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Influence of sublimation on stable isotope records recovered from high-altitude glaciers in the tropical Andes

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Abstract. Sublimation dominates the ablation process on cold, high-altitude glaciers in the tropical Andes. Transport of water vapor through the firn and exchange with ambient moisture alter the stable isotope composition of the surface layers. A sublimation experiment carried out during an ice core drilling campaign on Cerro Tapado (5536 m above sea level, 30°08′S, 69°55′W) revealed a strong enrichment in the ^{2}H and ^{18}O content in the surface layer. Concerning the deuterium excess, a decrease occurred at daytime, while during the night, the values remained comparatively constant. At daytime the sublimation is enhanced due to the higher moisture deficit of the ambient air accompanied by relatively high firn surface temperatures. Low surface temperatures at night cause condensation of water vapor in the firn pores near the surface and thus inhibit penetration of the isotopically enriched surface front into deeper firn layers. Measuring an isotope profile obtained through detailed sampling between the surface and 38 cm depth proved this mechanism. The observed modification of the isotopic composition at the surface was quantitatively described by a model, which also reproduced the mass loss measured with sublimation pans and calculated from relevant meteorological data. The results of this study suggest that the influence of sublimation on the preserved isotope record of ice cores under comparable environmental conditions is rather limited. In any case, simultaneous measurements of $\delta^{2}H$ and $\delta^{18}O$ help to identify layers in an ice core which might be effected by sublimation. However, since the mass loss due to sublimation was of the order of 2–4 mm per day during the experiment, important palaeoinformation from an isotope record could be eliminated during extended dry periods.

1. Introduction

Ice cores from the tropical Andes contain important information about physical and chemical changes during the past 25 kyr in the atmosphere close to a major source region of the global water cycle [*Thompson et al*., 1995, 1998]. Of particular interest are stable isotope records of the cores because they directly address the temperature and precipitation history in the region and therefore may also allow reconstructing climate anomalies caused by El Niño-Southern Oscillation (ENSO), beyond the limit of instrumental records [*Thompson et al*., 1992, 2000]. However, loss of accumulated snow at the surface due to sublimation is substantial at these high-altitude glacier sites. Within a dry axis between 18°S and 28°S, sublimation may be as high as 3 mm per day [*Vuille*, 1996] which inhibits the formation of glaciers even at altitudes over 6000 m above sea level (asl), under present-day climate [*Kull*, 1999]. Meter high snow pyramids ("penitentes") are impressive remnants of ablation processes which are forced by high global radiation, low relative humidity, strong winds, and dust deposition in cavities, which lower the albedo. However, an integral theory about the origin of penitentes [*Lliboutry*, 1954] is still missing. Changes in the isotopic composition at the surface of penitentes were already reported from two Chilean glaciers (Parinacota, 18°S and Echaurren, 33°S) where a modification was found to be strongly dependent on the exposure to solar radiation [*Peña*, 1989]. Furthermore, on the Quelccaya ice cap it was also found that seasonal changes in evaporation of snow could remarkably amplify seasonal changes in $\delta^{18}O$ [*Grootes et al*., 1989]. It is evident that under such extreme environmental conditions the various phase transitions of the water molecule also influence the isotopic composition in deeper layers. Diffusive mixing of water vapor which smoothes the original isotope signal in firn is well known and described in detail [e.g., *Johnsen*, 1977; *Jouzel et al*., 1983; *Whillans and Grootes*, 1985]. Especially the difference in firn diffusivity of $\delta^{2}H$ and $\delta^{18}O$ may cause post-depositional changes in deuterium excess, defined as $d = \delta^{2}H - 8\delta^{18}O$, and denoted d-excess [*Johnsen et al*., 2000].

To clearly verify a possible penetration of isotopically modified surface layers by sublimation into greater depths of a glacier, complementary $\delta^{2}H$ and $\delta^{18}O$ measurements are required. Plotting the experimental data in a $\delta^{2}H - \delta^{18}O$ diagram, the influence of evaporation (sublimation) can be seen if the slope of the trend line is lower than 8, the slope of the meteoric water line ($\delta^{2}H = 8\delta^{18}O + 10$). Furthermore, the d excess (which is only related to a slope of 8) can provide specific information about the source of the atmospheric moisture forming the precipitation [*Johnsen et al*., 1989]. To make full use of this information, the influence of diffusion and sublimation have to be ruled out first.

Experimental evidence of isotopic fractionation at the snow surface has been provided by earlier studies in the Alps [*Moser*

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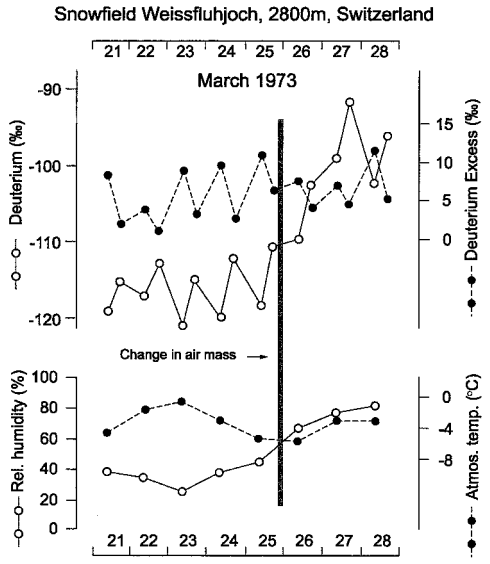

Figure 1. Diurnal variation of the δ^2H values and the deuterium excess at the surface of a late winter snow cover (topmost 1–2 cm) plotted together with the relevant meteorological parameters. During daytime the isotope values in the surface snow are being enriched due to the predominant sublimation process, while at night, recondensation of moisture partly balances further enrichment [after *Stichler et al*., 1982].

and Stichler, 1975]. During a fair weather period, which followed a snowfall, samples were collected twice a day from the surface layer with a thickness of 1–2 cm at Weissfluhjoch (2800 m asl, Switzerland). The measured data (Figure 1) show a general enrichment in the deuterium content, accompanied by a decrease of the *d* excess, during daytime when sublimation of snow prevailed. These effects are largely compensated during the first nights of the observation period, which is attributed to condensation of the air moisture in the snow cover. After the fifth day the weather conditions changed, as indicated by a general increase of the deuterium values, even during the nights, and by an increase of the humidity. It is assumed that the new air moisture transported into the study area is enriched in heavy isotopes with respect to the moisture of the previous days. It should also be noted that day–night changes of the *d* excess continued, which suggests that the new air moisture originated from the same source area as the preceding one (same *d* excess, higher humidity).

In the following, a similar experiment is described which was carried out during an ice core drilling campaign in the Chilean Andes, where sublimation dominates the ablation process. The aim was to describe the modification of the isotopic composition of the preserved snow cover due to sublimation and to assess the impact on the stable isotope record of the recovered ice cores. To detect any possible "penetration" of the isotopic changes at the surface into deeper layers, a small snow pit was sampled in detail.

2. Study Area and Meteorological Conditions

The Cerro Tapado glacier (5536 m asl, 30°08′S, 69°55′W) is located at the southern rim of a dry axis. This axis separates the tropical precipitation regime (with the main moisture sources originating from the Atlantic and the Amazon Basin) from the west-wind belt with moisture sources in the Pacific (Figure 2, left side). At a distance of ~200 km to the Pacific, Cerro Tapado peaks at the eastern margin of the Andean chain. According to meteorological data from the region (F. Escobar, DGA Santiago, personal communication, 1999), precipitation occurs mainly between May and August (austral winter). The dominant weather conditions leading to precipitation are a northward displacement of cold fronts from the Pacific and cutoffs of polar air interacting with tropical air [*Vuille and Amman*, 1997]. Convective summer storms can, in principle, also generate snowfall at summit regions around Cerro Tapado (as experienced during the drilling seasons 1998 and 1999). They may arrive from the east where a summer precipitation regime dominates. The influence of ENSO on the interannual variability of precipitation north of 35°S is substantial [*Escobar and Aceituno*, 1998]. The year after the 1997/1998 El Niño was extremely dry in this region (P. Aceituno, personal communication, 1999).

The southeast exposed glacier ranges from the summit plateau at 5536 m to a lowest point at 4600 m. The modern equilibrium line altitude (ELA) is found at 5300 m, the ratio of accumulation to ablation area is ~1.5–1. The size of 1.5 km^2 is exceptional in an otherwise completely dry environment. Even the 700 m higher neighboring Cerro Olivares is covered only by some patchy ice fields on the southeaster slopes. According to mass balance calculations an annual accumulation of 750 mm is needed to create and maintain a glacier. It is assumed that local effects (topography, wind-blown snow, albedo) are responsible for the needed surplus of accumulated snow. Radar measurements at the top of Cerro Tapado indicated a maximum ice thickness of 40 m (at the drilling site bedrock was reached at 38 m). The mean annual net accumulation rate, as derived from ^{3}H peaks of the nuclear weapon tests during the 1960s, is 300 mm water equivalent. The temperature in the borehole varied between −8.5°C at the surface and −12.5°C at bedrock [*Zweifel*, 2000]. From the distribution of few, thin ice lenses, percolating meltwater can be excluded. Nevertheless, density increases rapidly with depth reaching already values around 0.8 g/cm^3 at 20 m. Massive surface melting occurs only at the margins of the glacier near the uncovered rocks where the heating of the dark volcanic material is substantial. (Small frozen lakes covered with penitentes could be seen during the experiment). Near the drilling site (200 m apart from the rocks) the surface was flat and smooth (Figure 2, right side).

To obtain the necessary meteorological data, portable equipment was placed at 4550 m and at the summit, respectively. The lower station had already been operating for 1 year, the summit station only for the time of experiment and drilling (10 days). Continuous data collection integrating 30 min intervals included relative humidity, wind speed and direction, atmospheric temperature and pressure, and global radiation. Three temperature sensors measured firn temperatures at 7, 15, and 25 cm depth, respectively (Figure 3a). The moisture deficit during the day indicates maximum sublimation (Figure 3b). Sublimation was measured by weighing small pans filled with snow (sublimation lysimeters) during the whole period from sunset to sunrise and sunrise to sunset and thereafter modeled with the relevant meteorological parameters (P. Ginot et al., submitted manuscript, 2001) (hereinafter referred to as G2001).

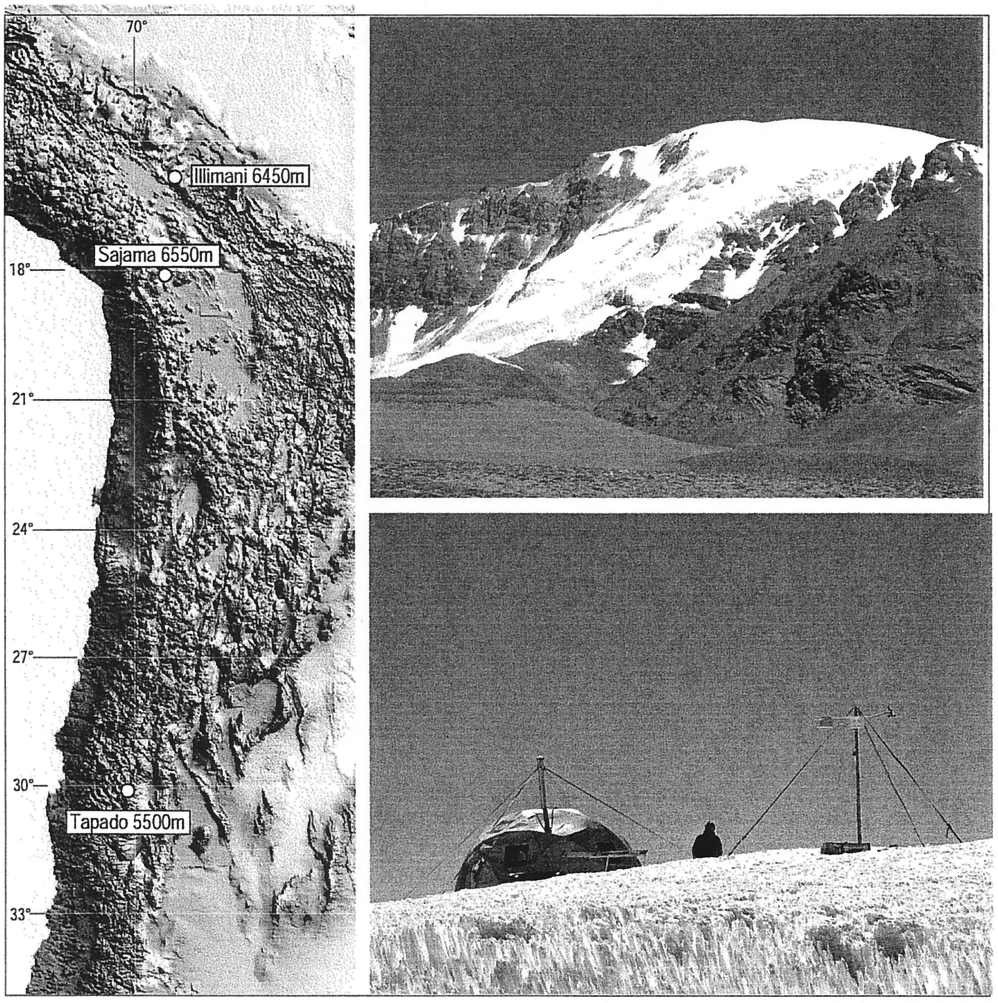

Figure 2. Geographic location, overview of the glacier, and drilling site at the top of the Cerro Tapado (5534 m). The tongue of the southeast exposed glacier terminates at 4600 m. The importance of sublimation is illustrated by the evolution of penitentes near the drilling site and the meteorological station.

3. Experiment

The experiment was carried out at the summit of Cerro Tapado during the drilling campaign in February 1999. It was designed to obtain the daily changes in the isotopic composition of the surface firn layer due to sublimation and refreezing of condensed air moisture according to the previous experiment described above. A flat snowfield, 50 m away from the drilling site, was chosen because the smooth undulating surface indicated little influence of penitentes formation. As a first step, a small pit was dug from which samples were taken in 1–3 cm intervals down to a depth of 38 cm where a hard firn layer marked a change in accumulation conditions. The whole profile appeared very homogeneous without ice lenses (except some small-scale icy crusts that where excluded from sampling). The overall density was 0.4 g/cm^3. Thereafter, the uppermost 7 cm were removed to create a new flat surface to be exposed to the influence of air moisture exchange forced by sublimation (Figure 4). Twice a day, after sunrise and before sunset, thin slices of ~1 cm thickness were collected corresponding to about 4 mm of water equivalent. This procedure was repeated for $3\frac{1}{2}$ days. The isotope content of the air moisture was derived from intensive riming that occurred in the evening on February 14. All samples were stored in precleaned plastic tubes and shipped to the laboratory in a frozen state. Beside the ^{2}H and ^{18}O contents a detailed set of chemical constituents was analyzed, including the major anions and cations and organic compounds as well. The stable isotope ratios were measured twice by standard mass spectrometry (analytical error of $\pm$ 0.5‰ for δ^2H and $\pm$ 0.05‰ for δ^{18}O, respectively) to obtain a high precision in d-excess values. A detailed discussion of chemical and meteorological results is given elsewhere (G2001).

4. Results and Discussion

The obtained δ^{18}O − depth profile (Figure 5) shows a steep decrease in the uppermost 7 cm followed by a more gradual decrease farther down. The d excess increases sharply with depth in those uppermost layers. At about 7 cm the d excess reaches a maximum and farther below remains rather constant at about 15‰. The drastic change of both parameters is also reflected in the δ^2H − δ^{18}O plot (Figure 6). The values are spread about a line with the slope of 8 (meteoric water line) except for the last three values, which define a typical sublimation (evaporation) line with a slope of $s = 4.88$. These findings indicate that there is a modification of the isotopic

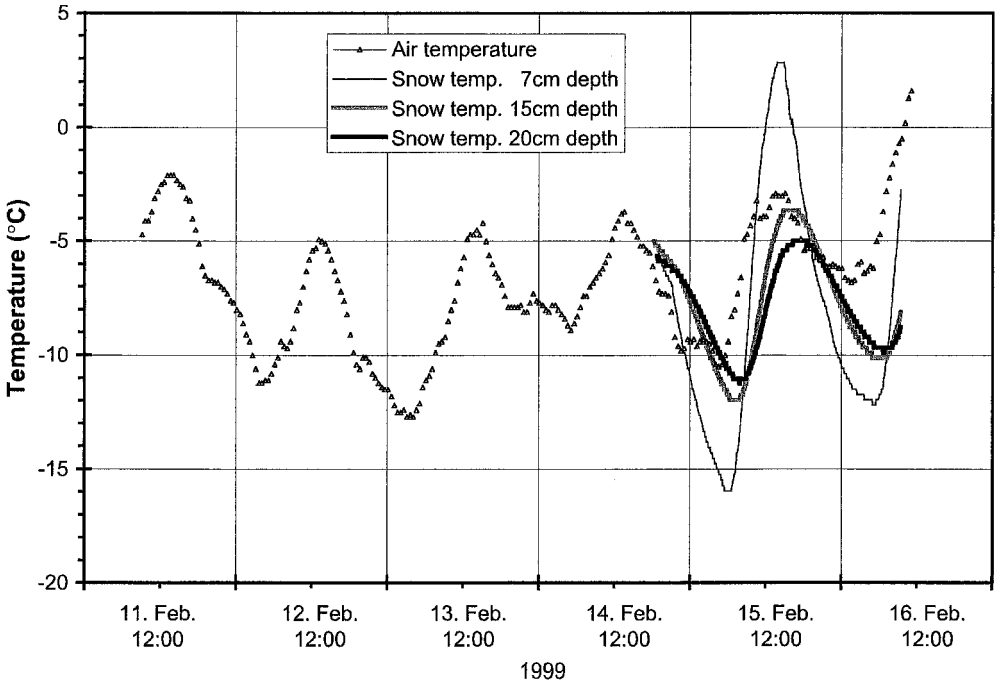

Figure 3a. Diurnal variations of air temperature at 2 m height (February 10–16, 1999) and firn temperature at three depths. Note that the near-surface temperature during night is lowest due to strong reemitted infrared radiation (clear sky), which is additionally enforced by cooling of continuing sublimation.

composition of the firn by sublimation, which is restricted to a depth of 7 cm only.

The surface sublimation experiment shows a steady increase of $\delta^{18}O$ of about 5‰ and a stepwise decrease of the d excess by 10‰ during the observation period (Figure 7). Concerning the d excess, the decrease occurs mainly at daytime, reflecting the influence of the kinetic isotope effect during intense sublimation, while at night, the values remain more or less constant. The δ^2H and $\delta^{18}O$ values are plotted also in Figure 6. The calculated regression line results with the same slope (s = 4.86) as that of the uppermost pit samples. The (rather incidentally so close) agreement of the two observed slopes caused by the same process indicates a dynamic equilibrium between mass loss and depth penetration of the sublimation front.

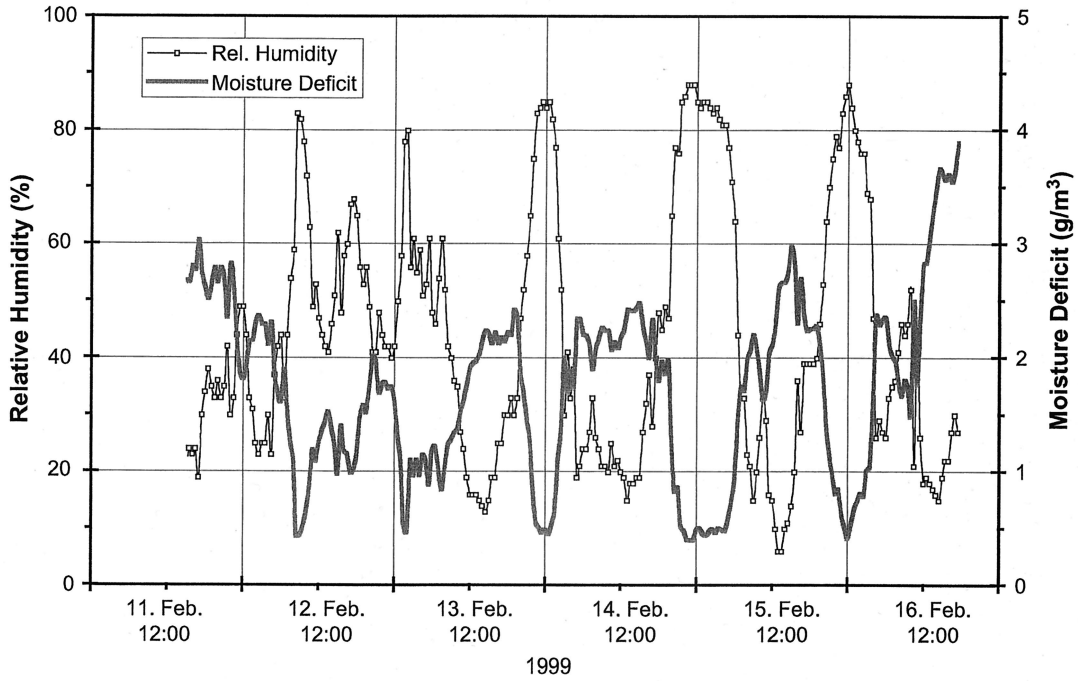

Figure 3b. Diurnal variations of relative humidity and moisture deficit (difference in absolute and relative humidity) covering the time of sublimation experiment.

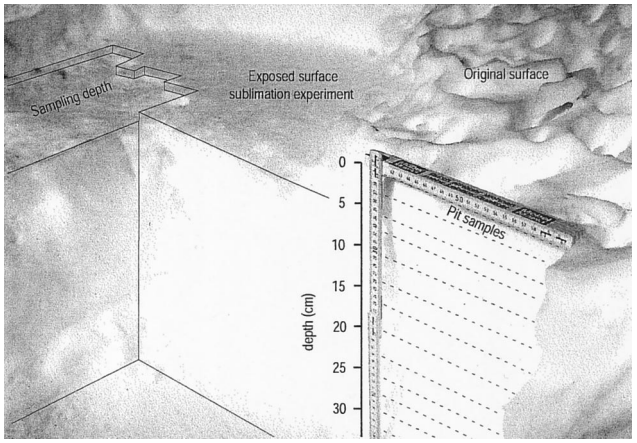

Figure 4. View of the surface experiment. The snow pit was dug down to a hard layer, indicating a change in accumulation conditions. The undulating surface containing little icy pieces is shaped by sublimation. The surface part was removed to provide a homogeneous surface for the experiment.

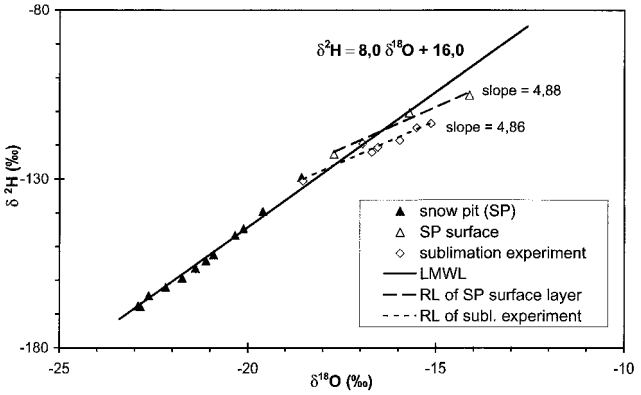

Figure 6. The $\delta^2H - \delta^{18}O$ diagram of the pit and the surface samples. The slope of the regression line (RL) of the uppermost pit samples and the samples from the surface experiment are characteristic for evaporation (sublimation), the samples from below 7 cm depth follow perfectly the meteoric water line.

These experimental findings can be explained as follows: The sublimation process is driven by the difference in the temperature of the ambient air and of the surface and deeper layers of the firn (see Figure 3a). The sublimation is strongest during daytime due to the highest moisture deficit of the ambient air accompanied by high firn surface temperature. This process results in an isotopic enrichment at the surface (Figure 6). The low temperature of the firn surface at night causes condensation of the vapor and thus prevents penetration of the isotopically enriched front into deeper layers of the firn profile. The observed higher d excess at a depth of about 7 cm also points to the existence of such a condensation front.

To quantitatively describe the effect of sublimation on the isotope composition of firn at the surface, a model has been derived which has two main features: (1) the isotopic enrichment at the surface, which is described by a net diffusive flux of the isotope species i (i stands for deuterium and oxygen 18, respectively) into the interior of the firn profile, and (2) a time-dependent coordinate system (its origin is defined by the firn surface) which accounts for the firn loss at the surface in terms of an apparent advective movement of the firn layers toward the surface. The velocity of this movement is equal to sublimation rate ν. Feature (1) can be expressed by

$$-D\,\frac{\partial R_i}{\partial x} = (a_i R_i + b_i R_i^a)\,\nu, \tag{1}$$

where D is an apparent diffusion coefficient (the small difference between its value for deuterium and oxygen-18 has been neglected), R_i (R_i^a) is the isotope ratio of the firn at the surface (of atmospheric water vapor above the firn surface), ν is the sublimation rate (in cm firn layer per day), and the factors a_i and b_i are defined by the expressions

$$a_i = 1 - \frac{1}{\alpha_i(1-h)(1+n\Theta C_D^i)}, \tag{2a}$$

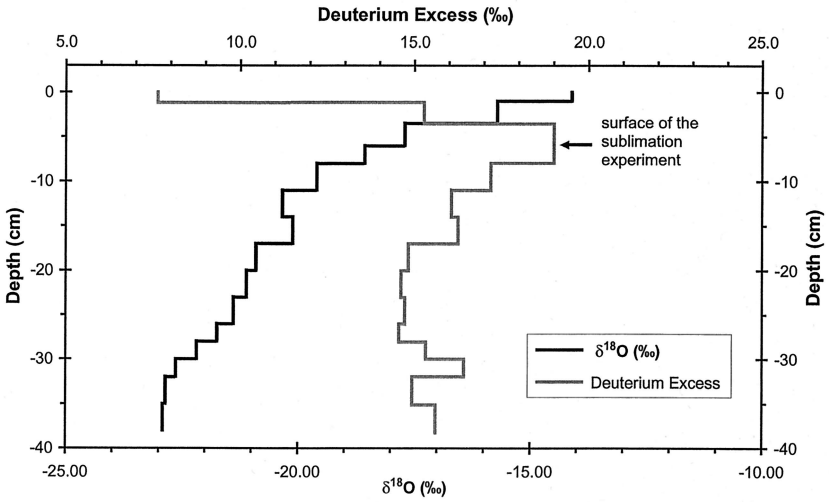

Figure 5. Oxygen 18 content and deuterium excess profiles of the pit samples. The $\delta^{18}O$ values show a strong decrease in the upper 7 cm of the profile followed by steady further decrease. After a sharp increase down to 7 cm, the deuterium excess remains rather constant. The latter might be due to diffusive mixing under equilibrium conditions.

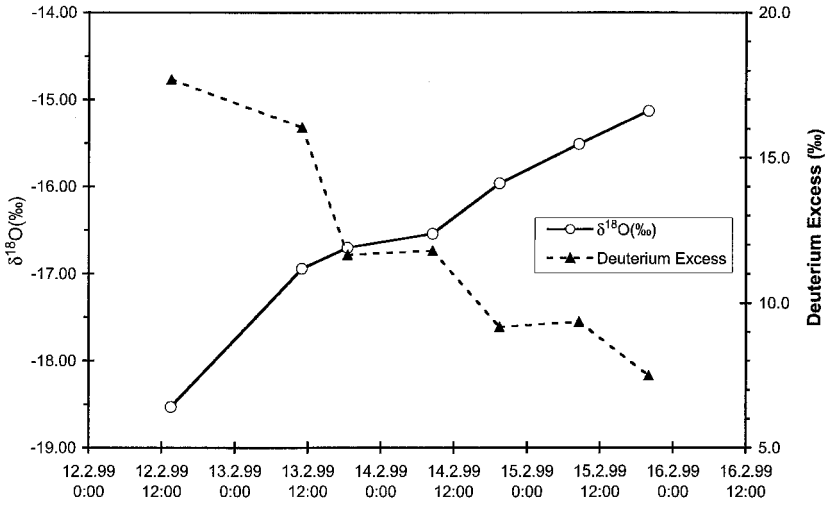

Figure 7. Oxygen 18 content and d-excess variations in the firn surface (1 cm) during the sublimation experiment.

$$b_i = \frac{h}{(1-h)(1+n\Theta C_D^i)}. \tag{2b}$$

In these expressions, h is the average relative humidity during observation ($h = 40\%$), α_i is the equilibrium fractionation factor, and the parameter n, θ, and C_D^i characterize the kinetic fractionation factor α_{ki} (J. Gat, manuscript in preparation, 2001) (hereinafter referred to as JGat):

$$\alpha_{ki} = 1 + (1-h)n\Theta C_D^i. \tag{3}$$

The parameter n reflects the wind conditions at the glacier surface ($0.5 \le n \le 1$), θ ($0.5 \le \theta \le 1$) accounts for the influence of sublimated water vapor on the isotopic composition of the free air above the firn surface, and C_D^i characterizes the diffusive transport at the interface to the atmosphere.

In a first approximation (neglecting diffusive transport in the pores of the interior of the profile), feature (2) is reflected by the equation

$$\partial R_i/\partial t = -\nu \partial R_i/\partial x. \tag{4}$$

The solution of (4) under the special boundary condition (equation (1)) provides a quantitative description of the spatial and temporal change of the isotopic composition of the firn near the surface. For the change of R_i at the surface between the observation times t_1 and t_2 we obtain

$$R_i(t_2) - R_i(t_1) = \left(R_i(t_1) + \frac{b_i}{a_i}R_i^a\right)\left(\exp\left(\frac{a_i\nu^2}{D}(t_2-t_1)-1\right)\right). \tag{5}$$

Furthermore, on the basis of (4) the sublimation rate ν can be estimated using the measured isotopic depth gradient at the surface (Figure 5) and the isotopic "enrichment rate," i.e., the measured temporal change of the isotopic composition of the firn at the surface of the glacier (Figure 7).

In the following, the parameters included in the above equations are determined, and the theoretical results derived by these equations are compared with the experimental data. The value of R_i^a has been calculated from the collected rime assuming isotopic equilibrium between the condensed (with values of $\delta^{18}O = -5.41‰$ and $\delta^2H = -23.6‰$) and the vapor phase. According to the equilibrium fractionation factor α of 1.016256 and 1.143587 at -6°C for oxygen 18 and deuterium, respectively [*Majoube*, 1971; *Merlivat and Nief*, 1967] the isotopic composition of the air moisture results in $\delta^{18}O = -21.31‰$ and $\delta^2H = -146.2‰$. Since the moisture, which caused the riming, was transported with the prevailing westerly winds, these values were adopted as the average isotopic composition during the experiment.

It should be noted that for longer time periods the temporal fluctuation of R_i^a must be taken into account. The temperature dependence of the equilibrium fractionation factor is of minor influence on the isotopic fraction during sublimation. For α calculation a value of -6°C was adopted, which is close to the average surface temperature during the experiment. The value of the parameter C_D^i is 0.0285 for oxygen 18 and 0.0251 for deuterium, respectively (J.Gat). The value of the product $n\theta$ has been derived from the slope s in the $\delta^2H - \delta^{18}O$ diagram (Figure 6). Using the expression

$$s = \frac{\partial R_2}{\partial x}\Big/\frac{\partial R_{18}}{\partial x}, \tag{6}$$

the slope can be calculated using (1). It should be noted that the slope in the $\delta^2H - \delta^{18}O$ diagram is, within the assumptions of the model, independent from the "kinetic" parameters D (diffusion of water vapor into the firn) and ν (sublimation of firn into the free atmosphere). The results are shown in Figure 8, where the product $n\theta$ is used as a free parameter. As mentioned above, both slopes in Figure 6 reflect the same process, namely, isotopic fractionation due to sublimation. With a mean value of the slope s of 4.87 and the average relative humidity during the observation period of $h = 40\%$, the value of the product $n\theta$ is 0.5. This result is in good agreement with the expected value. The prevailing strong wind regime observed at the glacier (turbulent conditions) suggests that n is close to 0.5. Moreover, the influence of sublimated water vapor (given the relatively small surface of the glacier) on the isotopic composition of the air moisture appears to be negligible under such conditions which results with a value of θ close to 1.

The sublimation rate ν can be estimated from the ratio of the measured temporal change (Figure 7) and depth gradient (Figure 5) of the isotopic composition of the firn at the surface.

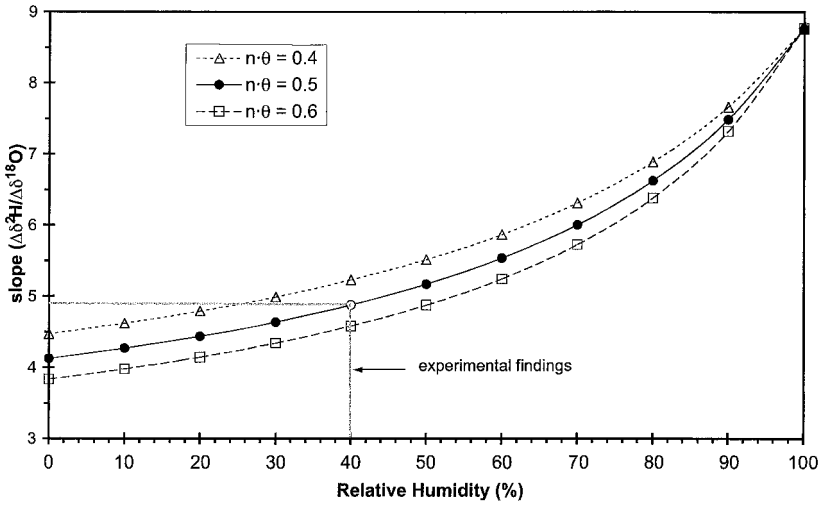

Figure 8. Plot of relative humidity versus slope ($\Delta\delta^2H/\Delta\delta^{18}O$) for estimating the product of n and θ, parameters involved in the kinetic processes during sublimation. From the measured slope of $s = 4.88$ and under the experimental conditions ($h = 40\%$), $n\theta$ results in 0.5.

The value derived from the relevant oxygen 18 data and for an average relative humidity of $h = 40\%$ is 1 cm firn per day (4 mm weq). It has been used to estimate the diffusion coefficient by (1). The obtained value is 20 cm^2/day. Furthermore, the temporal change of the isotopic composition of the firn at the surface of the glacier could be calculated using (5). The results are plotted in Figure 9 using the measured initial isotope values for deuterium and oxygen 18 of −130.6 and −18.53‰, respectively. (It should be noted that in the equations derived above, the isotopic composition is given in terms of the isotope ratio, but in the figures, the corresponding δ values have been used). For the observation period the calculated curve fits well with the experimental data. Deviations between modeled and observed data might occur if the isotopic composition of the atmospheric moisture changes (the model assumes that this parameter is constant in time). The good agreement supports the assumption that the isotopic composition of the atmospheric moisture calculated from the rime was characteristic for the period of the experiment. Finally, a value of 0.7‰ per day has been derived for the rate of the temporal change of oxygen 18 at the surface. This result is comparable with earlier findings [*Grootes et al.*, 1989] where a value of 0.5‰ per day was obtained for an observation period of 12 days and more humid conditions than at the Tapado glacier.

5. Conclusions

Two important postdepositional processes may influence a palaeoclimatic reconstruction derived from stable isotope records in tropical ice cores: (1) diffusive mixing of water vapor within the firn layer and (2) sublimation at the surface of the snow cover. Especially the latter is crucial for applying the d excess as a source indicator for atmospheric moisture. However, from the $\delta^2H - \delta^{18}O$ relation (slope) it is evident, that layers affected by sublimation reach a depth of about 5–10 cm only, even under extreme dry environmental conditions as prevailing before and during the experiment. Condensation and refreezing of water vapor during night at the surface (the

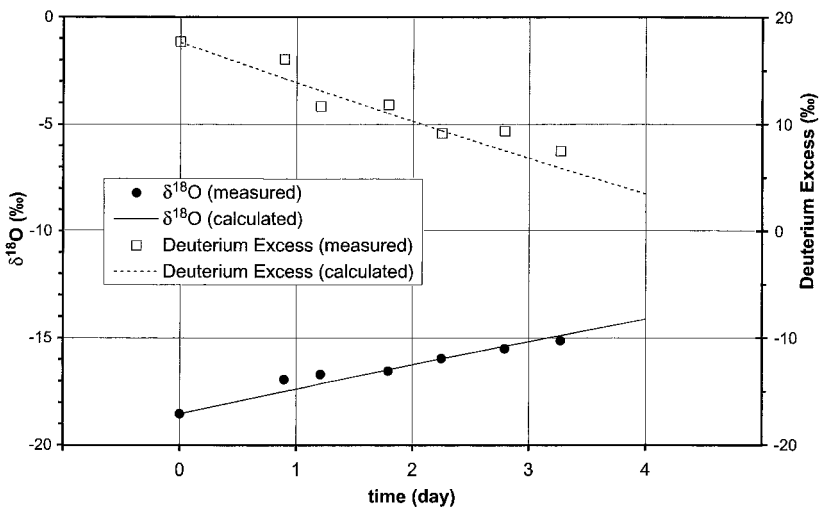

Figure 9. Measured and calculated $\delta^{18}O$ values and deuterium excess versus time (days) after starting the sublimation experiment.

coldest part of the profile at that time) blocks the penetration of the enriched isotope ratios to deeper layers. The total mass loss at the surface also has to be considered since it removes instantaneously the enriched layer, thus limiting the actual isotopic enrichment. The process ends with the next snowfall. Remnants of the sublimation process may be preserved always by a new snow cover. Amount of disturbed layers and their subsequent smoothing by diffusion will depend on the duration of dry periods and/or on amount and frequency of precipitation events. In any case, suspicious samples from an ice core record may be identified within the $\delta^2H - \delta^{18}O$ diagram.

The experimental data could be described by a model, which also reproduced the amount of sublimation sufficiently. The average loss of 4 mm weq per day seems to be an upper limit when comparing it to 2 mm weq as derived from sublimation pans. Nevertheless, one has to take into account that the latter does not include the moisture transport from deeper firn layers to the surface during night and might therefore be considered as a lower limit. The mass loss itself may have consequences for a palaeorecord too because extended dry periods could remove important isotopic information from previous precipitation events.

Moreover, the result of this experiment will have major consequences for the interpretation of chemical species obtained from glaciers under comparable environmental conditions (low humidity, small and event-based accumulation rate, high sublimation rate). The large differences in changes caused by sublimation among volatile, soluble, and insoluble components are discussed in detail elsewhere (G2001).

Since sublimation is known to be an important process in cold, dry environments too, the experiment should be repeated, and the model could be adapted to the different ambient conditions at sites where sublimation is expected to influence palaeoenvironmental records from ice core measurements.

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