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Evidence of isotopic fractionation during vapor exchange between the atmosphere and the snow surface in Greenland

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Key points:

Evidence of isotopic fractionation during vapor exchange between the snow surface and atmosphere

Model simulations suggest diurnal variation in the snow surface isotopic composition

Propose an enhanced effective isotopic exchange between the surface of the snow grain and its interior.

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Abstract

Several recent studies from both Greenland and Antarctica have reported significant changes in the water isotopic composition of near-surface snow between precipitation events. These changes have been linked to isotopic exchange with atmospheric water vapor and sublimation-induced fractionation, but the processes are poorly constrained by observations. Understanding and quantifying these processes are crucial to both the interpretation of ice core climate proxies and the formulation of isotope enabled general circulation models. Here, we present continuous measurements of the water isotopic composition in surface snow and atmospheric vapor together with near-surface atmospheric turbulence and snow-air latent and sensible heat fluxes, obtained at the East Greenland Ice-Core Project drilling site in summer 2016. For two 4 day-long time periods, significant diurnal variations in atmospheric water isotopologues are observed. A model is developed to explore the impact of this variability on the surface snow isotopic composition. Our model suggests that the snow isotopic composition in the upper sub-centimeter of the snow exhibits a diurnal variation with amplitudes in $\delta^{18}\text{O}$ and δD of $\sim 2.5\text{‰}$ and $\sim 13\text{‰}$, respectively. As comparison, such changes correspond to 10-20% of the magnitude of seasonal changes in interior Greenland snow pack isotopes and of the change across a glacial-interglacial transition. Importantly, our observation and model results suggest, that sublimation-induced fractionation needs to be included in simulations of vapor-ice transitions on diurnal timescales during summer cloud-free conditions in northeast Greenland.

1 Introduction

Climate reconstructions derived from both Antarctic and Greenland ice cores constitute a cornerstone in paleo-climate science (e.g. Masson-Delmotte et al., 2015; Jouzel et al., 2007; Johnsen et al., 2001; Vimeux et al., 1999), extending to 129 thousand years (kyr) before present (BP; before 1950) in Greenland (North Greenland Ice-Core Project (NorthGRIP) Members, 2004; NEEM community members, 2013), and to 800 kyr BP in Antarctica (EPICA community members, 2006; Jouzel et al. 2007). Interpretations of past climate variability using ice core water isotopes were determined using precipitation-weighted isotopic composition and observations of mean annual temperature either from in-situ observations (e.g. Dansgaard, 1964; Jouzel et al., 1997; Johnsen et al., 2001), borehole temperature reconstruction (e.g. Vinther et al., 2010), or from use of distillation models (e.g. Johnsen et al., 1989; Uemura et al.,

2012; Masson-Delmotte et al., 2005). These previous studies commonly assume that post-depositional processes do not influence the mean annual isotopic signature.

Recent advances in laser spectroscopy allow for field measurements of water isotopologue exchange between the snow surface and the atmosphere overlying the ice sheets. Steen-Larsen et al. (2014) reported concurrent isotopic variations in near-surface snow and atmospheric vapor at the NEEM ice core camp, northwest Greenland. Over several precipitation-free periods (3-7 days), the surface (top 5 mm) snow $\delta^{18}\text{O}$ varied by up to 6‰, attributable to vapor-exchange between the surface snow and atmospheric vapor. Ritter et al. (2016) deployed a laser spectrometer for measuring water vapor isotopes at Kohnen Station, East Antarctica. They showed that both surface snow and near-surface water vapor exhibit significant concurrent diurnal variations in water isotopic composition.

In a study by Casado et al. (2018), the authors combine a comprehensive dataset consisting of several years of precipitation collection from Dome C, Antarctica with $\delta^{18}\text{O}$ records from snow pits. A clear discrepancy between the average precipitation isotopic composition and the average snow pit isotopic composition was observed. This demonstrated that the climate signal initially stored in the precipitation is not necessarily stored in the surface snow and subsequently buried, suggesting that the water isotopic composition of ice cores is not solely governed by precipitation. These studies highlight that isotopic exchange between atmospheric vapor and surface snow must be considered to accurately interpret observed variations in snow isotopic composition.

These observations of post-depositional change challenge the current parameterization of snow-air isotope exchange in isotope-enabled global circulation models (isoGCMs) which are based on the assumption that sublimation does not change the surface snow isotopic composition (Werner et al., 2011; Risi et al., 2010; Wong et al., 2017). To link simulations using isoGCMs with ice core isotope records, it is therefore important to understand and quantify the impact of post-depositional processes.

Here, we examine processes that control diurnal variations in snow and vapor isotopic composition in Greenland as a case study for the processes at play during sublimation

and condensation. We pursue the hypothesis that snow and vapor isotopic composition is controlled through surface fluxes of water by both sublimation and deposition. To test our hypothesis we combine measurements of the isotopic composition of surface snow and near-surface atmospheric water vapor with estimates of atmospheric boundary layer turbulence. To quantify the impact of post-depositional processes we advance upon previous studies and use a 1-dimensional model to simulate our observed vertical profiles of atmospheric water vapor mixing ratio and isotopic composition above the snow surface, and the accompanying change in the isotopic composition of the surface snow. Our aim is to show that fluxes of water vapor between the snow surface and the atmosphere have the potential to change the snow isotopic composition. We acknowledge here that other relevant processes controlling the snow-air isotope exchange are neglected in this study. Development of a fully coupled atmosphere-snow boundary layer model with enabled isotopes is beyond the scope of the present study, but is an important direction for future research.

The paper is organized as follows. In section 2, we describe our observational methodology, reviewing the measurement site, characteristic meteorology, and instrumental configuration, along with the data acquisition, calibration, and the time series of observed variations in near-surface atmospheric humidity and water isotopologues. In section 3, we describe our near-surface atmospheric model. The model results are discussed in section 4, followed by conclusions and recommendations for further work in section 5.

2 Site Description and Methods

2.1 EastGRIP site location and meteorological characteristics

Sampling and measurements were conducted as part of the international deep ice core drilling project EastGRIP from April to August 2016. The campsite was located in the northeast Greenland ice stream (75.63°N, 35.99°W; 2700 m above sea level).

Meteorological observations were obtained from the Program for the Monitoring of the Greenland Ice Sheet (PROMICE) (Ahlstrøm et al., 2008) using an automatic weather station (AWS), which was installed ~500 m southeast of the EastGRIP camp in May 2016. The

summer 2016 (June-July-August; JJA) meteorological observations reported by the AWS are summarized in Table 1. The prevailing wind at the camp was westerly (Figure 1D). The surface air temperature (~2.5 meter above the surface) varied between -35.0°C and -2.1°C, with a mean of -15.8°C.

During the measurement period (beginning of May to beginning of August), six precipitation events, corresponding to a total of 9 cm of snowfall, were recorded. The accumulation was estimated from measurements of snow heights along an array of 200 small bamboo sticks (1 cm diameter) deployed at the beginning of the season.

Table 1 Summer 2016 (JJA) minimum, average, and maximum meteorological values reported by the PROMICE automatic weather station at EastGRIP.

	Minimum	Average	Maximum
Ambient air pressure	708 hPa	727 hPa	740 hPa
Wind speed	0.01 ms ⁻¹	4.7 ms ⁻¹	12.4 ms ⁻¹
Air temperature	-35.0 °C	-15.8 °C	-2.1 °C
Relative humidity w.r.t. ice	54.6%	92.7%	113.7 %

2.2 Cavity Ring-Down Spectrometry measurements on water vapour and surface snow

During the 2016 field season water stable isotopologues (¹H₂¹⁶O, ¹H²H¹⁶O, and ¹H₂¹⁸O) in near-surface vapor were measured continuously from June 14th to August 4th. The vapor measurement site (Figure 1) was located to the southwest (i.e. upwind) of camp at the edge of the clean air sector. Vapor samples were collected from 4 inlets mounted on a tower at initial heights of 0.52 m, 1.06 m, 2.07 m, and 7.20 m above the snow surface (Figure 1). For the rest of this study, these inlet heights are approximated as $z = 0.5$ m, 1 m, 2 m and 7 m, respectively. No significant amount of accumulation occurred around the tower during the water vapor isotope measurement campaign. The tower consisted of an open aluminum frame with a triangular footprint of ~20 cm wide sides. The air was sampled through the inlets using a 10 L/min KNF pump (N811 KN.18) and measured using a Picarro L-2130 cavity ring-down spectrometer (CRDS). The CRDS was housed in a small heated tent (Figure 1), erected ~10 m downwind from the tower. The full sampling protocol is described in Steen-Larsen et al. (2013), including regulation of both the vapor intake and analysis apparatus, which was done using solenoid valves measuring 15 minutes at each level.

Isotopic composition is reported using the notation $\delta^* = (R^*/R^*_{\text{VSMOW}} - 1) \cdot 1000\text{‰}$, where R^* is the concentration ratio of the heavier isotopic species (with * denoting either $^1\text{H}^2\text{H}^{16}\text{O}$ or $^1\text{H}_2^{18}\text{O}$) to the light abundant species ($^1\text{H}_2^{16}\text{O}$) of water (Craig, 1961). R^*_{VSMOW} is the relative composition of the VSMOW (Vienna Standard Mean Ocean Water) standard. δ^* represents the abundance of either $^1\text{H}^2\text{H}^{16}\text{O}$ or $^1\text{H}_2^{18}\text{O}$. The second order parameter deuterium excess is defined by Dansgaard (1964) as $dxs = \delta\text{D} - 8\delta^{18}\text{O}$.

Calibration of the CRDS data was performed following the protocol outlined in Steen-Larsen et al. (2013). Humidity-isotope calibrations were conducted 4 times throughout the field season to correct for humidity-induced bias. VSMOW-SLAP calibrations were carried out 6 times during the field campaign using three standards ($\delta^{18}\text{O}$: 0.4‰, -33.56‰, -54.05‰; δD : 2.8‰, -257.6‰, -424.1‰). The uncertainties are assumed to be equivalent to the uncertainties estimated by Steen-Larsen et al. (2014), which are for $\delta^{18}\text{O}$ and δD are 0.23‰ and 1.4‰, respectively. Propagation of errors gives an uncertainty on the vapor dxs of 2.3‰. The humidity mixing ratio measured by the spectrometer was calibrated using the humidity measurements from the nearby AWS.

Throughout the field season, snow samples were routinely collected for isotopic analysis. Along a 1 km marked transect, 26 samples of the upper 1 cm of snow were collected on a daily basis. These samples have been analyzed on a Picarro L-2130-i CRDS and calibrated to the VSMOW-SLAP scale using 4 standards ($\delta^{18}\text{O}$: -19.8‰, -33.8‰, -42.39‰, -50.12‰; δD : -152.93‰, -266.7‰, -341.24‰, -392.0‰) at the Alfred-Wegener-Institute, Bremerhaven. In this study, only the average value and standard deviation of these 26 samples for each day are shown. These values will be referred to as the observed snow isotopic composition with standard deviation σ_{snow} .

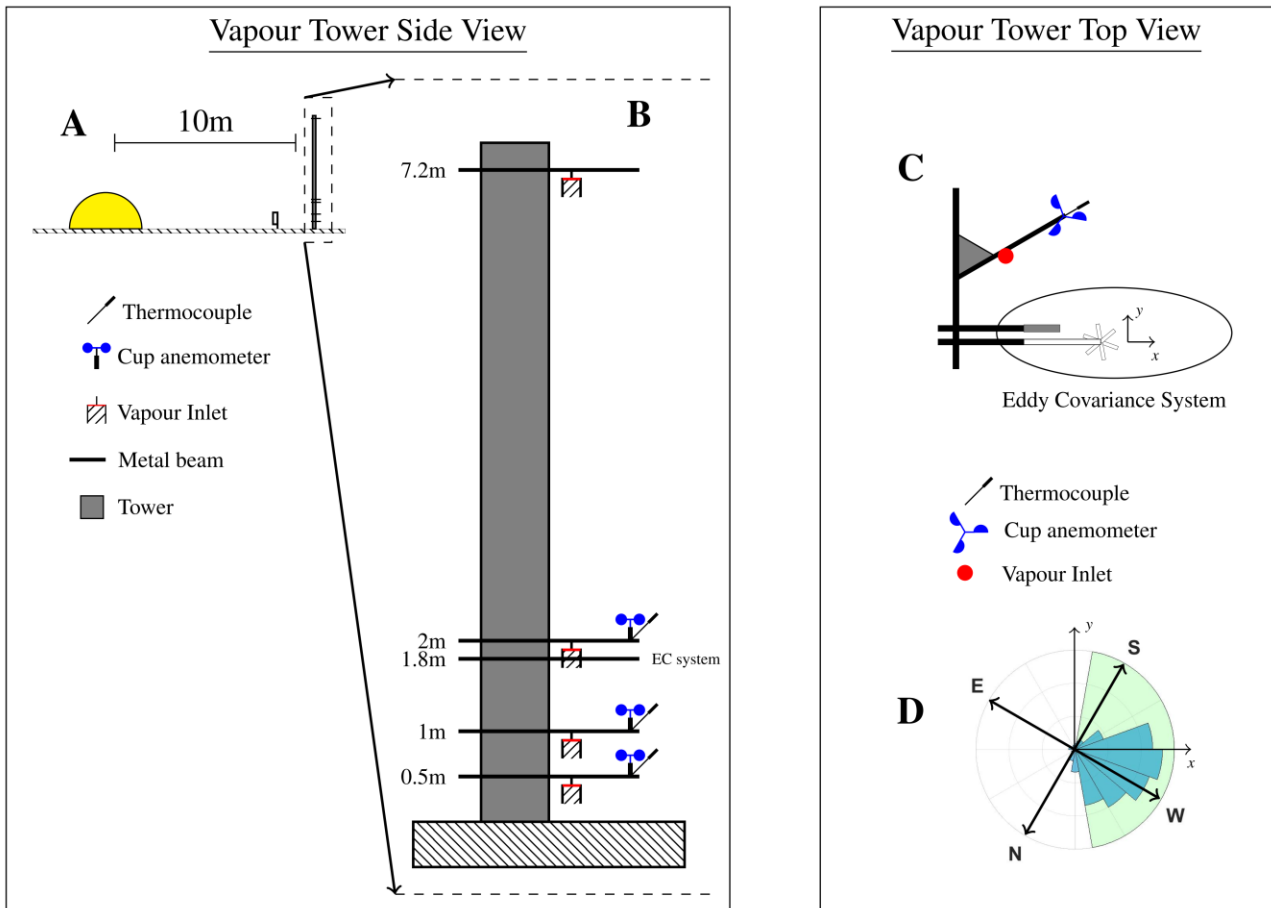


Figure 1 Schematic overview of the field site and instrument configuration. Side view: (A) Position of the tent, CR3000 micrologger, and vapor tower. The prevailing wind is approximately from right to left (see D). Vertical discretization of the model domain representation the lower boundary in contact with the snow surface. (B) Approximate position of vapor inlets, cup anemometers, fine wire thermocouples and the eddy covariance system. Top view: (C) Relative position of vapor inlets, cup anemometers, thermocouples, and eddy covariance instruments on each beam. A KH20 hygrometer and CSAT3 ultrasonic anemometer comprise the eddy covariance system. Note that instruments are not drawn to scale. The $x - y$ coordinate system is the internal coordinate system of the ultrasonic anemometer. (D) The wind rose observed by the ultrasonic anemometer (10 min averages) where directions are given both with respect to the orientation of the anemometer ($x - y$ coordinate system) and the approximate north-south compass (N-S, E-W). The green wedge indicates the angles within 80° of the x -axis of the CSAT3.

2.3 Atmospheric Eddy Covariance Measurements

To estimate the atmospheric flux of water vapor at EastGRIP, an eddy covariance system (hereafter EC) was mounted on the tower, 1.8 m above the snow surface (Figure 1). The EC system consisted of a fast response krypton hygrometer (KH20) and a highly sensitive omnidirectional ultrasonic anemometer (CSAT3), both produced by Campbell Scientific Inc. With this setup, we calculated the turbulent fluxes of momentum, heat, and moisture between the surface and atmosphere (Box and Steffen, 2001; Cullen et al., 2007; Forrer and Rotach, 1997). Stably stratified conditions prevail at EastGRIP, strong and persistent katabatic winds are expected to maintain shear-driven instabilities and reduce intermittency, allowing reliable calculation of turbulent fluxes from the eddy covariance statistics.

The raw data was sampled at 20 Hz and relayed to a micro logger (Campbell Scientific Inc. CR3000) placed approximately 1.5 m downwind from the tower (Figure 1). For the turbulent flux calculation, raw covariances were averaged over 10 min intervals. Three cup-anemometers and fine-wire thermocouples were also mounted at heights 0.54 m, 1.05 m and 2.07 m above the snow surface. These instruments have been included in Figure 1 for completeness, but the associated time series are not discussed in this paper.

2.3.1 Calibration

We correct for errors in our turbulent flux measurements following Cullen et al. (2007). Outliers are excluded iteratively using criteria adopted from Hojstrup (1993). Errors induced by wind deflection around nearby structures have been corrected by excluding all measurements taken at times when the wind is directed from the camp towards the mounted sensors. By only retaining winds with an incident angle of $\pm 80^\circ$ relative to the x-axis of the anemometer (Figure 1D), all potentially corrupted data have been discarded.

Errors associated with the anemometer tilt (Hyson et al., 1977; Tanner and Thurtell, 1969) and frequency response loss (Moore, 1986; Moncrieff et al., 1997) have been corrected. Tilt corrections are required to prevent cross-contamination of velocities by small misalignment of the sensors. On average, tilt corrections change the sensible and latent heat flux by 0.4% and -0.3%, respectively. Spectral corrections are required to account for bandpass filtering due to the separation and limited frequency response of the instruments. The CSAT3 and KH20 sensors were mounted 20 cm apart. The internal path lengths of the CSAT3 and the KH20 sensors were set to 11.5 cm and 1 cm, respectively. Average flux increases of 0.8%

and 13% for the sensible and latent heat flux have been obtained, respectively.

2.4 Observations of water vapour

We focus now on two periods with distinct diurnal cycles in the atmospheric state: June 25th to 29th (DOY 177-181) and July 21st to 25th (DOY 203-207). These periods were chosen based on the criteria that we wanted at least four clear diurnal cycles with minimal change in mean synoptic conditions and mostly clear sky conditions all the time. Diurnal cycles are observed on other days, but were not chosen as they did not fulfill the requirements. During the June period, weak atmospheric instability is observed from 12:00-18:00 UTC, whereas neutral stability is observed during these hours in the July period. Measurement of the eddy momentum and heat flux by the EC system allows for the calculation of the friction velocity u^* and the Monin-Obukhov length, L , where L is proportional to the height at which buoyancy forcing dominates mechanical production of turbulence. The non-dimensional stability parameter is defined as $\zeta = z/L$, where z is the height above the surface. Timeseries of ζ and u^* are shown in Figure 2.

Although both June and July periods exhibit similar variation in atmospheric humidity, there are notable differences in observed vapor isotopic composition. Values of dxs throughout the June period show diurnal variations, but are relatively constant during the July period.

Furthermore, time-averaged dxs is larger in the earlier period. For reference, we note that in the June period, the time-average $\delta^{18}\text{O}$ and δD is -43.5‰ and -317.5‰ , respectively, compared to July values of -39.6‰ and -290.5‰ . The supplementary material S2 gives an overview of the water isotope observations from all 4 inlets for both the June and July period.

We shortly discuss relationships between the Eddy Covariance, humidity, and isotope observations. Typically, high (positive) stability is associated with a stable stratified lower atmosphere, where the snow surface is colder than the air above. This condition gives rise to a negative (downward) latent heat flux in the form of deposition or condensation causing the atmosphere to become less humid and more isotopic depleted. Further, in stable conditions little vertical mixing would occur and we would expect a gradient in both humidity and isotopic composition in the vapour (Supplementary S2), where the vapour closest to the surface is more depleted and less humid than the air above. Opposite, unstable or near-neutral

conditions result in an upward transport, positive heat fluxes and increasing humidity, and a uniform humidity and isotopic composition of the lower atmosphere (Supplementary S2). We therefore expect, as also observed, a phase shift between the latent heat flux and the isotope observations since a positive latent heat flux infers sublimation from the surface, and the maximum humidity will occur at the time where the latent heat flux shifts from positive to negative.

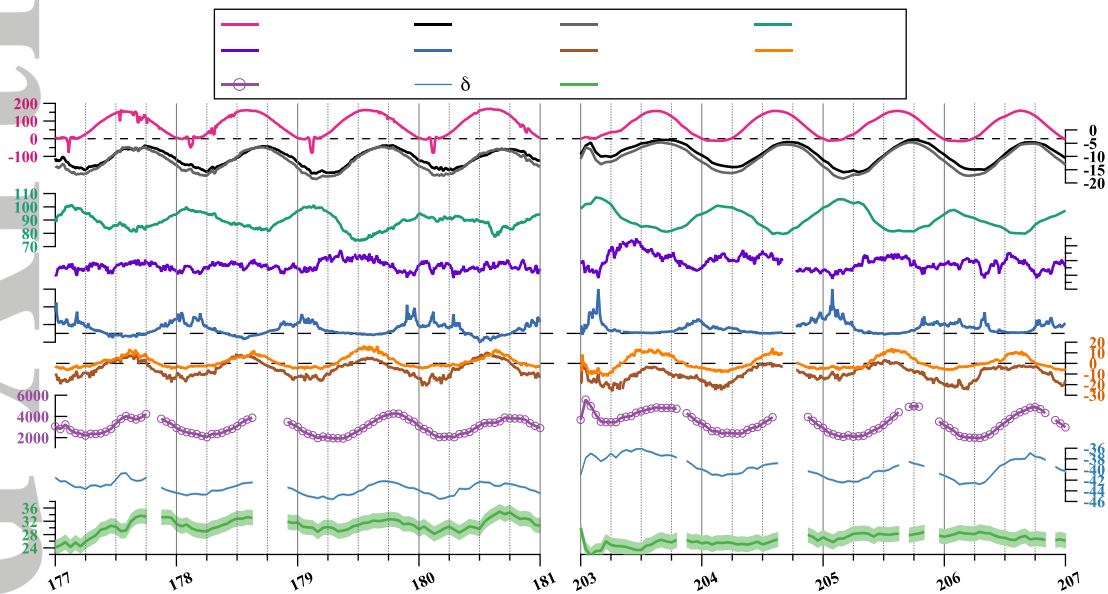


Figure 2 Left panel: June period (DOY 177-181, June 25th to 29th). **Right panel:** July period (DOY 203-207, July 21st to 25th). **From above:** PROMICE automatic weather station (AWS) observations of net in-coming shortwave (SW) radiation, air and snow surface temperature, and relative humidity with respect to ice. Eddy Covariance observations of friction velocity, atmospheric stability (z/L) evaluated at a height of 1.8 m, and turbulent sensible and latent heat flux. Specific humidity, $\delta^{18}O$, and dxs measured by the CRDS at 2 meter above the snow surface. The shading on both $\delta^{18}O$ and dxs indicates 1 measurement uncertainty.

3 Model

In this section, we construct a model to explore the observed variation of humidity, $q(z,t)$, and the vapor isotopic composition of $\delta^{18}O(z,t)$ and $\delta D(z,t)$, with respect to time (t) and

displacement from the surface (z). We aim to simulate the two periods with distinct dxs variations presented in Section 2.4. The periods will be referred to as the June and July period, respectively. Both periods were cloud-free and characterized by repeating diurnal cycles of latent and sensible fluxes of heat, near-surface temperature, and humidity (Figure 2). The aim is to model the snow surface isotopic composition consistent with our humidity and isotope observations for these two cases.

The model consists of three boxes representing (1) the immediate snow surface, (2) a viscous sub-layer (VSL), and (3) the near-surface atmospheric boundary layer (ABL) (Craig and Gordon, 1965).

The VSL has thickness Δz and is characterized by mixing dominated by molecular diffusion. At all times, it is assumed that the lower boundary of the VSL is saturated with respect to ice at the snow surface temperature T_s .

The model domain simulating the near-surface ABL extends from the top of the VSL to the height $z = H$ and is characterized by turbulent mixing and no isotopic fractionation. This mixing rate is assumed to be the same for all isotopologues of water, in contrast to the molecular diffusion in the VSL, which is modeled with an isotopologue-dependent molecular diffusion. We set $H = 7.2$ m, corresponding to the top inlet on the tower.

3.1 Numerical Formulation

We model the humidity and vapor isotopic composition with a diffusion equation

$$\frac{\partial R^* q}{\partial t} = \frac{\partial}{\partial z} \left(\kappa^*(z, t) \frac{\partial R^* q}{\partial z} \right) \quad (1)$$

where R^* is the ratio of the concentration of the rare isotopic species to the abundant $^1\text{H}_2^{16}\text{O}$ and q is the mixing ratio. κ^* is the isotopologue-specific diffusion coefficient. To provide higher resolution near the surface where we expect the largest vertical gradients of $q(z)$, $\delta^{18}\text{O}(z)$, and $\delta\text{D}(z)$, we introduce a vertically stretched coordinate system (Figure 1). The height z of a grid point given by $z(s) = H [\exp(a s) - 1] / [\exp(a) - 1]$, where s is a normalized coordinate used to transform a linearly spaced coordinate system into the stretched

coordinate. We set $a = 8.2$, generating 200 grid nodes that allow for reasonable computation times. Stable solutions to Eq. (1) are achieved using a Crank-Nicholson discretization scheme, with a time step of 2 min. Our discretization is independent of the VSL thickness Δz , which allows us to explore solutions to Eq. (1) under a broad range of Δz , without compromising numerical stability or increasing the computational cost of the model.

3.2 Diffusion Coefficient

We use the formulation of eddy diffusivity for momentum and heat inspired by Brost and Wyngaard (1978), and assume that the eddy diffusivity for sensible heat equals that of latent heat (Box and Steffen, 2001; Moore, 1986). In the near-surface ABL, we parameterize the turbulent diffusion coefficient, $K_H(z,t)$, as:

$$K_H(z, t) = \frac{ku^* z' (1 - \frac{z'}{h})^{1.5}}{\phi_m(\frac{z}{L}) \phi_H(\frac{z}{L})} \quad (2)$$

Here, z is the height above the snow surface and $z' = z - \Delta z$ is the height over the VSL. The distinction between z' and z is set so that $K_H(z = \Delta z) = 0$. u_* the friction velocity and the von Karmán constant $k = 0.4$. We use the non-dimensional functions ϕ_m and ϕ_H for momentum and heat (Högström, 1988) for both stable and unstable stratifications. h is the total height of the ABL and we assume $h > H$. In this work, we use h as a free parameter to minimize the misfit between the observations and the model. The time dependency of K_H is contained in u_* and L , which are both derived directly from the eddy covariance measurements. The full diffusion coefficient is:

$$\kappa^*(z, t) = \begin{cases} D^*(T_s, p) & \text{if } 0 \leq z \leq \Delta z \\ D^{16O}(T_s, p) + K_H(z, t) & \text{if } \Delta z < z \leq H \end{cases} \quad (3)$$

where $D^*(T_s, p)$ is the isotopologue specific molecular diffusion, T_s is the snow surface temperature, and p is the ambient atmospheric pressure. We use the molecular diffusivity of water vapor in air given by Hall and Pruppacher (1976). The isotopologue specific diffusivities in the VSL are given by the ratios $D^{18O}/D^{16O} = 0.9723$ and $D^D/D^{16O} = 0.9755$

(Merlivat, 1978).

3.3 Modelling Humidity

When modelling the humidity we solve Eq. 1, with $R^* = R^{16O} = 1$. At the snow-VSL interface we force the model with the AWS observed radiative snow surface temperature and assume saturation with respect to ice. The saturation vapor pressure over ice is calculated following Flatau et al. (1992). The upper boundary of the model is forced with the observed humidity-mixing ratio obtained from the CRDS measurements. The model is initialized with a constant humidity throughout the box, prescribed as the saturation humidity at the snow surface temperature. We use a spin-up of 1 day. This means that to model for example the June period (26th - 29th June) we use one-day integration forced by CRDS, EC, and AWS data from June 25th as spin-up.

3.4 Modelling isotopic composition of water vapor

We solved Eq. 1 for $R^{18O}q$ and R^Dq , and initialized the simulations with uniform isotopic composition. The initialization values based on observational means were $\delta^{18O} = -45\text{‰}$ and $\delta D = -320\text{‰}$. Similar to the humidity simulations, a 1-day spin-up is used. We force the upper boundary at $z = H$ with the observed isotopic composition, $R^{18O}q$ and R^Dq . We do not have any measurements of the vapor isotopic composition at $z = 0$. Instead we assume that the vapor isotopic composition at the snow-vapor interface varies diurnally (See Figure 2) following:

$$\delta^*(z = 0, t) = A^* + B^* \sin\left(\frac{2\pi t}{T_{day}} + C^*\right) \quad (4)$$

where $T_{day} = 24$ hours, A^* is the mean isotopic composition, B^* is the amplitude and C^* is the phase offset, for each isotopologue. A^* , B^* , and C^* are unknown model-parameters for each isotopologue.

We use a least squares optimization approach to minimize the total model-data misfit. The model parameters we seek to optimize are A^* , B^* and C^* in Eq. (4), along with the VSL thickness, Δz , and the ABL height, h . To compute the isotopologue misfit, the modeled isotopic composition is linearly interpolated onto the height of the 3 inlets on the tower at $z =$

[0.56, 1.06, 2.07] m.

We have computed best fit values of A^* , B^* and C^* , referred to as A^*_{best} , B^*_{best} and C^*_{best} , respectively, for 3 different boundary layer heights $h = [25, 75, 150]$ m and VSL thicknesses in the range $0.0005\text{m} \leq \Delta z \leq 0.1\text{m}$. Values for A^* and B^* have been run with a resolution of 0.1‰ and 0.5‰ for $\delta^{18}\text{O}$ and δD , and the phase offset, C^* with a resolution of 30 minutes. No *a priori* constraints have been placed on the values of A^* and B^* .

4 Results & Discussion

Figure 3 shows values of A^*_{best} , B^*_{best} and C^*_{best} , as a function of the VSL thickness Δz , and boundary layer height, h . In general, we find that the value of C^*_{best} for $\delta^{18}\text{O}$ and δD is nearly independent of Δz and h during both the June and July period. A^*_{best} and B^*_{best} are almost independent of h , but vary approximately linearly with Δz . A positive linear relation between B^*_{best} and Δz is expected since the influence of the bottom boundary condition is more attenuated for a thicker VSL. For the rest of this study, we will only consider results from Eq. (4) using the optimized values of the three model coefficients A^*_{best} , B^*_{best} , and C^*_{best} (Figure 3).

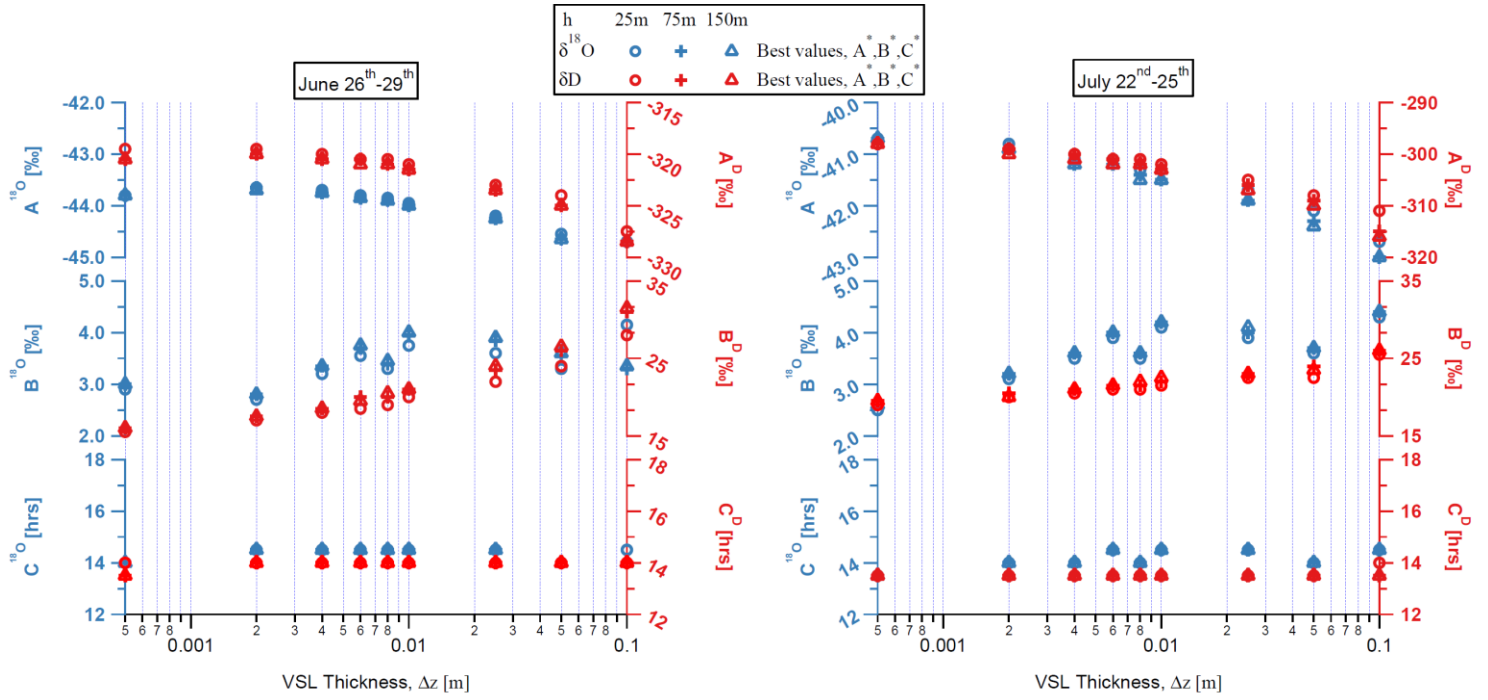


Figure 3 Values of the coefficients A^* , B^* and C^* in Eq. (4) for different combinations of VSL thickness (Δz , x -axis) and ABL height (h , symbols - see key), shown for both (blue) $\delta^{18}O$ and (red) δD producing the best fit to the observations. **Left:** June period. **Right:** July period.

4.1 The June Period

The model-data misfits, calculated as described in section 3.4, of $\delta^{18}O$, δD and specific humidity, q , as a function of Δz are shown in Figure 4. The model-data misfit of q is shown at each of the 3 observed heights $z = [0.5 \text{ m}, 1 \text{ m}, 2 \text{ m}]$. For the investigated range of Δz and h , the model-data misfit in q is consistently smaller for the lowest level ($z = 0.5 \text{ m}$). This misfit is strongly dependent on the choice of the VSL thickness, Δz , and weakly dependent on the ABL height, h . The optimal choice of Δz , depends on the height above the surface; the minimum misfit at heights $z = [0.5, 1, 2] \text{ m}$ are found for a VSL thicknesses of $\Delta z \sim [0.008, 0.006, 0.03] \text{ m}$. At heights $z = [0.5, 1, 2] \text{ m}$ the optimal combination of Δz and h has a [50%, 25%, 25%] reduction in model-data misfit, relative to the worst possible combination of Δz and h used in this study.

Ideally, minimization of model-data misfits at the 3 levels should suggest the same

optimal values of Δz and h . We find that the modeled humidity is slightly phase shifted relative to the observations at $z = 2$ m on DOY 179. Furthermore, observed humidity at $z = 1$ m on DOY 180 exhibits more noise relative to DOY 178 and 179, which cannot be reproduced by the model. As a result, larger model-data misfits are found at the $z = [1, 2]$ m levels, relative to the $z = 0.5$ m level (Supplementary S3, Figures S7, S8, S9).

Despite these issues, our idealized model reproduces a significant fraction of the observed variability. Specifically, we are able to simulate 90-95 % of the observed variance in q (i.e. modeled q variations are within 1 measurement uncertainty of the observations), by assuming a VSL thickness in the range $0.006 \text{ m} < \Delta z < 0.01 \text{ m}$, independent of the ABL height.

The model-data misfit in $\delta^{18}\text{O}$ is maximized for a VSL thickness of $\Delta z = 0.006 \text{ m}$ and minimized for thicknesses in the range $0.05 \text{ m} < \Delta z < 0.1 \text{ m}$. The model-data misfit in δD is minimized for a VSL thickness in the range $0.004 \text{ m} < \Delta z < 0.008 \text{ m}$. For both $\delta^{18}\text{O}$ and δD , the optimal choice of Δz depends on the assumed ABL height, h . We find that the total model-data misfit for $\delta^{18}\text{O}$ and δD can be reduced by 9% and 3% given the choice of Δz and h , respectively.

We select $\Delta z = 0.008 \text{ m}$ and $h = 25 \text{ m}$ to minimize the total model-data misfit for the June period. The values of A^*_{best} , B^*_{best} , and C^*_{best} for the June period are shown in Table 2. See Supplementary S3 for a comparison between model and observations with these settings.

4.2 The July Period

We now focus on optimization of the model for the July period (DOY 204 to 207). Both humidity and the isotopologues dependence of model-data misfit on the VSL thickness Δz , and ABL height, h , are shown in Figure 5.

We find that the humidity model-data misfit is minimized for $0.025 \text{ m} < \Delta z < 0.05 \text{ m}$; as mentioned above, the optimal choice depends on the height above the surface. However, in contrast to the June period, we find that the worst model-data misfit in

July is obtained for the lowest level ($z = 0.5$ m). (Supplementary S3, Figures S10, S11, S12).

We observe trends for the total model-data misfit for $\delta^{18}\text{O}$ and δD that are similar to those during the June period. Surprisingly, we note that the misfits for the two isotopes behave independently of the fit to the overall humidity, i.e. that the minimum of the humidity is not aligned with the minimum in the total 2-norm of δD . The humidity misfit is also more drastically reduced due to the choice of Δz compared to the isotope misfits. Therefore, the best overall fit to the observations is obtained by settings $\Delta z = 0.025$ m and $h = 25$ m. The values of A^*_{best} , B^*_{best} , and C^*_{best} using these settings are shown in Table 2. We refer to Supplementary S3 for a comparison between model and observations with these settings.

panel: humidity misfit for each individual level; the misfit at the 0.5 m level (purple) is consistently smaller than that at the 1 m (black) and 2 m (green) levels. **Mid panel:** total $\delta^{18}\text{O}$ model-data misfit (blue). **Bottom panel:** total model-data misfit for δD (red).

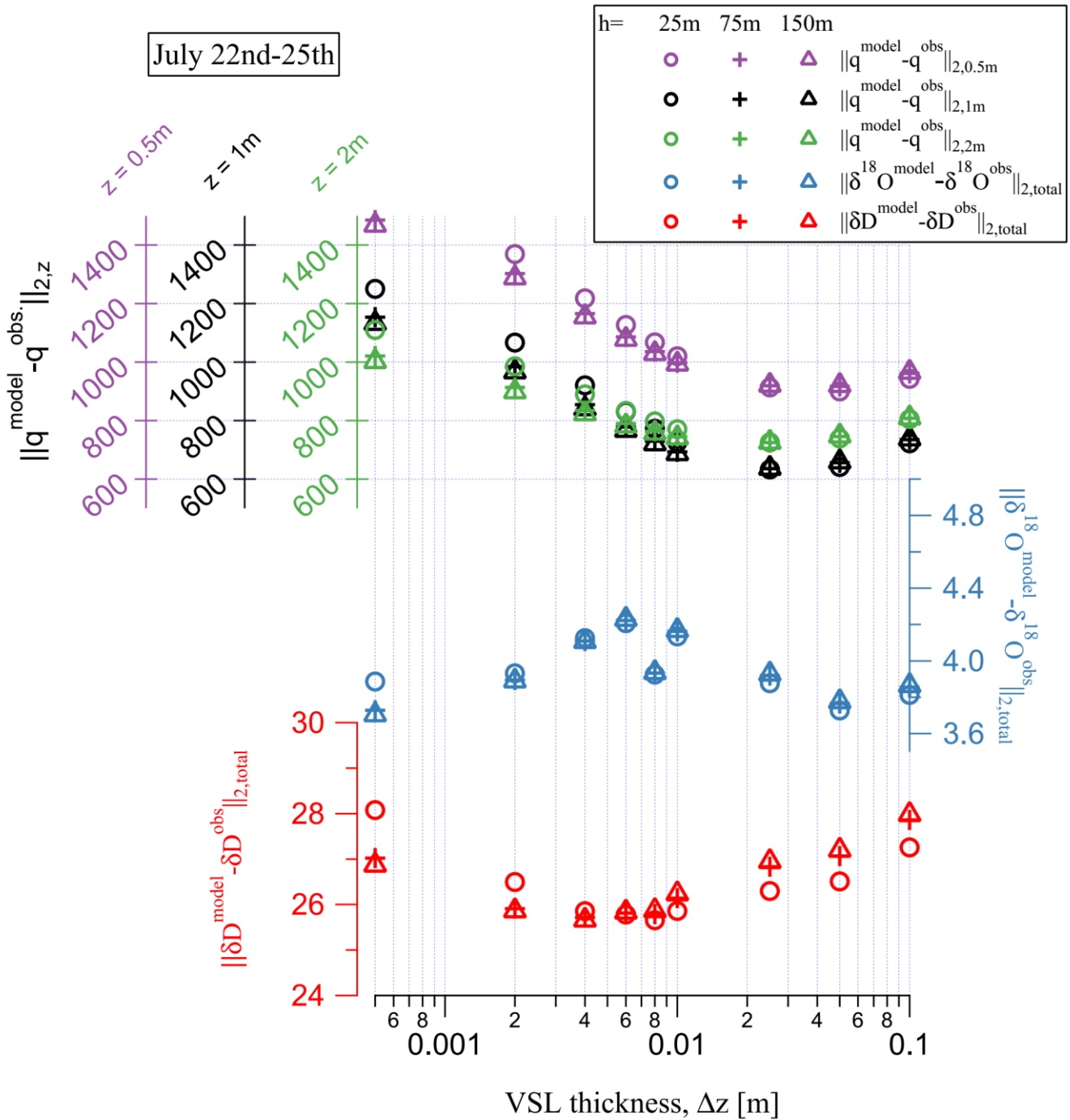


Figure 5 July period model-data misfit dependency on the thickness of the viscous sub-layer Δz for 3 different values of h : 25 m (circles), 75 m (+), and 150 m (triangles). **Top panel:** humidity misfit for each individual level; the misfit at the 0.5 m level (purple) is consistently smaller than that at the 1 m (black) and 2 m (green) levels. **Mid panel:** total $\delta^{18}\text{O}$ model-data misfit (blue). **Bottom panel:** total model-data misfit for δD (red).

		June 26-29			July 22-25		
		A[‰]	B[‰]	C[hrs]	A[‰]	B[‰]	C[hrs]
Vapor	$\delta^{18}O$	-43.9	3.3(1.7, 4.6)	14.5	-41.7	3.9(2.4, 4.6)	14.5
	δD	-320.5	19.0(10, 27.5)	14.0	-305.0	22.5(13.5, -)	13.5
	dxs	31	-8	-	28	-11	-

Table 2 Best-fit values for A^* , B^* , and C^* for the June and July period. To achieve the overall best fit to both humidity and isotopic composition measurements, we find $\Delta z = 0.008m$ and $h = 25m$ for the June period, and $\Delta z = 0.025m$ and $h = 25m$ for the July period. The 95% confidence bound on B^* is given in the parenthesis, an upper limit on B^D for the July period has not been determined (see Appendix).

4.3 Snow Isotopic Composition

The results in the previous sections allow us to estimate the diurnal changes in the snow isotopic composition during the June and July periods, consistent with the water vapor isotope observations. We assume equilibrium fractionation at the interface between the snow surface and the VSL. Using the optimized parameters A^*_{best} , B^*_{best} , C^*_{best} (Table 2), we compute the snow isotopic composition using the fractionation coefficients α for ice-vapor fractionation from Ellehoj et al. (2013) and the observed snow surface temperature. We note that using fractionation values from Majoube (1971) or Merlivat and Nief (1967) does not change our conclusions. We have computed the average and maximum amplitude of the snow isotopic composition, and have propagated the 95% confidence limit of the vapor amplitudes into snow amplitudes. The model is compared with the observed snow isotopic composition at three times during both the June and July periods (Figure 6).

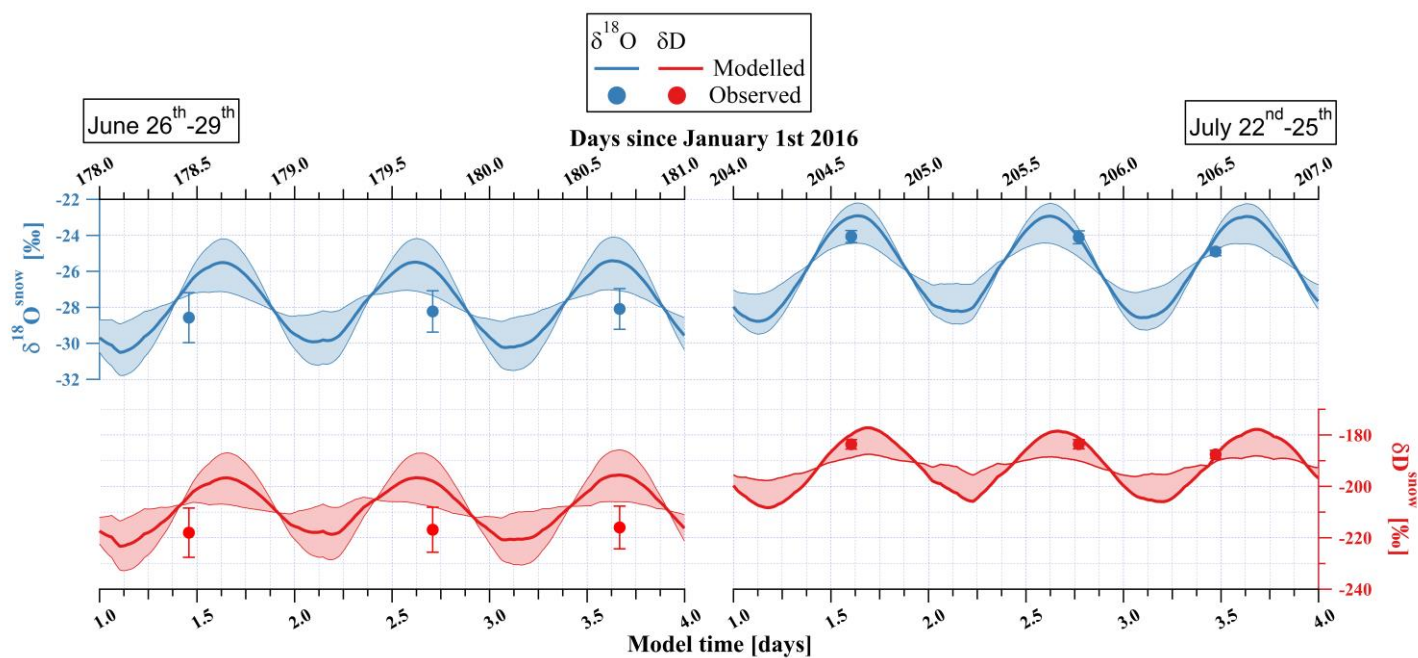


Figure 6. Snow isotopic composition using the ice-vapor fractionation coefficient from Ellehøj et al. (2013), assuming equilibrium fractionation in the viscous sub-layer. **Left:** June period. **Right:** July period. For each period, three observations of snow isotopic composition are also shown. The standard deviation (σ_{SNOW}) on the mean observed snow isotopic composition is comparable to the marker size for the July period.

In Figure 6, we observe that the top 1 cm of the snow surface isotope measurements and the modeled snow isotopes are consistent with each other under the assumption of isotopic fractionation at the interface, but due to the low temporal sampling frequency of the snow samples they are not directly comparable. Furthermore, it is important to note that it is still unresolved to which depth the atmospheric water vapor is in contact with the top of the snow pack. To verify or reject the hypothesis that the snow surface is in isotopic equilibrium with the vapor at the snow-air interface, the surface snow would have to be sampled in higher vertical and temporal resolution (millimeter and hourly, respectively). However, it is possible to model the depth to which the snow should be in isotopic equilibrium with the vapor.

In Table 3, we have estimated the depth of the snow surface that remains in equilibrium with the vapor at the lower boundary of the VSL, using the principle of

conservation of isotopic composition and assuming fractionation. We do this using EC measurements of the latent heat flux, the fractionation coefficients given by Ellehoj et al. (2013), and the constants given in Table 3. The required depth of the snow surface, which is in equilibrium with the vapor at the lower boundary of the VSL interphase, is computed for both the June and July period using the amplitudes and the confidence interval given in Table 2. As a result of these calculations we observe that within the uncertainty range of our tuned parameters, the snow depth of the layer in equilibrium with the vapor will be in the sub-millimeter to centimeter range (Table 3).

In conclusion, our model simulates that during summer cloud-free conditions at EastGRIP, the snow isotopic composition exhibits diurnal variations with an amplitude of around 2.5 ‰ and 13 ‰ for $\delta^{18}\text{O}$ and δD , respectively. Such variations are significant as they are on the order of 10-20% of seasonal variations measured in snow pack isotopes (Shuman et al., 1998; Steen-Larsen et al., 2011). Similarly do the estimated diurnal changes in the snow isotopes also correspond to 10-20% of glacial-interglacial transitions in Greenland (e.g. Johnsen et al., 2001). It is possible that these large diurnal variations in isotopic composition may be limited to the upper few millimeters of snow. Further work to model vapor diffusion within the snow pack could help determine the maximum depth at which the snow is influenced by these processes. Validation of our model results will require carefully conducted snow sampling in future field experiments.

Table 3: Top table: Values used for estimating snow surface thickness in equilibrium with the vapor in the viscous sub-layer. Bottom table: Estimates of the snow thickness at which the snow is in equilibrium with the vapor above the surface. The 95% confidence bounds are giving in the parenthesis.

	Symbol	Value
Latent heat of sublimation at 0 °C	λ	2838 kJ kg ⁻¹
Snow density	ρ_s	150 kg m ⁻³
Snow surface temperature	T_s	-11.5°C
Average day positive latent heat flux (June/July)	$L_E > 0$	6.5/6.7 W m ⁻²
Average day negative latent heat flux (June/July)	$L_E < 0$	-2.5/-3.8 W m ⁻²
Initial snow surface isotopic composition	$\delta^{18}\text{O}$	-30‰

Initial snow surface isotopic composition		δD	-240‰
$L_E > 0$	$\delta^{18}O$	2.5(7.1, 1.8) mm	2.3 (4.5, 1.9) mm
	δD	3.2(14.4, 1.9) mm	2.0 (9.9, -) mm
$L_E < 0$	$\delta^{18}O$	0.7 (2.5, 0.4) mm	0.9 (2.2, 0.7) mm
	δD	1.0 (5.3, 0.5) mm	1.2 (5.2, -) mm

We suggest that the simulated and observed snow isotopic compositions are evidence of fractionation during the diurnal vapor to ice and ice to vapor phase transitions. For the June period, this conclusion is based on the observation that the snow samples are consistent with the average value of the modeled snow isotopic composition within $1\sigma_{snow}$ for both isotopic species. This agreement is independent of the specific choice of fractionation coefficients from the available range published in the literature. For the July period, we observe an agreement within $1\sigma_{snow}$ and the 95% confidence bound on the modeled snow isotopic composition. We conclude that accounting for isotopic fractionation is important in modeling snow-atmosphere isotopic exchange. This implies that the snow isotopic composition can change while the snow is subjected to exchange with the atmosphere.

Up until this point we have not considered how the model performs in terms of dxs . In summary, given that we use the optimized values for A^* , B^* , and C^* , we find that we are able to simulate the dxs such that on average 95% of the modeled dxs is within one standard deviation of the observed values. However, the modeled dxs limits the maximum deviation of $B^{18}O$ from B^D . For example, by selecting the upper bound of the confidence limit on δD and the lower bound on the confidence limit of $\delta^{18}O$, we find that we no longer simulate the dxs within 95% confidence. This implies that an optimization of the parameters A^* and B^* with respect to dxs will result in a decrease of the confidence limits given in Table 1. Since a decrease in the confidence bounds on B^* does not undermine our results we find that another optimization of the

parameters with respect to dxs is unnecessary. Nonetheless, it is important to note that we find that the modeled vapor at the snow-VSL interface have a diurnal cycle in the dxs for both the June and July period (Table 2). For both periods we find that the dxs is in anti-phase with the δD and $\delta^{18}O$, even though there is no diurnal cycle in the atmospheric vapor for the July period. This is a result of the presences of the VSL, where the difference in molecular diffusivities determines how the dxs attenuates with displacement from the surface.

We now compare our results to existing studies. Ritter et al. (2016) find evidence in their snow samples of a diurnal cycle with amplitude $\sim 0.2\text{‰}$ and $\sim 1.5\text{‰}$ for $\delta^{18}O$ and δD , respectively. This amplitude is smaller than our modeled amplitude, which in part can be explained by both lower temperatures and lower specific humidity, since the observations of Ritter et al. (2016) are conducted at Kohnen Station, Antarctica. To verify this, we have conducted sensitivity studies (not shown) and found that a 15-20% reduction in snow isotope amplitude is achieved for a cooling of 10 K, consistent with summer conditions at Kohnen Station. However, the most important factor is probably related to the difficulties of sampling the exact top of the snow pack layer. Steen-Larsen et al. (2014) present two summer seasons of snow samples collected from the top 0.5 cm. Their morning and evening samples indicate a diurnal cycle with maximum amplitudes of 0.6‰ for $\delta^{18}O$.

Isotopes have recently been implemented in the complex snowpack model CROCUS (Touzeau et al., 2018). The authors propose, similar to Ebner et al. (2017), that a snow grain has an inner and outer isotopic composition, which is similar upon snowfall, but changes independently as the snow grain undergoes post-depositional processes. We propose that throughout a single day, the outer snow grain undergoes substantial changes in both volume and isotopic composition, whereas the inner snow grain isotopic composition stays constant. This can partly explain the difference between the modeled and observed change observed in this work, since a snow sample would be biased towards inner grain isotopic composition, and thus the observed diurnal variability in the surface snow isotopic composition would be damped.

It is unclear how this conclusion is compatible with Pinzer et al. (2012), who used controlled lab experiments with X-ray tomography to show that an average snow crystal has a lifetime of 2-3 days, with a daily mass turnover of up to 60%. Further studies are needed to address the interplay between changes in the snow isotopic composition caused by snow metamorphism and equilibration of the outer snow grain with the near-surface atmospheric water vapor.

5 Conclusions

We have presented near-continuous, high-precision measurements of water isotopic composition in atmospheric vapor, as well as eddy covariance measurements from two periods of stable diurnal cycles, taken at the East Greenland Ice Core Project camp during summer 2016. We observe substantial changes in the isotopic composition of the near-surface atmosphere on diurnal timescales, which prompted an investigation as to whether these high frequency isotopic variations are also present in the surface snow. We focus on simulating two distinct cloud free periods from the 2016 field season, spanning three days each. Although both periods exhibit similar variation in atmospheric humidity, there are notable differences in observed vapor isotopic compositions.

We have developed a numerical model to simulate changes in humidity and water vapor isotopic composition along a vertical profile extending from the snow surface up into the near-surface atmosphere. With this model, we are able to compute the snow isotopic composition and quantify the amplitude of snow isotope variability across diurnal cycles. We find that the uppermost millimeters of the snow surface in northeast Greenland exhibits a diurnal variability with an amplitude of approximately 2.5‰ and 13‰ for $\delta^{18}\text{O}$ and δD , respectively. The magnitude of these diurnal variations in the snow is significant and equivalent to 10-20% of the seasonal change in the snow isotopic composition in Greenland, or of the magnitude of the change across a glacial-interglacial transition.

We also compared our modeled snow isotopic composition with measurements of the integrated top 1 cm of snow. Based on the snow and vapor isotope measurements, we conclude that the observations are consistent with the assumption of isotopic equilibrium at the snow-air interface. Our findings highlights the need for a high resolution sampling campaign in order to improve our understanding on the processes controlling of isotopic

fractionation of snow during sublimation. Our results strongly support the earlier findings that a diurnal signal exists in the snow isotopic composition. Further laboratory experiments and fieldwork can address the following questions: Does a viscous sub-layer exist as an interface between the snow and the near-surface atmosphere? What is the thickness of the viscous sub-layer? To what depth is diurnal variability in snow isotopic composition significant? It is needed to sample the uppermost millimeters of the snow at high frequency in both laboratory and field experiments to answer this question.

We have found evidence that fractionation during sublimation and solid-condensation is important for modeling vapor exchange and snow isotopic composition on the diurnal scale, supporting recently published results by Ritter et al. (2016). This implies that the snow isotopic composition can change while the snow is subjected to exchange with the atmosphere. This work therefore contributes to the understanding of how the isotopic composition of snow is subject to changes after deposition. The ability of the presented model to simulate the diurnal cycle in isotopic composition of the vapor and change in the snow isotopic composition yield confidence in the ability to further parameterize the snow-air interaction and eventually implement this into higher complexity climate models. This is relevant for both present-day and paleo climate modeling of Greenland isotopes and comparison to ice core records.

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Data

Data are available as supplementary material in –ascii and excel format. Questions regarding data should be address to H. C. Steen-Larsen (Hans.Christian.Steen-Larsen@uib.no).

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