

Supplementary material

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1 Calibrations

In this section we detail the data treatment of two calibrations: the instrumental humidity-isotope response and the estimation of the uncertainties related to the drift correction. δ^* stands either for δD or $\delta^{18}O$, and we will use the notation introduced in Sec. 3.4 of the paper.

5 1.1 Instrumental humidity-isotope response

We present in Fig. S1 the data from a humidity-isotope response calibration performed during ~ 24 hours on 2013/12/06 following the protocol of Steen-Larsen et al. (2013). A moving average has been calculated for δ^* vs q every 5 ppmv in a range of 10 ppmv. The fit obtained with the moving average is used as a correction function, called Γ_* in the paper. This function Γ_* depends on q , but
10 also on the time, because the humidity-isotope response slightly varies from day to day. During our monitoring period we had to repeat the calibration procedure on five different dates as this correction is time dependent. Figure S2 shows the different humidity-isotope responses $\Gamma_*^{\text{day}}(q)$ associated with the day of the calibration. We set $q_0 = 1000$ ppmv with $\Gamma_*^{\text{day}}(q_0) = 0$ as a humidity reference level. We need to get a humidity correction Γ_*^{day} for each day of our monitoring period to be able to
15 correct the data. We therefore calculate a linear interpolation of the humidity corrections from two consecutive calibrations. For example, if we want to get the humidity correction on 2013/12/25, we calculate for a given q an interpolation between $\Gamma_*^{2013/12/14}(q)$ and $\Gamma_*^{2013/12/28}(q)$, with 2013/12/14 and 2013/12/28 the closest calibration dates before and after 2013/12/25. The uncertainty associated with $\Gamma_*^{2013/12/25}(q)$ is calculated as $d\Gamma_*^{2013/12/25}(q) = |\Gamma_*^{2013/12/14}(q) - \Gamma_*^{2013/12/28}(q)|$.
20 Finally we have for every day of our monitoring period a humidity correction function Γ_* with an associated uncertainty $d\Gamma_*$.

1.2 Uncertainties related to the drift correction

During our monitoring period, an automatic calibration was performed every 111 minutes for 12 minutes using the working standard. We first apply the humidity correction function Γ_* to the data from this calibration. We then multiply them with α_* in order to convert them on the VSMOW scale. After these corrections, we calculate mean values over 11.5 min, the missing 30 seconds being discarded at the beginning of each calibration to remove the memory effect. Then we calculate a linear interpolation between two successive mean values and define the function $f^*(t)$ as the juxtaposition of all the linear interpolations for δ^* vs t . The drift correction is defined as $\mu_*(t) = \delta_{\text{standard}}^* - f^*(t)$, with $\delta_{\text{standard}}^*$ the isotopic value of the working standard for the isotope δ^* (we assume no fractionation during the calibration from the liquid state to the vapor state).

In order to estimate the uncertainty associated with the drift correction μ_* , we have performed a ~ 24 h calibration on 2014/02/01 using the working standard, keeping a stable humidity of 1800 ± 150 ppmv. The data from this calibration are shown in Fig. S3. We use the red dots to calculate the mean values over 11.5 minutes (as previously described), leading to the construction of $f^*(t)$ labeled "standard drift interpolation" in Fig. S3. From the black dots, we calculate mean values every 30 minutes, and construct $f_{\text{ref}}^*(t)$ (labeled "reference drift") in a similar way than $f^*(t)$, but using more mean values. We have estimated the uncertainty $d\mu_*$ associated with the drift correction μ_* as the standard deviation of $(f^* - f_{\text{ref}}^*)(t)$.

2 Air-snow exchanges

We describe in the two following sections the fundamental equations leading to the equations (2), (3), (4) and (5) of the paper. We will use all the notations introduced in Fig. 5 of the paper and use the following relationships in the demonstrations:

$$m_t^s = m_0^v + m_0^s - m_t^v \quad (1)$$

$$m_0^s = \rho_s h_0 S \quad (2)$$

$$m_t^v = q_t \rho_d H_0 S \quad (3)$$

$$\delta^* = \left(\frac{R_*}{R_{\text{VSMOW}}} - 1 \right) \times 1000 \quad (4)$$

The first equation is the mass conservation of water molecules inside the closed system {air reservoir + snow reservoir}. The second equation is the amount of water molecules in the snow reservoir

at the beginning of the cooling phase ($t = 0$). The third equation comes from $m_t^v = q_t \rho_d H_t S$, knowing that $\forall t, \zeta_t \ll H_0$. The fourth equation is a simple definition of δ^* in ‰. S is the area of the box,
55 but it will not appear in the final equations.

2.0.1 Cooling phase

From t to $t + 1$, the loss of water vapor mass in the air reservoir during the cooling phase is $(m_t^v - m_{t+1}^v)$. This quantity is assumed to condensate on the snow surface because the box model is closed. The condensate is formed in equilibrium with the vapor at time t , its isotopic ratio is therefore
60 $\alpha_t R_t^v$ with α_t the fractionation coefficient with respect to ice, and R_t^v the isotopic ratio of the vapor. We assume from t to $t + 1$ an immediate removal of the condensate from the air reservoir and an immediate mixing of the condensate with the snow reservoir.

We simply write the mass conservation of the heavy isotopes in the air reservoir:

$$m_{t+1}^v R_{t+1}^v = m_t^v R_t^v - \alpha_t R_t^v (m_t^v - m_{t+1}^v)$$

65 And the mass conservation of the heavy isotopes in the snow reservoir:

$$m_{t+1}^s R_{t+1}^s = m_t^s R_t^s + \alpha_t R_t^v (m_t^v - m_{t+1}^v)$$

With these elements, getting equations (2) and (3) of the paper is straightforward.

The study of the supersaturated case is described in Jouzel and Merlivat (1984). When the relative humidity with respect to ice is higher than 1, we need take the possible kinetic effects into account.

70 We replace α_t by α_t^{RMK} with:

$$\alpha_t^{\text{RMK}} = \alpha_t \times \frac{\text{RH}}{\alpha_t \times \frac{1}{D'/D} \times (\text{RH} - 1) + 1}$$

RMK is for Rayleigh Model taking the Kinetic effects into accounts. The parameter D'/D is given in Jouzel and Merlivat (1984) equal to 0.9723 for $\delta^{18}\text{O}$, and to 0.9755 for δD . We set in our paper the relative humidity RH with respect to ice equal to 1.1 in the supersaturated case.

75 2.0.2 Warming phase

The reasoning is the same for the warming phase, except that the air reservoir is receiving mass from the snow reservoir. We therefore have the equations:

$$m_{t+1}^v R_{t+1}^v = m_t^v R_t^v + R_t^{\text{sub}} (m_{t+1}^v - m_t^v)$$

$$80 \quad m_{t+1}^s R_{t+1}^s = m_t^s R_t^s - R_t^{\text{sub}} (m_{t+1}^v - m_t^v)$$

The different hypotheses concerning the isotopic ratio R_t^{sub} of the sublimate are detailed in the section 4.3.2 of the paper. These two equations lead to equations (4) and (5) in the paper.

References

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- Steen-Larsen, H. C., Johnsen, S. J., Masson-Delmotte, V., Stenni, B., Risi, C., Sodemann, H., Balslev-Clausen, D., Blunier, T., Dahl-Jensen, D., Ellehøj, M., et al.: Continuous monitoring of summer surface water vapor isotopic composition above the Greenland Ice Sheet, *Atmospheric Chemistry and Physics*, 13, 4815–4828, 2013.

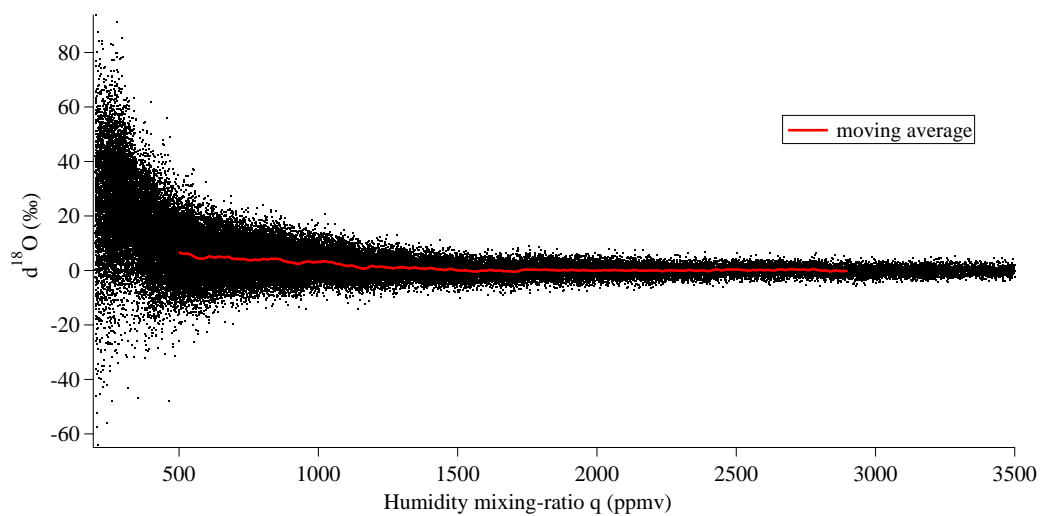


Figure 1. Humidity isotope response calibration performed during ~ 24 h on 2013/12/06. The moving average has been calculated every 5 ppmv over a range of 10 ppmv.

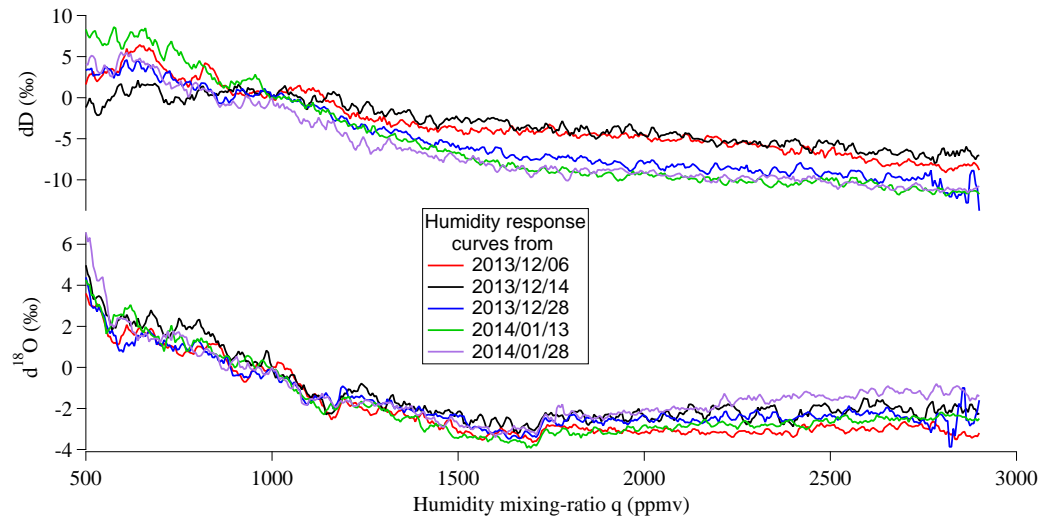


Figure 2. Moving averages calculated from 5 different humidity isotope response calibrations. The humidity $q_0 = 1000$ ppmv is chosen as a reference level.

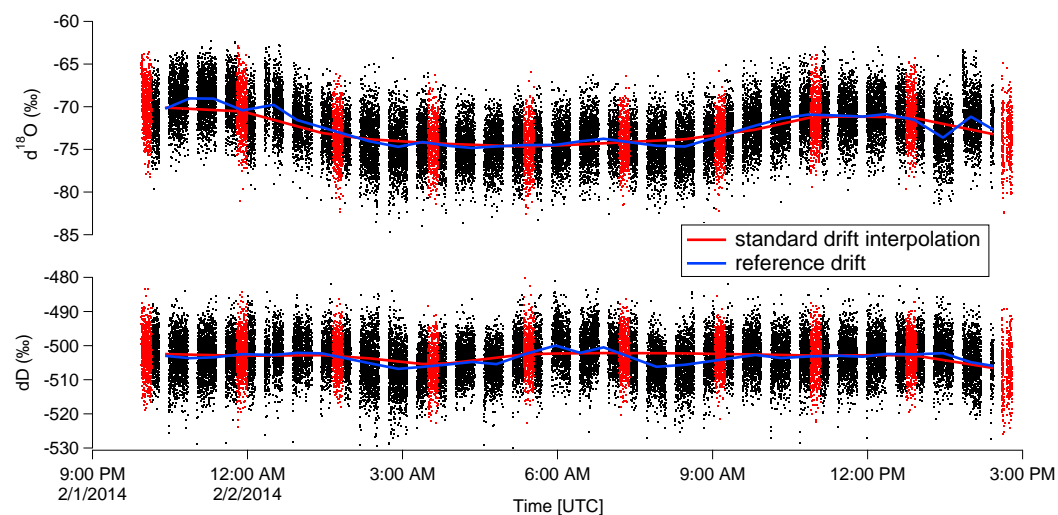


Figure 3. Calibration performed on 2014/02/01 during ~ 24 h at a stable humidity of 1800 ± 150 ppmv in order to quantify the uncertainty associated with the drift correction (labelled "standard drift correction")