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MASTER'S THESIS

Influence of Post-Depositional Processes on the Stable Water Isotopic Composition in Snow and Air

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Submitted by

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Abstract

Stable water isotopes ($H_2{}^{16}O, HD{}^{16}O, H_2{}^{18}O$) obtained from snow and ice samples of polar regions are used to reconstruct past climate variability. However, post-depositional processes like snow sublimation and snow metamorphism can affect the isotopic composition of the snow which forms later the ice. In order to fully understand and interpret the ice core proxy it is important to understand the mechanisms possibly changing the snow signal even after deposition. In this work, an experimental study on the effect of snow metamorphism and snow sublimation on the snow isotopic composition in controlled laboratory conditions at temperatures of -2 °C, -7 °C, -16.5 °C and -40 °C is presented. The influence of isothermal snow temperatures and snow structures on the isotopic content in the snow and interstitial water vapor is elucidated. Further, the impact of sublimation on a snowpack was analyzed. Snow metamorphism inside snow packs with different properties (SSA & density) led to a vapor pressure gradient. This induces an exchange of stable water isotopes between the layers, altering the isotopic content of each snow layer. A rearranging of more than 3 ‰ is already visible after four days for snow with same isotopic composition but with snow layers of different structural properties in all measured temperatures. The difference of 13 ‰ in $\delta^{18}O$ (additionally to the difference in the snows structural properties) decreased over 32 days 8 ‰ respectively 1 ‰ in the neighboring layers (depending on the temperature: the warmer the temperature the larger the change). Sublimation of a snow cover showed a decrease of $\delta^{18}O$ in water vapor over time, while the snow cover got enriched. In the experiments at -2 °C an isotopic gradient evolved in the snowpack. Compared to the top layers the lower layers of the snow were enriched the most. The vertical gradient increased with ongoing snow sublimation from 0,06 ‰ after 12 h to 0,59 ‰ after 65 h. These results show that snow metamorphism and sublimation need to be taken into account when using stable water isotopes as proxies for climate reconstruction or even for understanding the hydrological cycle. These findings might help to think about refining the interpretation of ice core data. Furthermore, the results of this thesis highlight that post-depositional processes should be incorporated into isotope-enabled numerical earth system models to be able to correctly simulate the evolution of the isotope composition of the cryosphere and atmosphere in cold regions.

Contents

1 Introduction

Currently climate change confronts humanity with new challenges. To better understand currant climate change and to estimate future scenarios, reconstructions of the past climate help to identify (natural) drivers of climate change. Many different proxies are used to reconstruct past climate variabilities, such as the chemical and isotopic composition of speleotherms, microfossils or ice cores. A well-established proxy used for climate recoonstruction are stable water isotopes in ice cores ($\mathrm{H_2}\,^{16}\mathrm{O}, \mathrm{HD}\,^{16}\mathrm{O}, \mathrm{H_2}\,^{18}\mathrm{O}$) (Dansgaard, 1964) (see for example orange data in Figure 1).

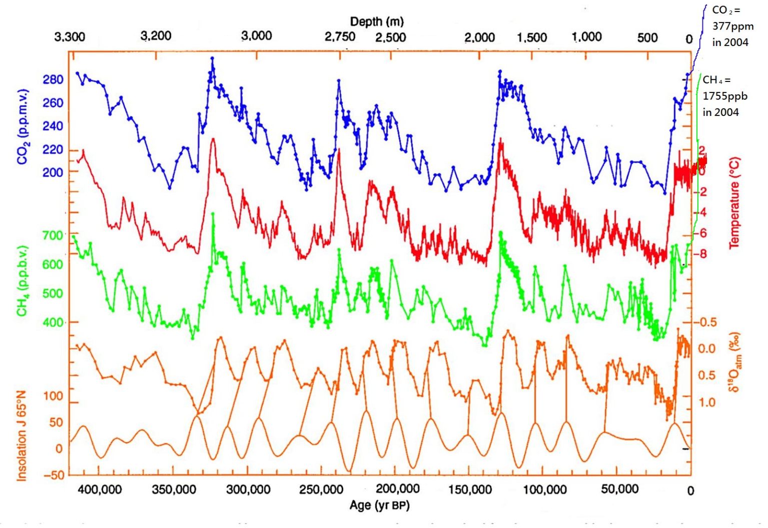


Figure 1: Climate reconstruction of the past 400'000 years using CO_2, CH_4, insolation, $\delta^{18}O$ and temperature variations. "File: Vostok 420ky 4curves insolation.jpg - Wikimedia Commons". (n.d.)., available at: https://commons.wikimedia.org/wiki/File: Vostok_420ky_4curves_insolation.jpg mediaviewer/File:Vostok_420ky_4curves_insolation.jpg (accessed 6 February 2020).

1.1 Stable Water Isotopes in Snow

The applicability of stable water isotopes as climate proxy is derived from the so-called isotopic fractionation, which describes the enrichment of one isotopologue (from now on always referred to as isotope) relative to another during a phase change. There are two types of isotopic fractionation. Equilibrium fractionation occurs due to the thermodynamic effect that lighter isotopes ($\mathrm{H_2}\,^{16}\mathrm{O}$) have higher vibrational and rotational energies (thermodynamic property) and therefore are more volatile. Due to its quantum mechanical nature, equilibrium fractionation is temperature dependent. This fractionation process is well-constrained theoretically (Bigeleisen, 1961) and from laboratory experiments (Majoube, 1971; Horita and Wesolowski, 1994; Merlivat and Nief, 1967). The second type is the non-equilibrium fractionation which is dependent on the molar mass and is controlled by the diffusion velocity of the different molecules.

To quantify the isotopic enrichment or depletion of a water sample, a standard reservoir to calculate a relative abundance is defined. The relative abundance is defined by the δ-notation, which is the ratio (R) between heavier and lighter isotopes compared to the defined standard ratio of the Vienna Standard Mean Ocean Water (R_{VSMOW}) from the International Atomic Energy Agency:

$$\delta = \left(\frac{R_{sample}}{R_{VSMOW}} \right) * 1000\% \tag{1}$$

$$R = \frac{\text{heavy molecules}}{\text{light molecules}} \tag{2}$$

For δ^{18}O, the lighter molecule is ($H_2{}^{16}O$) and the heavier molecule is ($H_2{}^{18}O$), for δD the lighter molecule is ($H_2{}^{16}O$) and the heavier molecule is ($D\,{}^{16}O$). In addition, a second-order isotope variable deuterium excess (d-excess) can be used as a measure of non-equilibrium effects (Dansgaard, 1964):

$$\mathrm{d-excess} = \delta\mathrm{D} \ - 8 \ * \ \delta^{18}\mathrm{O} \tag{3}$$

Once snow is deposited, it undergoes a variety of different processes affecting the properties of each snow layer, which also affect the isotopic composition of the snow: Redistribution and mixing by wind, metamorphism induced and controlled by temperature gradients and moisture content, changes induced by new precipitation, sublimation, condensation, rimming and evaporation (Figure 2).

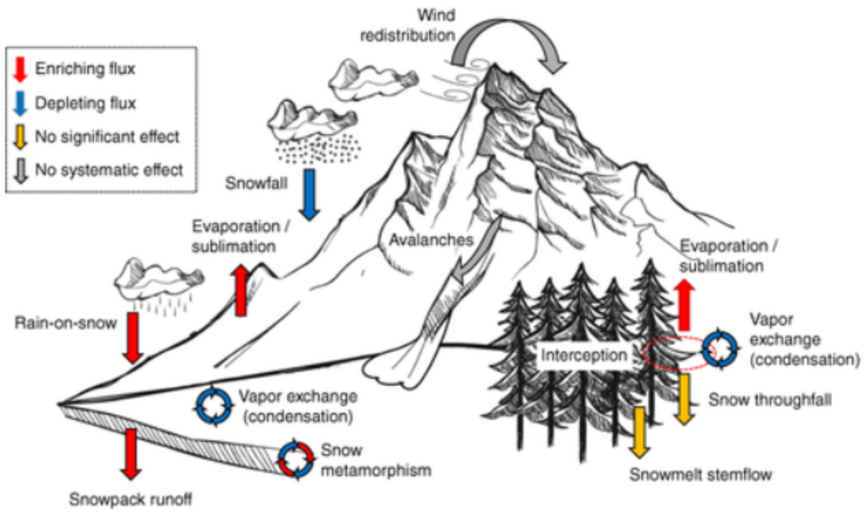


Figure 2: Fluxes leading to an enrichment or depletion of stable water isotopes in the snowpack, showing sublimation as enriching flux and metamorphism as enriching as well as depleting flux. (From Beria et al., 2018, Graphic based on original work from www.freepik.com)

1.2 Stable Water Isotopes During Post-Depositional Processes

Accurate knowledge about precipitation, vapor and the isotopic composition of snow is needed in order to properly interpret the variability of stable water isotopes in snow that later forms the ice from which ice cores are retrieved.

1.2.1 Snow Sublimation

Simple schemes like trajectory-based boxmodels as well as more recent general circulation models use the basic assumption that the sublimation of snow causes no isotopic fractionation (Sokratov and Golubev, 2009; Risi et al., 2010; Werner et al., 2011). Already in 1975, Moser and Stichler suspected that isotopic fractionation at the snow-air interface leads to an enrichment in heavy isotopes of the snow. Recent studies confirm this early finding by showing that sublimation of a snow cover indeed causes isotope fractionation (Sokratov and Golubev, 2009; Steen-Larsen et al., 2014; Christner et al., 2017; Ebner et al., 2017). As surface snow sublimates, the residual snowpack is enriched in heavier isotopes (Beria, 2018).

There are three different concepts on isotopic fractionation during snow metamorphism and sublimation. The first concepts suggests no change, the second and third concept suggest change in the isotopic signal triggered by sublimation.

1. The so-called onion model suggests a "layer by layer" sublimation (Taylor et al., 1991). Therefore, no fractionation would take place in the snowcover and the isotopic signal of the sublimation flux/snow crystal should not change over time .

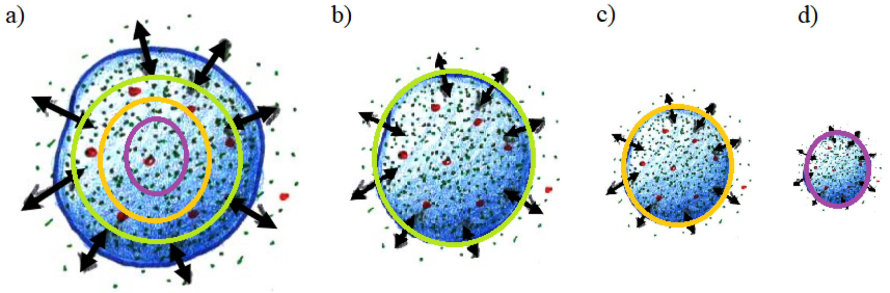


Figure 3: The onion model: layer by layer the snow crystal size decreases without changing the crystals isotopic composition.

2. The second concept is based on the idea that due to recrystalisation of snow fractionation also takes place during sublimation, whereby ^{18}O preferentially stays in the snow and ^{16}O goes into the vapor phase. In Figure 3 this would mean that the green snow crystal (Figure 3b) would be enriched in $\delta^{18}O$ compared to the blue snow crystal (Figure 3a) and the smallest crystal (Figure 3d) would have the highest $\delta^{18}O$ value. This then also means that the recrystalisation cycle due to snow metamorphism is able to transfer the fractionated vapor in a snow cover therefore moving the isotopic signal.

3. The third concept splits the isotopic signal change due to sublimation into two regimes. In the cold regime with temperatures below -7 °C no fractionation happens (corresponding to the onion model) and a warm regime over -7 °C where fractionation takes place because of a melt water formation at the snow surface (Christner et al., 2017). Therefore, change in the isotopic composition of the sublimated vapor depends on the surrounding temperature.

If fractionational processes during snow sublimation and metamorphism take place, then not only the climatic conditions at deposition are reflected in the isotope signature but also post-depositional processes such as sublimation, recrystallisation and diffusion shape the water isotope signal in cores. There is still a lack of understanding regarding these post-depositional processes, which limits the interpretation of isotopic signals from ice cores (Casado et al., 2018; Ritter et al., 2016). Casado et al.(2018) found, that for these post-depositional processes the continuous exchange between the atmosphere and the snowpack is particularly important.

1.2.2 Air-Snow Interactions

The lower atmospheric conditions at high altitudes is mainly controlled by the large-scale atmospheric flow. This results in time-varying micro-climatic conditions influencing the top snow layer between precipitation events (Trachsel et al., 2019). Depending on the large-scale flow situation strong moisture fluxes between the snow and the air can impact the water isotope signal of the snow (Casado et al., 2018). Thus, post-depositional processes can lead to variations in the isotopic signals of the surface snow which are strongly influenced by the variability of the atmospheric forcing. The isotopic signal of the surface snow can show a different signal than expected from precipitation input, as shown by Casado et al. (2018) for several measurement sites in Antarctica. Changes in δ^{18}O caused by sublimation penetrate to a snow layer depth of about 5-10 cm (Stichler et al., 2001). Steen-Larsen et al. (2014) establish a quantitative link between the near-surface vapor and the surface snow by showing that the temporal variability of δ^{18}O of the snow surface is similar to δ^{18}O in water vapor in the boundary layer. Furthermore, they observed a strong correlation between δ^{18}O in near-surface water vapor and air temperature.

Based on air temperature, Christner et al. (2017) suggested two regimes of post-depositional isotope variation, a cold regime defined as surface temperature (T_{skin}) maximal sublimation temperature ($T_{\text{subl,max}}$)= -7.7 °C and a warmer regime defined as $T_{\text{subl,max}}< T_{\text{skin}}< 0$ °C. They suggest a non-fractionating sublimation of snow for the cold regime and fractionating evaporation of meltwater forming at the snow surface for the warmer regime. The uncertainty of the determined threshold temperature ranges from -11,9 °C to -2,9 °C. An isothermal and temperature gradient experiment carried out by Ebner et al. (2017) at around -15 °C, where δ^{18}O-interaction between snow and air was observed, showed a change of the isotopic signal in snow of about 7.64 ‰ after 24 h and 15.06 ‰ after 84 h, compared to the original δ^{18}O isotope signal. The change in δ^{18}O of the atmospheric water vapor after 24 h was much higher at 19,9 ‰. The water-vapor-saturated airflow used in this experiment had an isotopic difference of up to 55 ‰ to the snow. Measurements at about -6 °C of Stichler et al. (2001) show a change in δ^{18}O change of snow 4 ‰ in 78 h. For comparison, between a glacial and an interglacial climate state δ^{18}O changes by around 5 ‰ (Ruddiman, 2001).

A mechanistic explanation of the change in isotopic ratio due to snow sublimation is the process of re-crystallization and diffusion of vapor to be the main factors influencing the change in isotopic content (Sokratov and Golubev, 2009). The repetitive phase transition in the re-crystallization process as well as the preferential diffusion of light water isotopes in the unsaturated pore space are thought to be responsible for the observed fractionation effect. Both processes are highly temperature dependent. Steen-Larsen et al. (2014) observed a δ^{18}O change in near surface vapor δ^{18}O of 0.85 ± 0.11 ‰ per degree air temperature change. Changes in δ^{18}O of vapor and δ^{18}O of snow occur simultaneously but the amplitude of the changes in δ^{18}O in snow is smaller most of the time. Although 6-20 % of the surface snow mass is exchanged with the atmosphere Steen-Larsen et al. (2014) were not able to identify any systematic relationships between sublimation rates and the trends in δ^{18}O in snow. They conclude that changes in δ^{18}O in snow are driven by synoptic changes in atmospheric δ^{18}O in the vapor composition.

Laboratory experiments established equilibrium fractionation factors describing the partitioning between the condensed phase and the vapor phase under saturated conditions as a function of temperature (so-called equilibrium fractionation factors) (Merlivat and Nief, 1967; Neumann et al., 2008; Ellehoj et al., 2013). However, non-equilibrium effects in the snow cover in under saturated conditions can lead to departures from the fractionation predicted by the equilibrium fractionation factors. These non-equilibrium effects during snow sublimation have not yet been addressed in detail in dedicated laboratory experiments.

The isotopic signal from precipitation in ice cores used for climate reconstructions can thus be superimposed by a signal from air-snow interactions in between precipitation events, if the analyzed snow-layer is exposed to the overlaying/overflowing air mass for a long time. An example for this would be in a low accumulation area. The overflowing air masses carrying water vapor, with a different isotopic signal than the snow, can have an impact on the snow if air-snow exchange fluxes are strong. This mechanism therefore introduces a "post-depositional noise" (Ebner et al., 2017) and thus air snow interactions might play an important but yet underestimated role for past climate reconstructions.

The studies mentioned above highlight the importance of recrystallization and bulk mass exchange within the snow surface layer. To incorporate these processes into numerical atmospheric models and to be able to realistically simulate the temporal variability of the isotopic signal of atmospheric and cryospheric water masses, their influence on the isotopic signal needs to be better understood and quantified. To achieve this, especially the role of metamorphism has to be better understood.

1.2.3 Snow Metamorphism

Through vapor exchange, heat flow and pressure the size and shape of a snow grain changes when undergoing metamorphosis. There are different types of snow metamorphism. Firstly there is wet and dry metamorphism (Colbeck, 1982). In the experiments carried out in this project only dry metamorphism occurred. The main factor forcing dry metamorphism is the snow surface energy balance which leads to a decrease in the snow surface area (SSA) in order to get to a better balance between surface area and volume and reach thermodynamic equilibrium. A differentiation in dry snow metamorphism is made due to different temperature gradient regimes. There is an equi-temperature (isothermal) metamorphism (ETM) and a temperature gradient metamorphism (Pinzer and Schneebeli, 2009). ETM produces rounded grains through a coarsening process induced by a sintering stress, resulting in a densification over time. In this process large grains grow at the expense of smaller grains (Colbeck, 1982). The sintering stress is mainly controlled by temperature. The process is faster at warmer temperatures as seen in the 3-D structure of the ice matrix during isothermal metamorphism at different temperatures (Kaempfer and Schneebeli, 2007). Similar ice matrix structures were found after 11 weeks at -2 °C and at -8 °C after 23 weeks, at -19 °C a similar structure was not reached until week 45 (Kaempfer and Schneebeli, 2007). Important to mention is that at -54°C almost no snow metamorphism was seen (Kaempfer and Schneebeli, 2007).

Over 12h 60% of the ice mass is redistributed and after about two days a complete turnover of the ice mass is seen (Pinzer et al., 2012). Therefore, a massive vapor exchange takes place. The question that arises is if an isotope fractionation process also takes place alongside it. Diffusion of water at the ice surface depends on the temperature but a free diffusion following a Brownian pattern is not expected until the inter facial liquid layer is at least three full molecular layers thick (Bartels-Rausch, 2014). If there is only a thin layer of free ions the exchange is described as an ice surface hopping mechanism (Carignano et al., 2007). Therefore, temperature dependent fractionation during metamorphism could be possible. Gofiantini et al. (1963) observed different δ^{18}O measurements in the fine grained unmetamorphosed winter layer of summer snow (higher δ^{18}O values) and the coarse-grained recrystallized summer layer of winter snow (lower δ^{18}O values). They speculated if the metamorphism/temperature or the air circulation above were responsible for this change. A strong correlation between near-surface vapor δ^{18}O and air temperature was found by Steen-Larsen et al. (2014).

Summer being the most important season for post-depositional isotopic exchange in firn, Neumann and Waddington (2004) suggests that higher temperatures and longer periods of air-snow interaction are more important for post depositional change in the isotopic composition. Furthermore, they found that air-snow isotopic composition is realistically never in equilibrium. A mass redistribution is governed by different vapor pressure. Therefore, if there is a temperature gradient material is redistributed into the direction of colder temperatures, trying to reach an equilibrium in vapor pressure (Pinzer et al., 2012).

1.3 Objectives

The objective of this thesis is to verify the hypothesis that the isotopic signal in the air and the snow changes over time due to post-depositional processes like snow sublimation and snow metamorphism. Furthermore, we would like to assess the sensitivity of these isotopic changes with respect to the prescribed isothermal temperature regime. We will address the following research questions:

1. How can metamorphism between snow layers with different properties change the isotope signal over time?
2. How does snow sublimation influence the isotopic composition of water vapor and the snow cover in an environment in which we expect strong effects of vapor diffusion in the snow cover?
3. Does isotopic fractionation during snow sublimation depend on temperature in a highly undersaturated environment?

The experiments were performed in the cold chambers at the WSL Institute for Snow and Avalanche Research (SLF) in Davos, Switzerland.

2 Instruments

2.1 Artificial Snow Generation

The snowmaker (Figure 4) at SLF producing nature-identical snow was used to create snow for the experiments. The snow sample was created with de-ionized tap water in the cold laboratory at around -16.5 °C following a procedure similar as described in Schleef et al. (2014).

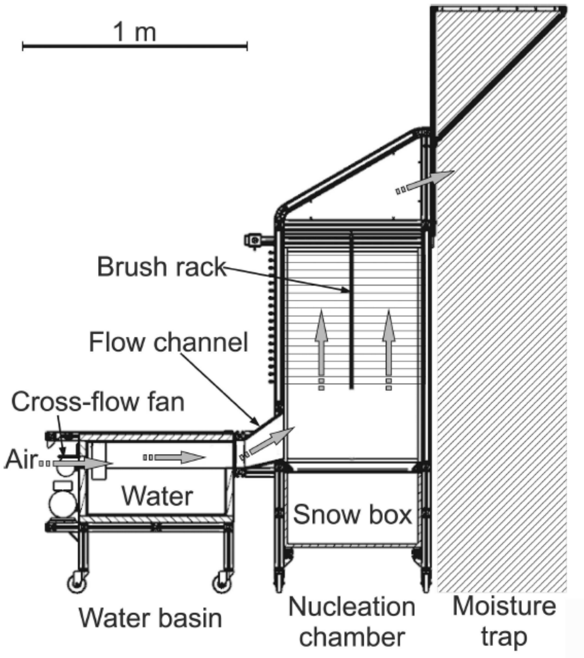


Figure 4: Sectional drawing of the snowmaker from Schleef et al. (2014). The gray arrows indicate the flow of the airstream.

Based on the supersaturation principle a water bath was heated to 30 °C, cold air was blown over the water. The resulting vapor was blown into a chamber at -16.5 °C containing nucleation strings on which snow crystals can grow. A brush rack brushes the snow crystals from the strings into the collecting container. In these conditions the snow has a SSA of around 59 mm^{-1}, a density of about 100 $\mathrm{kg/m}^3$ and crystals which can be most closely classified as bundles of elementary needles grow (see Figure 5)(Schleef et al., 2014).

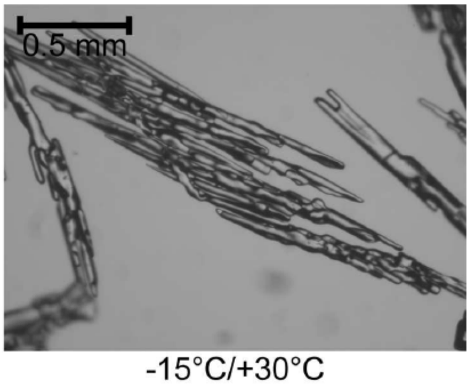


Figure 5: Picture of a typical snow crystal grown at -15 °C from Schleef et al. (2014).

As this machine might have an influence on the isotopic content of snow because of the fractionation during phase changes, the snow was always mixed before being used to get a snow mass as homogeneous as possible. The δ^{18}O content of that snow measured in 10 samples taken at the same time at a mean of -12,97 ‰ with standard deviations between 0,03 and 0,15 and a variance of 0,52.

2.2 Laser Spectrometric Measurements of Snow Samples and the Vapor Phase

To measure the isotopic content in the snow samples and in the sublimated vapor, a piccaro water isotope cavity ring-down laser spectrometer was used (Set-up in Figure 6). Different isotopic molecules differ in rotational-vibrational energy which leads to an isotope characteristic transition frequency in the near-infrared region of the spectrum (Kerstel, 2004). Laser spectoscopic systems use nearby absorption peaks in the near-infrared regions to identify the isotopes (Aemisegger et al., 2012).

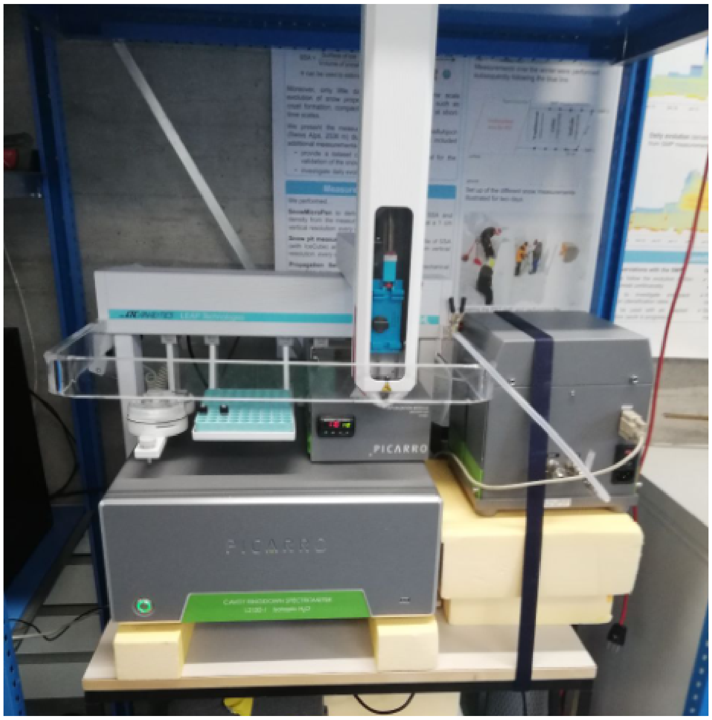


Figure 6: Set-up of the picarro with the SDM on the right.

Room air was sucked in to the standard delivery module (SDM) through a first desiccant before traversing a pump. Afterwards, the air traversed a filter (added because of the black powder produced by the malfunctioning pump) before going through a second desiccant. This dry air then was lead into the vaporizer. For the calibration a depleted standard (UBG) and an enriched standard (Millipore) were used. These standard waters were lead into the vaporizer to produce the vapor to be measured in the picarro. In the laboratory in Davos only the vapor measurements of Experiment 3 were taken, the measurements of the snow samples were taken with a picarro at ETH Zurich (by the Sustainable Agroecosystems group at ETH). For this the samples had to be taken, melted and refilled into the measuring tubes which were then sealed with parafilm and transported to Zurich.

2.2.1 Post Processing: Calibration

To analyze the measurements of the picarro analyzer they had to be calibrated. Especially because the vapor measurements were done by a different analyzer than the snow sample measurements. To get a stable signal high enough and stable water vapor values are needed, therefore only these runs were used for the calibration process. The calibration runs of the depleted standard (shown in Figure 7) measured at a mean of 34.43 ‰.

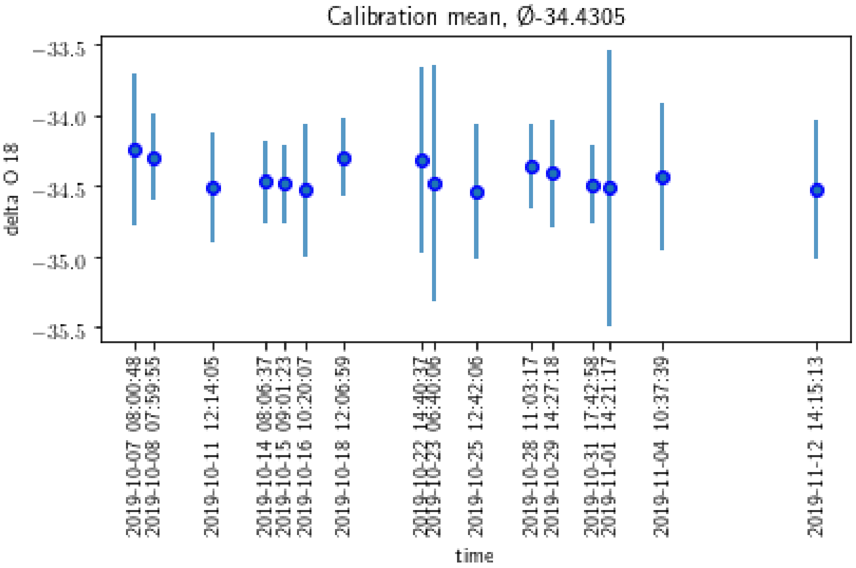


Figure 7: All calibration runs over the measuring period, standard deviation of the measurement as error bar.

Unfortunately no calibration runs of the enriched standard were usable. None of the calibration runs had high and stable enough water vapor values because of the malfunctioning pump of this standard. The values of the depleted standard (compared to earlier calibration runs of this analyzer) were in the measuring uncertainty. Therefore, the value of the enriched standard of earlier calibration runs were used to calibrate the data.

2.3 Computer Tomography of Snow Samples

To measure the 3D structure of snow and to characterize the snow sample (SSA and density) the micro-computed tomography (micro-CT) scanner at SLF in Davos was used (see Figure 8). The CT scanner preserves the snow structure which made it possible to measure the snow evolve over time using the same sample. Many other methods to characterize snow destroy the snow while taking the measurements. In the CT scanner a snow sample is irradiated from the front by a micro-focus energy source. In the back of the measuring chambre a sensor measures the radiation that the sample does not absorb. The extent of the materials X-ray attenuation depends on the selected energy source and the scanned material. For our measurements default values for fresh snow were chosen. Layer by layer the sample is irradiated. The measurement of each of our samples took 88 minutes at a diameter of 30 mm and an approximate height of 20 mm and a resolution of 18 micrometer voxel size. Using hagenmuller segmentation the density and SSA of the samples was then calculated.

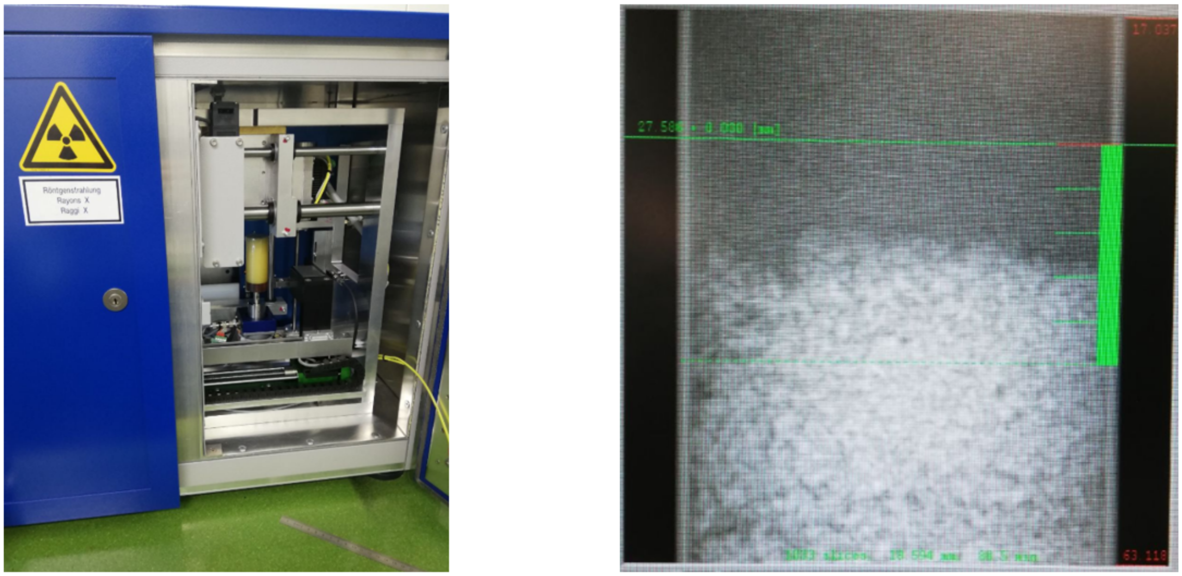


Figure 8: CT scanner with a sample in it (left) and a picture of choosing the section of the sample which was to be measured (right).

3 Methods

In order to investigate possible changes in oxygen isotope composition caused by post depositional processes like snow metamorphism and sublimation, a number of experiments were set-up. To investigate if in the experiments a fractionation would take place, each experiment was carried out in different isothermal temperature regimes. Firstly, a “warm” regime was tested with temperatures close to 0 °C (comparable to the non-fractionating sublimation regime described by Christner et al. in 2017). For practical reasons at least -2 °C were used because the temperature in the cold chamber can vary slightly and therefore snow could easily thaw at 0 °C. Secondly, an “intermediate” regime was tested with temperatures close to -8 °C (comparable to the cold regime described by Christner et al. in 2017). And thirdly, a “cold” regime was tested with temperatures close to -15 °C and below (comparable to measurements of Ebner et al., 2017). Temperatures fluctuated in and around the snow during the measuring period ±1 °C. Therefore, mainly dry metamorphism is expected to occur since all temperatures are below -2 °C.

The first step for all three experiments was the preparation of snow with a known isotopic composition. The snow was produced as described in Section 2.1 Artificial snow generator. An exception was the isotopic depleted snow in experiment two, for this experiment older natural snow was used.

3.1 Experiment 1: Isothermal Snow Metamorphism in a Two Layer Snow Sample With an Old and New Snow Layer

In order to produce an age difference in our snowprofile the snow for the bottom layer had to be produced in advance and sintered for some time. The to be sintered snow was sieved (2 mm) into an isotherm box and sintered at -5 °C for 10 days before preparing the “new” snow and filling the samples. The density of the sintered snow measured at 205 kg/m^3 and the fresh snow at around 125 kg/m^3. Approximately 15 cm high aluminum cans with a diameter of 6.4 cm were used as sample holders. They were cut open at the top and filled with a layer of wax to level the bottom. The sintered snow was gouged with those cans and the snow was cut at the desired height of 6 cm (see Figure 9, left). As the cans were now a little less than half full, new snow was sieved

(4 mm) into them to fill them to the rim (see Figure 9, middle). Each can was sealed air tight using cling film and tape.

Figure 9: Filling of the cans. Left: filling of the sinthered layer. Middle: filling of the fresh snow layer. Right: filled cans, ready to seal.

Then the cans were sealed and put into an isothermal box. 15 cans were filled following the same procedure. Three isothermal boxes each containing five cans were stored at temperatures of -2 °C, -8 °C and -16.5 °C. Samples were taken after 2, 4, 8, 16 and 32 days (Figure 10).

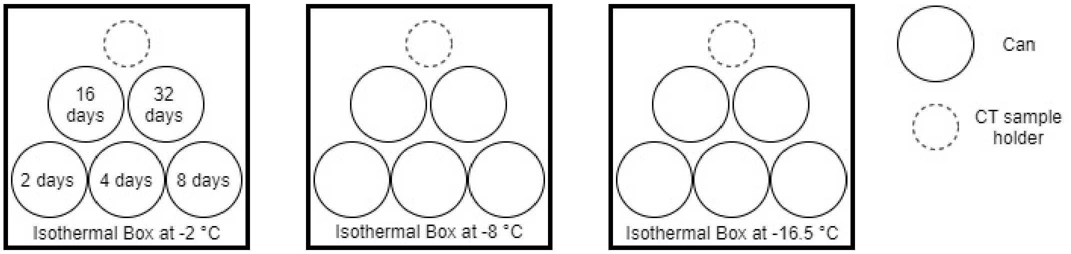


Figure 10: Experimental set-up, metamorphism Experiments.

To sample these snow profiles each can was split horizontally into six samples which then were filled into 15 ml sample holders (see Figure 11 and Figure 12). These bottles were additionally sealed with parafilm to avoid any fractionation when thawing. After thawing the sample was transferred into a 1.5 ml phial to analyze the isotopic composition. Additionally, for every temperature regime a CT sample holder was filled half and half with both snow types and scanned at the beginning and after 16 days. To control if the seen change between these layers can really be attributed to the different kind of snows an additional homogeneous filled can was put into each temperature regime.

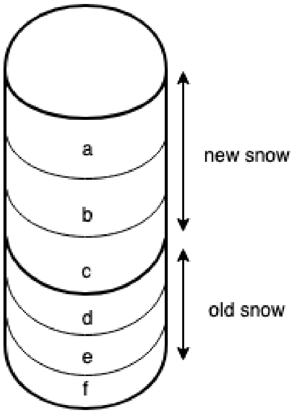


Figure 11: Scheme of a single can and the six samples, new snow on top and older snow on the bottom.

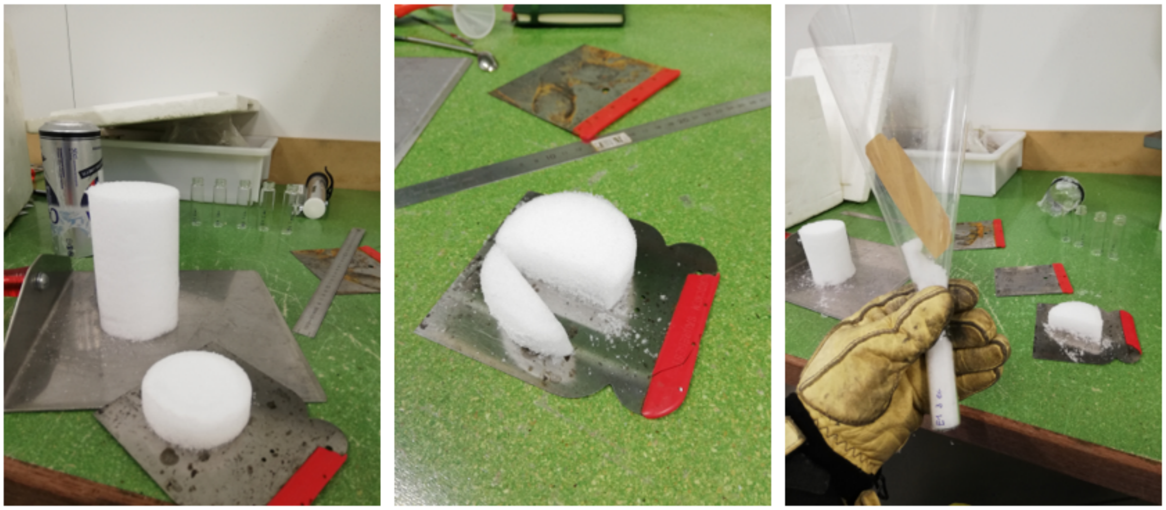


Figure 12: Slicing of the snow profile into the six samples, filling of the snow sample into the sample holder.

3.2 Experiment 2: Isothermal Snow Metamorphism With an Imposed Vertical δ^{18}O Gradient in Snow

For this experiment snow with different isotopic content was needed. There are many different ways to achieve that (see Appendix A). In the end snow that had been collected in Davos Tschuggen two years prior (28.01.2017) and then stored at -20 °C, was used as bottom layer. This snow had a δ^{18}O content of -23.53 ‰ ± 0,02 compared to the new produced snow from Davos tap water at around -11.66 ‰ ± 0,03.

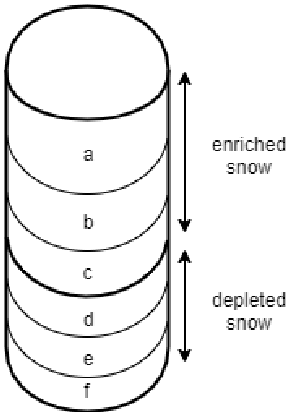


Figure 13: Scheme of a single can and the six samples, enriched snow on top and depleted snow on the bottom.

The two different kinds of snow were filled half and half into cans (Figure 13). The samples were taken following the same procedure as in experiment one. In addition to the three temperatures in the first experiment, measurements at -40 °C were taken also with an additional can that was not sealed.

3.3 Fractionational Sublimation of Snow

In order to investigate pure sublimation of snow in a vacuum, a series of experiments was set-up. The set-up of those experiments was the same, the only changing factor being the temperature and the running time. Temperature regimes were chosen similar to those in the metamorphism experiments at temperatures of -2 °C, -7 °C and -16.5 °C. The duration of the experiments was chosen to be 12 h, 24 h, 48 h and 60 h. After every experiment the box was opened and a snow profile with a resolution of 1 cm was taken.

For every experiment the snow was freshly sieved (4 mm) in, the snow was stored at the respective experiment temperatures a few hours before the experiment to get acclimatized. In addition, an experiment with ice was done using the same set-up at -2 °C/24 h.

To estimate the size of the box, a rough calculation for the needed snow volume was made. To calculate the snow volume (10) the exchange (8) (derived from the sublimation speed (4)) and the for the picarro needed flow rate (9) were approximated. The sublimation speed in (4) was estimated from Neumann et al. (2008). Using the molar mass of water (divided by the avogadro number) (5) the exchange speed was calculated (6). From this the amount of time for the exchange of the needed particles at 1 hPa (7) could be calculated (8).

$$\text{Sublimation speed(Sm)} \approx 0.05\text{g(g)/m}^3\text{(g)/s} \tag{4}$$

$$\text{Molar mass of Water: } 18.02 g/mol \rightarrow m = 2.99 \cdot 10^{-23} g/p \tag{5}$$

$$\text{Exchange speed (Es)} = \frac{Sm}{m} \rightarrow 1.67 \cdot 10^{21} p(s)/m^3(s)/s \tag{6}$$

$$\text{Pressure (P)} = 1hPa : 10^{16} p/cm^3 = 10^{22} p/m^3(g) \tag{7}$$

$$\text{Exchange (Ex)} = \frac{P}{Es} \cdot 1000 \rightarrow 5988s = \underline{99.8min} \tag{8}$$

$$\text{Flowrate (F)} \; = \underline{30ml/min} \tag{9}$$

$$\rightarrow \textbf{Vsnow=Ex} \cdot \textbf{F=2.99 l} \tag{10}$$

The box was constructed holding 9 l. Therefore, the box only has to be filled 1/3 with snow to achieve the minimally needed sublimation. To endure pressure the box was built out of acrylic glass in a cylindric form (Figure 14).

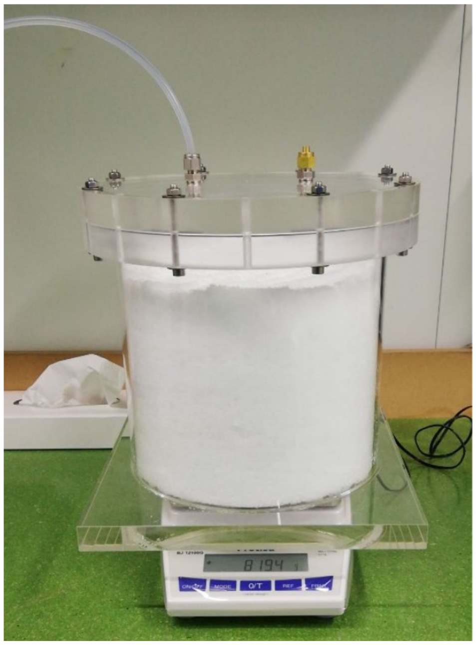
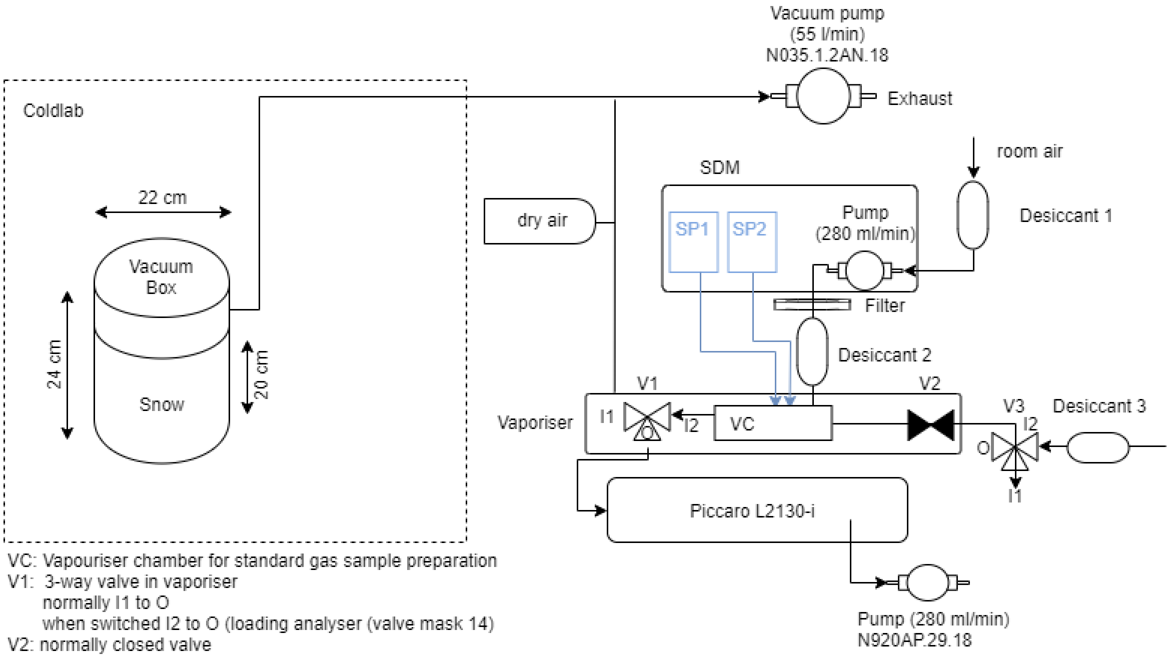


Figure 14: Picture of the vacuum box.



VC: Vapouriser chamber for standard gas sample preparation
V1: 3-way valve in vaporiser
normally I1 to O
when switched I2 to O (loading analyser (valve mask 14)
V2: normally closed valve
when switched vacuum overflow during sample preparation for calibration (valve mask 2)
V3: 3-way valve outside of vaporiser
normally I1 to O
when switched I2 to O (taking additional dry air during analyser loading, valve mask 14)
V4: Needle valve, for flow regulation of inlet pump

Figure 15: Schematic of the experimental set-up for the sublimation experiment.

The schematic of the general set-up of the sublimation experiment is shown in Figure 15. It is separated into the left part showing the set-up in the cold lab (dotted line around) and the right part showing the set-up outside at room temperature. Only the snow filled vacuum box was placed in the cold lab. The temperatures in the cold lab were varied between -2 °C, -7 °C and -16.5 °C. The box had to be screwed open and then close again to take measurements and refilled with new snow. The sealing ring between cover and box had to be warmed every time before the box was sealed so that the rubber was soft and could be compressed while closing so the box was sealed completely air tight. After sealing the box was weighed and affiliated to a tube reaching out of the cold lab to the measuring tool. To be sure that no small temperature changes were induced by the cooling system or by opening the laboratory door and disturbed the measurements, the box was put into an isotherm box and the tube was isolated and warmed with an anti freezing device. The rest of the set-up was stored outside the cold laboratory at room temperature to protect these machines from the cold temperatures. The airflow in the tube went from cold to warm air, therefore no measures had to be taken to prevent condensation in the tube outside the cold lab. The tube is connected to a vacuum pump to generate an under-saturated environment in the box to force the snow to sublimate. To find the ideal pumping rate, the rate was changed until the system generated the highest possible pressure in the box while still being able to generate a flow to the picarro. This stable system was reached when the pump was pumping at a pressure of 550 mbar introducing a pressure of 450 mbar onto the box. At this pressure the needed flow to the vapor analyzer of about 4.5 Ncc/m (Normalized cubic centimeter per minute) could be generated over the whole measuring period. In these conditions a flow directly out of the box starting at about 400 Ncc/m was measured, getting lower over time down to 17.5 Ncc/m after 90 h. The pumping induces a vapor pressure gradient inside the box respectively along the snow profile. Through a T-segment in the tube from the box to the vacuum pump, air was channeled off to the picarro (bottom right in Figure 15). If the needed airflow of 30 ml/min to the picarro would not have been attained, a bottle of dry air could be connected along the way. This airflow then traversed the vaporizer before being measured in the picarro. To calibrate the picarro a SDM was used. Between every experiment the syringes were rinsed before performing a calibration run. During the experiments temperatures in the snow, on top of the snow and next to the box were measured using IButtons.

4 Results and Discussion

4.1 Influence of isothermal snow metamorphism on the isotopic content of snow with different properties

In this section, the results of Experiments 1 and 2 are presented. Firstly, in Section 4.1.1 the results of Experiment 1 show how the isotopic content in the snow profile changes due to the vapor pressure gradient, induced by a different SSA and density of two snow layers. Secondly the results of Experiment 2 show how the isotopic content in the snow profile changes due to a isotopic gradient and a vapor pressure gradient.

4.1.1 Influence of the Vapor Pressure Gradient in a Snow Profile

In Figure 16, the time evolution of the isotopic profile in snow is shown. For δ^{18}O the starting profile is homogeneous over all layers. The difference in δ^{18}O between the top layers (a-c, fresh snow) and the bottom layers (d-f, 10 day old snow) value lies within the measurement uncertainty (standard deviation of the measurements of 0,04 and 0,07 ‰). After two days a shift in δ^{18}O can be seen. The top layers become enriched by approximately 3 ‰ at all temperatures. Layers d to f show as well an increase in δ^{18}O but not as constantly as layers a to c. The bottom layer stays at the starting value while d and e show a weak increase. After four days, a gradient in δ^{18}O starts to form more clearly. The bottom layer with old snow is now depleted while the top layer with fresh snow is still enriched. After eight days the δ^{18}O content in layers d to f increase again to the starting values. After 16 days the δ^{18}O gradient is very consistent between the three temperature regimes. All regimes show an increase in δ^{18}O from the bottom to the top. After 32 days, the green (-8 °C) and the blue (-16.5 °C) δ^{18}O gradient stay the same as after 16 days. Only the red line (-2 °C) shows a further increase in δ^{18}O in the bottom layers d to f.

To get a clearer view on how the gradient between the upper and the lower layer of snow evolved over time, Figure 18 summarizes the evolution of the δ^{18}O gradient over time. Four phases emerge, they are seen in all temperature regimes, but take longer at lower temperatures. The first phase is a rapid increase, a maximal difference is reached after two days in the warm regime, respectively four days in the intermediate and cold regime. In the second phase the difference decreases. In the third phase the difference

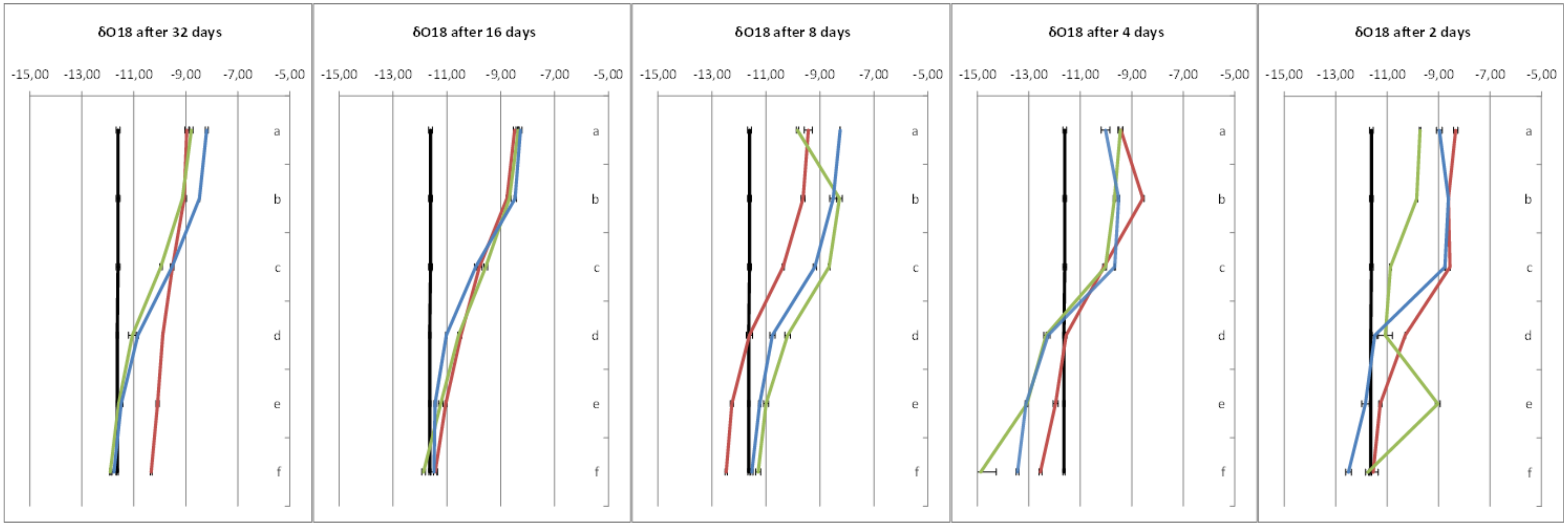


Figure 16: δ^{18}O content change over time at different temperatures in a snow profile. Each graph stands for one time step which show the snow profile after 2,4,8,16 and 32 days (from right to left). The x axis shows the isotopic content. The y axis shows the profile of the can from a on top to f on the bottom. The black line shows the profile of a hypothetical profile of the start (values were only once measured for the top snow and the bottom snow). The other colors each represent a temperature regime; in red the measurements at -2 °C (warm), in green the measurements at -8 °C (intermediate) and in blue the measurements at -16,5 °C (cold). Temperatures in and around the snow were in the measuring period ±1 °C those values. For each measuring point the standard deviation of the measurement is shown as error bar.

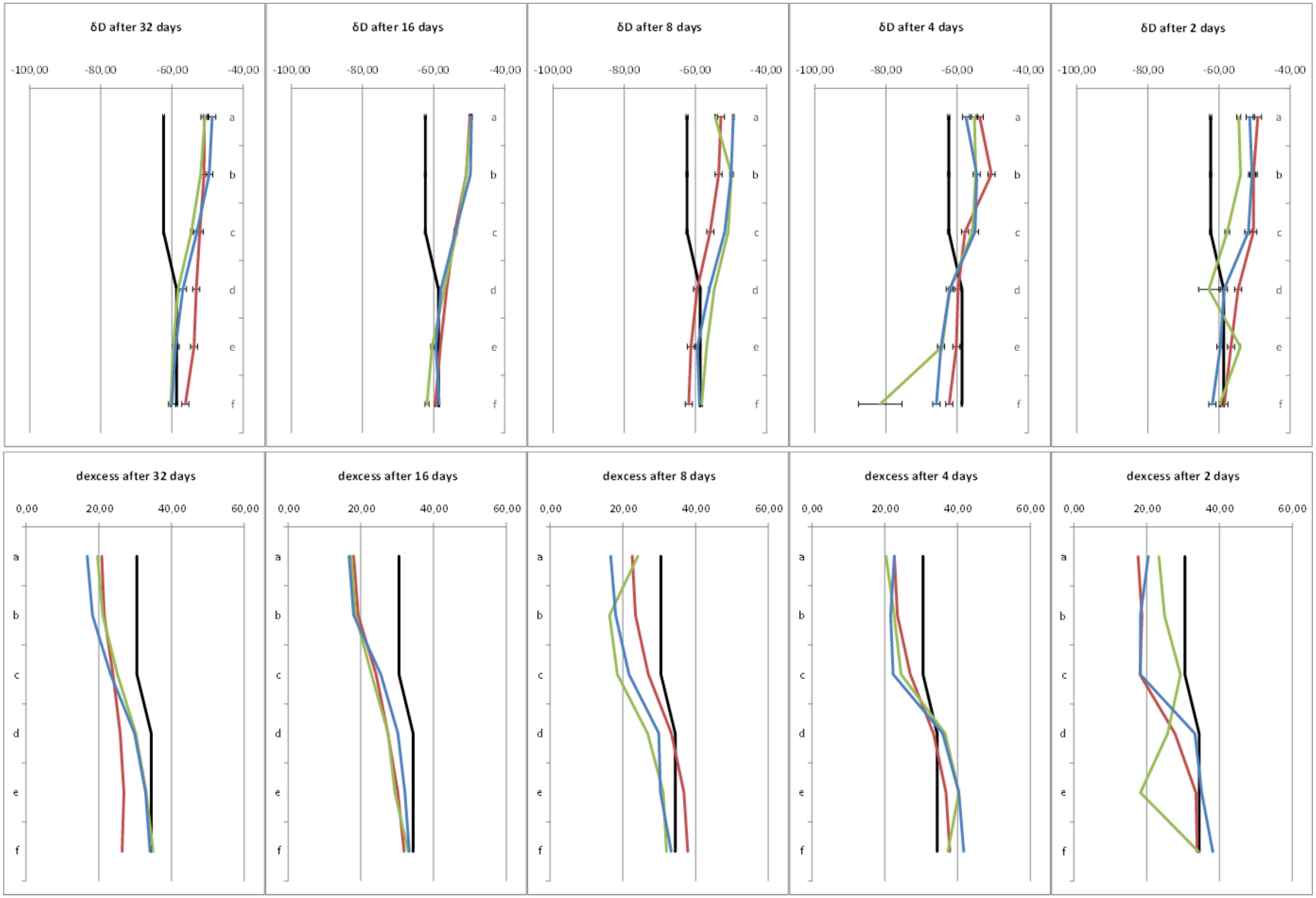


Figure 17: Figure 16 but for δD (top) and d-excess (bottom) over time at different temperatures in a snow profile

grows again, but do not reach the maximum. The fourth phase can only been seen in the intermediate and warm regime where the difference diminishes again.

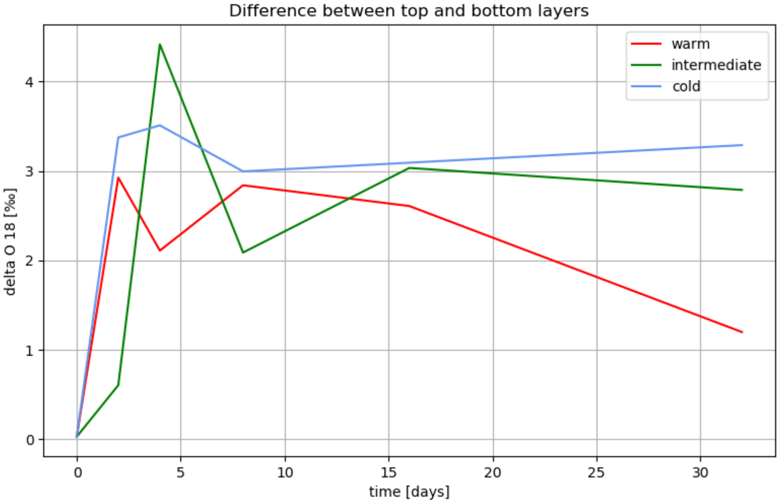


Figure 18: Evolution of the gradient between the top and the bottom two layers.

The measurements in δD generally show a similar evolution as δ^{18}O do (Figure 17 top). The enrichment of the top layers is already visible after two days, the gradient is strongest after four days and the values are most consistent between the temperature regimes until after 32 days. Except for the warm regime, which shows an enrichment in the bottom layers after 32 days, similar to δD. An explanation for the timelag in enrichment between the bottom and top layers could be isotopic fractionation during snow sublimation. The sublimation rates in old snow are lower than in fresh snow. Therefore, a possible enrichment of the snow due to snow sublimation during recrystallisation, occurs later in old snow compared to fresh snow.

The results of d-excess (shown in Figure 17 bottom) support this theory. D-excess shows a decrease in the top layers with time. The bottom layers show from days 2-8 an increase and from days 8-32 a decrease in d-excess. These results show that the isotopic signal changes during metamorphism. A combination of isotopic fractionation during snow sublimation and different saturation vapor pressure for old and fresh snow could explain the observed evolution in isotopic composition of snow in Experiment 1.

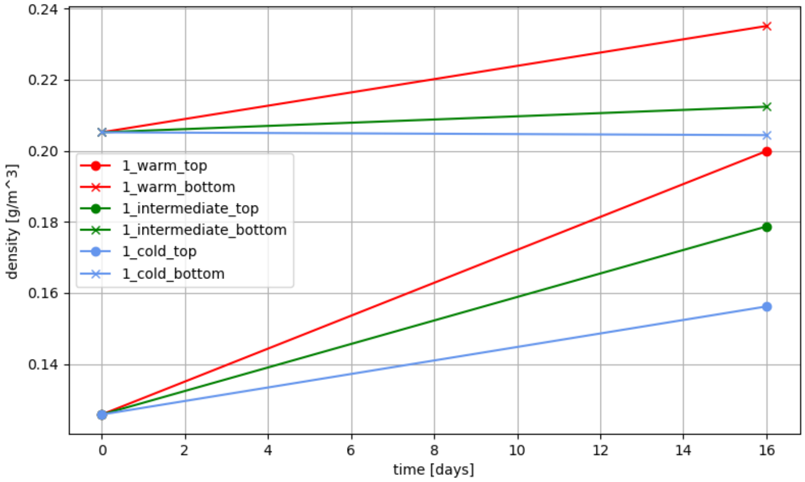


Figure 19: Density change of the top (points) and bottom (cross) layers at different temperatures over time.

In Figure 19 the development of the density in the two different layers of snow is seen. Clearly visible is the fact that at warmer temperatures the densification happens faster than at colder temperatures. Also it is visible, that the difference between the upper and the lower layer density gets smaller over time.

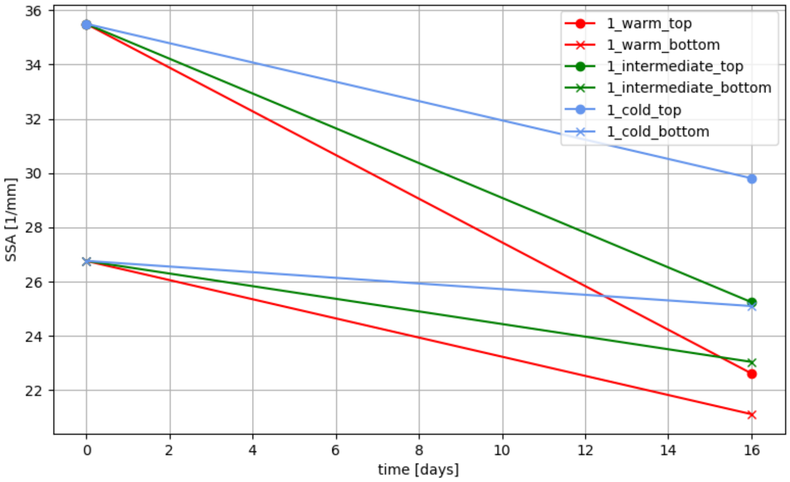


Figure 20: SSA change of the top (points) and bottom (cross) layers at different temperatures over time.

In Figure 20 the development of the SSA in the two different layers of snow is shown. After 16 days in the warm regime the SSA of the two snow layers is almost the same. In the intermediate and the cold regime the difference between the two layers also gets smaller but not as much.

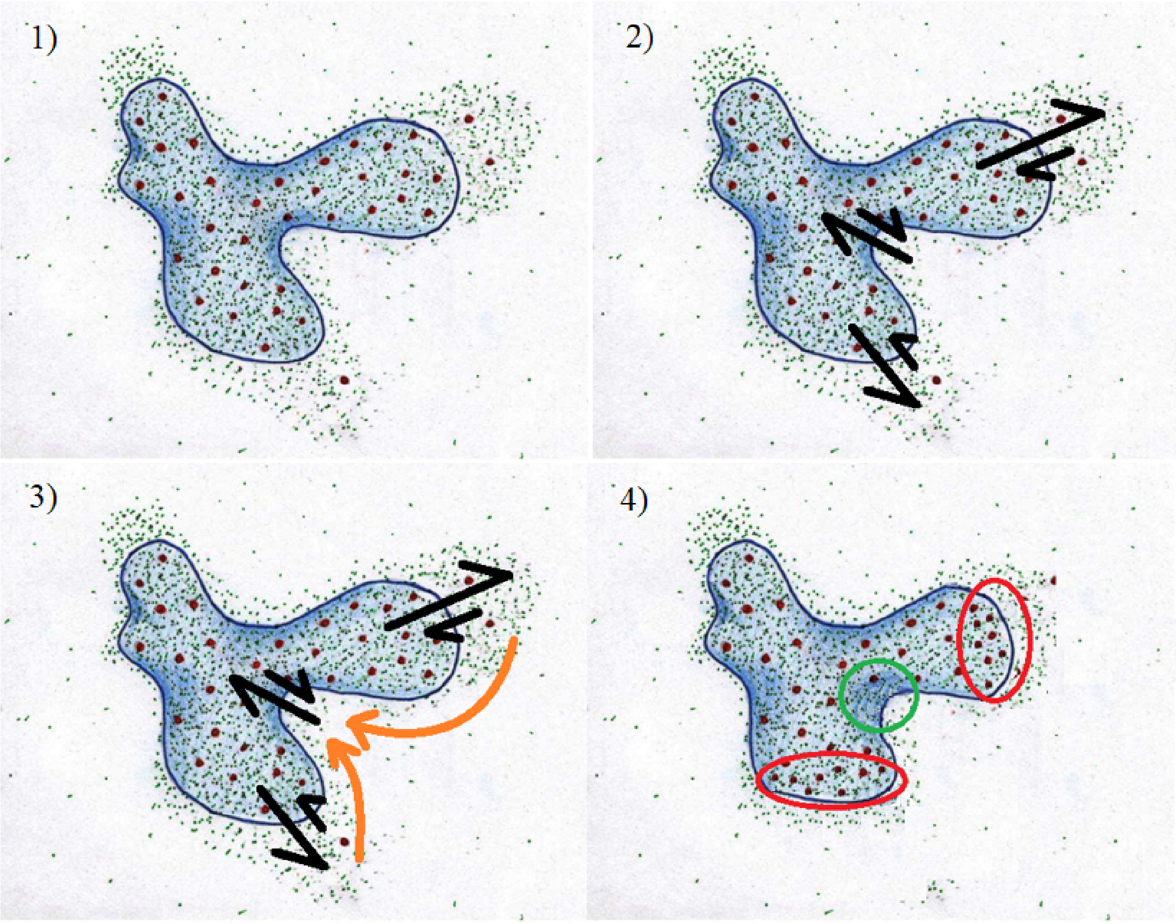


Figure 21: Isotopic fractionation during snow sublimation of a single snow crystal, showing the process step by step. In blue the snow crystal is shown, in red the heavy isotopes and in green the light isotopes. Large amounts of dots indicate high vapor pressure. The black arrows show the phase changes (2%3). The orange arrows show the vapor transport due to vapor pressure differences (3). As the metamorphosis progresses the snow crystal changes its form (4) and due to the fractionational process "shrinking" parts get enriched (red circle) and "growing" parts get depleted (green circle).

During snow metamorphism, the convex parts of a snow crystal shrink while the concave parts grow (Figure 21). If there is isotopic fractionation during snow sublimation, the concave and convex parts of a snow crystal have opposite δ^{18}O evolutions. On the one hand the convex parts of a snowflake becomes enriched in δ^{18}O because of a net flux into the vapor phase. The concave parts of the snow crystal on the other hand accumulate molecules into the solid phase. Therefore, δ^{18}O of the concave regions decreases. A small vapor pressure gradient between those parts emerges. Therefore, the depleted vapor flows from convex parts to concave parts (orange arrows in Figure 21) where it re-sublimates on the crystal. An indicator for snow sublimation during Experiment 1, is the observed increase in pressure in the cans during the experiment. This was visible by a rising of the foils which were tightened over the cans. Furthermore the mass balance for δ^{18}O is off balance after 16 days (around 1.5 ‰), there seem to be more heavier isotopes over all in the snow compared to the beginning. As the air got saturated in water vapor it also got depleted in δ^{18}O.

If these processes during snow metamorphism are translated to the bigger picture in Experiment 1 where new snow lies over old snow a shift in the isotopic signal is possible. The new snow exchanges molecules much faster because of the bigger SSA and faster metamorphosis than the old snow. This means, a vapor pressure gradient is created between the layers and a flow of the vapor from the upper to the lower layers takes place (black arrows in Figure 22). The depleted vapor travels to the lower snow layer, re-sublimates on the old snow crystals and depletes the lower snow layer isotopically (light green in the right of Figure 22), measured after four days. Additionally, the upper snow layer is isotopically enriched (red in the right part of Figure 22) because of the fractionation during sublimation. This increase in δ^{18}O and δD in the new snow and decreases in the old snow can be seen after two days of Experiment 1 (see Figure 16 and 17)).

Diffusion from the upper to the lower layers is also supported by the d-excess-profiles (Figure 17 bottom). The decrease in d-excess in the upper layers compared to the starting composition can be caused by diffusion. Because water molecules with a heavy hydrogen have a lighter diffusion velocity than water molecules with a heavy oxygen, d-excess decreases in the upper layers (new snow). A simultaneous increase in d-excess in the lower layers is seen, which would be expected due to diffusive effects.

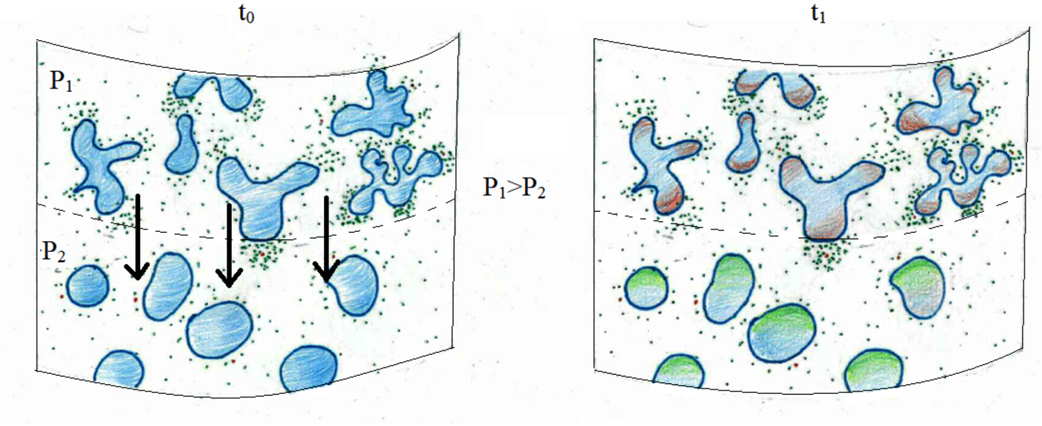


Figure 22: Isotopic frctionation during metamorphism. P_1 and P_2 are the saturation vapor pressure of the upper and lower layer, respectively. The difference between P_1 and P_2 is getting smaller over time (t_0 beginning, t_1 end of the experiment). Green crystals are depleted in δ^{18}O as green points symbolize molecules with ^{16}O, red crystals are enriched in δ^{18}O as red points symbolize molecules with ^{18}O.

The up and down of the difference between layers a&b and layers e&f (Figure 18) could be explained by the complexity of this process. The transport of the water vapor and the exchange between snow and air might vary in strength and speed over time.

In Experiment 1 with two different snow layers the three temperature regimes behave differently after the peak in δ^{18}O difference between lower and upper layers (Figure 18). The δ^{18}O-difference decreases for the warm and intermediate regime and stays constant for the cold regime. In the warm and intermediate regime, snow metamorphism is faster and the upper and lower layers have similar snow properties towards the end (Figure 20 & 27). Therefore, the layers equilibrate and the δ-values approach each other.

4.1.2 Homogeneous Snow

To test if the observed evolution of isotopic gradients in the snow profiles in experiments really are caused by the different properties of the sinthered old and the new snow three cans were filled with homogeneous freshly produced snow and stored at the three temperature regimes for 32 days.

The measured isotopic profile of homogeneous snow masses stored for 32 days at three different temperatures do not show any visual trend (Figure 23). The different temperature regimes do not show different changes over this time period. The values of each can varies within 0.5 ‰ which lies within the variance of the snowmaker of 0,52 ‰. The standard deviation of the measurements were between 0,03 ‰ and 0,12 ‰. Compared to the starting value (black) the snow gets slightly enriched in δ^{18}O. These results suggest, that the formation of an isotopic gradient (Figure 18) in Experiment 1 is due to the differences in snow properties, not due to the experimental set-up.

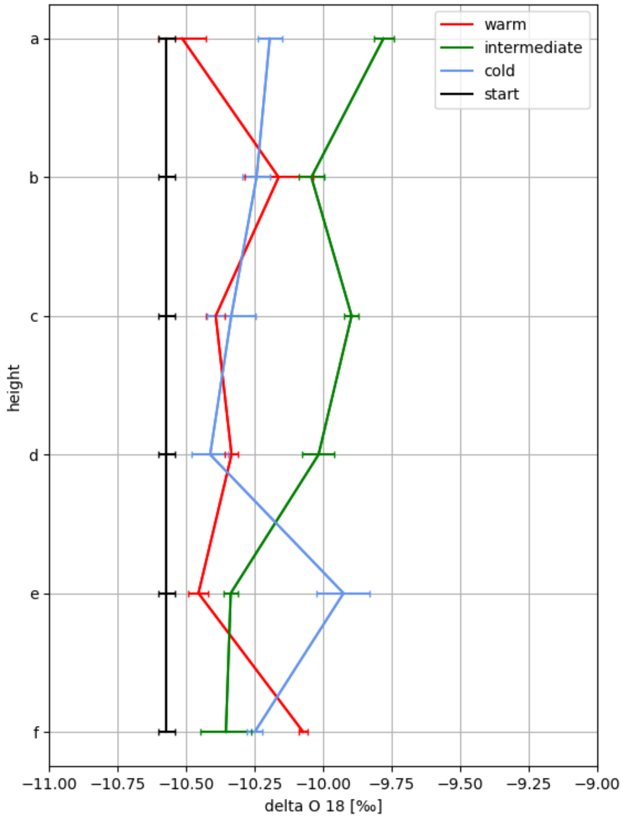


Figure 23: Isotopic profile of a 32 day old, homogeneous snow mass of fresh snow at different temperatures.

4.1.3 Influence of a Snow Isotopic Gradient in a Snow Profile

As seen in the previous experiment the isotopic difference gets smaller again after 32 days in the warm regime. In this section the interaction of two snow layers starting with a big δ-gradient between each other are looked at.

In Figure 24, the time evolution of the isotopic signal in a snow profile is shown. For δ^{18}O, the difference between the top layers (a-c) and the bottom layers (d-f) value is 13 ‰ at day 0. After two days, a shift of δ^{18}O in layer c and d is seen. Layer d becomes enriched, layer c depleted in heavy isotopes. This trend of an enrichment of the bottom layers and a depletion of the top layers continues until day 32, except in layer f where there is no change occurs in all temperature regimes over the whole period. The changes in the upper three layers is stronger than in the bottom three layers over the whole measuring time. In the four temperature regimes of Experiment 2, the changes in the isotopic composition of the snow are of various strength. The largest shift happens in the warmest regime at -2 °C. The cold and the freezing regime show only small changes over the entire time period. Furthermore, changes in the isotopic composition of the snow layers occur earlier for the warmer regimes, for which the first changes are seen after two days. For the coldest regime at -40 °C these changes are clearly visible after eight days. The measurements in δD (Figure 25) generally show the same trends as δ^{18}O. First changes are already seen after two days, increase with time and are largest in the warmest regime.

A temporal evolution of d-excess (Figure 25) in the snow profile is clearly seen in the top layers, where d-excess decreases with varying strength over time. In the bottom layers, d-excess stays constant in layers e and f and increase slightly in layer d. The decrease in d-excess in the top layers indicates diffusion from the top to the bottom layer. In accordance with Experiment 1, the difference in SSA between the top and the bottom layer could cause this downward flow in the snow profile.

In Figure 26 the development of the density in the two different layers of snow is shown. The bottom layer is already much denser and therefore changes less than the lower layer. The difference between the two layers is getting smaller over time, but only slightly. After 32 days the bottom layers is still much denser than the top layers in all temperature regimes.

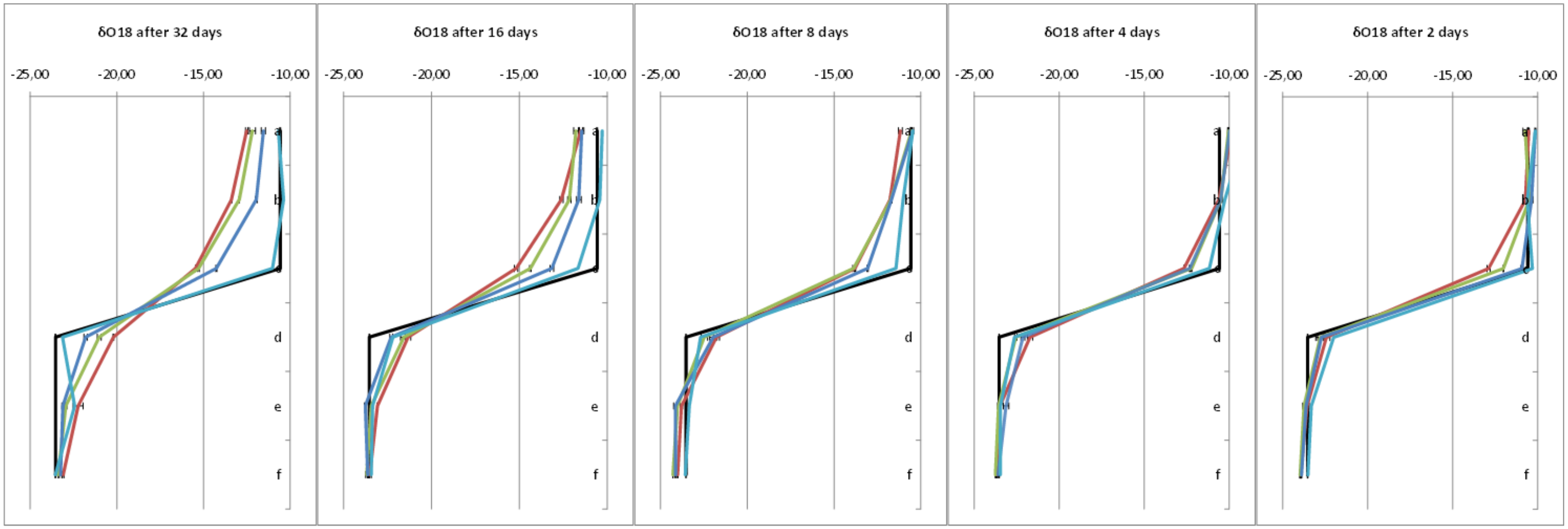


Figure 24: δ^{18}O content in snow over time at different temperatures in a snow profile. Each graph stands for one time step which show the snow profile after 2, 4, 8, 16 and 32 days (from right to left). The x-axis shows δ^{18}O in the snow. The y-axis shows the profile of the can from the top sublayer a to the bottom sublayer f. The black line shows the profile of a start profile. The other colors each represent a temperature regime; in red the measurements at -2 °C (warm), in green at -8 °C (intermediate), in blue at -16,5 °C (cold) and in light blue at -40°C (freezing) are shown. For each measuring point the standard deviation of the measurement is shown as error bar.

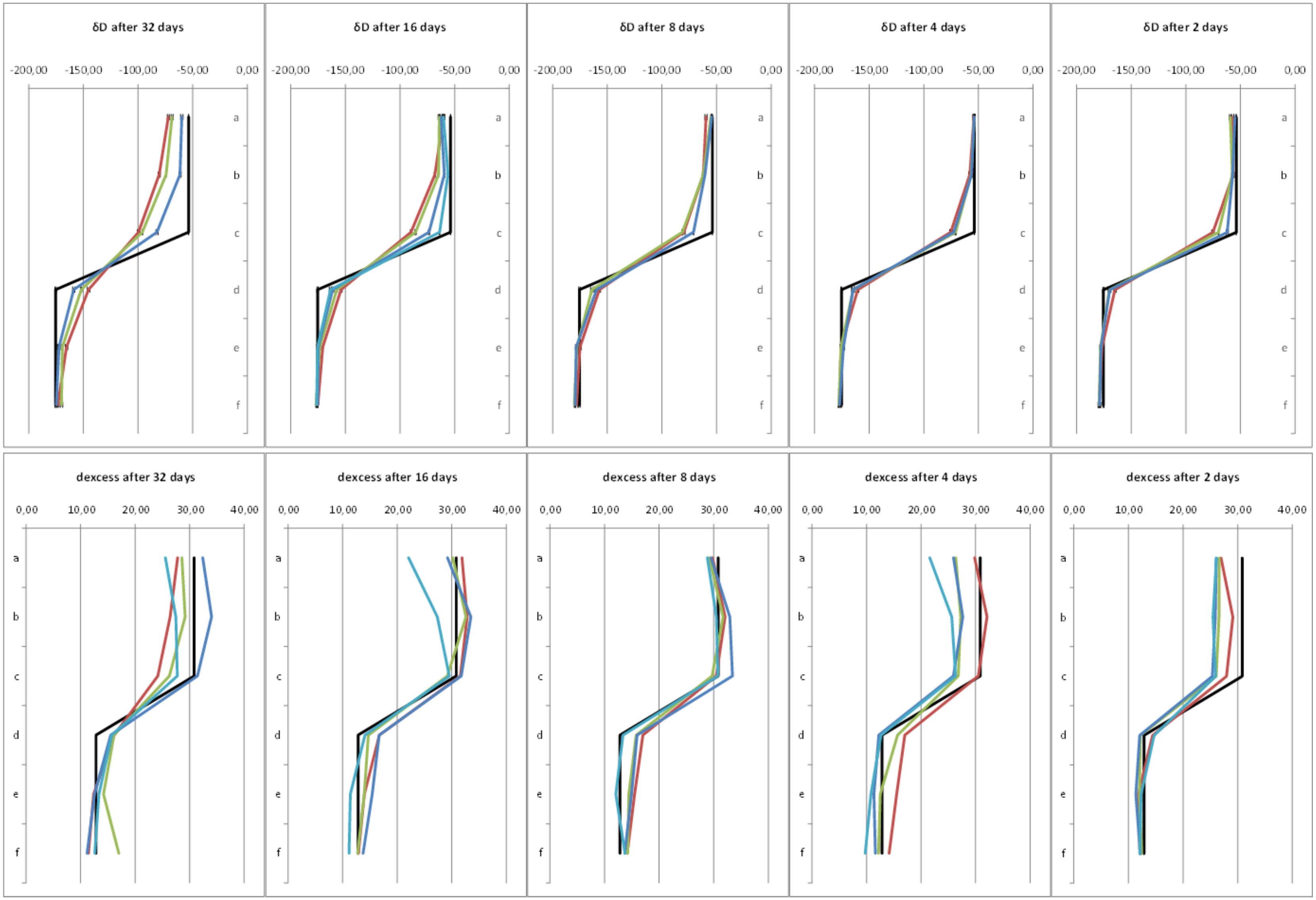


Figure 25: Same as Figure 24 but for δD (top) and d-excess (bottom)

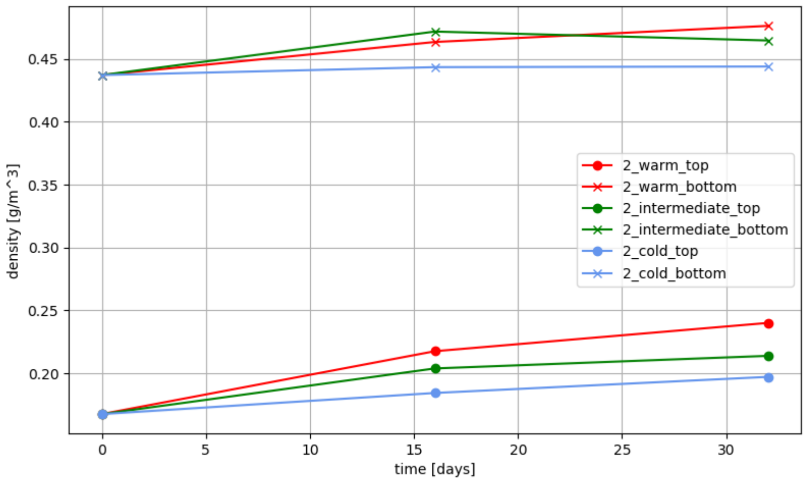


Figure 26: Density change of the top (points) and bottom (cross) layers at different temperatures over time.

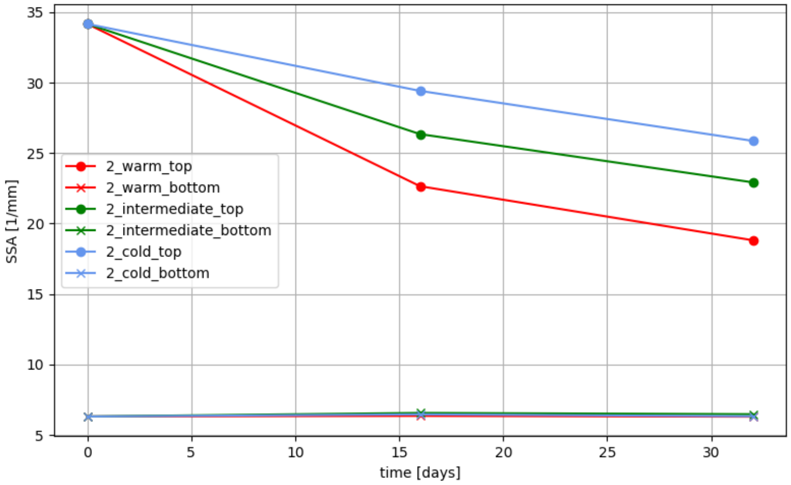


Figure 27: SSA change of the top (points) and bottom (cross) layers at different temperatures over time.

In Figure 27 the development of the SSA in the two different layers of snow is shown. The SSA of the fresh snow top layer decreases over the 32 days fastest at warmest temperatures and faster in the first half then the second half. The SSA of the old snow bottom layer stays pretty much the same over this measuring period.

The difference between layers c and d decrease over time (Figure 28), except the increase after 32 days at the freezing temperatures. The rate of change in δ^{18}O is decreasing with time. Furthermore, the difference between the two layers decreases fastest at warm temperatures and slowest in the freezing temperature regime, except after four days, where the cold regime seems to have a smaller difference than the intermediate regime. For example after 32 days in the warm regime the difference decreased by 50 % compared to the beginning. The decrease in rate of change over time as well as the larger changes at higher temperatures could be explained by the strength of metamorphism. Metamorphism occurs fastest at warm temperatures and in younger snow with high SSA. Therefore the exchange of molecules is fastest at warmer temperatures in fresh snow and the isotopic values of the different snow layers are able to reach an equilibrium faster. Compared to the decrease of 50 % in δ^{18}O in the warm regime over the whole measuring period the SSA decreased by 55 % and the density increased by 43 % .

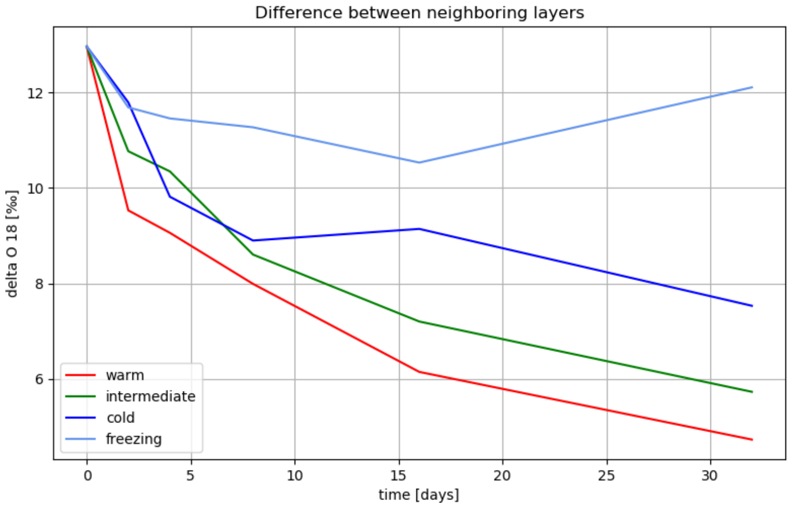


Figure 28: Evolution of the δ^{18}O gradient between layers c and d for the four temperature regimes.

The change in isotopic δ^{18}O-difference between layers c and d represents a small distance of the entire snow profile. If the top two layers were compared with the bottom two layers (Figure 29) the temporal evolution is similar to changes between layers c and d, but is shifted by eight days. During the first eight days almost no change in the difference in δ^{18}O is seen. In the first days the difference even grows. Starting from day eight, the vertical difference in δ^{18}O decreases and splits up again into the temperature regimes after 32 days similar as seen in the neighboring layers in Figure 28. The difference between the top and bottom snow layers is reduced by 3,26 ‰ after 32 days in a warm regime.

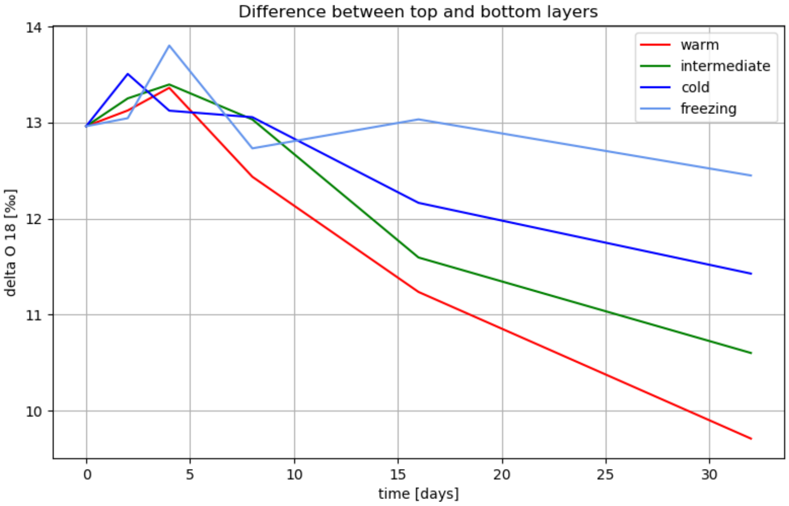


Figure 29: Evolution of the gradient between the top (mean a&b) and the bottom (mean e&f) layers for the four temperature regimes.

These results show that the vapor pressure gradient (the same mechanism as explained in Experiment 1) forces an exchange of water vapor between the bottom and top layers. Because of this exchange the difference in isotopic composition of the bottom and top layer decrease (Figure 30). The changes in isotopic content are larger in the upper than the lower layers. This is thought to be because of the faster exchange of molecules in the younger top snow.

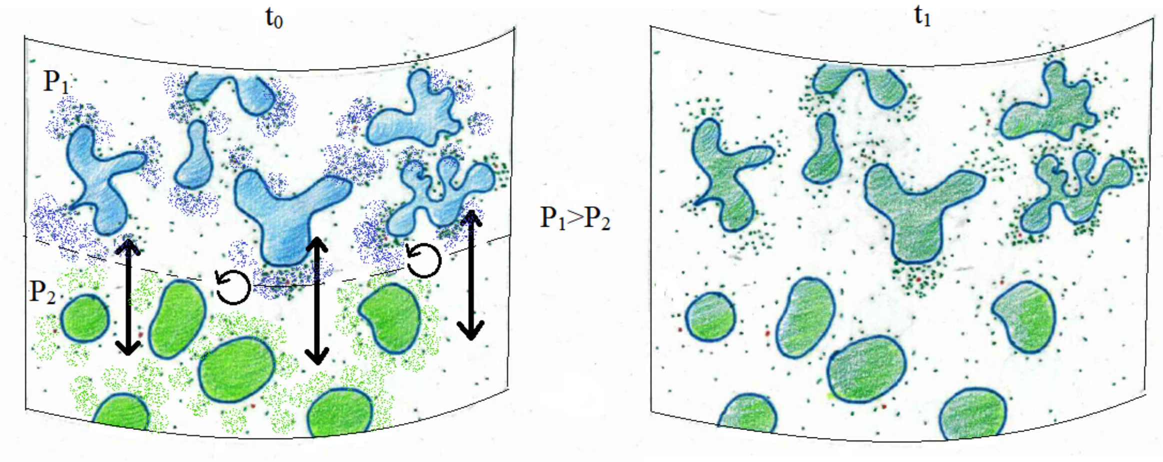


Figure 30: Figure 22 but for Experiment 2. Starting position on the left, upper snow is enriched (blue) compared to the depleted lower snow layer (green). After some time the vapor from the top (enriched) and the vapor from the bottom (depleted) mix and re-sublimate. The bottom layer gets enriched and the top layer gets depleted.

4.1.4 Isotopic Exchange in Open Versus Closed Systems

In this experiment, a can was stored without being sealed air tight at -40 °C. The difference in δ^{18}O between the layers c and d is slightly smaller for the closed can compared to the open can (Figure 31). This could be explained by a smaller vapor pressure gradient in the open can, because the top layers did not only exchange water vapor with the bottom layer but there was also a vapor flow upwards into the atmosphere. Due to the low temperatures (-40 °C) during the experiment for this comparison, the observed changes in δ^{18}O are small for the open and closed can. A repetition in a future study of this experiment at higher temperatures might reveal a stronger signal.

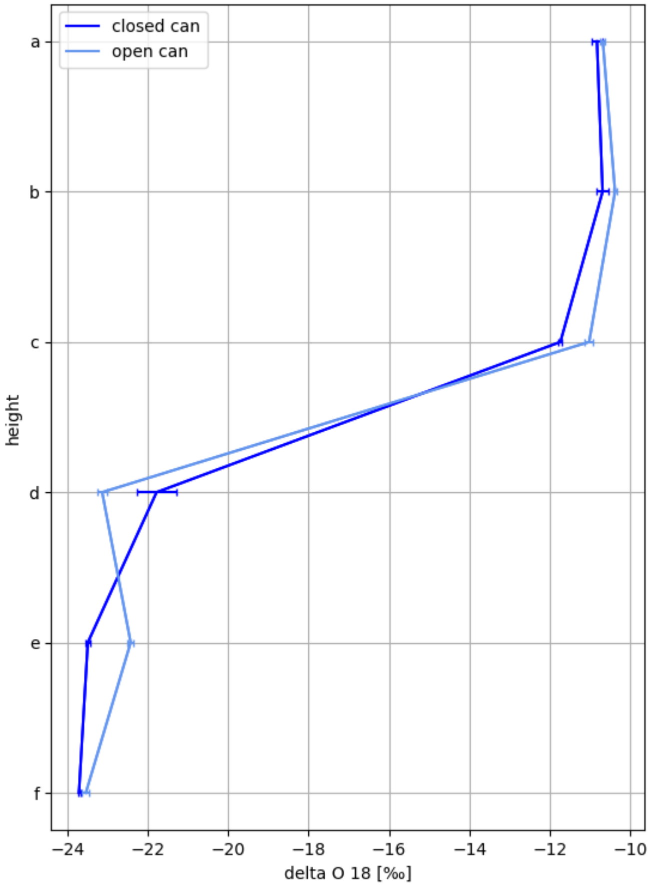


Figure 31: δ^{18}O profile of an open (light blue) and a closed (dark blue) can stored at -40 °C for 32 day, error bars show standard deviation of measurement.

4.1.5 Comparing Experiment 1&2

In contrast to Experiment 1, we do not see an increase (decrease) in δ^{18}O and δD in the upper (lower) layers due to the isotopic fractionation during snow metamorphism, but a decrease (increase) in δ^{18}O and δD in the upper (lower) layers. There are two main differences between Experiment 1 and 2. In Experiment 2, the difference in isotopic composition between the top and bottom layers is large from the beginning and the snow at the bottom is very old with a small SSA (6.3 1/mm) and, therefore, only weak snow metamorphism is expected in the lower layers. Therefore:

1. In Experiment 2 the vapor pressure gradient is large. This means that diffusion and exchange between the layers are more important than the effects from the isotopic fractionation during snow sublimation.
2. In Experiment 2 the difference in δ^{18}O and δD between the two snow layers is large. This means that mixing of water vapor from the top and bottom layers and subsequently re-sublimaiton of the water vapor on the snow crystal strongly changes bulk isotopic composition of snow in each layer.
3. In Experiment 2 are larger changes in isotopic content seen in the top layers. On one side this might have something to do with the faster metamorphism processes in the upper much younger snow layer on top much faster than in the old bottom layer. Therefore, the exchange is much faster and the vapor from below is incorporated into the snow much faster. On the other side it has something to do with the fractionation of depleted versus the fractionation of enriched snow. As the bottom layer already is depleted in δ^{18}O the leaving vapor is compared to the upper layer extremely depleted (fractionation increases this difference as well) but the signal of the leaving vapor of the enriched top layer is damped by the fractionation. If these two water vapor from top and bottom layers mix, difference in isotopic composition between snow and the mixed-in water vapor is smaller for the bottom than for the top layers.
4. In Experiment 1 the difference in δ^{18}O and δD between the two snow layers builds up in the first days. This difference then gets smaller after 32 days in the warm regime. This might show a similar process as seen in Experiment 2. Furthermore, is the faster changes in warmer regimes similar in both experiments.

4.2 Temporal Evolution of the Isotope Composition Content in Vapor and Snow Induced by Snow Sublimation

4.2.1 Influence of Temperature

To get a better understanding of how the different temperature regimes influence the measurements, this section shows the measurements of 12 h in the different temperature regimes. In Figure 32, all water vapor measurements lasting 12 h are shown (for the results of the longer lasting experiments see Appendix B.3). The warmest regime starts at the lowest δ^{18}O values, the cold regime starts at the highest δ^{18}O values and the intermediate regime is in between. The decrease is biggest in the warmest regime, it is faster at the beginning and is getting more constant after 8 hours. The intermediate regime shows a nearly linear decrease over the whole time period. The coldest regime shows a rapid decrease in the first two hours, afterwards this decrease stagnates but the values keep getting smaller.

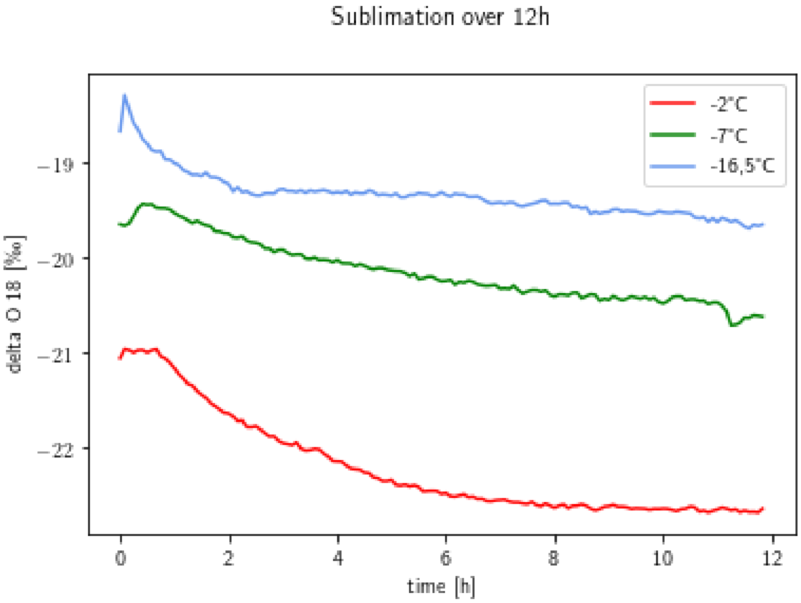


Figure 32: δ^{18}O evolution of water vapor in the first 12 h of forced sublimation in different temperature regimes.

In Figure 33 all snow measurements lasting 12 h are shown. All snow profiles are slightly enriched in δ^{18}O over the whole profile compared to the starting sample. At temperatures of -2 °C the snow was enriched the most and at -16.5 °C the snow was enriched the least. Over the whole profile the mass balance shows an enrichment in

δ^{18}O of 1,21 ‰ for the warm regime, 0,91 ‰ for the intermediate regime and only 0,15 ‰ for the cold regime.

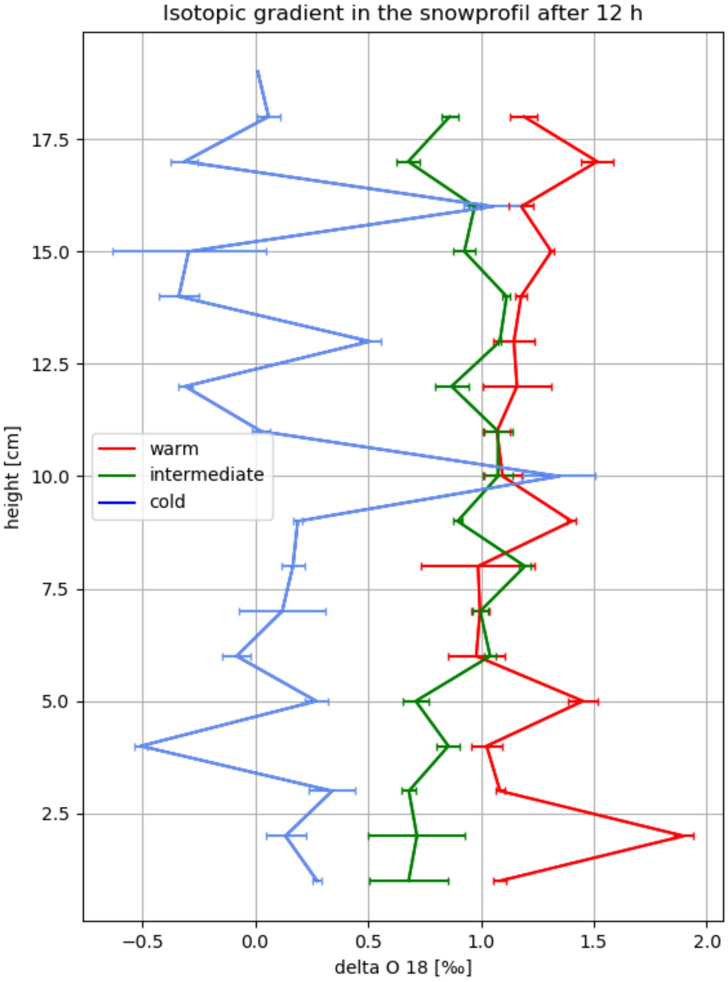


Figure 33: Evolution of the isotopic gradient over 12 h. On the y-axis 0 cm is the bottom of the profile, 18 respectively 19 cm is the top of the snow profile. One measurement every 1 cm was made. The profile is shown in perspective to the isotopic content of the snow at the beginning of the experiment. Different colors show the different temperature regimes of the experiment.

These results show, that at warmer temperatures the sublimated vapor gets more depleted and the snow gets more enriched in δ^{18}O compared to colder temperatures. Therefore, temperature can be directly linked to fractionation strength.

4.2.2 Influence of Sublimation on the Isotopic Content in Snow Over Time

This section shows the evolution of a snow profile at -2 °C after 12 h, 24 h, 48 h, 65 h and 90 h of sublimation. The isotopic water vapor measurements of these experiments and the snow profiles at -7 °C and -16.5 °C can be found in the Appendix B.2. In Figure 35 each profile is shown as variance in perspective to their own top three layers. All five profiles look more or less homogeneous in the upper half of the profile. In the lower 10 cm they split up. The values of the 12 h and the 24 h experiment still fluctuate around 0, however the amplitude of this fluctuation seems to get bigger towards the bottom for the 12 h experiment. The results of the 48 h and 65 h experiment show a shift towards a positive variance (enriched in δ^{18}O) compared to the top layers. The 48 h profile shows negative values in the middle part but then turns towards clearly positive values in the lower 5 cm. Therefore, the bottom snow is enriched compared to the top. This enrichment towards the bottom is even more visible in the 65 h profile. These results suggest that over time, a gradient in the snow emerges and increases (Figure 34). Due to the constant pumping at the top of the box, the snow is forced to sublimate and it also creates a vapor pressure gradient along the profile. Therefore, we have a flow of vapor from the bottom to the top. As the snow sublimates, a fractionation happens and like explained in Experiment 1, this depleted vapor then moves to upper layers, leaving an enriched snow layer on the bottom. As the upper layers get more depleted over time, the measured water vapor is as well getting more depleted (Figure 32).

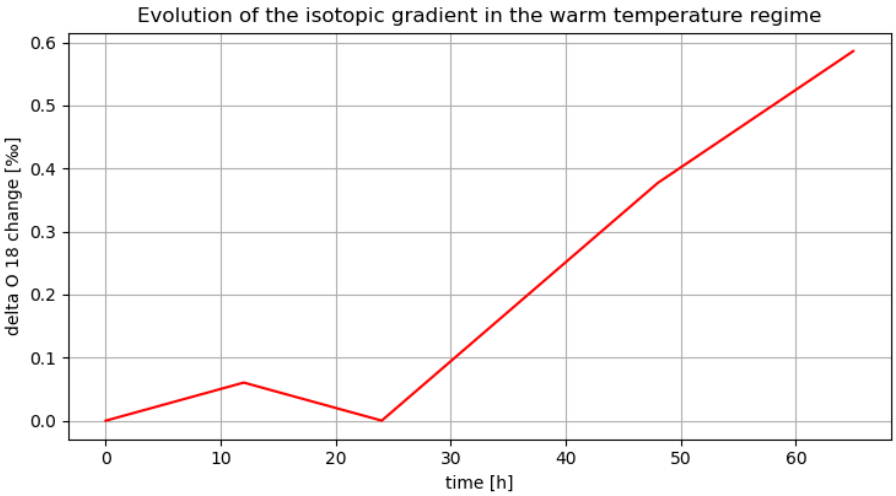


Figure 34: Evolution of an isotopic gradient at -2°C, top three minus bottom three layers.

The 90 h profile could not be taken over the full length, only the top 12 cm were sampled. These values do not seem to correlate with the results of the other profiles.

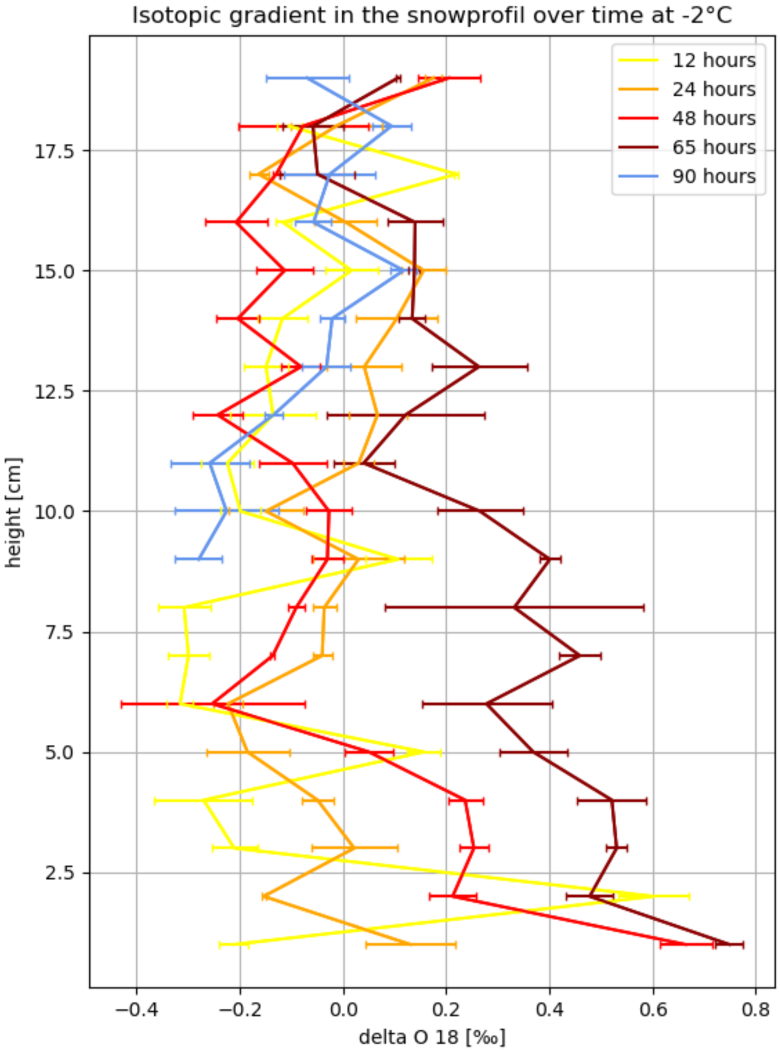


Figure 35: Evolution of the isotopic gradient at -2°C. The standard deviation in each point is between 0,01 and 0,25 ‰ but only for 5 measurements in all snow profiles at -2 °C a bigger standard deviation than 0,1 ‰ was measured. On the y-axis 0 cm is the bottom of the profile, 18 respectively 19 cm is the top of the snow profile. One measurement every 1 cm was made. The profile is shown in perspective to the mean of the top three layers. Different colors show the different duration of the experiment.

4.2.3 Comparison of Sublimation of Ice and Snow at -2 °C

In Figure 36 the sublimation of ice over 24 h at -2 °C is compared to the sublimation of snow over 24 h at -2 °C. The snow measurements had a gap between the first hour and the 14th hour. The ice experiment stopped completely between the 19th to the 21st hour, not only the measuring device turned off but also the pump because of a turn off of the power. The snow measurement shows a decrease in the δ^{18}O content. The ice measurement on the other hand shows at first a increase (until hour 10) and then after it a rather stable phase until the power was cut. After the power turned on again the δ^{18}O signal was back at the starting value. At first vapor that has been in an equilibrium with the ice is pumped off, then more and more the forced sublimation of the ice takes place. Because of the much lower surface area the ice offers the fractionation can not take place anymore and a stable δ^{18}O value gets sublimated. After the break of the pump, again something like an equilibrium over the ice could form and the values of the air that was pumped off later are lower again.

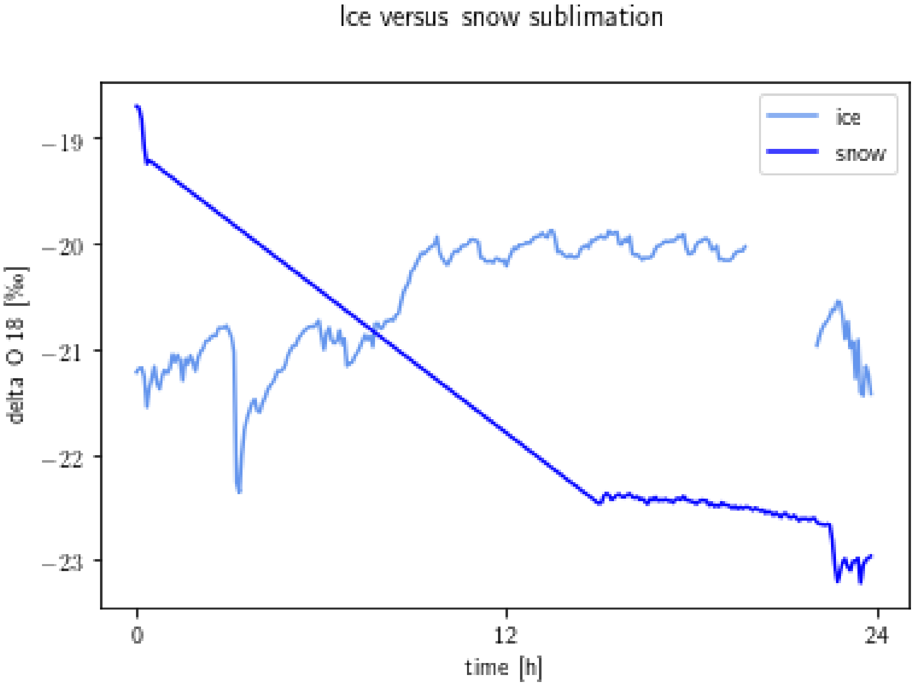


Figure 36: Sublimation of ice and snow over 24 hours at -2 °C.

In addition the isotopic content of the filled in water and then of the ice were measured. The filled in water had a δ^{18}O content of -14,18 ‰ ± 0,03 ‰. After the experiment the ice was melted and a sample of this water measured at -14,44 ‰ ± 0,09 ‰ compared to the other measurement slightly lower and therefore slightly depleted in δ^{18}O. This can not be explained by the single fractionational process form ice to vapor, nonetheless it could show that previous fractionational processes taking place while freezing, influenced this signal. However the whole ice volume was melted and the sublimation only took place at the surface. The water volume was therefore way to big to see the effect of sublimation. If the ice surface had been scratched and therefore only the upper millimeters would have been measured a change might have been visible.

5 Conclusions and Outlook

This thesis addresses fractionation effects related to phase changes that occur during snow metamorphism and during snow sublimation with dedicated laboratory experiments. Two experiments address directly the effect of metamorphism between two snow layers with different properties and its impact on their isotopic content. The third experiment addresses the effect of sublimation on the isotopic content of vapor and snow over time.

Metamorphism seems to have an important influence on the distribution of isotopes in a snow cover. In a closed system such as in Experiments 1 and 2, the redistribution respectively the re-sublimation of sublimated vapor due to a vapor pressure gradient seems to be the most important process. There are three physical parameters that control the isotopic composition of snow:

1. Vapor pressure gradient in the snow pack (SSA, temperature & curvature)
2. Temperature
3. Isotopic gradient between layers

Depending on these three properties, different dominating processes shape the isotopic composition of snow. The SSA and temperature mainly have an influence on the speed/strength of metamorphism respectively the redistribution. As mentioned in Section 1.2.3, a mass redistribution in snow is governed by the existing vapor pressure gradient. This can be induced by a temperature gradient (temperature gradient metamorphism) or, as seen in Experiments 1 and 2, a vapor pressure imbalance can also occur when neighboring layers have different SSA. Older snow layers have typically a lower SSA compared to newer snow layers due to the minimization of surface free energy during metamorphism. If a fractionation takes place during sublimation, the depleted vapor therefore changes the isotopic content in the profile. When the depleted vapor moves into one direction and deposits on different snow crystals, the previous isotopic signal is altered. This process smooths the isotopic differences in different snow layers and changes the isotopic content in deposited snow layers generally due to the predominant vapor pressure gradient in the snow profile. Furthermore, the SSA and curvature influence the amount of change because of the area vs volume imbalance. A small ice crystal with much curvature might have the same SSA as a bigger ice crystal with almost no curvature therefore they have the same amount of area they can interact with the air around themselves. If the isotopic change is then measured, the small one could have changed much more than the big one because of its starting volume. The third property, the isotopic gradient between layers has something to do with the isotopic signal of the sublimated vapor. If the snow itself of one layer (for example from one snowfall to an other) shows a different signal, the vapor produced in this layer will also have a different signal. If this vapor then moves and mixes with the vapor of another snow layer, due to re-sublimation, the signal in the snow is altered as well. Therefore, the effect is larger if the starting signal of those two snow layer is more diverse. However, the transport itself and therefore the impact is induced by the gradient of vapor pressure.

This shows that metamorphism has an influence on the isotopic signal in snow and therefore onto the air above the snow. Different SSA can, over a timescale of days, induce signal changes into an isotopic homogeneous snow cover as big as the difference in the isotopic signal between warm and cold periods in an ice core (around 5 ‰). Looking at longer time periods, the isotopic signal in the deposited snow is being smoothed. Single events of enriched or depleted precipitation are therefore ”filtered” for ice core measurements if the snow layers interact long enough. As a snow layer gets buried deeper, temperature gets more constant and the snow itself gets older (SSA gets smaller, difference of SSA gets smaller to neighboring layers as well), these processes get slower. If there is no more vapor pressure moving vapor around in the profile the isotopic change stops. As these changes are strongly dependent on many different factors that interact with each other (such as temperature, precipitation, wind, metamorphism,...), it is hard to extract the influence of one single factor. Furthermore, it is important to remember that at different locations the importance of one factor might be more important than somewhere else.

Sublimation of a free snow layer seems to change the isotopic content of the sublimated water vapor and the snow cover over time. In the set-up of Experiment 3, a vapor pressure gradient was induced onto the snow cover at all times. Temperature and length of the experiment influence the isotopic signal in air and snow. The water vapor gets depleted in heavier isotopes as the snow gets enriched. The snow cover gets more enriched at the bottom because of the upwards traveling depleted vapor. While the bottom layers only loose depleted vapor, the higher layers get sublimated as well and loose depleted vapor, but from underneath new depleted vapor ascends and re-sublimates, leaving them isotopically balanced. Because of this ascending depleted vapor, the top layers get more and more depleted as well. Therefore, the vapor leaving the snow cover at the top gets more and more depleted. To see this process more clearly, longer time periods of measurement and a higher resolution in the snow profiles are thought to be needed.

These findings suggest that depending on conditions such as temperature, how long the snow surface is air exposed, wind respectively pressure at the snow surface have an influence on how fast and how strong the isotopic signal is altered after the snow is deposited. This is thought to explain why some ice cores are more suitable for climate reconstructions than others. Furthermore is the dynamic of the isotopic signal of the water vapor of sublimated snow more complicated than previously assumed. Not only the top layer of the snow influences this signal. Snow deeper down might not have a direct influence on this signal but by exchange with the top layer the water vapor signal is influenced as well. To make specific statements on how these processes influence the isotopic content in a snow cover and the sublimated water vapor, the vapor pressure gradient and the isotopic gradient of this snow cover need to be known.

The importance of these experiments could be questioned regarding their rather short time frame compared to the duration of the formation of an ice shield. However, were these experiments carried out at higher temperatures than the ones occurring during the formation of an ice shield. While being exposed to higher temperatures, the alteration of the isotopic signal in the snow is thought to occur much faster than at lower temperatures. Therefore, the shown rearrangement processes are assumed to play an important role over a longer period of time in colder climates.

To get an even better understanding it would be interesting to take those measurements over longer measuring periods. For Experiment 1 it would be intriguing to see what would happen at -40 °C and in all temperatures how long it would take until a new equilibrium is found. For Experiment 2 it would be compelling to see what would happen if the depleted and enriched snow had the same age/properties. In Experiment 3 it would be fascinating to see what happens if the snow cover had different layers and how the isotopic content in air and snow would change then. Furthermore, it would be interesting to see what would happen at different sublimation rates. To understand the fractionation of ice better it would be thought-provoking to see how an ice ball compared to the ice layer would sublimate.

Overall, this thesis was able to identify processes like sublimation and metamorphism to alter the isotopic composition of snow after its deposition and the air above it. It is therefore important to improve this knowledge with further research to be able to quantify these changes with regard to their importance in paleoclimate reconstructions and to incorporate them into isotope-enabled numerical earth system models to correctly simulate the evolution of the isotope composition of the cryosphere and atmosphere in cold regions.

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A Additions to Experiment 2

A.1 Isotopic Difference in Water

One way to produce more depleted snow than using tap water could be running the snowmaker several times in a row, thaw the produced snow and then producing snow again using the fractionation process during the phase change in the machine. To save energy, only the evaporation over the water bath would be enough without producing snow, but for this to work a tent of some sort would have been built to catch the vapor. The sample to measure if this method would work was therefore produced using a regular pan. The pan was filled with some water and a glass was put into the middle of the pan. Then a foil was tightened over it to catch the vapor. To create a low point where the water could assemble and then drop into a glass, a golf ball was used as weight (Figure 37).

Figure 37: Producing the water sample of one evaporation cycle.

Measurements of the content in water after one evaporation showed only a change of about 1‰. Therefore, this process would have had to be repeated several times. Because of the time and energy consuming aspect and it being a rather complicated method an alternative method was searched for.

A creek with mainly glacier drain could have a different signal than a lake so different locations were sampled (five in Davos and one of Walensee (Figure 38)).

Figure 38: Different sample locations. From left to right: Walensee, Dischmabach, Flüelabach, Davosersee.

Unfortunately, the difference in these locations was insignificant.

Location	δ^{18}**O** [‰]	**StDev**
Davosersee	-13.39	0.04
Flüelabach	-13.54	0.04
Dischmabach	-13.32	0.34
Dischmabach Teufi	-13.76	0.03
Walensee	-13.28	1.0

Table 1: δ^{18}O measurements of different water samples.

As seen in Rossmann et al. (1998) wines from Germany, Italy and France have a different stable oxygen isotope content which lead to the assumption that the geographical distance of our locations were probably not big enough. To test this theory, the most southern water in the supermarket, in this case Salo in Italy, was also tested. It measured at -8,87 ‰ ± 0,01 and therefore showed a difference to the one in Davos of about 4.5 ‰. Even though using this water as a source for producing snow could work, a simpler method was chosen in the end.

B Additions to Experiment 3

B.1 Measuring Problem: Drop in Vapor δ^{18}O Measurements

One of the biggest challenges in water vapor measurements using laser spectrometry were the suddenly occurring drops in water vapor mixing ratio and δ^{18}O. One example of such a drop is shown in Figure 39. Between 5:45 AM and 5:53 AM a stable signal is measured. At 5:53 am a drop of over 2000 ppm in water vapor and 2 ‰ in δ^{18}O occurs. Over the following 10 minutes the signal recovers again and increases, almost reaching the starting values.

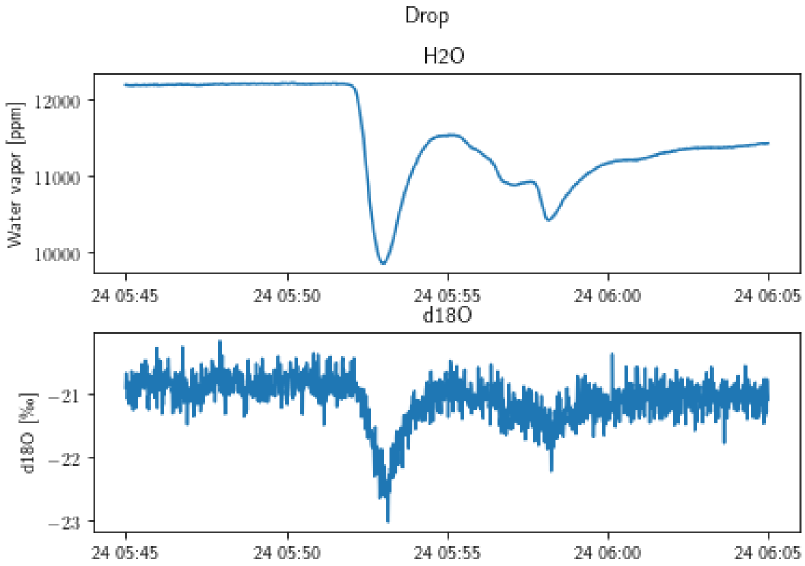

Figure 39: Drop in water vapor and δ^{18}O.

Such drops always occurred shortly after a laboratory door was opened. This did not only happen for the door of the cold lab, where the snow box was stored, drops were also seen when any other door to a different cold lab in the whole building was opened. The intensity of the drop seemed to correlate to the length of the door opening. This points to the conclusion, that these drops had something to do with the set-up outside the cold lab. These drops are also visual in Figure 46 for example in the warm regime between hours 0 to 4, 20 to 26 and 43 to 48. The more stable periods correlate to night time when the cold lab was closed.

B.2 Comparison of Vapor and Snow Isotope Signal Evolution

In this section the measurements of the sublimated vapor and the end snow profile are compared. In all Figures 12 h measurements are shown in yellow, 24 h measurements are shown in orange, 48 h measurements are shown in red, 65 h measurements are shown in dark red and the 90 h measurement is shown in blue. First the vapor measurements and the snow profile of the warm regime are shown, then the ones from the intermediate regime and in the end the ones from the cold regime. The vapor data is shifted so that every experiment starts at hour 0 and then goes as long as the experiment took. The snow data shows the profile in the end of the measuring period. It is shown in perspective to the top three layer so that the change in the profile itself is visible more clearly.

In Figure 40 the time evolution of the isotopic content of the sublimated vapor is shown. The measurements of the 65 h experiment stopped at hour 33 due to a computer update. All measurements seem to show a decrease in δ^{18}O. The amount of this decrease however is different. The 12 h and 24 h experiments show a much faster decrease at the beginning compared to the 48 h and 65 h experiments. This is thought to have something to do with the time slots where the measurements were done because of the before mentioned drops during the day. Interestingly the 12 h experiment and the 65 h experiment were started in the evening (12 h at eight, 65 h at five) but they do not show the same results at all. Therefore, the difference has probably more to do with the age and storage of the sieved in snow. Snow with different properties such as SSA or density might show different fractionational behavior.Even thought for every experiment the same procedure was followed it might be that one or the other snow might have been some hours older than the other when the experiment started. This difference however is bigger for storing the snow at warmer temperatures what might explain why this is not seen in the comparisons of the other experiments at -7°C and -16.5°C. Totally different values showed the measurements for the 90 h experiment. The drop in the beginning is faster and higher in the beginning and afterwards the values fluctuate a lot.

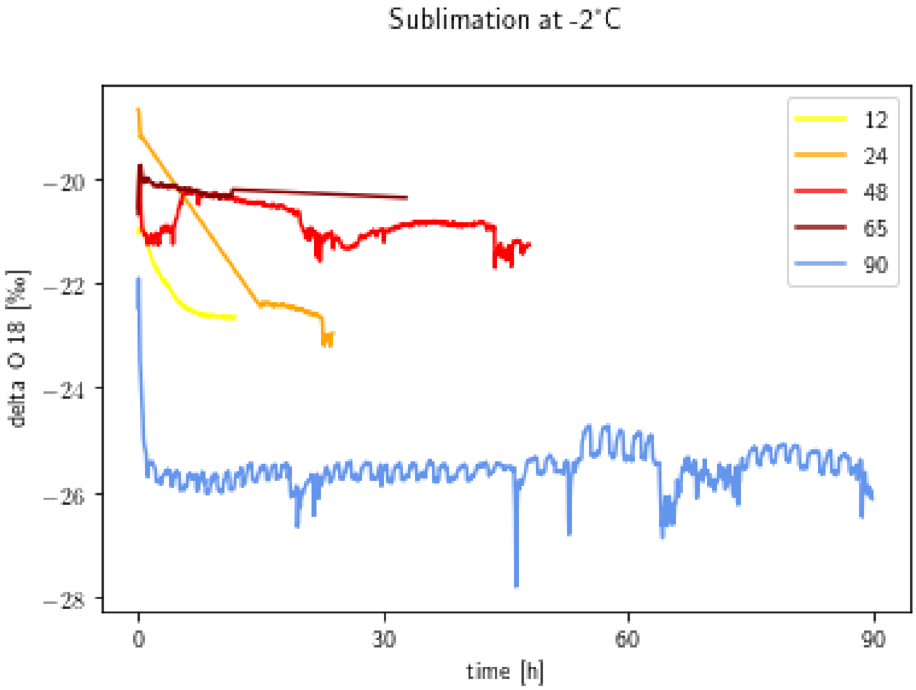

Figure 40: All Sublimation measurements at -2°C. Different colors show the different duration of the experiment. All experiments start at hour zero, they started at different times during the day.

The results of the snow profiles at -2 °C are presented in Section 4.2.2 Influence of Sublimation on the Isotopic Content in Snow Over Time.

In Figure 41 the time evolution of the isotopic content of the sublimated vapor is shown. The measurements of the 65 h experiment stopped at hour 33 due to the daylight savings. The measurements show a decrease in δ^{18}O except for the 24 h experiment. The experiment of 65 h and 48 h correlate really good, if we imagine the drops during the day seen in the 48 h experiment were not there. The experiments 12 h, 48 h and 65 h show a decrease of 1 to 1.5 ‰ over the first 12 hours. The measurements of 48 h and 65 h show that that decrease seems to stagnate after those first hours.

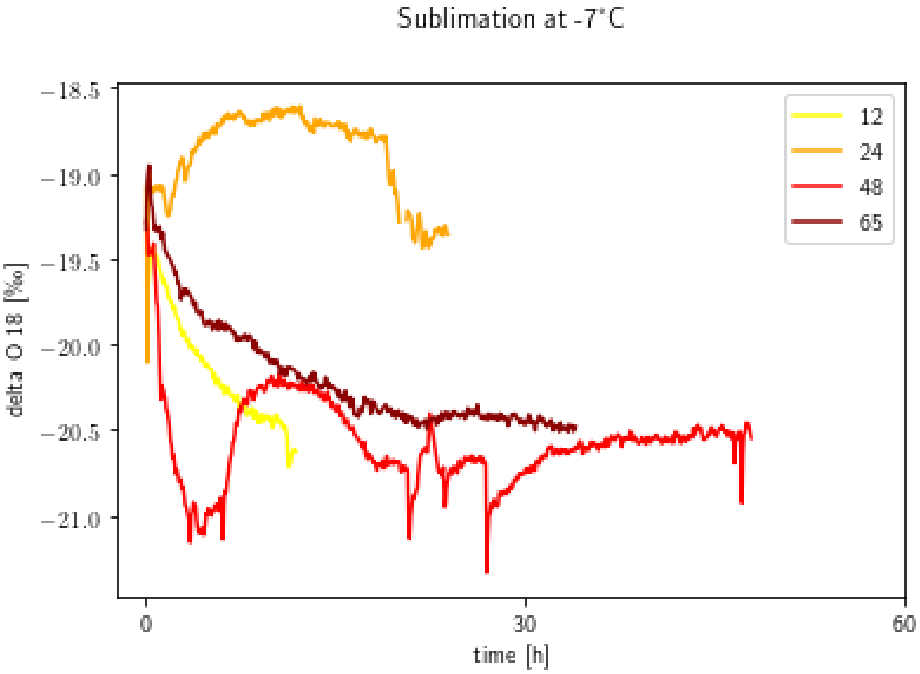

Figure 41: Figure 40 but for all sublimation measurements at -7°C

In Figure 42 the snow profiles of all experiments at -7 °C are shown. Each profile is shown as variance in perspective to their own top three layers.
All four profiles look more or less homogeneous in the upper half of the profile. In the lower 10 cm they seem to get negative, the longer the experiment lasted the more negative the values get. One exception is the measurement of the bottom 1 cm in the 65 h profile. Therefore, the bottom snow is depleted compared to the top. Compared to Figure 35 this is exactly the opposite, the amplitude of this change is about the same.

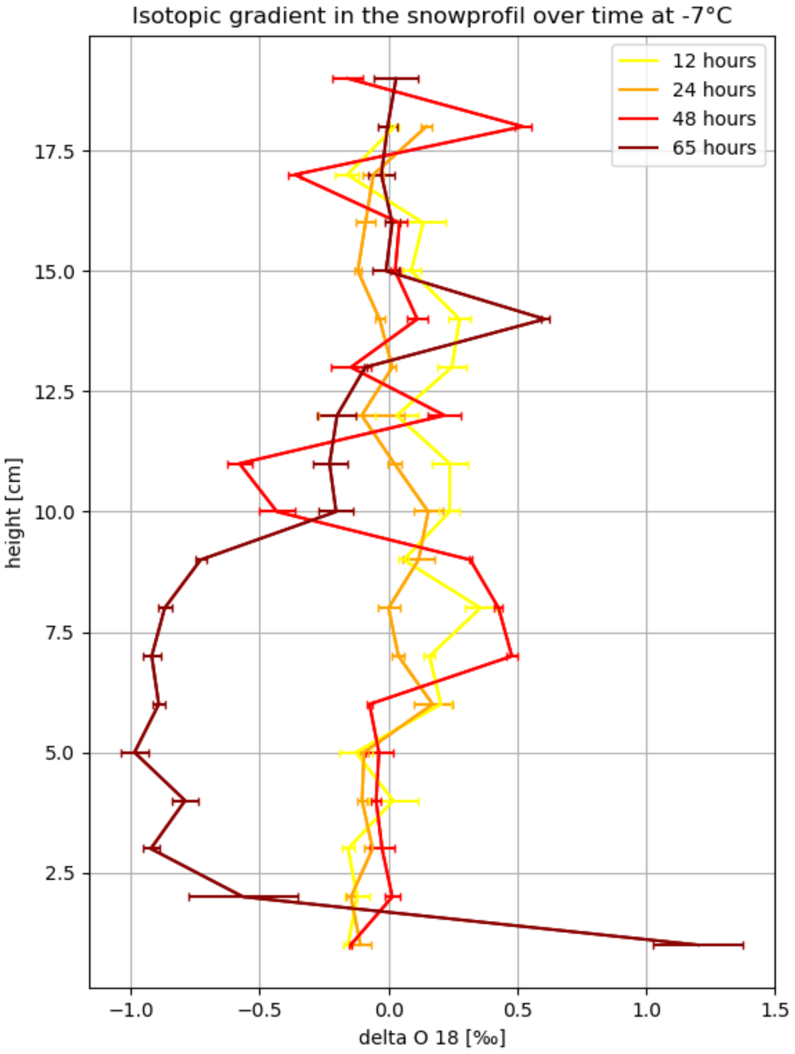

Figure 42: Figure 35 but for the evolution of the isotopic gradient at -7°C. The standard deviation in each point is between 0,01 and 0,52 ‰ but only for 7 measurements in all snow profiles at -7°C have a bigger standard deviation than 0,1 ‰ was measured.

The decrease in water vapor δ^{18}O might have something to do with the metamorphism that transports a low δ^{18}O signal to the top and accumulates there. Therefore, the top snow is depleted compared to the bottom snow. When this depleted snow is sublimated, it producing an even lower isotopic signal in the air due to fractionation. However in the snow profiles for the -7°C this process can not be seen (as in Figure 35). This could have something to do with the speed of metamorphism that is already much slower at -7°C compared to at -2 °C. This process might just happen in the upper few cm that can not be detected with the resolution of only 1 cm.

In Figure 43 the time evolution of the isotopic content of the sublimated vapor is shown. The measurements are more similar to each other compared to the ones at the other temperature regimes. All of them show a decrease in their values at some point. This decrease is in all measurements around 1 ‰. The biggest decrease is seen in the 12 h measurement, where it is at first faster and then slows down. In the 24 h experiment the decrease is constant over time, there is a an inexplicable drop after 17 h in this measurement. In the 48 h experiment te decrease seems to happen in the first hours. In the 65 h experiment on the other hand the decrease happens in the second half of the measuring period.

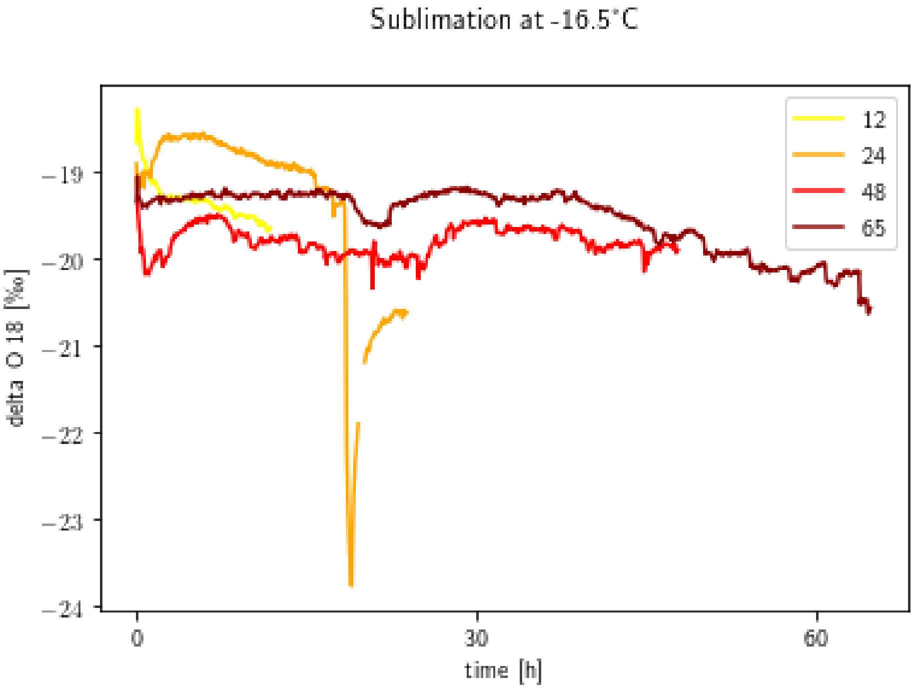

Figure 43: Figure 40 but for all Sublimation measurements at -16.5 °C.

In Figure 44 the snow profiles of all experiments at -16.5 °C are shown. Each profile is shown as variance in perspective to their own top three layers. No clear trend is visible. The variance in the profile is rather positive than negative over all. The amplitude of this variance seems to be bigger for shorter measuring periods. This might show that the snow itself is smoothing the original signal from sieving over time and because this being a really fast process it is not seen in the other temperature regimes. But it also could be from the bigger measuring uncertainties in these measurements.

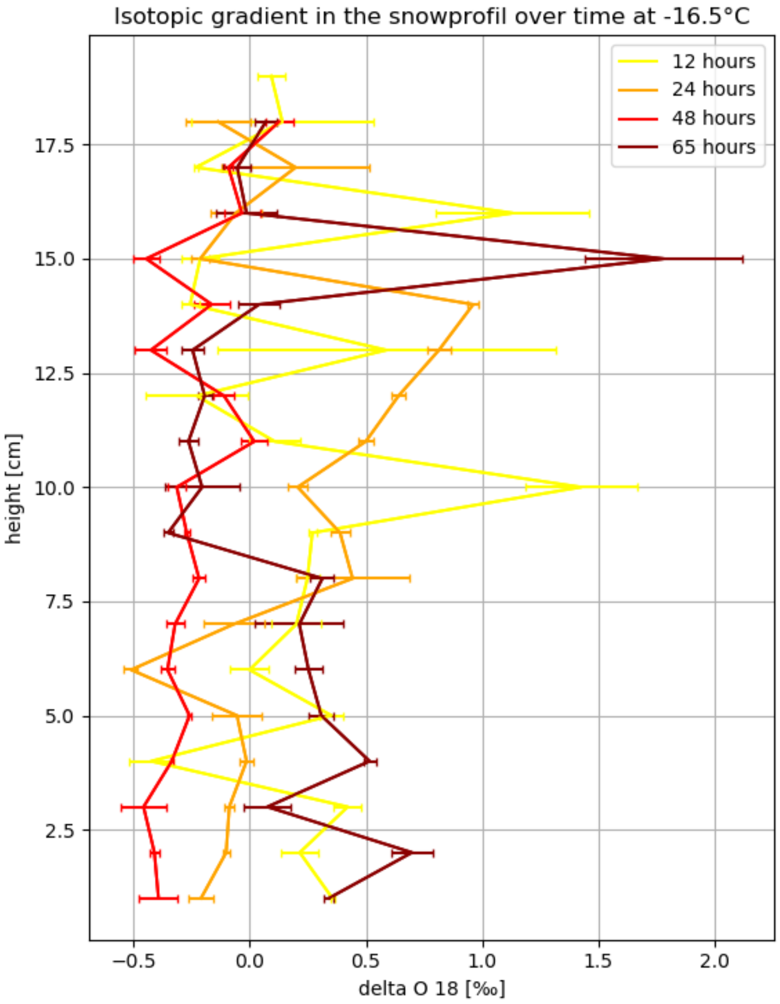

Figure 44: Figure 35 but for the evolution of the isotopic gradient at -16.5°C. The standard deviation in each point is between 0,01 and 0,72 ‰ but only for 8 measurements in all snow profiles at -16.5 °C have a bigger standard deviation than 0,2 ‰ was measured.

To compare these gradients Figure 45 shows the difference between the top three layers and bottom three layers. In the warm temperature regime a gradient evolves over time. In the intermediate and cold regime no such thing as a gradient evolving can be spotted.

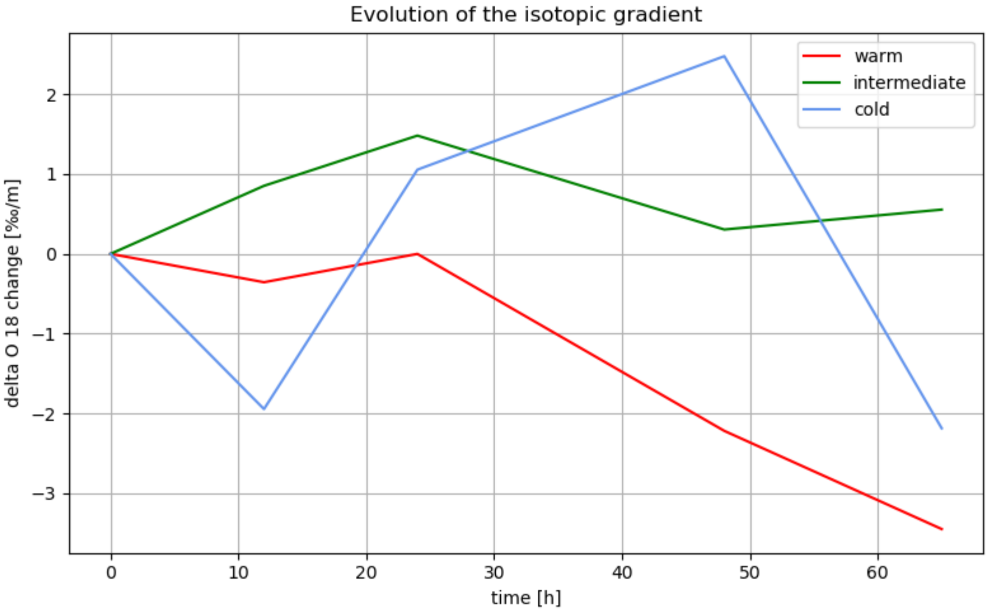

Figure 45: Evolution of the isotopic gradient, top three layers minus bottom three layers. Measurements are given in ‰/m.

B.3 Air Measurements of Different Temperature Regimes

This section shows the measurements of 48 h in the different temperature regimes. Additionally in Figure 47 all measurements are shown in the same plot, divided into the colors of the temperature regimes.

In Figure 46 all measurements lasting 48 h are shown. The warm regime shows again the lowest δ^{18}O values, the cold regime the highest δ^{18}O values and the intermediate regime is somewhere in between with some exceptions crossing the warm regime between 4 and 8 hours and crossing the cold regime right in the beginning. In this plot the problems with occurring drops at daytime are clearly visible. The starting times of the experiments were different: the warm experiment started at 12:50 p.m., the intermediate experiment started at 11:05 a.m. and the cold experiment started 4:15 p.m.. For example from hour five to hour 19 in the warm regime it is clearly nighttime with no disturbance. Around hour 24 in all regimes drops are visible.

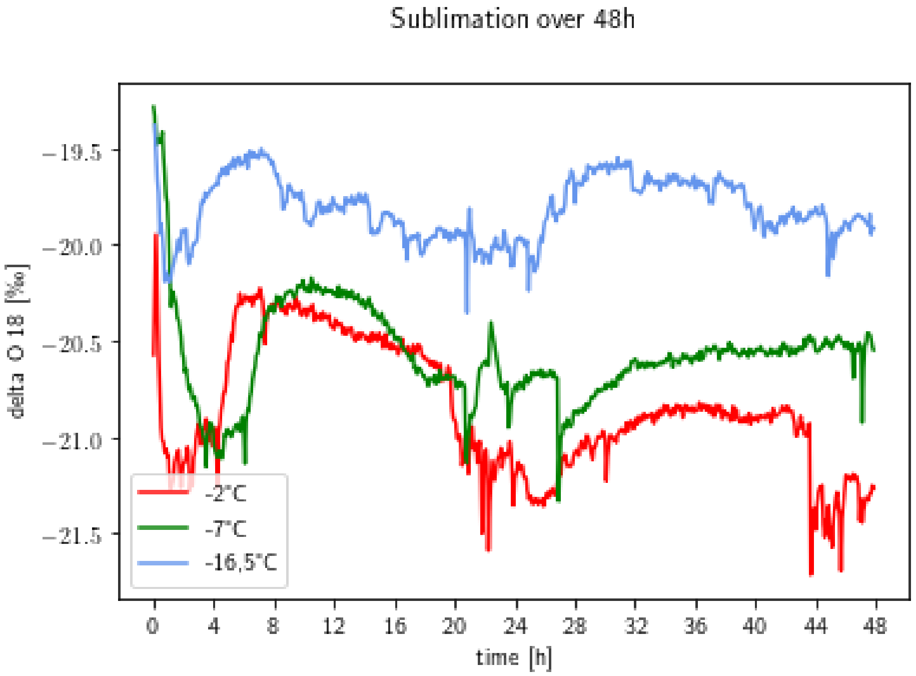

Figure 46: Isotopic content evolution of water vapor in the first 48 h of forced sublimation in different temperature regimes.

In Figure 47 all measurements are plotted according to their temperature regime. Again the measurements of the warm regime form the lower border of the values and the measurements of the cold regime form mostly the upper border of the values. Furthermore the values of the cold regime seem to be closer together than the values of the intermediate or the warm regime. The values of the red regime are spread the most.

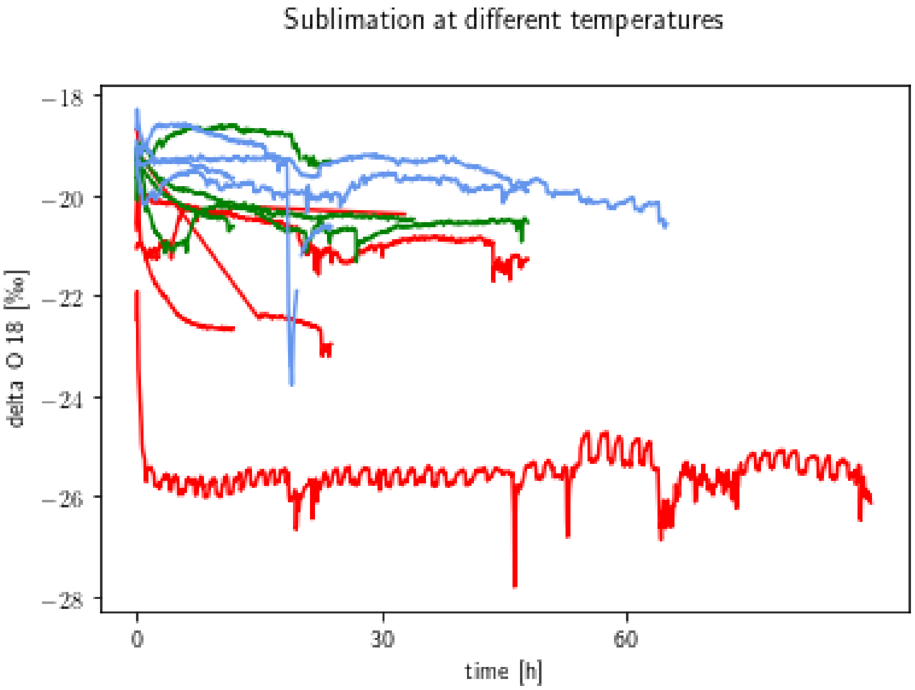

Figure 47: Isotopic content evolution at different temperatures, in red experiments at -2 °C, in green experiments at -7 °C and in blue experiments at -16.5 °C.

The results that the δ^{18}O values are lowest at warmer temperatures can be explained by a higher fractionation of the snow. The faster decrease during sublimation in the warmer regime in Figure 32 might be explained by the faster metamorphism. The faster metamorphism at warmer temperatures might also be the driving factor that the difference in the results of the warm regime, was biggest (see Figure 47). The snow was after the production refilled into a box and then stored for some hours in the temperature the experiment later would take place. The snow was not always stored for exactly the same amount of time. The difference in the structure of the snow might therefore be biggest at the warmer temperatures because one hour more or less in the warm regime would have a bigger influence on the structure compared to in the cold regime.

Figure 48 shows the evolving gradients in absolute values. It shows the difference between the top three layers and the bottom three layers. Over all it seems as if the amplitude of these changes are similar in all three temperature regimes and are bigger for longer time periods. This points to the conclusion, that longer lasting experiments would be needed to better understand the process happening in snow.

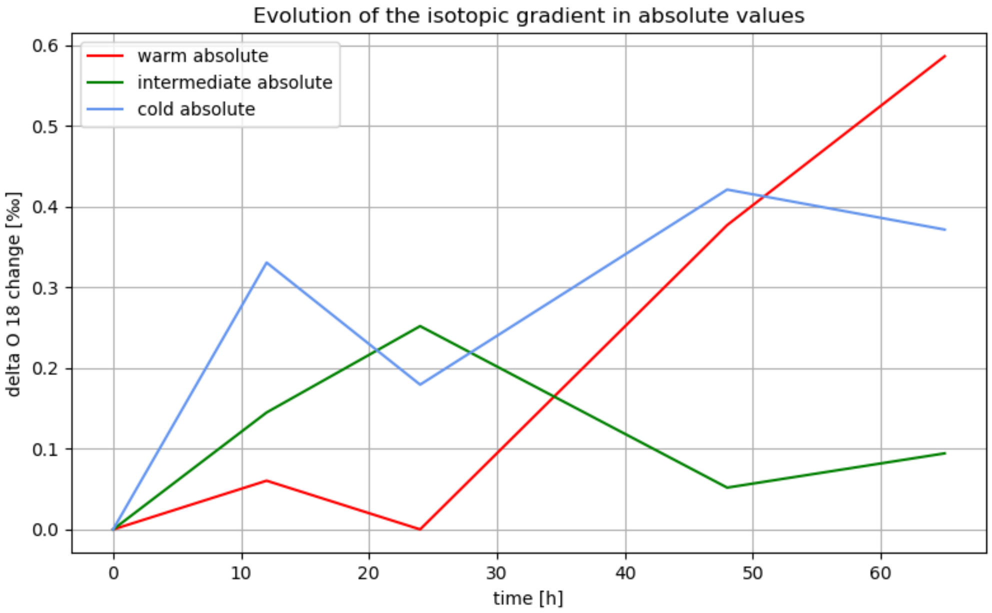

Figure 48: Figure 45 but in absolute values.

B.4 Same Age Snow Profiles

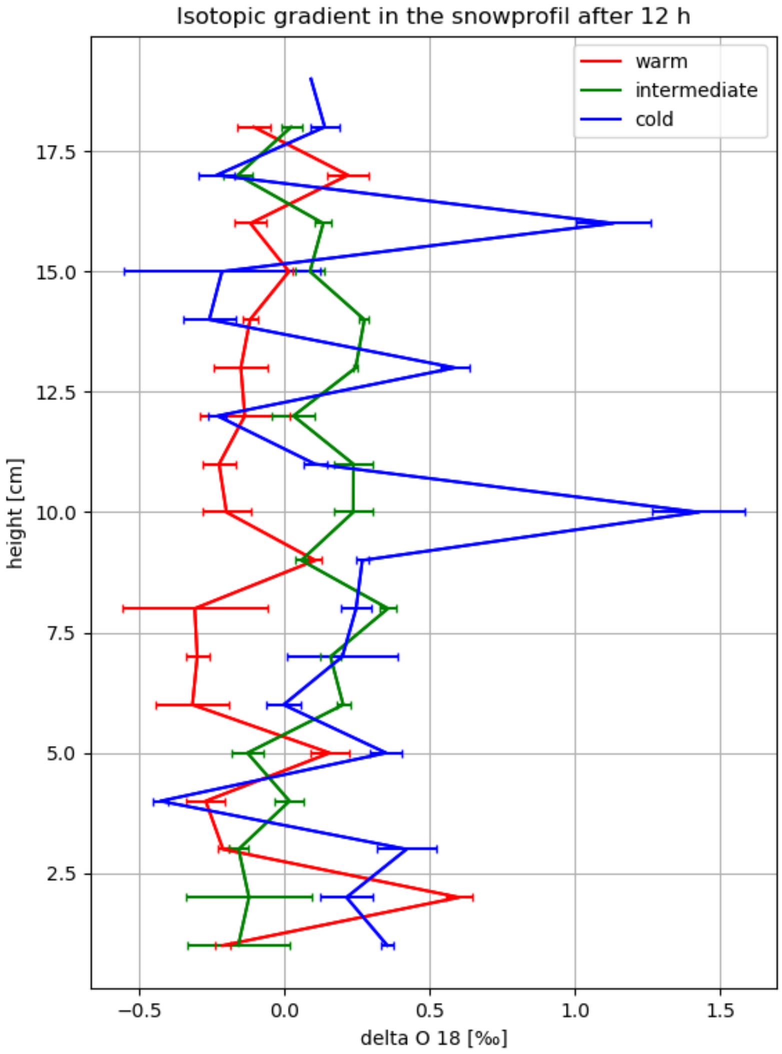

Figure 49: Evolution of the isotopic gradient over 12 hours at different temperatures. On the On the y-axis 0 cm is the bottom of the profile, 18 respectively 19 cm is the top of the snow profile. One measurement every 1 cm was made. The profile is shown in perspective to the mean of the top three layers.

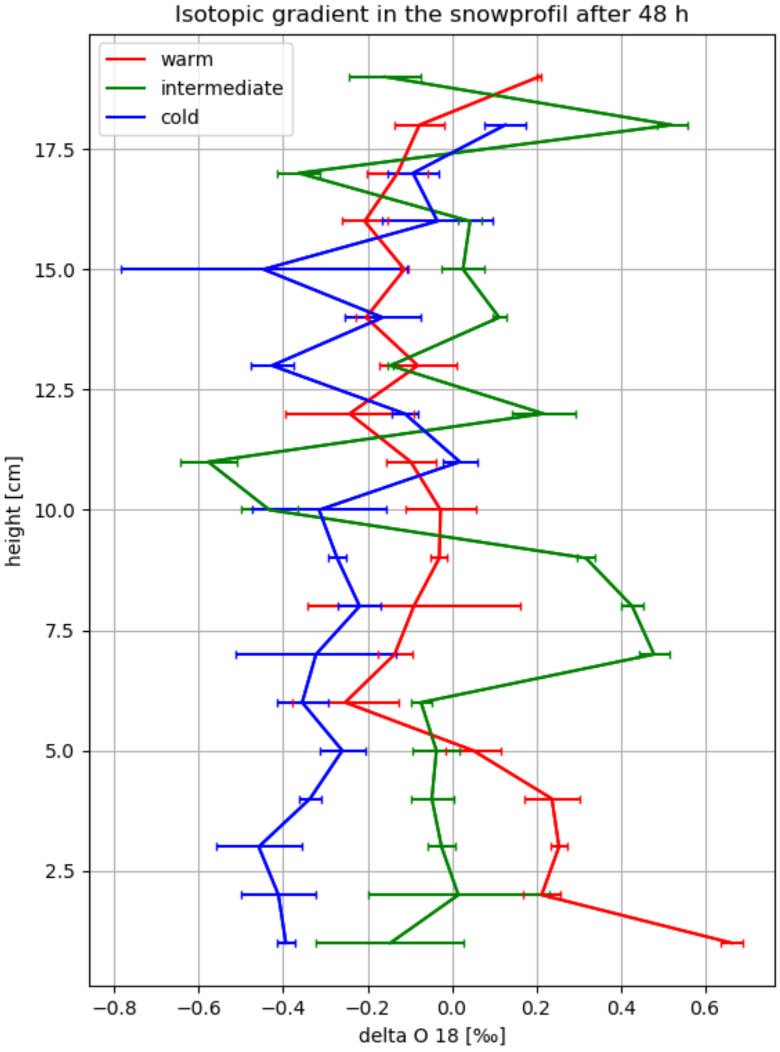

Figure 50: Evolution of the isotopic gradient over 48 hours at different temperatures. On the On the y-axis 0 cm is the bottom of the profile, 18 respectively 19 cm is the top of the snow profile. One measurement every 1 cm was made. The profile is shown in perspective to the mean of the top three layers.

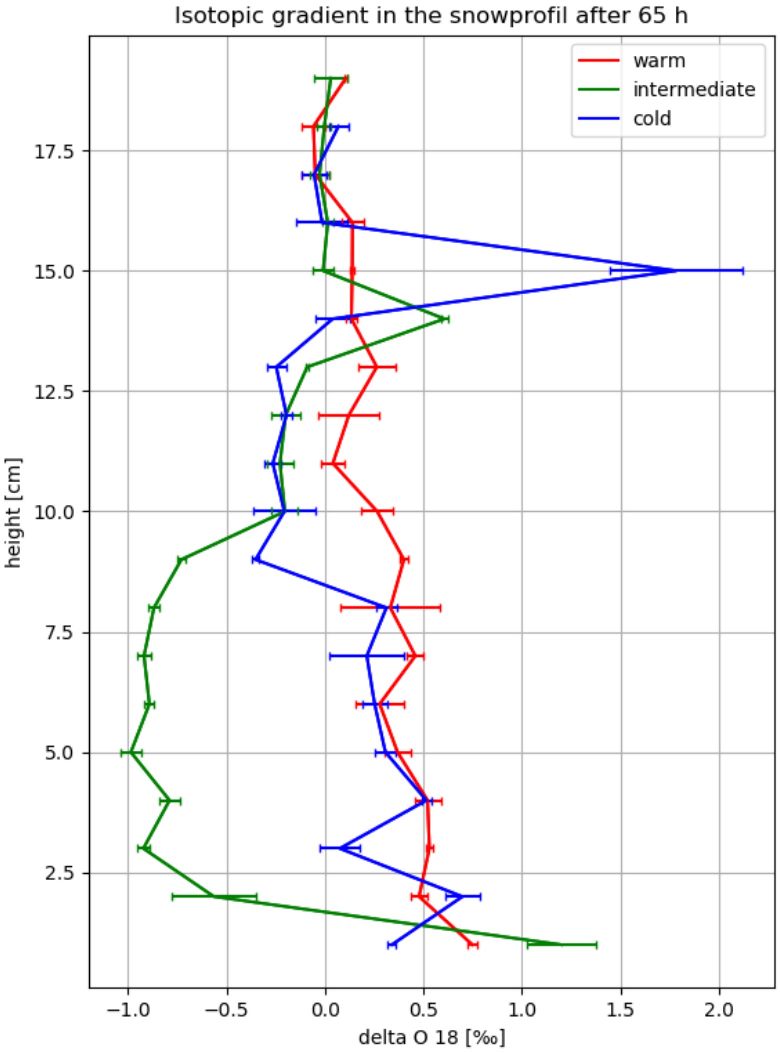

Figure 51: Evolution of the isotopic gradient over 65 hours at different temperatures. On the On the y-axis 0 cm is the bottom of the profile, 18 respectively 19 cm is the top of the snow profile. One measurement every 1 cm was made. The profile is shown in perspective to the mean of the top three layers.

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