

Experimental determination of snow sublimation rate and stable-isotopic exchange

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ABSTRACT. Snow sublimation is a fundamental process that affects the snow crystal structure and is important for ice-core interpretation, remote sensing, snow hydrology and chemical processes in snow. Prior studies have shown that sublimation can change the isotopic content of the remaining snow; these studies have inferred sublimation rates using field data, and were unable to control many of the environmental parameters that determine sublimation rate (e.g. temperature, relative humidity, snow microstructure). We present sublimation rate measurements on snow samples in the laboratory, where we have controlled many of these parameters simultaneously. We use the same experimental apparatus to determine sublimation rate, investigate the isotopic effects of sublimation, and study the isotopic exchange between vapor and solid. Our results suggest that pore spaces in snow are almost always at saturation vapor pressure; undersaturation may be possible in large pore spaces or in regions of rapid interstitial airflow. We present a revised formulation for determining the mass-transfer coefficient for snow as a linear function of Reynolds number ($h_m = 0.566Re + 0.075$), estimate the fractionation coefficient for sublimating snow, and provide evidence for isotopic exchange between vapor and solid.

INTRODUCTION

The sublimation of ice or snow is driven by an imbalance between the saturation vapor pressure (or vapor density) at a given temperature, and the vapor pressure in the immediate vicinity of an ice surface. If the former exceeds the latter, ice or snow sublimates to eliminate the imbalance. The sublimation rate of ice or snow is an important component of the surface energy balance, mass balance, and may play a significant role in isotopic exchange. Physically based studies of isotopic change (e.g. Neumann and Waddington, 2004) are limited in part by the unknown effects of sublimation on isotopic ratios and the mass-transfer coefficient from snow to vapor. Field studies (Sturm and Benson, 1997; Stichler and others, 2001) have documented the magnitude of post-depositional isotopic change, but have not determined the relative importance of several processes that are likely active in natural snowpacks.

Models of vapor movement through variably saturated firn (Albert, 2002) have had to estimate the mass-transfer coefficient to calculate sublimation rates, owing to a lack of laboratory data. Prior work on determining the sublimation rate of snow or ice in the laboratory has focused on sublimation of single ice particles during forced convection under high airflow rates (e.g. Thorpe and Mason, 1966), while fieldwork has typically used meteorological observations to infer sublimation rate (e.g. Box and Steffen, 2001) from energy-balance considerations.

Prior studies of stable-isotopic exchange have noted an isotopic enrichment of the remaining snow as a result of sublimation. Moser and Stichler (1975) measured a linear increase in $\delta^{18}\text{O}$ of a snow sample in the Alps after

successive days of sublimation, which suggests some degree of isotopic fractionation during sublimation. Stichler and others (2001) measured the isotopic evolution of near-surface snow over several days in the tropical Andes and found that during periods of sublimation the $\delta^{18}\text{O}$ of the remaining snow increased by several permil. Satake and Kawada (1997) inferred that samples from East Antarctica had lost about 30% of their original mass due to sublimation, leading to a measured isotopic enrichment of $\sim 6\text{‰}$ in $\delta^{18}\text{O}$. Other investigators (e.g. Sommerfeld and others, 1991; Sturm and Benson, 1997) have shown that temperature-gradient metamorphism also leads to isotopic enrichment in the high-temperature regions. Although each of these studies shows the net effect of vapor motion or loss on stable-isotope ratios, it is difficult to estimate the fractionation coefficient for sublimation because there are multiple processes active in temperature-gradient metamorphism, or unknown environmental conditions during sublimation at field sites.

In this paper, we present direct measurements of the sublimation rate of a snow sample under forced convection in the laboratory, and present isotopic measurements to investigate isotopic exchange between water vapor and the snow sample. The laboratory setting allows us to control many of the parameters that influence sublimation rate in nature (i.e. grain size, microstructure, temperature, rate of airflow rate through snow (ventilation)). Our methodology relies on precise frost-point measurements of an airstream prior to and after passing through a snow sample, and measurements of the isotopic content of the vapor in the airstream before and after passing through the snow sample.

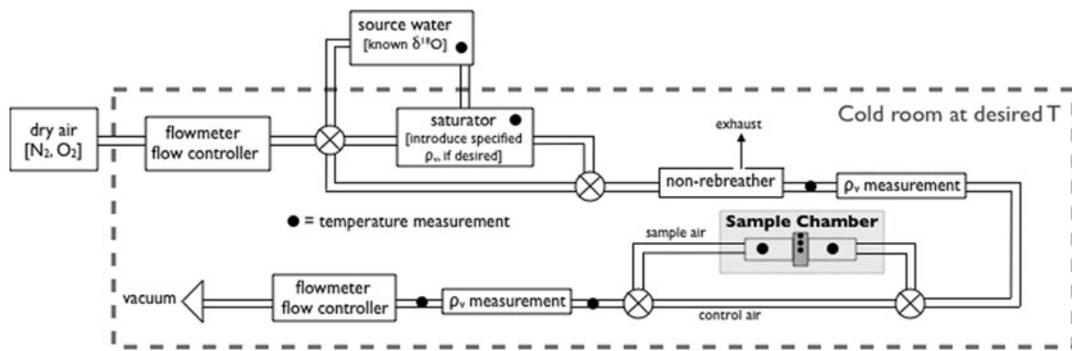


Fig. 1. Diagram of apparatus. Air is drawn through the sample and apparatus via vacuum at lower left. The cold room is maintained at a constant temperature to within $\sim 1^\circ\text{C}$; a recirculating bath maintains a constant temperature in the sample chamber to within 0.1°C . Adapted from Neumann and others (in press).

METHODS

We infer the snow sublimation rate by drawing air through a snow sample in a sealed chamber and measuring the change in relative humidity (via a chilled-mirror hygrometer, which measures the frost point) as the air passes through the sample. We record the snow sample temperature, the vapor density (ρ) of the air both up- and downstream of the sample, the air temperature and flow rate, and the pressure drop across the sample. We also measure the isotopic content of the water vapor in the airstream, both before and after passing through the snow sample, allowing us to determine the extent of isotopic exchange between the vapor and solid. The apparatus is similar to that of Conklin and others (1993); a schematic is shown in Figure 1.

The experimental set-up is described fully in Neumann and others (in press). Briefly, we use sieved natural snow of a specified grain size (~ 1 mm diameter) to form disc-shaped snow samples of radius 7 cm and thickness 1–5 cm. The sample is sifted into a PVC ring, with fittings to allow thermocouple wire to be incorporated into the sample during formation. The sample is clamped between two chambers with smaller radii; foam gaskets are used between the snow sample and the chamber to prevent air exchange between the sample chamber and the surrounding air. The chambers allow the airflow to diffuse from the small-diameter tubing of the airstream (0.635 cm) to the larger diameter of the snow sample. The entire sample chamber is housed in an insulated box connected to a constant-temperature recirculating bath.

Upstream of the sample chamber, the flow of dry air (vapor density $\rho = 0 \text{ kg m}^{-3}$) is controlled with a needle valve and the flow rate is recorded. Water vapor with a measured isotopic content and vapor density is introduced via a saturator, constructed following the method of Morris (1997). Our saturator is ~ 3 m of coiled copper tubing inserted in a recirculating bath. Frost is deposited in the saturator by bubbling dry air through a water source (at 25°C), and then forced through the saturator coil (at -15°C) at a high flow rate (~ 20 SLPM (standard liters per minute)). Frost is deposited on the copper coil for ~ 30 min. After frost deposition, passing dry air through the saturator after setting the recirculating bath temperature appropriately can generate air with any ρ . This method is capable of generating an airstream with a constant frost point to within our measurement precision ($\pm 0.2^\circ\text{C}$).

After passing through the saturator, the air is directed into a collapsible ~ 1 L reservoir with an exhaust port. Air is

drawn via vacuum from this reservoir, sequentially through a chilled-mirror hygrometer, the sample chamber containing the snow sample, a second hygrometer, a second airflow meter, a needle valve to control vacuum strength, and finally a vacuum pump. The collapsible reservoir acts as the source for air drawn through the sample; we insure that the flow rate into the reservoir is greater than the flow rate out of the reservoir; consequently, the air drawn through the snow sample has a known water-vapor content. If desired, the water vapor leaving the snow sample is captured in a second copper coil submerged in a bath cooled by solid CO_2 ($T \sim -75^\circ\text{C}$).

RESULTS

Sublimation rate

We measured the sublimation rate for 34 different simulations using a range of sample temperature (-5 , -9 , -13 , -19 and -23°C) and airflow rates (1–10 SLPM). These flow rates correspond to residence times of air in the snow sample of 26–0.5 s (depending on the sample thickness). These conditions were selected to approximate the temperature and airflow rates through polar snow during firm ventilation (Albert, 2002). Ideally, the sublimation rate can be controlled by varying the vapor density of the air entering the sample chamber (ρ_{in}) using the saturator. In order to bracket the range of possible sublimation rate for a given temperature and flow rate, we used dry air (frost point $T < -50^\circ\text{C}$, or $\rho < 3.8 \times 10^{-5} \text{ kg m}^{-3}$) to produce the results presented here. Our sublimation rate measurements are presented in Figure 2.

We calculate the sublimation rate (kg s^{-1}) during a given simulation by converting the frost-point data from the downstream sensor ($^\circ\text{C}$) to vapor pressure (Pa) and then to vapor density (kg m^{-3}). The sublimation rate is found by multiplying the vapor density by the airflow rate (measured as a volumetric flux, $\text{m}^3 \text{ s}^{-1}$). We calculate the sublimation rate from each pair of frost-point and flowmeter data during the run, and then average these discrete data over the duration of the run to generate a single sublimation rate. These average sublimation rates are indicated by the open circles in Figure 2. The vertical bars on each circle denote the standard deviation of the sublimation rate for a given run. This variation is primarily due to uncertainty in the frost-point measurement ($\pm 0.2^\circ\text{C}$). A second, much smaller, source of uncertainty is due to uncertainty in the flowmeter data. In Figure 2,

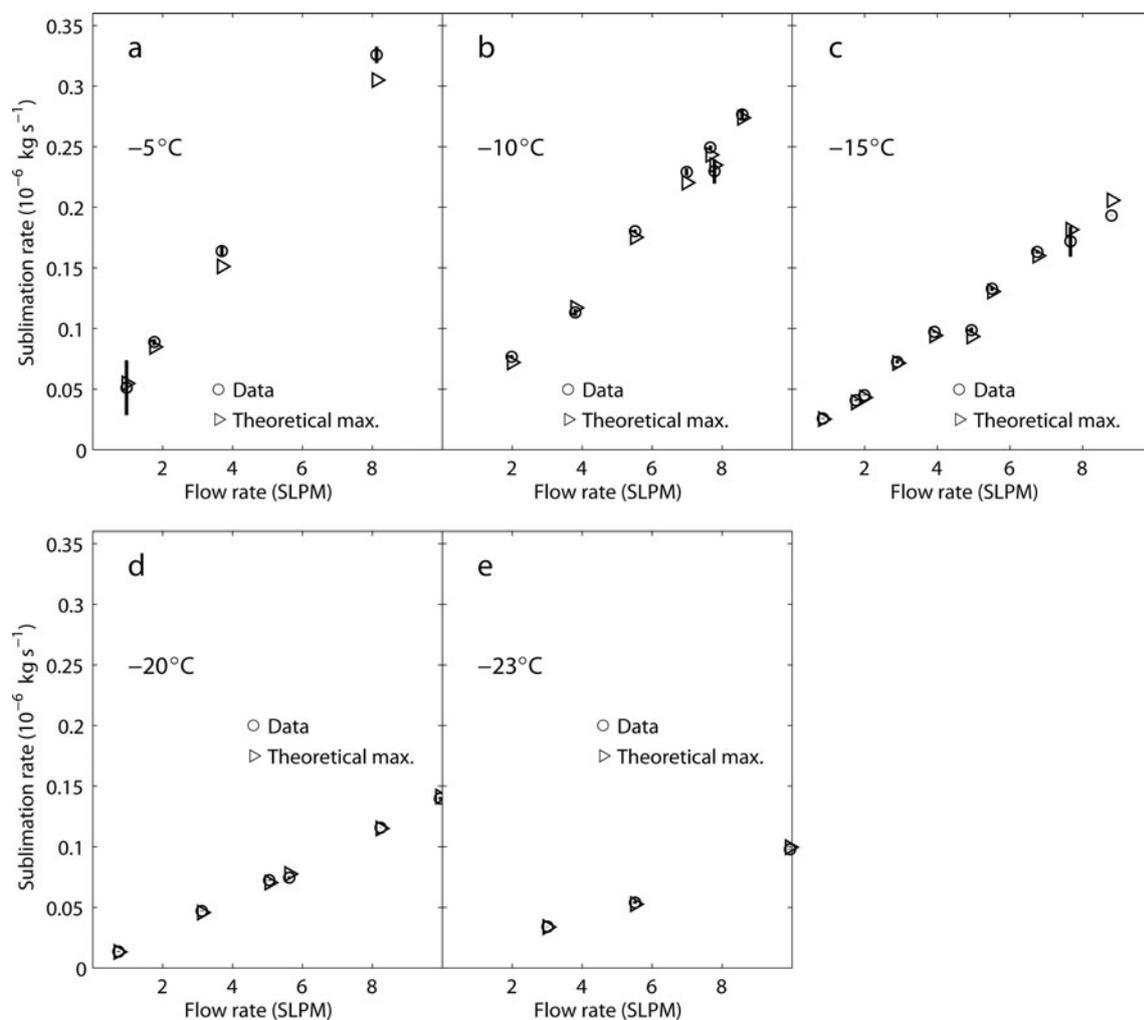


Fig. 2. Sublimation rate as a function of flow rate, for five different temperatures. Open circles are data from each run; open triangles represent the theoretical maximum sublimation rate at the same temperature and flow rate used in each run. Adapted from Neumann and others (in press).

each panel corresponds to the mean sample temperature during the series of runs.

The open triangles in Figure 2 represent the theoretical maximum possible sublimation rate for each run. The theoretical maximum sublimation rate is calculated using the average sample temperature (measured at the sample center), the average flow rate during the run, and by assuming that $\rho_{in} = 0$, and that $\rho_{out} = \rho_{sat}$, where $\rho_{sat}(T)$ is given by the Clausius–Clapeyron relation with respect to ice. For a given flow rate, the Clausius–Clapeyron relation between ρ_{sat} and T results in a decreasing maximum sublimation rate (expressed in kg s^{-1}) with decreasing temperature, simply because colder air has a lower ρ_{sat} . It is evident that, regardless of flow rate, sample thickness or temperature, our measured sublimation rates are very close to the theoretical maximum. This analysis shows that 94% (32 of 34) of our measurements lie within 5% of the theoretical maximum value.

Isotopic exchange

The $\delta^{18}\text{O}$ content of the isotopic samples is shown in Table 1. The analyses show that the isotopic content of the snow samples is homogeneous ($-18.8 \pm 0.2\text{‰}$). In order to generate vapor that was significantly different isotopically than the snow sample, we used enriched ‘heavy’

($27.6 \pm 1.6\text{‰}$) water as our vapor source; isotopically depleted water could also have been used. We created $\sim 5\text{ L}$ of heavy water by adding a small amount of 10% D_2O^{18} water to distilled water. Vapor was derived from this water and deposited as frost in the saturator, as described above. In order to measure the isotopic content of the frost in the saturator, we heated the coil with the recirculating bath to $\sim 10^\circ\text{C}$ to melt the frost. Due to the relatively small amount of water in the coil (typically $< 5\text{ mL}$) and the large surface area of the coil interior, it was not possible to pour the water sample out (due to surface tension or wetting of the copper surface). Instead, we evacuated the water from the coil with a jet of dry air. We determined that this method of extraction enriches the measurement by $\sim +3\text{‰}$ by forcing source water through the saturator (some of these results are shown in Table 1). The third column in Table 1 shows the $\delta^{18}\text{O}$ of our tests after correcting for the offset introduced by evacuation with the air jet.

Our measurements on frost deposited in the saturator demonstrate that the deposition of frost in the saturator from the source water approximately follows a Rayleigh process (e.g. Dansgaard, 1961). We calculated the expected isotopic content of the frost deposited in the saturator using measurements of the initial isotopic content and temperature of the source water and the saturator temperature. Our

Table 1. Isotopic measurements on snow sample, source water and captured vapor. The rightmost column indicates values corrected by -3‰ to account for the effect of evacuation by jet of dry air

Sample description	$\delta^{18}\text{O}$	$\delta^{18}\text{O}$ corr.
	‰	‰
Snow sample (six samples)	-18.8 ± 0.2	
Source water (six samples)	27.6 ± 1.6	
Source water flushed through saturator	31.2	28.2
Source water flushed through saturator	32.6	29.6
Source water flushed through saturator	31.5	28.5
Source water flushed through saturator	33.3	30.3
Frost deposited in saturator (-19°C)	19.8	16.8
Frost deposited in saturator (-5°C)	21.4	18.4
Frost deposited in saturator (-1°C)	19.1	16.1
Frost drawn through sample (-5°C , 1 SLPM)	-33.0	-36.0
Frost drawn through sample (-5°C , 0.75 SLPM)	-24.3	-27.3
Frost drawn through sample (-5°C , 0.75 SLPM)	-11.9	-14.9
Sublimed snow (1 SLPM)	-30.7	-33.7
Sublimed snow (1 SLPM)	-23.8	-26.8
Sublimed snow (1.5 SLPM)	-30.6	-33.6
Sublimed snow (2.2 SLPM ¹)	-27.1	-30.1

measurements show that the content of the frost in the saturator is typically 1–2‰ heavier than expected from a Rayleigh process. This is not surprising, given the high airflow velocity during frost deposition (20 SLPM), and suggests some non-equilibrium (kinetic) processes are active.

Using the methods above, we sublimated frost from the saturator and drew it through the snow sample. We set the saturator temperature equal to the snow sample temperature (-5°C) to insure that the airstream was fully saturated prior to entering the snow sample. We captured the vapor leaving the snow sample in a copper coil immersed in a dry-ice bath. After exiting the dry-ice bath, the airstream frost point was below our detection limit; we calculate that the dry-ice bath captures $\sim 99.9\%$ of the water vapor. We conducted tests at two flow rates (1 and 0.75 SLPM). Given the low flow rate, each test ran for ~ 40 hours in order to collect a measurable amount of water. The results (Table 1) show that the isotopic content of the vapor collected downstream of the snow sample (-25‰) is significantly different than the content of the vapor in the saturator (17‰), suggesting extensive isotopic exchange between vapor and solid.

Additional tests involved passing dry air through the snow sample and collecting the resulting sublimated vapor. In each case, the sample temperature was -5°C . The isotopic content of the sublimating vapor (-30‰) is significantly different than the mean content of the snow grains (-18‰).

DISCUSSION

Albert and McGilvary (1992) presented a model to calculate sublimation rates directly in a volume of snow. The sublimation (or condensation) rate S in Albert and McGilvary (1992) is driven by the difference between the local vapor density (ρ_v) and the saturation vapor density (ρ_{sat}):

$S = h_m a_s (\rho_{\text{sat}} - \rho_v)$, where a_s is the specific surface area and h_m is the mass-transfer coefficient. We update the values of h_m estimated by Albert and McGilvary (1992) using our data for S , ρ_v and a_s , and solving for h_m in each test. In Figure 3a, we plot our values of h_m as a function of temperature. The stars in Figure 3a indicate the value of h_m for each run, assuming sublimation occurs in the first 4 mm of the sample (a mean value suggested by applying the theory of Thorpe and Mason (1966) to our aggregate snow sample); the solid line indicates the best-fit line to these values. The circles indicate the value of h_m assuming sublimation occurs throughout the initial 1 cm of the sample; the thick dashed line indicates the best-fit line to these data. The squares indicate the value of h_m assuming sublimation occurs in the first 1 mm (the minimum value suggested by Thorpe and Mason (1966)); the thin dashed line indicates the best-fit line to these data. It is apparent that there is not a strong correlation between h_m and temperature ($r^2 = 0.12$), and that the mass-transfer coefficient is essentially temperature-independent.

In Figure 3b, we plot our values of h_m from all experiments as a function of the modified Reynolds number ($\text{Re} = d_p v / \nu_a (1 - \phi)$, where v is the velocity, ν_a is kinematic viscosity of air, d_p is the mean particle diameter and ϕ is porosity) as in Albert and McGilvary (1992), using the same notation used in Figure 3a. We find a statistically significant linear relationship between h_m and the modified Reynolds number ($r^2 = 0.99$), suggesting that the modified Reynolds number can be used to reliably calculate h_m for our data. The data suggest that the true relationship between h_m and Re lies in the region between the two dashed lines; the solid line is our preferred solution ($h_m = 0.566\text{Re} + 0.075$) and assumes that sublimation occurs over the first 4 mm of the sample. Estimating the actual surface area of sublimating snow grains using measurements of the pore space geometry (e.g. Freitag and others, 2002) would allow for a more accurate determination of the slope of this relationship.

Our isotopic measurements of the vapor sublimated from the snow samples are consistent with field-based studies and suggest that during sublimation, fractionation occurs as heavier isotopes are preferentially left in the solid phase. For example, Sommerfeld and others (1991) collected vapor coming off a sublimating snow sample and inferred a fractionation coefficient of 1.11 for deuterium. We can use our data to estimate the fractionation coefficient for ^{18}O at -5°C . By definition, the fractionation coefficient between two phases is the ratio of heavy to light isotopes in each phase (e.g. Criss, 1999). Converting our measurements in Table 1 from delta notation into ratios of heavy and light isotopes allows us to determine that the fractionation coefficient for our sublimation experiments is 1.013 for $\delta^{18}\text{O}$. This produces a somewhat smaller fractionation than that suggested by the thermal-gradient experiment of Sommerfeld and others (1991).

We note that our calculated fractionation coefficient for the ice–vapor system (1.013) is indistinguishable from the fractionation coefficient calculated for $\delta^{18}\text{O}$ for the water–vapor system at -5°C (1.012). This suggests that at temperatures where a quasi-liquid surface layer is expected, isotopic exchange in snow may be described by a water–vapor system or an ice–water–vapor system rather than an ice–vapor system. The experimental methods outlined above could be used to further test this assertion, and determine a

functional form of the fractionation coefficient as a function of temperature or sublimation rate.

The results of drawing vapor from the saturator through the snow sample are more difficult to interpret. It is evident that the isotopic content of the vapor after passing through the sample is significantly different than the frost in the saturator. Given that sublimation causes isotopic fractionation, the isotopic content of the frost leaving the saturator will probably change during the experiment. However, if all of the frost is sublimed from the saturator, mass conservation dictates that the vapor leaving the saturator will have the same average composition as the frost in the saturator. Consequently, this may not be a major concern for our experimental design. An additional complication is that after all of the frost in the saturator is sublimed, continued airflow causes sublimation in the snow sample. This sublimating vapor would contaminate our measurement of isotopic exchange between vapor and solid. Thus, it is important to use all of the frost in the saturator and then terminate the run. It is likely that two of our tests were compromised by saturator desiccation (measurements at -36.0% , -27.3%), based on frost-point measurements collected between the saturator and sample chamber. The third test (-14.9%) does not seem to have had that complication. While it is not possible to draw broad conclusions from these data, it is apparent that water-vapor advection through snow results in isotopic exchange between vapor and solid, even at the low flow rates considered here. Further tests will be used to determine the isotopic equilibration rate constant of Neumann and Waddington (2004).

CONCLUSIONS

We have conducted laboratory experiments to measure the mass-transfer coefficient for snow, investigate the isotopic effects of sublimation, and devise a method to determine the rate of isotopic equilibration between solid and vapor. Our revised formulation for the mass transfer coefficient ($h_m = 0.566\text{Re} + 0.075$) can now be used to update the estimates of Albert and McGilvary (1992). While these results are strictly valid only for the grain sizes, porosity and permeability of our snow samples, future work using our experimental approach on natural snow samples could improve on the relationship between h_m and Reynolds number presented here.

Our isotopic measurements are consistent with the work of prior field-based investigations and suggest that significant isotopic fractionation occurs during snow sublimation, although our data suggest a smaller effect. Our results also suggest that the presence of liquid water on ice grain surfaces could be an important factor in determining the fractionation coefficient for sublimating snow. Our tests for isotopic equilibration between vapor and solid are inconclusive, but suggest that this is also an important effect. The net result of these two effects (sublimation and equilibration between vapor and solid) will be most pronounced in areas with relatively low annual accumulation rate, and significant mass loss due to sublimation. These conditions are most frequently found on the East Antarctic plateau. The methods presented here should be used to further quantify these two effects, and to determine to what extent snow properties (such as grain size, porosity or permeability) impact the isotopic exchange rate.

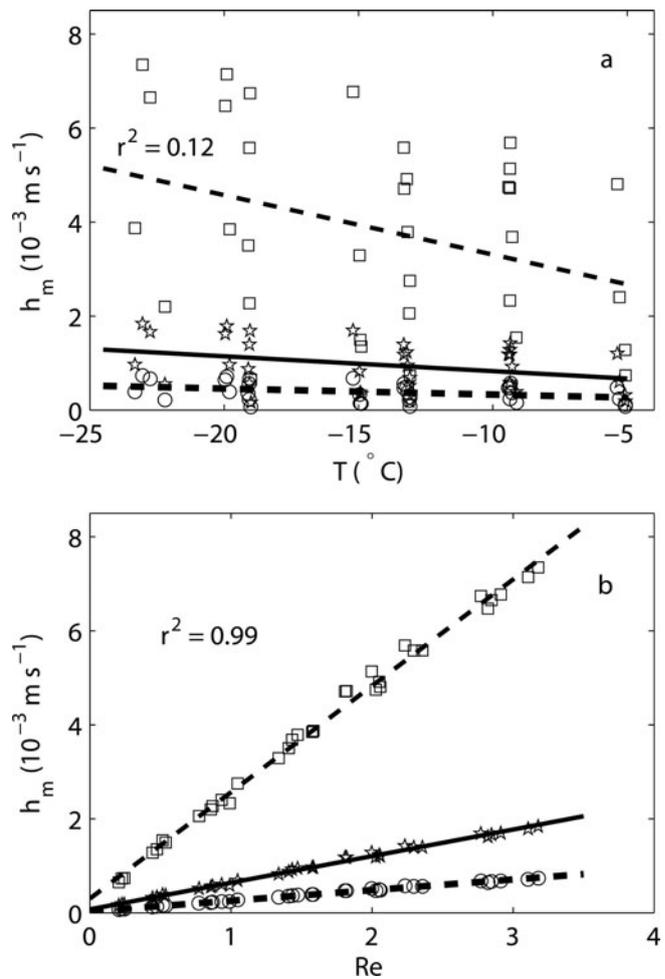


Fig. 3. Mass-transfer coefficient from all runs plotted (h_m) as a function of temperature (a) and modified Reynolds number (b). The stars in each panel indicate the preferred value of h_m for each run, assuming sublimation occurs in the first 4 mm of the sample; the solid line indicates the best-fit line to these values. The circles (squares) in each panel indicate the value of h_m assuming sublimation occurs evenly throughout the initial 1 cm (1 mm) of the sample; the thick (thin) dashed line indicates a best-fit line to these data. It is evident that there is only a weak relationship between h_m and temperature ($r^2 = 0.12$), while the relationship with Re is much stronger ($r^2 = 0.99$). These data suggest that Re can be used to reliably predict h_m , but snow temperature cannot.

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