ISOTOPIC CONSTRAINTS ON ATMOSPHERIC MOISTURE TRANSPORT PROCESSES IN SOUTH AMERICA

Kimberly Samuels-Crow

Follow this and additional works at: http://digitalrepository.unm.edu/eps_etds

Recommended Citation
Samuels-Crow, Kimberly. "ISOTOPIC CONSTRAINTS ON ATMOSPHERIC MOISTURE TRANSPORT PROCESSES IN SOUTH AMERICA." (2014). http://digitalrepository.unm.edu/eps_etds/76

This Dissertation is brought to you for free and open access by the Electronic Theses and Dissertations at UNM Digital Repository. It has been accepted for inclusion in Earth and Planetary Sciences ETDs by an authorized administrator of UNM Digital Repository. For more information, please contact kevco@unm.edu.
Kimberly E. Samuels-Crow
Candidate

Earth & Planetary Sciences
Department

This dissertation is approved, and it is acceptable in quality and form for publication:

Approved by the Dissertation Committee:

Joseph Galewsky, Chairperson

Zachary D. Sharp

David S. Gutzler

Douglas R. Hardy
ISOTOPIC CONSTRAINTS ON ATMOSPHERIC MOISTURE TRANSPORT PROCESSES IN SOUTH AMERICA

BY

KIMBERLY E. SAMUELS-CROW

B.S. Earth & Planetary Sciences, University of New Mexico, 2006
M.S. Geochemistry, New Mexico Institute of Mining and Technology, 2008

DISSERTATION

Submitted in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy in
Earth & Planetary Sciences

The University of New Mexico
Albuquerque, New Mexico

DECEMBER 2014
DEDICATION

This dissertation is dedicated to Ryan, Natalie, and Joey. Thank you for your love and support!
ACKNOWLEDGMENTS

Many people assisted in the research that went into this dissertation. First, I would like to thank my committee members, Joseph Galewsky, Zachary Sharp, David Gutzler, and Douglas Hardy for their help and support. Additional thanks to Carsten Braun, John Worden, and Kate Dennis, who are coauthors on the manuscripts that have come from this dissertation.

I used a number of publicly available climate data sets for this study. I obtained TES data for chapters 2 and 3 from the Jet Propulsion Laboratory, California Institute of Technology. AIRS data were obtained from the Mirador online database, developed and maintained by GES DISC. I gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model, which was used in chapters 2 and 4. I obtained NCEP-NCAR Reanalysis data from the Earth System Research Laboratory Physical Science Division (www.esrl.noaa.gov/psd/). Data on local weather conditions on the Chajnantor Plateau (Chapter 4) were acquired from ALMA and from the weather station of the Atacama Pathfinder Experiment (APEX), which is a collaboration between the Max-Planck-Institut für Radioastronomie, the European Southern Observatory, and the Onsala Space Observatory.

Field work was an integral part of this research. Thanks to Vicencio Expeditions for making our 2011 field work at Quelccaya Ice Cap both possible and pleasant. Thanks to Dylan Ward, Alex Lechler, Lauren Vargo, Alec Tunner, and Jason Cesta for field assistance on the Chajnantor Plateau. Additional thanks to the ALMA staff, particularly Richard Hills, Jim Murray, David Rabanus and Joaquin Penroz, for their hospitality and assistance. Thanks to Ryan Crow for assistance in generating topographic profiles for Chapter 2.

I was fortunate to have financial support for my graduate studies from NM EPSCoR and a National Science Foundation grant (NF-ATM 1158582) along with generous scholarship support from the Department of Earth and Planetary Sciences.

A special thanks to all of my friends in the Earth and Planetary Sciences Department (past and present) who made graduate school much more fun: Magdalena, Bekah, Maarten, Scott, Mark, Justin, Leah, Jason, Jesse, Dylan, and many, many others!
ISOTOPIC CONSTRAINTS ON ATMOSPHERIC MOISTURE TRANSPORT PROCESSES IN SOUTH AMERICA

by

Kimberly Ellen Samuels-Crow

B.Sc. Earth & Planetary Sciences, University of New Mexico, 2006

M.S. Geochemistry, New Mexico Institute of Mining and Technology, 2008

Doctor of Philosophy in Earth & Planetary Sciences,

University of New Mexico, December 2014

ABSTRACT

The water cycle in the tropics and subtropics exerts a strong influence on Earth’s climate. Isotopic ratios in modern water vapor can provide us with insights into low-latitude moisture-transport processes in the modern climate system, recorded in paleoclimate proxy records, and in general circulation models that we rely on to understand how our climate is changing. Advances in satellite and ground-based instruments in the past decade have improved measurements of isotopes in water vapor. In this study, I focus on satellite (chapters 2 and 3) and ground-based (chapters 2 and 4) measurements of isotopes in atmospheric water vapor to evaluate processes responsible for moisture transport in tropical and subtropical South America. Satellite-measured hydrogen isotope ratios (δD), mixing ratios (q), and outgoing longwave radiation (OLR) show that upwind convective intensity controls the seasonal variability in isotopic ratios in tropical Andean water vapor and leads to lower isotopic ratios than predicted by
equilibrium isotope fractionation models (i.e. $D\delta D = \delta D_{\text{measured}} - \delta D_{\text{Rayleigh}} < 0\%$)

(chapter 2). Deep convection in the South American Summer Monsoon domain in austral summer and in the Inter-tropical Convergence Zone in austral winter leads to zones where $D\delta D$ is negative from the Lifted Condensation Level through the mid- to upper-troposphere and possibly above the Level of Neutral Buoyancy (chapter 3). In subtropical South America, nearly continuous measurements of isotopic ratios, mixing ratios, and deuterium-excess (i.e. $d$-excess = $\delta D - (8*\delta^{18}O)$) indicate that condensation under ice supersaturated conditions and mixing with moister air play important roles in controlling moisture transport to the hyperarid Chajnantor Plateau.
PREFACE

The purpose of this preface is to outline the role of each coauthor in multi-author papers included in this dissertation in accordance with the Department of Earth and Planetary Sciences’ guidelines. The second chapter of this dissertation was published in the *Journal of Geophysical Research – Atmospheres* after undergoing the peer-review process. The fourth chapter has been accepted pending minor revisions to the journal *Geophysical Research Letters* after undergoing peer review. The third chapter is in preparation for submission to *Journal of Climate*. Kimberly E. Samuels-Crow is the primary author of, and conducted more than 51% of the work for, each manuscript.

Chapter two focuses on the isotopic composition of water vapor over the tropical Andes and is based on a combination of field sampling and satellite data from the Tropospheric Emission Spectrometer (TES). Joseph Galewsky provided guidance through all aspects of this project. Air samples were collected by Kimberly Samuels-Crow during a July 2011 field campaign at Quelccaya Ice Cap in southern Peru with help from Joseph Galewsky, Douglas Hardy (University of Massachusetts, Amherst, MA), and Carsten Braun (Westfield State University, MA). Kimberly Samuels-Crow prepared and analyzed all samples in the stable isotope lab at UNM under Zachary D. Sharp’s guidance. Kimberly Samuels-Crow obtained TES data from NASA and analyzed the data. John Worden (NASA Jet Propulsion Laboratory, CA) provided guidance and technical support for filtering and interpreting the TES data.

Chapter three focuses on vertical variations in isotopic ratios and water-vapor concentration over South America in austral summer and austral winter with special emphasis on the South American Summer Monsoon region. This study is based on TES
satellite data. Joseph Galewsky provided guidance and feedback during all aspects of this analysis. John Worden (NASA Jet Propulsion Laboratory, CA) provided guidance and technical support for filtering and interpreting the TES data.

Chapter four focuses on deuterium excess in water vapor measured at the Chajnantor Plateau in northern Chile. Joseph Galewsky deployed a Picarro, Inc. cavity ringdown spectrometer in the Central Weather Station at the Atacama Large Millimeter Array (ALMA) in July 2012. The instrument made continuous measurements of water-vapor concentration and isotopic ratios until 2013. Kimberly Samuels-Crow conducted concentration-dependence experiments on the instrument at ALMA in June 2013 and in the stable isotope lab at UNM in October 2013 in order to calibrate the instrument measurements at low water-vapor concentration. Analyzing standards is crucial to getting reliable measurements and quantifying uncertainties. Kimberly Samuels-Crow calibrated the standards used in this study to international standards under Zachary D. Sharp’s guidance at UNM in 2011. Kate Dennis of Picarro Inc. provided information about uncertainties in the instrument’s water-vapor concentration measurements. Kimberly Samuels-Crow analyzed the continuous data generated by the instrument from 2012-2013 under Joseph Galewsky’s guidance.
# TABLE OF CONTENTS

DEDICATION ........................................................................................................ iii

ACKNOWLEDGMENTS .......................................................................................... iv

ABSTRACT ............................................................................................................... v

PREFACE ................................................................................................................. vii

LIST OF FIGURES ................................................................................................. xii

1. INTRODUCTION ................................................................................................ 1

  1.1. References for Chapter 1 ................................................................................ 6

2. UPWIND CONVECTIVE INFLUENCES ON THE ISOTOPIC COMPOSITION OF ATMOSPHERIC WATER VAPOR OVER THE TROPICAL ANDES ........................................................................................................ 8

  2.1. Introduction ..................................................................................................... 9

  2.2. Methods .......................................................................................................... 12

    2.2.1 Satellite measurements of isotopic ratios ..................................................... 12

    2.2.2. Ground-based sample collection ................................................................. 14

    2.2.3. Theoretical curves ..................................................................................... 15

    2.2.4 Lagrangian back-trajectories and outgoing longwave radiation ................. 17

  2.3. Results ............................................................................................................. 19

    2.3.1 Seasonal δD and q variations ...................................................................... 19

    2.3.2 Upwind convective intensity ....................................................................... 24

  2.4. Discussion ....................................................................................................... 28

  2.5. Conclusions .................................................................................................... 30
2.6. References for Chapter 2 ................................................................. 32

3. SEASONAL VARIATIONS IN THE VERTICAL INFLUENCE OF THE
ISOTOPE AMOUNT EFFECT OVER SOUTH AMERICA............................ 38

3.1. Introduction...................................................................................... 38

3.2. Methods.......................................................................................... 41
  3.2.1 Satellite measurements ................................................................. 41
  3.2.2. ΔδD calculation........................................................................... 42
  3.2.3. Characterizing regional convective intensity............................... 44
  3.2.4. Characterizing the vertical extent of clouds................................. 45

3.3. Results........................................................................................... 46
  3.3.1. ΔδD over South America in DJF and JJA .................................... 46
  3.3.2. Seasonal variations in convective precipitation, OLR, and θ_{EB} over South
          America .......................................................................................... 51
  3.3.3. ΔδD and convective parameters................................................ 52
  3.3.4. LCL and cloudtop pressures over South America in DJF and JJA ....... 56

3.4. Discussion ...................................................................................... 58

3.5. Conclusions .................................................................................... 61

3.6. References for Chapter 3 .............................................................. 61

4. HIGH DEUTERIUM-EXCESS IN SUBTROPICAL FREE TROPOSPHERE
WATER VAPOR: CONTINUOUS MEASUREMENTS FROM THE
CHAJNANTOR PLATEAU, NORTHERN CHILE ........................................ 68

4.1. Introduction...................................................................................... 68

4.2. Methods.......................................................................................... 72
4.2.1. Isotope measurements ........................................................................................................... 72

4.2.2. Calculating theoretical curves ............................................................................................. 80

4.2.3 Quantifying water vapor mixing ratios and evaluating local conditions ...... 81

4.2.4. Evaluating the influence of moisture source on d-excess ............................................. 87

4.3. Results ........................................................................................................................................ 89

4.4. Discussion .................................................................................................................................... 93

4.5. Conclusions ............................................................................................................................... 98

4.6. References for Chapter 4 .......................................................................................................... 99

5. CONCLUDING REMARKS AND FUTURE WORK ......................................................... 105

5.1. Conclusions ............................................................................................................................... 105

5.2. Future Work ............................................................................................................................. 106

5.3. Chapter 5 References .............................................................................................................. 108
LIST OF FIGURES

Figure 1.1. An idealized plot showing Rayleigh fractionation (solid line) and mixing (dashed line) for an air parcel with an initial hydrogen isotope composition ($\delta D$) of -90‰. ................................................................. 3

Figure 1.2. Locations of areas of interest in this study (filled rectangles) along with annual average relative humidity (contours) at 500 hPa measured by the Atmospheric Infrared Sounder (AIRS) satellite instrument. The study areas shown here are (1) Chimborazo, (2) Huascarán, (3) Quelccaya, (4) Sajama, and (5) Chajnantor Plateau. .................................................................................................. 4

Figure 2.1. Maps of South America showing Tropospheric Emission Spectrometer (TES) water-vapor concentration for (A) DJF and (B) JJA along with TES $\delta D$ for (C) DJF and (D) JJA. Filled rectangles denote the locations of ice caps in the (1) northern tropical Andes (Chimborazo), (2) central tropical Andes (Huascarán), (3) southern tropical Andes (Quelccaya), and (4) northern subtropics (Sajama). The white square shows the location of the Cruzeiro do Sul sounding data. The white circle shows the location of Illimani ice cap. ................................................................. 10

Figure 2.2. Maps of sample back trajectories launched from the southern tropical Andes (Quelccaya) in (A) DJF and (B) JJA. The glacier at the center of the domain is shown with a white star. The heavy dashed line shows the boundary of the $10^\circ \times 10^\circ$ domain. The white circle shows the location of Cruzeiro do Sul. ......................... 18

Figure 2.3. Maps of South America showing seasonal differences in TES (A) $q$ ($q_{DJF} - q_{JJA}$) and (B) $\delta D_{vapor}$ ($\delta D_{DJF} - \delta D_{JJA}$) with the locations of tropical ice caps (filled
rectangles) in the (1) northern tropical (Chimborazo), (2) central tropical (Huascaran), (3) southern tropical (Quelccaya), and (4) northern subtropical (Sajama) Andes and the site of Cruzeiro do Sul sounding data (white square) shown. Illimani is shown with the white circle.

Figure 2.4. 2-D histograms (light solid lines) of TES $\delta D_{\text{vap}}$ and $q$ in the tropical and northern subtropical Andean glacier region in (A) DJF and (B) JJA with QIC flask measurements from 2011 (white squares). The contours indicate the frequency of TES measurements with a particular $\delta D$ and $q$, and the contour interval for the TES data is number of measurements = 50. Filled rectangles indicate the mean seasonal values for $10^\circ\times10^\circ$ domains centered on the (1) northern tropical, (2) central tropical, (3) southern tropical, and (4) northern subtropical Andes. The heavy lines are the calculated Rayleigh (solid line) and mixing (dashed line) curves. The Rayleigh curve was calculated with $\delta D_{\text{initial}} = -90\%$ and $q_{\text{initial}} = 26479$ ppmv. The mixing curve was calculated using a wet end member with $\delta D = -86\%$ and $q = 19162$ ppmv and a dry end member with $\delta D = -496\%$ and $q = 574$ ppmv.

Figure 2.5. Histograms showing the variability of $\Delta \delta D$ ($\Delta \delta D = \delta D_{\text{TES}} - \delta D_{\text{Rayleigh}}$) in the (A) northern tropical, (B) central tropical, (C) southern tropical, and (D) northern subtropical Andes in DJF (solid lines) and JJA (dashed lines). Shaded region indicates that $\Delta \delta D$ is negative.

Figure 2.6. $\Delta \delta D$ ($\Delta \delta D = \delta D_{\text{Rayleigh}} - \delta D_{\text{TES}}$) for (A) DJF and (B) JJA. Measurements that fall below the Rayleigh curve (i.e. $\Delta \delta D < 0\%$) are designated by solid lines while measurements that lie above the Rayleigh curve are designated by dashed lines. The $0\%$ contour is drawn with a heavy solid line. In DJF, measurements with $\Delta \delta D <$
0‰ are centered over the tropical Andes and upper Amazon Basin. In JJA, measurements with $\Delta\delta D < 0‰$ are located north of the tropical Andes. Filled rectangles indicate the locations of glaciers included in the study as in Figure 2.1 and Figure 2.3. The contour interval is $\Delta\delta D = 20‰$. 

Figure 2.7. Histograms of minimum OLR encountered en route to the tropical Andes show that minimum OLR along trajectories is lower for measurements with $\Delta\delta D < 0‰$ (solid lines) than for measurements with $\Delta\delta D \geq 0‰$ (dashed lines) in both (A) DJF and (B) JJA. OLR $\leq 240$ W m$^{-2}$ (gray field) is diagnostic of periods of intense convection in tropical South America.

Figure 2.8. Contour maps of minimum OLR encountered along back trajectories upwind of each TES $\delta D$ measurement in (A) DJF and (B) JJA. Trajectories launched from measurements with the highest $\Delta\delta D$ (see Figure 2.6) encountered OLR $\leq 200$ W m$^{-2}$ in DJF and JJA. Filled rectangles indicate the locations of glaciers included in the study as in Figure 2.1 and Figure 2.3. The contour interval is 20 W m$^{-2}$.

Figure 2.9. 2-D histograms showing the locations where minimum OLR was encountered along trajectories in (A) DJF and (B) JJA. The gray scale indicates the number of trajectories that encountered minimum OLR at each location. Filled rectangles indicate the locations of glaciers included in the study as in Figure 2.1 and Figure 2.3.

Figure 2.10. Maps showing the difference between the time of the TES measurement and minimum OLR for (A) DJF and (B) JJA along with maps of the distance between the location of the TES measurement and the minimum OLR encountered along trajectories in (C) DJF and (D) JJA. This analysis shows that the $\delta D$ measured by
the TES instrument is typically the product of upwind, rather than local, processes.

Figure 3.1. TRMM convective precipitation in A) DJF and B) JJA. Rectangles indicate locations of domains discussed in this study: 1) tropical Pacific, 2) SASM, 3) subtropics. The white squares indicate locations of sounding data used in section 3.2.4. Black dots indicate location of transects in Figure 3.12.

Figure 3.2. Percentage of each vertical profile with $\Delta \delta D < 0\%$ in A) DJF and B) JJA. Rectangles indicate locations of domains discussed in this study (see Figure 3.1).

Figure 3.3. Thickness of the $\Delta \delta D < 0\%$ zone in km in A) DJF and B) JJA. Rectangles indicate locations of domains discussed in this study (see Figure 3.1).

Figure 3.4. $\Delta \delta D_{\text{vapor}}$ in DJF at A) 1000 hPa, B) 681 hPa, C) 511 hPa, D) 422 hPa, E) 350 hPa, F) 287 hPa. Rectangles indicate locations of domains discussed in this study (see Figure 3.1).

Figure 3.5. As in Figure 3.4 for JJA.

Figure 3.6. OLR in A) DJF and B) JJA. Rectangles indicate locations of domains discussed in this study (see Figure 3.1).

Figure 3.7. $\theta_{\text{EB}}$ calculated from NCEP-NCAR Reanalysis data in A) DJF and B) JJA. Rectangles indicate locations of domains discussed in this study (see Figure 3.1).

Figure 3.8. 2D histograms showing the joint distribution of $\Delta \delta D_{\text{vapor}}$ and daily precipitation rates in each domain for DJF (A, C, E) and JJA (B, D, F). Contour interval = 50 measurements.

Figure 3.9. As in Figure 3.8 for the joint distribution of $\theta_{\text{EB}}$ and maximum $\Delta \delta D$. Contours indicate percentage of measurements.
Figure 3.10. Histograms showing the pressure of the LCL from atmospheric soundings within each domain................................................................. 56

Figure 3.11. AIRS cloudtop pressures in A) DJF and B) JJA. Rectangles indicate locations of domains discussed in this study (see Figure 3.1)......................... 58

Figure 3.12. Profiles showing ΔD in A) DJF and B) JJA along 70°W. The heavy dotted lines indicate cloudtop pressure and the small dashed lines indicate the approximate location of the LCL........................................................................ 59

Figure 4.1. Location of the Chajnantor Plateau in northern Chile (star). Annual mean relative humidity at 500 hPa (color scale and contours) is taken from the level 3 monthly Atmospheric Infrared Sounder satellite data............................. 71

Figure 4.2. Linear relationship between measured and accepted values for SMOW, GISP, and SLAP for (A) δ18O and (B) δD. ................................................................. 75

Figure 4.3. Linear relationship between measured and corrected values for secondary standards, including NM-3 and ANT, which are used to correct measurements in this study for A) δ18O and B) δD................................................................. 76

Figure 4.4. Mean isotopic ratios of standards did not vary systematically over time in NM-3 (panels A and C) and ANT (panels B and D). ........................................... 78

Figure 4.5. Comparison of q calculated from meteorological measurements at (A) ALMA and (B) APEX along with (C) q as reported by the CRDS. Reported q fluctuates with calculated q from the weather stations, but it is, on average, 21% higher than q calculated from ALMA data and 28% higher than q calculated from APEX data... 86

Figure 4.6. Scatter plot showing the linear relationship between q(ALMA) and q(CRDS)...... 87
Figure 4.7. Example of mean trajectory location at $t = -240$ hours for a suite of trajectories launched in a $1^\circ \times 1^\circ \times 500$ m domain around ALMA and for single trajectories launched from each measurement on August 12, 2012. The average source region latitude for the 3-dimensional region ($n = 15200$) was $19^\circ S \pm 5^\circ$ while the average source region for single trajectories launched from each measurement on 8/12/12 ($n = 129$) was $16^\circ S \pm 2^\circ$. Average $d$-excess on 8/12/12 was $+54\%o$. ........ 88

Figure 4.8. Histograms for trajectory locations at $t = -240$ hours shows that there is no distinct source area for high $d$-excess measurements. ................................................. 90

Figure 4.9. Water vapor (A) $\delta D$, (B) $\delta^{18}O$, and (C) $d$-excess measurements from the Chajnantor Plateau (black dots) plotted versus mixing ratio. The heavy black line shows Rayleigh fractionation at RH = 100%. The suite of gray lines shows $d$-excess at RHi ranging from 105% to 130% (contour interval = 5%). ............................................. 92

Figure 4.10. An idealized model for dehydration via condensation under ice supersaturation at RHi = 105% (gray line) followed by mixing en route to Chajnantor Plateau (thin black line) can produce the observed distribution of (A) $\delta D$, (B) $\delta^{18}O$, and (C) $d$-excess. Rayleigh fractionation at RH = 100% (thick black line) is shown for reference. ................................................................. 95

Figure 4.11. $D$-excess and mixing ratios for the Chajnantor Plateau from our dataset and theoretical Rayleigh curves at a range of relative humidity (as in Figure 4.9) along with model output, shown as monthly averages, in a $2^\circ \times 2^\circ$ domain around study area from (A) IsoGSM [Yoshimura et al., 2008] and (B) LMDZ [Risi et al., 2010], which are included in the SWING2 project......................................................... 97
Figure 5.1. Variations in measured (A) mixing ratio, (B) δD, (C) δ^{18}O, and (D) d-excess

on December 30, 2012. ........................................................................................................107
1. INTRODUCTION

Water vapor is a principal greenhouse gas that amplifies temperature changes initiated by forcings such as increases in anthropogenic CO$_2$ [e.g. Held and Soden, 2000]. This water-vapor feedback leads to significant uncertainties in climate change predictions because climate models do not accurately simulate the processes that contribute to the vertical and lateral distribution of tropospheric water vapor and precipitation [e.g. Risi et al., 2010; Bindoff et al., 2013]. Stable isotopologues of water (e.g. H$_2^{16}$O, H$_2^{18}$O, HD$^{16}$O) evaporate and condense at different rates, providing natural tracers of different processes that control atmospheric humidity and more information than water vapor amount alone.

Research over the past several decades has shown that stable isotopes in meteoric water can provide insights into precipitation source regions and processes that control moisture transport [e.g. Craig, 1961; Dansgaard, 1964; Craig and Gordon, 1965; Gat and Carmi, 1970; Gat and Dansgaard, 1972; Salati et al., 1979; Jouzel and Merlivat, 1982; Jouzel and Merlivat, 1984; Thompson et al., 1986; Grootes et al., 1989; Broecker, 1997; Pierrehumbert, 1999; Hoffman et al., 2003; Good et al., 2014]. The direct study of isotopes in atmospheric water vapor, however, has been limited by sampling technology. Many studies have relied on condensing water vapor over periods of hours from boundary layer air [e.g. Craig and Gordon, 1965; Uemura et al., 2008] or taking flask samples in order to measure hydrogen isotope ratios only [e.g. Strong et al., 2007]. Studies of water vapor in the free troposphere and lower stratosphere have relied on airborne cavity ringdown spectroscopy (CRDS) surveys [e.g. Moyer et al., 1996; Keith, 2000; Webster and Heymsfield, 2003; Sayres et al., 2010]. These studies are limited in
that they either provide an integrated view of water vapor isotopic ratios over periods of
hours (in the case of condensation of atmospheric water vapor) or they provide only a
snapshot of atmospheric conditions in the case of flask measurements and airborne CRDS
campaigns. The development and improvement of satellite and commercially available
CRDS instruments over the past ten years provides us with an opportunity to examine
processes that control isotopic ratios in water vapor over broader areas and longer
timeframes.

The Rayleigh model serves as a theoretical framework in which to understand
processes that control isotopic ratios in atmospheric water vapor. Rayleigh distillation is
an open-system process in which water vapor is immediately removed after condensation.
Isotopic ratios (R) produced by Rayleigh distillation are a function of water vapor amount
(q) and of temperature-dependent fractionation factors (α):

\[ d \ln R = (\alpha - 1) d \ln q \] (1.1)

Although Rayleigh distillation rarely completely describes isotopic ratios in low-latitude
water vapor, deviations from the idealized curves can provide first-order insights into the
processes that control isotopic ratios [Brown et al., 2008; Figure 1.1]. When a
measurement falls on the Rayleigh curve, equilibrium processes likely control isotopic
ratios, which are generally expressed as the permil difference between ratios of heavy and
light isotopes in a measurement relative to a standard:

\[ \delta = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) * 1000 \] (1.2)

Measurements that lie above the Rayleigh curve have likely undergone mixing between
moist and dry air, and measurements that fall below the Rayleigh curve have likely
undergone moisture recycling in convective clouds [e.g. Noone, 2012]. I rely on this diagnostic tool throughout this dissertation.

Each chapter focuses on isotopic ratios in different parts of South America (Figure 1.2) in order to understand 1) processes that controlled isotopic ratios in paleoprecipitation, 2) seasonal variations in the influence of the isotope amount effect, and 3) non-equilibrium processes that control moisture transport to the hyperarid subtropics. The analysis in chapter two relies on the spatial coverage provided by the Tropospheric Emission Spectrometer (TES) on-board the Aura satellite [e.g. Worden et al., 2012] to evaluate processes that control seasonal variations in atmospheric water vapor HDO/H$_2$O values ($\delta$D$_{\text{vapor}}$) over the tropical Andes. $\delta$D$_{\text{vapor}}$ is lower in austral summer (DJF) than austral winter (JJA), which is broadly consistent with precipitation studies and with $\delta^{18}$O$_{\text{snow}}$ preserved in tropical Andean glaciers. In DJF, 64% of $\delta$D$_{\text{vapor}}$ measurements over the tropical Andes are lower than predicted by Rayleigh distillation (i.e. $\Delta\delta$D = $\delta$D$_{\text{TES}}$ - $\delta$D$_{\text{Rayleigh}}$ < 0‰) while 40% of JJA $\delta$D$_{\text{vapor}}$ measurements are lower than predicted by Rayleigh distillation. Air that has lower $\delta$D$_{\text{vapor}}$ than predicted by
Rayleigh distillation at a given water-vapor concentration \((q)\) encounters low minimum outgoing longwave radiation \((< 240 \text{ W m}^{-2})\) en route to the tropical Andes, suggesting convective intensity controls the isotopic ratios of these measurements. The broad regional coverage of the satellite data allows mapping of the spatial extent of the region where isotopic ratios reflect convective processes in different seasons. In DJF, convection strongly influences \(\delta D_{\text{vapor}}\) in the central tropical Andes. In JJA, convection influences \(\delta D_{\text{vapor}}\) north of the tropical Andes. This pattern suggests that monsoon convection controls \(\delta D_{\text{vapor}}\) in austral summer while large-scale advective mixing controls Andean \(\delta D_{\text{vapor}}\) in austral winter. Isotopes in the region where \(\Delta \delta D < 0\%\) are generally controlled by the isotope “amount effect.”

![Figure 1.2](image.png)

*Figure 1.2. Locations of areas of interest in this study (filled rectangles) along with annual average relative humidity (contours) at 500 hPa measured by the Atmospheric Infrared Sounder (AIRS) satellite instrument. The study areas shown here are (1) Chimborazo, (2) Huascaran, (3) Quelccaya, (4) Sajama, and (5) Chajnantor Plateau.*

Chapter three is an extension of the analysis in chapter two and examines the vertical extent of the region influenced by the isotope amount effect over South America in DJF and JJA. Understanding the vertical structure of the amount effect over South
America is essential for improving theoretical constraints and models of convective influence on Southern Hemisphere moisture in DJF and JJA. In DJF, the thickest $\Delta \delta D < 0^\circ$ zone occurs over the South American Summer Monsoon (SASM) region while the thickest zone of negative $\Delta \delta D$ occurs north of 10°S over the tropical Pacific in JJA. The thickest tropical $\Delta \delta D < 0^\circ$ zones coincide with high convective precipitation rates and high boundary layer equivalent potential temperature ($\theta_{EB} \geq 340K$) in both DJF and JJA, linking these regions to high convective intensity. In both DJF and JJA, maximum $\Delta \delta D$ values occur in the subtropics, where values exceed $+50^\circ$ at pressures below 681 hPa.

Chapter four focuses on subtropical South America and continuous ground-based CRDS measurements taken from July 2012 to March 2013 on the hyperarid Chajnantor Plateau (Figure 1.2). The CRDS instrument measures both $\delta D$ and $\delta^{18}O$, making it possible to calculate a secondary parameter, deuterium-excess ($d$-excess) and use it to examine the range of processes responsible for transporting water vapor to the hyperarid subtropics:

$$d\text{-excess} = \delta D - (8 \times \delta^{18}O)$$ (1.3)

$D$-excess is an indicator of non-equilibrium isotope fractionation and results from the different evaporation rates of oxygen and hydrogen ratios. Globally, $d$-excess in meteoric water is approximately $+10^\circ$ [e.g. Dansgaard, 1964]. General Circulation Models estimate that $d$-excess in atmospheric water vapor from the surface through the mid-troposphere ranges from $+10^\circ$ to $+20^\circ$ [e.g. Yoshimura et al., 2008; Risi et al., 2010]. However, cloud-resolving models and microphysical models predict a broader range of $d$-excess for water vapor in the free troposphere. The data set presented in chapter four has a mean $d$-excess of $46^\circ \pm 5^\circ$ and frequently exceeds $100^\circ$ at low water vapor
concentration ($q \leq 500$ ppmv). The $d$-excess measured at this site can be understood in terms of supersaturation with respect to ice at relative humidities between 100% and 130%, followed by mixing en route to the plateau. The $d$-excess measured at Chajnantor is consistent with predictions for $d$-excess in the upper troposphere from isotope-enabled general circulation models and with high vapor saturation over ice in cloud-resolving and microphysical models.

1.1. References for Chapter 1


Thompson, L., E. Mosley-Thompson, W. Dansgaard, and P. Grootes (1986), The Little Ice Age as recorded in the stratigraphy of the tropical Quelccaya ice cap, Science, 234(4774), 361.


2. UPWIND CONVECTIVE INFLUENCES ON THE ISOTOPIC COMPOSITION OF ATMOSPHERIC WATER VAPOR OVER THE TROPICAL ANDES
2.1. Introduction

The seasonal cycle of modern water-vapor transport over the tropical Andes is strongly influenced by a complex interplay between the intertropical convergence zone (ITCZ) [Martínez et al., 2011], the strength of the South American Monsoon [Vuille and Werner, 2005], and the resulting position of the Bolivian High [Lenters and Cook, 1999]. Precipitation is strongly seasonal in modern tropical and subtropical South America. During the austral winter (JJA), most of South America experiences a dry season with convective precipitation focused north of the equator in the ITCZ [e.g. Garreaud et al., 2008]. In austral summer (DJF), a deep continental low-pressure zone forms over the Chaco region of eastern Brazil, feeding convective precipitation associated with the South American Summer Monsoon [e.g. Garreaud et al., 2008] and leading to an upper-level high-pressure zone, the Bolivian High [e.g. Lenters and Cook, 1999], which is absent in JJA [e.g. Garreaud et al., 2008]. Easterly winds associated with the Bolivian High transport moisture to the Altiplano and lead to the development of deep convection in the Andes during DJF [e.g. Garreaud et al., 2003; Garreaud et al., 2008]. Researchers have used paleoclimate proxies preserved in ice cores from Quelccaya Ice Cap [e.g. Grootes et al., 1989; Thompson et al., 2013], Huascarán [e.g. Thompson et al., 1995; Broecker, 1997; Pierrehumbert, 1999], Illimani [e.g. Ramirez et al., 2003; Hoffmann et al., 2003], and Chimborazo [e.g. Vimeux et al., 2009] (Figure 2.1) to reconstruct past tropical climate variability and from Sajama [e.g. Thompson et al., 2000] to reconstruct past climate variability in the northern subtropics [Kaser and Osmaston, 2002]. However, the interpretation of the oxygen isotope ratios in the ice (δ¹⁸Osnow) [e.g. Thompson et al., 2013] remains challenging.
Figure 2.1. Maps of South America showing Tropospheric Emission Spectrometer (TES) water-vapor concentration for (A) DJF and (B) JJA along with TES δD for (C) DJF and (D) JJA. Filled rectangles denote the locations of ice caps in the (1) northern tropical Andes (Chimborazo), (2) central tropical Andes (Huascaran), (3) southern tropical Andes (Quelccaya), and (4) northern subtropics (Sajama). The white square shows the location of the Cruzeiro do Sul sounding data. The white circle shows the location of Illimani ice cap.

Seasonal variations in observed tropical Andean δ¹⁸O³⁶⁰ are the central issue. Whereas there is a positive correlation between air temperature and δ¹⁸O³⁶⁰ in polar ice ("isotope temperature effect") [Dansgaard, 1964], tropical Andean δ¹⁸O³⁶⁰ is lower in DJF than JJA despite relatively uniform annual temperatures [Thompson, 2000]. Many researchers have concluded that regional δ¹⁸O³⁶⁰ preserves information about upwind precipitation history [e.g. Hoffmann et al., 2003; Vuille et al., 2003a; Vuille et al., 2003b; Vimeux et al., 2005; Vuille and Werner, 2005; Sturm et al., 2007; Villacís et al., 2008; Vimeux et al., 2011] instead of temperature [Thompson et al., 2003], suggesting that the
“isotope amount effect” [Dansgaard, 1964] primarily controls the isotopic composition of tropical ice.

Isotopic ratios in precipitation from valleys adjacent to Chimborazo [Villacís et al., 2008] and Cerro El Consuelo [Windhorst et al., 2013] in Ecuador and Illimani in Bolivia [Vimeux et al., 2005] have been linked to upwind, rather than local, processes, but the data are spatially and temporally limited. Joint measurements of atmospheric water-vapor concentration ($q$) and hydrogen isotope ratios ($\delta D_{\text{vapor}}$) may constrain the relative importance of large-scale advective mixing and convective processes in different seasons throughout the region [Worden et al., 2007; Noone, 2012]. The joint distribution of $\delta D_{\text{vapor}}$ and $q$ has been used to distinguish between processes that transport water vapor through the tropics [Worden et al., 2007], to the subtropics [e.g. Risi et al., 2010; Galewsky et al., 2011], and to monsoon regions [Brown et al., 2008]. Other studies have used the joint distribution of $q$ and $\delta D_{\text{vapor}}$ to quantify convective processes, including entrainment of vapor from the unsaturated downdraft into the subcloud layer, that govern observed decreases in isotopic ratios with increased precipitation [Risi et al., 2008].

The goal of this study is to use satellite measurements from NASA’s Tropospheric Emission Spectrometer (TES) to determine seasonal variability in $\delta D_{\text{vapor}}$ over the tropical Andes and to explore the links between modern $\delta D_{\text{vapor}}$ and upwind convective intensity. Satellite data provide spatial coverage impossible to achieve in ground-based studies, allowing us to evaluate how processes change from north to south along the spine of the Andes and through the region affected by the South American Summer Monsoon [Zhou and Lau, 1998], when most of the accumulation takes place on tropical glaciers [e.g. Vuille et al., 2000; Hardy et al., 2003]. Many processes are
involved in the conversion of atmospheric water vapor to glacial ice, including postdepositional processes such as wind scour, sublimation, and melting, in this topographically complex region [e.g. Hardy, 2003]. Our goal is to advance our knowledge of modern water-vapor dynamics in the tropical Andes, which may provide insights into past processes preserved in the ice-core record, and to map out the regions of South America where isotopic ratios in water vapor are affected by convection in different seasons.

2.2. Methods

2.2.1 Satellite measurements of isotopic ratios

Water isotopologues (e.g. HDO, H$_2^{16}$O, H$_2^{18}$O) fractionate during phase changes with evaporation and condensation concentrating the heavier isotopologues in the liquid. We can, therefore, use isotopic ratios in water vapor to trace atmospheric processes, including Rayleigh distillation, subcloud raindrop evaporation, diffusion, and large-scale mixing [Worden et al., 2006; Galewsky and Hurley, 2010; Noone, 2012]. HDO/H$_2$O ratios are reported as the per mil (‰) difference (δ) between the isotopic ratio of the sample ($R_{sample}$) and standard ($R_{std}$), in this case Vienna Standard Mean Ocean Water (VSMOW):

$$\delta D = (R_{sample} / R_{std} - 1) * 1000 \text{ (2.1)}$$

TES, aboard NASA’s Aura satellite launched in 2004, provides near-global measurements of infrared radiation from Earth’s surface and atmospheric gases, including H$_2$O and HDO. TES is a Fourier Transform Spectrometer that measures infrared radiation from 650 cm$^{-1}$ to 3050 cm$^{-1}$ in limb and nadir mode [Worden et al., 2006; Noone, 2012]. We used Level 2 nadir measurements from the TES Lite v006 data
set to calculate seasonal and monthly averages of $\delta D_{\text{vapor}}$ ($\overline{\delta D_{\text{vapor}}}$) and $q$ ($\overline{q}$) over $10^\circ \times 10^\circ$ boxes centered around Chimborazo (0.9°S, 74.5°W; northern tropical Andes), Huascaran (9°S, 78°W; central tropical Andes), Quelccaya Ice Cap (14°S, 71°W; southern tropical Andes), and Sajama (18°S, 69°W; northern subtropical Andes) at 510.9 hPa, and over a broad region of South America that incorporates the tropical and northern subtropical Andes (Figure 2.1). TES nadir measurements have a ground footprint of 5.3 km × 8.3 km. TES Lite data are bias-corrected for known problems in HDO measurements and have greater vertical resolution than previous versions of the TES [Worden et al., 2012], and other satellite data [e.g. Lacour et al., 2012], allowing us to distinguish between the boundary layer and free troposphere. TES data have peak sensitivity ~500 hPa, and averaging kernels strongly overlap at this level [Worden et al., 2012], so free troposphere measurements require no further correction and a single level can be used rather than a weighted average in the vertical.

To ensure high data quality, we used TES measurements from 2004 to 2011 with degrees of freedom for signal (DOFS) > 0.7 in the free troposphere and a retrieval quality flag of 1. We determined DOFS in the free troposphere by summing the averaging kernel diagonal for HDO from 750 to 100 hPa. Mean DOFS was greater than 1 in each domain in DJF and JJA and differed by less than 0.1 between seasons in each domain. At Quelccaya Ice Cap, 763 DJF and 772 JJA measurements met these criteria. At Chimborazo, 830 and 795 measurements met these criteria for DJF and JJA respectively. At Huascaran, 777 and 723 measurements met these criteria for DJF and JJA respectively, and, at Sajama, 716 and 564 measurements met these criteria for DJF and JJA respectively. On average, these measurements occurred every 3.9 days within each
10°×10° domain and include more than half of the TES measurements in the study area. The broader South American region shown in Figure 2.1 incorporates more than 20,000 measurements in both DJF and JJA. Mean DOFS, the primary means to quantify the sensitivity of TES retrievals to a number of factors, including clouds, shows little seasonal variation in the domains described above. Therefore, variations in interferences have little impact on seasonal variability in δD_{vapor} measurements [e.g. Worden et al., 2007; Lee et al. 2011].

2.2.2. Ground-based sample collection

We collected eleven air samples at the summit of Quelccaya Ice Cap in evacuated glass flasks [Strong et al., 2007] from July 7 to 9, 2011. Local conditions were measured simultaneously with a handheld Kestrel weather meter and an automated weather station installed at the summit of the ice cap in August 2003 [e.g. Hardy and Hardy, 2008; Bradley et al., 2009; Hardy, 2011]. The average atmospheric pressure at the summit of Quelccaya Ice Cap during the sampling period was 512 hPa, making these samples directly comparable to the TES measurements. We cryogenically isolated the water vapor in the University of New Mexico’s stable isotope lab following methods described by Strong et al. [2007] and Johnson et al. [2011] and converted the water vapor to H₂ gas using a zinc reduction method [Friedman, 1953]. We then determined the δD of the H₂ gas on a Finnegan MAT-252 mass spectrometer at the University of New Mexico. Small sample size precluded δ^{18}O_{vapor} measurements.
2.2.3. Theoretical curves

The Rayleigh model, which describes progressive, open-system isotopic change, is a first-order tool for diagnosing processes that control $\delta D_{\text{vapor}}$ and $q$. The Rayleigh model assumes condensed water vapor is completely removed from the system, decreasing the isotopic ratios of the remaining vapor. This process results in decreased $\delta D_{\text{vapor}}$ with decreased $q$, decreased temperature, increased elevation, and increased distance from the source region [e.g. Dansgaard, 1964; Gat, 1996]. Deviations from the Rayleigh model can provide insights into other processes that contribute to the isotopic composition of water vapor in the tropics and monsoon regions [e.g. Brown et al., 2008]. $\delta D_{\text{vapor}}$ that falls below the Rayleigh curve is generally associated with moisture recycling in convective clouds while $\delta D_{\text{vapor}}$ that lies above the Rayleigh curve is typically associated with advective mixing [e.g. Worden et al., 2007; Noone, 2012].

We calculated Rayleigh curves as a function of $q$ at saturation based on vertical temperature profiles from atmospheric soundings at Cruzeiro do Sul, Brazil (http://weather.uwyo.edu/upperair/sounding.html), which is upwind of the central and southern tropical Andean glaciers (Figure 2.1), based on equation 2.2:

$$d\ln R = (\alpha - 1)d\ln q \quad (2.2)$$

where $R$ is the D/H ratio, $\alpha$ is the temperature-dependent fractionation factor, and $q$ is the water vapor mixing ratio [e.g. Dessler and Sherwood, 2003]. We calculated mixing curves based on equation 2.3:

$$\delta D_{\text{mix}} = 1000 \left[ \frac{\left( \frac{f[D]}{1 + (1-f)[D]} \right)}{\left( \frac{f[H]}{1 + (1-f)[H]} \right)^2} \right]^{1/2} \left( \frac{D}{H} \right)_{\text{VSMOW}} - 1 \quad (2.3)$$
where $f$ is the mixing fraction [e.g. Gedzelman, 1988; Dessler and Sherwood, 2003].

In order to calculate the Rayleigh curve, we used an initial $\delta D_{\text{vapor}}$ of -90‰, consistent with $\delta D_{\text{vapor}}$ in equilibrium with the tropical Atlantic [Craig and Gordon, 1965], and an initial $q$ of 26479 ppmv, consistent with the saturation vapor pressure at low elevations over Cruzeiro do Sul. We used fractionation factors of Majoube [1971] for fractionation between liquid and vapor above 0°C and Merlivat and Nief [1967] for fractionation between solid and vapor at temperatures below 0°C. We tested the sensitivity of the Rayleigh curve calculations to choice of sounding data by comparing Rayleigh curves calculated from Cruzeiro do Sul sounding data to Rayleigh curves calculated based on soundings from locations in the Amazon Basin, but these calculations did not yield significantly different results.

In order to determine how the measured $\delta D_{\text{vapor}}$ deviates from Rayleigh predictions, we found the difference between the measured $\delta D_{\text{vapor}}$ and the Rayleigh prediction at the given $q \pm 100$ ppmv:

$$\Delta \delta D = \delta D_{\text{TES}} - \delta D_{\text{Rayleigh}} \ (2.4).$$

When a measurement lies on the Rayleigh curve (i.e. $\Delta \delta D = 0$‰) open-system equilibrium fractionation controls the isotopic composition of the water vapor. Measurements that lie above the Rayleigh curve have a $\Delta \delta D > 0$‰, suggesting that advective mixing between moist air with relatively high $\delta D$ and dry air with relatively low $\delta D$ controls the isotopic composition of the water vapor. Measurements that fall below the Rayleigh curve have a $\Delta \delta D < 0$‰ and are associated with convective moisture recycling, whereby the vapor and liquid coexist after condensation, and entrainment of
low δD water vapor from unsaturated downdrafts decreases the isotopic ratios in the
convective system [e.g. Risi et al., 2008].

2.2.4 Lagrangian back-trajectories and outgoing longwave radiation

We investigated links between δD$_{vapor}$ and convective intensity by determining
the minimum outgoing longwave radiation (OLR) along back trajectories upwind of each
TES measurement. Low OLR is primarily controlled by high cirrus clouds, which are
produced by deep convection and cannot persist longterm without convective conditions
[Zhang, 1993]. Therefore, low OLR is often used to identify intense tropical convection
and the onset of monsoon precipitation in monsoon regions [e.g. Kousky, 1988; Kousky
and Kayano, 1994; Moron, 1995; Singh, 2005; Vuille and Werner, 2005; Susskind et al.,
2012]. In Amazonia, a seasonal average OLR of 240 W m$^{-2}$ or lower is considered
diagnostic of the South American Summer Monsoon [Kousky, 1988]. Average cloudtop
temperatures in the study region are approximately 255 K, suggesting that cirrus clouds
fed by deep convection likely control OLR encountered along trajectories [Zhang, 1993]
and confirming that low OLR can be used as a proxy for regional convection.

In order to determine the minimum OLR air encounters en route to the tropical
Andes, we first calculated 5-day Lagrangian back trajectories from each TES
measurement using NOAA’s HYSPLIT model driven by NCEP-NCAR Reanalysis data
[Draxler and Hess, 1997]. Vertical motion is based on vertical velocity fields from the
Reanalysis dataset [Draxler and Hess, 1997; Draxler, 1999]. Sample trajectories are
shown in Figure 2.2.
In order to determine the sensitivity of the trajectory location to vertical motion in this highly convective and topographically complex region, we launched a subset of trajectories from 1000 m above TES measurements in 10°×10° domains above Quelccaya Ice Cap, eastern Brazil (10.2°S, 40.8°W), and the Pacific (14°S, 90°W) and compared the location of the trajectory launched from the TES measurement to the trajectory launched 1000 m above the TES measurement. Additionally, we calculated a subset of the trajectories using the Global Data Assimilation System (GDAS1) to test the sensitivity of HYSPLIT to variations in meteorological input.

Once back trajectories were calculated for each TES measurement, we used daily level 3 OLR data from the Atmospheric Infrared Sounder (AIRS) version 6 to determine the OLR within a 2°×2° domain around each trajectory 24, 48, 72, 96, and 120 hours before the TES measurement. OLR data from the AIRS instrument are consistent with OLR data from the Clouds and Earth’s Radiant Energy System (CERES) data and have been used to link variability in tropical OLR with the El Niño-Southern Oscillation Index.
[Susskind et al., 2012]. We determined the minimum OLR along each 5-day trajectory as a proxy for maximum upwind convective intensity. In order to evaluate the influence of local convection, we determined average OLR on the day of each TES measurement and the average distance, both spatially and temporally, between the TES measurement and minimum OLR.

Despite the discrepancies in the precise locations of trajectories calculated based on different meteorological input and between trajectories launched at different elevations, each trajectory encountered minimum OLR in the same region (not shown), and minimum OLR encountered along trajectories was consistent. Mean minimum OLR along back trajectories launched from the elevation of the TES measurement and from 1000 m above the TES measurement varied by only 2 W m\(^{-2}\) at Quelccaya Ice Cap, 4 W m\(^{-2}\) over the Pacific, and 10 W m\(^{-2}\) over eastern Brazil. In DJF, OLR along the subset of trajectories driven by GDAS1 was, on average, 7 W m\(^{-2}\) higher than OLR along trajectories driven by the Reanalysis dataset. In JJA, OLR along the subset of trajectories driven by GDAS1 was, on average, 2 W m\(^{-2}\) higher than OLR along trajectories driven by the Reanalysis dataset.

2.3. Results

2.3.1 Seasonal \(\delta D\) and \(q\) variations

Seasonal variations in \(q\) are consistent with precipitation patterns in tropical South America [e.g. Garreaud et al., 2008]. In DJF, \(q\) is highest over Brazil (Figure 2.1A) while \(q\) is highest in the vicinity of the equator in JJA (Figure 2.1B). \(\delta D_{\text{vapor}}\) does not follow the same spatial pattern as \(q\) in DJF (Figure 2.1C) or JJA (Figure 2.1D). Seasonal \(\delta D_{\text{vapor}}\) in the tropical Andes is lower in DJF (Figure 2.3A) when \(q\) is higher than it is in JJA.
(Figure 2.3B). This seasonal pattern is broadly consistent with seasonal variations in tropical Andean precipitation [e.g. Vimeux et al., 2005] and $\delta^{18}O_{snow}$ [Thompson, 2000] but is inconsistent with Rayleigh distillation based on starting $\delta D_{vapor}$ and $q$ consistent with a tropical source region. Seasonal $\overline{\delta D_{vapor}}$ in DJF is lower in the central tropical Andes (-260‰), than in the northern tropical Andes (-238‰), southern tropical Andes (-247‰), or the northern subtropical Andes (-236‰). In JJA, $\overline{\delta D_{vapor}}$ is 14‰ to 33‰ higher than it is in DJF while $\overline{\delta D_{vapor}}$ in the northern subtropical Andes is 4‰ lower than in DJF (Figure 2.4).

Figure 2.3. Maps of South America showing seasonal differences in TES (A) $q$ ($q_{DJF} - q_{JJA}$) and (B) $\delta D_{vapor}$ ($\delta D_{DJF} - \delta D_{JJA}$) with the locations of tropical ice caps (filled rectangles) in the (1) northern tropical (Chimborazo), (2) central tropical (Huascaran), (3) southern tropical (Quelccaya), and (4) northern subtropical (Sajama) Andes and the site of Cruzeiro do Sul sounding data (white square) shown. Illimani is shown with the white circle.
Figure 2.4. 2-D histograms (light solid lines) of TES $\delta D_{\text{vapor}}$ and $q$ in the tropical and northern subtropical Andean glacier region in (A) DJF and (B) JJA with QIC flask measurements from 2011 (white squares). The contours indicate the frequency of TES measurements with a particular $\delta D$ and $q$, and the contour interval for the TES data is number of measurements = 50. Filled rectangles indicate the mean seasonal values for $10^\circ \times 10^\circ$ domains centered on the (1) northern tropical, (2) central tropical, (3) southern tropical, and (4) northern subtropical Andes. The heavy lines are the calculated Rayleigh (solid line) and mixing (dashed line) curves. The Rayleigh curve was calculated with $\delta D_{\text{initial}} = -90\%$ and $q_{\text{initial}} = 26479$ ppmv. The mixing curve was calculated using a wet end member with $\delta D = -86\%$ and $q = 19162$ ppmv and a dry end member with $\delta D = -496\%$ and $q = 574$ ppmv.

In the tropical Andes, 67% to 73% of the DJF TES measurements fall below the Rayleigh curve (i.e. $\Delta \delta D < 0\%$) with the highest proportion of measurements below the Rayleigh curve in the central tropical Andes. In the northern subtropical Andes, 52% of the DJF TES measurements fall below the Rayleigh curve. Average $\Delta \delta D_{\text{vapor}}$ in DJF is $-18\%$ to $-28\%$ in the northern and southern tropical Andes and $-36\%$ in the central tropical Andes. In contrast, in the northern subtropical Andes, average $\Delta \delta D$ is $+12\%$. 
Figure 2.5. Histograms showing the variability of ΔδD (ΔδD = δD_{TES} – δD_{Rayleigh}) in the (A) northern tropical, (B) central tropical, (C) southern tropical, and (D) northern subtropical Andes in DJF (solid lines) and JJA (dashed lines). Shaded region indicates that ΔδD is negative.
Figure 2.6. $\Delta \delta D$ ($\Delta \delta D = \delta D_{\text{Rayleigh}} - \delta D_{\text{TES}}$) for (A) DJF and (B) JJA. Measurements that fall below the Rayleigh curve (i.e. $\Delta \delta D < 0\‰$) are designated by solid lines while measurements that lie above the Rayleigh curve are designated by dashed lines. The $0\‰$ contour is drawn with a heavy solid line. In DJF, measurements with $\Delta \delta D < 0\‰$ are centered over the tropical Andes and upper Amazon Basin. In JJA, measurements with $\Delta \delta D < 0\‰$ are located north of the tropical Andes. Filled rectangles indicate the locations of glaciers included in the study as in Figure 2.1 and Figure 2.3. The contour interval is $\Delta \delta D = 20\‰$.

While DJF $\Delta \delta D$ is negative in the tropical Andes, JJA $\delta D_{\text{vapor}}$ is higher than predicted by the Rayleigh model (i.e. $\Delta \delta D > 0\‰$). JJA $\Delta \delta D$ ranges from $+142\‰$ in the northern subtropical Andes to $+6\‰$ in the northern tropical Andes (Figure 2.6B). This is consistent with water vapor sampled at the summit of Quelccaya Ice Cap in July 2011, which has an average $\Delta \delta D_{\text{vapor}}$ of $+148\‰$ (Table 2.1). Whereas DJF $\Delta \delta D$ is highest in the central tropical Andes, there is a linear relationship ($r = -0.99$, $p = 0.006$) between latitude and mean $\Delta \delta D$ along the spine of the Andes in JJA, and the region where $\Delta \delta D \leq 0\‰$ shifts north of the equator (Figure 2.6B). This spatial difference in $\Delta \delta D$ suggests that the dominant processes controlling the isotopic composition of water vapor over the tropical Andean glaciers differ seasonally.
Table 2.1. δD_{vapor}, \( q \), and local conditions for Quelccaya Ice Cap flask samples

<table>
<thead>
<tr>
<th>Date</th>
<th>Time 1</th>
<th>( T ), °C</th>
<th>( T_d ), °C</th>
<th>q, ppmv</th>
<th>δD_{vapor}, ‰</th>
<th>ΔδD, ‰</th>
</tr>
</thead>
<tbody>
<tr>
<td>7/7/11</td>
<td>1300</td>
<td>-6.5</td>
<td>-16.1</td>
<td>2940</td>
<td>-134</td>
<td>+183</td>
</tr>
<tr>
<td>7/7/11</td>
<td>1852</td>
<td>-9.5</td>
<td>-18.0</td>
<td>2460</td>
<td>-153</td>
<td>+185</td>
</tr>
<tr>
<td>7/8/11</td>
<td>0700</td>
<td>-9.5</td>
<td>-16.5</td>
<td>2830</td>
<td>-164</td>
<td>+158</td>
</tr>
<tr>
<td>7/8/11</td>
<td>1300</td>
<td>-7.1</td>
<td>-12.0</td>
<td>4280</td>
<td>-162</td>
<td>+111</td>
</tr>
<tr>
<td>7/8/11</td>
<td>1600</td>
<td>-7.0</td>
<td>-12.9</td>
<td>3940</td>
<td>-155</td>
<td>+129</td>
</tr>
<tr>
<td>7/8/11</td>
<td>1900</td>
<td>-9.5</td>
<td>-14.4</td>
<td>3440</td>
<td>-148</td>
<td>+151</td>
</tr>
<tr>
<td>7/9/11</td>
<td>0100</td>
<td>-10.0</td>
<td>-16.8</td>
<td>2750</td>
<td>-161</td>
<td>+164</td>
</tr>
<tr>
<td>7/9/11</td>
<td>0100²</td>
<td>-10.0</td>
<td>-16.8</td>
<td>2750</td>
<td>-161</td>
<td>+164</td>
</tr>
<tr>
<td>7/9/11</td>
<td>0540</td>
<td>-10.5</td>
<td>-13.1</td>
<td>3870</td>
<td>-168</td>
<td>+118</td>
</tr>
<tr>
<td>7/9/11</td>
<td>0700</td>
<td>-10.6</td>
<td>-10.7</td>
<td>4810</td>
<td>-168</td>
<td>+91</td>
</tr>
<tr>
<td>7/9/11</td>
<td>1300</td>
<td>-4.3</td>
<td>-16.4</td>
<td>2860</td>
<td>-166</td>
<td>+155</td>
</tr>
</tbody>
</table>

1Local time (UTC/GMT – 5 hours), ²Duplicate sample, \( T \) = temperature, \( T_d \) = Dewpoint, \( q \) = water vapor concentration

2.3.2 Upwind convective intensity

More than half (64%) of the DJF and 40% of the JJA δD_{vapor} measurements in the tropical and northern subtropical Andes have \( \Delta \delta D < 0 \%, \) consistent with an interpretation that the air parcels have undergone intense convection \cite{Worden et al., 2007; Noone, 2012}. The goal of this section is to explicitly evaluate the link between TES measurements with \( \Delta \delta D < 0 \% \) and OLR, a proxy of upwind convective intensity.

5-day back trajectories indicate that air parcels with \( \Delta \delta D < 0 \% \) travel through regions with mean minimum OLR < 240 W m\(^{-2}\) (Figure 2.7). Air parcels with \( \Delta \delta D \geq 0 \% \) encounter higher average minimum OLR prior to arriving in the tropical Andes.
Histograms of minimum OLR along trajectories show that in DJF (Figure 2.7A) mean minimum OLR along all trajectories is 224 W m$^{-2}$. This is consistent with intense convection throughout the region during the monsoon season. DJF measurements with ΔδD < 0‰ encounter lower average minimum OLR along trajectories (204 W m$^{-2}$) than DJF measurements with ΔδD ≥ 0‰ (237 W m$^{-2}$) (Figure 2.7A). In JJA (Figure 2.7B), average minimum OLR along all trajectories is 228 W m$^{-2}$. JJA measurements with ΔδD < 0‰ also encounter lower average minimum OLR (209 W m$^{-2}$) than other JJA measurements (243 W m$^{-2}$; Figure 2.7B).

![Histograms of minimum OLR encountered en route to the tropical Andes](image)

**Figure 2.7.** Histograms of minimum OLR encountered en route to the tropical Andes show that minimum OLR along trajectories is lower for measurements with ΔδD < 0‰ (solid lines) than for measurements with ΔδD ≥ 0‰ (dashed lines) in both (A) DJF and (B) JJA. OLR ≤ 240 W m$^{-2}$ (gray field) is diagnostic of periods of intense convection in tropical South America.

Contour maps of minimum OLR encountered along air parcel trajectories show that, in DJF, air encounters the lowest OLR en route to the central tropical Andes and to the east of the central tropical Andes (Figure 2.8A). Spatially, this relationship forms a bull’s eye with a minimum OLR ≤ 200 W m$^{-2}$ that extends from around 50°W to 80°W
and 20°S to 5°N (Figure 2.6A). In JJA, air passes through regions with OLR ≤ 200 W m⁻² en route to the area between the equator and the northern tropical Andes (Figure 2.8B). In contrast, the central and southern tropical and northern subtropical Andes are influenced by upwind OLR > 240 W m⁻² in JJA (Figure 2.8B). Maps that show the probability density function of the location where minimum OLR was encountered en route to the 10°×10° domains around each glacier show that minimum OLR in DJF (Figure 2.9A) was encountered slightly further south and west of where it was encountered in JJA (Figure 2.9B).

Figure 2.8. Contour maps of minimum OLR encountered along back trajectories upwind of each TES δD measurement in (A) DJF and (B) JJA. Trajectories launched from measurements with the highest ΔδD (see Figure 2.6) encountered OLR ≤ 200 W m⁻² in DJF and JJA. Filled rectangles indicate the locations of glaciers included in the study as in Figure 2.1 and Figure 2.3. The contour interval is 20 W m⁻².
Figure 2.9. 2-D histograms showing the locations where minimum OLR was encountered along trajectories in (A) DJF and (B) JJA. The gray scale indicates the number of trajectories that encountered minimum OLR at each location. Filled rectangles indicate the locations of glaciers included in the study as in Figure 2.1 and Figure 2.3.

Local convection appears to exert only a minor influence over $\delta D_{\text{vapor}}$ measured in the tropical Andes (Figure 2.10). Regardless of season, less than 1% of the back trajectories launched from each TES measurement encountered minimum OLR the day the trajectory was launched (Figure 2.10A and Figure 2.10B). In DJF, the average distance between the measurement location and the location where minimum OLR was encountered ranged from 793 km in the southern tropical Andes to 1208 km in the northern tropical Andes (Figure 2.10C). In JJA, there were more than 1500 km between the measurement location and the location where minimum OLR was encountered in the tropical Andes and more than 2000 km in the northern subtropical Andes (Figure 2.10D). Average regional OLR at the time of trajectory initiation was 261 W m$^{-2}$ and 265 W m$^{-2}$ in DJF and JJA respectively. These results suggest that local convection does not exert a primary control over $\delta D_{\text{vapor}}$ or $\Delta \delta D$ in either austral summer or austral winter.
2.4. Discussion

There is a significant correlation ($r = 0.41$, $p < 0.0001$) between $\Delta \delta D$ and minimum OLR along back trajectories, suggesting that $\delta D_{\text{vapor}}$ that falls below the Rayleigh curve is associated with intense upwind convection during DJF. Negative $\Delta \delta D$ values are generally associated with mesoscale, organized convective systems upwind of the measuring site rather than local storms [e.g. Lawrence et al., 2004]. There are two main mechanisms proposed for decreasing the $\delta D_{\text{vapor}}$ in convective storms: low saturation temperatures in high cumulonimbus clouds [e.g. Lawrence, 2003; Thompson et
or increased entrainment of low δD water vapor from the unsaturated downdraft into the subcloud layer that feeds the convective system along with diffusive exchanges [e.g. Risi et al., 2008].

It is difficult to directly evaluate the influence of temperature at last saturation on the isotopic composition of water vapor measured over the tropical Andes. Cloud-top temperature data are available, but previous studies have shown that water vapor typically condenses at lower altitudes and higher temperatures than the top of the cloud during convective storms [e.g. Smith, 1992]. It is, therefore, impossible to directly evaluate saturation temperatures without echo-top data [e.g. Scholl et al., 2009], which can be obscured by high clouds in the tropics [Riley and Mapes, 2009]. Models indicate that condensation altitude and temperature variations play no role in the decreased δD_vapor associated with the amount effect [Risi et al., 2008]. More significant factors include the decreased isotopic composition of subcloud layer vapor with increased entrainment of low δD water vapor from the unsaturated downdraft [e.g. Risi et al., 2008] and converged water vapor [e.g. Moore et al., 2014] along with diffusive exchanges, which become more efficient at high relative humidity [e.g. Dansgaard, 1964; Risi et al., 2008]. Therefore, relatively low DJF δD_vapor likely records upwind convective intensity, most likely associated with the South American Summer Monsoon, rather than atmospheric temperature. This is consistent with the Andean Isotope Index [Hoffmann, 2003], precipitation studies from the northern and southern tropical Andes [Vimeux et al., 2005; Villacís et al., 2008], and models [Vuille et al., 2003a; Vimeux et al., 2009].

The majority of JJA TES measurements have positive ΔδD values. Processes that produce this relationship between q and δD_vapor include large-scale advective mixing
[Dessler and Sherwood, 2003; Noone, 2012] and ice lofting with subsequent sublimation in convective clouds [e.g. Smith, 1992]. JJA δDvapor generally falls on a mixing curve. Although mixing can occur between any number of air parcels last saturated in different regions [Galewsky and Hurley, 2010], we can simplify the process into a simple 2-component mixing model. The curve that best describes the data has a moist end member with $q = 19162$ ppmv and δDvapor = -86‰ and a dry end member with $q = 574$ ppmv and δDvapor = -496‰ (Figure 2.2B). The moist end member may itself be the product of mixing between marine boundary layer air and recycled moisture from the Amazon Basin. The dry end member has an isotopic composition consistent with water vapor in the upper tropical troposphere [e.g. Bony et al., 2008; Blossey et al., 2010] and may represent subsidence of air dehydrated via convection [e.g. Galewsky et al., 2011] in the ITCZ, which lies to the north of the equator in JJA.

2.5. Conclusions

Our goal was to investigate the relationship between water-vapor isotopic ratios and upwind convection in the tropical and northern subtropical Andes in order to improve our understanding of large-scale water vapor dynamics that, ultimately, deliver moisture to tropical glaciers. Specifically, this study shows that:

1. average δDvapor in the tropical Andes is 13‰ to 43‰ lower in austral summer than austral winter despite relatively uniform annual air temperatures;

2. δDvapor is, on average, 18‰ to 36‰ lower than predicted by the Rayleigh model in the tropical Andes in austral summer and 6‰ to 142‰ above the Rayleigh curve in austral winter;
(3) $\delta D$ is lower than predicted by Rayleigh fractionation (i.e. $\Delta \delta D < 0$‰) for more than half of the DJF TES $\delta D_{\text{vapor}}$ measurements but for only ~40% of the JJA TES measurements;

(4) more than 90% of negative $\Delta \delta D$ measurements in DJF have minimum upwind $\text{OLR} \leq 240 \text{ W m}^{-2}$ (high convective intensity), and all of the measurements with negative $\Delta \delta D$ encountered lower minimum upwind $\text{OLR}$ than measurements with positive $\Delta \delta D$ regardless of season.

Previous studies have linked upwind convection to lower $\delta D_{\text{vapor}}$ than predicted by the Rayleigh model at the given $q$ [e.g. Noone, 2012] and to $\delta ^{18} \text{O}_{\text{snow}}$ in the tropical Andes [e.g. Vimeux et al., 2005; Villacís et al., 2008]. The regional coverage of the satellite data allows us to explore this link between low isotopic ratios and upwind convection and to examine the spatial extent of the region where convection controls isotopic ratios of water vapor. TES measurements with negative $\Delta \delta D$ in DJF are centered in the central tropical Andes and to the east of the central tropical Andes in the area affected by the South American Summer Monsoon. The JJA measurements with $\Delta \delta D < 0$‰ are north of the tropical Andes and north of the equator. This result suggests that deep convection associated with the South American Summer Monsoon controls $\delta D_{\text{vapor}}$ in DJF while convection in the ITCZ controls the small proportion of relatively low $\delta D_{\text{vapor}}$ in austral winter.

Pacific SST and SST anomalies associated with the El Niño-Southern Oscillation strongly influence convective intensity upwind of the glaciers by controlling the position of the ITCZ, strength of the Hadley Circulation, Atlantic SST variations [Wang, 2004], South American precipitation [Lenters and Cook, 1999], and Altiplano climate [Vuille et
Modeling studies and studies based on reconstructed SST have linked isotopic profiles through tropical Andean ice cores to both Pacific SST and SST anomalies [Henderson et al., 1999; Vuille et al., 2003a; Thompson et al., 2013]. Overall, our results, based on satellite observations, are consistent with modeling studies [Vuille et al., 2003b] and with studies based on individual glaciers [Hardy, 2003; Vimeux et al., 2005; Villacís et al., 2008] and suggest that tropical convection, rather than temperature, exerts a primary control over $\delta^{18}$O$_{\text{snow}}$ in the tropical Andes.

2.6. References for Chapter 2


Singh, C. V. (2005), Principal component analysis of satellite-observed outgoing longwave radiation during the monsoon period (June–September) over India, Theor Appl Climatol, 84(4), 207–211, doi:10.1007/s00704-005-0170-z.


Villacís, M., F. Vimeux, and J. D. Taupin (2008), Analysis of the climate controls on the isotopic composition of precipitation (δ18O) at Nuevo Rocafuerte, 74.5°W, 0.9°S, 250 m, Ecuador, *Comptes Rendus Geoscience*, 340(1), 1–9, doi:10.1016/j.crte.2007.11.003.


3. SEASONAL VARIATIONS IN THE VERTICAL INFLUENCE OF THE ISOTOPE AMOUNT EFFECT OVER SOUTH AMERICA

3.1. Introduction

Processes that control tropical and subtropical humidity are a significant source of uncertainty in future climate change predictions [e.g. Wright et al., 2009; Risi et al., 2012] because water vapor exerts a strong positive feedback in the climate system [e.g. Held and Soden, 2000; Zhang et al., 2006]. Understanding the vertical and lateral extent of the region influenced by the isotope amount effect may provide an additional constraint on the influence of convection on moisture transport and humidity in the tropics and subtropics. Tropical convection can exert a particularly strong influence on the global water-vapor distribution as a source of stratospheric water vapor [e.g. Gettelman et al., 2002] and as a potential player in moistening the subtropics [e.g. Wright et al., 2009].

As discussed in chapter 2, variations in isotopic ratios in atmospheric water vapor can help distinguish between moisture-transport processes [e.g. Lawrence et al., 2004; Worden et al., 2007; Noone, 2012, Risi et al., 2012; Risi et al., 2013]. Theoretical studies show that deep convection in mesoscale storm systems injects relatively low δD water vapor from the unsaturated downdraft into the subcloud layer where it gets reincorporated into the cloud and progressively decreases isotopic ratios in water vapor [e.g. Risi et al., 2008; Moore et al., 2014]. This decrease leads to the observed isotope “amount effect” [e.g. Dansgaard, 1964] in which δ values are lower than predicted by Rayleigh distillation at a given water vapor concentration (q).
The distinct seasonality of the spatial distribution of convection in South America (Figure 3.1) allows us to evaluate the relationship between the amount effect and convection (chapter 2). In tropical South America, the influence of convection in the austral summer (DJF) has been recognized in the isotopic ratios of glacial ice in the tropical Andes [e.g. Hoffmann et al., 2003; Vuille et al., 2003a; Vuille et al., 2003b; Vimeux et al., 2005; Vuille and Werner, 2005; Sturm et al., 2007; Villacís et al., 2008; Vimeux et al., 2011], speleothems [Kanner et al., 2013], modern precipitation [e.g. Lawrence et al., 2004; Vimeux et al., 2009], and modern atmospheric water vapor [e.g. Worden et al., 2007; Samuels-Crow et al., 2014].

![Figure 3.1. TRMM convective precipitation in A) DJF and B) JJA. Rectangles indicate locations of domains discussed in this study: 1) tropical Pacific, 2) SASM, 3) subtropics. The white squares indicate locations of sounding data used in section 3.2.4. Black dots indicate location of transects in Figure 3.12.](image)

Water isotopologues (e.g. HDO, H$_2^{16}$O, and H$_2^{18}$O) serve as natural tracers of moisture transport processes because they fractionate during condensation and evaporation, concentrating the heavier isotopologues in the liquid [e.g. Craig, 1961;
Craig and Gordon, 1965; Dessler and Sherwood, 2003; Worden et al., 2006; Risi et al., 2008; Galewsky and Hurley, 2010; Noone, 2012]. Isotopic composition is reported as the permil (‰) difference (δ) in the measured isotopic ratios (e.g. \( R_{\text{sample}} = (\text{HDO}/\text{H}_2^{16}\text{O})_{\text{sample}} \)) relative to the isotopic ratios in Vienna Standard Mean Ocean Water, VSMOW, (e.g. \( R_{\text{standard}} = (\text{HDO}/\text{H}_2^{16}\text{O})_{\text{VSMOW}} \)):

\[
\delta D_{\text{vapor}} = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000 \quad (3.1)
\]

The Rayleigh distillation model describes open-system isotope fractionation in saturated air parcels (i.e. relative humidity = 100%). This model provides a first-order tool for diagnosing processes that control the joint distribution of isotopic ratios and water vapor mixing ratios \( q \):

\[
d \ln R = (\alpha - 1) d \ln q \quad (3.2)
\]

where \( R \) is the HDO/\( \text{H}_2^{16}\text{O} \) ratio, \( \alpha \) is the temperature-dependent fractionation factor, and \( q \) is the saturation water-vapor mixing ratio [e.g. Dessler and Sherwood, 2003].

The Rayleigh model assumes that condensate is immediately removed from saturated air parcels, decreasing \( \delta D_{\text{vapor}} \) and \( \delta ^{18}\text{O}_{\text{vapor}} \) as temperature and \( q \) decrease and elevation and distance from the source area increase [e.g. Dansgaard, 1964; Gat, 1996]. Deviations from this idealized case provide insights into moisture-transport processes [e.g. Worden et al., 2007; Brown et al., 2008; Hurley and Galewsky, 2010; Galewsky et al., 2011; Noone, 2012; Samuels-Crow et al., 2014]. Convective recycling typically leads to \( \delta D_{\text{vapor}} \) that is lower than predicted by Rayleigh distillation at a given \( q \) [e.g. Risi et al., 2008]. In contrast, advective mixing between moist and dry air typically leads to \( \delta D_{\text{vapor}} \) that is higher than predicted by the Rayleigh model because the moist air parcel contributes more water vapor with relatively high \( \delta D \) to the mixture, thereby exerting
greater influence over $\delta D_{\text{vapor}}$ [e.g. Galewsky and Hurley, 2010]. We use $\Delta \delta D = \delta D_{\text{measured}} - \delta D_{\text{Rayleigh}}$ to distinguish between these scenarios. When $\Delta \delta D$ is positive, $\delta D_{\text{measured}}$ is higher than $\delta D_{\text{Rayleigh}}$ and mixing plays a more important role than moist convection in setting the measured isotope ratios and humidity. In contrast, negative $\Delta \delta D$ indicates that $\delta D_{\text{measured}}$ is lower than predicted by the Rayleigh model and that the isotope amount effect plays a major role in controlling the isotopic ratios and humidity as shown in chapter 2.

The goal of this chapter is to examine the vertical structure of the isotope amount effect (i.e. $\Delta \delta D < 0$‰) and how the vertical structure is related to 1) convective intensity and 2) the vertical extent of clouds in the tropics and subtropics. We focus on the South American Summer Monsoon (SASM) domain ($16^\circ$-$2^\circ$S, $70^\circ$-$40^\circ$W; Hurley and Boos, 2013), the tropical Pacific domain ($5^\circ$S to $10^\circ$N, $100^\circ$-$70^\circ$W), and the subtropics ($20^\circ$-$35^\circ$S, $50^\circ$-$75^\circ$W) (Figure 3.1). We use satellite data from NASA’s Tropospheric Emission Spectrometer (TES) to map vertical variations in $\Delta \delta D$.

3.2. Methods

3.2.1 Satellite measurements

NASA’s TES instrument, a Fourier Transform Spectrometer aboard the Aura satellite, makes near-global measurements of infrared radiation from $650 \text{ cm}^{-1}$ to $3050 \text{ cm}^{-1}$ emitted by tropospheric gases [Worden et al., 2006]. We use Level 2 nadir measurements of $H_2O$ and HDO mixing ratios from the TES Lite v08 dataset to evaluate the deviation of measured $\delta D$ ($\delta D_{\text{TES}}$) from $\delta D_{\text{Rayleigh}}$. Recent aircraft validation studies have improved processing algorithms and decreased the error in TES HDO/$H_2O$ estimates at different pressure levels [Herman et al., 2014]. To ensure high data quality,
we use TES measurements from 2004 to 2013 with degrees of freedom for signal (DOFS) ≥ 0.7 and a retrieval quality flag of 1. In South America, 29585 and 32625 vertical profiles met these quality-control criteria in DJF and JJA respectively. Each profile includes measurements from 1000 hPa to 0.1 hPa, but we restrict our analysis to the 14 pressure levels measured from 1000 to 100 hPa. ΔδD is below 0% on at least 1 pressure level in 98% of the profiles from both DJF and JJA.

3.2.2. ΔδD calculation

We calculated an idealized Rayleigh curve as a function of the temperature-dependent fractionation factor and q (equation 3.2) at 100% relative humidity (Figure 1.1). We calculated saturated q based on average TES temperature and pressure profiles over South America. We then used an initial δDvapor of -90‰ and q of 26479 ppmv, which is consistent with δDvapor over the tropical Atlantic [Craig and Gordon, 1965] and an initial q of 26479 ppmv as a starting point for calculating idealized δDRayleigh. We used fractionation factors of Majoube [1971] for isotopic fractionation above 0°C and Merlivat and Nief [1967] for fractionation below 0°C, following methods of Gedzelman [1988].

In order to evaluate processes that control vertical variations in δDvapor over South America, we need to compare δDRayleigh with the true isotopic variation at each pressure level (δDtrue). However, each TES retrieval (\(\hat{x} = ln(HDO/H_2O)_{TES}\)) is a function of the true isotopic profile (\(x_{true} = ln(HDO/H_2O)_{true}\)), the difference between TES averaging kernel and the averaging kernel cross term (\(A = A_{HDO} - A_{cross}\)), and the a priori constraint vector (\(x_a = ln(HDO/H_2O)_{a priori}\); equation 3.3) [Worden et al., 2006]:

\[
\hat{x}_{TES} = x_a + A(x_{true} - x_a) \quad (3.3)
\]
The averaging kernel is a matrix that accounts for the sensitivity of the retrieval to the true HDO mixing ratio. The averaging kernel cross-term accounts for the sensitivity of the retrieval to other jointly estimated quantities (e.g. H$_2$O mixing ratio). The \textit{a priori} constraint vector is an idealized estimate of isotopic ratios. For an ideal measurement with no instrumental errors, the averaging kernel approaches the identity matrix and $\mathbf{x}_a$ approaches $\mathbf{x}_{true}$ [Worden et al., 2006]. As discussed in chapter 2, peak sensitivity for the TES instrument occurs at 500 hPa where the averaging kernel is closest to the identity matrix so no adjustment is needed to compare measurements from this level to the Rayleigh model. Retrieval uncertainties increase at pressures higher than 500 hPa and sensitivity decreases at pressures below 300 hPa, leading to larger deviations between $\mathbf{x}_a$ and $\mathbf{x}_{true}$ with vertical distance from 500 hPa [Worden et al., 2012].

Ideally, when comparing $\delta D_{Rayleigh}$ to $\delta D_{TES}$, we would find the deviations of the true state from the model (i.e. $\Delta \delta D = \delta D_{true} - \delta D_{Rayleigh}$). However, the true isotopic ratio is unknown. In order to account for the differences between the TES retrieval and the true isotopic variability at pressure levels other than 500 hPa and compare the idealized Rayleigh model with the true profile, we must first calculate an idealized $(\text{HDO/H}_2\text{O})_{Rayleigh}$ and then adjust the calculated Rayleigh curve based on the averaging kernel and constraint vector for each TES profile:

$$\hat{\mathbf{x}}_{Rayleigh} = \mathbf{x}_a + A(\mathbf{x}_{Rayleigh} - \mathbf{x}_a) \quad (3.4)$$

where $\hat{\mathbf{x}}_{Rayleigh}$ is the adjusted $\ln(\text{HDO/H}_2\text{O})_{Rayleigh}$, and $\mathbf{x}_{Rayleigh}$ is the unadjusted $\ln(\text{HDO/H}_2\text{O})_{Rayleigh}$. Once this adjustment is made, we can compare the Rayleigh model at $q_{Rayleigh} = q_{TES} \pm 100$ ppmv to the TES retrieval directly:

$$\hat{\mathbf{x}}_{TES} - \hat{\mathbf{x}}_{Rayleigh} = \mathbf{x}_a + A(\mathbf{x}_{true} - \mathbf{x}_a) - [\mathbf{x}_a + A(\mathbf{x}_{Rayleigh} - \mathbf{x}_a)] \quad (3.5)$$
To calculate $\Delta \delta D$, we first calculate $\dot{x}_{\text{Rayleigh}}$, convert this ratio to a $\delta$-value, and then subtract it from the measured $\delta D_{\text{TES}}$, which has already been adjusted for measurement uncertainty.

3.2.3. Characterizing regional convective intensity

Previous work shows a connection between the isotope amount effect and convection [e.g. Worden et al., 2007; Risi et al., 2008; Samuels-Crow et al., 2014]. We extend this work here by examining the relationship between convective intensity and the vertical extent of water vapor with negative $\Delta \delta D$. A number of indices and diagnostic parameters have been developed to characterize convective intensity [e.g. Peppier et al., 1988; Doswell and Schultz, 2006; and references therein]. Measurements of convective precipitation and OLR indicate areas where convection is occurring at the time of measurement. We used $0.5^\circ \times 0.5^\circ$ daily level 3 convective precipitation rate data from TRMM and $1^\circ \times 1^\circ$ daily level 3 OLR data from the Atmospheric Infrared Sounder (AIRS) version 6 [Tian et al., 2013] as first-order approximations of convective intensity in each domain. In tropical South America, $\text{OLR} \leq 240 \text{ W m}^{-2}$ is diagnostic of deep convection associated with the summer monsoon [e.g. Kousky, 1988; Kousky and Kayano, 1994; Moron, 1995; Singh, 2005; Vuille and Werner, 2005; Susskind et al., 2012].

Calculated indices can provide thresholds for the probability of convection, although no single convective index serves as a “magic bullet” that completely constrains the probability that intense convection will occur [e.g. Doswell and Schultz, 2006]. We focus here on equivalent potential temperature ($\theta_E$) in the boundary layer ($\theta_{EB}$) as an indicator of convective intensity. $\theta_E$ is a thermodynamic quantity that indicates the
temperature a moist air parcel would attain if it rose adiabatically until all of its moisture condensed and then returned to a reference pressure (typically 1000 hPa) through adiabatic processes. Vertical variations in $\theta_E$ provide insights into conditional stability in the atmosphere [e.g. Rossby, 1932; Folkins et al., 2002]. In absolutely stable air, $\theta_E$ increases as air parcels rise and cool adiabatically. When $\theta_E$ decreases during air parcel ascent, the air is conditionally unstable, and convection will occur if moisture content is high [e.g. Rossby, 1932].

High $\theta_{EB}$ coincides with upper-tropospheric temperature maxima in monsoon regions, coupling this boundary layer thermodynamic quantity with deep convection [e.g. Nie et al., 2010; Hurley and Boos, 2013]. Previous studies show that $\theta_{EB} > 340K$ occurs poleward of convective precipitation maxima in monsoon regions and is a simple, but reliable, indicator of convective intensity [Hurley and Boos, 2013].

We used 2.5°×2.5° NCAR-NCEP daily average reanalysis data [Kalnay et al., 1996] from 2m above the surface to calculate saturated $\theta_{EB}$ based on equation 3.6:

$$\theta_E = T \left( \frac{P_0}{P} \right)^{\frac{g^e}{R}} \exp \left( \frac{Lq^*}{c_p T} \right) \quad (3.6)$$

where $T$ is the temperature, $P_0$ is the reference pressure (1000 hPa), $P$ is the pressure 2 m above the surface in the area of interest, $R$ is the gas constant for dry air, $c_p$ is the heat capacity at constant pressure, $L$ is latent heat of evaporation, and $q^*$ is the saturation mixing ratio, calculated from temperatures and pressures from the Reanalysis data set.

3.2.4. Characterizing the vertical extent of clouds

In this chapter, we examine the vertical structure of the amount effect over South America in DJF and JJA and how it relates to the vertical extent of clouds in convective
regions. We use the Lifted Condensation Level (LCL) from 4-times daily atmospheric soundings at Corozal Panama (MPCZ, 8.98°N, 79.58°W), Alta Floresta Brazil (SBAT, 9.86°S, 56.10°W), Puerto Velho Brazil (SBPV, 8.76°S, 63.91°W), and Cordoba Argentina (SACO, 34.81°S, 58.53°W) as a proxy for cloud base. Sounding data are relatively sparse in South America, and each of the above stations is representative of a different domain. MPCZ is located on the eastern side of the tropical Pacific domain. SBAT and SBPV provide information about the central and western edge of the SASM domain respectively. SACO is located in the center of the subtropical domain. We obtained 6-hourly sounding data from 2004 to 2013 from the Department of Atmospheric Sciences at the University of Wyoming (http://weather.uwyo.edu/upperair/sounding.html).

We used 1°×1° daily level 3 cloudtop pressure data from AIRS to estimate cloud heights over the study region in each season. This method provides an average view of the vertical extent of clouds on a daily basis [Kahn et al., 2008], but it does not capture sub-degree variability on shorter timescales.

3.3. Results

3.3.1. ΔδD over South America in DJF and JJA

The vertical and lateral distribution of ΔδD varies seasonally. In DJF, ΔδD is negative over the SASM domain at pressures below 825 hPa and falls below -50‰ from 681 hPa to ~237 hPa. More than 40% of each vertical profile has ΔδD < 0‰ in this region (Figure 3.2A), and the ΔδD < 0‰ zone is more than 6 km thick in the center (Figure 3.3A). The lowest ΔδD values, which are less than -150‰, are concentrated along the western edge of the SASM domain from pressures of 422 hPa to 287 hPa.
(Figure 3.4D-E). At lower pressures, $\Delta\delta D$ increases. In contrast to the SASM domain, $\Delta\delta D$ values in the subtropical and tropical Pacific domains are generally positive at pressures below 511 hPa in DJF.

In JJA, $\Delta\delta D$ is negative north of 10°S and falls below -50‰ from 619 hPa to 287 hPa (Figure 3.5). As in DJF, minimum $\Delta\delta D$ values are below -150‰, but they are
centered over the equator at pressures below 500 hPa (Figure 3.5D-F). More than 40% of each vertical profile in the tropical Pacific region has \( \Delta\delta D \) values below 0‰ (Figure 3.2B), and the negative \( \Delta\delta D \) zone over the tropical Pacific in JJA can be more than 6 km thick (Figure 3.3B). In the SASM and subtropical domains, \( \Delta\delta D \) is generally positive in JJA (Figure 3.5). In these domains, only 20% to 30% of each profile has \( \Delta\delta D < 0‰ \) (Figure 3.2B).

In both DJF and JJA, \( \Delta\delta D \) is also negative poleward of 25°S to 30°S. Minimum \( \Delta\delta D \) values in this area are typically between 0‰ and -50‰ (Figure 3.4 and Figure 3.5). In DJF, negative \( \Delta\delta D \) extends from the surface to 350 hPa (Figure 3.4) and 40% of each vertical profile has \( \Delta\delta D < 0‰ \) (Figure 3.3). In JJA, negative \( \Delta\delta D \) water vapor at higher latitudes is discontinuous from the surface to 422 hPa (Figure 3.5).
Figure 3.4. $\Delta \delta D_{\text{vapor}}$ in DJF at A) 1000 hPa, B) 681 hPa, C) 511 hPa, D) 422 hPa, E) 350 hPa, F) 287 hPa. Rectangles indicate locations of domains discussed in this study (see Figure 3.1)
Figure 3.5. As in Figure 3.4 for JJA.
3.3.2. Seasonal variations in convective precipitation, OLR, and $\theta_{EB}$ over South America

Convective intensity also varies spatially and temporally over South America. In DJF, convective precipitation is highest in the SASM domain and along the spine of the Andes with low daily convective precipitation rates in the subtropics and tropical Pacific domain (Figure 3.1A). In JJA, convective precipitation generally occurs north of 5°S with maximum convective precipitation rates centered north of the equator over the Amazon Basin and in the tropical Pacific (Figure 3.1B). The distribution of convective precipitation is similar to the spatial distribution of OLR, which is 240 W m$^{-2}$ or below in the SASM domain in DJF and in the tropical Pacific in JJA (Figure 3.6).

![Figure 3.6. OLR in A) DJF and B) JJA. Rectangles indicate locations of domains discussed in this study (see Figure 3.1).](image)

$\theta_{EB}$ provides an indicator of atmospheric stability even when there is no precipitation. In DJF, high $\theta_{EB}$ (≥ 340 K) occurs north of 25°S over the South American continent with maximum values in a NNW trend across the SASM domain. In JJA, the
region where $\theta_{EB}$ is 340 K or higher lies north of 5°S over land and is slightly poleward of the zone of maximum convective precipitation (Figure 3.7).

![Figure 3.7. $\theta_{EB}$ calculated from NCEP-NCAR Reanalysis data in A) DJF and B) JJA. Rectangles indicate locations of domains discussed in this study (see Figure 3.1).](image)

3.3.3 $\Delta \delta D$ and convective parameters

We now examine the relationships between the magnitude of negative $\Delta \delta D$, an indicator of the isotope amount effect, the vertical extent of the negative $\Delta \delta D$ zone, and indicators of deep convection. Convective precipitation rates are highest in the center of the SASM domain in DJF and north of the equator in JJA (Figure 3.1). In DJF, higher maximum daily precipitation rates are typically associated with lower maximum $\Delta \delta D$ in the SASM domain while lower maximum precipitation rates in the subtropical and tropical Pacific domains are associated with relatively high maximum $\Delta \delta D$ (Figure 3.8A, C, E). In JJA, however, high daily maximum precipitation rates in the tropical Pacific domain are associated with relatively low maximum $\Delta \delta D$ values (Figure 3.8F) while lower maximum daily precipitation rates are associated with higher maximum $\Delta \delta D$ in the
SASM domain (Figure 3.8B). The subtropical domain receives very little rainfall during JJA, but maximum $\Delta \delta D$ in this domain is generally higher than $+100\%$ (Figure 3.8D).

Figure 3.8. 2D histograms showing the joint distribution of $\Delta \delta D_{\text{vap}}$ and daily precipitation rates in each domain for DJF (A, C, E) and JJA (B, D, F). Contour interval = 50 measurements.
In the previous section, we saw that the highest precipitation rates were associated with the lowest maximum \( \Delta \delta D \) values. We now focus on the relationship between \( \theta_{EB} \) and maximum \( \Delta \delta D \). \( \theta_{EB} \) is useful for understanding conditional stability throughout the region, not just in areas with measurable precipitation. \( \theta_{EB} \) of 340 K or higher can signify deep monsoon convection [e.g. Hurley and Boos, 2013]. In DJF, maximum \( \Delta \delta D \) values below 0‰ in the SASM domain (Figure 3.9A) and below +50‰ in the subtropics (Figure 3.9C) are associated with \( \theta_{EB} \) between 340 K and 345 K. In the subtropics, maximum \( \Delta \delta D \) greater than +50‰ are associated with \( \theta_{EB} \) between 310 K and 340 K (Figure 3.9C). In the tropical Pacific domain, there is no clear relationship between \( \theta_{EB} \) and maximum \( \Delta \delta D \) (Figure 3.9E). In JJA, maximum \( \Delta \delta D \) values below 0‰ in the tropical Pacific domain (Figure 3.9F) and below +100‰ in the SASM domain (Figure 3.9B) are associated with \( \theta_{EB} \) values between 340 K and 345 K. In contrast, maximum \( \Delta \delta D \) values greater than +100‰ in the subtropics are associated with \( \theta_{EB} \) below 320 K (Figure 3.9D).
Figure 3.9. As in Figure 3.8 for the joint distribution of $\theta_{EB}$ and maximum $\Delta \delta D$. Contours indicate percentage of measurements.
3.3.4. LCL and cloudtop pressures over South America in DJF and JJA

In the previous section, we found that maximum $\Delta\delta D$ decreases with increased precipitation rates and $\theta_{EB}$. We now examine the relationship between the vertical extent of the amount effect and cloud depth in convective regions by examining the relationships between the base of the negative $\Delta\delta D$ zone and LCL and the top of the negative $\Delta\delta D$ zone and cloud top pressures. LCL was relatively uniform year-round in all regions (Figure 3.10). Average LCL was 953 hPa at MPCZ. At SBPV in the western part of the SASM domain, average LCL was 918 hPa year round. In the central part of the SASM domain, however, pressure at the LCL ranged from 500 hPa to 900 hPa.

![Figure 3.10. Histograms showing the pressure of the LCL from atmospheric soundings within each domain.](image)

The distribution of cloudtop pressures also varied seasonally. In DJF, cloudtop pressures were lowest ($P \leq 400$ hPa) over the SASM domain and tropical Andes north of 20°S (Figure 3.11). In JJA, cloudtop pressures below 400 hPa are restricted to the tropical Pacific domain and the Amazon Basin between 5°S and 5°N (Figure 3.11). The top of the
ΔδD < 0‰ zone extends to lower pressures than the tops of the clouds in all cases. In DJF, clouds reach minimum pressures of 132 hPa (~15 km) over the SASM domain, 179 hPa (~13 km) over the subtropics, and 102 hPa (~17 km) over the tropical Pacific (Figure 3.11A). On average, DJF cloudtops are at pressures of 400 hPa or below in the western part of the SASM domain and as high as 600 hPa over the eastern part of the SASM domain. Cloudtops are around 500 hPa (~5 km) over the tropical Pacific, and at pressures above 500 hPa over the subtropics east of the Andes (Figure 3.11A). In JJA, clouds reach minimum pressures of ~114 hPa (~16 km) in the SASM and subtropical domains and 134 hPa in the tropical Pacific domain (~15 km). Average JJA cloudtops, however, are found at 725 hPa (~2.4 km) over the SASM domain, 650 hPa (~3 km) over the subtropics, and 561 hPa (4.3 km) over the tropical Pacific (Figure 3.11B).
3.4. Discussion

Independent indicators of convective intensity support the hypothesis that low \( \Delta \delta D \) is related to deep convection associated with the South American monsoon in austral summer and ITCZ in austral winter. High convective precipitation and low OLR are coincident with low maximum \( \Delta \delta D \). Negative maximum \( \Delta \delta D \) is associated with \( \theta_{EB} \) of 340 K or higher in the SASM in DJF and tropical Pacific domain in JJA. We now investigate the relationship between cloud thickness and the vertical structure of the negative \( \Delta \delta D \) zone over South America in DJF and JJA.
Figure 3.12 shows vertical profiles along 70°W in austral summer (Figure 3.12A) and winter (Figure 3.12B). Although the LCL measurements are discontinuous through the study area, they are generally near the base of the ΔδD < 0‰ zone in the areas with greatest convective intensity in each season. Below the LCL level, δD is higher than predicted by the Rayleigh model (ΔδD > 0‰). Relatively high ΔδD in the tropical boundary layer may be the result of surface evaporation [e.g. Yoshimura et al., 2011; Insel et al., 2012], which has been shown to increase isotopic ratios in tropical speleothems when local, rather than upwind, precipitation exerts dominant control [Lee et al., 2009]. The LCL, therefore, appears to constrain the base of the ΔδD < 0‰ zone in the tropics.

![Figure 3.12. Profiles showing ΔδD in A) DJF and B) JJA along 70°W. The heavy dotted lines indicate cloudtop pressure and the light dotted lines indicate the approximate location of the LCL.](image)

In contrast, cloud tops in regions with deep convection intersect zones where ΔδD is below -150‰. The tops of convective clouds may represent the level of neutral buoyancy (LNB) where unstable air masses cease to rise unstably. The upper limit for the LNB in the tropics is estimated from soundings as 14 km above the surface [e.g.
Gettelman et al., 2002; Liu and Zipser, 2005, Takahashi and Luo, 2012; Uma et al., 2014]. However, there are other methods to estimate the LNB [e.g. Sherwood et al., 2004; Mullendore et al., 2013]. Estimates based on cloud tops (10-16 km), the level of maximum mass detrainment (9.5-11.5 km), and the height at the base of detraining anvils (7.5 to 9.5 km) are much lower than estimates of the LNB based on sounding data [Takahashi and Luo, 2012].

Convective overshooting occurs when cloud tops exceed the LNB. This process is one major mechanism by which water vapor enters the stratosphere [e.g. Gettelman et al., 2002]. Convective overshooting is an ephemeral process that occurs at length scales of tens of kilometers and timescales of tens of minutes [Gettelman et al., 2002]. The climatological features of cloud heights from 2004 to 2013 at 1°×1° daily resolution may, therefore, fail to capture convective overshooting. Intense convection likely generates persistent ΔδD < 0‰ zones that exceed 10 km, and these zones may overshoot the LNB. Although the links between low ΔδD and convective overshooting are far from definitive, it is clear that clouds that persist to higher elevations are associated with more vertically extensive ΔδD < 0‰ zones and lower ΔδD minima.

Mid-latitude ΔδD < 0‰ zones do not appear to be related to high θ_{EB}. However, previous studies have documented that the high terrain in this area triggers convective storms [Rasmussen and Houze, 2011]. This convection likely contributes to the low ΔδD values over midlatitudes.
3.5. Conclusions

Our goal was to examine the relationship between convective intensity and the amount effect and to determine the relationship, if any, between the vertical structure of water vapor isotopologue variability and clouds. We find that:

1) The zone where $\Delta \delta D$ is negative is centered over the SASM domain in DJF and in the ITCZ in JJA and that regions with $\theta_{EB}$ between 340 K and 350 K experience maximum $\Delta \delta D$ below 0‰ and $\Delta \delta D < 0$‰ zones that are more than 5 km thick. These observations support the link between convection and $\delta D$ that is lower than predicted by Rayleigh distillation;

2) The base of the $\Delta \delta D < 0$‰ zone closely corresponds to the LCL in regions with greatest convective intensity, suggesting that the base is limited by cloudbase in convective regions;

3) The thickest negative $\Delta \delta D$ zones extend above the cloudtops. These zones have $\delta D$ values up to 150‰ lower than predicted by Rayleigh distillation. It is possible that these features of the $\Delta \delta D$ zones are indicative of overshooting convection and provide isotopic evidence of overshooting convection that potentially contributes to southern hemisphere stratospheric moisture.

3.6. References for Chapter 3


Craig, H., and L. Gordon (1965), *Deuterium and oxygen 18 variations in the ocean and the marine atmosphere*, edited by E. Tongiorgi, Laboratorio de Geologia Nucleare,


Villacís, M., F. Vimeux, and J. D. Taupin (2008), Analysis of the climate controls on the isotopic composition of precipitation (δ18O) at Nuevo Rocafuerte, 74.5°W, 0.9°S, 250 m, Ecuador, *Comptes Rendus Geoscience*, 340(1), 1–9, doi:10.1016/j.crte.2007.11.003.


Vuille, M., R. S. Bradley, M. Werner, and F. Keimig (2003b), 20th century climate
change in the tropical Andes: observations and model results, *Climatic Change*, 59(1), 75–99.


4. HIGH DEUTERIUM-EXCESS IN SUBTROPICAL FREE TROPOSPHERE WATER VAPOR: CONTINUOUS MEASUREMENTS FROM THE CHAJNANTOR PLATEAU, NORTHERN CHILE

4.1. Introduction

Stable isotope ratios in water and water vapor constrain parameters, such as the convective history of air parcels [e.g. Worden et al., 2007] and contain information about moisture source-area conditions [e.g. Steen-Larsen et al., 2013], not evident from precipitation or water vapor amount alone [Noone, 2012]. Isotopic ratios of oxygen and hydrogen in meteoric water covary linearly, fitting the equation $\delta D = 8*\delta ^{18}O + d$-excess [Craig, 1961] where $\delta D$ and $\delta ^{18}O$ are the permil difference in the ratio of heavy to light isotopes (R) in a sample relative to a standard (i.e. $\delta = ([R_{sample}/R_{standard}-1]*1000)$, and $d$-excess is the deuterium-excess parameter [Dansgaard, 1964]. Variations in $d$-excess result from kinetic fractionation that arises from different evaporation and condensation rates for the different isotopologues (e.g. H$_2^{16}$O, HD$_{16}$O, H$_2^{18}$O) of water [Dansgaard, 1964]. Globally, average $d$-excess in meteoric water is 10‰ [Craig, 1961], but it ranges from -5‰ [Rozanski et al., 1993] to +35‰ [e.g. Gat et al., 2003]. Theoretical studies [e.g. Bony et al., 2008; Yoshimura et al., 2008; Blossey et al., 2010; Bolot et al., 2013] indicate that $d$-excess in atmospheric water vapor should vary little from the surface to the mid-troposphere but can exceed 100‰ in the upper tropical troposphere (UTT). In general, this increase in $d$-excess with altitude is a straightforward consequence of the different evaporation and condensation rates of isotopologues of water.
Deviations from the slope of 8 and $d$-excess of 10‰ provide important information about non-equilibrium processes involved in moisture transport and precipitation. Microphysical processes associated with ice cloud formation or deep tropical convection can increase or decrease $d$-excess. Jouzel and Merlivat [1984] evaluated the role of condensation under conditions of supersaturation over ice in setting isotopic ratios of snow. Their work focused on fully glaciated clouds in polar regions and showed that condensation under ice supersaturation lowers water vapor $d$-excess relative to that predicted by an equilibrium Rayleigh distillation process at relative humidity (RH) of 100%. Ciais and Jouzel [1994] extended this work and found that, even in polar clouds, the range of $d$-excess in precipitation requires some balance between saturation over ice and saturation over liquid. Bony et al. [2008] used a single-column model that incorporates isotope physics to show that $d$-excess reaches a maximum as $\delta D$ reaches a minimum around 175 hPa in a convective atmosphere. In this simulation, $\delta D$ increased from 175 hPa to 100 hPa, decreasing $d$-excess. Blossey et al. [2010] used a cloud-resolving model with explicit representation of large-scale tropospheric and stratospheric (i.e. Brewer-Dobson) circulation to simulate isotope ratios in water vapor entering the stratosphere. They found that deep convection and cirrus cloud formation play an important role in setting the isotopic composition of water vapor in the upper troposphere and that air with characteristics associated with the UTT can be found beneath the subsiding branches of both the Hadley and Walker circulations. Bolot et al. [2013] used a one-dimensional microphysical model to extend Jouzel and Merlivat’s [1984] work and evaluate the role of microphysical processes in setting isotopic ratios in deep tropical convection. They found that isotope ratios and $d$-excess are sensitive to a variety of
microphysical parameters, including glaciation temperature, glaciation processes, and degree of supersaturation. Although $d$-excess can span a broad range in convective systems, it is generally calculated to be around 10‰ from the surface to 500 hPa and positive in the UTT.

It is difficult to validate theoretical predictions of $d$-excess in the free troposphere. Despite satellite instruments that measure $\delta D$ [e.g. Kuang et al., 2003; Worden et al., 2007; Lacour et al., 2012], there are few $\delta^{18}O$ measurements in free-troposphere water vapor. The CRYSTAL-FACE experiment showed that mean $\delta^{18}O$ in the upper troposphere is $-179^{\circ\circ} \pm 72^{\circ\circ}$ and mean $\delta D$ is $-600^{\circ\circ} \pm 180^{\circ\circ}$, yielding a mean $d$-excess of $832^{\circ\circ} \pm 603^{\circ\circ}$ [Webster and Heymsfield, 2003]. These upper troposphere $\delta D$ values are within measurement uncertainty of water vapor entering the stratosphere, which is around $-670^{\circ\circ}$ to $-650^{\circ\circ}$ [Moyer et al., 1996; Keith, 2000]. The CR-AVE and TC4 experiments showed that $d$-excess can exceed 200‰ and that water vapor mixing ratio ($q$) can be on the order of 200 ppmv at pressures of 250 hPa [Sayres et al., 2010; Pfister et al., 2010]. However, these experiments provide only a snapshot of the upper troposphere rather than continuous measurements that span seasons.

Advances in cavity ringdown spectroscopy (CRDS) have made reliable, longterm, continuous measurements of $\delta D$ and $\delta^{18}O$ possible from the surface [e.g. Johnson et al., 2011; Welp et al., 2012; Steen-Larsen et al., 2013; Bailey et al., 2013; Steen-Larsen et al., 2014]. Galewsky et al. [2011] showed that subsiding air with specific humidity and isotopic composition consistent with the UTT can be measured from surface at the Chajnantor Plateau (23ºS, 68ºW, elevation = 5080 m, P ~500 hPa) in the subtropical Chilean Andes (Figure 4.1). The version of the instrument used in that study had
relatively large uncertainties in $\delta^1$D and $\delta^{18}$O, making it impossible to reliably quantify $d$-excess in water vapor measured at the site. Advances in spectroscopy in commercial analyzers have reduced these uncertainties by an order of magnitude.

Figure 4.1. Location of the Chajnantor Plateau in northern Chile (star). Annual mean relative humidity at 500 hPa (color scale and contours) is taken from the level 3 monthly Atmospheric Infrared Sounder satellite data.

A diverse range of processes dehydrates air parcels that reach the arid subtropics [e.g. Galewsky et al., 2005; Couhert et al., 2010], including deep tropical convection and condensation in midlatitude storm tracks [e.g. Hurley et al., 2012]. Dehydrated air parcels are then subjected to mixing with moist air from the mid- or lower-troposphere en route to the subtropics [e.g. Galewsky and Samuels-Crow, 2014] Therefore, we would expect the $d$-excess of subtropical water vapor to be relatively high and reflect a diverse range of non-equilibrium processes. To quantify the range of water vapor $d$-excess in the hyperarid subtropics and to evaluate the processes responsible for delivering moisture to
this region, we measured \( q \) and isotopic ratios in atmospheric water vapor from July 2012 to March 2013 at the Atacama Large Millimeter Array (ALMA) observatory [Wootten and Thompson, 2009] on the Chajnantor Plateau in northern Chile (Figure 4.1). ALMA, located in the subtropical Andes adjacent to the Atacama Desert is one of the driest sites on Earth’s surface outside of Antarctica. Annual median precipitable water vapor (PWV) at this site is 1.2 mm. PWV averages less than 1mm from March to November but frequently exceeds 10 mm in austral summer (DJF) [Giovanelli et al., 2001]. The Plateau is unvegetated above 4000 m, and isotopic ratios measured at low \( q \) are consistent with airplane measurements in the free troposphere [Galewsky et al., 2011]. The unique conditions at this site allow us to use these measurements to evaluate theoretical predictions of free troposphere \( d \)-excess.

4.2. Methods

4.2.1. Isotope measurements

A Picarro L2130-i water vapor analyzer, which simultaneously measures \( H_2^{16}O \), \( H_2^{18}O \), and \( HD^{16}O \), was deployed at the climate-controlled Central Weather Station (CWS) at ALMA. We used a 4.8 L min\(^{-1}\) pump to transfer air to the instrument from a height of ~5m above the ground via an unheated teflon tube. Only 0.3% of the measurements were taken when local RH exceeded 95%, so we do not believe condensation of water vapor in the inlet skewed the results at this hyperarid site. This study is based on 5-minute averages of nearly continuous data collected from July 2012 to March 2013.
4.2.1.1. Measurement calibrations

The water vapor analyzer was equipped with a Standards Delivery Module that delivered two liquid standards to a vaporizer operated at 140°C prior to delivery to the instrument. The two standards, NM-3 and Antarctic Snow, were calibrated to international standards in 2011 at the University of New Mexico’s stable isotope lab: Vienna Standard Mean Ocean Water (VSMOW), Standard Light Antarctic Precipitation (SLAP), and Greenland Ice Sheet Precipitation (GISP) [Gröning et al., 1999; and references therein]. During this calibration effort, isotopic ratios of thirty aliquots of VSMOW, SLAP, and GISP obtained from the National Institute of Standards and Technology were analyzed conventionally on a Finnigan Delta Plus XL mass spectrometer and via cavity-ringdown spectroscopy on a Picarro 1102-i water vapor analyzer. Thirty aliquots each of five secondary standards were analyzed alongside the international standards. These secondary standards include bottled water from Hawaii (Kona) and Tibet, tap water from Georgia in the southeastern U.S., distilled tap water from New Mexico (NM-3), and melted Antarctic snow (ANT) obtained from the Climate Change Institute at the University of Maine. Results are shown in Table 4.1.
Table 4.1. Results of the 2011 lab standards calibration effort

<table>
<thead>
<tr>
<th>Standard Name</th>
<th>Mass spec Mean (\delta^{18}O), %</th>
<th>Mass spec Mean (\deltaD), %</th>
<th>CRDS Mean (\delta^{18}O), %</th>
<th>CRDS (1\sigma) (\delta^{18}O), %</th>
<th>CRDS Mean (\deltaD), %</th>
<th>CRDS (1\sigma) (\deltaD), %</th>
<th>accepted or corrected (\delta^{18}O), %</th>
<th>accepted or corrected (\deltaD), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>VSMOW</td>
<td>0.01</td>
<td>0.18</td>
<td>0.005</td>
<td>0.007</td>
<td>0.1</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>GISP</td>
<td>-24.79</td>
<td>-190.37</td>
<td>-24.79</td>
<td>0.01</td>
<td>-190</td>
<td>1</td>
<td>-24.8</td>
<td>-189.7</td>
</tr>
<tr>
<td>SLAP</td>
<td>-55.5</td>
<td>-427.86</td>
<td>-55.494</td>
<td>0.006</td>
<td>-427.9</td>
<td>0.4</td>
<td>-55.5</td>
<td>-428</td>
</tr>
<tr>
<td>Kona</td>
<td>0.12</td>
<td>-0.49</td>
<td>0.5</td>
<td>0.2</td>
<td>0.59</td>
<td>0.02</td>
<td>0 (^2)</td>
<td>0.6 (^2)</td>
</tr>
<tr>
<td>Georgia</td>
<td>-2.36</td>
<td>-14.07</td>
<td>-2.2</td>
<td>0.4</td>
<td>-15.4</td>
<td>0.7</td>
<td>-2.2 (^2)</td>
<td>-15 (^2)</td>
</tr>
<tr>
<td>NM3(^1)</td>
<td>-13.16</td>
<td>-97.64</td>
<td>-13.1</td>
<td>0.3</td>
<td>-97</td>
<td>1</td>
<td>-13.1 (^2)</td>
<td>-96 (^2)</td>
</tr>
<tr>
<td>Tibet</td>
<td>-19.07</td>
<td>-144.82</td>
<td>-19.1</td>
<td>0.2</td>
<td>-144</td>
<td>1</td>
<td>-19.1 (^2)</td>
<td>-144 (^2)</td>
</tr>
<tr>
<td>ANT(^1)</td>
<td>-49.53</td>
<td>-394.94</td>
<td>-49.7</td>
<td>0.2</td>
<td>-388.2</td>
<td>0.5</td>
<td>-49.6 (^2)</td>
<td>-388 (^2)</td>
</tr>
</tbody>
</table>

\(^1\)Secondary standards used to calibrate CRDS measurements at ALMA; \(^2\)Corrected value after applying stretching factor

Water isotopologue abundance cannot be analyzed directly via mass spectrometry, so it is necessary to convert the water to dry gases (CO\(_2\) and H\(_2\)) that retain the isotopic ratios of the original sample. Samples and standards were prepared for oxygen isotope analysis on the mass spectrometer using the CO\(_2\) equilibration method first described by Cohn and Urey [1938]. Two mL of each sample or standard was added to a vacutainer flushed with high-purity CO\(_2\) (5%) in He. The tubes were held at a constant 25°C in a block heater for 12 hours to allow the water to equilibrate with the CO\(_2\). The CO\(_2\) was extracted in continuous flow and measured for its \(\delta^{18}O\) value.

Samples and standards were reduced to H\(_2\) gas by reacting 2 \(\mu\)l of water with zinc [Friedman, 1953; Coleman et al., 1982] at 500°C for 30 minutes using Bloomington,
Indiana zinc (http://geology.indiana.edu/biogeochemistry/references.html). This process quantitatively converts the H₂O to H₂ gas and ZnO [Friedman, 1953]. The H₂ gas was analyzed in a Finnigan MAT-252 mass spectrometer in dual inlet mode.

We calculated stretching factors to account for the differences between the measured and accepted isotopic values of each international standard [Sharp, 2007]. The stretching factors (equation 4.1) are based on the linear relationship between the measured and accepted values of VSMOW, SLAP, and GISP (Figure 4.2):

\[ \delta_{\text{measured}} = M\delta_{\text{accepted}} + b \] (4.1)

where \( M_D = M_{\delta^{18}O} = 0.99996 \), \( b_D = -0.0035351 \), and \( b_{\delta^{18}O} = -0.0012332 \).

These stretching factors allow us to calculate calibrated values for the secondary standards (Table 4.1). There is a linear relationship between the calibrated and measured values for the secondary standards, so we can use just 2 standards to calibrate the instrument deployed on the Chajnantor Plateau (Figure 4.3).

![Figure 4.2. Linear relationship between measured and accepted values for SMOW, GISP, and SLAP for (A) \( \delta^{18}O \) and (B) \( \delta D \).](image-url)
4.2.1.2. Concentration bias characterization and correction

Prior to field deployment, a concentration-dependence experiment was conducted on the instrument at Picarro, Inc. to quantify biases in δD and δ¹⁸O at low q. This experiment utilized a bubbler apparatus to progressively dilute water vapor of known isotopic composition with dry air and nitrogen gas as described by Johnson et al. [2011] and Galewsky et al. [2011]. We corrected q_{CRDS} based on the linear regression between q_{ALMA} and q_{CRDS} described below in section 2.3. This experiment was conducted from q_{corrected} of 109 ppmv to 16572 ppmv. The measurements at q_{corrected} = 158 ppmv are outside of the 1-σ uncertainty for δD and δ¹⁸O. An assessment of spectral features stored in the full Picarro Private Data Log files suggests there may have been a frequency offset within the Wavelength Monitor control loop during data acquisition at this concentration step. Although the frequency offset is minor (on the order of 10⁻⁴), the resultant ~3‰ shift in δ¹⁸O results in a large (~14‰) offset in the calculated d-excess parameter for this data point. We do not consider this outlier representative of uncertainty at low
concentrations, and we have excluded it from the concentration bias correction. The 1-σ uncertainty in 5-minute averages of individual measurements increased with decreased \( q \) but was less than \( \pm 1\% \) at the average \( q \) (~3200 ppmv) measured during the study period (Table 4.2). The 1-σ uncertainty in \( d \)-excess was calculated by propagating the errors in \( \delta D \) and \( \delta^{18}O \) at different concentrations according to equation 4.2:

\[
1\sigma_{d\text{-excess}} = (\sigma_{\delta D}^2 + (8\sigma_{\delta^{18}O})^2)^{1/2} \quad (4.2)
\]

Table 4.2. Results of the 2012 concentration-dependence experiment

<table>
<thead>
<tr>
<th>( q_{CRDS}, \text{ppmv} )</th>
<th>( q_{corr}, \text{ppmv} )</th>
<th>( 1\sigma, \text{ppmv} )</th>
<th>( \delta D, % )</th>
<th>( \delta D, 1\sigma, % )</th>
<th>( \delta^{18}O, % )</th>
<th>( \delta^{18}O, 1\sigma, % )</th>
<th>d-excess 1\sigma, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>171</td>
<td>109</td>
<td>3</td>
<td>-127</td>
<td>5</td>
<td>-18.2</td>
<td>0.4</td>
<td>5.9</td>
</tr>
<tr>
<td>1231</td>
<td>158</td>
<td>27</td>
<td>-134.2</td>
<td>0.9</td>
<td>-21.0</td>
<td>0.6</td>
<td>4.9</td>
</tr>
<tr>
<td>1323</td>
<td>1046</td>
<td>9</td>
<td>-135.1</td>
<td>0.9</td>
<td>-18.6</td>
<td>0.3</td>
<td>2.6</td>
</tr>
<tr>
<td>1440</td>
<td>1141</td>
<td>12</td>
<td>-133</td>
<td>1</td>
<td>-18.7</td>
<td>0.2</td>
<td>1.9</td>
</tr>
<tr>
<td>3063</td>
<td>2462</td>
<td>5</td>
<td>-135.0</td>
<td>0.2</td>
<td>-18.81</td>
<td>0.04</td>
<td>0.4</td>
</tr>
<tr>
<td>3196</td>
<td>2570</td>
<td>12</td>
<td>-133.5</td>
<td>0.4</td>
<td>-18.7</td>
<td>0.1</td>
<td>0.9</td>
</tr>
<tr>
<td>5860</td>
<td>4737</td>
<td>10</td>
<td>-134.86</td>
<td>0.07</td>
<td>-18.82</td>
<td>0.05</td>
<td>0.4</td>
</tr>
<tr>
<td>6054</td>
<td>4895</td>
<td>23</td>
<td>-133.8</td>
<td>0.1</td>
<td>-18.78</td>
<td>0.08</td>
<td>0.6</td>
</tr>
<tr>
<td>11802</td>
<td>9571</td>
<td>18</td>
<td>-134.4</td>
<td>0.2</td>
<td>-18.78</td>
<td>0.02</td>
<td>0.3</td>
</tr>
<tr>
<td>11856</td>
<td>9615</td>
<td>20</td>
<td>-134.43</td>
<td>0.07</td>
<td>-18.83</td>
<td>0.02</td>
<td>0.2</td>
</tr>
<tr>
<td>16482</td>
<td>13378</td>
<td>20</td>
<td>-134.9</td>
<td>0.1</td>
<td>-18.77</td>
<td>0.03</td>
<td>0.3</td>
</tr>
<tr>
<td>16697</td>
<td>13553</td>
<td>61</td>
<td>-134.3</td>
<td>0.2</td>
<td>-18.70</td>
<td>0.03</td>
<td>0.3</td>
</tr>
<tr>
<td>20408</td>
<td>16572</td>
<td>43</td>
<td>-134.7</td>
<td>0.2</td>
<td>-18.80</td>
<td>0.02</td>
<td>0.3</td>
</tr>
</tbody>
</table>

\({}^1\text{excluded from the bias-correction calculation}\)
As found in previous studies, the instrument concentration bias is linear as a function of $1/q$ [Galewsky et al., 2011], allowing us to apply a correction (equation 4.3):

$$\delta_{\text{corrected}} = \delta_{\text{measured}} - X/q \ (4.3)$$

where $X_D = 1367.8$ and $X_{\delta^{18}O} = 180.42$. The correction factor applied to the L2130-1 analyzer is half of that applied in an earlier study for $\delta^{18}O$ and an order of magnitude less than previous corrections in $\delta D$ [Galewsky et al., 2011]. At $q < 1400$ ppmv, bias-corrected $\delta D_{vapors}$ is up to 6‰ lower than uncorrected values.

4.2.1.3. Instrument stability over time

We evaluated instrument stability over the course of deployment at ALMA by monitoring standards and by repeating the concentration-dependence experiment in June 2013. Due to the remote location of the site, we were unable to conduct concentration-dependence experiments more frequently. Standard values were stable over time with little variability in $\delta D$ and $\delta^{18}O$ and no systematic change in standard values over time (Figure 4.4).

![Figure 4.4. Mean isotopic ratios of standards did not vary systematically over time in NM-3 (panels A and C) and ANT (panels B and D).](image)
We conducted the June 2013 concentration-dependence experiment at ALMA’s Operations Support Facility (OSF). For this experiment, we bubbled dry nitrogen gas from the headspace of a liquid nitrogen tank through one liter of ALMA tap water in a sealed Erlenmeyer flask. ALMA tap water is transported to the OSF from Calama (22.5°S, 66.9°W, elevation = 2260 m). Because the water used in this experiment differed from the water used in the 2012 experiment and was of unknown isotopic composition, we took samples of water from the bubbler apparatus before and after the experiment and analyzed them on the Picarro 1102-i at UNM. The isotopic ratios were the same within 1-σ uncertainty before \((δD = -69‰ ± 3‰, δ^{18}O = -9.5‰ ± 0.2‰)\) and after \((δD = -62‰ ± 4‰, δ^{18}O = -9.48‰ ± 0.03‰)\) the experiment.

As in the 2012 concentration-dependence experiment, the 1-σ uncertainty of the measurements increased as \(q\) decreased. We used 5-minute averages of the 5-second measurements to determine the uncertainty in \(δD\) and \(δ^{18}O\) measurements and \(d\)-excess calculations (Table 4.3).
Table 4.3. Results of June 2013 concentration-dependence experiment

<table>
<thead>
<tr>
<th>q_{CRDS}, ppmv</th>
<th>q_{Corr}, ppmv</th>
<th>q_{1\sigma}, ppmv</th>
<th>δD, %</th>
<th>δD_{1\sigma}, %</th>
<th>δ^{18}O, %</th>
<th>δ^{18}O_{1\sigma}, %</th>
<th>d-excess</th>
<th>d-excess_{1\sigma}, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>217</td>
<td>146</td>
<td>16</td>
<td>-136</td>
<td>2</td>
<td>-17.8</td>
<td>0.2</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>228</td>
<td>155</td>
<td>7</td>
<td>-140</td>
<td>2</td>
<td>-19.2</td>
<td>0.3</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>444</td>
<td>331</td>
<td>5</td>
<td>-150</td>
<td>1</td>
<td>-19.9</td>
<td>0.1</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>608</td>
<td>464</td>
<td>8</td>
<td>-150.2</td>
<td>0.2</td>
<td>-20.5</td>
<td>0.7</td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>458</td>
<td>9</td>
<td>-147</td>
<td>1</td>
<td>-18.9</td>
<td>0.1</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>701</td>
<td>539</td>
<td>8</td>
<td>-147.4</td>
<td>1</td>
<td>-19.2</td>
<td>0.2</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>810</td>
<td>699</td>
<td>3</td>
<td>-148.1</td>
<td>0.7</td>
<td>-19.3</td>
<td>0.2</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>954</td>
<td>746</td>
<td>5</td>
<td>-150</td>
<td>2</td>
<td>-20.1</td>
<td>0.3</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>1009</td>
<td>791</td>
<td>7</td>
<td>-148.6</td>
<td>0.8</td>
<td>-19.71</td>
<td>0.09</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>1437</td>
<td>1139</td>
<td>15</td>
<td>-148.8</td>
<td>0.1</td>
<td>-20.0</td>
<td>0.4</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>3657</td>
<td>2945</td>
<td>27</td>
<td>-149.2</td>
<td>0.7</td>
<td>-19.6</td>
<td>0.1</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>5961</td>
<td>4819</td>
<td>66</td>
<td>-150.3</td>
<td>0.3</td>
<td>-19.78</td>
<td>0.07</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>16963</td>
<td>13769</td>
<td>65</td>
<td>-149.04</td>
<td>0.09</td>
<td>-19.57</td>
<td>0.04</td>
<td>0.3</td>
<td></td>
</tr>
</tbody>
</table>

4.2.2. Calculating theoretical curves

Rayleigh distillation at saturation vapor pressure (i.e. RH = 100%) is a first-order, open-system model for predicting progressive isotopic change in precipitation and atmospheric water vapor [e.g. Dansgaard, 1964]. As water vapor condenses, heavier isotopes preferentially go into the condensed phase, and the Rayleigh model assumes the condensate is immediately removed, leaving water vapor with lower isotopic ratios than the initial vapor [e.g. Craig, 1961; Dansgaard, 1964; Gat, 1996]. High d-excess at low q is a natural consequence of Rayleigh distillation because water vapor isotopic ratios
approach 0% as the fraction of vapor remaining approaches 0. By definition, δ-values then approach -1000‰ and d-excess approaches 7000‰ [e.g. Bony et al., 2008]. In ice clouds, Rayleigh fractionation usually takes place under ice-supersaturated conditions (i.e. RH > 100%) [Jouzel and Merlivat, 1984; Jensen and Pfister, 2005], which requires a modification of the Rayleigh model to account for non-equilibrium kinetic processes that take place under these conditions [Jouzel and Merlivat, 1984].

We calculated theoretical Rayleigh curves as a function of $q$ (equation 4.4):

$$d\ln R = (\alpha - 1)d\ln q$$

where $\alpha$ is the fractionation factor [e.g. Dessler and Sherwood, 2003] for saturated (RH = 100%) and ice-supersaturated conditions, ranging from RHi = 101% to RHi = 140%, as well as mixing curves. We calculated saturated $q$ at the range of RH based on temperatures and pressures from atmospheric soundings (http://weather.uwyo.edu/upperair/sounding.html). We used fractionation factors of [Majoube, 1971] for hydrogen-isotope fractionation between liquid and vapor above 0°C and oxygen-isotope fractionation at all temperatures and those of [Merlivat and Nief, 1967] for hydrogen-isotope fractionation between solid and vapor at temperatures below 0°C. We used starting isotopic ratios and $q$ consistent with evaporation in a tropical setting ($\delta D = -66‰$, $\delta^{18}O = -11‰$, $q = 26444$ ppmv) [e.g. Craig and Gordon, 1965].

4.2.3 Quantifying water vapor mixing ratios and evaluating local conditions

Despite improvements in isotopic measurements, empirical calibration efforts at Picarro, Inc. show that the L2130-i analyzer overestimates $q$. In order to accurately determine mixing ratios at this hyperarid site, we relied on independent measurements from weather stations on the Chajnantor Plateau. We calculated $q$ based on RH,
temperature, and pressure measured by automated weather stations (http://weather.aiv.alma.cl/) installed at ALMA approximately 400 m from the CWS where our instrument is housed. In order to characterize moisture across the Plateau, we also calculated $q$ based on measurements made at the Atacama Pathfinder Experiment (APEX) observatory (http://archive.eso.org/wdb/wdb/eso/meteo_apex/form), which is approximately 2.3 km northwest of, and 70 m higher than, the CWS.

The automated weather stations at ALMA are equipped with Vaisala’s PTU300 instrument, which simultaneously measures pressure, relative humidity, and ambient temperature [Mangum, 2009]. Data from both ALMA weather stations are recorded at sub-second intervals. We based our calculations on 5-minute averages of these measurements. See Table 4.4 for technical details on the sensors that measure each parameter.

**Table 4.4. Technical specifications for meteorological equipment at ALMA AOS**

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Parameter</th>
<th>Precision</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class B</td>
<td>P</td>
<td>±0.25 hPa</td>
<td>50-1100 hPa/ -40°C to +60°C</td>
</tr>
<tr>
<td>PT100 RTD 1/3 Class B</td>
<td>Ambient T</td>
<td>±0.20 to 0.30 °C</td>
<td>-20°C to + 40°C</td>
</tr>
<tr>
<td>IEC 751 HUMICAP</td>
<td>RH</td>
<td>±(1.0 ± 0.008 × reading) %</td>
<td>-20°C to + 40°C / 0-100%</td>
</tr>
<tr>
<td>WMT50</td>
<td>W$_s$ and W$_d$*</td>
<td>max(±0.3m/s,±3%)/±3 deg</td>
<td>0–35 m/s / 0–360 deg</td>
</tr>
</tbody>
</table>

*W$_s$ = wind speed; W$_d$ = wind direction

The automated weather station at APEX is mounted on a free-standing tower approximately 5 m above the ground and is equipped with Vaisala instruments that measure dewpoint and pressure. Data is recorded every minute, and we based our calculation of $q$ on 5-minute averages of these measurements. See Table 4.5 for technical details on the sensors that measure each parameter.
Table 4.5. Technical specifications for meteorological equipment at APEX

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Parameter</th>
<th>Precision</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTB240</td>
<td>P</td>
<td>±0.20 hPa</td>
<td>50-1100 hPa/ -40°C to +60°C</td>
</tr>
<tr>
<td>Vaisala HMT243</td>
<td>T_d</td>
<td>±0.50 to 1.0°C*</td>
<td>-40°C to +100°C</td>
</tr>
</tbody>
</table>

*Under mean conditions at APEX with mean T = -1.5°C, mean T_d = -19.8°C, and mean dewpoint difference (i.e. T – T_d = 18.3°C).

4.2.3.1. Calculating water vapor mixing ratios and quantifying uncertainties

We calculated 5-minute averages of q in parts per million by volume (ppmv) (equation 4.5) based on relative humidity (RH) at ALMA (equation 4.6) and dewpoint temperature (T_d) at APEX (equation 4.7), using the following equations from UMA [2013]:

\[
q = \frac{P_w}{P - P_w} \times 10^6 \quad (4.5)
\]

where \( q \) is the water vapor mixing ratios in ppmv, \( P \) is the total pressure in hPa, and \( P_w \) is the water vapor pressure in hPa.

\( P_w \) can be calculated based on RH or \( T_d \):

\[
P_w = P_{ws} \times \frac{RH}{100} \quad (4.6)
\]

\[
P_w = A \times 10^{\left[\frac{m(T_d)}{T_n+T_d}\right]} \quad (4.7)
\]

where RH is the relative humidity, \( P_{ws} \) is the saturation water vapor pressure in hPa, \( T_d \) is the dewpoint temperature in °C, and A, m, and \( T_n \) are constants defined within a given temperature range. We used the constants as defined for liquid water, rather than ice, between -20°C and +50°C (A = 6.116441; m = 7.591386; \( T_n = 240.7263 \)).
We calculated $P_{ws}$ using equation 4.8:

$$P_{ws} = A * 10^{\left(\frac{m*T}{T+273}\right)}$$ (4.8)

where $T$ is the ambient temperature in °C and $A$, $m$, and $T_n$ are constants as defined above.

Because $q$ in ppmv is a derived quantity based on a number of measurements, each with their own error, we propagated uncertainties through the calculation to determine the uncertainty in $q$ ($\Delta q$) (equation 4.9)


Uncertainty in $q$ ($\Delta q$):

$$\Delta q = \sqrt{\left(\frac{\Delta P_{ws}}{P_w}\right)^2 + \left(\frac{\Delta S}{S}\right)^2}$$ (4.9)

Where

$$S = P - P_w$$ (4.10)

and

$$\Delta S = \sqrt{(\Delta P)^2 + (\Delta P_w)^2}$$ (4.11)

Uncertainty in $P_{ws}$ ($\Delta P_{ws}$) in calculations based on RH (ALMA) or $P_w$ in calculations based on $T_d$ (APEX):

$$\Delta P_x = \left| \frac{dP_x}{dT_y} \right| * \Delta T_y$$ (4.12)
Where

\[
\frac{dP_x}{dT} = \frac{m^* A^* T_n^* \log_{10}(10) \cdot 10^{[\frac{m^* T_y}{T_n + T_y}]}}{(T_n + T_y)^2}
\]  

(4.13)

and

\( P_x \) is \( P_{ws} \) for ALMA and \( P_w \) for APEX, \( T_y \) is ambient temperature for ALMA and \( T_d \) for APEX, and \( \Delta T_y \) is the error in ambient temperature (ALMA – see table 4.4) or dewpoint (APEX – see table 4.5).

**Uncertainty in \( P_w (\Delta P_w) \) at ALMA:**

\[
\Delta P_w = P_w \sqrt{\left( \frac{\Delta P_{ws}}{P_{ws}} \right)^2} + \left( \frac{\Delta RH}{RH} \right)^2
\]

(4.14)

At maximum \( q \), \( \Delta q \) was approximately 2% of calculated \( q \) at both APEX and ALMA. At minimum \( q \), \( \Delta q \) was 6% at APEX and 4% at ALMA. At mean \( q \) (~3200 ppmv), mean \( \Delta q \) was approximately 3% of the calculated \( q \).

4.2.3.2 **Comparison of humidity measurements from ALMA, APEX, and CRDS**

Calculated \( q \) is identical between the two ALMA weather stations and consistent between the ALMA weather stations and the weather station at APEX. ALMA \( q \) ranges from 68 ppmv ± 3 ppmv to 12400 ± 250 ppmv with a mean value of 3230 ± 84 ppmv. APEX \( q \) ranges from 0.36 ppmv ± 0.02 ppmv to 11700 ppmv ± 275 ppmv with a mean value of 3210 ± 84 ppmv. Due to its proximity to the CWS, we used \( q \) calculated from the meteorological measurements at ALMA rather than APEX for this study.

CRDS measurements of \( q \) are consistently higher than \( q \) calculated from meteorological measurements at ALMA, but they rise and fall consistently with calculated \( q \) from both ALMA and APEX (Figure 4.5). CRDS-reported \( q \) is, on average
21% higher than $q$ calculated based on ALMA measurements and 28% higher than $q$ calculated based on APEX measurements. There are strong linear correlations between $q$ calculated from ALMA and APEX data ($r = 0.94$, $p < 0.001$) and between CRDS-reported $q$ and $q$ calculated from ALMA ($r = 0.99$, $p < 0.001$) (Figure 4.6) and APEX ($r = 0.93$, $p < 0.001$) data.

![Graphs showing comparisons of $q$ from ALMA, APEX, and CRDS](image)

Figure 4.5. Comparison of $q$ calculated from meteorological measurements at (A) ALMA and (B) APEX along with (C) $q$ as reported by the CRDS. Reported $q$ fluctuates with calculated $q$ from the weather stations, but it is, on average, 21% higher than $q$ calculated from ALMA data and 28% higher than $q$ calculated from APEX data.
Figure 4.6. Scatter plot showing the linear relationship between $q_{\text{ALMA}}$ and $q_{\text{CRDS}}$.

We also used 5-minute averages of RH, dewpoint, temperature, wind speed, and wind direction measured at ALMA to evaluate the influence of local weather on isotopic ratios and $d$-excess measured at the site. During the measurement period, average local dewpoint was -19.7°C. Winds were predominantly from the west at speeds up to 27.9 m s$^{-1}$. There is a statistically significant correlation between $d$-excess and local dewpoint ($r = -0.33, p < 0.001$) during the study period.

4.2.4. Evaluating the influence of moisture source on $d$-excess

$D$-excess variations are often linked to variations and conditions in water-vapor source regions. In order to test the relationship between $d$-excess and source region, we calculated 5-day and 10-day Lagrangian back trajectories, using NOAA’s HYSPLIT model [Draxler et al., 1997; Draxler, 1999] driven by NCEP-NCAR Reanalysis data. We tested the sensitivity of the model to starting location and elevation by calculating a
subset of trajectories (n = 3200) in a 1°×1°×500 m domain around the measuring site. We found no significant difference in the average source latitude and longitude for this subset of trajectories (Figure 4.7) versus the full dataset.

![Figure 4.7. Example of mean trajectory location at t = -240 hours for a suite of trajectories launched in a 1°×1°×500 m domain around ALMA and for single trajectories launched from each measurement on August 12, 2012. The average source region latitude for the 3-dimensional region (n = 15200) was 19°S ± 5° while the average source region for single trajectories launched from each measurement on 8/12/12 (n = 129) was 16°S ± 2°. Average d-excess on 8/12/12 was +54‰.](image)

Source areas for trajectories launched at the measurement times varied from low to high latitudes with most of the trajectories arriving at ALMA along the prevailing westerlies. We tested the sensitivity of trajectories to meteorological input files by calculating a subset of 5-day back trajectories (n = 5643) using GDAS1 meteorological data. We found that at t = -120 hours, the source areas for trajectories were in the same general vicinity as they are in trajectories calculated based on Reanalysis data. Furthermore, the relationship between RH at t = -120 hours and d-excess is similar in trajectories calculated using GDAS1 and Reanalysis data. We, therefore, focus our
discussion of source area on trajectories calculated with the NCEP-NCAR Reanalysis data.

4.3. Results

During the study period, $q$ on the Chajnantor Plateau ranged from 96 ± 4 ppmv to 12400 ± 250 ppmv with a mean value of 3208 ± 84 ppmv. $\delta D_{\text{vapor}}$ ranged from -46‰ ± 5‰ to -46‰ ± 0.2‰ and $\delta^{18}O_{\text{vapor}}$ ranged from -66.6‰ ± 0.6‰ to -8.8‰ ± 0.1‰. Average $d$-excess over the full data set was 20 ± 0.5‰, with measurements ranging from -37‰ ± 2‰ to 234 ± 1‰ (October 2012; $q = 2046 ± 61$ ppmv). At $q \leq 1000$ ppmv, approximately 20% of the dataset, average $d$-excess was 31‰ ± 1.3‰. At $q \leq 500$ ppmv, average $d$-excess was 46‰ ± 4.8‰. Uncertainties are based on standard deviation at the appropriate $q$ in the concentration-dependence experiment conducted prior to instrument deployment in 2012 (see section 2.1.2).

Back-trajectory analysis indicates that there is no distinct source area for high (i.e. $d$-excess ≥ 40‰), low (i.e. $d$-excess ≤ 0‰), or average (i.e. 0‰ < $d$-excess < 40‰) $d$-excess measurements (Figure 4.8). More than half of all 5- and 10-day back trajectories launched from the Chajnantor Plateau had source areas in the subtropics and midlatitudes regardless of $d$-excess. Another 45% of the trajectories were in the tropics 5- to 10-days before arriving at the Plateau, and less than 2% were poleward of 50°S. There was no correlation between $d$-excess and RH for trajectories that originated in the boundary layer. Additionally, boundary layer $d$-excess values range between -5‰ [Uemura et al., 2008] and +35‰ [[Gat et al., 2003], suggesting that variability in boundary layer $d$-excess can explain only a small part of the observed $d$-excess variability.
Figure 4.8. Histograms for trajectory locations at $t = -240$ hours shows that there is no distinct source area for high $d$-excess measurements.

High $d$-excess measured at ALMA is, therefore, more likely related to in-cloud processes than to source area. Figure 4.9 shows the joint distribution of $q$, $\delta D$ (Figure 4.9A), $\delta^{18}O$ (Figure 4.9B), and $d$-excess (Figure 4.9C) along with several theoretical curves. The dark lines show $\delta$- and $d$-excess values predicted for RH = 100% while the suite of lighter curves shows values predicted for condensation at RH$\iota$ ranging from 105% to 130% calculated using the technique of Jouzel and Merlivat [1984]. The $\delta$-values generally lie above the theoretical Rayleigh curves, a distribution diagnostic of mixing between dry and moist air [e.g. Galewsky and Hurley, 2010; Galewsky et al., 2011; Hurley et al., 2012; Noone, 2012; Galewsky and Samuels-Crow, 2014]. While $\delta$-values show the importance of mixing between moist and dry air in controlling isotopic
ratios measured at the Chajnantor Plateau, the range of $d$-excess provides insights into condensation processes prior to mixing.

Rayleigh distillation at RH = 100% generally marks the upper bound of $d$-excess. Condensation under RHi > 100% lowers the $d$-excess at a given $q$ relative to Rayleigh distillation at RH = 100%. Dewpoint temperatures at ALMA were as low as -52°C during the study period, and 17% of the $d$-excess measurements are associated with dewpoint below -30°C, suggesting that the air was processed through regions cold enough to support fully glaciated clouds where RHi can be as high as 155% [Korolev and Isaac, 2006; Ström et al., 2003]. Most of the $d$-excess data can be explained by condensation at RHi between 105% and 130%, and the $\delta$-values show that a modest degree of mixing must occur en route to the Plateau (Figure 4.9). However, no single combination of initial $\delta$-values, initial $d$-excess, RHi, and mixing fraction can fit the entire dataset.
Figure 4.9. Water vapor (A) $\delta D$, (B) $\delta^{18}O$, and (C) $d$-excess measurements from the Chajnantor Plateau (black dots) plotted versus mixing ratio. The heavy black line shows Rayleigh fractionation at RH = 100%. The suite of gray lines shows $d$-excess at RH ranging from 105% to 130% (contour interval = 5%).
4.4. Discussion

High $d$-excess in atmospheric water vapor has been attributed to different processes, including: 1) distinct source areas where low RH or high sea-surface temperature enhance evaporation [e.g. Gat et al., 2003 Steen-Larsen et al., 2013; Pfahl and Sodeman, 2014] and 2) moisture transport processes, including vertical mixing between subsiding air and boundary layer air [e.g. Blossey et al., 2010] or condensation under ice supersaturation conditions in ice clouds at high latitudes [e.g. Jouzel and Merlivat, 1984] or mixed-phase clouds in the tropics [e.g. Bolot et al., 2013]. Studies of polar regions [e.g. Jouzel and Merlivat, 1984; Rozanski et al., 1997] showed a coherent link between $d$-excess in snow and source area properties such as RH, temperature, or sea-surface temperature. Back-trajectory analysis in the current dataset shows no coherent relationship between $d$-excess and either source area or source area conditions.

Rather than an indicator of source area conditions, $d$-excess in subtropical water vapor results from a different balance of processes than $d$-excess from polar regions. Our analysis of the dataset suggests that certain processes are required to produce the observed $d$-excess range. We focus now on an idealized case in which an air parcel condenses at a temperature of $-55^\circ$C and RHi of 105% and then mixes with moister air. This situation arises throughout the low $q$ portion of the data set, and we propose an idealized model that reproduces this observed relationship between $\delta D$, $\delta^{18}O$, and $d$-excess (Figure 4.10). First, water vapor measured at the Chajnantor Plateau undergoes condensation at RH between 100% and 130% with most of the measurements condensing between RHi of 105% to 120% (Figure 4.9). We chose RHi = 105% and a minimum $q$ of 100 ppmv for this idealized case (gray lines in Figure 4.10), but the measurements with
\( d\)-excess below 0\(^\circ\) (less than 1% of the dataset) likely reflect highly supersaturated conditions [Jouzel and Merlivat, 1984; Bolot et al., 2010]. In order to produce the observed relationship between \( \delta D \), \( \delta^{18}O \), and \( d\)-excess in low \( q \) measurements, this dehydrated air must mix with moister air en route to the measuring site (shown as a thin black line in Figure 4.10). The dry air comprises 80% to 95% of the mixture.

The joint distribution of \( \delta \)-values and mixing ratio (Figure 4.9) highlight the importance of mixing, which has been substantially documented in the subtropics [Galewsky and Hurley, 2010; Hurley et al., 2012] in general and at the Chajnantor Plateau in particular [Galewsky et al., 2011; Galewsky and Samuels-Crow, 2014]. There is no unique combination of RHi, initial \( \delta \)-values, or degree of mixing that fully constrains the full dataset or even individual measurements. However, it is clear that both condensation under a range of RH up to ~130\(^\circ\) followed by mixing are required to produce the range of \( \delta D \), \( \delta^{18}O \), and \( d\)-excess measured at Chajnantor Plateau.
Figure 4.10. An idealized model for dehydration via condensation under ice supersaturation at RH \(\text{Hi} = 105\%\) (gray line) followed by mixing en route to Chajnantor Plateau (thin black line) can produce the observed distribution of (A) \(\delta D\), (B) \(\delta^{18}O\), and (C) \(d\)-excess. Rayleigh fractionation at RH = 100\% (thick black line) is shown for reference.
Isotope-enabled general circulation models provide a means to evaluate complex processes that control isotopic ratios, but $d$-excess is a difficult parameter to simulate [Risi et al., 2010]. IsoGSM [Yoshimura et al., 2008], included in the second generation of the Stable Water Isotope Intercomparison Group (SWING2) models, incorporates parameterized ice supersaturation, and predicts relatively uniform $d$-excess values ~10‰ through the mid-troposphere. At 500 hPa in the vicinity of ALMA, IsoGSM predicts monthly mean $d$-excess values between 20‰ and 27‰ and $q$ values between 1000 ppmv and 3000 ppmv. At 250 hPa, IsoGSM starts to predict $q$ below 500 ppmv and $d$-excess between 37‰ and 65‰. The trends in the highest $d$-excess values, measured when $q \leq 250$ ppmv, are consistent with IsoGSM predictions for $d$-excess at pressures below 250 hPa (Figure 4.11). The isotope-enabled version of the LMDZ model [Risi et al., 2010], which is also included in SWING2 but uses a constant ice supersaturation parameter to best simulate Antarctic $d$-excess, is able to reproduce the average values we observe but cannot reproduce the broad range of $d$-excess we measured at the Chajnantor Plateau.
Figure 4.11. $D$-excess and mixing ratios for the Chajnantor Plateau from our dataset and theoretical Rayleigh curves at a range of relative humidity (as in Figure 4.9) along with model output, shown as monthly averages, in a $2^\circ \times 2^\circ$ domain around study area from (A) IsoGSM [Yoshimura et al., 2008] and (B) LMDZ [Risi et al., 2010], which are included in the SWING2 project.

In general, of course, one should not expect individual measurements to match precisely with a coarse GCM grid, but two points emerge. First, IsoGSM and LMDZ do show a correspondence between mixing ratio and $d$-excess similar to what we measure on Chajnantor, but they do not produce the broad range of $d$-excess values we measure at low $q$, suggesting that these models may not sufficiently capture high RHi processes. Second, most GCMs exhibit a moist bias in the subtropics [i.e. Risi et al., 2012], which may be the reason high $d$-excess measurements do not appear at the 500 hPa level in IsoGSM, and low values ($d$-excess $< 0\%$) do not appear at all in monthly averages.
4.5. Conclusions

This study presents a unique data set of in-situ isotopic measurements from the Chajnantor Plateau in northern Chile, where it is possible to measure free troposphere water vapor from the surface [Galewsky et al., 2011]. These high-precision measurements provide us with new insights into the mechanisms required to produce a broad range of $d$-excess values in the subtropics. Specifically, we find that:

(1) water vapor $d$-excess on the Chajnantor Plateau ranges from $-37\%$ to $+234\%$ with a mean of $46\%$ when $q$ is 500 ppmv or below. This range of $d$-excess values is consistent with condensation over a broad range of ice supersaturation values up to $130\%$;

(2) variations in $d$-excess measured on the Chajnantor Plateau are generally unrelated to source area location, RH$_{source}$, or $d$-excess$_{initial}$, but they are likely related to different in-cloud condensation temperatures;

(3) While condensation under ice supersaturation conditions can explain much of the joint distribution of $d$-excess and $q$, the joint distribution of isotopic ratios ($\delta D$ or $\delta^{18}O$) and $q$ requires that mixing exert a primary control over isotopic variability in the dataset.

Our results provide empirical support for the broad range of $d$-excess predicted by microphysical [e.g. Bolot et al., 2010], single column [e.g. Bony et al., 2008], cloud-resolving [e.g. Blossey et al., 2010], and general circulation [e.g. Yoshimura et al., 2008; Risi et al., 2010] models. Although general circulation models predict the broad range of $d$-excess in the upper troposphere, they do not accurately predict the variability that we observe at 500 hPa in the subtropics. Examining the full data set allows us to see that
some balance of condensation under ice supersaturated conditions and mixing produce
the range of isotopic ratios and $d$-excess we observe at Chajnantor Plateau. The full data
set provides a general overview of the range of processes involved, but the analysis is
underconstrained in that a range of RH$i$, $\delta D_{\text{initial}}$, $\delta^{18}O_{\text{initial}}$, $q$, and amount of mixing can
produce each measurement. Determining precise processes that set specific isotopic ratios
and $d$-excess values will require detailed analysis of specific events with high, low, and
median $d$-excess values.

4.6. References for Chapter 4

Bailey, A., D. Toohey, and D. Noone (2013), Characterizing moisture exchange between
the Hawaiian convective boundary layer and free troposphere using stable isotopes in

Blossey, P. N., Z. Kuang, and D. M. Romps (2010), Isotopic composition of water in the
tropical tropopause layer in cloud-resolving simulations of an idealized tropical

Bolot, M., B. Legras, and E. J. Moyer (2013), Modelling and interpreting the isotopic
composition of water vapour in convective updrafts, *Atmos. Chem. Phys.*, 13(16),

Bony, S., C. Risi, and F. Vimeux (2008), Influence of convective processes on the
isotopic composition ( $\delta^{18}O$ and $\delta D$) of precipitation and water vapor in the tropics:
1. Radiative-convective equilibrium and Tropical Ocean–Global Atmosphere–
Coupled Ocean-Atmosphere Response Experiment (TOGA-COARE) simulations, *J.

Ciais, P., and J. Jouzel (1994), Deuterium and oxygen 18 in precipitation: Isotopic model,
2012)*, 99(D8), 16793–16803.

Cohn, M., and H. C. Urey (1938), Oxygen exchange reactions of organic compounds and


UMA (2013), Humidity Conversion Formulas: Calculation formulas for humidity, Vaisala Oyj.


5. CONCLUDING REMARKS AND FUTURE WORK

Isotopic ratios in water vapor can serve as a valuable tool for distinguishing between processes that control the vertical and lateral distribution of humidity, and advances in satellite and commercially available CRDS instruments provide a means to make long-term measurements of atmospheric water vapor over large regions. In this dissertation, I have focused on processes that control humidity over tropical and subtropical South America in an effort to understand: 1) controls on paleoprecipitation preserved in tropical Andean glaciers, 2) seasonal variations in the vertical extent of the isotope amount effect, and 3) the range of processes involved in setting isotopic ratios in subtropical water vapor.

5.1. Conclusions

There are several common themes that came out of this study. First, theoretical studies show that convective intensity is likely responsible for the observed “isotope amount effect” in which isotopic ratios decrease with increased precipitation or water vapor amount. We link water vapor with δD values that are lower than predicted by Rayleigh fractionation (i.e. ΔδD < 0‰) with indicators of convection, including low upwind outgoing longwave radiation, convective precipitation, and high equivalent potential temperature. In the tropical Andes, water vapor with negative ΔδD is associated with South American Summer Monsoon (SASM) convection in austral summer and convection in the Intertropical Convergence Zone in austral winter (chapter 2). Maximum ΔδD is lowest over the SASM domain in austral summer and over the tropical Pacific in austral winter. Low maximum ΔδD and vertically extensive zones of negative ΔδD are associated with deep convection over these regions in different seasons (chapter 3).
In subtropical South America, $\Delta \delta D$ is generally higher and most isotopic measurements lie above the Rayleigh curve. This pattern underscores the importance of advective mixing in controlling isotopic ratios in subtropical atmospheric water vapor. Continuous measurements of $\delta D$, $\delta^{18}O$, and $q$ on the Chajnantor Plateau in northern Chile show that mixing exerts a primary control over isotopic ratios in water vapor that reaches the site. These measurements are more precise than previous measurements at this site, allowing us to formally examine the $d$-excess parameter, which is a measure of non-equilibrium fractionation. On dry days (i.e. $q \leq 500$ ppmv) $d$-excess in water vapor measured from the Chajnantor Plateau is consistent with condensation under ice supersaturation conditions with relative humidity between 101% and 120% prior to mixing with moister air en route to the measuring site.

5.2. Future Work

The tools described here can be used to answer a number of questions related to modern moisture transport and to inform the study of ancient climate. Further constraining conditions responsible for controlling the $d$-excess at the Chajnantor Plateau will require a detailed examination of the upwind meteorological conditions along trajectories launched from measurements representative of the range of $d$-excess (Figure 5.1) along with modeling to determine the optimal combination of RHi, $\delta_{\text{initial}}$, initial $d$-excess, and mixing fraction required to reproduce $d$-excess, $\delta D$, and $\delta^{18}O$. 
Figure 5.1. Variations in measured (A) mixing ratio, (B) $\delta$D, (C) $\delta^{18}$O, and (D) $d$-excess on December 30, 2012.

It is also possible to expand the study of the isotope amount effect over South America to the study of other areas influenced by monsoon convection, including the Tibetan Plateau. Understanding processes that influence moisture transport to high peaks on the Tibetan Plateau is important for understanding regional water resources [e.g. Kehrwald et al., 2008; Mölg et al., 2013], paleoclimate information encoded in glacial ice [Yao et al., 2013], Indian Summer monsoon (ISM) intensity [e.g. Vuille et al., 2005], and troposphere-stratosphere moisture exchanges that affect global climate [e.g. Tian et al., 2011]. A complex interplay between large-scale circulations, including westerlies in the northern Tibetan Plateau, the ISM, and the East Asian monsoon, along with local
moisture recycling leads to interseasonal and interannual variations in moisture delivered to high peaks in the region, and there is some debate over dominant processes that influence precipitation in the transition zone between the monsoon-dominated southern Plateau and westerlies-dominated northern Plateau. Satellite measurements of water vapor isotopologues may provide a tool to distinguish between processes that deliver moisture to different parts of the Tibetan Plateau at different times of year.

5.3. Chapter 5 References


Möl, T., F. Maussion, and D. Scherer (2013), Mid-latitude westerlies as a driver of glacier variability in monsoonal High Asia, Nature Climate Change, 4(1), 68–73, doi:10.1038/nclimate2055.
