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Variability in HDO/H_2O abundance ratios in the tropical tropopause layer

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[1] The dehydration of air in the tropical tropopause layer (TTL) and mechanisms for the entry of water vapor into the stratosphere are investigated by an analysis of ACE-FTS profiles of temperature, water vapor, and the ratio [HDO]/[H_2O] expressed in δD notation. Month-to-month comparisons indicate greater seasonal variability than interannual variability between 25°S–25°N, thus comparisons are made between February, April, August, and October averages for the years 2004 and 2005 combined. The data indicate a pattern of seasonal variability which is clearer in the Northern Hemisphere tropics and a relationship between minimum temperature, minimum water vapor, and maximum HDO depletion, which exists beyond the estimated uncertainty in these values. The range of values observed for HDO depletion and comparisons to modeled Rayleigh distillation curves indicate an important contribution from convection in addition to gradual dehydration. Multiple factors including the shape of the δD profiles suggest that a likely mechanism for the convective influence is the lofting of ice particles in the tropical troposphere.

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1. Introduction

[2] Water is known to enter the stratosphere by vertical transport across the tropical tropopause layer (TTL) then circulate to higher latitudes [*Brewer*, 1949]. As air ascends across the TTL, condensation occurs so that the humidity of the air entering the stratosphere is controlled by the coldest temperature region that it encounters, called the ''cold trap''. However, if gradual vertical transport through a cold trap were solely responsible for the abundance of water in the stratosphere, the stratospheric entry value $[H_2O]_e$ is estimated to be approximately 4.5 ppmv, whereas observed values of $[H_2O]_e$ were generally 3–4 ppmv throughout the 1980s and 1990s [*SPARC*, 2000].

[3] A modification to the cold trap mechanism was suggested by *Holton and Gettelman* [2001] by accounting for the velocities of horizontal motion which are about 10^4 times greater than vertical velocities, but were generally not factored into simple dehydration models. Since the temperature of the TTL is not uniform with longitude, *Holton and Gettelman* [2001] suggested that most air entering the stratosphere will at one time pass horizontally through the coldest part of the TTL, referred to as the western Pacific cold trap, where air becomes dehydrated; then the net ascent in the tropics, when all longitudes are considered, would gradually transport the air to the stratosphere.

[4] Convective processes may also affect the humidity of the stratosphere, and it has been suggested that they can either hydrate or dehydrate the stratosphere depending on whether the air injected carries more or less water than the mean stratospheric levels [*Danielsen*, 1982]. The rapid lofting of ice particles by convective updrafts would hydrate the stratosphere if these particles were lofted past the temperature minimum [*Dessler and Sherwood*, 2004]. The particles would then vaporize in the lower stratosphere where the air is slightly warmer and unsaturated with respect to water vapor. *Sherwood and Dessler* [2000] have suggested a mechanism for convective dehydration in which localized deep convection brings air across the TTL where it encounters very cold stratospheric temperatures and becomes severely dehydrated. The dehydrated air would later mix with moister air throughout the stratosphere, therefore lowering the mean stratospheric water vapor abundance. Convection is common throughout the tropical troposphere up to ~14 km, but the degree to which it can penetrate the TTL, as required for the above two mechanisms to occur, is still uncertain and is the subject of ongoing study [*Folkins et al.*, 1999, 2006; *Gettelman et al.*, 2002; *Liu and Zipser*, 2005; *Dessler et al.*, 2006a, 2006b].

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Table 1. The Four Most Abundant Isotopologues of Water in the Standard Reference Material Vienna Standard Mean Ocean Water (VSMOW) [*IUPAC*, 1994; *Coplen*, 1994]

Isotopologue	Standard Abundance
$H_2{}^{16}O$	0.997317
$H_2{}^{18}O$	0.00199983
$H_2{}^{17}O$	0.000372
$HD^{16}O$	0.00031069
Total of above species	0.99999952

[5] Long-term records indicate significant interannual variability for both stratospheric water vapor and $[H_2O]_e$ including a recent period where both quantities were elevated [*Oltmans et al.*, 2000; *Rosenlof et al.*, 2001; *Nedoluha et al.*, 2003; *Nassar et al.*, 2005] in spite of the fact that overall TTL temperatures decreased over the same time period [*Randel et al.*, 2001]. While this interannual variability is not well understood, seasonal variability in the tropical lower stratosphere with the maximum amount of water observed during the Northern Hemisphere (NH) summer and the minimum amount during the NH winter, has been known for some time [*Mastenbrook*, 1968]. The seasonal pattern of water vapor entering the stratosphere in the tropics is commonly referred to as the ''tape recorder'', since it contains a record of water vapor maxima and minima over time [*Mote et al.*, 1996].

[6] Multiple studies using measurements as well as models provide evidence for the transport of water across the TTL into the stratosphere by gradual ascent and/or convective processes [*Moyer et al.*, 1996; *Sherwood and Dessler*, 2000; *Holton and Gettelman*, 2001; *Schmidt et al.*, 2005; *Gettelman and Webster*, 2005; *Smith et al.*, 2006], and some studies even show evidence of the transport of water by convection at midlatitudes [*Dessler and Sherwood*, 2004; *Fu et al.*, 2006; *Hanisco et al.*, 2007]. A thorough understanding of the relative contributions of all important mechanisms for the transport of water to the stratosphere, as well as the variability in these contributions, should help to better understand the changes in $[H_2O]_e$ observed in recent years [*Oltmans et al.*, 2000; *Rosenlof et al.*, 2001; *Nedoluha et al.*, 2003; *Nassar et al.*, 2005].

[7] This work is an investigation of water vapor in the TTL region in order to gain a better understanding of processes relating to water entering the tropical stratosphere. Variability over a 2-a period is examined to determine if there is a pattern that may relate to the tropical tape recorder. The primary method for investigating these processes is by comparing profiles of temperature, volume mixing ratio (VMR) of water vapor $[H_2O]$, and $[HDO]/[H_2O]$ vapor ratios, all measured from the Atmospheric Chemistry Experiment (ACE) satellite.

2. Water Isotopologues

[8] The International Union of Pure and Applied Chemistry (IUPAC) defines isotopes as atoms with the same number of protons but a different number of neutrons, whereas isotopologues are molecules which differ only by their isotopic composition [*Brenninkmeijer et al.*, 2003]. The main water isotopologues and their abundances are shown in Table 1. Species such as those in Table 1 are often called isotopes, although this is not consistent with IUPAC nomenclature since the term isotopes should be used in reference to atoms, not molecules. The term isotopomer (short for isotopic-isomer) is sometimes used, but it is incorrect in this case since it should be used to refer to a molecule with the same isotopic atoms as another molecule, but in a different arrangement. Water does not have any isotopomers, whereas ozone, for example, has multiple isotopomers including $^{16}O^{18}O^{16}O$ and $^{18}O^{16}O^{16}O$, which are also minor isotopologues. Mass numbers for each atom can be shown as left superscripts as above, but since no isotopologues with more than one nonprimary isotope (i.e., D_2O or $HD^{17}O$) are dealt with in this work, mass numbers are only included when it would otherwise not be clear from the context if referring to a specific isotopologue or the total of all isotopologues in a chemical species.

[9] Since HDO and the other heavy isotopologues of water have a lower vapor pressure than H_2O, fractionation will occur during certain processes such as condensation or sublimation. These processes result in the condensed phase (liquid or ice) becoming enriched in the heavier isotopologue and the vapor becoming depleted. For this reason the isotopic composition of water vapor in the TTL region can act as a useful tracer for determining the type of hydration or dehydration processes which have occurred. The standard convention is to express the VMR ratio of a less abundant isotopologue to the primary isotopologue, relative to the standard abundance in the reference Vienna Standard Mean Ocean Water (VSMOW) [*Coplen*, 1994] using the following relationship:

$$\delta D = 1000 \times \left[\frac{([HDO]/[H_2O])_{measurement}}{([HDO]/[H_2O])_{VSMOW}} - 1 \right] \qquad (1)$$

Water vapor with 67% of its HDO removed would be described as $\delta D = -670‰$ or -670 per mil.

[10] Some early atmospheric δD ratios were measured in samples of upper tropospheric air collected during an aircraft campaign [*Ehalt*, 1974]. The Aircraft Laser Infrared Absorption Spectrometer (ALIAS) instrument [*Webster and Heymsfield*, 2003], the Integrated Cavity Output Spectroscopy (ICOS) instrument, and the Hoxotope instrument [*Hanisco et al.*, 2007] are some examples of direct in situ measurements from aircraft. Remote measurements have been made by the balloon-borne Michelson Interferometer for Passive Atmospheric Sounding (MIPAS-B) [*Stowasser et al.*, 1999] and Far Infrared Spectrometer (FIRS-2) [*Johnson et al.*, 2001a], but the main set of remote measurements analyzed in the literature come from the Atmospheric Trace Molecule Spectroscopy (ATMOS) experiment [*Rinsland et al.*, 1991; *Moyer et al.*, 1996; *Ridal*, 2002; *Ridal and Siskind*, 2002; *Kuang et al.*, 2003] and are mostly stratospheric measurements. *Moyer et al.* [1996] were the first to suggest that δD could be used to investigate dehydration and stratospheric water entry mechanisms, but the ATMOS data set only included 16 tropical occultations, with only four extending below the stratosphere to span the TTL region. More recently, MIPAS on ENVISAT [*Steinwagner et al.*, 2007; *Payne et al.*, 2007] and the Tropospheric Emission Spectrometer (TES) on the Aura satellite [*Worden et al.*, 2006] have begun retrieving both

HDO and H_2O from measurements of the troposphere and lower stratosphere. The first scientific study utilizing TES HDO data has focused on precipitation in the tropical lower troposphere [*Worden et al.*, 2007].

3. ACE-FTS H_2O and HDO Retrievals and the Tropical Data Set

[11] The Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS) is a high-resolution infrared Fourier transform spectrometer (FTS) on the SCISAT-1 or ACE satellite, launched in August 2003 to an orbit with an altitude of ~650 km and an inclination of 74° [*Bernath et al.*, 2005]. A description of the ACE-FTS retrieval approach is given by *Boone et al.* [2005], although the retrievals have undergone many recent improvements. The ACE-FTS measures the four water isotopologues listed in Table 1, as well as multiple isotopologues of other species including CH_4 and N_2O. HDO is included as an update to version 2.2; however, data for the other non-primary isotopologues have not yet been released. The v2.2 H_2O retrieval used in this work utilizes 67 microwindows to retrieve H_2O from 5.5 to 88.5 km in altitude. Four of these microwindows are in the 953–975 cm^{-1} range, and one is near 2137 cm^{-1}, but the majority are in the 1362–2004 cm^{-1} range. The HDO retrieval utilizes 26 microwindows in the 1402–1498 cm^{-1} and 2612–2724 cm^{-1} ranges to retrieve HDO from 6.5 to 37.5 km in altitude. Deviations from the Voigt line shape yield large *W*-shaped residuals at low altitudes in the analysis of both H_2O and HDO. These line shape problems could deteriorate the accuracy of the retrievals, particularly below about 15 km. Future processing of H_2O from the ACE-FTS measurements will employ a different line shape function, such as the speed-dependent Voigt profile, as soon as the appropriate spectroscopic constants become available [*Boone et al.*, 2007]. About 30 of the approximately 500 occultations used in this work were processed with a slightly modified v2.2 update for HDO. The modified retrieval was necessary when the initial retrieval did not process to completion in v2.2, and in a few cases HDO was retrieved for a second time when the initial retrieved result had unphysical oscillations or spikes due to clouds in the field of view (FOV). Of the retrievals attempted a second time, any that still had obvious problems were not used. Although the large number of species studied by the ACE-FTS is a major strength of infrared FTS remote sensing, the retrieval difficulties that result from clouds in the FOV are a limitation which results in a clear-sky bias, since retrievals of measurements near appreciable cloud thickness frequently fail.

[12] For all ACE-FTS species, including both primary and minor isotopologues, VMR values provided represent the total VMR for all isotopologues of the species on the basis of a retrieval using that specific isotopologue and an assumed abundance. The ACE-FTS data are provided in this way as a direct result of the manner in which line intensities are given in the HTRAN database [*Rothman et al.*, 2005], which is the primary source of spectroscopic parameters for ACE-FTS retrievals. HITRAN line intensities have been divided by their standard abundance so that spectral lines of any isotopologue can be used to retrieve directly the total VMR of a species by assuming it was measured at standard abundance conditions. Stating the combined VMR of all isotopologues is the most straightforward method for the majority of ACE-FTS data users who most likely want profiles of total water and not just the $H_2^{16}O$ isotopologue, or total methane and not just $^{12}CH_4$. To obtain the actual HDO or $H_2^{16}O$ VMR, the given VMR value must be multiplied by its standard abundance as given in the HITRAN database.

[13] Since ACE is primarily a solar occultation mission and the ACE orbit is optimized for measurements over the poles and midlatitudes, tropical measurements are sparse. As a general rule, ACE only has the opportunity for tropical measurements during even-numbered months (February, April, August, June, October, and December), and these measurements occur only at times in the ACE orbit when the beta angle (β) is high. β is the angle between the satellite orbital plane and the Earth-Sun vector. When $\beta = 0$, the Earth-Sun vector is in the orbital plane and the Sun sets (or rises) rapidly in a vertical direction with respect to the horizon as viewed from the satellite. For high β occultations the Sun appears to set (or rise) at an inclined angle with respect to the horizon. High-β occultations have a greater number of individual tangent point measurements than lower-β occultations, and this causes problems for two reasons. First, this makes the time for a single sounding longer, resulting in a profile that is not quite vertical since the occultation is smeared over a large horizontal distance, mostly in the north-south direction. For an occultation with $\beta = 60°$ the horizontal change between the surface and 17 km is ~6370 km if the effects of refraction are included. The second problem results from having more individual FTS spectra in an occultation and thus a larger volume of data for downlink. With a limited amount of downlink capacity available to ACE, very high β occultations are frequently not measured because a single one can have the same data volume as three low-β occultations, and tropical measurements are generally of a lower priority than middle and high-latitude measurements for the ACE mission.

[14] Figure 1 shows a map of the locations of the 17.5 km altitude point for all ACE-FTS HDO tropical profiles (defined here as 25°S–25°N) in 2004 and 2005. Figure 2 shows an example of temperature, [H_2O] vapor, and δD profiles for the Southern Hemisphere (SH) tropics during the months of April 2004 and 2005 averaged together. (Note that by design the ACE orbit repeats annually.) Much of the stratospheric variability in the [H_2O] profiles is a result of methane oxidation [*Nassar et al.*, 2005, and references therein]. The temperature profiles and [H_2O] profiles have a comparable amount of variability, although the temperature profiles have a smoother shape. The δD profiles exhibit the most variability, much of which can be attributed to spectral noise because of the lower signal-to-noise ratio for HDO, as well as the fact that δD is derived from two quantities ([H_2O] and [HDO]), each contributing to the error. The position of the hygropause (or water vapor minimum) is located at a slightly higher altitude than the temperature minimum, and both are above the altitude of maximum HDO depletion indicated by the minimum in the δD profile.

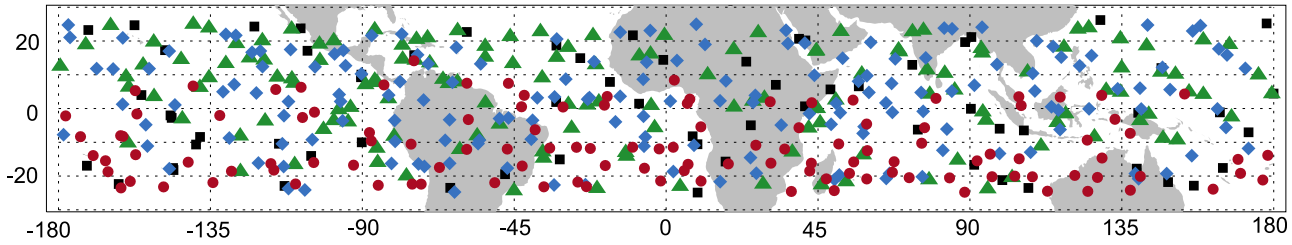

Figure 1. Distribution of ACE-FTS tropical (25°S–25°N latitude) measurements during 2004 and 2005 (based on the position of the 17.5 km point) used in this work. Different markers indicate the month: February (black squares), April (green triangles), August (blue diamonds), and October (red circles), with more details given in the text and Table 2.

[15] The δD profiles can be corrected for the stratospheric production of H_2O by CH_4 and the production of HDO via the net reaction

$$CH_3D + 2O_2 \rightarrow CO_2 + H_2O + HDO \quad (2)$$

[16] Application of a correction for the oxidation of methane was tested with ACE-FTS δD profiles. Ultimately, we decided not to apply the correction in order to avoid potentially introducing a bias from assumed profiles, since the stratospheric chemistry of CH_3D may differ from that of $^{12}CH_4$ [*Irion et al.*, 1996], which would contribute error with this method of correction. Future investigations may use ACE-FTS retrievals of the minor methane isotopologues to correct for methane oxidation in the stratosphere, but Figure 2 indicates that the correction is insignificant

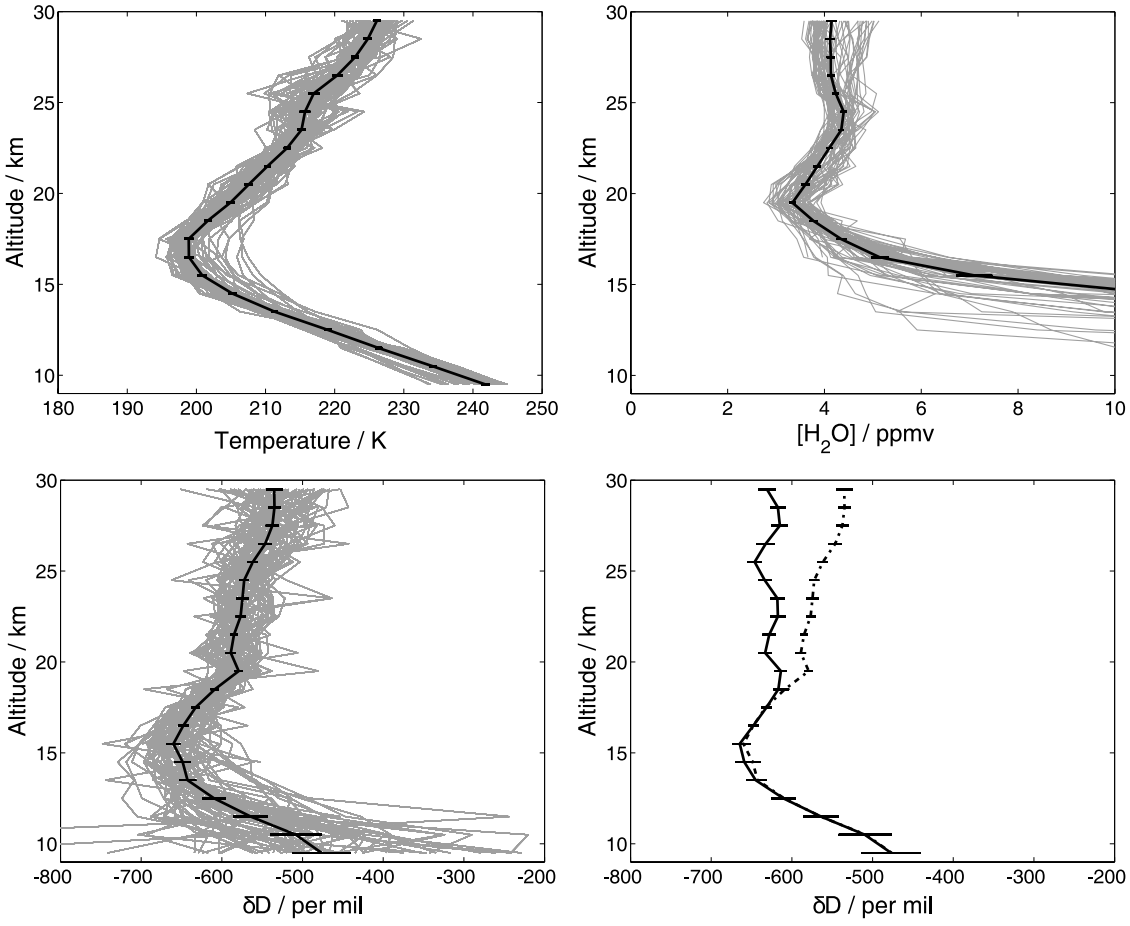

Figure 2. Sixty-eight temperature, [H_2O] vapor, and δD profiles for the SH tropics (0–25°S) during August 2004 and 2005 (gray lines). Thicker black lines are the combined August 2004–2005 mean profiles. (bottom, right) SH tropics August mean δD profiles with no correction for methane oxidation (dash-dot line) and with a correction based on assumed abundances of $^{12}CH_4$, $^{13}CH_4$, and CH_3D (solid line). All error bars indicate the 2σ precision of the mean profiles.

Table 2. The Number of Tropical Occultations in Each Hemisphere Sorted by Month, Along With the Mean Latitude of the 17.5 km Tangent Point in the Measurements

		2004		2005		2004 and 2005	
		n	Mean Latitude	*n*	Mean Latitude	*n*	Mean Latitude
NH	Feb	24	13.7°	8	17.5°	32	14.7°
	Apr	31	12.3°	67	13.6°	98	13.2°
	Aug	51	13.3°	44	11.2°	95	12.3°
	Oct	6[a]	3.4°	20	4.3°	26	4.1°
SH	Feb	7	−5.5°	27[b]	−15.2°	34	−13.2°
	Apr	10	−6.1°	38	−12.4°	48	−11.1°
	Aug	30	−11.1°	38	−11.1°	68	−11.1°
	Oct	39	−14.1°	56	−16.6°	95	−15.6°

[a]Includes one equatorial profile with the 17.5 km point in the SH, but the troposphere is mostly in the NH.
[b]Includes one profile with a reference date and time of 2005-01-31, 2301 UT.

below ∼18.5 km, which is the most important altitude range in the present work.

4. Month-to-Month Comparisons

[17] Tropical monthly averages in each hemisphere for ACE-FTS measurements in 2004 and 2005 will now be examined. For some of the reasons mentioned in the previous section, there are not enough June or December occultations available to obtain monthly averages, so only February, April, August, and October are compared. These months approximately correspond to the NH seasons (February: winter; April: spring; August: summer; and October: autumn). The number of occultations averaged in each hemisphere for each month is shown in Table 2, along with the mean latitude of the measurements. Figure 3 shows the separate hemisphere comparisons of the monthly averaged temperature, [H_2O] vapor, and δD profiles. In an initial analysis, profiles were only separated by month and year; however, close examination indicated significant hemispheric asymmetry, so in a second trial, profiles were separated by month, year, and hemisphere. If fewer than ∼15 profiles are averaged, δD profiles often have a jagged shape which can be attributed to a combination of both noise and small-scale atmospheric variability. To prevent basing averages on low numbers of profiles, while still adequately examining seasonal and hemispheric variability, equivalent months in 2004 and 2005 were combined in the current comparison and for the majority of this work. When a sufficient number of profiles were available for a given month in both 2004 and 2005, large differences between the years were not observed, as shown in Figure 4.

[18] The latitude and longitude values for the 17.5 km point (the approximate position of the cold point tropopause) were determined from a model which accounts for the ACE orbit and the effects of refraction of infrared light through the atmosphere. These coordinates, rather than the more commonly used 30-km reference point for ACE-FTS measurements, were used to determine if an occultation was tropical, to which hemisphere it belonged, and the mean latitude in Table 2. If a latitude and longitude array was not available from the model (which occurred less than 5% of the time), then the coordinates were determined by interpolating between latitude and longitude shifts in neighboring occultations which have a very similar β effect.

[19] Figure 3 indicates that for both hemispheres the coldest TTL temperatures occurred in February, followed by April, then October, and finally August. In the NH the ACE-FTS mean profiles exhibited larger seasonal differences than in the SH, where February and April profiles were very similar, as were the October and August profiles. In addition, the altitude of the temperature minimum in the NH was lowest in August and highest in February, while in the SH an altitude variation of the temperature minimum is not as clear. All of these results are consistent with the conclusions of *Seidel et al.* [2001] based on radiosonde measurements.

[20] For water vapor profiles in both hemispheres the lowest VMR values occurred in February, followed by April, then August, and finally October; however, the shape of the profiles changed significantly from one month to the next. The changing shape of these profiles can be understood to some extent by examining the modeled profiles of *Holton and Gettelman* [2001]. The ordering of ACE-FTS water vapor profiles by season was very similar to the model, but minima in the measured profiles were not as sharp. The lack of sharp minima is expected on the basis of the vertical resolution (typically 3–4 km) of the ACE-FTS measurements, but an additional reduction in the sharpness of the minima can also be attributed to the horizontal averaging of multiple profiles exhibiting differences in the altitude of their minima.

[21] In the ACE-FTS water vapor profiles it appears that the minimum in the profile, corresponding to the most dehydrated air, is propagating upward in time, while the air is simultaneously undergoing mixing and chemical production of water from methane. This upward propagation demonstrates the tropical tape recorder effect. In both hemispheres the April profiles even show a weak secondary minimum in the lower stratosphere which may be from the previous winter. The minima appear to be separated by ∼9 km, which implies a mean upward propagation rate of 9 km/a or ∼0.285 mm/s, whereas the separation between tape recorder minima modeled by *Mote et al.* [1996] is about 10–11 km. The slightly lower rate of upward propagation in the ACE data may just be a result of a relaxed definition of the tropics, including measurements up to 25° latitude, which is close to the subtropical jets where net downward motion in the troposphere dominates. It may also result from minima being dampened by averaging, where there was variability in the individual profile minimum heights. It is not clear why the secondary minimum is more prominent in April than during other months (although for October it would be partially above the altitude range shown). In the stratosphere the extent of methane oxidation will have a large impact on the profiles. The minima at 15.5 and 25.5 km in the methane-corrected δD profile in Figure 2 are further evidence of the tape recorder effect, where the 10 km/a separation is in better agreement with *Mote et al.* [1996], but the profile in Figure 2 also shows a small unexplained local minimum around 20 km, perhaps due to noise. It should be noted that there is a larger than expected vertical offset for the NH October [H_2O] vapor minimum in Figure 3, which may be the result of a latitudinal bias, since it has a lower mean latitude than the other averages.

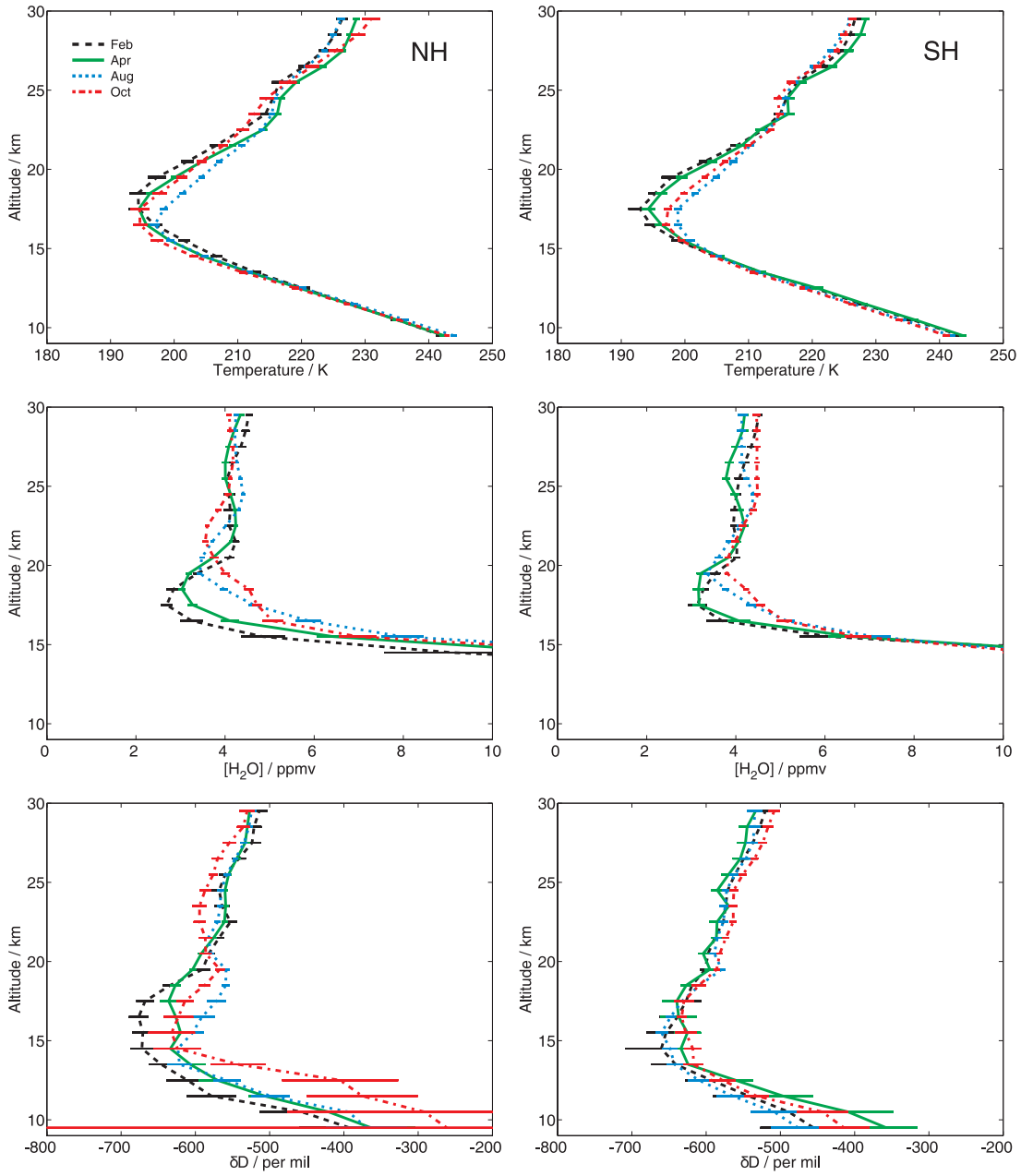

Figure 3. Combined 2004–2005 monthly averaged NH tropics (left) and SH tropics (right) profiles of temperature, water vapor, and δD. Error bars indicate the 2σ precision of the mean profiles.

[22] The δD profiles in the NH exhibit a large amount of seasonal variability, while those in the SH show much less. In both hemispheres, February profiles are the most depleted, with the NH February average reaching −676‰ at 16.5 km and the SH February average reaching −660‰ at 14.5 km. In the NH the ordering of the amount of depletion in the δD profiles is the same ordering as for the minimum temperature values. In the SH the August profiles are depleted nearly as much as the February profiles, and the SH April and October δD profiles were very similar although their temperature and water vapor profiles were different.

[23] The monthly averaged profiles in each hemisphere indicate a relationship between tropopause temperature, water vapor, and the degree of HDO depletion, although the minima in the δD profiles are found at lower altitudes than the temperature or water vapor minima.

[24] In general, there is a good seasonal correspondence between the lowest water vapor and largest depletion. In the NH above ~22 km the seasonal cycle of depletion is reversed from that at ~14–17 km. This seasonal δD pattern is indicative of vertical transport similar to that of water vapor and could potentially be clearer if a correction for methane oxidation were applied. In the TTL below the cold point, there are broad regions where near-maximum depletion is reached with much higher water vapor concentrations. *Gettelman and Webster* [2005] noted that high supersaturations which occur in cirrus clouds in the TTL

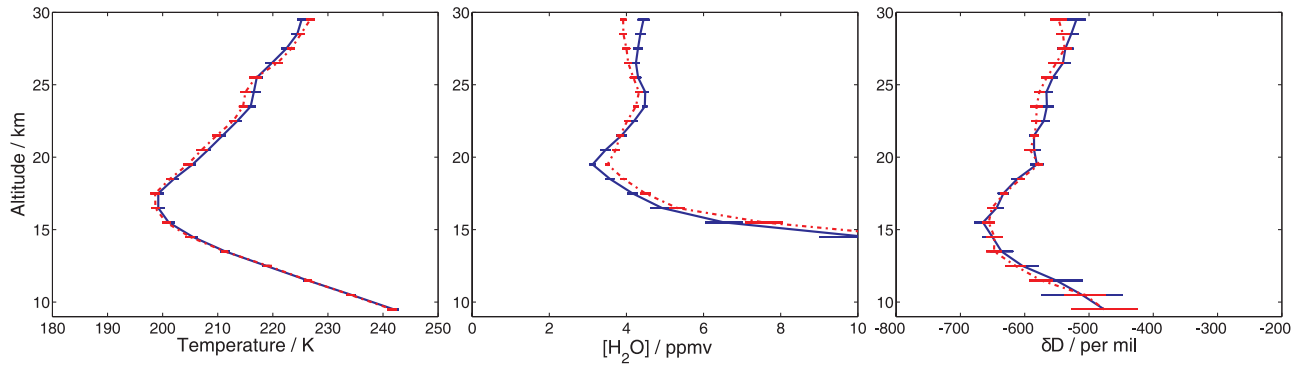

Figure 4. A comparison of SH tropics August 2004 (blue solid line) and 2005 (red dash-dotted line) mean temperature, $[H_2O]$, and δD profiles, showing that all pairs of profiles, especially the temperature and δD profiles, are very similar. Error bars indicate the 2σ precision of the mean profiles.

tend to inhibit fractionation. This may also be a region where lofted ice is most important. These relationships are not as strong in the Southern Hemisphere, although it is not obvious why this hemispheric difference should occur, aside from the sampling differences between seasons and hemispheres shown in Figure 1. Figure 1 also indicates that only one February profile is located in the tropical western Pacific region, which is the region of coldest tropopause temperatures and lowest water vapor, which also complicates the analysis.

[25] The most common method for determining whether or not convective processes have played a role in regulating $[H_2O]_e$ is by comparing the observed δD values to those predicted for the equilibrium fractionation for a given temperature profile, referred to as Rayleigh distillation. The method for calculation of Rayleigh distillation profiles is described in detail by *Johnson et al.* [2001b]. Our Rayleigh distillation curves were calculated using the analytic model described by *Gettelman and Webster* [2005] which is based on similar principles. For these model runs we used the mean ACE-FTS temperature profiles and assumed 80% humidity initially, then allowed condensation to begin when 100% was reached. A critical relative humidity for ice was set at 100% in the calculation. The individual points from each ACE-FTS δD profile up to 18.5 km (shown in Figure 5) clearly differ from a Rayleigh distribution, with very few points below -800‰, although a small number of extraneous points (defined as points with $\delta D \leq -1000$‰) were omitted. Deviation from the Rayleigh distribution is usually cited as evidence for convective processes enriching air in HDO; but on its own it cannot definitively be used to distinguish whether the HDO enrichment relative to the Rayleigh curve has occurred via convective dehydration or the lofting of ice particles [*Keith*, 2000].

5. Discussion

[26] *Moyer et al.* [1996] state that isotopic data from the stratosphere alone may be sufficient to demonstrate whether the final dehydration of stratospheric air occurs in slow ascent rather than in convective penetration, if a clear seasonal cycle in stratospheric δD is detectable. *Ridal* [2002] and *Ridal and Siskind* [2002] modeled δD ratios throughout the stratosphere including seasonal factors and suggest that their results are consistent with ATMOS. However, it is not definitively stated in these three papers what the authors believe a seasonal cycle means in the context of mechanisms for entry of water into the stratosphere. *Sherwood and Dessler* [2003] state that one might interpret a seasonal cycle in δD at the TTL as an indication that convective processes do not often go beyond $\sim$16–17 km, because these processes would cause mixing and thus remove any seasonal signature, but they refute this by stating that it really depends on the details of the convective process. For example, processes that dilute water vapor, such as injecting dry air into the stratosphere, do not alter δD values, although injecting ice particles which introduces water would cause a change. *Keith* [2000] suggested that in order to determine if ice was lofted through the tropopause by convection or of it evaporated in the upper troposphere then ascended to the stratosphere, observations of isotopic fractionation at the top of the TTL are much more helpful than those in the stratosphere.

[27] Our measurements indicate seasonal cycles in temperature, water vapor, and δD profiles in the TTL and a relationship between the variability in these quantities. The relationship is clearer in the NH tropics where minimum values for these quantities occur in the NH winter and maximum values occur in the NH summer. Minima in δD can occur below the hygropause in a relatively wet region, which suggests that convective lofting of ice (enriched in HDO) which hydrates moist regions [*Dessler and Sherwood*, 2004] could frequently occur there. In addition, fractionation of water vapor is diffusion limited under supersaturated conditions, and so the limited depletion gradients at the top of the TTL (e.g., in February in the Northern Hemisphere) may be due to much of the remaining dehydration occurring within cirrus clouds as postulated by *Gettelman and Webster* [2005].

[28] In the ACE-FTS $[H_2O]$ versus δD plots shown in Figure 5, only points up to 18.5 km were included, below which methane oxidation is negligible. Deviation from the Rayleigh distribution in these plots is clear, implying a role for convective processes. The range of δD values that the points span for a given $[H_2O]$ value emphasizes the degree of variability which occurs, as has been noted previously by *Webster and Heymsfield* [2003], *Gettelman and Webster*

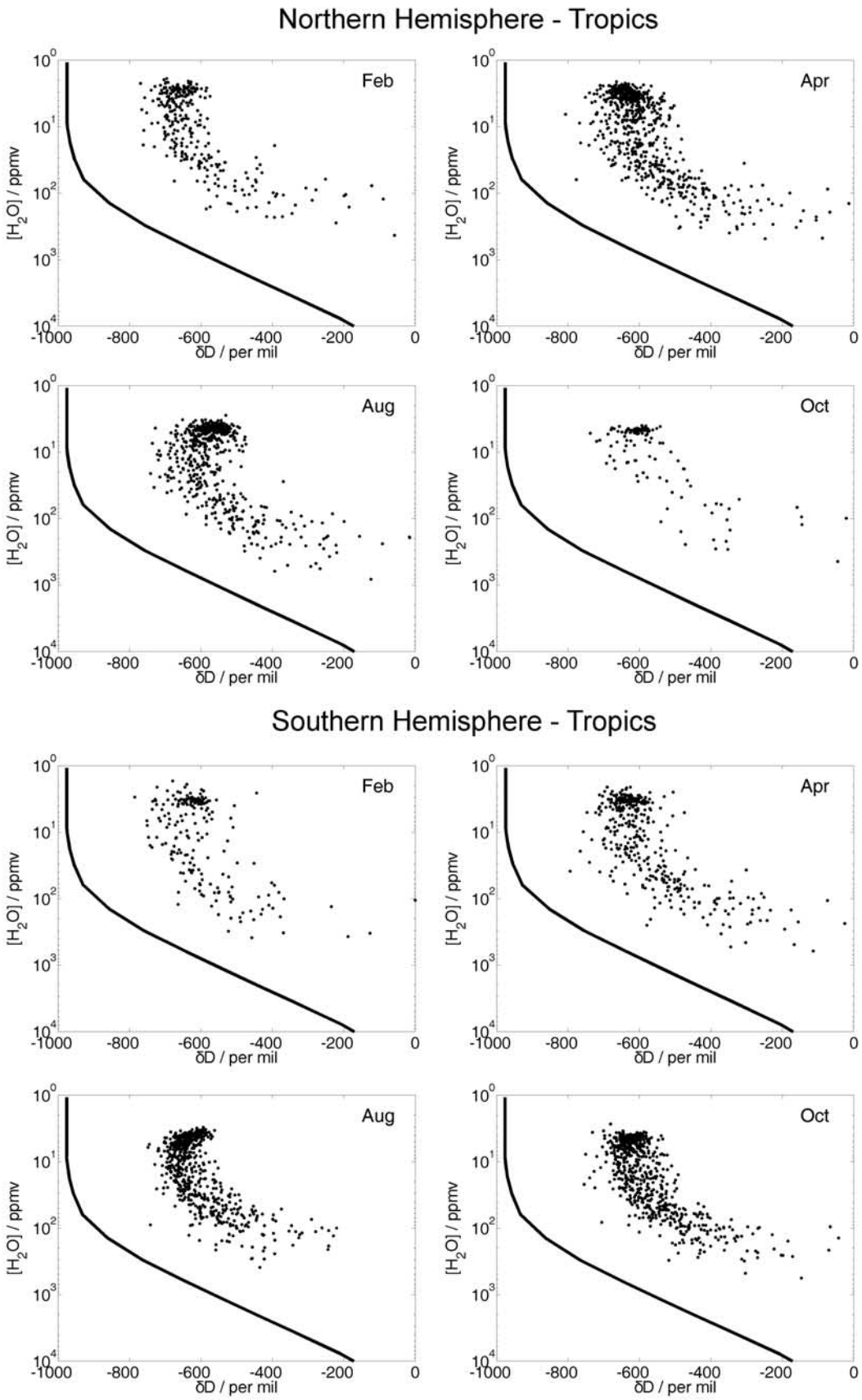
Northern Hemisphere - Tropics
Feb
Apr
Aug
Oct
Southern Hemisphere - Tropics
Feb
Apr
Aug
Oct
[H2O] / ppmv
δD / per mil
10^0
10^1
10^2
10^3
10^4
-1000
-800
-600
-400
-200
0

Figure 5

[2005], *Smith et al.* [2006], and others and suggests that multiple mechanisms may be involved. One implication of the fact that convective processes which dilute water vapor, such as injecting dry air into the stratosphere, do not alter δD values is that convective dehydration should produce a near-uniform altitude versus δD profile, but convective ice lofting should not. Localized convective episodes which loft ice particles would be consistent with a variable shape in the altitude versus δD profiles.

[29] *Kuang et al.* [2003] examined ATMOS [HDO] and [H_2O] in 11 tropical occultations from November 1994, which used better spectroscopic constants than were available in the past and found a near-uniform altitude versus δD distribution with a value of about -670‰ after correcting for methane oxidation. The ACE-FTS δD profiles show much less depletion in the stratosphere as a result of opting not to apply a methane correction, but they also show less depletion in the troposphere which is unrelated to methane oxidation. Some of the mean δD profiles shown in Figure 3 (NH February, NH April, SH April, and SH October) have a small, near-uniform range between $\sim$14–19 km corresponding to the TTL, but none are uniform over as wide of a range as given by *Kuang et al.* [2003].

[30] One possible reason for the discrepancy between the ACE-FTS results and the work of *Kuang et al.* [2003] may be their use of slant columns rather than VMR profiles retrieved by inversion. Although using slant columns avoids errors from the inversion process, profiles based directly on slant columns have a lower vertical resolution than profiles obtained by inversion. Each point in a profile derived directly from slant columns measured by a limb sounder does not represent the VMR at that altitude, but rather the integrated VMR for a slant column with a tangent height equal to that altitude, so contributions from higher altitudes effectively contaminate the measurement if they are not accounted for by inversion. This effect is negligible only if the true VMR profile decreases rapidly with altitude, which is not the case for H_2O or HDO at the TTL. This may explain why *Kuang et al.* [2003] have a near-uniform distribution of δD and values of about -650‰ as low as 11 km, while the ATMOS δD profiles given by *Moyer et al.* [1996] showed less depletion and a deviation from uniformity below $\sim$20 km (but did not reach as low in altitude). *Gettelman and Webster* [2005] have also shown that the ATMOS δD profiles are not uniform, especially when traceable to convection. *Dessler and Sherwood* [2003] cite the nearly uniform depletion with altitude obtained by *Kuang et al.* [2003] as evidence for the dominance of convective dehydration, but on the basis of the use of slant columns this interpretation should be questioned.

[31] *Gettelman and Webster* [2005] have shown that deviation from the Rayleigh curve does not require convective dehydration and can be explained by ice lofting during convective episodes. Although it is common to describe the tropical upper troposphere as a region of net ascent, clear-sky regions of the tropics have a net subsidence, while localized convection in clouds which is common up to $\sim$14–15 km [*Folkins et al.*, 1999] is responsible for most of the ascent. The frequency of convection overshooting the TTL and reaching the lower stratosphere is much less common [*Gettelman et al.*, 2002; *Liu and Zipser*, 2005; *Dessler et al.*, 2006a, 2006b], and for this reason alone one might expect that it would be difficult for convective dehydration to provide enough dry air to regulate the humidity of the stratosphere. Since we find no evidence of convective dehydration in the present work, it is unlikely to have a major role in determining the quantity of water in the stratosphere, but its contribution cannot be completely ruled out. Ice lofting would not need to reach the lower stratosphere to influence δD profiles, since lofting to altitudes at or just below the TTL would enrich those altitudes in HDO, some of which may subsequently be transported upward by gradual ascent, as suggested by *Moyer et al.* [1996]. Although the observed increases in δD with increasing altitude or decreasing water vapor are both consistent with ice lofting which penetrates the TTL, the degree to which this occurs versus lofting which stops below the TTL (thus providing a source of HDO-enriched air directly below it) cannot be determined from our results.

[32] This work was only intended as a first look at ACE-FTS HDO measurements and was not intended to settle all remaining questions about atmospheric transport or dehydration. A more sophisticated analysis of the data could involve separating the hemispheres by the variable position of the center of the intertropical convergence zone (ITCZ) rather than the equator, in order to avoid averaging together measurements of air which may be physically isolated. An analysis of tracers could also be used to discern tropical air from subtropical air rather than using the 25°N/S boundaries. Although only $\sim$500 occultations considered tropical were available for this work, the ACE-FTS is continuing to accumulate tropical measurements. With more measurements a study of longitudinal variability in the tropics may be possible. Investigations are also possible involving HDO at middle and high latitudes, for which many more measurements are currently available. An analysis of cloud locations inferred from ACE data would be a very useful aid in understanding convection. $H_2^{17}O$ and $H_2^{18}O$ can also be used [*Kaye*, 1990] to try to confirm the present findings or in conjunction with HDO, e.g., examining plots of δD versus $\delta^{18}O$.

6. Summary and Conclusions

[33] This work examined the seasonal variability in tropical temperature, water vapor, and δD profiles in 2004 and 2005, using ACE-FTS measurements. The minimum temperature and altitude of the cold point tropopause were found to exhibit a significant seasonal cycle in the NH, while only the minimum temperature varied in the SH. The δD also showed a seasonal variation which was stronger in the NH than in the SH, with the lowest δD values occurring during February in the NH, corresponding to the coldest temperature. In both hemispheres a relationship between

Figure 5. [H_2O] versus δD plots for all individual points from 9.5–18.5 km for each month shown with the Rayleigh distillation curve. No part of the distribution of ACE-FTS points approaches -970‰, as seen near the tropopause under Rayleigh distillation.

temperature, water vapor, and δD profiles was observed which suggests a role for gradual dehydration (including horizontal transport through a cold trap) and also indicates an important role for convective processes, evidenced by the range of δD values for a given [H_2O] value and the deviation from Rayleigh distillation curves which begins in the troposphere. Convection, which lofts ice crystals enriched with HDO, occurs throughout the tropics with the ability to reach a range of altitudes. In some cases the convection may penetrate the TTL, while at other times it will not, but can still have an affect on the pattern of HDO depletion at higher altitudes. It is difficult to determine from the present work how frequently convective episodes may loft ice particles directly into the TTL or into the lower stratosphere. A significant amount of dry air convection reaching the lower stratosphere would be necessary to lower the overall humidity of the stratosphere as required by the convective dehydration mechanism. Convective dehydration is expected to produce a uniform distribution in altitude versus δD profiles if it were the dominant mechanism [*Dessler and Sherwood*, 2003], which is not observed in these results over a significant altitude range. Consideration of these ACE-FTS results along with work described in the literature indicates that the entry of water into the tropical stratosphere likely occurs by a combination of gradual processes and convective ice lofting, which should be sufficient to explain the quantity of water in the stratosphere and the observed δD signature.

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