Post-depositional changes in snow isotope content: preliminary results of laboratory experiments

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Abstract

Isotopic content of the snow and firn thickness is assumed to be altered significantly due to the post-depositional (PD) mass- and isotope exchange with the atmospheric water vapor. If so, these effects should be accounted for in the ice core-based isotope-temperature paleo-reconstructions. In order to study the intensity of the PD processes we set up a series of laboratory experiments. In this paper we describe in detail the experimental technique and briefly overview preliminary results. It is shown that the PD modifications in the upper layer of snow thickness are noticeably strong even under such a low temperature as $-35^\circ$C (the value typical for the Central Antarctic summer).

It is demonstrated that the PD isotopic changes in snow can be approximated as a linear function of the relative mass loss due to snow sublimation. Possible applications for improving the isotope-temperature paleo-reconstructions are shortly discussed.

1 Introduction

Data on isotope content of ice cores, obtained as a result of the polar ice sheets deep drilling, are widely used to reconstruct the paleo-temperature in the remote past since the mid 1960s (Dansgaard et al., 1971). The detailed study of the deuterium and oxygen 18 concentrations in the successively deposited ice layers has allowed reconstructing climate variability over the past 120 kyr in Greenland (NorthGRIP, 2004) and about 800 kyr in Antarctica (Jouzel et al., 2007). However, the calibration of the isotopic paleo-thermometer (i.e., defining the relationship between temporal changes of temperature and isotope content) is subjected to a number of assumptions, which introduce some error to the estimated values of air temperature in the past. Main uncertainties in the paleo-reconstructions are related to the past changes in moisture source conditions, seasonal cycle of precipitation, ratio between condensation and near-surface air temperature, microphysical conditions of condensation (see review in Ekaykin, 2003; Jouzel et al., 1997, 2003). Recently more and more attention is drawn to the alter-
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The PD changes of the snow cover isotope content are mainly attributed to two processes: 1) smoothing of vertical isotopic profiles due to molecular diffusion in the pore space and ice matrix (Johnsen, 1977; Johnsen et al., 2000) without alteration of mean isotope content of snow-ice thickness, and 2) change of the upper snow isotope content due to the isotopic and mass-exchange between snow and atmosphere (see next section).

Note that these two processes are in fact two sides of one single mechanism of mass exchange between snow ice grains and water vapor in pore space and lower atmosphere. (A first attempt to physically describe it as a single process was made by Neumann and Waddington, 2004). Thus, the above differentiation is somewhat conventional and is related to the fact that process 1 (diffusive smoothing) is relatively well studied and is accounted for in ice core isotopic studies, while the impact of process 2 on isotope-temperature reconstruction is not sufficiently investigated. The physical difference between the both processes consists in their temporal and spatial scales: intensive mass exchange of snow with atmosphere takes place in upper 0.4–2 m, while diffusive smoothing reveals itself in the whole firn-ice thickness. Finally, process 1 by definition does not affect the mean isotopic content of snow and ice depositions, whereas atmosphere-snow exchange usually results in heavier isotope content of the remaining snow, which may be important for the ice core-based isotope-temperature reconstructions.

Hereinafter in this work the “PD processes” are attributed only to the above process 2, i.e., isotope-mass exchange of snow with atmosphere.

In order to quantitatively describe the intensity of the PD changes in snow, we devel-
oped a program of laboratory experiments. In this work we present the experimental set-up, as well as preliminary results of the experiments. This is preceded by a brief review of the published evidence of the PD effects in nature supported by experiments and modeling.

2 Physical basis and experimental evidence of the isotopic PD effects in snow

The PD changes of the snow isotope content are based on the isotope fractionation during the molecule transition between vapor and solid phase. This process has some features comparing to the vapor-liquid phase transition. It is believed (Dansgaard et al., 1973) that “layer-by-layer” sublimation of ice (unlike to water evaporation) does not change the isotope content of the remaining ice, and that the isotope content of the forming vapor is equal to that of the sublimated material. This is explained by a very small coefficient of self-diffusion of water molecules in ice matrix (Ramseier, 1967), which prevent the exchange of the sublimating surface with the deeper ice layers. However, it should not be understood *ad verbum* in case of natural process of snow sublimation, since in natural conditions pure sublimation is met very rarely. The observed mass decrease of snow may be viewed as the difference of two opposite mass fluxes, from snow to atmosphere and back. Sublimation part of this process may take place without isotope fractionation, as mentioned above, but the condensation part of it is accompanied by isotope modification due to preferential deposition of heavy molecules (HD\(^{16}\)O and H\(_2\)\(^{18}\)O) on ice matrix. The process of isotope fractionation is further promoted by the fact that during snow metamorphism different snow grains do not behave equally in terms of their mass balance. Tendency to equilibrium in the whole snow matrix requires that small grains disappear while bigger ones become larger (Colbeck, 1982). Thus, growing grains may be easily enriched in heavy isotopes.

\(^1\)Here we use the term “condensation” for vapor-to-solid phase transition instead of more correct terms “resublimation” or “inverse sublimation” to simplify the text.
Finally, even during the “layer-to-layer” processes the isotope fractionation may not be totally ruled out, because the low diffusion coefficients may be compensated by huge isotope gradients forming in the upper layers of the snow grains, and by huge specific area of grains in snow thickness (Golubev et al., 2000).

The physical parameters affecting the intensity of the PD processes are described in Town et al., 2008; Waddington et al., 2002. The most important factor is snow temperature which defines the water vapor pressure, as well as the coefficients of diffusion and fractionation. Second important parameter is snow accumulation rate which is inversely related to the time that a given snow stratum spend in the active upper layer of snow thickness exposed to the influence of atmosphere. The vertical scale of this active layer is of the order of 0.4–2 m (Neumann and Waddington, 2004; Town et al., 2008). Note that these two factors usually counteract one another due to positive correlation between air temperature and precipitation rate in the cold regions of our planet (Schwerdtfeger, 1984). Third important factor is the intensity of so-called “wind pumping” of air into snow, that accelerates mass exchange and, in turn, depends on wind speed and surface roughness (form and size of micro-relief). Finally, snow properties are also important, first of all, ice grain size and shape and, to less extent, snow density. They determine mass exchange between ice matrix and water vapor in the pore space.

One of the first evidence of possible alteration of snow isotope content after deposition were given by Epstein and Sharp (1965), who pointed out at enrichment of snow by heavy isotopes due to the depth hoar formation in the vicinities of the South Pole. This effect was then repeatedly noted at various sites in Antarctica (Ekaykin et al., 2002; Satake and Kawada, 1997; Watanabe et al., 1988) and other world’s regions (Friedman et al., 1991; Golubev et al., 2002; Hachikubo et al., 1997; Stichler and Schotterer, 2000; Stichler et al., 2001; Sturm and Benson, 1997; Wang et al., 2008).

Noticeable change of the upper snow isotope composition due to intensive sublimation in the Alps region was demonstrated by Moser and Stichler (1974). Negative correlation was shown between isotope content of snow in Siberia and correspond-
ing snow thickness, which is interpreted as the above mentioned dependence of the PD processes on the accumulation rate (Konishchev et al., 2003). Similar result was achieved in Antarctica on the scale of ~1 km during the study of isotope content and snow build-up in the vicinity of Vostok Station (Ekaykin et al., 2002). This may be explained both by mechanism of “relief-related” noise formation and by the PD effects (Ekaykin, 2003). The PD changes of snow isotope content was used to explain the isotope record in ice core drilled at site “Taylor Mouth” (Neumann et al., 2005) which otherwise would be difficult to interpret.

A possible importance of the PD effects for the formation of the snow isotope content in central Antarctica (Vostok and Komsomolskaya) was demonstrated by the fact that the isotopic records extracted from the snow thickness better correlate with “effective” temperature of upper snow thickness (mainly defined by summer temperature) than by mean annual air temperature (Ekaykin et al., 2007; Golubev, 2001; Lipenkov et al., 2004).

A few laboratory experiments were undertaken to demonstrate and quantitatively describe the alteration of snow isotope content due to mass exchange of snow with atmosphere, or inside the snow (Golubev and Sokratov, 1991; Hachikubo et al., 2000; Moser and Stichler, 1974; Neumann et al., 2008; Satow and Watanabe, 1985; Sokratov and Golubev, 2009; Sommerfeld, 1983; Sommerfeld et al., 1987, 1991). As a result of them, the existence of the isotope alteration due to mass-exchange was proven. It was shown that the intensity of these PD changes is positively related to the snow temperature, and is additionally strengthen by the vertical temperature gradient in snow which causes water vapor density gradient and thus enhances the mass exchange. It was also demonstrated that the isotopic fractionation during the PD processes takes place in non-equilibrium conditions, as is evident from low deuterium-oxygen 18 slope (of the order of 3–4 comparing to the value of 8 typical for the initial snow, Dansgaard et al., 1973).

However, these experiments have not brought enough data to give quantitative characteristic of the isotopic alteration during the PD processes in different natural condi-
tions. Partly this is because the experiments were made in relatively warm range of temperature (mostly above −15°C and none below −30°C).

This is why we developed an experimental program aimed to broaden the databank on the PD modifications, and to extend the data to the range of the low temperatures. In the next sections we present the experimental set-up and methods, and discuss the preliminary results of the experiments.

3 Experimental methods

3.1 Set-up

The laboratory experiments were carried out in 2007–2008 at Institute of Low Temperature Sciences (ILTS) of Hokkaido University (Sapporo), Japan. The set-up was developed by the authors with participation of S. Sokratov (Moscow State University, Russia) and J. Okuyama (then at ILTS), and constructed by technical staff of ILTS (M. Ikeda).

The set-up was designed to achieve the aim of the experiments: to monitor the evolution of the vertical profile of snow isotope content under controlled conditions in the temperature range down to that typical for central Antarctic summer season (−35°C).

The requirements for the experimental set-up were stated as follows:

1. Isothermal conditions in snow under controlled value of temperature.

2. Possibility to monitor mass- and isotope balance, and snow properties during experiment.

The scheme of the set-up used in experiments that is believed to meet the above requirements is given in Fig. 1.

The main component of the set-up is the experimental box made of thermo-insulated material (foam plastic) with the dimensions 52×52×51 cm, and with the wall thickness...
of 15 cm. Inner (work) chamber of the box has horizontal dimensions of 20×20 cm and the volume of about 9920 cm³. In the cover of the box there is a hole (about 1.5 cm in diameter) for the access of the pump tube (see below) and electrical wires.

The walls of the work chamber were sheathed by copper plates (about 1 mm in thickness) to improve the insulating properties and to equalize the temperature in the chamber.

On the lower side of the cover (i.e., in the upper part of the work chamber) the following equipment is placed: a 50-watt electrical lamp used as a heater, and a fan (the same type as used as a PC processor cooler). The lamp is placed near the mouth of the pump tube (through which the cold outer air is pushed into the chamber) and its work is governed by the temperature controller. The fan works constantly during the experiments to create the isothermal conditions in the chamber, as well as to simulate the natural process of wind pumping. In order to shield the snow samples from the direct influence of the fan, the transparent plastic screen was placed below it.

In the work chamber four equal plastic containers are placed having cubic shape with sides of 10 cm. Thus, in each experiment 4 equal snow samples participated with the total snow volume of up to 4000 cm³. Initial snow height in all the experiments was 10 cm, except the first one where it was 6.8 cm. Each container is placed on the separate drawer (Fig. 1), which allowed fast access to samples during experiments without significant disturb of the temperature conditions. However, for the “warm” experiments (above −15°C) it proved out that the drawers became frozen to box by the frost, so we had to open the cover to take out the samples. The influence of temperature jumps related to the sample treatment on the results of experiment may be considered as negligible.

The temperature and humidity sensor was placed between the plastic screen and the containers, just above the initial snow surface. As the sensor we used logger MR6662 by “Chino” (Japan) with the following characteristics: measurements range of temperature and humidity is from −40 to +60°C and from 0 to 100%, respectively; accuracy of temperature is ±0.5°C in the range −5~50°C and ±1°C beyond this range;
accuracy of humidity is ±3% in the range 5–60°C, while for the negative temperatures
the accuracy is not given in the certificate (not defined).

Aside from the box, the laboratory set-up comprises the temperature controller (to
govern the heater in the box), the pump to push air inside the box (with the discharge of
10 l/min), as well as the moisture source. The latter represents a cardboard box filled
with 10–15 kg of snow. The inhaust tube of the pump is pushed in the center of this
snow. Since the isotope content and temperature of the snow are known (the latter
is equal to the average temperature in the cold room), we may calculate the absolute
humidity of the air sucked by the pump, as well as the isotope content of the water
vapor of this air. The calculations are based on the assumption that the pumped air is
always in mass and isotope equilibrium with the snow in the moisture source. Indeed,
the time needed to establish the equilibrium between the ice grains and the pore air in
snow is of the order of few (tens) of seconds (Neumann et al., 2008). During this time
the pump sucks roughly 1–4 liters of air, which is 1–2 orders of magnitude less than
the total volume of pore air in the moisture source. Moreover, the mass of water vapor
pumped during this time interval is at least 5 orders of magnitude less than the mass
of the snow in the moisture source.

Thus, the introduction of the moisture source to the experimental set up has allowed
us to control the mass and isotope content of the moisture coming into the work cham-
ber.

We made 2 identical experimental set-ups and placed them to different cold rooms
with air temperature of −50 and −20°C. The −20°C room set-up was equipped by an
additional controller which switched off the pump in case when the air in the room rose
above the temperature of an experiment. This could happen during periodical shut
down the compressors to defrost.

A number of preliminary experiments have been carried out to study the thermo-
insulation properties of the box, which showed that it may be used for the experiments
with the difference between inside and outside temperature of at least 60°C. The max-
imum real difference during our experiments was about 25°C, which is well below this
limit. In case if the heater is switched off (and so is the pump), the temperature inside the box is equilibrating with that in the cold room with the rate of about 0.15 h\(^{-1}\) (i.e., when the difference is 10°C, the temperature in the box would change by 1.5°C in 1 h). This value is for an empty box, while the box filled with snow would be more thermally inert due to increased mass.

### 3.2 Procedure

As the snow samples we used natural snow of two types: hard winter precipitation at Sapporo with an isotope content of −67‰ (for δD) and deposited snow from the upper part of Vostok (central Antarctica) firn with an isotope content of −440‰. The samples were prepared by a dry method, i.e., the snow was thoroughly mixed under the temperature of −20°C, without melting, in order to homogenize its isotope content. The snow was put to the containers and weighted, followed by taking samples for the grain size and isotope content.

The containers are placed into the work chamber, and an experiment begins. The pump constantly pushes air from the moisture source, which is then heated by the lamp and mixed by the fan. The relative humidity of the incoming air is always 100%, but it drops in the chamber due to the heating. Together with the ventilation, it favors the sublimation of the snow samples.

On the 1st and the 5th days of experiment preliminary weighting of the samples are done in order to estimate the mass loss rate and to define the duration of the experiment. The experiment lasts until the loss of roughly 80% of the initial mass, but not longer than 60 days. The latter restriction is defined by the length of the warm period in central Antarctica, during which most of the PD changes take place. On estimating the total duration of the experiment (τ), the timing of the successive sampling is defined as 1/4 τ, 1/2 τ, 3/4 τ and τ.

Before each sampling, volume and weight are measured for all the samples to calculate snow density, and then the snow is cut for the isotopic probes. For it, the snow is taken out from the containers (even under the temperature of −35°C the snow grains...
freeze to each other so that the sample represents consolidated, rather than loose, material) and cut into horizontal layers with the thickness of 1 cm. Each of these layers represents an individual isotope probe, while the ensemble of the probes taken from one snow sample describes the vertical profile of the isotope content of this sample. Then, the successive isotope probing of all the four samples during and in the end of the experiment allows to follow the evolution of this vertical profile in time, as long as the sublimation proceeds. The only assumption behind this scheme is that the isotopic properties of all the snow samples in the work chamber are identical in given moment of time.

The air temperature and humidity in the work chamber was logged with the interval of 1 min for the first three experiments (which proved to be an oversampling), and 10 min for the rest of the experiments.

3.3 Mass and isotope balance

The experimental scheme described above allows monitoring all the components of the mass balance during the experiment (Fig. 2). Installation of the moisture source into the scheme gave the possibility to estimate the mass of the water vapor coming into the work chamber \((m_{\text{in}})\). The outcoming part of the balance \((m_{\text{out}})\) may be calculated based on the temperature and relative humidity inside the chamber, assuming that the latter equal to the humidity of the air leaving the chamber. The difference between outcome and income gives the net snow sublimation \((s)\), which, in turn, can be defined directly by successive weighting of the snow samples. Finally, the mass balance is expressed as:

\[
dM_{\text{snow}} = -s = m_{\text{in}} - m_{\text{out}}.
\]

Here \(M_{\text{snow}}\) is the snow sample mass; \(m_{\text{in}}=F\ p_v\), where \(F\) is the incoming air flux equal to the pump discharge, and \(p_v\) is the absolute humidity of the air \((\text{g m}^{-3})\) coming from the moisture source, \(p_v=217\ e_{\text{ms}}/(273.15+T_{\text{ms}})\) where \(e_{\text{ms}}\) is the saturated vapor pressure under the temperature of the moisture source, \(T_{\text{ms}}\) \((\text{°C})\);
\[ m_{\text{out}} = F 217 h \frac{e_{\text{ex}}}{(273.15 + T_{\text{ex}})} \]
where \( h \) is the relative humidity as measured by the logger inside the work chamber, \( e_{\text{ex}} \) is the saturated vapor pressure under the temperature of the experiment, \( T_{\text{ex}} \).

The scheme of the isotope balance is significantly more complicated, and its components cannot be defined robustly. The main problems are unknown isotope content of the water vapor inside the chamber, and impossibility to measure the gross mass fluxes into and out of the snow.

We developed a simple model of the isotope balance for our experiments. The isotope content of the water vapor of the air inside the work chamber above the snow samples is defined as (Fig. 2):

\[
d(M_{\text{air}} R_{\text{air}}) = m_{\text{in}} R_{\text{in}} + m_{s-} R_{\text{snow}} - m_{s+} R_{s+} - m_{\text{out}} R_{\text{out}}, \quad (2a)
\]

where \( M \) – mass, \( R \) – isotope content of, correspondingly, water vapor in the box (air), incoming (in) and outcoming (out) moisture, snow (snow), as well as of the moisture fluxes into and out of the snow (\( s+ \) and \( s- \)). The values of \( M_{\text{air}}, m_{\text{in}}, R_{\text{in}}, R_{\text{snow}} \) and \( m_{\text{out}} \) are known \((R_{\text{in}} = \alpha_T R_{\text{ms}})\), where \( \alpha_T \) is the temperature-dependant fractionation coefficient (Merlivat and Nief, 1967) and \( R_{\text{ms}} \) is the isotope content of snow in the moisture source; isotope content of outcoming moisture is taken equal to that inside the chamber \((R_{\text{out}} = R_{\text{air}})\); the isotope content of the vapor condensating into the snow is related to the isotope content of the air moisture by the fractionation coefficient \((R_{s+} = \alpha_T R_{\text{air}})\); and the sum of the moisture fluxes from and to the snow is equal to the measured sublimation \((s = m_{s-} - m_{s+} = m_{\text{out}} - m_{\text{in}})\). \( R_{\text{air}} \) is set equal to \( R_{\text{in}} \) in the beginning of the model run, and then it is calculated as \( R_{\text{air}} + dR_{\text{air}} \) at each computational step.

In turn, the isotope balance of the snow is defined as:

\[
d(M_{\text{snow}} R_{\text{snow}}) = m_{s+} R_{s+} - m_{s-} R_{\text{snow}} \quad (2b)
\]

An uncertainty remains related to the values of fluxes \( m_{s+} \) and \( m_{s-} \). In our model, we assume that the gross moisture flux from the snow to the air is equal to the net snow sublimation taken with an amplification factor \( k \):

\[
m_{s-} = k s \quad (3)
\]
Then, the $k$ value may be defined by tuning the model in such a way that the simulated function $R_{\text{snow}} = f(M_{\text{snow}})$ corresponds to the measured one.

4 Preliminary results of the experiments

4.1 Experimental conditions and snow properties

In Fig. 3 we showed as an example the data recorded by the temperature/humidity logger during Experiment 6 carried out in the $-20^\circ\text{C}$ cold room of ILTS with the temperature of experiment being about $-5^\circ\text{C}$. The duration of the experiment was 61 days, the data resolution was 10 min, and the total number of the data points is about 17 600.

The data show that the temperature conditions were quite stable during the experiment with the standard deviation of the values being $\pm0.17^\circ\text{C}$. According to the relationship between experimental temperature and the corresponding isotope PD effect, this temperature error can be translated into the $\delta D$ error of roughly $\pm0.2‰$ (see Sect. 4.2), which is well below the standard accuracy of mass-spectrometric isotopic measurements. Thus we conclude that the stability of the temperature conditions was sufficient for the aims of the experiment.

The results of the humidity measurements demonstrate three step-like drops of the values from 73% in the beginning of the experiment to 36% in its end that correspond to the time of the successive snow sampling. Obviously, the humidity in the box is proportional to the sublimation rate ($\text{g day}^{-1}$), which is, in turn, related to the area of the snow surface.

The data shown in Fig. 3 has allowed to calculate the sublimation rate in the way described by Eq. (1) and compare it with the measured values, as shown in Fig. 4. Average values of calculated and measured sublimation are very similar, though their variability differs. The measured sublimation rate slightly grows in the course of the experiment likely due to decreasing humidity in the chamber, which fosters sublimation. At the same time, the calculated values of the sublimation demonstrate considerable
decrease from about 600 to about 350 g m$^{-2}$ day$^{-1}$. This discrepancy may be explained by the uncertainty of measured humidity values in the chamber, which is due to 2 main reasons:

1. the instrumental error, related to the difficulty of measuring relative humidity under low temperatures;

2. the methodological uncertainty, i.e. systematic difference between the measured value and the true value of humidity in the air outcoming from the chamber. Unlike the air temperature that is supposed to be similar in the different part of the chamber (except the immediate neighborhood of the heater and the tube supplying cold air) due to the air mixing, the air humidity by definition cannot be homogeneously distributed inside the chamber. The humidity is minimal in the upper part of the chamber (close to the source of the dry cold outer air) and maximal at the snow surface, where it should tend to 100%. This gives the negative vertical gradient of humidity, which make the sublimation possible. Thus, the lowering of the calculated sublimation, which in fact means an overestimation of the decrease of the humidity in the outcoming air, may be attributed to the increased distance between the humidity sensor and the snow surface due to snow mass loss by sublimation (during Experiment 6 the snow height decreased from 10 to 3.4 cm).

The sublimation rate measured in the different experiments (with the chamber temperature between $-5^\circ$C and $-35^\circ$C) ranged by 1 order of magnitude between 40 and 570 g m$^{-2}$ day$^{-1}$. As expected, sublimation rate is significantly related ($R^2=0.89$) to the temperature:

$$s = 559.16 \times e^{0.0737T}.$$  

Interestingly, the present-day typical values of summer surface air temperature and sublimation rate at Vostok Station, $-32^\circ$C and 50 g m$^{-2}$ day$^{-1}$ (Ekaykin, 2003), correspond well to this relationship. We thus suggest that this equation may likely be used for rough estimation of Vostok sublimation rate under different temperature conditions.
The snow density of the samples during nearly all the experiments remained stable or slightly increased, which may be related to the snow compaction and metamorphism. The only exception is Experiment 6, during which the density decreased from 0.43 to 0.32 g cm$^{-3}$. Partly it may be related to the error of density measurements, since in the end of the experiment the snow surface became highly uneven, which prevented precise measurement of the snow volume. Another possible reason is the intensive snow sublimation at the surface that could have led to the hoar layer formation, which is confirmed by slight increase of the crystal grain size by the end of the experiment.

4.2 Isotope modifications

Figure 5 summarizes the isotope data currently available as a result of the experiments. A preliminary analysis of the curves reveals several characteristic features, of which the main are as follows:

1. The PD modification of the snow isotope content does exist, and is noticeable even for the low temperature ($-35^\circ$C).

2. The PD effect strongly and positively depends on temperature.

3. Influence of minor factors can be seen that disturb the influence of temperature (note that the PD effects for Exp. 2, $-15^\circ$C, are apparently weaker than those for Exp. 5, $-25^\circ$C), which will be the focus of future studies.

4. The time evolution of the vertical isotope profiles seems to have some general features for all the experiments. At first, a strong isotope modification takes place in the uppermost snow layer. Then this wave of isotope changes propagates deeper into the snow thickness, while the previously enriched uppermost snow layer is removed by the sublimation. Thus, the isotopic enrichment of the snow surface tends to a certain limit, which is defined by counteracting of the enrichment rate and sublimation rate, both being dependant on temperature. The depth of the
“isotope wave” propagation tends to a limit, too, varying from 1–2 cm for lower temperature (−35°C) to about 4 cm for higher temperature (−5°C).

In Fig. 6 we plotted the isotope change due to the PD processes in the course of the experiments (i.e., mean isotope content of the snow remaining after sublimation minus that of an initial snow sample), ΔD, as a function of the relative mass loss, Δm. Interestingly, for all the experiments except Experiment 4, all the data can be approximated by a single line, disregarding the experimental temperature, sublimation rate and initial snow properties\(^2\). Thus the relative mass loss of the snow thickness due to sublimation may be an integral characteristic of the PD process intensity, which comprises the other factors.

The only parameter that is similar for these experiments, but different for Experiment 4, is the air circulation inside the work chamber. Usually, after sampling the snow from a plastic container, we turned the empty container upside down and put back to the chamber in order to maintain the geometry of the empty space in the latter. In case of Experiment 4, after sampling we did not turn the containers and put them back to the chamber by open side up in order to investigate the importance of the chamber geometry. This lead to larger volume of the empty space in the chamber and likely to a more effective mass exchange between snow and air, so that the same net sublimation resulted in stronger isotopic modification. In nature, similar effect may be achieved by stronger “wind pumping”.

We also calculated the relationship between the sublimation rate and the PD isotope change. It proved to be significantly \( r = 0.55 \pm 0.17 \) related by a linear function:

\[
\Delta \delta D = 0.00576 s + 1.1
\]

\(^2\)It can be easily shown that the \( \Delta \delta D/\Delta m \) slope remains nearly similar disregarding the initial snow mass. Indeed, if we multiply the initial mass by a factor of \( n \), the relative mass loss will be \( n \) times less; but the \( \Delta \delta D \) value will decrease by a factor close to \( n \), too. Only if relative mass loss is close to 100%, will the gradient be considerably affected.
We use the Eqs. (4) and (5) in order to translate the typical variability of temperature measurements into that of the final PD effects (see Sect. 4.1). According to Eq. (4), the error of ±0.17°C leads to uncertainty of the sublimation rate equal to about 4.8 g m\(^{-2}\) day\(^{-1}\) for the temperature of −5°C (the lower is the temperature, the less is the corresponding temperature effect, for −35°C the sublimation rate uncertainty being roughly 10 times less). In turn, the latter, according to Eq. (5), gives the uncertainty of ΔδD equal to 0.2‰, which is less than the mass-spectrometric instrumental accuracy and can be considered as negligible.

4.3 Mass transport inside the snow thickness

We used the data on the snow isotopic enrichment during the experiments to tune our simple isotope model, Eq. (2), and estimate the value of the gross mass flux between the snow and the overlying air. The calculations show that the isotopic modification of the uppermost 1-cm layer of snow samples corresponds to the amplification factor \(k\) (see Eq. 3) varying between \(10^1\) and \(10^2\). This means that real mass transport inside the snow thickness, and between snow thickness and atmosphere, is 1–2 orders of magnitude larger than the observed net sublimation. Similar results have been obtained by the 3-D X-ray tomography observations of metamorphism in snow pack (Sokratov et al., 2004).

We thus argue that the monitoring of the isotopic modifications in snow may be used as an indicator of mass transport in laboratory (and in some cases in field) studies of snow metamorphism and mass balance.

4.4 Implication for ice core isotope-temperature paleo-reconstructions

The results shown in Fig. 6, provided they are confirmed in the future studies, lead to a conclusion that is potentially important for the PD effect corrections in the ice core isotope-temperature paleo-reconstructions. In fact, the intensity of the PD changes in snow cover depends on two main factors: 1) wind pumping (or, generally, intensity of
air ventilation in the firn), which defines the slope of the PD changes versus relative mass loss, and 2) relative mass loss, which in turn is a function of the sublimation rate (mainly defined by temperature), the duration of the sublimation period, and the initial snow mass defined by precipitation rate.

We use this assumption to preliminary estimate possible changes of the PD isotopic effect in the remote past. For example, during the Last Glacial Maximum (LGM) epoch (about 25–30 kyr BP) at Vostok Station mean annual air temperature was \( \approx 10^\circ \)C lower, and the snow accumulation rate was about two times less than now (Salamatin et al., 2009). Assuming that the annual temperature amplitude has not changed (which is not obvious), then the summer surface snow temperature was \(-42^\circ\)C, and the sublimation rate (according to Eq. 4) was about two times lower than now. Since relative mass loss may be roughly calculated as the total summer sublimation divided by the annual accumulation, it was nearly the same at the LGM time as now, i.e. 10–20%. Then the isotopic enrichment of the snow thickness was the same, too (which requires another assumption that the wind pumping has not changed), and no significant correction of the isotope-temperature reconstruction is needed, in accordance with the results of the PD effects modeling (Town et al., 2008).

However, one cannot expect that the degree of the PD snow enrichment at Vostok was always constant. This is due to the non-linear relationship of sublimation rate and temperature, and due to not absolutely precise correlation between temperature and accumulation rate in the past.

### 5 Conclusions

In this work we described in detail the laboratory experiments aimed to investigate the PD isotope effects in snow thickness, and presented some preliminary results.

In total, 8 laboratory experiments on the snow PD processes have been carried out in the temperature range from \(-35\) to \(-5^\circ\)C. We found relatively strong isotopic enrichment in surface snow layers due to mass- and isotopic exchange with atmosphere
even for low temperatures (−35°C) typical for Central Antarctica. As the temperature increases, the isotopic modifications strengthen exponentially.

It has been demonstrated that isotopic enrichment in the snow thickness can be approximated by two main factors, air ventilation of the snow thickness and the relative mass loss due to sublimation. The latter is linearly related to the change of the mean isotopic content of the remaining snow, while the slope of the relationship is defined by the first factor. We tried to apply this approach to derive possible PD effects during the LGM period at Vostok Station and came to a conclusion that it was a similar value as present day, due to similar relative snow mass loss in the course of summer sublimation. However, this approach involves several assumptions, and its results are quite sensitive to the error of the estimations of the past values of temperature and accumulation rate.

We used a simple isotopic box-model to interpret the results of the experiments, which showed that the observed isotopic modifications can only be explained if the real mass transport between the snow thickness and atmosphere, as well as inside the snow, is 1–2 orders of magnitude larger than the observed net sublimation rate. It means that the resultant (net) sublimation can be considered as a small difference of two strong opposite fluxes, from snow to air and back. From our point of view, this is an example of how isotopic method can be used in the study of snow mass balance and metamorphism.

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Fig. 1. The scheme of the laboratory set-up designed to study the alteration of snow isotope content due to mass exchange with atmosphere. See details in the text. A photo of the set-up is shown on the right.
Fig. 2. The scheme illustrating the mass and isotope balance during the experiments. See explanations in the text.
Fig. 3. The changes of temperature and humidity in the work chamber of the experimental set-up during Experiment 6.
Fig. 4. The changes of snow sublimation rate during Experiment 6: calculated values are shown by dots, while real measurements are done by solid line.
Fig. 5. The changes of snow isotopic content during the experiments. All the experiments (8 in total) are grouped into 2 rows (according to the snow used, Sapporo or Vostok) and 4 columns (according to the temperature of an experiment). The isotope data are shown as the deviations from an initial value (about $-67\%$ in the case of Sapporo snow and about $-440\%$ in the case of Vostok snow). The samples from Experiment 8 and partly Experiment 7 are not yet processed.
Fig. 6. Isotope change in snow during the experiments (mean isotope content of snow remaining after sublimation minus mean initial isotope content of snow samples) as a function of relative mass loss due to the sublimation. Blue: data from all the experiments except Experiment 4. Red: data from Experiment 4. Open diamonds: data from Sokratov and Golubev (2009).