Isotopic Fractionation in Wintertime Orographic Clouds

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ABSTRACT

The Isotopic Fractionation in Snow (IFRACS) study was conducted at Storm Peak Laboratory (SPL) in northwestern Colorado during the winter of 2014 to elucidate snow growth processes in mixed-phase clouds. The isotopic composition (δ^{18} O and δ D) of water vapor, cloud water, and snow in mixed-phase orographic clouds were measured simultaneously for the first time. The depletion of heavy isotopes [¹⁸O and deuterium (D)] was greatest for vapor, followed by snow, then cloud. The vapor, cloud, and snow compositions were highly correlated, suggesting similar cloud processes throughout the experiment. The isotopic composition of the water vapor was directly related to its concentration. Isotopic fractionation during condensation of vapor to cloud drops was accurately reproduced assuming equilibrium fractionation. This was not the case for snow, which grows by riming and vapor deposition. This implies stratification of vapor with altitude. The relationship between temperature at SPL and δ^{18} O was used to show that the snow gained most of its mass within 922 m above SPL. Relatively invariant deuterium excess (d) in vapor, cloud water, and snow from day to day suggests a constant vapor source and Rayleigh fractionation during transport. The diurnal variation of vapor d reflected the differences between surface and free-tropospheric air during the afternoon and early morning hours, respectively. These observations will be used to validate simulations of snow growth using an isotope-enabled mesoscale model with explicit microphysics.

1. Introduction

Precipitation amounts can increase when wintertime storms encounter mountains or plateaus. Orographic lifting in cold mountain clouds results in the production of additional condensate in the form of supercooled liquid water (SCLW) that becomes available for accretion (riming) by snow falling from higher levels, as was the case in the Park Range in northwestern Colorado (Rauber and Grant 1986a) and in the Mikuni Mountains of Japan (Kusunoki et al. 2005). The extent and liquid water content (LWC) of near-surface SCLW depend on the mountain aspect, wind speed, and direction relative to the mountain, and proximity to the moisture source. The intensity and location of the liquid cloud depend on stability, the occurrence of blocking, and small-scale topographical features (e.g., Colle et al. 2005; Houze and Medina 2005; Rotunno and Houze 2007). Liquid water contents as high as 1.5 and 2 gm^{-3} have been observed in wintertime orographic clouds in the Sierra Nevada and Cascade Mountains, respectively (Lamb et al. 1976; Hobbs 1975). In contrast, significantly lower SCLW levels (<0.4 gm⁻³) were reported in wintertime orographic clouds in the Park Range (Rauber and Grant 1986a; Borys et al. 2000, 2003).

The effect of aerosols on orographic cloud microphysics and snowfall has been examined by Borys et al. (2000, 2003), Muhlbauer et al. (2010), Lowenthal et al. (2011), and Saleeby et al. (2013). Model simulations by Saleeby et al. (2013) confirmed the empirical studies by Borys et al. (2000, 2003) that suggested that higher cloud

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condensation nucleus (CCN) concentration increased cloud droplet number concentration, decreased their size, thereby reducing riming efficiency and snowfall amount. Muhlbauer et al. (2010) applied three cloudresolving models to orographic precipitation in an idealized 2D context to examine the aerosol effect on precipitation from mixed-phase orographic clouds. In most of the cases, the models showed a decrease in orographic precipitation with increasing aerosol number concentrations, but the sensitivity of precipitation to aerosol perturbations varied considerably among the models and scaled with the ice water path, suggesting that the presence of a well-developed mixed-phase layer may reduce the aerosol susceptibility of orographic precipitation due to compensating effects and microphysical buffers introduced by numerous icemicrophysical pathways.

Fractionation of stable isotopologues of water ($H_2^{18}O$, $H_2^{16}O$, $HD^{16}O$ [D, deuterium is ²H]) in the atmosphere occurs during phase changes between water vapor and liquid water or ice.

The heavier isotopologues (HD¹⁶O and H₂¹⁸O) are more plentiful in the condensed phase during the exchange between vapor and cloud drops or snow because their vapor pressures are lower than that of $H_2^{16}O$. Further, kinetic fractionation occurs during nonequilibrium exchange (e.g., deposition onto ice in supersaturated conditions) due to the differing diffusivities of heavier and lighter water molecules (Jouzel and Merlivat 1984). The isotopic composition of stream and tree sap waters was used to explore the drying of air columns as they passed across mountain barriers (Smith et al. 2005; Smith and Evans 2007). Drier air masses require colder temperatures for condensation, and the resulting connection between temperature and isotopic composition has been found in observations of precipitation in the North Atlantic (Dansgaard 1964) and Antarctica (Picciotto et al.1960; Jouzel and Merlivat 1984; Masson-Delmotte et al. 2008). Warburton and DeFelice (1986) estimated the altitude of ice production in wintertime Sierra Nevada storms from the isotopic composition of snow collected at the surface, the empirical relationship between ice crystal habit and formation temperature, and atmospheric soundings. Demoz et al. (1991) extended the work of Warburton and DeFelice (1986) by incorporating information on riming derived from visual observation of ice crystals at the surface. They found that ice formation temperatures based on ice crystal habit were consistently lower than those inferred from the isotopic composition of snow collected at the surface. The difference was attributed to riming of crystals at altitudes lower and warmer than those at which the crystals nucleated. This framework for understanding the isotopic content of precipitation has served as a basis for inferring past climate characteristics from the isotopic composition of polar snow and ice (Lorius et al. 1979; Steen-Larsen et al. 2011), the inference of past mountain range heights relative to sea level (Rowley et al. 2001; Poage and Chamberlain 2001), and the contribution of orographic cloud water to precipitation in mountain forest ecosystems (Scholl et al. 2007).

Representations of isotopic exchange have been included in general circulation models (GCMs), starting with the work of Joussaume et al. (1984), and have been applied to study many issues including, for example, troposphere-stratosphere exchange (Schmidt et al. 2005) and the relationships between the parameterization of moist processes and isotopic composition (Lee et al. 2009a; Wright et al. 2009). Isotope-enabled GCMs and regional models have been widely applied in an effort to reproduce current and past climates (e.g., Noone and Simmonds 2002; Ciais and Jouzel 1994; Sturm et al. 2007; Risi et al. 2010; Werner et al. 2011; Yoshimura et al. 2011). They have also been used to gain understanding of specific paleoisotopic records, as in the recent work of Lee et al. (2009b) and Pausata et al. (2011). Progress has been slower for incorporating water isotopologues in cloud-resolving/large-eddy simulation models, which resolve at least the largest scales of motions within clouds. Such models remove many of the uncertainties associated with moist convection parameterizations in GCMs but are typically constrained to be run in limited geographical domains due to their higher spatial resolution. Building on earlier work by Gedzelman and Arnold (1994) and others, isotopeenabled cloud-resolving models have been developed by Smith et al. (2006) and Blossey et al. (2010) to study isotopic fractionation in the tropical tropopause layer. Recently, Pfahl et al. (2012) used Consortium for Small-Scale Modelling Isotope model (COSMOiso) to study the isotopic composition of a frontal system over the eastern United States and validated that model against observations included in the work of Gedzelman and Lawrence (1990). The simulations of Pfahl et al. (2012) were not cloud-resolving and required the integration of water isotopologues into the convective parameterization.

The Isotopic Fractionation in Snow (IFRACS) study at Storm Peak Laboratory (SPL) in northwestern Colorado was conducted during the winter of 2014 to explore the impacts of microphysical processes in mixed-phase orographic clouds on the water isotopic composition of falling snow. In-cloud observations are being complemented by simulations with an isotopeenabled version of the Weather Research and Forecasting (WRF) Model (Blossey et al. 2015; Moore et al. 2016). In the model, the evolution of water isotopic composition is followed from the water vapor source(s) through snowfall at SPL. Measurement of the isotopic composition of water vapor, cloud droplets, and snow in mixed-phase clouds coupled with simulations that follow these isotopic tracers through phase changes is intended to improve our understanding of snow growth processes, including riming and vapor deposition in microphysical parameterizations. The contribution of isotope-enabled microphysical modeling will allow for broader application of these methodologies in studies of general circulation and the water cycle. In this paper, we present and discuss the first simultaneous measurements of water isotopologues in water vapor, cloud droplets, and snow in mixed-phase wintertime orographic clouds.

2. Methods

A field study was conducted at the Desert Research Institute's Storm Peak Laboratory (3210 m MSL; 40.456570°N, 106.739948°W) located on the summit of Mt. Werner in the Park Range near Steamboat Springs, Colorado, from 20 January to 27 February 2014. The study location is shown in Fig. 1 and in Wetzel et al. (2004). SPL is above cloud base in snowing clouds greater than 25% of the time during winter (Borys and Wetzel 1997). Synoptic-scale storms occur roughly weekly with snowfall under pre- and postfrontal conditions, with and without convection, and in large-scale stratiform cloud systems (Rauber et al. 1986b). Given sufficient moisture, orographic forcing typically produces a cap cloud at SPL, which may be embedded, and which produces persistent snowfall. During precipitation events, the flow is generally from the west or northwest. Cloud and precipitation under southwest flow are suppressed by the Flat Tops Range (maximum elevation: 3768 m MSL) (Fig. 1). The main source of moisture is the Pacific Ocean to the west. Snowing clouds were sampled during intensive operating periods (IOPs) with discrete durations averaging 37 min using methods described by Borys et al. (2000). Hydrometeor particle size distributions (PSDs) were measured at a frequency of 1Hz with Droplet Measurement Technologies Inc. (DMT) cloud probes mounted on a rotating wind vane to orient them into the wind. The probes were calibrated at the factory prior to but not immediately after the field study. Cloud droplet PSDs $(2-47 \,\mu\text{m})$ were measured with an aspirated DMT SPP-100 (forward scattering spectrometer probe). Ice particle PSDs were measured with DMT cloud imaging probe (CIP; $25-1550 \,\mu$ m) and precipitation imaging probe (PIP; $100-6200 \,\mu\text{m}$) optical array probes (OAP). An Applied Technologies Inc. SATI three-axis sonic



FIG. 1. Topographical profile of the study area and the location of Storm Peak Laboratory (red star) and the town of Steamboat Springs (black circle) in the Park Range in northwestern Colorado.

anemometer mounted on the probe vane supplied the airspeed for the array probes. The 2D probe images were analyzed using the System for OAP Data Analysis (SODA2) analysis software obtained from the National Center for Atmospheric Research Mesoscale and Microscale Meteorology Laboratory (NCAR MMM), which is based on work by Heymsfield et al. (2013) and Delanoe et al. (2014).

Super-cooled cloud water was collected with monofilament sieves that collect droplets with diameters > $2\,\mu m$ but not snow crystals (Hindman et al. 1992). If necessary, sequential sieve samples were taken during a snow collection period to avoid overloading the cloud sieves (Hindman et al. 1992). Immediately after sampling, rime ice was scraped off the sieves, placed in a storage bag, and transferred to a freezer. Snow was collected in polyethylene bags mounted in two 15-cmdiameter tubes oriented into the wind by a vane (Borys et al. 1988). This collector acts as a virtual impactor that excludes cloud droplets. Ice water content (IWC) was derived from the wind speed and the diameter of the tubes. Snow samples were transferred to a storage bag and stored in a freezer. After the study, aliquots of cloud and snow water samples were sent to the Institute of Arctic and Alpine Research (INSTAAR) in Boulder, Colorado, for analysis of stable isotopes of water (Lowenthal et al. 2011).

A weather station measured 5-min average temperature, relative humidity (RH), and wind speed and direction. The NCAR GPS Advanced Upper-Air Sounding 2666

System (GAUS) balloon-sonde system was deployed in the valley approximately 6.1 km upwind of SPL (2067 m MSL; 40.456250°N, 106.813863°W). Balloons were launched every 2 h during IOPs. Particle light absorption (Bap) was measured with a NOAA/Global Monitoring Division (GMD) continuous light absorption photometer (CLAP) that measures light absorption by particles at three wavelengths (467, 528, 652 nm). The CLAP is similar to the particle soot absorption photometer (PSAP; Bond et al. 1999), but it is designed to run unattended 8 times longer.

a. Water vapor isotopic composition

Water isotopic composition is expressed in terms of the ratio of the heavy to light isotopes, where $R = {}^{18}\text{O}/{}^{16}\text{O}$ or $D({}^{2}\text{H})/{}^{1}\text{H}$. In delta (δ) notation, for either isotope,

$$\delta = \left(\frac{R}{\text{Ro}} - 1\right) \times 1000,\tag{1}$$

where Ro is the ratio in a standard. The δ^{18} O and δ D in ambient water vapor were measured continuously with a Picarro L-2130-i analyzer equipped with a standards delivery module (SDM) and vaporizer. Ambient air was sampled at a flow rate of $1000 \,\mathrm{L\,min^{-1}}$ through a vertical 4-in. internal diameter, 3-m-high stainless steel aerosol inlet that was designed by Enertechnix (Maple Valley, Washington) using a coupled detached eddy simulation/discrete random walk computational fluid dynamics (CFD) model to exclude cloud droplets and snow (Hallar et al. 2016; Kumler and Ogren 2016). The theoretical transmission efficiency for particles larger than $10 \,\mu m$ is zero. The inlet cap is heated to avoid riming but according to the CFD model, the sample flow was high enough to preclude heat transfer to cloud droplets passing the inlet. The inlet is used routinely for aerosol sampling at SPL by the NOAA/ESRL/GMD program. The Picarro instrument was connected with copper tubing to the top of the manifold near the ceiling, where it passes through the roof. The temperature inside the manifold at the Picarro sampling port was the same as ambient. Had supercooled droplets been present in the manifold, they would have rimed the Picarro sampling port. A scope camera placed into the manifold revealed no such riming or the presence of droplets. The Picarro instrument malfunctioned on 19 February 2014 but was repaired by the first week in March 2014.

Two secondary standards were used to calibrate ambient vapor measurements: 1) distilled deionized water (DDI); and 2) filtered Antarctic ice water (POLAR) from the European Project for Ice Coring in Antarctica (EPICA) B40 core taken at a depth of 80 m (~1200 AD). Each secondary standard was divided into ten 125-mL bottles and a small aliquot from each was reserved and sent to INSTAAR for calibration against primary standards [Vienna Standard Mean Ocean Water (VSMOW)], Vienna Standard Light Antarctic Precipitation (VSLAP), and Greenland Ice Sheet Project (GISP)]. The isotopic composition was $\delta D = -68.68 \pm 0.20\%$ and $-342.80 \pm 0.46\%$ and $\delta^{18}O = -7.68 \pm 0.059\%$ and $-43.38 \pm 0.06\%$ for DDI and POLAR, respectively, where the uncertainties are the standard deviations of the 10 replicates [per mil (‰)]. Nearly all of the uncalibrated vapor measurements were within the range of the two standards: 99.2% for δD and 99.97% for $\delta^{18}O$. During routine operation, the SDM injected and vaporized the two secondary standards into the analyzer every 4-6 h for 75% of the time, every 12h for 14% of the time, and within 24 h for the remainder of the time. The standards were vaporized and mixed with room air dried with Drierite. A critical orifice in the SDM maintained a constant airflow rate. The vapor concentration during standardization was set by regulating the liquid flow rate into the vaporizer. During the experiment, standardizations were done at a vapor concentration of \sim 20 000 ppmv at a liquid flow rate of 0.04 μ L s⁻¹. Each of the standards was measured for 20 min, with 10 min of ambient air sampling between the two. The instrument allows the standard to stabilize for 10 min before reporting data for 20 min. The first 10 min after the second standard were eliminated to allow for stabilization of the ambient vapor measurements. In this manner, memory effects were minimized. The Picarro L-2130-i reports water vapor concentration (H₂O), although detailed calibrations beyond those performed by the manufacturer were not done. The average indicated water vapor concentration at which the standards were measured was 21780 ± 500 ppmv.

There were 97 valid two-point calibrations during the field study. These were used to correct the vapor isotope data for instrument drift and to align the indicated response to the standards. The average standard calibrations for δ^{18} O and δ D are as follows:

$$\delta^{18}O_{Actual} = \delta^{18}O_{Indicated} \times 1.01 \pm 0.01 - 2.41 \pm 0.14,$$
(2)

$$\delta D_{Actual} = \delta D_{Indicated} \times 1.01 \pm 0.01 + 12.7 \pm 0.9.$$
(3)

There was little instrument drift during the study, as evidenced by the small standard deviations of the slopes and intercepts in Eqs. (2) and (3). Further, the slopes are near unity, indicating that calibration was mainly a matter of applying an offset to the indicated values. For

any data point between two calibrations, corrected

values of δ^{18} O and δ D were calculated from the

respective end-member equations. A weighted average of the corrected values of δ^{18} O and δ D was then calculated, where the weighting was the ratio of the time between the data point and the end of the first calibration to the time between the end of the first calibration and the beginning of the second calibration.

The uncertainties of the vapor isotopic measurements have two components: accuracy and precision (repeatability of the measurement of a constant attribute). Accuracy, or bias, is the difference between the true (VSMOW, VSLAP, and GISP) and unknown values, which in this case is the secondary standards (POLAR and DDI). INSTAAR reported upper limits on accuracy of 0.09% for δ^{18} O and 0.78% for δ D. There is no error to minimize for a two-point calibration line. However, the calibration precision is a function of variability of the secondary standards (σ_{Std}^2), as determined by INSTAAR, and the variability of the measured values of the standards over the calibration period (σ_{Meas}^2). The uncertainties of the slope and intercept of the calibration line can be obtained by propagating $\sigma_{\rm Std}^2$ and $\sigma_{\rm Meas}^2$ through the calculation using the effective variance approach [Eq. (2) in Lowenthal et al. 1987]. The contributions of the calibration process to ambient vapor measurement precision were 0.33% and 1.73% for δ^{18} O and δD , respectively.

The response and measurement precision of the Picarro L-2130-i vary as a function of water vapor concentration (H₂O). Aemisegger et al. (2102) characterized these effects for Picarro analyzers with detailed laboratory experiments. They found that the response of the Picarro L-2130-i analyzer was nearly flat for δ^{18} O and δD for H₂O between 2500 and 30000 ppmv. To address these issues, the POLAR standard was introduced to the analyzer to produce indicated vapor concentrations from ~ 600 to ~ 15000 ppmv by diluting the vaporized standard with ultradry air and by varying the liquid standard flow rate (Bastrikov et al. 2014). This was done at the end of the field study on 5 and 6 March 2014 at SPL after the instrument had been repaired remotely by Picarro. Standard measurements at low vapor concentration could not be reliably done by only reducing the liquid flow rate below $0.01 \,\mu \text{L s}^{-1}$. Low vapor concentrations were obtained by removing the critical orifice in the SDM and manually regulating the flow of ultradry airflow into the vaporizer (Bastrikov et al. 2014). In this manner, we were able to obtain eight and seven data points for δ^{18} O and δ D, respectively. The isotopic response with respect to the indicated water vapor concentration is shown in Fig. 2. The response was flat above \sim 4000 ppmv, but it deviated nonlinearly below that concentration. The solid lines in Fig. 2 represent second- and third-order polynomial fits for δ^{18} O and δ D,



FIG. 2. Isotopic response of the Picarro L-2130-i (a) δ^{18} O and (b) δ D to water vapor concentration. Error bars are the standard deviations of the isotopic composition at each H₂O concentration. Data points in red were not included in the polynomial regressions.

respectively, for the indicated H₂O concentration between 644 and 4203 ppmv. One δD measurement at 1747 ppmv (Fig. 2) was not included in the regression. It is not known why δD was heavier than expected during this run. It is possible that there were problems with the vaporization, resulting in fractionation or that the manual regulation of the ultradry dilution air was not stable. Isotopic composition was corrected for the response bias at H₂O less than 4203 ppmv using these functions. Note that there were only 9 hourly average H₂O concentrations less than 1000 ppm and that these occurred during the clear period of 20–26 January 2014. During IOPs, there were 13 and 1 hourly average concentrations less than 3000 and 2000 ppmv, respectively.

Figure 2 shows that measurement precision decreased with decreasing H₂O concentration below \sim 4000 ppmv. Table 1 gives the precision (the standard deviation of measurements of the standard over an approximately 20-min period at constant H₂O) as a function of H₂O concentration for the points in the H₂O calibration. The

TABLE 1. Precision (the standard deviation of measurements of the standard over a 20-min period) as a function of H_2O concentration (ppmv) for the calibration of instrument response.

H ₂ O (ppmv)	δ^{18} O (‰)	δD (‰)	
644	2.8	15.2	
1131	1.23	7.8	
1747	0.85	6.1	
2973	0.60	3.0	
4203	0.54	2.2	
8724	1.25	1.78	
9767	0.39	0.99	
14 438	0.24	0.70	

precision of the POLAR standard measurement was 0.54% and 2.16% for δ^{18} O and δ D, respectively, at 4203 ppmv and 2.78‰ and 15.23‰ for δ^{18} O and δ D, respectively, at 644 ppmv. These values could be parameterized or interpolated to estimate measurement precision for the ambient data, but there are very few data points. Measurement precision may also be considered as the variance of ambient measurements over a time period where δ^{18} O and δ D are assumed to be constant, that is to say, over repeated measurements. To simulate repeated measurements, ambient vapor δ^{18} O and δ D were averaged over 5-min periods and a standard deviation was calculated. On average, there were 50 data points per 5-min period. The squares of these standard deviations were averaged over ranges of H₂O concentration. The square root of this average is the root-mean-square error (RMSE). The results are presented in Table 2, which gives the RMSE precision for δ^{18} O and δ D, and the number of 5-min averaging periods in each H₂O concentration range. Only 1.2% and 0.14% of the measurements had indicated H₂O concentrations less than 1000 and greater than 9000 ppmv, respectively. Figure 3 shows second-order polynomial fits of 5-min precision of ambient δ^{18} O and δ D measurements as a function of H₂O concentration (as the midpoints of the ranges in Table 2). For both of these regressions R^2 was greater than 0.999. To compare the two approaches for estimating precision, the data points from Table 1 are overlaid with the values from Table 2 in Fig. 3. The two approaches agree well; however, precision based on short-term averaging of the ambient data is clearly more robust. Measurement precision for each ambient data point was estimated from these functions. The overall precision was obtained by propagating the precisions associated with the standardization and the ambient measurements. These precisions were assigned to the 5-min average data points. Longer averages were calculated from the 5-min data, where the precision was reduced as the square root of the ratio of

TABLE 2. Average ambient vapor measurement precision^a as a function of the indicated H₂O concentration (ppmv).

H ₂ O (ppmv)	$\mathbf{N}^{\mathbf{a}}$	δ^{18} O (‰)	δD (‰)
500-600	10	2.6	15.6
600-700	19	2.2	13.4
700-800	19	1.90	11.6
800-900	13	1.67	10.8
900-1000	20	1.46	9.47
1000-2000	524	1.00	6.1
2000-3000	1131	0.64	3.6
3000-4000	1767	0.50	2.6
4000-5000	1534	0.43	2.1
5000-6000	977	0.38	1.82
6000-7000	622	0.34	1.57
7000-8000	680	0.32	1.38
8000-9000	388	0.30	1.27
9000-10 000	11	0.30	1.35

^a Ambient measurements of δ^{18} O and δ D were averaged in 5-min bins and their standard deviations (σ) were calculated. The values above represent the square root of the average of σ^2 (RMSE) for each H₂O range.

the number of minutes in the averaging period divided by 5.

b. Back trajectories

Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT) back trajectories based on 12-km-resolution North American Mesoscale Forecast System (NAM) data were used to locate the source of water vapor at SPL during IOPs (Draxler and Rolph 2015). The 72-h isentropic back trajectories were run (online) from an elevation of 3500 m ASL every 2h beginning 2h before and ending 2h after each IOP.

3. Results and discussion

a. Isotopic composition

Continuous vapor measurements with regular standardization began on 20 January 2014, although conditions were clear until 27 January 2014. There were 44 cloud sampling periods over 14 days from 27 January to 27 February 2014, representing 27.1 h when SPL was in cloud. Snowfall occurred during 35 of these periods for 21.7 h. Figure 4 presents daily average δ^{18} O and δ D compositions of water vapor, cloud water, and snow during the study. While there was considerable temporal variation, both δ^{18} O and δ D in the three phases tracked one another. The Pearson correlation coefficients (r) between daily vapor and cloud, vapor and snow, and cloud and snow δ^{18} O were 0.97, 0.94, and 0.93, respectively. The corresponding r values for δD were 0.96, 0.92, and 0.93. Vapor was the most isotopically depleted (more negative δ , i.e., lighter) in the heavy isotopologues (HD¹⁶O and H₂¹⁸O), followed by



FIG. 3. Precision (standard deviation) of 5-min ambient measurements of (a) δ^{18} O and (b) δ D as a function of water vapor (H₂O) concentration (open circles). Precision based on the calibration of isotopic composition vs H₂O concentration taken from Table 1 (closed circles).

snow, and then cloud. Daily average differences between vapor and cloud δ^{18} O and between vapor and snow δ^{18} O were 12.1 \pm 0.8‰ and 10.9 \pm 1.3‰, respectively. The corresponding differences for δ D were 98.2 \pm 7.0‰ and 89.7 \pm 12.0‰, respectively. The δ^{18} O and δ D were highly correlated during vapor (r = 1.00), cloud (r = 1.00), and snow (r = 0.99) sample periods. Figure 5 presents the relationships between δ^{18} O and δ D in cloud, snow, and vapor samples during IOPs. The regressions shown in Fig. 5 are close to the global meteoric water line (GMWL) (δ D = $8\delta^{18}$ O + 10) found by Craig (1961) in natural waters and precipitation, although the intercept for vapor is lower.

The temporal variation of vapor δ^{18} O and δ D reflects the history of precipitation (i.e., the fraction of vapor removed) and any processes that introduce vapor to the air mass en route to SPL. Daily average vapor δ^{18} O during IOPs varied from -36.0% to -23.8%. Based on equilibrium fractionation coefficients presented in Clark and Fritz (1997) from Majoube (1971), a



FIG. 4. Variation of daily average water vapor, cloud, and snow oxygen isotopic composition (δ^{18} O and δ D).

VSMOW-derived source vapor δ^{18} O at 100% RH would vary by only 1.73% for sea surface temperatures between 30°C and 10°C. As vapor moves inland, it becomes more and more isotopically depleted after successive precipitation events (Dansgaard 1964). Since the saturation vapor pressure is lower at lower temperatures, the final vapor δ^{18} O and δ D at SPL are determined by the temperature gradient between the vapor source and SPL (Dansgaard 1964; Harmon 1979). This gradient is enhanced by orographic lifting (Siegenthaler and Oeschger 1980). Dansgaard (1964) demonstrated that δ^{18} O in precipitation decreased linearly with decreasing mean annual air temperature with a slope of 0.7% °C⁻¹ at 38 coastal stations in the North Atlantic and Greenland, and that this decrease was theoretically consistent with the isotopic lightening of an air mass as it cools during transport from the oceanic vapor source. Isotopic fractionation during successive events of vapor condensation under equilibrium conditions followed by removal of the condensate is known as Rayleigh distillation. Similar relationships were found by Picciotto et al. (1960), Warburton and DeFelice (1986), and Lowenthal et al. (2011).

The expected isotopic lightening following removal of water from air masses was demonstrated in coastal Iceland (Steen-Larsen et al. 2015) and on the eastern slope of the Colorado Rockies (Noone et al. 2013). This was also the case during IFRACS. Figure 6 presents a time series and scatterplot of daily average water vapor concentration (H₂O) and δ^{18} O. The relationship was direct with a moderate correlation (r = 0.62), suggesting different airmass histories from day to day. However, Fig. 6 illustrates the effect of Rayleigh distillation upwind of SPL, whether or not there was cloud at SPL. While the isotopic composition of cloud water and snow at SPL varied from day to day, the differences between phases was relatively constant. This is consistent with Rayleigh distillation of the vapor with equilibrium fractionation en route to SPL.



FIG. 5. Relationship between δ^{18} O and δ D in cloud, snow, and vapor samples. Solid line is the global meteoric water line of Craig (1961): δ D = 8 δ^{18} O + 10.

b. Altitude of snow growth

The mass-weighted altitude (MWA) of snow growth by vapor deposition and riming may be inferred from the relationship between isotopic composition and temperature (Picciotto et al. 1960; Warburton and DeFelice 1986; Lowenthal et al. 2011). Based on δ^{18} O in precipitation and surface temperature at 38 coastal North Atlantic and Greenland sites, Dansgaard (1964, p. 443) concluded: "If the mean surface temperature [T] is supposed to vary parallel to the mean condensation temperature from one place to another," then $d\delta^{18}O/dT \approx 0.7^{\circ}_{00} \,^{\circ}C^{-1}$. When snow is more depleted than cloud droplets at SPL (Fig. 4), it follows that it formed aloft at a temperature colder than that at SPL. This temperature can be estimated as the difference (Δ) between δ^{18} O in cloud and snow divided by 0.7. To convert temperature aloft to altitude above SPL, Δ is multiplied by the average of the inverse ambient lapse rate derived from sounding data within 2 km above SPL during IOPs. This value was relatively stable over



FIG. 6. The relationship between daily water vapor concentration (H₂O) and vapor δ^{18} O: (a) time series, also indicating days on which cloud and snow sampling (IOPs) occurred; and (b) scatterplot for days without (clear, black circle) and with cloud and snow (IOPs, red circle) sampling (r = Pearson correlation).

the experiment $(158 \pm 20 \text{ m} ^{\circ}\text{C}^{-1})$. Figure 7 presents daily MWA, which ranged from just below SPL (-53 m) to 922 m above SPL. On 14 and 16 February, negative heights could represent growth of ice crystals from isotopically enriched vapor or drops in the upslope flow below SPL. Also plotted in Fig. 7 are the daily differences (Δ) between cloud and snow δ^{18} O. The seeder–feeder model (Reinking et al. 2000) suggests that ice nucleation occurs at a higher altitude than the liquid cloud, which, based on the soundings, extended from 1 to 2.5 km above SPL on 10 of 14 sampling days. While ice nucleation may occur above this level, most of the ice mass and its isotopic signature accrue much closer to the surface.

c. Isotopic fractionation

The isotopic composition of the vapor phase (V) and the condensed phase (C) for cloud droplet and ice crystal growth by vapor deposition is described as

$$\alpha_{C-V} \alpha_{K} = (\delta_{C} + 1000) / (\delta_{V} + 1000), \qquad (4)$$

where α_{C-V} is the equilibrium fractionation factor, α_K is the kinetic fractionation factor, and δ_C and δ_V are δ^{18} O



FIG. 7. Daily MWA above SPL of snow growth (bars). The solid circles are the differences between $\delta^{18}O$ in cloud and snow.

or δD in the condensed phase and vapor, respectively. This simple model is realistic for cloud droplets at SPL, since the vapor in the upslope flow is continuously replenished by advection and the cloud base is within a few hundred meters below SPL. The amount of condensed water is negligible compared to the vapor concentration. For sample periods when vapor was measured, daily average LWC (from the DMT SPP-100) and IWC (from the snow collectors) were 0.11 and $0.09 \,\mathrm{g \, m^{-3}}$, respectively, while the average vapor concentration was $4.6 \,\mathrm{g}\,\mathrm{m}^{-3}$. At equilibrium, where the vapor saturation ratio is one, the heavier isotopologues (HD¹⁶O and $H_2^{18}O$) are preferentially enriched in the condensed phases because their vapor pressures are lower than that of $H_2^{16}O$. Equilibrium fractionation factors increase with decreasing temperature (and increasing altitude). The degree of fractionation—that is, the difference between δ in the condensed and vapor phases—is approximately

$$\delta_C - \delta_V \approx 1000 \ln(\alpha_{C-V} \alpha_K). \tag{5}$$

Under nonequilibrium conditions-that is, evaporation into an unsaturated atmosphere or condensation of vapor to liquid or deposition to ice from a supersaturated atmosphere-a kinetic effect arises from the lower diffusivity of HD¹⁶O and H₂¹⁸O relative to H₂¹⁶O (Merlivat 1978; Jouzel and Merlivat 1984). During condensation (deposition), H₂¹⁶O becomes enriched relative to $HD^{16}O$ and $H_2^{18}O$ in the condensed phase. During evaporation, H₂¹⁶O becomes enriched relative to $H_2^{18}O$ and $HD^{16}O$ in the vapor phase. Given the much stronger equilibrium fractionation of HD¹⁶O compared to $H_2^{18}O$, and to a lesser extent the slightly higher diffusivity of HD¹⁶O than that of $H_2^{18}O$, these kinetic effects, relative to their equilibrium fractionation, are more important for H2¹⁸O than for HD¹⁶O and are manifested in the deuterium excess (d), defined as $\delta D - 8 \delta^{18} O$ (Craig 1961). Thus, evaporation leads to higher d in the vapor phase (lower d in the condensed phase) and condensation (deposition) leads to higher d in the condensed phase (lower d in the vapor phase). Note that while the $\delta D - 8 \delta^{18}O$ definition of d is a good indicator for nonequilibrium conditions at temperatures higher than $-20^{\circ}C$ (typical of conditions during IFRACS), curvatures in the Rayleigh distillation curve can generate nonzero d even for equilibrium processes.

The kinetic fractionation factor (α_K) is described by Jouzel and Merlivat (1984) as

$$\alpha_{K} = S/[\alpha_{V-C}D/D'(S-1)+1], \tag{6}$$

where *S* is the saturation ratio with respect to water or ice, and D/D' is the inverse of the ratio of the diffusivity of HD¹⁶O or H₂¹⁸O (D') to that of H₂¹⁶O (D). Merlivat (1978) estimated D'/D as 0.9723 for H₂¹⁸O and 0.9755 for HDO. Note that α_K is greater than 1, equal to 1, and less than 1 for S < 1, S = 1, and S > 1, respectively.

The isotopic composition of cloud water samples was estimated from the average vapor δ^{18} O and δ D during those sample periods and equilibrium fractionation factors from Majoube (1971), and from the combination of equilibrium and kinetic fractionation factors, as described above. Measured and estimated values were compared on a daily average basis. Figure 8 shows good agreement between measured and estimated cloud water δ^{18} O and δD considering equilibrium fractionation only (Fig. 8, Calc.¹). Lowenthal et al. (2002) estimated a typical supersaturation with respect to water of 0.5% in wintertime orographic clouds at SPL. The kinetic effect was evaluated assuming $S_{water} = 1.005$. Because S_{water} was so close to unity, the kinetic effect was negligible (Fig. 8, Calc.²), consistent with the work of Stewart (1975). A similar analysis was done for snow growth by vapor deposition only using equilibrium fractionation factors from Ellehoj et al. (2013) at the temperature and vapor composition at SPL. The maximum S with respect to ice was estimated assuming RH with respect to water equal to 100.5% using equations from Vaisala (2013). The results are presented in Fig. 9. Considering equilibrium fractionation only, estimated δ^{18} O and δ D were 4.6% and 29.5% less depleted than measured δ^{18} O and δ D, respectively. When kinetic fractionation was included, these differences decreased to 0.97% and 16.1%, respectively.

This treatment for snow is unrealistic in part because it does not account for snow growth by riming, which can be significant at SPL in mixed-phase clouds (Borys et al. 2003; Lowenthal et al. 2011; Saleeby et al. 2013). Snow will incorporate the isotopic signature of the cloud droplets at SPL to the extent that the snow is rimed by those drops. The daily average depletions of δ^{18} O and δ D in snow with respect to cloud were 1.44 ± 1.33% and



FIG. 8. Measured and estimated (a) δ^{18} O and (b) δ D for cloud water using the vapor composition at SPL and equilibrium fractionation only (Calc.¹) and equilibrium and kinetic fractionation (Calc.²).

 $11.1 \pm 10.6\%$, respectively. The difference for δ^{18} O was less than 1% on 7 of 14 days, suggesting that the rimed mass fraction was high and riming occurred close to SPL. Larger differences could be caused by riming of snow by more depleted droplets or by deposition of vapor that is lighter than at SPL. As discussed above, vapor is expected to be lighter aloft where temperatures are lower than at SPL. Preliminary modeling of a case study with a large difference between cloud and snow $\delta^{18}O$ on 13 February 2014 indicated vertical stratification (depletion) of δ^{18} O in water vapor above SPL (Blossey et al. 2015). On 13 February 2014, the difference between snow (-17.3%) and cloud $(-14.0\%)\delta^{18}$ O was 3.3%, the vapor δ^{18} O was $-25.5^{\circ}_{\circ\circ\circ}$, and the temperature at SPL was -4.7° C. The δ^{18} O estimated assuming equilibrium and equilibrium plus kinetic fractionation were -10.5%and -12.7‰, respectively. If vapor deposition occurred at a higher altitude but from the same vapor as at SPL, estimated δ^{18} O would be heavier than at SPL because of the increase in the equilibrium fractionation coefficient with decreasing temperature. Assuming an inverse lapse rate of $158 \text{ m}^{\circ}\text{C}^{-1}$ (above), the temperature at 1 km



FIG. 9. Measured and estimated (a) δ^{18} O and (b) δ D for snow using the vapor composition at SPL and equilibrium fractionation only (Calc.¹) and equilibrium and kinetic fractionation (Calc.²).

above SPL (above the highest mass-weighted altitude of snow growth in Fig. 7) would be -11° C. This corresponds to a vapor δ^{18} O of -31.5°_{00} based on the relationship between δ^{18} O and the temperature described above. Assuming that all vapor deposition occurred at this elevation, estimated snow δ^{18} O would be -15.5%and -19.7% considering equilibrium fractionation and equilibrium plus kinetic fractionation, respectively. While these estimates bracket the measured snow δ^{18} O, they do not fully account for the effect of riming on the snow's isotopic composition. While the isotopic composition of cloud water is theoretically consistent with equilibrium fractionation of the vapor at SPL, this is not the case for snow. Model estimates of the vertical structure of the vapor isotopic composition will provide better understanding of the mechanisms and level in the atmosphere where snow forms.

d. Deuterium excess

Deuterium excess *d* in polar ice has been used to infer source location, meteorological conditions, and longterm climate variations (Jouzel et al. 1982; Dansgaard et al. 1989; Vimeux et al. 1999; Jouzel et al. 2007), water vapor circulation and atmospheric mixing (Blossey et al. 2010), and cloud processes (Bolot et al. 2013; Ciais and Jouzel 1994; Samuels-Crow et al. 2014). Benetti et al. (2014) concluded that d was inversely related to RH above the sea surface and that it increased significantly as a function of increasing surface roughness, which is a function of wind speed. Pfahl and Sodemann (2014) concluded that d varied with RH but not sea surface temperature (SST). Steen-Larsen et al. (2014) found a relationship between d and RH on Bermuda, but the effect of wind speed on d was ambiguous. Steen-Larsen et al. (2015) concluded that neither wind speed nor SST had an effect on d in Iceland. The global meteoric water line of Craig (1961) is consistent with a d of 10% in water vapor over an oceanic source at RH~85% (Clark and Fritz 1997).

The temporal variations of daily average vapor, cloud, and snow d during IOPs are shown in Fig. 10a. Average vapor, cloud, and snow *d* were $11.1 \pm 1.7\%$, $12.6 \pm 2.8\%$, and $13.0 \pm 3.4\%$, respectively. On a daily basis, vapor d at SPL was roughly consistent with oceanic source vapor evaporated at 85% RH (Clark and Fritz 1997). This was also the case for cloud and snow d, although there were higher values prior to 9 February 2014. Figure 10a indicates the direction of the source area with respect to SPL derived from ensemble HYSPLIT back trajectories during IOPs on each day. All 72-h trajectories ended in the Pacific Ocean except for several on 29 February 2014, which ended in Nevada and California. For the 12 days with vapor measurements, the source directions were west, northwest, and westsouthwest on 8, 3, and 1 days, respectively. Deuterium excess during IOPs was estimated for cloud (Fig. 10b) and snow (Fig. 10c) from the estimated δ^{18} O and δ D. shown in Figs. 8 and 9, respectively. Cloud d after 6 February 2014 was estimated to within 1.3% and 0.3%, on average, based on equilibrium and equilibrium plus kinetic fractionation, respectively. Cloud d was underestimated on 27 January, and 4 and 6 February 2014. As was the case for δ^{18} O and δ D (Fig. 9), snow d could not be reproduced assuming growth by vapor deposition under equilibrium or equilibrium plus kinetic fractionation.

Welp et al. (2012) reported diurnal cycles of d in surface water vapor during summer at six urban, agricultural, and rural sites in the United States, Canada, and China. Deuterium excess increased from noon to midafternoon at all sites, with amplitudes ranging from $3.5\%_{00}$ to $17\%_{00}$. This was attributed to entrainment of upper-level air as the mixed layer deepened and/or evapotranspiration from plants.

The diurnal variation of water vapor d during IFRACS was examined using grand hourly averages for



FIG. 10. (a) Variation of daily d in vapor, cloud, and snow during IOP sample periods; comparison of measured and calculated d in (b) cloud and (c) snow. Calc.¹ and Calc.² are as in Figs. 9 and 10. Wind directions from ensemble HYSPLIT trajectories on each day are shown in Fig. 10a (W stands for west, NW is for northwest, WSW is for west-southwest).

all hours from 20 January to 19 February 2014. The average hourly vapor d was $8.9 \pm 3.8_{00}^{\circ}$. The diurnal cycles of d, temperature, water vapor concentration (H₂O), and the particle light absorption coefficient at 528 nm (Bap), an indicator of surface pollution, are shown in Fig. 11a. Peaks in Bap occurred from 2300 to 0100 mountain standard time (MST). These peaks were probably caused by snow grooming operations that occurred late at night and into the early morning. After eliminating the highest 1% of the data (i.e., statistical outliers), these peaks disappeared. The uncertainties of d were propagated from those of δ^{18} O and δ D. The correlations r between temperature and H₂O and between H₂O and d were 0.74 and 0.71, respectively. Maxima and minima in d, temperature, H₂O, and Bap



FIG. 11. Diurnal variation of (a) deuterium excess *d*, temperature, water vapor (H₂O), and Bap for the bottom 99% of the data; and (b) diurnal variation of δ^{18} O and δ D.

occurred during the afternoon (1300-1700 MST) and early morning (0400-0900 MST), respectively. Average afternoon and morning d and H₂O were 10.3 \pm 0.4% and 4600 \pm 140 ppmv and 7.7 \pm 0.4% and 4200 \pm 140 ppmv, respectively. Thus, the diurnal ranges of d and H_2O were only 2.5% and 400 ppmv. Note that based on the relationship shown in Fig. 6b, the diurnal variation in water vapor concentration (400 ppmv) corresponds to a change in vapor δ^{18} O of only 0.49‰. Water vapor concentration varies by 40% on a daily basis but only by 11% over the diurnal cycle. Figure 11b shows the diurnal variation of δ^{18} O and δ D. There was no clear diurnal trend for δ^{18} O and δ D (consistent with the small diurnal variation of water vapor concentration), although their divergence between 1300 and approximately 2000 MST is responsible for the afternoon peak in vapor d. The small variation of water vapor concentration and its isotopic composition at night supports the suggestion in section 3a (Fig. 6b) that their daily variation is related to Rayleigh distillation during transport to SPL.

SPL is above the surface inversion overnight and into the morning hours. Lower temperature and Bap during that period represent background or free-tropospheric air (Borys et al. 1986; Lowenthal et al. 2002; Obrist et al. 2008). During the daytime, surface-derived aerosols (as indicated by Bap) are mixed up to the level of SPL. As discussed above, kinetic fractionation during condensation increased estimated d in the condensate—for example, cloud (Fig. 10b) and snow (Fig. 10c)although the effect is much greater for snow. The effect is opposite for d in the vapor. Figure 12 shows a weak but direct relationship between daily average H2O concentration and vapor d at SPL. This is expected if the fraction (f) of water vapor remaining after transport to SPL is proportional to the vapor concentration at SPL and if kinetic fractionation occurred during condensation and precipitation upwind of SPL. This mechanism, which is seen on a day-to-day basis, is consistent with the diurnal variation in H₂O and vapor d. The diurnal variation in d suggests vertical stratification of water vapor,



FIG. 12. Relationship between daily average water vapor concentration (H_2O) and vapor d.

which becomes drier and more isotopically depleted with a lower d with increasing altitude. Another process that could elevate d during the daytime is evaporation from upwind surface snow. Kinetic fractionation could occur if there was melting followed by evaporation at the snow surface. This is certainly possible as even under cloudy conditions at SPL during IOPs, the average surface temperature and RH at the GAUS launch site were 1.3°C and 73%, respectively. Relatively small day-to-day variation of d in vapor, cloud water, and snow suggests a relatively constant vapor source. However, the diurnal variation of d demonstrates the influence of colder, drier free-tropospheric air with lower d during the nighttime and early morning hours in contrast with higher d in moister surface air during the afternoon hours.

4. Conclusions

Water isotopologues (HD¹⁶O and H₂¹⁸O) were measured in water vapor, supercooled cloud droplets, and falling snow in mixed-phase wintertime orgographic clouds at Storm Peak Laboratory (SPL, 3210 m MSL) from 20 January to 27 February 2014 during the Isotopic Fractionation in Snow (IFRACS) study. A Picarro L-2130-i analyzer continuously measured δ^{18} O and δ D in atmospheric water vapor until 19 February. Cloud and snow were sampled when SPL was enveloped in snowing cloud in discrete intervals totaling 21.7 h over 14 days.

a. Isotopic composition

Water vapor was the most isotopically depleted, followed by snow, and then cloud. The δ^{18} O and δ D were nearly perfectly correlated (r > 0.99) in all three phases and closely followed the global meteoric water line of Craig (1961). There were strong correlations between daily δ^{18} O in vapor and cloud (r = 0.97), vapor and snow (r = 0.94), and cloud and snow (r = 0.93). The differences between vapor and cloud and between vapor and snow δ^{18} O were similar from day to day, consistent with Rayleigh distillation and equilibrium fractionation during transport to SPL. This also suggests relatively consistent cloud condensation and snow growth processes during the experiment.

b. Altitude of snow growth

The altitude at which the snow accrued most of its mass was inferred from relationships between cloud and snow δ^{18} O, a literature-based $d\delta^{18}$ O/dT of $0.7\%^{\circ}$ °C⁻¹, and a consistent ambient lapse rate over the course of the field study. The estimated mass-weighted altitude of snow growth was within 1 km of SPL on all days and within 500 m of SPL on 9 out of 14 study days. These results are similar to those found in a previous study at SPL (Lowenthal et al. 2011). While ice crystals may nucleate under subsaturated conditions higher in the atmosphere, they gain most of their ice mass by vapor deposition and riming at much lower levels in the orographic cloud.

c. Isotopic fractionation

The isotopic composition of cloud water at SPL was closely reproduced from the vapor composition at SPL and literature-based equilibrium fractionation factors. Estimated δ^{18} O decreased by only 0.2‰, on average, if the potential effects of kinetic fractionation were considered. Estimating the isotopic composition of snow was more difficult. Assuming depositional growth only, the vapor composition observed at SPL, and equilibrium fractionation, the estimated snow composition was significantly heavier than that observed. Adding kinetic fractionation increased the estimated depletion; however, this treatment is unrealistic in part because snow growth occurs by riming as well as by vapor deposition.

The difference between cloud and snow δ^{18} O was less than 1‰ on 7 of 14 days, suggesting that snow on these days gained much of its mass and isotopic signature from riming close to SPL. Thus, near-surface riming can have a significant effect on the isotopic composition of deposited snow. For larger differences between cloud and snow δ^{18} O, growth likely occurred by deposition of vapor that was isotopically lighter than that observed at SPL or by riming of droplets derived from that vapor. This implies that the vapor and its isotopic composition were vertically stratified. Vapor depletion with increasing altitude is consistent with previous observations and our understanding of isotopic fractionation as a function of temperature. 2676

d. Deuterium excess

The daily average deuterium excess (d) in vapor, cloud, and snow was $11.1 \pm 1.7\%$, $12.6 \pm 2.8\%$, and $13.0 \pm 3.4\%$, respectively. The small variation of vapor d from day to day is consistent with Rayleigh distillation and equilibrium fractionation of water vapor from a similar source during transport of air masses to SPL. Cloud d was estimated to within 2.4 and 1.4% assuming equilibrium fractionation and equilibrium plus kinetic fractionation, respectively. In these cases, the vapor d signal was well preserved in the cloud water. The highest cloud d (19.9%) was estimated to within 3.4%, assuming both equilibrium and kinetic fractionation. The correlation between measured and estimated cloud d was 0.76. A diurnal trend in vapor d, peaking in the early to midafternoon, coincided with trends in temperature, water vapor concentration, and aerosol light absorption (Bap). This demonstrates a transition between surface air during the day and free-tropospheric air at night at SPL, and suggests vertical stratification of water vapor with lower concentration, more isotopic depletion, and lower deuterium excess at higher altitude. These observations will be used to help validate simulations of storms with an isotope-enabled mesoscale model.

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