Title
Mixed Phase Isotopes 2019

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Data Set Overview
Scientific relevance
Ice crystals and supercooled liquid droplets exist simultaneously in mixed-phase clouds. As a result, precipitation may form by distinct pathways. Water vapor in the atmosphere can deposit directly onto tiny particulates called ice nuclei, or supercooled droplets can freeze onto existing ice crystals, resulting in riming. Environmental conditions (such as temperature) and the presence of different particulate types are both thought to influence the balance of ice and liquid content in mixed-phase clouds, which has important implications for weather and climate. For instance, liquid droplets tend to be more efficient than ice crystals at scattering sunlight back to space, and riming is thought to increase the efficiency of precipitation, resulting in more intense storms. Understanding the processes that control mixed-phase cloud characteristics is thus critical for improving numerical predictions of weather and climate.

Description of scientific experiment
Because of their sensitivity to the temperature, efficiency, and microphysical pathway of precipitation formation, the stable isotopes of water provide insight into the processes controlling ice crystal growth. Theory suggests, for example, that ice crystals formed by vapor deposition should be more depleted (i.e., have lower isotope ratios) than ice crystals formed by riming. Knowing the isotope ratios of water vapor, liquid, and ice in mixed-phase clouds should thus provide a means to estimate the mass fraction of precipitation formed by riming. However, isotopic measurements of distinct cloud particle types are challenging to obtain.

During January 2019, a new observational strategy was tested for making simultaneous measurements of isotope ratios in mixed-phase cloud particles and water vapor at the Desert Research Institute's (DRI) high-elevation Storm Peak Laboratory (SPL, 3220 m) in northwestern Colorado, USA. Two water vapor isotopic analyzers were deployed: one targeting ice crystals and the other targeting interstitial vapor.

Interstitial vapor was measured by attaching a stainless steel backwards-facing inlet to a 1000 liter per minute ambient sampling stack. Vapor was drawn through the inlet to the isotopic analyzer via ¼-inch (outer diameter) copper sample tubing.

Ice crystals were separated from supercooled liquid and vapor using a new phase-separating inlet known as SPIDER, or the phaSe seParation Inlet for Droplets, icE crystals, and aeRosols, developed by researchers at the Massachusetts Institute of Technology and Purdue University. SPIDER separates cloud liquid and ice crystals from the interstial vapor by pulling air through two counterflow virtual impactors (CVIs), positioned on either end of a temperature-controlled cylinder. During passage through the first CVI, dry air flowing counter to the sample excludes molecules in the gas phase while allowing condensate to pass.

Once in the temperature-controlled cylinder, the supercooled droplets evaporate while the ice crystals remain intact, due to saturation vapor pressure differences between liquid and ice. The second CVI then separates the crystals from the newly vaporized liquid droplets. These were delivered to the second isotopic analyzer via ¼-inch copper sample tubing.

This dataset describes a number of distinct measurement periods associated with the 2019 Storm Peak deployment.
- Simultaneous measurements of isotope ratios in ice crystals and interstitial vapor were made over a two-hour intensive observational period on January 23, 2019.
- During the remainder of the SPL deployment (January 14-23, 2019), both isotopic analyzers sampled water vapor (in clear and mixed-phase cloud conditions) from the SPL ambient stack.
- One isotopic analyzer remained at SPL sampling water vapor beyond the main deployment period (January 23 - March 15, 2019).
- Extensive instrument characterization, including side-by-side water vapor sampling, was performed prior to deployment at the NCAR Research Aviation Facility (December 20, 2018 through January 7, 2019).

Study site
Storm Peak Laboratory (SPL) is a permanent mountaintop research facility in the Rocky Mountains of northwestern Colorado. The laboratory is located above the town of Steamboat Springs, near the summit of Mt. Werner, at 3220 m above sea level. Due to its unique setting, SPL is frequently exposed to mixed-phase clouds, as well as free tropospheric air.

Instrument Descriptions
Water vapor and ice crystal isotope ratios were measured with two Picarro L2130-i water vapor isotopic analyzers: Desert Research Institute's (DRI's) HIDS2034 and NCAR's HIDS2346. Both analyzers were operated at nominal 0.5 Hz frequency during the SPL deployment. HIDS2346 was operated in 5-Hz flight-ready mode during the instrument characterization, which took place December 20, 2018 – January 7, 2019.

Data Processing
Isotopic calibrations of the HIDS2034 analyzer were performed for the duration of its operation (December 2018 – March 2019) once every few days using a Picarro Standards Delivery Module (SDM). Calibration points from the SDM, averaged from the last five minutes of a ten-minute vapor stream, were used to correct for concentration-dependent biases and calibrate the HIDS2034 to the Vienna Standard Mean Ocean Water – Standard Light Antarctic Precipitation (VSMOW-SLAP) scale. Secondary (liquid) standards provided by the University of Colorado Boulder's Institute of Arctic and Alpine Research (INSTAAR) were used for these purposes (Table 1). Concentration-dependent biases were characterized using 4th and 5th order polynomial regressions for oxygen and hydrogen isotope ratios, respectively. Scale and offset values for transforming the HIDS2034 measurements to the VSMOW-SLAP scale were identified using only calibration points at water vapor concentrations near 17,000 ppmv (+/- 500 ppmv). Isotopic drift was also monitored over the course of the measurement period but found insignificant.

Table 1. Isotope ratios for the two secondary standards used in calibrations.

	Standard Name	Oxygen isotope ratio ($\delta^{18}O$)	Hydrogen isotope ratio (δD)
Standard 1	Boulder Water	-14.15 permil	-111.65 permil

Standard 2	Polar Water	-45.41 permil	-355.18 permil

Extensive side-by-side water vapor sampling prior to the field deployment at SPL provided a means to peg the HIDS2346 water isotope ratios to HIDS2034 and, conversely, to peg the HIDS2034 water vapor concentrations to HIDS2346. The accuracy of HIDS2346 water vapor concentrations was assessed using a LiCOR (LI-610) portable dew point generator (mixed with dry air of known mass flow) and found suitably accurate such that no correction was applied.

The pre-deployment side-by-side comparison was performed at the NCAR Research Aviation Facility (RAF) in Broomfield, Colorado, December 20, 2018 through January 7, 2019. During this time period, the analyzers sampled room air. Time series from both analyzers were smoothed using one-minute boxcar averaging in order to identify appropriate linear regression coefficients for pegging the water vapor concentration and isotope ratio measurements from one analyzer to the other. All correction models are reported in Table 2.

Table 2. Coefficients for the regression models used to correct water concentration and isotopic data, where X represents either the measured water vapor concentration in ppmv or the measured isotope ratio in permil.

Correction model description	Intercept	X	X^2	X^3	X^4	X^5	Units X
Concentration dependence HIDS2034 $\delta^{18}O$	-432.57052	166.21435	-24.84044	1.64760	-0.04082		ppmv
Concentration dependence HIDS2034 δD	5112.7259	-3369.1818	831.2219	-99.6228	5.8443	-0.1349	ppmv
VSMOW-SLAP scaling HIDS2034 $\delta^{18}O$	0.6204	0.9732					permil
VSMOW-SLAP scaling HIDS2034 δD	5.7597	0.9529					permil
Peg HIDS2034 H_2O concentration to HIDS2346	-5.1830	0.7561					ppmv
Peg HIDS2346 $\delta^{18}O$ to HIDS2034	0.329	1.088					permil
Peg HIDS2346 δD to HIDS2034	-2.6130	0.9028					permil

Even though the two analyzers sampled water vapor side-by-side for the majority of the SPL deployment period, only the pre-deployment period was used to peg the instruments to one another. Measured

discrepancies at SPL—estimated using one-minute boxcar averaging of the two analyzers' time series—were used, instead, as an independent estimate of uncertainty. These uncertainties are reported as root mean square errors (RMSE) in Table 3, alongside RMSE differences from the pre-deployment period.

Table 3. Root mean square errors quantifying the differences between the two isotopic analyzers.

Period name	Date coverage	H_2O (ppmv)	$\delta^{18}O$ (permil)	δD (permil)
Pre-deployment (RAF)	20 December 2018 – 7 January 2019	48.3012	0.1988	1.5394
"In field" deployment (SPL)	14 January 2019 – 23 January 2019	68.3928	0.5662	5.4951

Concentration-corrected and calibrated isotopic data, as well as calibrated water vapor concentration data, are archived separately for the pre-deployment and deployment periods. In addition, the deployment period is separated into three distinct timeframes: the mixed-phase cloud intensive observational period on January 23, 2019, the period of side-by-side water vapor sampling (January 14-23, 2019), and the extended water vapor sampling period, when only the HIDS2034 analyzer operated (January 23 – March 15, 2019). Data files for these periods are as follows:
- MixedPhaseIsotopes2019_PreDeploy_VaporComparison
- MixedPhaseIsotopes2019_InField_CloudSampling
- MixedPhaseIsotopes2019_InField_VaporComparison
- MixedPhaseIsotopes2019_Extended_VaporSampling

All calibration periods are removed from the "in field vapor comparison" dataset, as well as 6 (14) minutes following the end of each calibration period for $\delta^{18}O$ (δD). This ensures that isotopic biases introduced by the standard water as it desorbs from the HIDS2034 buffer volumes and lines are minimized. Periods in which other instruments were actively attached to or detached from the SPL ambient stack are also excluded.

The "pre-deployment vapor comparison" dataset includes only night, weekend, and holiday periods when both analyzers were sampling room air and the laboratory was undisturbed.

In all four processed datasets, isotopic values are provided at sample rate and for one-minute boxcar averages. Time offsets are applied in the first three. However, because the time difference between HIDS2346 and HIDS2034 appeared to drift over the course of the SPL deployment, both adjusted and un-adjusted time vectors are provided in the sample rate "in field vapor comparison" file.

All datasets also provide estimates of uncertainties for the water vapor concentration and isotope ratio measurements. For the sample rate data, these estimates are derived from uncertainties associated with the correction models (i.e., 95% confidence intervals on the fits, see Table 2 for model coefficients) and added in quadrature where necessary. For the one-minute averaged data, these uncertainties are propagated by adding uncertainties from each data point in quadrature and dividing by the number of data points per averaging window. The one-minute data files also contain standard errors for the one-minute averages. For time periods when both analyzers sampled the same medium simultaneously, root mean square errors quantify bulk differences between the isotopic analyzers.

Data Format

All processed (corrected and calibrated) data are provided as sample rate and one-minute averages in NetCDF format and are differentiated by the absence or presence of "_OneMinAvg" at the end of the filename. Each file contains water vapor concentrations, oxygen and hydrogen isotope ratios, and associated uncertainties for four different periods described in Table 4 below.

Table 4. The measurement periods, dates, and sample targets associated with each processed NetCDF.

Filename base	Period name	Date coverage	HIDS2034 target	HIDS2346 target
MixedPhaseIsotopes2019_ PreDeploy_VaporComparison	Pre-deployment (RAF)	20 December 2018 – 7 January 2019	Room air	Room air
MixedPhaseIsotopes2019_ InField_CloudSampling	Main deployment (SPL)	23 January 2019	Interstitial water vapor	Ice crystals
MixedPhaseIsotopes2019_ InField_VaporComparison	Main deployment (SPL)	14 January 2019 – 23 January 2019	Ambient water vapor	Ambient water vapor
MixedPhaseIsotopes2019_ Extended_VaporSampling	Extended deployment (SPL)	23 January 2019 – 15 March 2019	Ambient water vapor	NA

Missing values are denoted by -9999 in all processed NetCDFs.