



HAL
open science

Water isotopes as tools to document oceanic sources of precipitation

Jean Jouzel, G. Delaygue, Amaelle Landais, Valérie Masson-Delmotte,
Camille Risi, F. Vimeux

► **To cite this version:**

Jean Jouzel, G. Delaygue, Amaelle Landais, Valérie Masson-Delmotte, Camille Risi, et al.. Water isotopes as tools to document oceanic sources of precipitation. *Water Resources Research*, 2013, 49 (11), pp.7469-7486. 10.1002/2013WR013508 . hal-01108534

HAL Id: hal-01108534

<https://hal.science/hal-01108534>

Submitted on 12 Jan 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Water isotopes as tools to document oceanic sources of precipitation

Jean Jouzel,¹ Gilles Delaygue,² Amaëlle Landais,¹ Valérie Masson-Delmotte,¹ Camille Risi,³ and Françoise Vimeux^{1,4}

Received 13 January 2013; revised 26 September 2013; accepted 13 October 2013; published 18 November 2013.

[1] The isotopic composition of precipitation, in deuterium, oxygen 18 and oxygen 17, depends on the climatic conditions prevailing in the oceanic regions where it originates, mainly the sea surface temperature and the relative humidity of air. This dependency applies to present-day precipitation but also to past records which are extracted, for example, from polar ice cores. In turn, coisotopic measurements of deuterium and oxygen 18 offer the possibility to retrieve information about the oceanic origin of modern precipitation as well as about past changes in sea surface temperature and relative humidity of air. This interpretation of isotopic measurements has largely relied on simple Rayleigh-type isotopic models and is complemented by Lagrangian back trajectory analysis of moisture sources. It is now complemented by isotopic General Circulation Models (IGCM) in which the origin of precipitation can be tagged. We shortly review published results documenting this link between the oceanic sources of precipitation and their isotopic composition. We then present experiments performed with two different IGCMs, the GISS model II and the LMDZ model. We focus our study on marine water vapor and its contribution to precipitation over Antarctica and over the Andean region of South America. We show how IGCM experiments allow us to relate climatic conditions prevailing in the oceanic source of precipitation to its isotopic composition. Such experiments support, at least qualitatively, the current interpretation of ice core isotopic data in terms of changes in sea surface temperature. Additionally, we discuss recent studies clearly showing the added value of oxygen 17 measurements.

Citation: Jouzel, J., G. Delaygue, A. Landais, V. Masson-Delmotte, C. Risi, and F. Vimeux (2013), Water isotopes as tools to document oceanic sources of precipitation, *Water Resour. Res.*, 49, 7469–7486, doi:10.1002/2013WR013508.

1. Introduction

[2] Natural waters are mainly formed of H₂¹⁶O (about 99.7%) but also incorporate other stable isotopic molecules such as H₂¹⁸O (~2‰), H₂¹⁷O (~0.5‰), and HD¹⁶O (~0.3‰), where H and D (deuterium) correspond to ¹H and ²H, respectively. Owing to slight differences in physical properties of those molecules, essentially their saturation vapor pressure and their molecular diffusivity in air, fractionation processes occur at each phase change of the water except sublimation and melting of compact ice. As a result, the distribution of those water isotopes varies both

spatially and temporally in the atmosphere, in the precipitation and, in turn, in the various reservoirs of the hydrosphere and of the cryosphere.

[3] Isotopic concentrations are given with respect to a standard as:

$$\delta = (R_{\text{sample}} - R_{\text{SMOW}}) / R_{\text{SMOW}}$$

and expressed in per mill δ units (δD and $\delta^{18}\text{O}$, respectively). In this definition, R_{sample} and R_{SMOW} are the isotopic ratios of the sample and of the V-SMOW (the Vienna Standard Mean Ocean Water) with D/H and ¹⁸O/¹⁶O atomic ratios of 155.76×10^{-6} and 2005.2×10^{-6} , respectively [Hageman *et al.*, 1970; Baertschi, 1976; Gonfiantini, 1978]. As discussed in numerous articles [e.g., Jouzel, 2003], the use of water stable isotopes is largely based on the fact that their distribution in precipitation is strongly related to climatological parameters with applications in such fields as climatology, cloud physics, hydrology, and paleoclimatology. Of primary interest is the linear relationship between annual values of δD and $\delta^{18}\text{O}$ and annual mean temperature at the precipitation site that is observed at middle and high latitudes. No such relationship can be identified in tropical and equatorial regions where δD and $\delta^{18}\text{O}$ are more significantly influenced by the amount of precipitation. Second, δD and $\delta^{18}\text{O}$ are linearly related to each other along the so-called

¹Laboratoire des Sciences du Climat et de l'Environnement/Institut Pierre-Simon Laplace UMR 8212 (CEA-CNRS-UVSQ), Gif-sur-Yvette, Cedex, France.

²University of Grenoble Alpes/CNRS, Laboratoire de Glaciologie et de Géophysique de l'Environnement (LGGE), Grenoble, France.

³Laboratoire de Météorologie Dynamique/Institut Pierre-Simon Laplace, CNRS, UPMC, Paris, France.

⁴Institut de Recherche pour le Développement (IRD), Laboratoire Hydro Sciences Montpellier (HSM), Montpellier, France.

Corresponding author: J. Jouzel, Laboratoire des Sciences du Climat et de l'Environnement/Institut Pierre-Simon Laplace UMR 8212 (CEA-CNRS-UVSQ), CEA Saclay, L'Orme des Merisiers, Bt. 701, 91191 Gif-sur-Yvette, Cedex, France. (jean.jouzel@lsce.ipsl.fr)

Meteoric Water Line (MWL), $\delta D = 8 \times \delta^{18}O + 10\%$ [Craig, 1961]. From this linear relationship, Dansgaard [1964] defined the deuterium excess parameter, hereafter d-excess, $d = \delta D - 8 \times \delta^{18}O$, sensitive to small deviations of data to the MWL. $H_2^{17}O$ has only recently been considered, thanks to analytical developments allowing very precise measurements [Barkan and Luz, 2005; Landais et al., 2006, 2008].

[4] In 1965, Harmon Craig and Louis I. Gordon [Craig and Gordon, 1965] published a very comprehensive study entitled “Deuterium and oxygen 18 in the ocean and marine atmosphere” which can be considered as the starting point for linking the isotopic content of precipitation and the conditions prevailing at its oceanic sources. The great improvement of this work was to account for a kinetic isotopic fractionation at evaporation, which depends on both temperature and relative humidity. Earlier studies [Epstein and Mayeda, 1953; Dansgaard, 1954] assumed that this isotopic fractionation was at equilibrium, and hence that the isotopic composition of the vapor only (and weakly) depends on temperature. During phase transitions such as evaporation, the different isotopic forms of water (mostly H_2O , HDO, and $H_2^{18}O$) are not in the same proportions in the different phases, a process which is called isotopic fractionation. The equilibrium part of fractionation depends on the saturation vapor pressure of the water molecules, whereas the kinetic part depends on their molecular diffusivity in air.

[5] This kinetic fractionation directly influences the d-excess of the vapor above the ocean surface and is partly propagated along the vapor trajectory to precipitation. An improved theory of evaporation [Brutsaert, 1975] and experiments conducted in a wind tunnel [Merlivat and Coantic, 1975] were exploited by Merlivat and Jouzel [1979] to propose a climatic interpretation of the observed linear deuterium-oxygen 18 relationship (MWL). By assuming a steady-state regime for the evaporation of water at the ocean surface and for the subsequent formation of precipitation, Merlivat and Jouzel [1979] concluded that, at least for liquid precipitation, the observed $\delta D - \delta^{18}O$ relationship mainly depends on the physical characteristics of the air masses at the origin of this precipitation, i.e., the sea surface temperature (SST) and the relative humidity (h). This global interpretation of the MWL—complemented by more regional studies [e.g., Gat, 1980]—paved the way for using water isotopes of continental precipitation to reconstruct the characteristics of their oceanic sources.

[6] This possibility was first explored for precipitation in the Mediterranean region, characterized by high d-excess values which are attributed to low relative humidity values in the source areas [Gat and Carmi, 1970]. Such studies aiming to identify oceanic source characteristics are still active in this region [Rindsberger et al., 1983; Gat et al., 2003; Pfahl et al., 2008] and have developed in other parts of the world [e.g., Yamanaka et al., 2002; Tian et al., 2007; Vachon et al., 2010; Guan et al., 2013; Pfahl and Sodemann, 2013].

[7] This isotopic tool has also been extensively applied to reconstruct past oceanic conditions from water archives. Pioneering studies dealt with Pleistocene data measured on Saharan groundwaters, showing a d-excess deficit attributed to high relative humidity over the oceanic sources [Sonntag et al., 1978; Merlivat and Jouzel, 1979], and on

fluid inclusions from speleothems [Harmon and Schwarcz, 1981]. Since then, numerous publications dealt with the interpretation of δD and $\delta^{18}O$ profiles measured in Antarctic and Greenland ice cores which give access to continuous and potentially very detailed d-excess profiles.

[8] Since the first studies performed on the Antarctic Dome C ice core [Jouzel et al., 1982] and on the Greenland Dye 3 ice core [Dansgaard et al., 1989; Johnsen et al., 1989], both δD and $\delta^{18}O$ have been systematically measured along polar ice cores in order to estimate d-excess. As a first step, either δD or $\delta^{18}O$ measurements are classically used to derive quantitative or qualitative information about local (polar) temperature change at the drilling site. As a second step, their comparison with d-excess has been extensively used to get information about remote conditions prevailing at the ocean surface. Such a reconstruction is complicated by two processes, which alter the initial isotopic composition of moisture during its trajectory. Both processes are affected by the cooling which occurs between middle and high latitudes, where polar precipitation is archived as ice. First, the $\delta D/\delta^{18}O$ slope progressively deviates from its global value of 8, due to the temperature dependency of the isotopic fractionation. Second, kinetic fractionation occurs during solid condensation due to supersaturation of vapor with respect to ice crystals. Additionally, post deposition processes may alter the original isotopic composition of snow layers once deposited onto the firn surface: snow metamorphism involves sublimation and condensation within snow layers, and wind redistribution (“scouring”) can alter their stratigraphy. While it is well known that these post depositional effects can smooth the initial precipitation isotopic composition δ [Johnsen, 1977], their impacts on d-excess remain poorly documented and understood.

[9] More recently, technical improvements of spectrometry have made it possible to document a linear relationship between $\delta^{17}O$ and $\delta^{18}O$ in global precipitation [Meijer and Li, 1998]. This has led to the definition of a new isotopic parameter called ^{17}O -excess [Barkan and Luz, 2005; Landais et al., 2006] which brings additional information about oceanic sources due to differences in the kinetic effects affecting ^{18}O and ^{17}O [Landais et al., 2008, 2012; Winkler et al., 2012]. Although the ^{17}O -excess has been defined by analogy with the d-excess definition, it uses the logarithm system [Miller, 2002; Angert et al., 2004] with ^{17}O -excess = $\ln[1 + \delta^{17}O] - 0.528 \times \ln[1 + \delta^{18}O]$ [Barkan and Luz, 2007; Landais et al., 2008].

[10] Interpreting the d-excess and ^{17}O -excess data in snow is still largely based on simple isotopic models which describe the successive condensation steps of vapor along its trajectory from its oceanic origin to the precipitation site [Merlivat and Jouzel, 1979; Jouzel and Merlivat, 1984; Johnsen et al., 1989; Ciais and Jouzel, 1994; Landais et al., 2008; Steen-Larsen et al., 2011; Winkler et al., 2012]. Such Rayleigh-type models do not account for the complexity of moisture transport in the atmosphere, a possibility offered by atmospheric General Circulation Models (GCMs), especially those equipped with water isotopes (IGCM). This GCM approach is particularly well suited for examining the link between the evaporative origin of a precipitation and its isotope content. Water evaporating from a defined source region on the Earth’s surface can be “tagged” in the GCM and followed through the atmosphere until it precipitates. This

tagging approach allows one to consistently quantify, in the model world, the relative contributions of several evaporative sources to the precipitation of a given region [Joussaume *et al.*, 1986; Koster *et al.*, 1986; Delaygue, 2000; Werner *et al.*, 2001; Kelley, 2003]. By tagging and following not only moisture but its isotopic components, it is then possible to determine the relationship between the source characteristics and the isotopic content of precipitation [Koster *et al.*, 1992; Charles *et al.*, 1994; Delaygue *et al.*, 2000a; Lewis *et al.*, 2010, 2013; Risi *et al.*, 2010b, 2013b].

[11] A more recent development has been the emergence of GCM simulations nudged to large-scale wind fields from atmospheric analyses, which provides a framework for comparing realtime isotopic data and model results, and not only their time average [Yoshimura *et al.*, 2008, Risi *et al.*, 2010a; K. Gribanov *et al.*, Developing a Western Siberia reference site for tropospheric water vapor isotopologue observations obtained by different techniques (in-situ and remote sensing), submitted to *Atmospheric Chemistry Physics*, 2013]. Also, the Lagrangian analysis of moisture sources complements this GCM approach [Dirmeyer and Brubaker, 1999; Stohl and James, 2004, 2005; Gimeno *et al.*, 2010, Sodemann *et al.*, 2008; Sodemann and Stohl, 2009].

[12] In this article, we first summarize what we know from simple isotopic models on the link between oceanic source characteristics and d-excess in precipitation, and we then illustrate how such information has been used to interpret paleodata (section 2). This is followed by a short review of how IGCM have been used to examine this link (section 3.1). Section 3 (sections 3.2–3.5) is dedicated to new results derived from experiments that we have performed using two different GCMs, GISS model II and LMDZ, equipped with water isotopes. We specifically diagnose the drivers of d-excess in the marine water vapor and also investigate the impacts of moisture sources on polar and low-latitude precipitation, both for present-day and past climates. We conclude by pointing out the perspectives offered by combining d-excess and ^{17}O -excess data.

2. Oceanic Source Characteristics as Derived From Simple Isotopic Models

2.1. Simple Isotopic Models

[13] A Rayleigh-type model [Dansgaard, 1964] describes the moisture exhaustion of an isolated air parcel traveling from an oceanic source toward a polar region, in order to calculate its isotopic composition. The condensed phase is assumed to form in isotopic equilibrium with the surrounding vapor and to be removed immediately from the parcel by precipitation. Under simplistic hypothesis, the isotopic content of precipitation is a unique function of the initial isotopic content of the vapor, δ_0 , and of the ratio, F , of the left vapor mass to the initial vapor mass within the air parcel. In fact, measurements show that the real isotopic content of precipitation, δ_p (i.e., either δD , $\delta^{18}\text{O}$, $\delta^{17}\text{O}$) is very well approximated by

$$\delta_p = \alpha_c \left((1 + \delta_0) F^{(\alpha_m - 1)} \right) - 1 \quad (1)$$

in which α_m is the mean value of the fractionation coefficient over the trajectory, and α_c its value when

condensation occurs. The parcel water vapor content is modified according to the saturation vapor pressure, a function of temperature and phases (liquid and/or ice), and to the air pressure. Thus, in such a simple model, the isotopic content of precipitation can be expressed as a function of the initial isotopic composition of vapor and of the initial and final condensation temperatures and air pressures.

[14] If the trajectory conditions, in terms of temperature and pressure, can be easily defined, the initial isotopic composition of vapor is poorly constrained by observations. Merlivat and Jouzel [1979] showed that the initial isotopic content of vapor in an air parcel above the ocean, δ_{v0} , may, under certain simplifying assumptions, be expressed as a function of:

[15] 1. the liquid-vapor fractionation coefficient α for the sea surface temperature T_w ,

[16] 2. the relative humidity h , with respect to sea surface temperature,

[17] 3. a kinetic fractionation parameter k which depends on windspeed,

[18] 4. the isotopic composition of the sea surface, δ_{ocean} ,

$$\text{as : } \delta_{v0} = (1 + \delta_{\text{ocean}}) (1 - k) / (\alpha(1 - kh)) - 1 \quad (2)$$

[19] Merlivat and Jouzel [1979] pointed out the strong dependence of the isotopic fractionation on the regime of evaporation (smooth versus rough), depending on wind speed. Based on the observation that more than 95% of the ocean is in the smooth regime, Merlivat and Jouzel [1979] interpreted the well obeyed MWL in terms of the mean evaporation temperature of the ocean surface ($\sim 25^\circ\text{C}$) and of the mean relative humidity of the air masses with respect to the sea surface temperature (h of $\sim 80\%$). These figures appeared quite reasonable (there was however no direct way to discuss the value of h at that time).

[20] In order to correctly simulate the isotopic composition of snow, Jouzel and Merlivat [1984] accounted for the kinetic fractionation associated with the condensation of vapor onto ice. This extended model can reproduce the isotopic data observed for midlatitudes and high-latitudes and even for East Antarctica [see also Masson-Delmotte *et al.*, 2008]. The importance of the kinetic fractionation at condensation was further confirmed by Ciais and Jouzel [1994] who introduced mixed clouds (with liquid and ice) into the Rayleigh-type model (hereafter called MCIM for mixed cloud isotopic model).

2.2. Deuterium Excess and Source Characteristics

[21] Following Merlivat and Jouzel [1979] and Johnsen *et al.* [1989] derived how the d-excess of moisture evaporated from the oceanic surface depends on surface temperature and humidity, assuming a smooth regime of evaporation (Figure 1). The d-excess value decreases when the relative humidity over the ocean increases, or when the temperature of the ocean surface decreases; it would also decrease for higher windspeed leading to rough evaporation regime (above ~ 7 m/s; not shown). Figure 1 shows that the d-excess of vapor is more sensitive to relative humidity than to surface temperature. The observed meteoric water line (MWL) implies, at first order, a fairly constant d-excess of vapor, which means that it is not too much modified by condensation along the trajectory of the vapor mass.

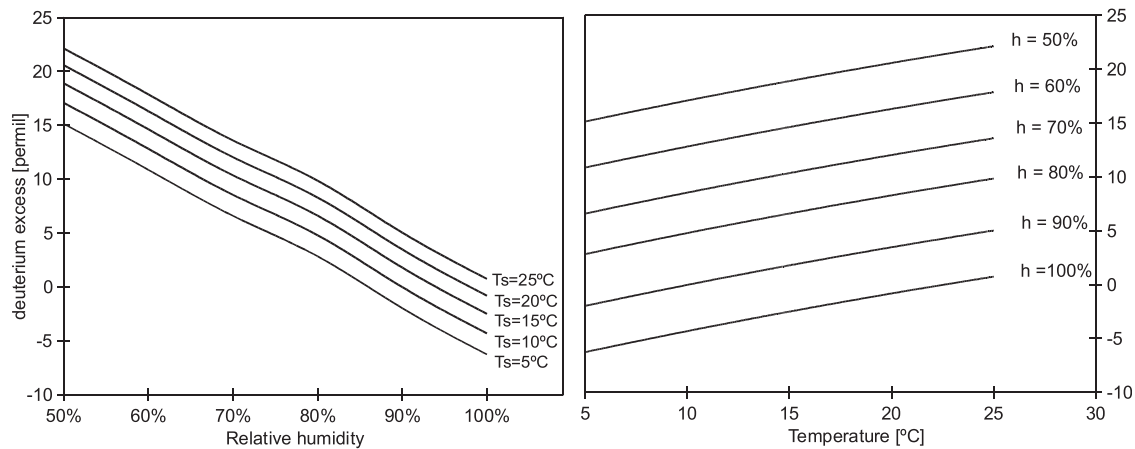


Figure 1. d-excess of vapor formed above the ocean as a function of the relative humidity h and surface temperature (T_w), calculated under simplifying assumptions [adapted from Merlivat and Jouzel, 1979; Johnsen *et al.*, 1989].

From these features has emerged the possibility to use isotopic data to constrain the relative humidity of the oceanic source, or at least a (T_w , h) couple.

[22] Simple Rayleigh-type models can correctly reproduce the observed d-excess values in precipitation, even in polar regions where it is strongly influenced by the kinetic effect occurring at snow formation [Jouzel and Merlivat, 1984; Johnsen *et al.*, 1989; Petit *et al.*, 1991; Ciais and Jouzel, 1994]. These models show that the sensitivity of d-excess to T_w and h in the initial vapor (Figure 1) is modified by condensation along the air mass trajectory. Hence, the actual sensitivity in polar regions has to be determined in order to use the isotopic content of precipitation to constrain the initial source characteristics T_w and h . Petit *et al.* [1991] first simulated the influence of source temperature on the d-excess of Antarctic snow especially for inland sites. Later, sensitivity tests conducted with the MCIM have suggested that the initial source relative humidity is better preserved in the d-excess at coastal sites than at central sites in Antarctica [Ciais *et al.*, 1995; Vimeux *et al.*, 2001a]. These modeling studies have tried to quantify how much of the information on initial oceanic conditions can be inferred from the isotopic content of precipitation, especially from its d-excess. The difficulties in inferring these oceanic conditions from the d-excess are twofold: (1) the d-excess of vapor is affected by the changes in air temperature during the distillation path (due to the ratio of equilibrium fractionation coefficients and to the impact of supersaturation on ice crystals) and (2) the sensitivity of precipitation d-excess to local temperature, T_{site} , is not well constrained by models because it depends on several free parameters [Uemura *et al.*, 2012].

2.3. Case Studies

[23] We illustrate here how isotopic data allow us to retrieve information about the oceanic sources of precipitation, with examples related to firn and ice core data.

[24] In the Antarctic Peninsula, at the site of Dalinger Dome in James Ross Island, the $\delta D - T_{\text{site}}$ relationship could be inferred by combining isotopic measurements in firn to temperature measurements from meteorological

stations, over the last decades [Aristarain *et al.*, 1986]. Such relationship (a temporal one) is rarely available: usually the $\delta D - T_{\text{site}}$, used to interpret ice core isotopic measurements, is inferred by combining annual averages from different stations (which gives a spatial relationship). It was found that, over the last decades, the temporal $\delta D - T_{\text{site}}$ slope is about twice lower than the spatial $\delta D - T_{\text{site}}$ slope: this is a critical result since it implies that temperature variations inferred from ice core isotopic profiles are twice stronger than when applying the spatial $\delta D - T_{\text{site}}$ slope, as usually done. This difference in slopes can be explained with the assumption of a simultaneous and parallel change in the source and site temperatures over the last decades, which is a reasonable assumption for such a coastal site [Aristarain *et al.*, 1986]. Other interpretations of such a low temporal $\delta D - T_{\text{site}}$ slope are changes in the seasonality and covariation between site temperature and precipitation rate [Sime *et al.*, 2009]; and changes in vapor recycling [Lee *et al.*, 2008]. Note also that the $\delta D - T_{\text{site}}$ slope may be sensitive to the regression technique applied to data [Abram *et al.*, 2011]. More generally, Boyle [1997] suggested that the cooling of the tropical source of precipitation in central Greenland, at the Last Glacial Maximum (LGM, 20,000 years ago), could explain such a discrepancy over the glacial-interglacial timescale. However, these assumptions remained to be tested by constraining changes in the source temperature: such information can be provided by the d-excess.

[25] The first d-excess profile measured along a polar ice core over a full glacial-interglacial transition was at the former Dome C, in central East Antarctica: it revealed lower values of d-excess at the LGM, which were interpreted as reflecting a higher relative humidity over the oceanic source of precipitation [Jouzel *et al.*, 1982]. Instead, the d-excess profile of Vostok, East Antarctica, which covers a full glacial-interglacial cycle, was interpreted by Vimeux *et al.* [2001b] in terms of changes in SST (rather than h), taking into account the relationship between SST and surface humidity simulated by GCMs. This interpretation of changes in d-excess by changes in the temperature of moisture source, rather than by changes in the humidity of

moisture source, has led to deconvolve, with an inversion procedure, temperature changes at the moisture source and at the precipitation site, over glacial timescales. Such a deconvolution has been applied to the Vostok, Dome C, and EDML isotopic records in Antarctica [Stenni *et al.*, 2001, 2003, 2010; Cuffey and Vimeux, 2001; Vimeux *et al.*, 2002] and to the GRIP isotopic record in Greenland [Masson-Delmotte *et al.*, 2005a, 2005b; Jouzel *et al.*, 2007a]. Studies on shorter timescales also interpreted d-excess measurements with temperature changes at the precipitation source: for instance, Delmotte *et al.* [2000] have shown that the seasonality in d-excess at Law Dome (coastal Antarctica) is influenced by the southern ocean temperature cycle.

[26] We illustrate this deconvolution of source and site temperature changes with the reconstruction based on the EPICA Dome C (EDC) isotopic data by Stenni *et al.* [2010] for the last climatic cycle (Figure 2). Basically, a linear inversion procedure is applied to the isotopic data, based on sensitivities derived from a simple isotopic model. However, there are too many unknown parameters to allow us to constrain the deconvolution from only $\delta^{18}\text{O}$ and δD data: source and site temperatures, relative humidity and wind speed at the source, simple model parameterizations of cloud microphysics. To reduce the number of unknowns, the simple model (MCIM) parameterizations were adjusted to fit isotopic data from the coast to Dome C [Masson-Delmotte *et al.*, 2004]. In practice, the MCIM was run for different source temperatures, and for different site temperatures within the range of the present day to glacial temperatures at Dome C. For each set of source and site temperature, the model simulates the isotopic composition of precipitation at Dome C, i.e., $\delta^{18}\text{O}$, δD , and d-excess. From these data, multivariate regressions were performed in order to infer the best estimates of source and site temperatures based on the precipitation δD and d-excess at Dome C:

$$\Delta T_{\text{site}} = 0.16 \pm 0.02 \Delta \delta D_{\text{corr}} + 0.44 \pm 0.15 \Delta d_{\text{corr}} \quad (3)$$

$$\Delta T_{\text{source}} = 0.06 \pm 0.03 \Delta \delta D_{\text{corr}} + 0.93 \pm 0.15 \Delta d_{\text{corr}} \quad (4)$$

[27] In these formulas, $\Delta \delta D_{\text{corr}}$ and Δd_{corr} are, respectively, the changes in δD and d-excess measured in the ice at Dome C, corrected for the isotopic concentration of the oceanic surface [Jouzel *et al.*, 2003]. As illustrated in Figure 2, Stenni *et al.* [2010] also accounted for local elevation changes. Combining equations (3) and (4) give access to the change in the temperature gradient between the precipitation site and the oceanic source. Note that, because precipitation at Dome C is a mixture of different sources, the inferred source temperature T_{source} is an average value of these sources.

[28] The central Antarctic Dome F d-excess record was also interpreted in terms of oceanic information, but in a different way, by Uemura *et al.* [2004]. This d-excess record was compared to records of ocean-water $\delta^{18}\text{O}$ and SSTs derived from ocean sediments: d-excess changes are anticorrelated with ice volume changes, and correlated with SST changes.

[29] The interpretation of Greenland d-excess records [Masson-Delmotte *et al.*, 2005a, 2005b; Jouzel *et al.*, 2007a] is more complex in particular for the glacial period because, as for the local temperature interpretation, the precipitation intermittency and seasonality should be taken into account prior to the interpretation of d-excess data. This has been done by Masson-Delmotte *et al.* [2005b] who estimated the changes in the site and source temperatures from the GRIP $\delta^{18}\text{O}$ and δD records: these source temperature changes suggest that large changes in the location of moisture sources did occur, both at the orbital and millennial time scales. In fact, the high d-excess values during cold glacial stadials cannot be simulated by only accounting for colder temperatures: they also require changes in moisture sources and/or evaporation conditions. Hence,

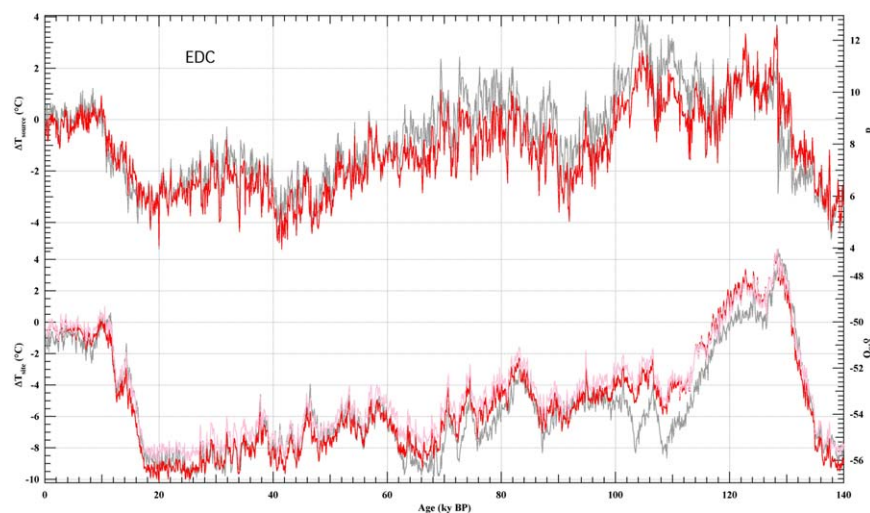


Figure 2. This figure illustrates how the temperature of the oceanic source (red, top curve and left axis) is inferred from the d-excess profile (gray, top curve and right axis) measured along the EPICA Dome C (EDC) ice core over the last climatic cycle [adapted from Stenni *et al.*, 2010]. The bottom curves correspond to the local temperature at the EDC site (pink and red curves without and with elevation correction, and left axis) and to the $\delta^{18}\text{O}$ record (gray curve and right axis).

Masson-Delmotte et al. [2005b] interpreted higher d-excess values as a shift of moisture sources toward lower latitudes under extremely cold Arctic conditions. Alternatively, such high d-excess values could be due to the strong kinetic fractionation occurring at the sea ice margin, as documented for present day conditions [*Kurita*, 2011; *Steen-Larsen et al.*, 2013].

3. Isotopic GCMs: A Promising Tool to Identify Oceanic Sources of Precipitation

[30] Atmospheric GCMs can be used to tag vapor when it evaporates and to follow it until it precipitates. They are ideal tools to design experiments in which the origin of the vapor is tagged: for a given site, the contribution of different sources to precipitation can be then calculated. Unlike simple Rayleigh-type models that generally consider a unique source, GCMs make it possible to account for the mixing of several sources of vapor. The application of tagging approaches to water vapor pioneered by *Joussaume et al.* [1986] and *Koster et al.* [1986] was further extended to water isotopes. In section 3.1, we shortly review how this approach has developed. We then present and discuss unpublished results we have derived from experiments performed with two IGCMs equipped with water isotopes tagging, GISS Model II and LMDZ-iso run with $8^\circ \times 10^\circ$ and $2.5^\circ \times 3.75^\circ$ resolutions, respectively, both for present-day and LGM climate conditions.

[31] In this line, we successively examine the d-excess of marine vapor (section 3.2), its distribution in Antarctic precipitation (section 3.3) and how this distribution is influenced by cooling the ocean (section 3.4), and the usefulness of this parameter as a tracer of air masses in low latitudes (section 3.5).

3.1. IGCMs and Ocean Source Characteristics: A Review

[32] The first experiments addressing the oceanic origin of a precipitation and its isotopic content δ_p were performed using the NASA/GISS model II IGCM. They focused on polar regions both for present-day climate [*Koster et al.*, 1992] and for glacial climate [*Charles et al.*, 1994; *Delaygue et al.*, 2000b]. For Antarctica, the GISS model II simulates that oceanic sources of precipitation are mainly located at midlatitudes and in the subtropics, with a strong contribution of high latitude oceans to coastal area precipitation. The average SST of these sources, weighted by their relative contribution to Antarctic precipitation, is about 11°C (a complete analysis of these contributions, their seasonal and climatic variations, is given by *Delaygue et al.* [2000b]). *Charles et al.* [1994] analyzed the origin of Greenland precipitation and pointed out that very different distillation pathways exist: they showed that the moisture from the North Pacific source arrives at the Greenland coast with a much lower $\delta^{18}\text{O}$ than its North Atlantic counterpart.

[33] The result, inferred from simple Rayleigh-type model, that warmer sources provide precipitation with lower δ_p in Antarctica was confirmed by *Koster et al.* [1992]. Using the same IGCM, *Delaygue et al.* [2000b] further showed that the isotopic content δ_p also depends on the distance between the precipitation site and the oceanic

source: for the same source temperature, the more distant the oceanic source, the more isotopically depleted is δ_p . This is due to the fact that, in the GCM, more distant sources provide moisture that is transported at higher altitude and which undergoes colder conditions and stronger distillation. These different pathways for the vapor cannot be readily accounted for with a simple Rayleigh-type model, which considers a unique temperature of condensation at the precipitation site. The origin of polar precipitation, and its impact on the isotopic content, has been also studied with the ECHAM-4 IGCM from a similar tagging experiment by *Werner et al.* [2001]. In particular, they showed, as with the GISS IGCM, that the relationship between $\delta^{18}\text{O}$ and d-excess simulated for different sources is similar to the one simulated with a simple Rayleigh-type model.

[34] Results obtained with Rayleigh-isotopic models have been further compared with the help of IGCMs, which simulate more realistically the transport and mixing of vapor from different sources. In this context, *Jouzel and Koster* [1996] used the GISS IGCM to point out a limitation of the theoretical formula proposed by *Merlivat and Jouzel* [1979] for the isotopic composition of water vapor above the ocean, and used in Rayleigh isotopic models. Water vapor is more depleted than if it was determined only by surface evaporation, due to horizontal transport and vertical mixing. Such transport and mixing of vapor can only be accounted for by an IGCM.

[35] Using the same GISS IGCM as in previous studies, *Armengaud et al.* [1998] evaluated how the temperature of the oceanic moisture source affects the d-excess of Greenland precipitation. Each of these oceanic sources was also considered separately in independent simulations with the simple MCIM. The two types of models consistently show a link between the d-excess values of polar precipitation and the moisture source temperature. *Delmotte et al.* [2000] also combined an IGCM estimate of the initial vapor and a simple isotopic model to examine the origin of the d-excess seasonal cycle observed at Law Dome, Antarctica. This approach of describing separate trajectories for vapor from different sources has been recently extended thanks to the combination of MCIM results and back-trajectory analyses [*Helsen et al.*, 2006, 2007] and to a new Lagrangian diagnostic for identifying the sources of water vapor for precipitation using reanalysis data [*Sodemann et al.*, 2008; *Schlosser et al.*, 2008].

[36] These studies using IGCMs, in one way or another, have contributed to better understand the link between the isotopic characteristics of a polar precipitation and its oceanic origin. In this line, tagging water and both isotopes (δD and $\delta^{18}\text{O}$) for their oceanic source should provide a clue on the relationship between the d-excess of a precipitation and its oceanic origin. Such experiments have been performed with the GISS IGCM and have been partly presented in *Delaygue* [2000]. Interestingly, this link between d-excess in precipitation and oceanic sources has been recently examined [*Lewis et al.*, 2013] with the IGCM built by *Schmidt et al.* [2005] from a more recent version of the GISS GCM (model E-R). This IGCM is equipped by a suite of generalized vapor source distribution (VSD) tracers, a diagnostic tool with the advantage to be computationally more efficient than the regional tracers [*Kelley*, 2003; *Lewis et al.*, 2010]. The tagging approach is also used in

complement of VSD in the experiments described in *Lewis et al.* [2013].

3.2. Deuterium Excess of the Marine Vapor and Its Climatic Stability

[37] As recalled in section 2, the d-excess of oceanic vapor is partly preserved along the distillation pathway and in precipitation, leading to the MWL. The sensitivity of d-excess to source conditions is thus of primary interest in order to constrain the conditions at the origin of precipitation (see section 2 and Figure 1). Observations [*Uemura et al.*, 2008] and theoretical modeling show that the d-excess of marine vapor should be mostly determined by the sea surface temperature (SST) and the relative humidity h . Such a sensitivity can also be diagnosed in GCMs which physically simulate all processes at the origin of the d-excess of the vapor, with however some simplifying assumptions and attached uncertainties.

[38] As sensitivity tests, we conducted simulations with the GISS and LMDZ IGCMs for three different climatic scenarios. Present-day simulation was forced by observed SSTs and sea ice from the AMIP data set [*Gates*, 1992]. Glacial (LGM) simulations were forced with two different sets of SSTs. One set of SSTs uses the CLIMAP reconstruction [*CLIMAP*, 1976]. This reconstruction leads to a meridional gradient of temperature stronger than the present one. The other set of glacial SSTs is based on the CLIMAP one, by cooling the tropical ocean: this decreases the meridional gradient of temperature to a value similar to the present-day one. (The analysis of source contributions to Antarctic precipitation can be found in *Delaygue et al.* [2000b]; some contributions are given as percentage in Figure 7). For both LGM climates, greenhouse gas concentrations, orbital parameters, and ice-sheet topography were adapted to match LGM values (all details in *Delaygue et al.* [2000b] and *Risi et al.* [2010a]).

[39] Grid cells of the GISS model were aggregated in each oceanic basin, based on their SST, to determine 17 different sources of vapor in the southern hemisphere (see Figure 2 of *Delaygue et al.* [2000a]). Each source is thus characterized by its average SST and humidity (T_w and h). The same groups of grid cells were kept for glacial simulations, not the same range of SST, so that the characteristics of each source could change. The modern SST ranges of these sources were used to define the sources in the LMDZ model. Such source definition ensures that similar sources have similar area in both models, despite their different grid resolutions.

[40] Figure 3 shows the spatial relationship between the d-excess of the marine vapor and the SST of the southern hemisphere ocean, simulated with the GISS and the LMDZ IGCMs. Each point represents the d-excess-SST annual average values of one source of vapor. Note that similar GISS and LMDZ sources (gray square and black dot) have not exactly the same SSTs because they have been defined from ranges of SST, not from their average.

[41] For the modern climate (so-called “control simulation”), both models simulate a similar relationship, roughly linear, over approximately the range 0–23°C. The slopes are almost similar, close to 0.45‰/°C, with d-excess values ranging from 2–4‰ to 10–13‰. For SST warmer than ~23°C, the simulated relationships diverge: the GISS

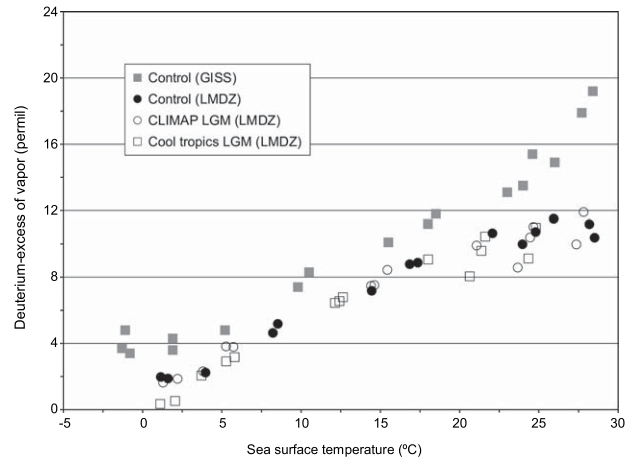


Figure 3. Spatial relationship between d-excess of the marine vapor and sea surface temperature in the Southern hemisphere, simulated by two GCMs under very contrasted climatic conditions.

model simulates a d-excess increase to values up to 19‰, whereas the LMDZ model simulates a very limited, barely significant, increase, with values up to 12‰. Over the full range 0–26°C, the d-excess/SST relationships are almost linear, with a slope close to 0.47‰/°C simulated by the GISS model and 0.39‰/°C by the LMDZ model. Note that the slope values calculated on all grid cells (i.e., with about 1000 values), instead on aggregated sources, are very close to these ones: this suggests that there is little bias on the slope values. A strong relationship with the relative humidity is simulated by the GISS model (not shown), with an approximate slope of $-1\text{‰}/\%$. Since h strongly covaries with SST, we used a multilinear regression to infer sensitivities of d-excess to SST (0.43‰/°C) and to relative humidity ($-0.22\text{‰}/\%$). On the contrary, the LMDZ model underestimates the imprint of relative humidity on d-excess compared to observations conducted in the southern ocean [*Uemura et al.*, 2008], a deficiency more likely related to free tropospheric processes [*Risi et al.*, 2013b].

[42] These simulated d-excess values are consistent with the ones measured over the Southern ocean by *Uemura et al.* [2008]. It is also noteworthy that the simulated d-excess/SST slopes match very well the one calculated from a multilinear regression of observations by *Uemura et al.* (0.45‰/°C). These observations do show a very strong anticorrelation between d-excess and h , with a slope between $-0.61\text{‰}/\%$ (simple regression) and $-0.45\text{‰}/\%$ (multilinear regression). Hence, the sensitivity of $-0.22\text{‰}/\%$ simulated by the GISS model seems too weak.

[43] In order to test the robustness of these d-excess/SST relationships to different climates and atmospheric circulations, we compared the outputs of the LMDZ for the present day and the glacial (LGM) conditions. As shown in Figure 3, the d-excess/SST relationship is essentially the same under any of these very contrasted climatic conditions. This suggests that the relationship with SST is very strong and not appreciably affected by the meridional gradient of temperature (and thus by the meridional advection of vapor).

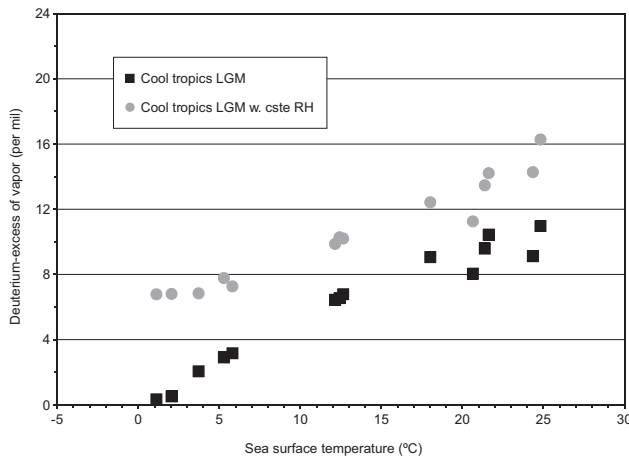


Figure 4. d-excess of marine vapor in different regions (see text) simulated by the LMDZ model with the cool tropics LGM conditions. Black squares: d-excess simulated with the standard model h . Gray circles: d-excess simulated with h artificially kept constant with the value of 60%.

[44] We further tried to disentangle the effects of SST and h on the d-excess of vapor, by conducting a simulation in which the effect of h is kept constant. In the LMDZ GCM, h was free to change except when calculating the isotopic fractionation at evaporation: a constant value of 60% for h was systematically used [Risi *et al.*, 2013b]. This value of 60% is the average over the southern hemisphere, lower than the actual values of about 80% over the ocean. Figure 4 shows the simulated values of d-excess in marine vapor versus SST, for the “cool tropics LGM” conditions as an example. With the lower h value of 60%, the d-excess of vapor is higher, by about 4‰: considering an actual average value of h of about 80% over the ocean, this increase of d is roughly consistent with a d-excess sensitivity of $-0.2\text{‰}/\%$, in line with the sensitivity inferred from the GISS model. The sensitivity of d-excess to SST (linear slope in Figure 4) is similar but slightly lower with constant h ($0.36\text{‰}/\text{°C}$) than with varying h ($0.42\text{‰}/\text{°C}$). A similar result is obtained with CLIMAP LGM conditions: $0.32\text{‰}/\text{°C}$ versus $0.36\text{‰}/\text{°C}$, respectively. Consistently with the multilinear regression of values for present-day conditions, these comparisons suggest that the sensitivity of d-excess to SST is slightly increased by the covariation between SST and h over the oceans.

[45] From these simulations with contrasted climatic conditions, we are able to calculate a “temporal” d-excess/SST slope instead of the “spatial” slope calculated above. What is interpreted in ice core records is the change in time of d-excess at one place: this requires to use a sensitivity of d-excess to varying SSTs over time, what has been coined as a “temporal slope.” Rather, what is calculated here from simulations (or observations) is the sensitivity of d-excess to varying SST in space, what is called a “spatial slope.” Here, by combining the different simulations with contrasted climatic conditions, we are able to infer such a temporal slope: we calculated the linear regressions of d-excess change versus SST change for all LMDZ data points in the southern hemisphere (1527 points). (Using only

averaged regions for such a regression leads to quite poor relationships.) Based on changes between the “Control” and CLIMAP LGM simulations, the average slope is $0.47\text{‰}/\text{°C}$ ($R^2 = 0.32$). Based on changes between the “Control” and “Cool tropics LGM” simulations, the average slope is $0.48\text{‰}/\text{°C}$ ($R^2 = 0.30$). Despite much lower correlation than for spatial slopes, it is remarkable that these values for temporal slopes are similar to those for spatial slopes.

3.3. Deuterium Excess of Antarctic Precipitation

[46] Quantitative calculation and modeling show that Antarctic precipitation mostly originates from marine vapor [Werner *et al.*, 2001]. Sublimation, especially of drifting snow, may provide some recycled moisture, but in specific conditions and to an extent which is still largely uncertain. The different approaches for defining precipitation origins, as recalled in section 3.1, consistently depict that these origins differ across Antarctica: Subtropics and midlatitudes are the main origins of precipitation on the Plateau, and high-latitudes contribute more to West Antarctic and coastal precipitation.

[47] If the d-excess of vapor were not modified during its trajectory to Antarctica, it would be possible to apply the sensitivity estimated in the previous section to the d-excess of precipitation to constrain its origin. However, theory suggests that it is not the case: d-excess of vapor is modified because the isotopic fractionation coefficients are temperature dependent and because kinetic fractionation is important in mixed clouds. We use here the GISS and the LMDZ models to study the d-excess of precipitation in Antarctica and how it relates to the SST of moisture sources. In complement, the MCIM is used in order to isolate the role of complex vapor trajectories on the isotopic fractionation.

[48] Despite its low spatial resolution, both surface temperature and isotopic contents of precipitation are realistically simulated by the GISS model, even over central Antarctica with minimum values (-55‰ for $\delta^{18}\text{O}$) comparable to present-day observations. LMDZ overestimates temperature in central Antarctica but simulates lower d-excess values in precipitation during the LGM over most high-latitude regions, which is consistent with d-excess records, and poorly simulated by other GCMs. Both models have a similar grid which presents a singularity at the South pole: in both models, it is accounted for by periodically averaging the fields of the grid cells adjacent to the South pole. In this way, this singularity should not affect too much the climate of Antarctica. A circulation across the South pole region does exist in the models; although indirectly. The extremely low temperatures on the Antarctic Plateau make the vapor flux drop down to very low values, so that the advection of vapor is essentially poleward.

[49] Figure 5 shows the simulated d-excess of precipitation on the Antarctic Plateau, in the area of the Vostok station, originating from each vapor source already depicted in Figure 3 and characterized by its average SST. We used the MCIM and the GISS model to simulate the trajectory, and the associated isotopic fractionation, of vapor from its source to the Antarctic Plateau. Black dots are d-excess values in the marine vapor of each source (the same values already shown in Figure 3 with gray squares), and each of them has two counterparts in Antarctic precipitation,

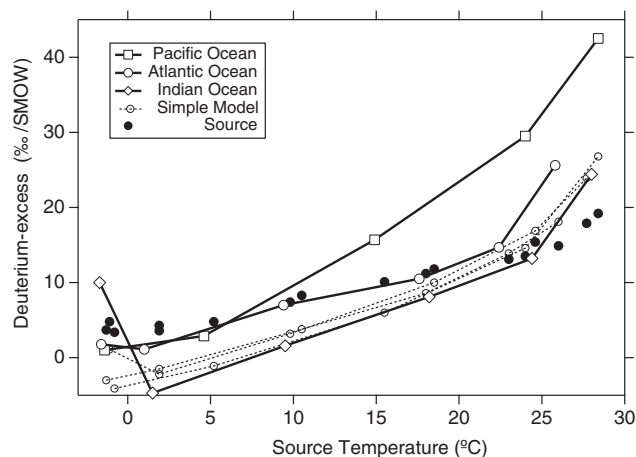


Figure 5. Simulated d-excess of precipitation in Eastern Central Antarctica (region of Vostok station) (open symbols), compared to d-excess of the initial vapor (black circles), plotted against the temperature of the vapor source. Both the simple isotopic model (MCIM, small open dots) and the GISS GCM (large open symbols) have been used to transport and fractionate the vapor. The origin of vapor in terms of oceanic basin is underlined by lines between sources belonging to the same oceanic basin.

plotted for the same SST with open symbols: the small open circles are values simulated by the MCIM, and the large open symbols are values simulated by the GISS model. Hence, the distance between each black dot and its open counterparts represents the change in d-excess from the initial vapor to precipitation in Antarctica. (Note that the large open symbols are slightly shifted in SST with respect to their counterparts, because of a slightly different averaging of SSTs, but the source characteristics are the same). The MCIM simulates d-excess values lower in Antarctic precipitation than in marine vapor, except for SSTs higher than $\sim 22^\circ\text{C}$. This shift is enhanced with latitudes, up to 7‰ for high latitude, colder, sources. The MCIM simulates a monotonic relationship between d-excess of precipitation and SST, with a linear slope of about $0.75\text{‰}/^\circ\text{C}$, which is stronger than the one for the marine vapor (about $0.45\text{‰}/^\circ\text{C}$, cf. section 3.2). A strong deviation from this relationship is obtained for very high SSTs (tropical sources). These features were already shown by earlier studies, e.g., *Petit et al.* [1991] (their Figure 10). The d-excess of vapor from subtropical to midlatitudes sources (SSTs range from 17 to 25°C) is the least modified: interestingly, the corresponding values in precipitation (10–15‰) match well the values measured in Central Antarctica, and these sources contribute the most to the Antarctic Plateau precipitation in the GISS GCM.

[50] Compared to the MCIM, the GISS GCM simulates a stronger spread of d-excess in precipitation, with large values up to 40‰. However, when d-excess values are grouped according to oceanic basins, a similar picture emerges: precipitation coming from the Indian Ocean (open diamonds), which contributes the most to the total (30–60% seasonally), has d-excess values very similar to the values simulated by the MCIM. Instead, precipitation coming from the Atlantic (open circles) and the Pacific

(open squares) oceans has higher d-excess values. Since both models start with the same vapor and d-excess values, such difference in precipitation must be caused by different trajectories and fractionation histories. In fact, the MCIM calculates the trajectory of an amount of vapor, from its source to the precipitation site, by assuming that, wherever the source is, the vapor is transported to the same elevation (and temperature) at the precipitation site. Hence, precipitations originating from two sources with close temperatures have close d-excess values (see, e.g., the two open dots close to 10°C). On the contrary, the GISS GCM simulates more realistic trajectories for the vapor, and accounts for the distance between the source and the precipitation site: between two sources with close temperatures, the more distant source provides precipitation in Antarctica with the higher d-excess value. This is because, in the GISS model, the average elevation of vapor increases during its trajectory, so that condensation and the associated isotopic fractionation take place at lower temperature. Hence, vapor originating from a more distant source is more fractionated when it arrives in Antarctica [*Delaygue et al.*, 2000b]. Sources of vapor located in the Pacific and Atlantic Oceans are more distant to the Antarctic Plateau than sources in the Indian Ocean: they provide less precipitation to the Antarctic Plateau, with higher d-excess values (compare, e.g., the open circle and open square for sources at $\sim 9^\circ\text{C}$). A similar difference in trajectories has been obtained from analyzing back-trajectories of vapor [*Masson-Delmotte et al.*, 2008], which gives some credit to the trajectories simulated by the GISS GCM.

[51] Does the LMDZ GCM also simulate different trajectories and isotopic fractionation according to the distance of the source? To show it differently, we plot in Figure 6 the d-excess of Antarctic precipitation simulated by the LMDZ model, versus the temperature at the precipitation site. Instead of separating all sources, as in Figure 5, we have grouped the sources from the same ocean: an open diamond represents the d-excess of precipitation falling at some place on Eastern Antarctica and coming from the whole Indian Ocean, a source which is the closest and

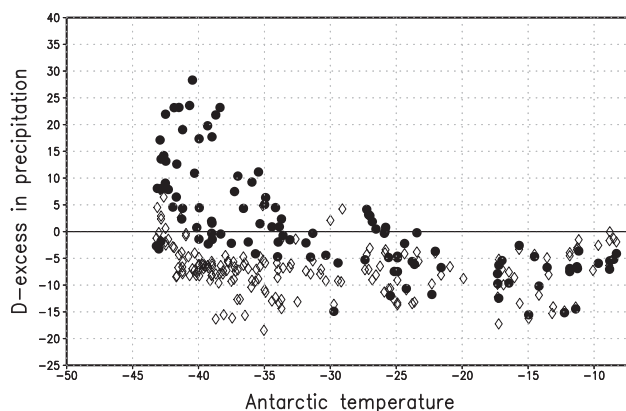


Figure 6. d-excess of precipitation across Eastern Antarctica ($60^\circ\text{--}150^\circ\text{E}$; $68^\circ\text{--}80^\circ\text{S}$), plotted against the local surface temperature, simulated with the LMDZ model with modern (“control”) climatic conditions. The oceanic origin of precipitation has been tagged: Indian ocean with open diamonds, Atlantic ocean with black circles.

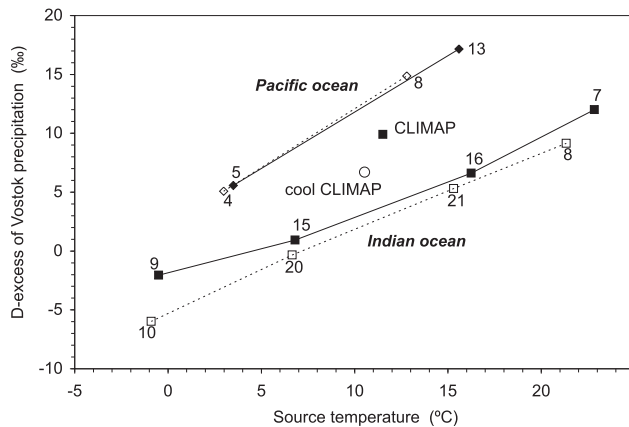


Figure 7. Same as Figure 5, but for glacial conditions: d-excess of precipitation over the Eastern Antarctic Plateau, simulated for two different sets of glacial climatic conditions by the GISS IGCM, versus marine source temperature (SST). Each point represents one specific oceanic region, with its contribution (in %) to the total precipitation as labeled. For clarity only sources contributing more than 5% to precipitation are displayed. Full symbols and lines represent glacial conditions using the CLIMAP reconstruction; open symbols and dashed lines represent glacial conditions with cooler tropics. The two isolated symbols are the average d-excess values of the total precipitation (all sources), plotted with respect to the average source temperature.

contributes the most (15–40%) to the total precipitation. It can be compared with its black-dot counterpart, which is the d-excess of precipitation falling *at the same place*, but coming from the whole Atlantic Ocean, a source which is on average further and contributes the least (less than 15%) to the total precipitation. (Note that, to reduce the spread of points and the noisiness of the figure, only contributions higher than 5% to the total precipitation have been retained, so that not all open diamonds have black-dot counterparts.) Figure 6 consistently shows that, except in coastal regions, precipitation originating from the Indian Ocean (open diamonds) has a lower d-excess than precipitation originating from the Atlantic Ocean (black dots), with difference up to 30‰. Hence, the LMDZ GCM also simulates, like the GISS GCM, different trajectories for the vapor depending on the distance.

[52] The fact that the d-excess of Antarctic precipitation depends not only on the conditions (T_w and h) at the source of vapor, but also to the absolute distance between the source of vapor and the precipitation site, complicates its interpretation in terms of source conditions. Such interpretation would be easier in Antarctic regions for which the precipitation origin is dominated by a limited oceanic area. The GISS and LMDZ GCMs suggest that precipitation on the Eastern Antarctic Plateau predominantly comes from the Indian Ocean, precipitation on the Dronning Maud land predominantly from the Atlantic Ocean, and precipitation on West Antarctica predominantly from the Pacific Ocean: these are probably places where the d-excess of precipitation (and ice) can be reliably interpreted in terms of source conditions.

3.4. Signature of a Tropical Cooling in Antarctic Precipitation d-Excess

[53] Interpreting the d-excess of Antarctic precipitation as oceanic temperature has been explored for years [e.g., Jouzel *et al.*, 1982], motivated by the fantastic isotopic archives available from the ice sheet. In the previous section, we have seen that the d-excess signature of source conditions acquired by vapor is modified when vapor is transported to Antarctica. Ideally, in favorable regions of Antarctica dominated by one ocean, this modification could be accounted for by applying a specific sensitivity of d-excess to SST (Figure 5). However, what happens when the global climate was radically different, as during glacial periods? Because the atmospheric transport of vapor was different, the contributions of the different oceanic regions to Antarctic precipitation have changed [e.g., Delaygue *et al.*, 2000a]. How does it affect the d-excess signature of sources in precipitation? Here, we focus on the particular sensitivity test of cooling the tropical oceans under glacial conditions, in order to limit changes in the atmospheric circulation. Additionally, the isotopic composition of the oceans, which changed along with climate, is kept constant: this is important since this composition directly affects the d-excess of precipitation [Jouzel *et al.*, 2003]. The idea of testing such a tropical cooling comes from the debate on the CLIMAP reconstruction of glacial SSTs, which shows little cooling in the tropical ocean (and even warming in the Pacific). For this sensitivity test, the CLIMAP SST reconstruction for LGM was modified to get a 2–3°C cooling in the tropical region compared to modern conditions, as described in Delaygue *et al.* [2000a]. This cooler SST reconstruction is coined “cool CLIMAP” in the following.

[54] Figure 7 shows the relationship between the d-excess of precipitation over the Antarctic Plateau (region of Vostok) and the temperature of the source of vapor (as in Figure 5 but for glacial conditions) as simulated by the GISS model. Note the cooling of the sources (shift between open and full symbols), especially strong in the subtropical Pacific. This tropical cooling reduces the contribution of the warmer sources to the precipitation in Antarctica, and increases the (relative) contribution of the cooler sources [Delaygue *et al.*, 2000b]. Note that the slight cooling of extratropical sources is due to a reduction in the evaporation flux, used to calculate the average SST of each source, and not to a change in SSTs. The shifts between full and open symbols (CLIMAP and cool CLIMAP climates) show that cooling the sources decreases the d-excess of precipitation. Both cooling and d-excess decrease define a temporal slope, since defined between different climates. It is noteworthy that this temporal slope is in general similar to the spatial slopes, defined between different sources for each particular climate. In other words, the GISS model simulates similar temporal and spatial slopes for the relationship between precipitation d-excess and source temperature. However, the practical question for reconstructing SST change from d-excess in ice record is whether such relationship is preserved in the total precipitation, i.e., the mixing of all sources. Total precipitation is represented with isolated symbols in Figure 7. In this particular sensitivity test, since the cooling is restricted to the tropical ocean, and because the relative contribution of the warmer sources to

the precipitation decreases, the average source cooling is only about 1°C whereas the associated decrease in the d-excess is about 3‰, dominated by the tropical sources. This simulated d-excess decrease by about 3‰ in the total precipitation would be interpreted as a 4°C cooling of the marine source by applying the slope of 0.75‰/°C inferred from the MCIM model for a Rayleigh distillation (see section 3.3). Hence, this inferred cooling would be too strong compared to the actual 2–3°C decrease of SST imposed in the simulation, a bias due to a change in the relative contributions of the vapor sources.

[55] Although based on GCM simulations, not necessarily realistic, this sensitivity test suggests that interpreting d-excess of precipitation in terms of SST change is qualitatively correct (the simulated d-excess change is consistent with the marine source cooling), but is quantitatively biased, even in this case of a limited change in climate. This approach also illustrates the possibility to test the realism of different LGM ocean surface conditions against ice core data.

3.5. How Useful is d-Excess to Identify the Origin of Air Masses at Low Latitude?

[56] We focus now on low-latitude regions, more specifically on tropical South America. From measurements performed on 1 year precipitation events (between September 1999 and August 2000) in the Bolivian Andes, *Vimeux et al.* [2011] showed that their isotopic composition is partly influenced by their geographic origin. The most isotopically depleted composition mostly corresponds to trajectories that originate in the Pacific and that cross the Andes, whereas the most isotopically enriched composition is often related to a southern origin, probably related to lower convective activity along air mass pathway. However, it is worth noting that the influence of geographic origin on the isotopic composition is not always obvious and that other processes or other origins than oceanic vapor (transpiration, bare soil evaporation) can be strong enough to offset the oceanic origin imprint. Moreover, no relationship is found between d-excess value and the geographic origin of precipitation (Austral, Pacific, or Atlantic). So far, d-excess has been interpreted to reflect the effect of fractionation during evaporation of standing water such as bare soil and lakes [*Gat and Matsui*, 1991].

[57] Using the LMDZ-iso IGCN model with water tagging, and new isotopic measurements, we revisit these interpretations of the $\delta^{18}\text{O}$ and d-excess in terms of water vapor origin. We focus on the $\delta^{18}\text{O}$ seasonality, which has traditionally been interpreted in terms of temporally and spatially integrated convection along air mass trajectories [*Villacis et al.*, 2008; *Vimeux et al.*, 2005, 2011], and we examine the possibility to explain this seasonality by seasonal changes in both water vapor sources and their isotopic compositions.

[58] LMDZ-iso was nudged toward the horizontal winds of the ECMWF reanalyses, to ensure a realistic large-scale circulation [*Risi et al.*, 2010a, *Yoshimura et al.*, 2008]. Three years are simulated with the sea surface and wind conditions corresponding to an arbitrarily chosen year (here, 2006). The last year of the simulation is analyzed and the first 2 years are discarded for spin up. We focus on the seasonal cycle, which is an order of magnitude larger

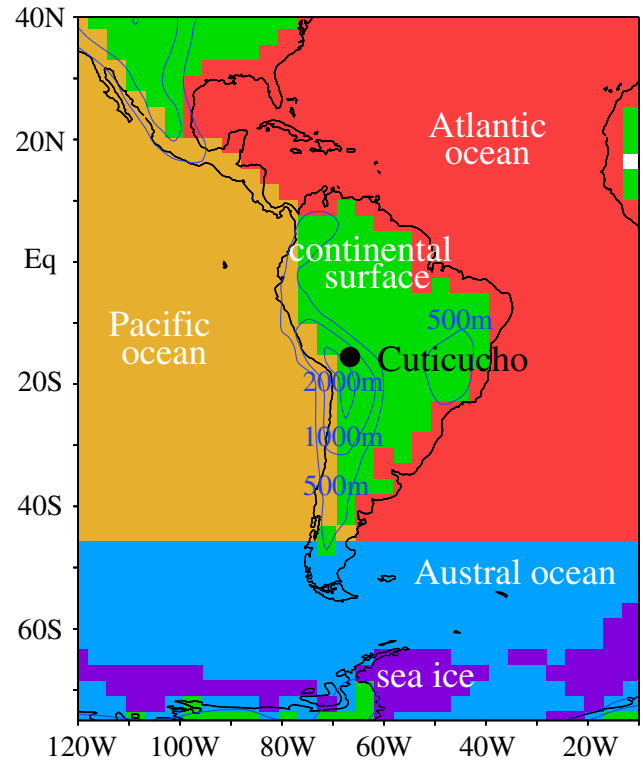


Figure 8. Map illustrating the tagging definition around South America: water evaporating over the red, orange, and blue areas is tagged as Atlantic, Pacific, and Austral, respectively. Water evaporating over purple areas (i.e., sea ice) is tagged as residual. Water evaporating over green areas is tagged as continental, and can be further tagged as transpiration or as bare soil evaporation. Sublimation of snow is included in the bare soil evaporation component. Note that LMDZ can represent different surface types (terrestrial, oceanic, or sea ice) over each grid box. For example, along the coasts, a fraction of the vapor is tagged as oceanic while another fraction is tagged as continental. The same applies over sea ice. The location of Cuticucho is also indicated together with contours of the altitude prescribed to the LMDZ model.

than interannual variations. Simulations are initialized with no water isotopes and no tracers, but we checked that 2 years were enough for reaching equilibrium. LMDZ is coupled to the land surface model ORCHIDEE [*Krinner et al.*, 2005], to distinguish between different sources of terrestrial precipitation: bare soil evaporation and transpiration [*Risi et al.*, 2010b, 2013b]. In ORCHIDEE, a detailed soil water budget is described [*Ducoudré et al.*, 1993]. Fractionation occurs during soil evaporation [*Barnes and Allison*, 1983] and is represented following *Risi* [2009]. We assume that transpiration has the composition of the soil water taken up by the roots [*Washburn and Smith*, 1934; *Barnes and Allison*, 1988]. Canopy interception was disabled. For oceanic sources, five oceanic basins are defined: Pacific, Atlantic, Indian, and Austral oceans, Mediterranean Sea. An additional tag is affected to all other nonterrestrial surfaces, including the Arctic ocean, interior seas, and sea ice surfaces. The definition of the tags in and around South America is illustrated in Figure 8.

Cuticucho from December 2011 to November 2012

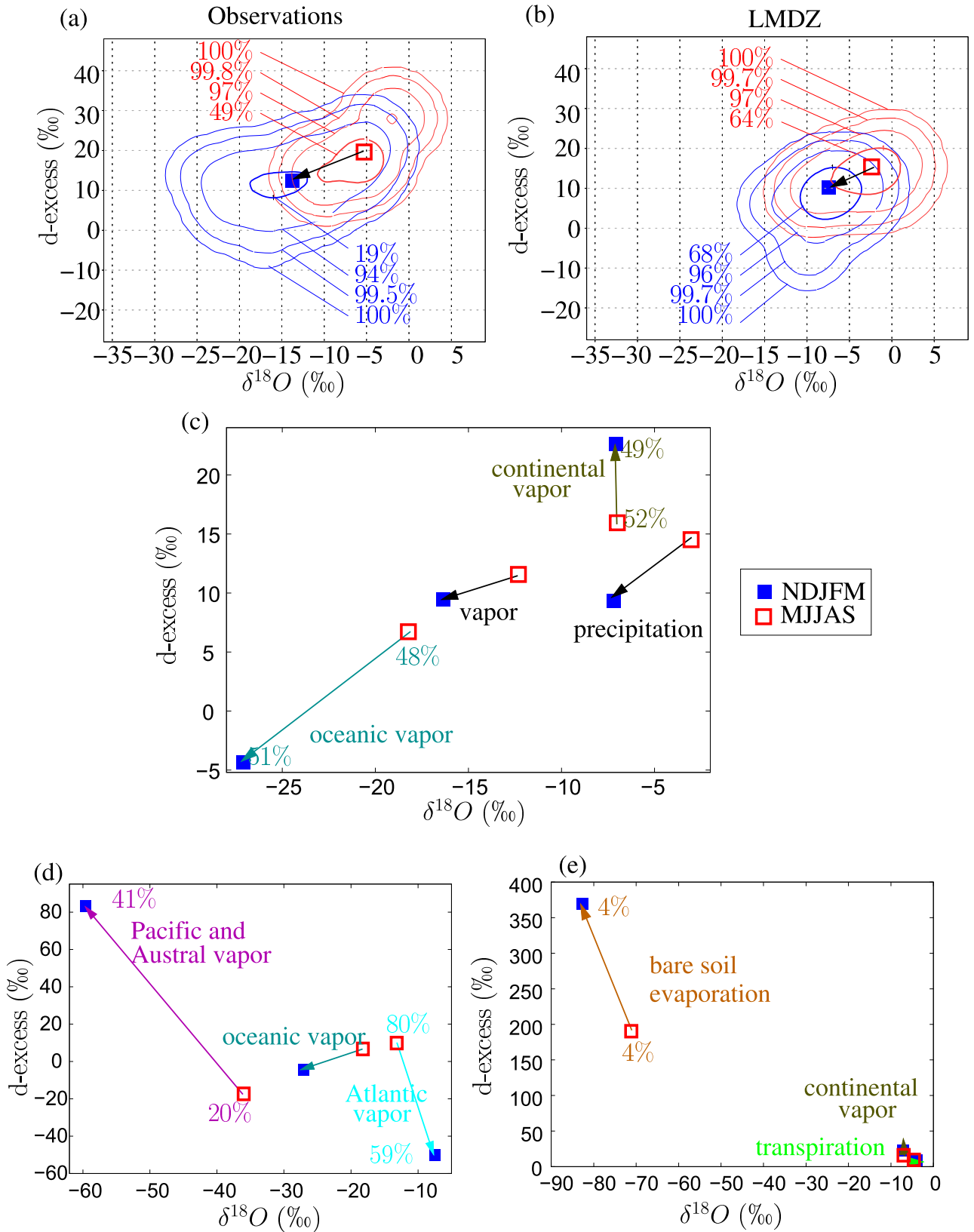


Figure 9.

[59] Precipitation was collected at an event basis from December 2011 to November 2012 in the Zongo valley (16°20'S–67°47'W), at the station of Cuticucho (2697 m). Its isotopic composition is plotted in Figure 9a as joint d-excess- $\delta^{18}\text{O}$ probability density function for the wet season (December to March) and the dry season (May to September). During the wet season, observed precipitation is 7.8‰ more depleted in $\delta^{18}\text{O}$ and has a 6.2‰ lower d-excess than during the dry season.

[60] LMDZ-iso captures qualitatively well the observed seasonality in the precipitation (Figure 9b) with $\delta^{18}\text{O}$ lower by 4.8‰ and d-excess lower by 4.7‰ during the wet season compared to the dry season. This seasonal shift in the isotopic composition of precipitation does also exist for the isotopic composition of vapor (Figure 9c, Table 1): to understand the seasonality in the precipitation we need to understand the seasonality in the vapor. Water vapor is tagged in LMDZ-iso to quantify the contributions of different evaporative origins: oceanic origins (including Atlantic, Pacific, Austral basins) and land origin (transpiration and bare-soil evaporation). Results are illustrated in Figures 9c–9e; and the contributions of different effects to $\delta^{18}\text{O}$ and d-excess changes are quantified in Table 1.

[61] From the dry to the wet season, the contribution from continental recycling changes little from 52 to 49% (Figure 9c). The change in water vapor composition is almost entirely due to the change in the oceanic component of the vapor (Figure 9c, Table 1). What causes the decrease of $\delta^{18}\text{O}$ and d-excess from the dry to the wet season in the oceanic water vapor?

[62] Figure 9d illustrates that half of the decrease in $\delta^{18}\text{O}$ in oceanic vapor is due to the increase in the proportion of water vapor coming from Pacific and Austral origins (from 20 to 41%), which is very depleted due to its long distillation pathway. It is worth noting that this contribution might be overestimated with the standard resolution of LMDZ-iso for which the Andes range reaches ~ 4000 m in elevation, allowing more transport from the Pacific ocean. The other half of the decrease in $\delta^{18}\text{O}$ is due to the decrease in $\delta^{18}\text{O}$ in the Pacific and Austral vapor itself (Table 1), due to longer distillation history or to more rain out along the way. Surprisingly, the $\delta^{18}\text{O}$ in the Atlantic water vapor does not change much from dry to wet season, in spite of the increased convection over the Amazon basin. In contrast,

the decrease in d-excess from dry to wet season is due to the decrease in d-excess in the Atlantic water vapor which remains the main water vapor contributor. This d-excess decrease may be due to a change in the evaporative origin of the water vapor within the Atlantic basin, as shown in *Vimeux et al.* [2005].

[63] The decrease of d-excess in the oceanic component of the vapor is partially compensated by an increase in the continental component (Figure 9c). More specifically, the increase of d-excess in the continental component is due to an increase in d-excess in the bare-soil evaporation component (Figure 9e). This is because the composition of the bare soil evaporation depends on the composition of the overlying water vapor, so that bare-soil evaporation always tends to attenuate variations in water vapor composition.

4. Concluding Remarks: What to Expect From $\delta^{17}\text{O}$?

[64] In a recent review article, *Gimeno et al.* [2012] examined the various methods used to establish source-sink relationships for atmospheric water vapor and discuss the advantages and caveats associated with each technique. They recognized the potential of stable water isotopes in this context, especially to interpret direct (ice cores) or indirect (e.g., speleothem calcite, lake sediment calcite, tree ring cellulose, plant wax) archives of past changes in the isotopic composition of precipitation. However, they pointed out the crucial need to improve our understanding of how moisture origin and transport affect isotopes in precipitation.

[65] The GCM approach discussed above, as well as the recent simulations published by *Lewis et al.* [2013], clearly contribute to this objective by following water evaporating from a given source region and its isotopic properties through the atmosphere until it precipitates. Such GCM studies largely confirm the link between the d-excess of water vapor over the ocean and surface parameters (SST and relative humidity h). More directly relevant to the interpretation of ice-core data is the similarity between the spatial and temporal slopes relating the d-excess in Antarctic precipitation and SST in the oceanic source region (section 3.4). The simple model (MCIM) and the IGCM approaches lead to an overall consistent picture, especially

Figure 9. (a) Joint d-excess/ $\delta^{18}\text{O}$ probability density function in the precipitation observed at Cuticucho from December 2011 to November 2012 at the event basis, for the wet season (NDJFM, blue) and the dry season (MJJAS, red). Contours show the 1%, 0.1%, 0.01%, and 0.001% isolines of probability for one given event to be in a surrounding 1–2‰ $\delta^{18}\text{O}$ –d-excess box. (b) Same as Figure 9a but for LMDZ outputs. The altitude of Cuticucho and of the corresponding LMDZ grid box are 2697 m and 2705 m, respectively, so that no altitude correction is needed. (c) Decomposition of the NDJFM-mean (blue) and MJJAS-mean (red) precipitation and vapor composition simulated by LMDZ into its oceanic (dark cyan) and continental components (brownish green). Fractions of oceanic vapor and continental vapor are indicated for each season in percent. (d) Same as Figure 9c but for the decomposition of the oceanic water vapor (dark cyan) into its Atlantic (light cyan) and Pacific/Austral (purple) components. The oceanic water vapor arrow corresponds to the one in Figure 9c. Fractions of Atlantic and Pacific/Austral vapor relatively to the total oceanic water vapor are indicated for each season in percent. (e) Same as Figure 9c but for the decomposition of continental vapor (brownish green) into its transpiration (light green) and bare soil evaporation (brown) components. The continental water vapor arrow corresponds to the one in Figure 9c. Fractions of transpiration and bare soil evaporation relatively to the total continental water vapor are indicated for each season in percent.

Table 1. First Two Rows: Simulated Seasonal ($\Delta = \text{NDJFM-MJJAS}$) Change in $\delta^{18}\text{O}$ and d-Excess in the Precipitation (Row 1) and in the Vapor (Row 2)^a

0	Seasonal Change and Its Contributions	$\Delta\delta^{18}\text{O}$ (‰)	$\Delta\text{d Excess}$ (‰)	Fraction of $\Delta\delta^{18}\text{O}$ Explained by Each Contribution (%)	Fraction of $\Delta\text{d-excess}$ Explained by Each Contribution (%)
1	Precipitation	−4.8	−4.7		
2	Water vapor	−5	−1	100	100
3	Contribution associated with the change in the fraction of continental vapor	−0.41	−0.48	4	6
4	Contribution associated with the change in the composition of oceanic vapor	−8.9	−11	90	136
5	Contribution associated with the change in the composition of continental vapor	−0.6	3.4	6	−42
6	Contribution associated with the change in the fraction of Pacific-Austral vapor	−7.6	10.8	53	51
7	Contribution associated with the change in the composition of Pacific-Austral vapor	−6.9	37.7	48	180
8	Contribution associated with the change in the composition of Atlantic vapor	0.2	−27.5	−1	−131
9	Contribution associated with the change in the fraction of bare soil evaporation	−0.1	0.5		14
10	Contribution associated with the change in the composition of bare soil evaporation	−0.2	3.4		94
11	Contribution associated with the change in the composition of transpiration	0.3	−0.3		−8

^aRows 3–5: Contribution of different effects to the simulated seasonal change in water vapor $\delta^{18}\text{O}$ and d-excess, based on water tagging (details on the quantification methodology are given in *Risi et al.* [2010a, 2013b]). The contributions are given in permil (first two columns) and in % of water vapor $\delta^{18}\text{O}$ and d-excess change. Their sum equals 100%. The contributions associated with the changes in composition of oceanic and continental water vapor are further decomposed in the following rows. Rows 6–8: Same as rows 5–7 but for the contribution of different effects to the simulated seasonal change in oceanic water vapor $\delta^{18}\text{O}$ and d-excess. The sum of these contributions equals 100%. Rows 9–11: Same as rows 5–7 but for the contribution of different effects to the simulated seasonal change in continental water vapor $\delta^{18}\text{O}$ and d-excess. The sum of these contributions equals 100%.

a similar d-excess/SST relationship; although the IGCMS simulate a dependency of this relationship to the absolute distance to the source, what is attributed to the elevation of vapor pathway [*Delaygue et al.*, 2000b]. This consistency gives some credit, at least qualitatively, to the current interpretation of ice-core d-excess based on a simple model, as illustrated in Figure 2. These results obtained with IGCMS could be assessed with the independent back trajectory approach, although IGCMS have the advantage to be compared to data over very different time scales and climatic conditions. We note that our comparison has however stressed that the two models investigated here may underestimate the impact of relative humidity at the sea surface on vapor d-excess, compared to existing data sets. Further investigations of these features are needed.

[66] In addition to the complexity of vapor pathway, not accounted for with simple model, there are other difficulties to infer quantitative information on climatic conditions at the evaporative regions from the d-excess parameter alone. In particular, the influence of changes in relative humidity is not explicitly taken into account. We owe to *Angert et al.* [2004] the idea that, by adding $\delta^{17}\text{O}$ to δD and $\delta^{18}\text{O}$ of precipitation, it could be possible to decouple changes in surface temperature and changes in relative humidity. While the ratio of fractionation intensities for δD and $\delta^{18}\text{O}$ is temperature dependent, the ratio for $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ is quite insensitive to temperature. Similarly to the d-excess parameter, the ^{17}O -excess parameter has been designed because its value in precipitation should be, in theory, primarily controlled by the kinetic fractionation at evaporation [*Angert et al.*, 2004]. Under the steady-state assumption of *Merlivat and Jouzel* [1979] for evaporation, *Landais et al.*

[2008] confirmed that the ^{17}O -excess of the initial vapor should be practically independent on SST. Measurements in surface water vapor and snow at the Greenland NEEM camp have confirmed the potential of ^{17}O -excess as a marker of relative humidity at the source of precipitation [*Landais et al.*, 2012]. In fact, this isotopic parameter shows seasonal variations with a minimum in July in phase with a maximum in source relative humidity, which happens earlier than the sea surface temperature maximum in a large northern Atlantic sector.

[67] However, a strong kinetic fractionation also occurs at snow formation. By using a simple isotopic model to account for this kinetic effect, *Winkler et al.* [2012] showed that this decoupling between relative humidity (h) and SST based on ^{17}O -excess of polar precipitation is not straightforward. In fact, interpreting ^{17}O -excess in ice core proved to be complex: the first profile measured along the Antarctic Vostok ice core [*Landais et al.*, 2008] suggests an LGM increase in the source relative humidity of up to 20%, which appears unrealistic. This raised the possibility that the ^{17}O -excess measured at Vostok is a local climatic signal rather than a more regional one. *Winkler et al.* [2012] addressed this question by analyzing the variations of ^{17}O -excess over the last deglaciation in ice from two other Antarctic sites: Dome C on the Plateau, and Talos Dome, which is a more coastal site. The comparison reveals differences in ^{17}O -excess mean level and changes between the three sites: While the Dome C data display a ^{17}O -excess change smaller than at Vostok by a factor of about 3, the Talos Dome data show no significant variation from the LGM to the Early Holocene. This suggests that the large increase measured at Vostok over the last deglaciation

[Landais *et al.*, 2008] is a local and not a general pattern for East Antarctica. In fact, a Lagrangian moisture source diagnostic reveals very different source regions for Vostok and Dome C compared to Talos Dome, and an analysis with the MCIM model points to the strong sensitivity of ^{17}O -excess to local effects under the conditions of the Antarctic Plateau [Winkler *et al.*, 2012]. This study confirms that combining δD , $\delta^{18}\text{O}$, and $\delta^{17}\text{O}$ measurements in ice cores is promising for getting access to variations of both SST and relative humidity in the oceanic source region, although it is more reliable for relatively coastal sites such as Talos Dome. The study of Risi *et al.* [2013a] is important in this context as it is the first time that both d-excess and ^{17}O -excess are fully simulated by an IGCM equipped with the four water isotopes (H_2^{16}O , HDO, H_2^{18}O , and H_2^{17}O). Such a modeling framework is needed to quantify the relative influences of SST and relative humidity on these isotopic compositions. At the current stage of model development, these authors recognized some shortcomings in the first simulation of ^{17}O -excess.

[68] Our focus on low-latitude precipitation (section 3.3) illustrates the potential of IGCMs to establish a link between the isotopic content of precipitation and its oceanic origin. The fact that the IGCM approach is promising is confirmed by the study of Lewis *et al.* [2013]. These authors recognize that d-excess is generally a faithful tracer of source temperatures as estimated with the MCIM, but point out that large discrepancies in the isotope-climate relationship occur around Greenland for the LGM, when precipitation seasonality and moisture sources were notably different from present-day ones. These results show that quantitative reconstruction from ice core d-excess should be treated with caution if the atmospheric transport and other climatic conditions were significantly different from the present-day ones. These authors also noted difficulties for interpreting Antarctic data from high elevation sites such as Dome C, while data from the lower elevation EDML site should be more reliable. They also strengthened the importance of humidity when interpreting d-excess values. Mapping the geographical distribution of d-excess of past precipitation from ice cores for different past periods may provide further information.

[69] An inherent difficulty for interpreting the longest d-excess time series from the EPICA Dome C site, covering more than 800,000 years [Jouzel *et al.*, 2007b; Stenni *et al.*, 2013], is the very cold temperature. In particular, isotopic ratios are, for these very cold sites, strongly influenced by the supersaturation of vapor over ice, which itself is temperature dependent. Sensitivity tests to the tuning of the MCIM model have evidenced the sensitivity of the results to poorly constrained model parameters [Uemura *et al.*, 2010]. Most of existing IGCMs—such as the LMDZ model used in our study and the GISS Model E-R used by Lewis *et al.* [2013]—have difficulties to simulate such very cold conditions (temperature is overestimated by 10°C or even more). This is not the case for the GISS model II (observed and simulated minima are within a few $^\circ\text{C}$) on which is based a large part of the IGCM results discussed in this article. This ability to correctly reproduce the very low temperatures of Central East Antarctica increases our confidence in the link between d-excess in the marine vapor and d-excess in Antarctic precipitation that we have

inferred from this IGCM, despite its low spatial resolution. Simulations conducted for present-day at very high resolution with the ECHAM-5 model are promising by showing a realistic distribution of precipitation isotopic composition, when compared with surface snow data [Werner *et al.*, 2011].

[70] Finally, a major breakthrough has been accomplished as infrared laser spectrometers, now commercially available, have reached the same level of precision as mass spectrometers for measuring water isotope ratio. These devices are sufficiently robust to allow continuous field measurements of the δD and $\delta^{18}\text{O}$ composition of water vapor and the possibility to develop an instrument for measuring $\delta^{17}\text{O}$ is currently explored. Field measurements of the δD and $\delta^{18}\text{O}$ composition in the marine atmosphere are now running in Bermuda, Iceland (H.C. Steen-Larsen, personal communication, 2013) and in south Greenland (J. L. Bonne, personal communication, 2013). This network should be extended to other polar sites, both in Greenland and Antarctica, to help establishing the link between the oceanic source characteristics, the isotopic ratio in the marine vapor and in precipitation.

[71] **Acknowledgments.** This work has benefited from the support of projects VANISH (Vulnerability of the Antarctic Ice Sheet and its Atmosphere, ANR-VULN-013) and GREEN-LAND (Groenland vert, ANR-10-CEPL-0008). We are indebted to the people who largely contributed to develop the GISS GCM and implement the water isotopes and tagging, especially Gary Russell and Randy Koster at NASA/GISS. LMDZ simulations were performed on the NEC supercomputer of the IDRIS computing center. We thank Romain Trasancos and Bénédicte Minster for their contribution to the program of isotopic measurements conducted on precipitation from the Zongo valley, and Randy Koster and Andreas Stohl for their very constructive reviews.

References

- Abram, N. J., R. Mulvaney, and C. Arrowsmith (2011), Environmental signals in a highly resolved ice core from James Ross Island, Antarctica, *J. Geophys. Res.*, *116*, D20116, doi:10.1029/2011JD016147.
- Angert, A., C. D. Cappa, and D. J. De Paolo (2004), Kinetic ^{17}O effects in the hydrologic cycle: Indirect evidence and implications, *Geochim. Cosmochim. Acta*, *68*(19), 3487–3495.
- Aristarain, A. J., J. Jouzel, and M. Pourchet (1986), Past Antarctic peninsula climate (1850–1980) deduced from an ice core isotope record, *Clim. Change*, *8*, 69–89.
- Armengaud, A., R. Koster, J. Jouzel, and P. Ciais (1998), Deuterium excess in Greenland snow: Analysis with simple and complex models, *J. Geophys. Res.*, *103*, 8947–8653.
- Baertschi, P. (1976), Absolute ^{18}O content of standard mean ocean water, *Earth Planet Sci. Lett.*, *31*, 341–344.
- Barkan, E., and B. Luz (2005), High precision measurements of $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ in H_2O , *Rapid Commun. Mass Spectrom.*, *19*, 3737–3742.
- Barkan, E., and B. Luz (2007), Diffusivity fractionations of $\text{H}_2^{16}\text{O}/\text{H}_2^{17}\text{O}$ and $\text{H}_2^{16}\text{O}/\text{H}_2^{18}\text{O}$ in air and their implications for isotope hydrology, *Rapid Commun. Mass Spectrom.*, *21*, 2999–3005.
- Barnes, C. J., and G. B. Allison (1983), The distribution of deuterium and ^{18}O in dry soils: 1. Theory, *J. Hydrol.*, *60*(1), 141–156.
- Barnes, C., and G. Allison (1988), Tracing of water movement in the unsaturated zone using stable isotopes of hydrogen and oxygen, *J. Hydrol.*, *100*, 143–176.
- Boyle, E. A. (1997), Cool tropical temperatures shift the global $\delta^{18}\text{O}$ -T relationship: An explanation for the ice core $\delta^{18}\text{O}$ borehole thermometry conflict?, *Geophys. Res. Lett.*, *24*, 273–276.
- Brutsaert, W. H. (1975), A theory for local evaporation (or heat transfer) from rough and smooth surfaces at ground level, *Water Resour. Res.*, *11*, 543–550.
- Charles, C., D. Rind, J. Jouzel, R. Koster, and R. Fairbanks (1994), Glacial interglacial changes in moisture sources for Greenland: influences on the ice core record of climate, *Science*, *263*, 508–511.

- Ciais, P., and J. Jouzel (1994), Deuterium and oxygen 18 in precipitation: An isotopic model including mixed cloud processes, *J. Geophys. Res.*, *99*, 16,793–16,803.
- Ciais, P., J. W. C. White, J. Jouzel, and J.-R. Petit (1995), The origin of present-day Antarctic precipitation from surface snow deuterium excess data, *J. Geophys. Res.*, *100*, 18,917–18,927.
- CLIMAP (1976), The surface of the ice-age Earth, *Science*, *191*, 1131–1137.
- Craig, H. (1961), Isotopic variations in meteoric waters, *Science*, *133*, 1702–1703.
- Craig, H., and L. I. Gordon (1965), Deuterium and oxygen 18 variations in the ocean and the marine atmosphere, in *Stables Isotopes in Oceanographic Studies and Paleotemperatures*, edited by E. Tongiorgi, pp. 9–130, CNR, Pisa, Italy.
- Cuffey, K. M., and F. Vimeux (2001), Covariation of carbon dioxide and temperature from the Vostok ice core after deuterium-excess correction, *Nature*, *421*, 523–527.
- Dansgaard, W. (1954), The ^{18}O abundance in fresh water, *Geochim. Cosmochim. Acta*, *6*, 241–260.
- Dansgaard, W. (1964), Stable isotopes in precipitation, *Tellus*, *16*, 436–468.
- Dansgaard, W., J. W. C. White, and S. J. Johnsen (1989), The abrupt termination of the Younger Dryas climate event, *Nature*, *339*, 532–534.
- Delaygue, G. (2000), Relationship between the oceanic surface and the isotopic content of Antarctic precipitation: Simulations for different climates, PhD thesis, Univ. of Aix-Marseille, France.
- Delaygue, G., V. Masson, J. Jouzel, R. D. Koster, and C. Healy (2000a), The origin of the Antarctic precipitation: A modelling approach, *Tellus*, *52*, 19–36.
- Delaygue, G., J. Jouzel, V. Masson, R. D. Koster, and E. Bard (2000b), Validity of the isotopic thermometer in central Antarctica: Limited impact of glacial precipitation seasonality and moisture origin, *Geophys. Res. Lett.*, *27*, 2677–2680.
- Delmotte, M., V. Masson, J. Jouzel, and V. Morgan (2000), A seasonal deuterium excess signal at Law Dome, coastal Eastern Antarctica: A southern ocean signature, *J. Geophys. Res.*, *105*, 7187–7197.
- Dirmeyer, P. A., and K. L. Brubaker (1999), Contrasting evaporative moisture sources during the drought of 1988 and the flood of 1993, *J. Geophys. Res.*, *104*, 19,383–19,397.
- Ducoudré, N., K. Laval, and A. Perrier (1993), SECHIBA, a new set of parameterizations of the hydrological exchanges at the land-atmosphere interface within the LMD atmospheric general circulation model, *J. Clim.*, *6*, 248–273.
- Epstein, S., and T. Mayeda (1953), Variation of ^{18}O content of waters from natural sources, *Geochim. Cosmochim. Acta*, *4*, 213–224.
- Gat, J. (1980), The isotopes of hydrogen and oxygen in precipitation, in *Handbook of Environmental Isotope Geochemistry*, vol. 1: *The terrestrial environment A*, edited by P. Fritz and J.-Ch. Fontes, vol. 1, pp. 22–46, Elsevier.
- Gat, J. R., and I. Carmi (1970), Evolution of the isotopic composition of atmospheric waters in the Mediterranean Sea area, *J. Geophys. Res.*, *75*, 3039–3048.
- Gat, J. R., and E. Matsui (1991), Atmospheric water-balance in the Amazon Basin—An isotopic evapotranspiration model, *J. Geophys. Res.*, *96*, 13,179–13,188, doi:10.1029/91JD00054.
- Gat, J. R., B. Klein, Y. Kushnir, W. Roether, H. Wernli, R. Yam, and A. Shemesh (2003), Isotope composition of air moisture over the Mediterranean Sea: An index of the air-sea interaction pattern, *Tellus, Ser. B*, 953–965.
- Gates, W. L. (1992), AMIP: The atmospheric model intercomparison project, *Bull. Am. Meteorol. Soc.*, *73*, 1962–1970.
- Gimeno, L., A. Drumond, R. Nieto, R. M. Trigo, and A. Stohl (2010), On the origin of continental precipitation, *Geophys. Res. Lett.*, *37*, L13804, doi:10.1029/2010GL043712.
- Gimeno, L., A. Stohl, R. M. Trigo, F. Domínguez, Y. L. Yoshimura, A. Drumond, A. M. Durán-Quesada, and R. Nieto (2012), Oceanic and terrestrial sources of continental precipitation, *Rev. Geophys.*, *50*, RG4003, doi:10.1029/2012RG000389.
- Gonfiantini, R. (1978), Standards for stable isotope measurements in natural compounds, *Nature*, *271*, 534–536.
- Guan, H., X. Zhang, G. Skrzypek, Z. Sun, and X. Xu (2013), Deuterium excess variations of rainfall events in a coastal area of South Australia and its relationship with synoptic weather systems and atmospheric moisture sources, *J. Geophys. Res. Atmos.*, *118*, 1123–1138, doi:10.1002/jgrd.50137.
- Hageman, R., G. Nief, and E. Roth (1970), Absolute isotopic scale for deuterium analysis of natural waters. Absolute D/H ratio for SMOW, *Tellus*, *2*, 712–715.
- Harmon, R. S., and H. P. Schwarcz (1981), Changes of ^2H and ^{18}O enrichment of meteoric water and Pleistocene glaciation, *Nature*, *290*, 125–128, doi:10.1038/290125a0.
- Helsen, M. M., R. S. W. van de Wal, M. R. van den Broeke, V. Masson-Delmotte, H. A. J. Meijer, M. P. Scheele, and M. Werner (2006), Modeling the isotopic composition of Antarctic snow using backward trajectories: Simulation of snow pit records, *J. Geophys. Res.*, *111*, D15109, doi:10.1029/2005JD006524.
- Helsen, M. M., R. S. W. van de Wal, M. R. van den Broeke, V. Masson-Delmotte, H. A. J. Meijer, M. P. Scheele, and M. Werner (2007), The isotopic composition of present-day Antarctic snow in a Lagrangian atmospheric simulation, *J. Clim.*, *20*, 739–756.
- Johnsen, S. J. (1977), Stable isotope homogenization of polar firn and ice, in *Proceedings of the Symposium on Isotopes and Impurities in Snow and Ice*, IUGG XVI General Assembly, Grenoble August/September 1975, IAHS-AISH Publ. 118, pp. 210–219.
- Johnsen, S. J., W. Dansgaard, and J. W. C. White (1989), The origin of Arctic precipitation under present and glacial conditions, *Tellus*, *41*, 452–468.
- Joussaume, S. J., R. Sadourny, and C. Vignal (1986), Origin of precipitating water in a numerical simulation of the July climate, *Ocean-Air Interact.*, *1*, 43–56.
- Jouzel, J. (2003) Water stable isotopes: Atmospheric composition and applications in ice core studies, in *Treatise of Geochemistry*, Vol. 4, *The Atmosphere*, edited by R. F. Keeling, H. D. Holland, and K. K. Turekian Exec, pp. 213–243, Pergamon, Oxford.
- Jouzel, J., and L. Merlivat (1984), Deuterium and oxygen 18 in precipitation: Modeling of the isotopic effects during snow formation, *J. Geophys. Res.*, *89*, 11,749–11,757.
- Jouzel, J., and R. Koster (1996), A reconsideration of the initial conditions used for stable water isotopes models, *J. Geophys. Res.*, *101*, 22,933–22,938.
- Jouzel, J., L. Merlivat, and C. Lorius (1982), Deuterium excess in an East Antarctic ice core suggests higher relative humidity at the oceanic surface during the last glacial maximum, *Nature*, *299*, 688–691.
- Jouzel, J., F. Vimeux, N. Caillon, G. Delaygue, G. Hoffmann, V. Masson, and F. Parrenin (2003), Magnitude of the isotope/temperature scaling for interpretation of central Antarctic ice cores, *J. Geophys. Res.*, *108*(D12), 4361, doi:10.1029/2002JD002677.
- Jouzel, J., M. Stiévenard, S. J. Johnsen, K. Fuhrer, A. Landais, V. Masson-Delmotte, A. E. Sveinbjörnsdóttir, F. Vimeux, and J. W. C. White (2007a), The GRIP deuterium-excess record, *Quat. Sci. Rev.*, *26*, 1–17.
- Jouzel, J., et al. (2007b), Orbital and millennial Antarctic climate variability over the past 800,000 years, *Science*, *317*(5839), 793–796, doi:10.1126/science.1141038.
- Kelley, M. (2003), Water tracers and the hydrologic cycle in a GCM, PhD thesis, Dep. of Earth and Environ. Sci., Columbia Univ., New York.
- Koster, R. D., J. Jouzel, R. Suozzo, G. Russell, W. S. Broecker, D. Rind, and P. Eagleson (1986), Global sources of local precipitations as determined by the NASA/GISS GCM, *Geophys. Res. Lett.*, *43*, 121–124.
- Koster, R. D., J. Jouzel, R. J. Suozzo, and G. L. Russell (1992), Origin of July Antarctic precipitation and its influence on deuterium content: A GCM analysis, *Clim. Dyn.*, *7*, 195–203.
- Krinner, G., N. Viovy, N. de Noblet-Ducoudre, J. Ogee, J. Polcher, P. Friedlingstein, P. Ciais, S. Sitch, and I. C. Prentice (2005), A dynamic global vegetation model for studies of the coupled atmosphere-biosphere system, *Global Biogeochem. Cycles*, *19*, GB1015, doi:10.1029/2003GB002199.
- Kurita, N. (2011), Origin of Arctic water vapor during the ice-growth season, *Geophys. Res. Lett.*, *38*, L02709, doi:10.1029/2010GL046064.
- Landais, A., E. Barkan, D. Yakir, and B. Luz (2006), The triple isotopic composition of oxygen in leaf water, *Geochim. Cosmochim. Acta*, *70*, 4105–4115.
- Landais, A., E. Barkan, and B. Luz (2008), The record of ^{18}O and ^{17}O -excess in ice from Vostok Antarctica during the last 150,000 years, *Geophys. Res. Lett.*, *35*, L02709, doi:10.1029/2007GL032096.
- Landais, A., H. C. Steen-Larsen, M. Guillevic, V. Masson-Delmotte, B. Vinther, and R. Winkler (2012), Triple isotopic composition of oxygen in surface snow and water vapor at NEEM (Greenland), *Geochim. Cosmochim. Acta*, *77*, 304–316.
- Lee, J. E., I. Fung, D. J. DePaolo, and B. OttoBliesner (2008), Water isotopes during the Last Glacial Maximum: New general circulation model calculations, *J. Geophys. Res.*, *113*, D19109, doi:10.1029/2008JD009859.

- Lewis, S. C., A. N. LeGrande, M. Kelley, and G. A. Schmidt (2010), Water vapour source impacts on oxygen isotope variability in tropical precipitation during Heinrich events, *Clim. Past*, 6, 325–343, doi:10.5194/cp-6-325-2010.
- Lewis, S. C., A. N. LeGrande, M. Kelley, and G. A. Schmidt (2013), Modeling insights into deuterium excess as an indicator of water vapor source conditions, *J. Geophys. Res.*, 118, 243–262, doi:10.1029/2012JD017804.
- Markle, B. R., N. A. N. Bertler, K. E. Sinclair, and S. B. Sneed (2012), Synoptic variability in the Ross Sea region, Antarctica, as seen from back-trajectory modeling and ice core analysis, *J. Geophys. Res.*, 117, D02113, doi:10.1029/2011JD016437.
- Masson-Delmotte, V., B. Stenni, and J. Jouzel (2004), Common millennial scale variability of Antarctic and southern ocean temperatures during the past 5000 years reconstructed from EPICA Dome C ice core, *Holocene*, 14, 145–151.
- Masson-Delmotte, V., J. Jouzel, A. Landais, M. Stiévenard, S. J. Johnsen, J. W. C. White, M. Werner, A. Sveinbjornsdottir, K. Fuhrer (2005a), GRIP deuterium excess reveals rapid and orbital-scale changes in Greenland moisture origin, *Science*, 309, 118–121.
- Masson-Delmotte, V., et al. (2005b), Holocene climatic changes in Greenland: Different deuterium excess signals at Greenland Ice Core Project (GRIP) and North GRIP, *J. Geophys. Res.*, 110, D14102, doi:10.1029/2004JD005575.
- Masson-Delmotte, V., et al. (2008), A review of Antarctic surface snow isotopic composition: Observations, atmospheric circulation, and isotopic modeling, *J. Clim.*, 21(13), 3359–3387, doi:10.1175/2007JCLI2139.1.
- Meijer, H., and W. J. Li (1998), The use of electrolysis for accurate dO-17 and dO-18 isotope measurements in water, *Isot. Environ. Health Studies*, 34(4), 349–369.
- Merlivat, L., and M. Coantic. (1975), Study of mass transfer at the air-water interface by an isotopic method, *J. Geophys. Res.*, 80, 3455–3464.
- Merlivat, L., and J. Jouzel (1979), Global climatic interpretation of the Deuterium-Oxygen 18 relationship for precipitation, *J. Geophys. Res.*, 84, 5029–5033.
- Miller, M. F. (2002), Isotopic fractionation and the quantification of ^{17}O anomalies in the oxygen three-isotope system: An appraisal and geochemical significance, *Geochim. Cosmochim. Acta*, 66, 1881–1889.
- Petit, J. R., J. W. C. White, N. W. Young, J. Jouzel, and Y. S. Korotkevich (1991), Deuterium excess in recent Antarctic snow, *J. Geophys. Res.*, 96, 5113–5122.
- Pfahl, S., and H. Wernli (2008), Air parcel trajectory analysis of stable isotopes in water vapor in the eastern Mediterranean, *J. Geophys. Res.*, 113, D20104, doi:10.1029/2008JD009839.
- Pfahl, S., and H. Sodemann (2013), What controls deuterium excess in global precipitation?, *Clim. Past Discuss.*, 9, 4745–4770, doi:10.5194/cpd-9-4745-2013.
- Rind, D. (1987), Components of the ice age circulation, *J. Geophys. Res.*, 92, 4241–4281, doi:10.1029/JD092iD04p04241.
- Rindsberger, M., M. Magaritz, I. Carmi, and D. Gilad (1983), The relation between air mass trajectories and the water isotope composition of rain in the Mediterranean Sea area, *Geophys. Res. Lett.*, 10, 43–46.
- Risi, C. (2009), Les isotopes stables de l'eau: Applications à l'étude du cycle de l'eau et des variations du climat, PhD thesis, Univ. Pierre & Marie Curie, France.
- Risi, C., S. Bony, F. Vimeux, and J. Jouzel (2010a), Water-stable isotopes in the LMDZ4 General Circulation Model: Model evaluation for present-day and past climates and applications to climatic interpretation of tropical isotopic records, *J. Geophys. Res.*, 115, D12118, doi:10.1029/2009JD013255.
- Risi, C., S. Bony, F. Vimeux, C. Frankenberg, D. Noone, and J. Worden (2010b), Understanding the Sahelian water budget through the isotopic composition of water vapor and precipitation, *J. Geophys. Res.*, 115, D24110, doi:10.1029/2010JD014690.
- Risi, C., A. Landais, R. Winkler, and F. Vimeux (2013a), Can we determine what controls the spatio-temporal distribution of d-excess and ^{17}O -excess in precipitation using the LMDZ general circulation model?, *Clim. Past*, 9, 2173, doi:10.5194/cp-9-2173-2013.
- Risi, C., D. Noone, C. Frankenberg, and J. Worden (2013b), The role of continental recycling in intra-seasonal variations of continental moisture as deduced from model simulations and water vapor isotopic measurements, *Water Resour. Res.*, doi:10.1002/wrcr.20312.
- Schlosser, E., H. Oerter, V. Masson-Delmotte, and C. Reijmer (2008), Atmospheric influence on the deuterium excess signal in polar firn: Implications for ice-core interpretation, *J. Glaciol.*, 54(184), 117–124, doi:10.3189/002214308784408991.
- Schmidt, G. A., G. Hoffmann, D. T. Shindell, and Y. Hu (2005), Modelling atmospheric stable water isotopes and the potential for constraining cloud processes and stratosphere-troposphere water exchange, *J. Geophys. Res.*, 110, D21314, doi:10.1029/2005JD005790.
- Sime, L. C., G. J. Marshall, R. Mulvaney, and E. R. Thomas (2009), Interpreting temperature information from ice cores along the Antarctic Peninsula: ERA40 analysis, *Geophys. Res. Lett.*, 36, L18801, doi:10.1029/2009GL038902.
- Sodemann, H., and A. Stohl (2009), Asymmetries in the moisture origin of Antarctic precipitation, *Geophys. Res. Lett.*, 36, L22803, doi:10.1029/2009GL040242.
- Sodemann, H., V. Masson-Delmotte, C. Schwierz, B. M. Vinther, and H. Wernli (2008), Interannual variability of Greenland winter precipitation sources: 2. Effects of North Atlantic Oscillation variability on stable isotopes in precipitation, *J. Geophys. Res.*, 113, D12111, doi:10.1029/2007JD009416.
- Sonntag, C., et al. (1978) Palaeoclimatic information from deuterium and oxygen-18 in carbon-14 dated north Saharian groundwaters; groundwater formation in the past, paper presented at the International Symposium on Isotope Hydrology, Neuherberg, Germany, IAEA Proceedings Series, pp. 569–581.
- Stenni, B., V. Masson, S. J. Johnsen, J. Jouzel, A. Longinelli, E. Monnin, R. Roethlisberger, and E. Selmo (2001), An oceanic cold reversal during the last deglaciation, *Science*, 293, 2074–2077.
- Steen-Larsen, H. C., et al. (2011), Understanding the climatic signal in the water stable isotope records from the NEEM shallow firn/ice cores in northwest Greenland, *J. Geophys. Res.*, 116, D06108, doi:10.1029/2010JD014311.
- Steen-Larsen, H. C., et al. (2013), Continuous monitoring of summer surface water vapour isotopic composition above the Greenland Ice Sheet, *Atmos. Chem. Phys.*, 13, 4815–4828, doi:10.5194/acp-13-4815-2013.
- Stenni, B., et al. (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(1–2), 183–195.
- Stenni, B., et al. (2010), The deuterium excess records of EPICA Dome C and Dronning Maud Land ice cores (East Antarctica), *Quat. Sci. Rev.*, 29(1–2), 146–159.
- Stohl, A., and P. James (2004), A Lagrangian analysis of the atmospheric branch of the global water cycle: 1. Method description, validation, and demonstration for the August 2002 flooding in Central Europe, *J. Hydrometeorol.*, 5, 656–678.
- Stohl, A., and P. James (2005), A Lagrangian analysis of the atmospheric branch of the global water cycle. Part II: Moisture transports between Earth's ocean basins and river catchments, *J. Hydrometeorol.*, 6(6), 961.
- Tian, L., T. Yao, K. MacClune, J. W. C. White, A. Schilla, B. Vaughn, R. Vachon, and K. Ichiyanagi (2007), Stable isotopic variations in west China: A consideration of moisture sources, *J. Geophys. Res.*, 112, D10112, doi:10.1029/2006JD007718.
- Uemura, R., N. Yoshida, N. Kurita, M. Nakawo, and O. Watanabe (2004), An observation-based method for reconstructing ocean surface changes using a 340,000-year deuterium excess record from the Dome Fuji ice core, Antarctica, *Geophys. Res. Lett.*, 31, L13216, doi:10.1029/2004GL019954.
- Uemura, R., Y. Matsui, K. Yoshimura, H. Motoyama, and N. Yoshida (2008), Evidence of deuterium excess in water vapour as an indicator of ocean surface conditions, *J. Geophys. Res.*, 113, D19114, doi:10.1029/2008JD010209.
- Uemura, R., E. Barkan, O. Abe, and B. Luz (2010), Triple isotope composition of oxygen in atmospheric water vapor, *Geophys. Res. Lett.*, 37, L04402, doi:10.1029/2009GL041960.
- Uemura, R., V. Masson-Delmotte, J. Jouzel, A. Landais, H. Motoyama, and B. Stenni (2012), Ranges of moisture-source temperature estimated from Antarctic ice cores stable isotope records over glacial-interglacial cycles, *Clim. Past*, 8, 1109–1125, doi:10.5194/cp-8-1109-2012.
- Vachon, R. W., J. M. Welker, J. W. C. White, and B. H. Vaughn (2010), Monthly precipitation isoscapes ($\delta^{18}\text{O}$) of the United States: Connections with surface temperatures, moisture source conditions, and air mass trajectories, *J. Geophys. Res.*, 115, D21126, doi:10.1029/2010JD014105.
- Villacis, M., F. Vimeux, and J.-D. Taupin (2008), Analysis of the climate controls on the isotopic composition of precipitation ($\delta^{18}\text{O}$) at Nuevo Rocafuerte (74,5°W; 0,9°S; 250 m) Ecuador, *C. R. Geosci.*, 340, 1–9, doi:10.1016/j.crte.2007.11.003.
- Vimeux, F., V. Masson, J. Jouzel, J. R. Petit, E. J. Steig, M. Stiévenard, R. Vaikmae, and J. W. C. White (2001a), Holocene hydrological cycle

- changes in Southern Hemisphere documented in East Antarctic deuterium excess records, *Clim. Dyn.*, *17*, 503–513.
- Vimeux, F., V. Masson, G. Delaygue, J. Jouzel, M. Stiévenard, and J. R. Petit (2001b), A 420,000 year deuterium-excess record from East Antarctica: Information on past changes in the origin of precipitation at Vostok, *J. Geophys. Res.*, *106*, 31,863–31,873.
- Vimeux, F., K. Cuffey, and J. Jouzel (2002), New insights into Southern Hemisphere temperature changes from Vostok ice cores using deuterium excess correction, *Earth Planet. Sci. Lett.*, *203*, 829–843.
- Vimeux, F., R. Gallaire, S. Bony, G. Hoffmann, J. Chiang, and R. Fuenes (2005), What are the climate controls on isotopic composition (δD) of precipitation in Zongo Valley (Bolivia)? Implications for the Illimani ice core interpretation, *Earth Planet. Sci. Lett.*, *240*, 205–220.
- Vimeux, F., G. Tremoy, C. Risis, and R. Gallaire (2011), A strong control of the South American SeeSaw on the intra-seasonal variability of the isotopic composition of precipitation in the Bolivian Andes, *Earth Planet. Sci. Lett.*, *307*, 47–58.
- Washburn, E., and E. Smith (1934), The isotopic fractionation of water by physiological processes, *Science*, *79*, 188–189.
- Werner, M., M. Heimann, and G. Hoffmann (2001), Isotopic composition and origin of polar precipitation in present and glacial climate simulations, *Tellus B*, *53*, 53–71.
- Werner, M., P. M. Langebroek, T. Carlsen, M. Herold, and G. Lohmann (2011), Stable water isotopes in the ECHAM5 general circulation model: Toward high-resolution isotope modeling on a global scale, *J. Geophys. Res.*, *116*, D15109, doi:10.1029/2011JD015681.
- Winkler, R., A. Landais, H. Sodemann, L. Dümbgen, F. Prié, V. Masson-Delmotte, B. Stenni, and J. Jouzel (2012), Deglaciation records of ^{17}O -excess in East Antarctica: Reliable reconstruction of oceanic relative humidity from coastal sites, *Clim. Past*, *8*, 1–16, doi:10.5194/cp-8-1-2012.
- Yamanaka, T., J. Shimada, and K. Miyaoka (2002), Footprint analysis using event-based isotope data for identifying source area of precipitated water, *J. Geophys. Res.*, *107*(D22), 4624, doi:10.1029/2001JD001187.
- Yoshimura, K., M. Kanamitsu, D. Noone, and T. Oki (2008), Historical isotope simulation using reanalysis atmospheric data, *J. Geophys. Res.*, *113*, D19108, doi:10.1029/2008JD010074.