Measured HDO/H_2O ratios across the tropical tropopause

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[1] We present the first simultaneous measurements of HDO and H_2O in the tropical upper troposphere (UT) and lower stratosphere (LS) as derived from infrared solar absorption spectra acquired by the Atmospheric Trace Molecule Spectroscopy (ATMOS) experiment. We find, surprisingly, that the observed HDO/H_2O ratio does not decrease with altitude in this region despite a factor of 4–5 decrease in the water vapor mixing ratio. This observation is inconsistent with the view that dehydration in the tropical UT/LS is by gradual processes, and suggests a major role by convective processes. *INDEX TERMS:* 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 0399 Atmospheric Composition and Structure: General or miscellaneous; 3362 Meteorology and Atmospheric Dynamics: Stratosphere/troposphere interactions. **Citation:** Kuang, Z., G. C. Toon, P. O. Wennberg, and Y. L. Yung, Measured HDO/H_2O ratios across the tropical tropopause, *Geophys. Res. Lett.*, *30*(7), 1372, doi:10.1029/2003GL017023, 2003.

1. Introduction

[2] A recent assessment of stratospheric water observations obtained over the last 50 years concludes that there has been an approximate doubling in stratospheric humidity [*Rosenlof et al.*, 2001; *SPARC*, 2000]. Such a trend causes concern because stratospheric water plays important roles in the Earth's climate through its influences on radiation and ozone chemistry [*Forster and Shine*, 2002; *Kirk-Davidoff et al.*, 1999; *Shindell*, 2001]. The reason for the increase, however, is not well understood because the dehydration processes in tropical upper troposphere (UT) and lower stratosphere (LS) are poorly constrained.

[3] The amount (or volume mixing ratio - VMR) of stratospheric water vapor is determined both by the water VMR of air entering the stratosphere from the troposphere (primarily in the tropics for the part of the stratosphere that is above the 380 K isentrope, sometimes known as the "overworld") and by *in situ* production from oxidation of methane [*Hurst et al.*, 1999]. The latter source has increased significantly in the last 50 years, but can account for only about half of the observed change in stratospheric humidity. If the assessed trends in H_2O are correct, they could imply a substantial increase in the H_2O VMR of air entering the stratosphere. Much interest has been drawn to the dehydration processes in the tropical UT/LS, also known as the tropical tropopause layer, or the TTL, in order to understand what controls the stratospheric entry humidity [*Holton and Gettelman*, 2001; *Sherwood and Dessler*, 2001].

[4] There is a longstanding debate on the relative importance of the two processes that determines the stratospheric entry humidity - here labeled "gradual dehydration" and "convective dehydration" [*Holton et al.*, 1995]. Above ~13–14 km in the tropics (base of the TTL), the clear sky radiative heating is positive. Diabatic heating therefore causes air to ascend "gradually" towards the stratosphere. If at some point, this air becomes sufficiently supersaturated, ice crystals will form, grow and fall, leading to dehydration. In this "gradual dehydration" process, the humidity of the air entering the stratosphere is controlled by the coldest temperature, or more precisely the lowest saturation water VMR that it has experienced, often at or near the tropopause. The cold episodes can be induced by, for example, horizontal advection through a cold trap [*Holton and Gettelman*, 2001] or wave perturbations [*Potter and Holton*, 1995]. In contrast, in "convective dehydration", air detrained in the TTL from deep convection is already dehydrated to stratospheric abundances, and experiences little further freeze-drying during its subsequent gradual ascent towards the stratosphere [*Sherwood and Dessler*, 2001]. "Freeze-drying" here refers to the process of condensation and precipitation of ice particles. It is important to distinguish between these two processes because each is likely to have changed differently over the last several decades. If gradual dehydration dominates, we should look to changes in the temperature of the cold point as the primary forcing of stratospheric entry humidity. On the other hand, if convective processes control stratospheric entry humidity, we should look to changes in convection and cloud microphysics.

[5] A useful tracer for diagnosing the dehydration processes in the TTL is the isotopic composition of water vapor [*Moyer et al.*, 1996]. The minor water isotopic species, such as HDO, $H_2{}^{18}O$, and $H_2{}^{17}O$, have lower vapor pressures than $H_2{}^{16}O$. Hence, when vapor is in equilibrium with the condensed phases, greater portions of the minor isotopic species are partitioned in the condensed phases, a process termed "fractionation". As vapor condenses out of an air parcel, these minor isotopic species are preferentially removed and become progressively depleted in the residual vapor. Measurements of the isotopic composition can, therefore, be used to infer the condensation and evaporation history of the moisture. Among these minor isotopic species, HDO is particularly useful because of its large vapor pressure fractionation effect [*Merlivat and Nief*, 1967].

[6] Based on the measured isotopic composition of the stratospheric water, a HDO abundance of $\delta D = \sim -670‰$ was inferred for the vapor that enters the stratosphere [*Johnson et al.*, 2001b; *Moyer et al.*, 1996]. Following the convention, the HDO abundance has been expressed as deviations from that of the standard mean ocean water

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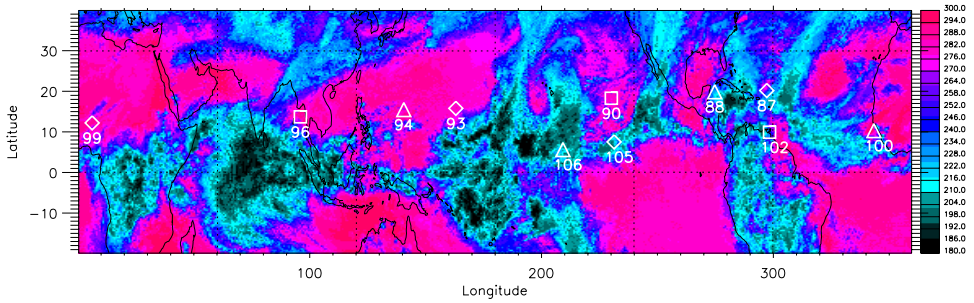

Figure 1. The locations of 11 tropical ATMOS altas-3 sunset occultations (white symbols) that extended below the tropopause. They were taken during Nov. 10–12, 1994. We also plot the minimum 11-μm brightness temperature over this period. The numbers refer to the occultation number in the ATMOS database.

(SMOW) in the so-called δ notation: $\delta D(‰) = 1000 \times \left[\frac{(\langle HDO\rangle/\langle H_2O\rangle)_{sample}}{(\langle HDO\rangle/\langle H_2O\rangle)_{SMOW}} - 1\right]$. This observation has been used to reveal the inadequacy of simple models that assume the air being steadily dehydrated as it ascends from the surface to the stratosphere, as these models predict a much reduced HDO abundance ($\delta D \sim -900‰$) at the tropopause [*Keith*, 2000; *Moyer et al.*, 1996]. Evaporation of lofted cloud ice, which is enriched in HDO relative to the environmental vapor, was suggested to resolve this discrepancy [*Keith*, 2000; *Moyer et al.*, 1996].

[7] It was also realized, however, that the stratospheric isotopic measurements provide little constraint for discriminating between the two proposed dehydration scenarios in the TTL [*Keith*, 2000]. For instance, convection could loft ice particles above the tropopause where they would evaporate, adding HDO-enriched moisture, as in the "convective dehydration" scenario. On the other hand, it is equally plausible that cloud lofting and evaporation occur well below the tropopause to provide a source of HDO-enriched moisture, which is then subject to further condensation and fractionation during the subsequent gradual ascent into the stratosphere. In order to discriminate between the two proposed dehydration scenarios in the TTL, observations throughout the tropical tropopause region are needed [*Keith*, 2000; *Moyer et al.*, 1996].

2. Data and Analysis

[8] We have derived the first profiles of HDO/H_2O ratios across the tropical tropopause from high spectral resolution (~0.01 cm^{-1}), infrared solar absorption spectra acquired by the Atmospheric Trace Molecule Spectroscopy (ATMOS) experiment during the ATLAS-3 space shuttle mission in 1994 [*Gunson et al.*, 1996]. We present data from 11 tropical occultations taken between 5°N and 20°N from Nov. 10 to Nov. 12. Figure 1 shows the locations of these occultations (white symbols) together with the minimum 11-μm brightness temperature obtained by geostationary satellites. Each occultation used one of the following three optical band pass filters: filter 3 (Δ), 1580–3340 cm^{-1}, filter 4 (◇), 3150–4800 cm^{-1}, and filter 9 (□), 600–2450 cm^{-1}. The minimum 11-μm brightness temperature was derived from 3-hourly geostationary satellite images averaged to a 0.3° × 0.7° resolution. Deep convection is marked by the low brightness temperatures. The tropical occultations that we chose in general reside in or near the inter-tropical convergence zone (ITCZ) region and are distributed over all longitudes. Tracers such as CO in these occultations show tropospheric concentrations (> ~80 ppbv) up to near tropopause (~16.5 km) altitudes and quickly decrease to a stratospheric value (<20 ppbv) (not shown). This is an indication that the upper tropospheric air sampled in these occultations is not significantly affected by recirculated air from higher latitudes. In contrast, the CO concentrations in the subtropical occultations start to decrease well below the tropopause (not shown). Since no ATMOS measurements were possible when the sun was blocked by optically thick clouds, our retrieved profiles are generally in the regions outside of deep convection. It is worth noting, however, that based on vertical velocity measurements [*Gage et al.*, 1991], tropospheric air may indeed enter the "overworld" stratosphere largely in the regions outside of deep convection [*Sherwood and Dessler*, 2001].

[9] While the raw data used are the same as in Moyer et al. [*Moyer et al.*, 1996], accurate retrievals of the HDO/H_2O ratio in the TTL has become possible only recently with the improved spectroscopic parameters of H_2O and HDO [*Toth*, 1998; *Toth*, 1999] and the extended retrievals deeper into the troposphere. We have identified appropriate spectral windows for each filter in order to retrieve the HDO and H_2O abundances. For spectra with tangent altitudes in the TTL, we identified ~25 suitable HDO absorption lines between 1300 and 1500 cm^{-1} for filter 9, ~30 lines between 2675 cm^{-1} and 2795 cm^{-1} for filter 3, and ~10 lines between 3760 and 3800 cm^{-1} for filter 4. We have used relatively weak absorption lines for retrieving $H_2{}^{16}O$ abundances to avoid saturation at the TTL altitudes. The consistency among the three filters is examined using spectra obtained during the Mark IV balloon flights [*Toon et al.*, 1999], which covered the spectral range of 650–5650 cm^{-1}. We find that the filter 9 windows consistently give a HDO mixing ratio ~12% higher than the other two filters at all altitudes. After this bias is corrected, the three filters agree within their individual errors. This correction has been applied to the HDO abundances retrieved from the filter 9 spectra in this study. Until the cause for the systematic difference between the spectral regions is understood, the absolute values of δD are subject to a ~50‰ uncertainty. It is therefore important to realize that the results presented in this work are based on the relative variations in δD and not its absolute accuracy.

3. Results and Discussions

[10] The HDO/H_2O ratios, expressed as δD, show little further fractionation above ~12 km (Figure 2a). For the

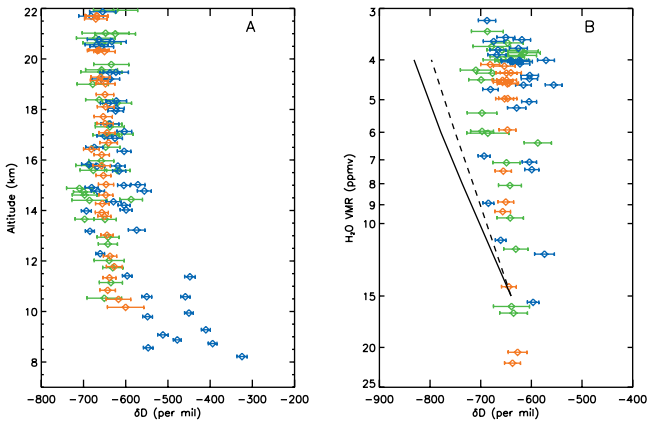

Figure 2. (a) The δD profiles from the 11 tropical occultations. (b) δD is plotted against the water mixing ratio [H_2O] for the altitude range of 11–19 km. The different filters are represented by different colors: filter 3, blue, filter 4, green, filter 9, red. The δD vs. [H_2O] relationship predicted by the Rayleigh distillation model, appropriate for the ''gradual dehydration'', is over-plotted in b (solid). The kinetic isotopic fractionation effect from a 20% supersaturation was included in calculating the dashed curve.

altitude range 11–19 km, there is little systematic change in δD despite a five-fold decrease in the water mixing ratio [H_2O] (Figure 2b). The HDO and H_2O abundances that we report are for the slant columns along the line of sight as measured by the instrument, not VMR profiles retrieved from these slant columns. In this way, errors associated with this extra step of retrieval are avoided. Effects due to errors in the tangent pressure (2%), the tangent temperature (3K), and the zero level offset (1%) have been folded into our error bars. The effect of methane oxidation has been removed [*Irion et al.*, 1996]. Unlike inferring the entry composition from the stratospheric measurements, our results are not sensitive to errors in this correction, as the effect of methane oxidation is small in the TTL.

[11] Because most convection does not extend above ~14 km [*Folkins et al.*, 1999], it was commonly assumed that convection did not have major effects on the characteristics of the bulk of the TTL [*Holton and Gettelman*, 2001]. If this is indeed the case, freeze-drying during the gradual ascent would have to be mainly responsible for the decrease of [H_2O] in this layer. During the gradual ascent, the air is in general stably stratified, and the sedimentation time for ice particles is rather short (a few hours) [*Jensen et al.*, 2001] compared to the timescale of the cold episodes (several days) [*Holton and Gettelman*, 2001]. Under these conditions, the fractionation of water vapor may be described by a Rayleigh distillation process, which assumes that the condensates formed are in equilibrium with the vapor and are removed as soon as they form[*Keith*, 2000]. Despite its simplicity, the Rayleigh model has been successfully used to describe the distributions of water isotopic compositions in the lower and middle troposphere when stably stratified conditions prevail [*Gedzelman*, 1988]. In Figure 2b, we show the δD vs. [H_2O] relationship predicted by the Rayleigh model with a starting composition of δD = −640‰ and [H_2O] = 15 ppmv, appropriate for the base of the TTL (solid curve). The fractionation coefficients that we use are extrapolated from the data by *Merlivat and Nief* [1967]. The predicted additional 200‰ depletion in δD as [H_2O] decreases from 15 ppmv to 4 ppmv is completely absent in the observations. Possible supersaturation during the gradual ascent [*Jensen et al.*, 2001] may reduce the fractionation, however, is insufficient to explain the difference. For instance, a 20% supersaturation reduces the fractionation by only ~30‰ (dashed line). The isotopic measurements therefore provide strong evidence that dehydration in the TTL cannot be mostly accomplished by gradual processes. In order to explain the lack of change in the isotopic ratios when the water VMR decreases by a factor of 4–5, convective influence in the TTL appears necessary.

[12] One possible and widely suggested way that convection may reduce the depletion of HDO is by lofting cloud ice to the TTL, which later evaporates. The water VMR still decreases with altitude, because air detrained at higher altitudes is still drier even with the evaporation of some lofted cloud ice. On the other hand, as the lofted ice particles are enriched in HDO, if their evaporation contributes substantially to the water vapor in the TTL, they can greatly affect the isotopic ratio distributions. Under certain assumed conditions, the isotopic ratio may even increase as [H_2O] decreases with altitude[*Keith*, 2000]. We note that isotopic evidence of ice lofting and evaporation has been documented near the midlatitude tropopause [*Smith*, 1992]. It is conceivable that the same process operates in the tropics as well.

[13] A model recently proposed for transport across the tropical tropopause [*Sherwood and Dessler*, 2001] may also help to explain the lack of δD gradient in the TTL. In this model, for the region outside of deep convection, less energetic convection supplies relatively moist air ([H_2O] ~ 15 ppmv) to the base of the TTL. During the air's subsequent gradual ascent (by radiative heating) towards the stratosphere, it further interacts with drier air supplied by the more energetic convective events that penetrate deeper into the TTL and reach colder temperatures. The water VMR of the air decreases as the air ascends, since the moisture is progressively diluted through mixing with the drier air. This water VMR decrease can be accomplished without significantly changing the isotopic ratio, because it is not directly related to condensation, thus does not involve further isotopic fractionation. As an illustrative, albeit unrealistic, example, consider the case when the air detrained from the more energetic convections has a negligible amount of moisture compared to the air that is gradually rising from the base of the TTL. In this case, the isotopic ratio would be constant all the way across the TTL, as all moisture in the TTL originates from the base of the TTL and has undergone no further phase change since then. The effect of this ''mix-drying'' mechanism on the isotopic composition of stratospheric water vapor was examined by *Johnson et al.* [2001a]. In reality, both evaporation of lofted ice and the ''mix-drying'' mechanism are likely to have contributed to the lack of δD gradient in the TTL.

[14] The difference between the HDO/H_2O ratios in the tropical UT and LS may be used to place an upper bound to the extent of gradual ''freeze-drying'' that can be accomplished by the tropical tropopause. For this purpose, it is

important that there is no significant altitude dependent bias in the derived δD. We have examined the effects of systematic errors in the zero level offset, tangent temperature, and the pressure broadening coefficients. The altitude dependent biases are estimated to be less than 10‰ across the TTL region.

[15] The averaged δD is −648‰ between 13 km and the tropopause (∼16.5 km) with a standard deviation of 40‰ (37 samples) and −639‰ between the tropopause and 19 km, with a standard deviation of 15‰ (23 samples). The samples are weighted by their individual uncertainties when we calculate the mean and the standard deviation. The estimated measurement uncertainty of individual samples in each region is on average about 21‰ and 25‰, respectively. The scatter in the upper troposphere thus exceeds what one expects from measurement errors by a factor of 2. This larger scatter may be a consequence of convection. More consistent values are found in the lower stratosphere where the convective influence diminishes. On the other hand, a 20% decrease in [H_2O] (from 5 ppmv to 4 ppmv) by gradual freeze-drying would produce additional depletion of ∼50‰ in δD. There is no evidence for such depletion. We note, however, that the coarse resolution (∼2 km vertical, ∼200 km horizontal) of the ATMOS measurements may hide localized depletions of this magnitude if ice lofting and evaporation produce a thin layer (<1 km) of HDO-enriched moisture beneath the tropopause. In situ data are needed to resolve these fine scale structures.

4. Conclusions

[16] The isotopic data presented here provide evidence for convective influence on the moisture in the TTL, and constrain the extent of gradual "freeze-drying" that can be accomplished by the tropical tropopause (either by going through a cold trap or by wave perturbations). These results suggest that viewing the tropopause temperature as the only control on stratospheric humidity may be too simplistic; changes in convection and cloud microphysics may be important for understanding past and future stratospheric humidity changes [*Sherwood*, 2002]. Our results demonstrate the value of water isotopic composition measurements in the TTL in understanding the dehydration processes in this region. As our observations are limited in temporal coverage, additional data of this sort are needed, particularly in establishing possible seasonal behavior and interannual variability.

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