.E., Ruth, U., 2006. A new Greenland ice core chronology for the last glacial termination. *J. Geophys. Res. Atmos.* 111 (6), 1–16. <http://dx.doi.org/10.1029/2005JD006079>.
- Risi, C., Bony, S., Vimeux, F., Jouzel, J., 2010. Water-stable isotopes in the LMDZ4 general circulation model: Model evaluation for present-day and past climates and applications to climatic interpretations of tropical isotopic records. *J. Geophys. Res. Atmos.* 115 (12), <http://dx.doi.org/10.1029/2009JD013255>.
- Ritter, F., Steen-Larsen, H.C., Werner, M., Masson-Delmotte, V., Orsi, A., Behrens, M., Birnbaum, G., Freitag, J., Risi, C., Kipfstuhl, S., 2016. Isotopic exchange on the diurnal scale between near-surface snow and lower atmospheric blowing snow transport events in East Antarctica. *Cryosphere* 10, 1647–1663. <http://dx.doi.org/10.5194/tc-10-1647-2016>.
- Salamatin, A.N., Lipenkov, V.Y., Barkov, N.I., Jouzel, J., Petit, J.R., Raynaud, D., 1998. Ice core age dating and paleothermometer calibration based on isotope and temperature profiles from deep boreholes at Vostok Station (East Antarctica). *J. Geophys. Res.* 103 (8), 8963. <http://dx.doi.org/10.1029/97JD02253>.
- Scarchilli, C., Frezzotti, M., Grigioni, P., De Silvestri, L., Agnoletto, L., Dolci, S., 2010. Extraordinary blowing snow transport events in East Antarctica. *Clim. Dynam.* 34 (7), 1195–1206. <http://dx.doi.org/10.1007/s00382-009-0601-0>.
- Schmidt, G.A., Hoffmann, G., Shindell, D.T., Hu, Y., 2005. Modeling atmospheric stable water isotopes and the potential for constraining cloud processes and stratosphere-troposphere water exchange. *J. Geophys. Res. Atmos.* 110 (21), 1–15. <http://dx.doi.org/10.1029/2005JD005790>.
- Schmidt, G.A., LeGrande, A.N., Hoffmann, G., 2007. Water isotope expressions of intrinsic and forced variability in a coupled ocean-atmosphere model. *J. Geophys. Res. Atmos.* 112 (D10), D10103. <http://dx.doi.org/10.1029/2006JD007781>.
- Schneider, D.P., Steig, E.J., Van Ommen, T.D., Dixon, D.A., Mayewski, P.A., Jones, J.M., Bitz, C.M., 2006. Antarctic temperatures over the past two centuries from ice cores. *Geophys. Res. Lett.* 33 (16), 1–5. <http://dx.doi.org/10.1029/2006GL027057>.
- Severinghaus, J.P., Brook, E.J., 1999. Abrupt climate change at the end of the last glacial period inferred from trapped air in polar ice. *Science* 286, 930–933. <http://dx.doi.org/10.1126/science.286.5441.930>.
- Sime, L.C., Wolff, E.W., Oliver, K.I.C., Tindall, J.C., 2009. Evidence for warmer interglacials in East Antarctic ice cores. *Nature* 462 (7271), 342–345.
- Steen-Larsen, H.C., Masson-Delmotte, V., Hirabayashi, M., Winkler, R., Satow, K., Prié, F., Bayou, N., Brun, E., Cuffey, K.M., Dahl-Jensen, D., Dumont, M., Guillemin, M., Kipfstuhl, S., Landais, A., Popp, T., Risi, C., Steffen, K., Stenni, B., Sveinbjörnsdóttir, A.E., 2014. What controls the isotopic composition of Greenland surface snow? *Clim. Past* 10 (1), 377–392. <http://dx.doi.org/10.5194/cp-10-377-2014>.
- Steen-Larsen, H.C., Masson-Delmotte, V., Sjolte, J., Johnsen, S.J., Vinther, B.M., Bréon, F.-M., Clausen, H.B., Dahl-Jensen, D., Falourd, S., Fettweis, X., Gallée, H., Jouzel, J., Kageyama, M., Lerche, H., Minster, B., Picard, G., Punge, H.J., Risi, C., Salas, D., Schwander, J., Steffen, K., Sveinbjörnsdóttir, A.E., Svensson, A., White, J., 2011. Understanding the climatic signal in the water stable isotope records from the NEEM shallow firn/ice cores in northwest Greenland. *J. Geophys. Res. Atmos.* 116 (D6), <http://dx.doi.org/10.1029/2010JD014311>.
- Stenni, B., Jouzel, J., Masson-Delmotte, V., Röthlisberger, R., Castellano, E., Cattani, O., Falourd, S., Johnsen, S.J., Longinelli, A., Sachs, J.P., Selmo, E., Souchez, R., Steffensen, J.P., Udisti, R., 2003. A late-glacial high-resolution site and source temperature record derived from the EPICA Dome C isotope records (East Antarctica). *Earth Planet. Sci. Lett.* 217, 183–195.
- Stenni, B., Masson-Delmotte, V., Selmo, E., Oerter, H., Meyer, H., Röthlisberger, R., Jouzel, J., Cattani, O., Falourd, S., Fischer, H., Hoffmann, G., Iacumin, P., Johnsen, S.J., Minster, B., Udisti, R., 2010. The deuterium excess records of EPICA Dome C and Dronning Maud Land ice cores (East Antarctica). *Quatern. Sci. Rev.* 29 (1), 146–159.
- Stenni, B., Scarchilli, C., Masson-Delmotte, V., Schlosser, E., Ciardini, V., Dreossi, G., Grigioni, P., Bonazza, M., Cagnati, A., Karlické, D., 2016. Three-year monitoring of stable isotopes of precipitation at Concordia Station, East Antarctica. *Cryosphere* 10 (5), 2415.
- Touzeau, A., Landais, A., Stenni, B., Uemura, R., Fukui, K., Fujita, S., Guilbaud, S., Ekaykin, A., Casado, M., Barkan, E., Luz, B., Magand, O., Teste, G., Le Meur, E., Baroni, M., Savarino, J., Bourgeois, I., Risi, C., 2016. Acquisition of isotopic composition for surface snow in East Antarctica and the links to climatic parameters. *Cryosphere* 10, 837–852. <http://dx.doi.org/10.5194/tc-10-837-2016>.
- Town, M.S., Warren, S.G., Walden, V.P., Waddington, E.D., 2008. Effect of atmospheric water vapor on modification of stable isotopes in near-surface snow on ice sheets. *J. Geophys. Res. Atmos.* 113 (24), 1–16. <http://dx.doi.org/10.1029/2008JD009852>.
- Van Hook, W.A., 1968. Vapor pressures of the isotopic waters and ices. *J. Phys. Chem.* 72 (4), 1234–1244.
- Vimeux, F., Masson, V., Delaygue, G., Jouzel, J., Petit, J.R., Stievenard, M., 2001. A 420,000 year deuterium excess record from East Antarctica: Information on past changes in the origin of precipitation at Vostok. *J. Geophys. Res. Atmos.* 106 (D23), 31863–31873.
- Werner, M., Haese, B., Xu, X., Zhang, X., Butzin, M., Lohmann, G., 2015. Glacial-interglacial changes of H_2^{18}O , HDO and deuterium excess—results from the fully coupled Earth System Model ECHAM5/MPI-OM. *Geosci. Model Dev. Discuss.* 8 (10), 8835–8894. <http://dx.doi.org/10.5194/gmdd-8-8835-2015>.
- Werner, M., Langebroek, P.M., Carlsen, T., Herold, M., Lohmann, G., 2011. Stable water isotopes in the ECHAM5 general circulation model: toward high-resolution isotope modeling on a global scale. *J. Geophys. Res. Atmos.* 116 (D15).
- Winkler, R., Landais, A., Sodemann, H., Dumbgen, L., Prie, F., Masson-Delmotte, V., Stenni, B., Jouzel, J., 2012. Deglaciation records of ^{17}O -excess in East Antarctica: Reliable reconstruction of oceanic normalized relative humidity from coastal sites. *Clim. Past* 8 (1), 1–16. <http://dx.doi.org/10.5194/cp-8-1-2012>.
- Wolff, E.W., Barbante, C., Becagli, S., Bigler, M., Boutron, C.F., Castellano, E., de Angelis, M., Federer, U., Fischer, H., Fundel, F., Hansson, M., Hutterli, M., Jonsell, U., Karlin, T., Kaufmann, P., Lambert, F., Littot, G.C., Mulvaney, R., Röthlisberger, R., Ruth, U., Severi, M., Siggaard-Andersen, M.L., Sime, L.C., Steffensen, J.P., Stocker, T.F., Traversi, R., Twarloh, B., Udisti, R., Wagenbach, D., Wegner, A., 2010. Changes in environment over the last 800,000 years from chemical analysis of the EPICA Dome C ice core. *Quat. Sci. Rev.* 29 (1–2), 285–295. <http://dx.doi.org/10.1016/j.quascirev.2009.06.013>.