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Experimental observation of transient $\delta^{18}O$ interaction between snow and advective airflow under various temperature gradient conditions

Pirmin Philipp Ebner[1], Hans Christian Steen-Larsen[2, 3], Barbara Stenni[4,5], Martin Schneebeli[1,*], and Aldo Steinfeld[6]

[1] *WSL Institute for Snow and Avalanche Research SLF, 7260 Davos Dorf, Switzerland*

[2] *LSCE Laboratoire des Sciences du Climat et de l'Environnement, Gif-Sur-Yvette Cedex, France*

[3] *Center for Ice and Climate, Niels Bohr Institute, University of Copenhagen, Copenhagen, Denmark*

[4] *Department of Environmental Sciences, Informatics and Statistics, University Ca' Foscari of Venice, Venice, Italy*

[5] *Institute for the Dynamics of Environmental Processes, CNR, Venice, Italy*

[6] *Department of Mechanical and Process Engineering, ETH Zurich, 8092 Zurich, Switzerland*

Abstract

Stable water isotopes ($\delta^{18}O$) obtained from snow and ice samples of polar regions are used to reconstruct past climate variability, but heat and mass transport processes can affect the isotopic composition. Here we present an experimental study on the effect on the snow isotopic composition by airflow through a snow pack in controlled laboratory conditions. The influence of isothermal and controlled temperature gradient conditions on the $\delta^{18}O$ content in the snow and interstitial water vapor is elucidated. The observed disequilibrium between snow and vapor isotopes led to exchange of isotopes between snow and vapor under non-equilibrium processes, significantly changing the $\delta^{18}O$ content of the snow. The type of metamorphism of the snow had a significant influence on this process. These findings are pertinent to the interpretation of the

* Corresponding author. email: schneebeli@slf.ch

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25 records of stable isotopes of water from ice cores. These laboratory measurements
26 suggest that a highly resolved history is relevant for the interpretation of the snow
27 isotopic composition in the field.

28

29 *Keywords*: snow, isotope, isothermal, metamorphism, advection, tomography, post-depositional process

30

31 1. Introduction

32 Water stable isotopes in polar snow and ice have been used for several decades as
33 proxies for global and local temperatures (e.g. Dansgaard, 1964; Lorius et al., 1979;
34 Grootes et al., 1994; Petit et al., 1999; Johnsen et al., 2001; EPICA Members, 2004).
35 However, the processes that influence the isotopic composition in high-latitude
36 precipitation are complex, making direct inference of paleo temperatures from the
37 isotopic record difficult (Cuffey et al., 1994; Jouzel et al., 1997, 2003; Hendricks et al.,
38 2000). Several factors affect the vapor and snow isotopic composition, which give rise
39 to ice core isotopic composition, starting from the process of evaporation in the source
40 region, until the air mass arrives on top of the ice sheets, and even after snow deposition
41 (Craig and Gordon, 1964; Merlivat and Jouzel, 1979; Johnsen et al. 2001; Ciais and
42 Jouzel, 1994; Jouzel and Merlivat, 1984; Jouzel et al., 2003; Helsen et al., 2005, 2006,
43 2007; Cuffey and Steig, 1998; Krinner and Werner, 2003). Mechanical processes such
44 as mixing, seasonal scouring, or spatial redistribution of snow can alter seasonal and
45 annual records (Fisher et al., 1983; Hoshina et al., 2014). Post-depositional processes
46 associated with wind scouring and snow redistribution are known to introduce a "post-
47 depositional noise" in the surface snow. Comparisons of isotopic records obtained from

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nearby shallow ice cores have allowed for estimation of a signal-to-noise ratio and a common climate signal (Fisher and Koerner, 1988, 1994; White et al., 1997; Steen-Larsen et al., 2011; Sjolte et al., 2011; Masson-Delmotte et al., 2015). After deposition, interstitial diffusion in the firn and ice affects the water-isotopic signal but back-diffusion or deconvolution techniques have been used to establish the original isotope signal (Johnsen, 1977; Johnsen et al., 2000).

The interpretation of ice core data and the comparison with atmospheric model results implicitly rely on the assumption that the snowfall precipitation signal is preserved in the snow-ice matrix (Werner et al. 2011). Classically, ice-core stable-isotope records are interpreted as reflecting precipitation-weighted signals, and compared to observations and atmospheric model results for precipitation, ignoring snow-vapor exchanges between surface snow and atmospheric water vapor (e.g. Persson et al., 2011). However, recent studies carried out on top of the Greenland and Antarctic ice sheets combining continuous atmospheric water vapor isotope observations with daily snow surface sampling document a clear day-to-day variation of isotopic composition of surface snow in-between precipitation events as well as diurnal change in the snow isotopes (Steen-Larsen et al., 2014a; Ritter et al., 2016, Casado et al., 2016). This effect was interpreted as being caused by the uptake of the synoptic-driven atmospheric water-vapor isotope signal by individual snow crystals undergoing snow metamorphism (Steen-Larsen et al., 2014a) and the diurnal variation in moisture flux (Ritter et al., 2016). However, the impact of this process on the isotope-temperature reconstruction is not yet sufficiently understood, but crucial to constrain. This process, compared to interstitial diffusion (Johnsen, 1977; Johnsen et al., 2000), will alter the isotope mean value. The field observations challenge the previous assumption that sublimation occurred molecular layer-by-layer with no resulting isotopic fractionation

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(Dansgaard, 1964; Friedman et al., 1991; Town et al., 2008; Neumann and Waddington, 2004). It is assumed that the solid undergoing sublimation would not be unduly enriched in the heavier isotope species due to the preferential loss of lighter isotopic species to the vapor (Dansgaard, 1964; Friedman et al., 1991). Because self-diffusion in the ice is about three orders of magnitude slower than molecular diffusion in the vapor, the amount of isotopic separation in snow is assumed to be negligible.

Snow is a bi-continuous material consisting of fully connected ice crystals and pore space (air) (Löwe et al., 2011). Because of the proximity to the melting point, the high vapor pressure causes a continuous recrystallization of the snow microstructure known as snow metamorphism, even under moderate temperature gradients (Pinzer et al., 2012). The whole ice matrix is continuously recrystallizing by sublimation and deposition, with vapor diffusion as the dominant transport process. Pinzer et al. (2012) showed that a typical half-life of the ice matrix is a few days. The intensity of the recrystallization is dictated by the temperature gradient. Temperature, and geometrical factors (porosity and specific surface area) also play a significant role (Pinzer and Schneebeli, 2009; Pinzer et al., 2012). Snow has a high permeability (Calonne et al., 2012; Zermatten et al., 2014), which facilitates diffusion of gases and, under appropriate conditions, airflow (Gjessing, 1977; Colbeck, 1989; Sturm and Johnson, 1991; Waddington et al., 1996). Modeling of the influence of the so-called 'wind pumping'-effect (Fisher et al., 1983; Neumann and Waddington, 2004), in which the interstitial water vapor is replaced by atmospheric air pushed through the upper meters of the snow pack by small scale high and low pressure areas caused by irregular grooves or ridges formed on the snow surface (dunes and sastrugi), have assumed that the snow grains would equilibrate with the interstitial water vapor on timescales governed by ice self-diffusion. However, no experimental data are available to support this assumption.

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With this in mind the experimental study presented here is specifically developed to investigate the effect of ventilation inside the snow pack on the isotopic composition. Only conditions deeper than 1 cm inside a snowpack are considered. Previous work showed that (1) under isothermal conditions, the Kelvin effect leads to a saturation of the pore space in the snow but does not affect the structural change (Ebner et al., 2015a); (2) applying a negative temperature gradient along the flow direction leads to a change in the microstructure due to deposition of water molecules on the ice matrix (Ebner et al., 2015b); and (3) a positive temperature gradient along the flow had a negligible total mass change of the ice but a strong reposition effect of water molecules on the ice grains (Ebner et al., 2016). Here, we measured continuously the isotopic composition of an airflow containing water vapor through a snow sample under both isothermal and temperature gradient conditions. Micro computed-tomography (μCT) was applied to obtain the 3D microstructure and morphological properties of snow.

2. Experimental setup

Isothermal and temperature gradient experiments with fully saturated airflow and defined isotopic composition were performed in a cold laboratory at around $T_{lab} \approx$ -15 °C with small fluctuations of ± 0.8 °C (Ebner et al., 2014). Snow produced from de-ionized tap water in a cold laboratory (water temperature: 30 ºC; air temperature: -20 ºC) was used for the snow sample preparation (Schleef et al., 2014). The snow was sieved with a mesh size of 1.4 mm into a box, and isothermally sintered for 27 days at -5 ºC to increase the strength, in order to prevent destruction of the snow sample due to the airflow, and to evaluate the effect of metamorphism of snow. The morphological properties of the snow are listed in Table 1. The sample holder (diameter 53 mm, height 30 mm, 0.066 liter) was filled by a cylinder cut out from the sintered snow. To prevent that air can flow between the snow sample and the sample holder walls, the undisturbed

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snow disk was filled in at a higher temperature (about -5 °C) and sintering was allowed for about 1 h before cooling down and start of the experiment. The setup of Ebner et al. (2014) was modified by additionally inserting a water vapor isotope analyzer (Model: L1102-I Picarro, Inc., Santa Clara, CA, USA) to measure the isotopic ratio $\delta^{18}O$ of the water vapor contained in the airflow at the inlet and outlet of the sample holder. The experimental setup consisted of three main components (humidifier, sample holder, and the Picarro analyzer) were connected with insulated copper tubing and Swagelok fitting (Fig. 1). The tubes to the Picarro analyzer were heated to prevent deposition of water vapor and thereby fractionation. The temperature was monitored with thermistors inside the humidifier and at the inlet and outlet of the snow sample. A dry air pressure tank controlled by a mass flow controller (EL-Flow, Bronkhorst) generated the airflow. A humidifier, consisting of a tube (diameter 60 mm, height 150 mm, 0.424 liter volume) filled with crushed ice particles (snow from Antarctica with low $\delta^{18}O$ composition), was used to saturate the dry air entering the humidifier with water vapor at an almost constant isotopic composition. The air temperature in the humidifier and at the inlet of the snow sample was maintained at the same value (accuracy ± 0.2 K) to limit changes influence of variability in absolute vapor pressure and isotopic composition. We measured the $\delta^{18}O$ of the water vapor produced by the humidifier before and after each experimental run ($\delta^{18}O_{hum}$). The outlet flow ($\delta^{18}O_a$) of the sample holder was continuously measured during the experiment to analyze the temporal evolution of the isotopic signal. All data from the Picarro analyzer were corrected to the humidity reference level using the established instrument humidity-isotope response (2013; 2014b). In addition, VSMOW-SLAP correction and drift correction were performed. We followed the calibration protocol and used the calibration system described in detail by Steen-Larsen et al. (2013; 2014b).

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148 The sample holder described by Ebner et al. (2014) was used because it already had
149 the appliance to analyze the snow by µCT. Tomography measurements were performed
150 with a modified µ-CT80 (Scanco Medical). The equipment incorporated a microfocus
151 X-ray source, operated at 70 kV acceleration voltage with a nominal resolution of 18
152 µm. The samples were scanned with 1000 projections per 180º in high-resolution
153 setting, with typical adjustable integration time of 200 ms per projection. The field of
154 view of the scan area was 36.9 mm of the total 53 mm diameter, and subsamples with a
155 dimension of 7.2 × 7.2 × 7.2 mm^3 were extracted for further processing. The
156 reconstructed µCT images were filtered using a 3 × 3 × 3 median filter followed by a
157 Gaussian filter (σ = 1.4, support = 3). The Otsu method (Otsu, 1979) was used to
158 automatically perform clustering-based image thresholding to segment the grey-level
159 images into ice and void phase. Morphological properties in the two-phase system were
160 determined based on the exact geometry obtained by the µCT. Tetrahedrons
161 corresponding to the enclosed volume of the triangulated ice matrix surface were
162 applied on the segmented data to determine porosity (ε) and specific surface area (SSA).
163 Opening size distribution operation was applied in the segmented µCT data to extract
164 the mean pore size (d_{mean}) (Haussener et al., 2012).

165 Three experiments with saturated advective airflow through the snow sample were
166 performed to record the following parameters and analyze their effects: (1) isothermal
167 conditions to analyze the influence of curvature effects (Kaempfer al et., 2007); (2)
168 positive temperature gradient applied to the snow sample where cold air is heated up
169 while flowing through the sample in order to analyze the influence of sublimation; (3)
170 negative temperature gradient applied to the snow sample where warm air is cooled
171 down while flowing across the sample, to analyze the influence of net deposition.
172 During the temperature gradient experiments, a temperature difference of 1.4 ºC and 1.8

ºC was imposed resulting in a gradient of +47 K m^{-1} and -60 K m^{-1}, respectively. The runs were performed at atmospheric pressure and with a volume flow rate of 3.0 liter min^{-1} corresponding to an average flow speed in the pores of ≈ 30 mm s^{-1}. In experiment (2) the outlet temperature and in experiment (3) the inlet and also the humidifier temperature was actively controlled using thermo-electric elements. Variations in temperature of up to ± 0.8 ºC were due to temperature fluctuations inside the cold laboratory, leading to slightly variable temperature gradients and mean temperature in experiment (2) and (3). Table 1 presents a summary of the experimental conditions and the morphological properties of the snow samples. At the end of each experiment, the snow sample was cut into five layers of 6 mm height and the isotopic composition of each layer was analyzed to examine the spatial $\delta^{18}O$ gradient in the isotopic composition of the snow sample.

A slight increase with a maximum of 0.7 ‰ of $\delta^{18}O$ in the water vapor produced by the humidifier was observed during the experiments (Table 2). This change of ~0.7‰ is not significant compared to the difference between the isotopic composition of the water vapor and the snow sample in the sample holder of ~53‰ and the temporal change of the water vapor isotopes on the back side of the snow sample.

3. Results

3.1 Isothermal condition

The experiment (1) was performed for 24 h at a mean temperature of T_{mean} = -15.5 ºC. $\delta^{18}O_a$ decreased exponentially in the outlet flow was observed throughout the experimental run as shown in Fig. 2. Initially, the $\delta^{18}O_a$ content in the flow was -27.7 ‰ and exponentially decreased to -47.6 ‰ after 24 h. The increase of $\delta^{18}O_a$ in the first approximately 30 min was due to memory effects from air and possible condensed

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197 water left in the tubes from a prior experiment. The small fluctuations in the $\delta^{18}O_a$
198 signal at $t \approx 7$ h, 17 h and 23 h were due to small temperature changes in the cold
199 laboratory.

200 We observed a strong interaction between the airflow and the snow was observed in
201 the isotopic composition of the snow. The $\delta^{18}O_s$ signal in the snow decreased by 4.75 –
202 7.78 ‰ and an isotopic gradient in the snow was observed after the experimental run,
203 shown in Fig. 3. Initially, the snow had a homogeneous isotopic composition of $\delta^{18}O_s$ =
204 -10.97 ‰ but post-experiment sampling showed a decrease in the snow $\delta^{18}O$ at the inlet
205 side to -17.75 ‰ and at the outlet side to -15.72 ‰. The spatial $\delta^{18}O_s$ gradient of the
206 snow had an approximate slope of 0.68 ‰ mm^{-1} at the end of the experimental run.
207 Table 2 shows the $\delta^{18}O$ value in snow at the beginning (t = 0) and end (t = 24 h) of the
208 experiment.

209 **3.2 Air warming by a positive temperature gradient along the airflow**

210 The experiment (2) was performed over a period of 24 h with an average
211 temperature gradient of approximatively +47 K m^{-1} (warmer temperatures at the outlet
212 of the snow) and an average mean temperature of -14.7 ºC. We observed again a
213 relaxing exponential decrease of $\delta^{18}O_a$ in the outlet flow was observed throughout the
214 measurement period as shown in Fig. 2, but the decrease was slower compared to the
215 isothermal run. Initially, the $\delta^{18}O_a$ content in the flow coming through the snow disk
216 was -29.8 ‰ and exponentially decreased to -41.9 ‰ after 24 h. The increase of $\delta^{18}O_a$
217 in the first 30 min was due to memory effects as explained previously. The small
218 fluctuations in the $\delta^{18}O_a$ signal at $t \approx 2.7$ h, and 12.7 h were due to small temperature
219 changes in the cold laboratory.

220 The $\delta^{18}O_s$ signal in the snow decreased up to 4.66 – 7.66 ‰ and a gradient in
221 isotopic composition of the snow was observed after the experimental run, shown in

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222 Fig. 3. Initially, the snow had a homogeneous isotopic composition of $\delta^{18}O_s$ = -11.94
223 ‰, but post-experiment sampling showed a decrease at the inlet side to -19.6 ‰ and at
224 the outlet side to -16.6 ‰. The spatial $\delta^{18}O_s$ gradient of the snow had an approximate
225 slope of 1.0 ‰ mm^{-1} at the end of the experimental run. Table 2 shows the $\delta^{18}O_s$ value
226 in snow at the beginning (t = 0) and end (t = 24 h) of the experiment.

227 **3.3 Air cooling by a negative temperature gradient along the air flow**

228 The experiment (3) was performed for 84 h instead of 24 h to better estimate the
229 trend in $\delta^{18}O_a$ in the outlet flow. An average temperature gradient of approximately -60
230 K m^{-1} (colder temperatures at the outlet of the snow) and an average mean temperature
231 of -13.2 ºC were observed during the experiment. As in the previous experiments, a
232 relaxing exponential decrease of $\delta^{18}O_a$ in the outlet flow was observed throughout the
233 experimental run as shown in Fig. 2, but the decrease was slower compared to the
234 isothermal run and temperature gradient opposed to the airflow. Initially, the $\delta^{18}O_a$
235 content in the flow was -29.8 ‰ and exponentially decreased to -37.7 ‰ after 84 h. The
236 increase of $\delta^{18}O_a$ in the first 30 min was again due to memory effects. The small
237 fluctuations in the $\delta^{18}O_a$ signal at $t \approx$ 7.3 h, 21.3 h, 31.3 h, 45.3 h, 55.3 h, 69.3 h, and
238 79.3 h were due to small temperature changes in the cold laboratory.

239 The $\delta^{18}O_s$ signal in the snow decreased up to 4.46 – 15.09 ‰ and a gradient in the
240 isotopic composition of the snow was observed after the experimental run, shown in
241 Fig. 3. Initially, the snow had an isotopic composition of $\delta^{18}O_s$ = -10.44 ‰ but post-
242 experiment sampling showed a decrease at the inlet side to -25.53 ‰ and at the outlet
243 side to -15.00 ‰. The spatial $\delta^{18}O_s$ gradient of the snow had an approximate slope of
244 3.5 ‰ mm^{-1} at the end of the experimental run. Table 2 shows the $\delta^{18}O_s$ value in snow
245 at the beginning (t = 0) and end (t = 84 h) of the experiment.

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4. Discussion

All experiments showed a strong exchange in $\delta^{18}O$ between the snow and water-vapor saturated air resulting in a significant change of the value of the stable isotopes in the snow. The advective conditions in the experiments were comparable with surface snow layers in Antarctica and Greenland, but at higher temperature, especially compared to interior Antarctica. In wind pumping theory, an airflow velocity of $u_D \approx 10$ mm s^{-1} (corresponding Reynolds number Re ≈ 0.65) was estimated inside the surface snow layers ($d_{mean} \approx 1$ mm) for a high wind speed above the snow surface (≈ 10 m s^{-1}) (Neumann, 2003). We performed experiments with airflow velocities inside the snow sample of around 30 mm s^{-1} (corresponding Reynolds number Re = 0.7), which was a factor three higher than in natural conditions, but still in the feasible flow regime according to the Reynolds number.

The results also showed strong interactions in $\delta^{18}O$ between snow and air depending on the different temperature gradient conditions. The experiments indicate that temperature variation and airflow above and through the snow structures (Sturm and Johnson, 1991; Colbeck, 1989; Albert and Hardy, 1995) seem to be dominant processes affecting water stable isotopes of surface snow. In a typical Antarctic and Greenland snow profile, strong interactions between the atmosphere and snow occurs, especially in the first 2 m (Neumann and Waddington, 2004; Town et al., 2008), called the convective zone. In the convective zone, air can move relatively freely and therefore exchange between snow and the atmospheric air occurs. Air flowing into the snow reaches saturation vapor pressure nearly instantly through sublimation (Neumann et al., 2008; Ebner et al., 2015a). Our results support the interpretation that changes in surface snow isotopic composition are expected to be significant if large day-to-day surface changes in water vapor occur in between precipitation events, wind pumping is efficient

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and snow metamorphism is enhanced by temperature gradients in the upper first centimeters of the snow (Steen-Larsen et al., 2014a).

We expect that our findings will lead to influence the interpretation of the water stable isotope records from ice cores. Classically, ice core stable isotope records are interpreted as paleo-temperature reflecting precipitation-weighted signals. When comparing observations and atmospheric model results for precipitation with ice core records, such vapor-snow exchanges are normally ignored (e.g. Persson et al. (2011) and Fujita and Abe (2006)). However, vapor-snow exchange enhanced by recrystallization rate seems to be an important factor for the high variation in the snow surface $\delta^{18}O$ signal as supported by our experiments. It was hypothesized that the changes in the snow-surface $\delta^{18}O$ reported by Steen-Larsen et al. (2014a) are caused by changes in large-scale wind and moisture advection of the atmospheric water vapor signal and snow metamorphism. The strong interaction between atmosphere and near-surface snow can modify the ice core water stable isotope records.

The rate-limiting step for isotopic exchange in the snow is isotopic equilibration between the pore-space vapor and surrounding ice grains. The relaxing exponential decrease of $\delta^{18}O$ in the outflow of our experiments predicted that full isotopic equilibrium between snow and atmospheric vapor will not be reached at any depth (Waddington et al., 2002; Neumann and Waddington, 2004) but changes towards equilibrium with the atmospheric state occurs, effectively changing the "target" towards which the snow is equilibrating (Steen-Larsen et al., 2013, 2014a).

As snow accumulates, the upper 2 m are advected through the ventilated zone (Neumann and Waddington, 2004; Town et al., 2008). In areas with high accumulation rate (e.g. South Greenland), snow is advected for a short time through the ventilated zone. Relatively short time vapor snow exchange would result in higher spatial

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296 variability compared to long-time. However, the effects of snow ventilation on isotopic
297 composition may become more important as the accumulation rate of the snow
298 decreases (< 50 mm a^{-1}), such that snow remains in the near-surface ventilated zone for
299 many years (Waddington et al., 2002; Hoshina et al., 2014; Hoshina et al., 2016). As the
300 snow remains longer in the near-surface ventilated zone, a larger $\delta^{18}O$ exchange
301 between snow and atmospheric vapor will occur. Consequently, the isotopic content of
302 layers at sites with high and low accumulation rates can evolve differently, even if the
303 initial snow composition had been equal, and the sites had been subjected to the same
304 histories of air-mass vapor.

305 We now discuss the fact that despite a relatively small change in the difference
306 between the isotopic composition of the incoming vapor and the snow, large differences
307 in the isotopic composition of the water vapor at the outlet flow exist for the three
308 different experimental setups. Based on the difference in the outlet water vapor isotopic
309 composition, we hypothesized that different processes are at play for the different
310 experiments. It is obvious that there is a fast isotopic exchange with the surface of the
311 ice crystals, and a much slower timescale on which the interior of the ice crystals gets
312 altered. Due to the low diffusivity of $H_2{}^{16}O$ and $H_2{}^{18}O$ in ice ($D_{H_2{}^{18}O} \approx D_{H_2{}^{16}O} = \sim 10^{-15}$
313 $m^2\ s^{-1}$ (Ramseier, 1967; Johnsen et al., 2000)), we assumed that the interior is not
314 altered on the timescale of the experiment. This explained why the net isotopic change
315 of the bulk sample is relatively small compared to the changes in the outlet water vapor
316 isotopes. The effective 'ice-diffusion depth' of the isotopic exchange during the
317 experiments is given as $L_D = \sqrt{D \cdot t}$, where D is the diffusion coefficient of $H_2{}^{16}O$ and
318 $H_2{}^{18}O$ in ice, respectively, and t the experimental time. The calculated 'ice-diffusion
319 depth' L_D, is ~ 9.3 μm for experiment (1) and (2), and ~17.4 μm for experiment (3),
320 respectively, indicating an expected low altering of the interior of the ice crystal.

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However, snow has a large specific surface area and therefore a high exchange area. This has an effect on the $\delta^{18}O$ snow concentration. The fraction of the total volume V_{tot} of ice that is close enough to the ice surface to be affected by diffusion in time t is then $\rho_{ice} \cdot SSA \cdot L_D$, where SSA is the specific surface area (area per unit mass), and L_D is the diffusion depth (above) for time t. For $t \approx 24$ hours, a large fraction (24 to 43 %) the total volume V_{tot} of the ice matrix can be accessed through diffusion. It is quite hard to see the total $\delta^{18}O$ snow difference between experiments (1) and (2) after the experiment compared to the $\delta^{18}O$ of the vapor in the air at the outlet. But there is still a notable effect in the $\delta^{18}O$ of the snow between experiment (1) and (2). Due to the higher recrystallization rate of experiment (2) the spatial $\delta^{18}O_s$ gradient of the snow (1.0 ‰ mm^{-1}) is higher than for experiment (1) (0.68 ‰ mm^{-1}). Increasing the experimental time, the $\delta^{18}O$ change in the snow increases (experiment (3)). In general, the calculated 'ice-diffusion depth' is realistic under isothermal conditions where diffusion processes are the main factors (Kaempfer and Schneebeli, 2007; Ebner et al., 2015). Applying a temperature gradient, the impact of diffusion is suppressed due to the high recrystallization rate by sublimation and deposition. Due to the low half-life of the ice matrix of a few days, the growth rates are typically on the order of 100 µm per day (Pinzer et al., 2012). Therefore, this redistribution of ice counteracts the diffusion into the solid ice.

By comparing similarities and differences between the outcomes of the three experimental setups we will now discuss the physical processes influencing the interaction and exchange processes within the snowpack between the snow and the advected vapor. We first notice that the final snow isotopic profile of experiment (1) (isothermal) and (2) (positive temperature gradient along the direction of the flow) are comparable to each other. Despite this similarity, the evolution in the outlet water vapor

346 of experiment (1) showed a significantly stronger depletion compared to experiment (2).
347 For experiment (3) (negative temperature gradient along the direction of the flow) we
348 observed the smallest change in outlet water vapor isotopes but the largest snow-pack
349 isotope gradient after the experiment. However, this change was caused by 84 hours
350 flow instead of 24 hours.

351 Curvature effects, temperature gradients and therefore the recrystallization rate
352 influence the mass transfer of $H_2{}^{16}O$/ $H_2{}^{18}O$ molecules. The higher the recrystallization
353 rate of the snow the slower the adaption of the outlet air concentration to the inlet air
354 concentration (see in experiment (2) and (3)). Under isothermal conditions (experiment
355 (1)) the only effect influencing the recrystallization rate is the curvature effect
356 (Kaempfer and Schneebeli, 2007). However, based on the experimental observations
357 (Kaempfer and Schneebeli, 2007) this effect decreases with decreasing temperature and
358 increasing experimental time. Applying an additional temperature gradient on a snow
359 sample, there are complex interplays between local sublimation and deposition on
360 surfaces and the interaction of water molecules in the air with the ice matrix due to
361 changing saturation conditions of the airflow. Therefore, the recrystallization rate
362 increases and thus the change in the $\delta^{18}O$ of the air. For experiment (2) there is a
363 complex interplay between sublimation and deposition of water molecules into the
364 interstitial flow (Ebner et al., 2015c) while for experiment (3) there are deposition of
365 molecules carried by the interstitial flow onto the snow crystals (Ebner et al., 2015b).
366 Furthermore, in the beginning of each experiment there is a tendency to sublimate from
367 edges of the individual snow crystals due to the higher curvature. As the edges were
368 sublimated and deposition occurred in the concavities, the individual snow crystals
369 became more rounded, slowing down the transfer of water molecules into the interstitial
370 airflow. We noticed for all three experiments that within the uncertainty of the isotopic

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371 composition of the snow, the initial isotopic composition of the vapor was the same and
372 in isotopic equilibrium with the snow. The difference between experiment (1) and (2)
373 lies in the fact that due to the temperature gradient in experiment (2) there is an
374 increased transfer of water vapor with the isotopic composition of the snow in to the
375 airflow. Hence the depleted air from the humidifier advected through the snow disk is
376 mixed with a relatively larger vapor flux from the snow crystals. Additionally, we also
377 expected less deposition into the concavities in experiment (2) compared to experiment
378 (1). However, it is interesting to note that the final isotopic profile of the snow disk is
379 similar in experiment (1) and experiment (2). We interpreted this as being a result of
380 two processes acting in opposite direction: although relatively isotope-depleted vapor
381 from the humidifier was deposited on the ice matrix there was also a higher amount of
382 sublimation of relatively isotope-enriched vapor from the snow disk in experiment (2).
383 Experiment (3) separates itself from the other two experiments in the way that as the
384 water vapor from the humidifier is advected through the snow disk there is a continuous
385 deposition of very depleted air due the negative temperature gradient. As for the case of
386 experiment (1) and (2) there was also in experiment (3) a constant sublimation of the
387 convexities into the vapor stream. We notice that despite the fact that experiment 3 ran
388 for 84 hours the snow at the outlet side of the snow-disk did not become more
389 isotopically depleted compared to experiment (1) and (2). However, the snow on the
390 inlet side became significantly more isotopically depleted. By having this observation in
391 mind, together with the fact that the vapor of the outlet of the snow-disk is less depleted
392 compared to experiment (1) and (2), lead us to hypothesize that there is a relatively
393 larger deposition of isotopically depleted vapor from the humidifier as the vapor is
394 advected through the snow disk. This means that a relatively larger component of the

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395 isotopic composition of the vapor is originating by sublimation from the convexities of
396 the snow disk and less from the isotopically depleted vapor from the humidifier.

397 Our hypotheses ask for additional validation by more detailed experiments.
398 Specifically, it would be crucial to know the mass balance of the snow disk more
399 precisely, which could be done by scanning the entire snow disk following the change
400 in density and morphological properties over the entire height, or gravimetrically.
401 Insights would also be achieved with experiments using snow of the same isotopic
402 composition, but different SSA, as this would allow calculating more precisely the
403 different observed exchange rates. Additionally, different and colder background
404 temperatures should be tested to better understand inland Antarctic environment and the
405 effect of the quasi-liquid layer, which is necessary for the development of a numerical
406 model. Isotopically different combinations of vapor and snow should be performed. In
407 the present manuscript, vapor with low $\delta^{18}O$ isotopic composition was transported
408 through snow with relative high $\delta^{18}O$ isotopic composition. It would be interesting to
409 reverse the combination and perform experiments with different combinations to
410 provide more insights on mass and isotope exchanges between vapor and snow.
411 Experiments with longer running time helps to understand the change in the ice matrix
412 better. Further, as in the humidifier we had not only sublimation but a complex interplay
413 of simultaneously sublimation and deposition due to the geometrical complexity of
414 snow, a further experiment is suggested to show isotopic fractionation during
415 sublimation. Dry air is blown over a flat ice surface and is immediately removed. With
416 the suggested experiment the actual statement whether there is no measurable
417 fractionation and the sublimated vapor has the same $\delta^{18}O$ value as the sublimating ice or
418 not can be proved. Based on the results of this paper, we expect a different $\delta^{18}O$ value
419 between vapor and ice, especially at the beginning (see Fig. 4). Due to the fact that

420 $H_2{}^{16}O$ is lighter in mass than $H_2{}^{18}O$, the energy required to change the state from solid
421 to vapor is less. Therefore, especially at the beginning of the experiment, the vapor is
422 depleted in $H_2{}^{18}O$ and thus a different $\delta^{18}O$ value in the vapor and ice should be seen.
423 After a while the ice interface is depleted in $H_2{}^{16}O$ molecules and because the self-
424 diffusion in ice is low, an approach of the $\delta^{18}O$ value of the vapor and ice should be
425 seen. Comparing the penetration depths for diffusion ($L_D = \sqrt{D \cdot t}$; where $D \approx 10^{-15}$ m^2 s^{-1}
426) and for sublimation ($L_{sub} = v_{sub}t$; where $v_{sub} \approx 100$ µm per day (Pinzer et al., 2012))
427 the time $t = D/v_{sub} \approx 10^3$ s represents the transition from diffusion-dominated behavior
428 (with fractionation on sublimation) to sublimation-dominated behavior (in which nearly
429 all $H_2{}^{18}O$ atoms are forced to enter the vapor phase). This is obviously not a precise
430 number but it suggests that after about 10^3 seconds, sublimation from the ice crystals
431 occurs without significant isotopic fractionation. However, as we have not performed
432 such experiments yet, these statements are only speculative.

433 **4. Summary and conclusion**

434 We analyzed the influence of airflow and metamorphism across a snow sample on
435 the $\delta^{18}O$ isotopic composition in controlled laboratory experiments. Three experiments
436 with saturated advective airflow across the snow sample with a volume flow rate of 3.0
437 liter min^{-1} ($u_D \approx 3$ cm s^{-1}) were performed: (1) isothermal run to analyze the influence of
438 the curvature effects; (2) positive temperature gradient run (approx. +47 K m^{-1}) along
439 the airflow where cold air heated up while flowing through the sample to analyze the
440 influence of net ice mass loss in a snowpack; and (3) negative temperature gradient run
441 (approx. -60 K m^{-1}) where warm air cooled down while flowing through the sample, to
442 analyze the influence of deposition. Air with low $\delta^{18}O$ content (-68 ‰ – -62 ‰) was
443 blown into the snow sample and the $\delta^{18}O$ outlet was continuously measured with a

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444 water vapor isotope analyzer. The $\delta^{18}O$ distribution through the snow disk was
445 measured at the beginning and end of each experiment. µCT measurements were
446 applied to obtain the 3D microstructure and the morphological properties, namely:
447 porosity (ε), specific surface area (SSA), and the mean pore size (d_{mean}) of the snow.

448 Laboratory experimental runs were performed where a transient $\delta^{18}O$ interaction
449 between snow and air was observed. The airflow altered the isotopic composition of the
450 snowpack and supports an improved climatic interpretation of ice core stable water
451 isotope records. The water vapor saturated airflow with an isotopic difference of up to
452 55‰ changed within 24 h and 84 h the original $\delta^{18}O$ isotope signal in the snow by up to
453 7.64 ‰ and 15.06 ‰. The disequilibrium between snow and air isotopes led to the
454 observed exchange of isotopes, the rate depending on the temperature gradient
455 conditions. Concluding, increasing the recrystallization rate in the ice matrix the
456 temporal change of the $\delta^{18}O$ concentration at the outflow decreases (experiment (2) and
457 (3)). Decreasing the recrystallization rate the temporal curve of the outlet concentration
458 is getting steeper reaching the $\delta^{18}O$ inlet concentration of the air faster (experiment (1)).

459 Additionally, the complex interplay of simultaneous diffusion, sublimation and
460 deposition due to the geometrical complexity of snow has a strong effect on the $\delta^{18}O$
461 signal in the snow and cannot be neglected. A temporal signal can be superimposed on
462 that cloud-temperature signal, (a) if the snow remains near the surface for a long time,
463 i.e. in a low-accumulation area, and (b) is exposed to a history of air masses carrying
464 vapor with a significantly different isotopic signature than the precipitated snow.

465 These are novel measurements and will therefore be important for allowing other
466 researchers formulate their research question based on and carry out further
467 experiments. Our results represent the first direct experimental observation showing
468 interaction between the water isotopic composition of the snow, the water vapor in the

air and recrystallization due to temperature gradients. Previous work on isotopic content of surface snow failed to incorporate the recrystallization process, and recrystallization and bulk mass exchange must be incorporated into future models of snow and firn evolution. Further studies are required on the influence of temperature and airflow as well as snow microstructure on the mass transfer phenomena for validating the implementation of stable water isotopes in snow models.

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709 **Table 1:** Morphological properties and flow characteristics of the experimental runs:
710 snow density (ρ), porosity (ε), specific surface area per unit mass (SSA), mean pore
711 space diameter (d_{mean}), superficial velocity in snow (u_D), corresponding Reynolds
712 number ($Re = d_{mean} \cdot u_D/\nu_{air}$), average inlet temperature of the humidifier and at the inlet
713 ($T_{in,mean}$), average outlet temperature at the outlet ($T_{out,mean}$), and average temperature
714 gradient (∇T_{ave}). Experiment (1) corresponds to the isothermal conditions; Experiment
715 (2) to air warming; and Experiment (3) to air cooling in the snow sample.
716

	ρ kg m^{-3}	ε –	SSA m^2 kg^{-1}	d_{mean} mm	u_D m s^{-1}	Re –	$T_{in,mean}$ °C	$T_{out,mean}$ °C	∇T_{ave} K m^{-1}
Experiment (1)	201.74	0.78	28.0	0.39	0.03	0.76	-15.5	-15.5	–
Experiment (2)	201.74	0.78	29.7	0.36	0.03	0.70	-15.4	-14.0	+47
Experiment (3)	220.08	0.76	27.2	0.37	0.031	0.74	-12.3	-14.1	-60

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718 **Table 2:** $\delta^{18}O$ in the vapor in the humidifier ($\delta^{18}O_{hum}$) and of the snow in the sample
719 holder ($\delta^{18}O_s$) at the beginning ($t = 0$) and end (t = end) of each experiment and the final
720 $\delta^{18}O$ content of the snow in the sample holder at the inlet ($z = 0$ mm) and outlet ($z = 30$
721 mm). Experiment (1) corresponds to the isothermal conditions; Experiment (2) to air
722 warming; and Experiment (3) to air cooling in the snow sample.

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	$\delta^{18}O_{hum}$ ‰		$\delta^{18}O_{s,\,t=0}$ ‰	$\delta^{18}O_{s,\,t=end}$ ‰	
	$t = 0$	t = end		$z = 0$ mm	$z = 30$ mm
Experiment (1)	-68.2	-67.5	-10.97	-17.75	-15.72
Experiment (2)	-66.3	-66.1	-11.94	-19.60	-16.60
Experiment (3)	-62.8	-62.2	-10.44	-25.53	-15.00

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Figure captions

Fig. 1. Schematic of the experimental setup. A thermocouple (TC) and a humidity sensor (HS) inside the humidifier measured the the mean temperature and humidity of the airflow. Two thermistors (NTC) close to the snow surface measured the inlet and outlet temperature of the airflow (Ebner et al., 2014). The Picarro Analyzer measured the isotopic composition $\delta^{18}O$ of the outlet flow. Inset: 3D structure of 110 × 42 × 110 voxels (2 × 0.75 × 2 mm^3) obtained by the μCT.

Fig. 2. Temporal isotopic composition of $\delta^{18}O$ of the outflow for each of the experimental run. The spikes in the $\delta^{18}O$ were due to small temperature changes in the cold laboratory (Ebner et al., 2014). Exp. (1) corresponds to the isothermal conditions; Exp. (2) to air warming; and Exp. (3) to air cooling in the snow sample. The higher the recrystallization rate of the snow the slower the adaption of $\delta^{18}O$ of the outlet air to the inlet air. The illustration in the lower right corner shows the relation between $\delta^{18}O$ of the initial snow, inlet, and outlet of the air.

Fig. 3. Spatial isotopic composition of $\delta^{18}O$ of the snow sample at the beginning (t = 0) and at the end (t = end) for each experiment. The air entered at z = 0 mm and exited at z = 30 mm. Exp. (1) corresponds to the isothermal conditions; Exp. (2) to air warming; and Exp. (3) to air cooling in the snow sample.

Fig. 4. Schematic of isotopic fractionation of vapor and ice during sublimation. Water molecules sublimate rapidly from a flat ice surface in dry air and are immediately removed. The different in relative mass of $H_2{}^{16}O$ and $H_2{}^{18}O$ led to an isotopic fractionation of vapor and ice. The isotopic fractionation is a

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750 brief transient effect, possibly lasting only a few minutes. Time *t* represents
751 the transition from diffusion-dominated behavior (with fractionation on
752 sublimation) to sublimation-dominated behavior (in which nearly all $H_2{}^{18}O$
753 atoms are forced to enter the vapor phase).
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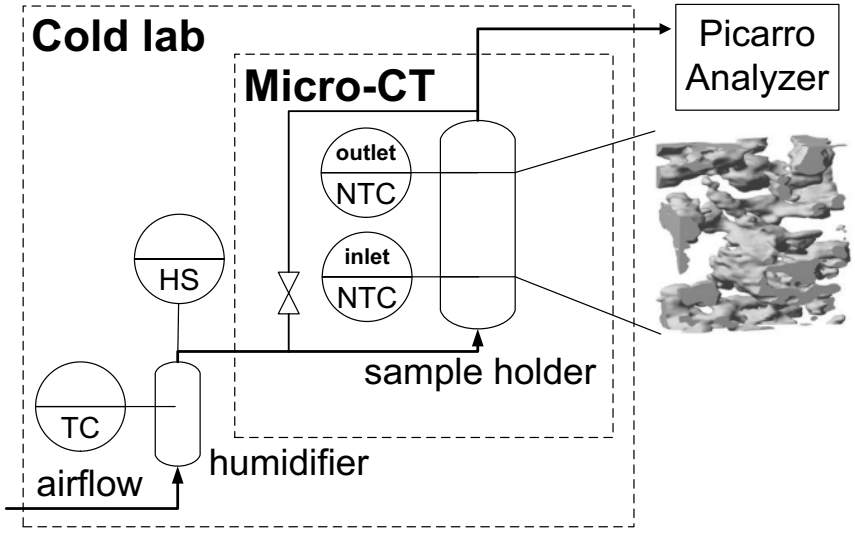

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756 Fig. 1
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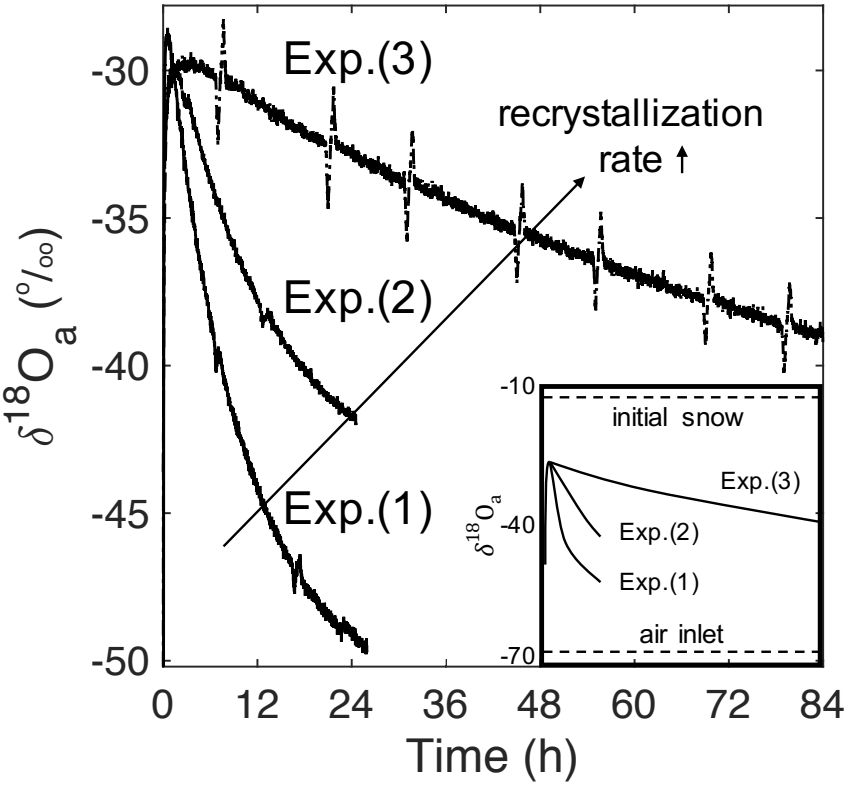

Fig. 2

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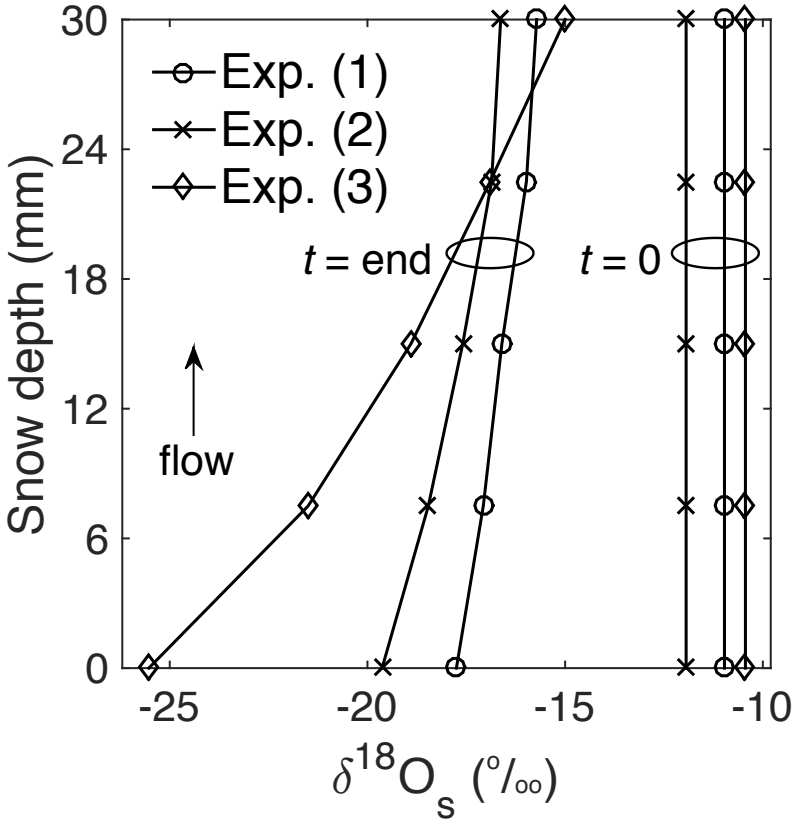

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762 Fig. 3

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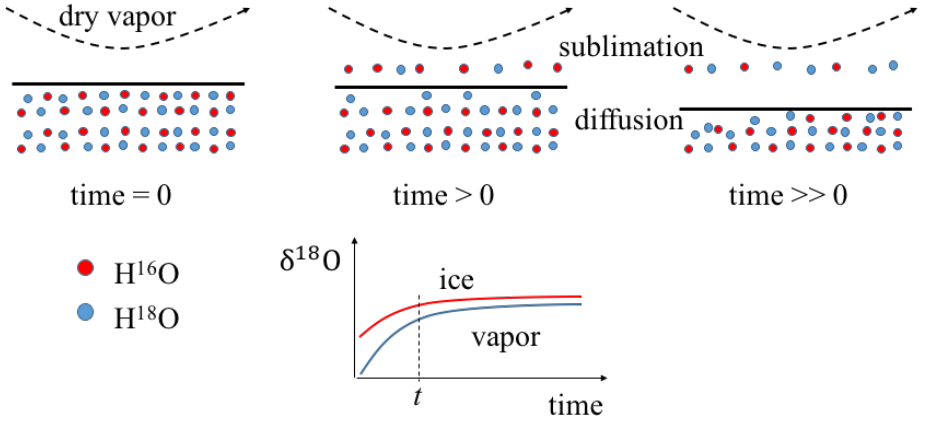

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766 Fig. 4