Stratosphere-troposphere exchange: Inferences from the isotopic composition of water vapor

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Abstract. Air may cross the tropical tropopause either by gradual ascent or in localized episodes associated with convection. While observations demonstrate that water vapor mixing ratios of air entering the tropical stratosphere are consistent with the mean tropical tropopause temperature, they do not resolve key mechanistic questions, such as the relative contribution of gradual or episodic transport, or the role of thin cirrus. As *Moyer et al.* [1996] clearly argue, observations of the isotopic content of water entering the tropical stratosphere can provide a strong constraint on models of water vapor transport across the tropopause. For example, stratospheric HDO is too abundant to be compatible with the assumption that all moisture enters the stratosphere as vapor during convection. Analysis of recent $H_2{}^{18}O$ observations shows that kinetic effects cannot explain the HDO excess. Lofting and evaporation of cloud ice can explain the observed stratospheric water vapor content and its isotopic composition, but the relative importance of gradual or episodic transport remains unresolved.

1. Introduction

Water vapor plays a key role in stratospheric chemistry by regulating the threshold temperature at which heterogeneous chemistry on cold aerosols becomes important, and as the dominant source for HO_x. Water vapor in the overworld (the stratosphere above $\theta \approx 390\,\mathrm{K}$) enters the stratosphere near the equator and is supplemented by water formed from methane oxidation. While the methane oxidation source is well understood [*Hurst et al.*, 1999], mechanistic understanding of tropical stratosphere-troposphere exchange (T-STE) is weak, particularly with respect to the processes that control the water vapor mixing ratio of air entering the stratosphere ($[H_2O]_e$). A mechanistic understanding is needed to predict the influence of changing tropical tropospheric temperatures on stratospheric chemistry via changes in $[H_2O]_e$

Here we focus on the possibility that measurements of the isotopic fractionation of moisture in the tropical upper troposphere and lower stratosphere could provide a valuable tool to further our understanding of T-STE.

1.1. T-STE: Historical Development and Current Understanding

In order to place current uncertainty about the mechanisms of T-STE in context, we first reexamine two assumptions that have played a central role in analysis of T-STE: (1) that extensive clouds do not occur in the tropical upper troposphere, and (2) that $[H_2O]_e$ is too low to be explained by freeze-drying of air as it moves uniformly through the tropical tropopause. We will argue that both assumptions are false.

Robinson [1980] noted that *Brewer's* [1949] freeze-drying mechanism assumed that air entered the tropical stratosphere uniformly within ~10° of the equator. Robinson noted that such gradual, uniform, ascent would make the tropical upper troposphere saturated and cloudy. Because such clouds were not observed, and because then-current observations suggested that the tropical subtropopause region was undersaturated (assumption 1 above) Robinson concluded that T-STE must be associated with episodic convective events that penetrate the tropopause.

Holton et al. [1995] summarized and extended arguments showing that the net mass flux through the tropical tropopause is controlled nonlocally by angular momentum forcing in the extratropical stratosphere. While the mass flux through the ~400 K isentrope is likely controlled nonlocally, circulation in the tropical tropopause region (defined here as $350 < \theta < 400$ K) is poorly understood, particularly with respect to the magnitude of the convective mass flux. Following Holton et al., we will use "underventilated" to denote the state in which the convective mass flux into the tropopause region is smaller than the upward flux through 400 K that is controlled nonlocally and "hyperventilated" for the converse. Following the argument of *Robinson* [1980], *Holton et al.* [1995, p. 426] noted that "absence of a large-scale cirrus veil can be taken as evidence against such underventilation".

While there is no visible cirrus veil in the tropics, subvisual cirrus appear to be ubiquitous near the tropical tropopause. Observations include satellite infrared instruments [*Prabhakara et al.*, 1993], satellite limb occultation [*Wang et al.*, 1996], ground-based lidar [*Nee et al.*, 1998], aircraft lidar

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(Received January 29, 1999; revised October 11, 1999; accepted February 11, 2000)

Paper number 2000JD900130.
0148-0227/00/2000JD900130$09.00

and in situ instruments [*Heymsfield and McFarquhar*, 1996] and satellite lidar [*Winker and Trepte*, 1998]. The ubiquity of thin cirrus suggests that the tropical subtropopause region is frequently saturated, and thus that large-scale uplift is common. In contrast to *Holton et al.* [1995], we infer that the presence of a large-scale cirrus veil can be taken as evidence for underventilation.

Early observations [*Jones et al.*, 1986; *Kley et al.*, 1979] showed that air entering the tropical stratosphere was drier than predicted by freeze-drying at the zonal-mean tropopause temperature. Two explanations were advanced to explain the discrepancy. First, *Newell and Gould-Stewart* [1981] proposed that T-STE occurred preferentially at the times and in the locations with the coldest tropopause temperatures. *Danielsen* [1982] proposed an alternative dehydration mechanism in which convective events penetrate the stratosphere where subsequent differential radiative heating of the clouds induces mixing that efficiently removes cloud ice by precipitation. This hypothesis was attractive because it explained the dryness of both the stratosphere and the tropical uppertroposphere, the two key assumptions analyzed here.

Data from the NASA Water Vapor Exchange Experiment [*Kley et al.*, 1982; *Knolenberg et al.*, 1982] and Stratosphere-Trposophere Exchange Program topical mission (STEP/Tropical) [*Danielsen*, 1993] demonstrated that cumulonimbus clouds can penetrate the stratosphere and mix irreversibly with stratospheric air. Despite a measurement campaign focused on the most favorable season and location, only one such event was observed during STEP/Tropical, so these observations could not establish the frequency of such penetration, nor the magnitude of its contribution to T-STE. Satellite observations of cloud top temperatures suggest that optically thick clouds very rarely approach the height (inferred from brightness temperature) of the tropical tropopause [*Highwood and Hoskins*, 1998].

The mean mixing ratio of water entering the tropical stratosphere has remained controversial. *Dessler* [1998] combined five recent measurements yielding an overall estimated $[H_2O]_e$ of 3.8±0.3 ppmv. Using quality-controlled radiosonde data, and calculating the minimum mixing ratio for each sounding prior to averaging, Dessler found a tropical average minimum saturation mixing ratio (SMR) of 4.0±0.8 ppmv, in good agreement with the observed $[H_2O]_e$. The discrepancy between Dessler's work and earlier analyses arises both because early estimates of $[H_2O]_e$ were too low and because estimates for the tropical average minimum tropopause mixing ratio were too high. For example, *Newell and Gould-Stewart* [1981] used average 100 hPa temperatures to compute minimum SMR. Dessler shows that this method produces SMRs 50% larger than the mean of the minimum SMRs.

Analysis of recent in situ measurements allows a high-accuracy estimate of $[H_2O]_e$ to be obtained by extrapolation of the measured H_2O versus CH_4 correlation to the known tropospheric concentration of CH_4, yielding $[H_2O]_e$=4.0±0.3 ppmv [*Hurst et al.*, 1999]. Very similar results were obtained using two water vapor instruments that are independently calibrated and use different fundamental measurement methods: the Jet Propulsion Laboratory (JPL) tunable diode-laser hygrometer, and the Harvard Lyman α hygrometer, which itself has demonstrated in-flight agreement between Ly α absorption and photofragment fluorescence. At altitudes of 19-21 km the JPL and Harvard instruments agree to better than 1% with an offset of less than 0.1 ppmv [*Hintsa et al.*, 1999]. This close agreement strongly suggests that these measurements are correct, and that previous lower estimates of $[H_2O]_e$ are not reliable.

In summary, recent observations and analysis imply that (1) large-scale uplift is common in the tropical subtropopause region, and (2) that $[H_2O]_e$ matches the mean SMR of the tropopause. Together these observations suggest, but do not prove, that T-STE primarily occurs via large-scale slow ascent through the tropopause region.

1.2. "Gradual" Versus "Convective" T-STE

We now assume that the $[H_2O]_e$ is equal (within experimental uncertainties) to the mean minimum SMR of the tropical tropopause. This does not imply that air crosses the tropical tropopause at a spatially uniform rate. Indeed, such uniform T-STE is unlikely given the robust reasons to expect an anticorrelation between upward velocity and temperature. If we assume that air predominately enters the stratosphere at colder than average temperatures, then the observations imply that the stratosphere is moister than we expect from a freeze-drying process in which $[H_2O]_e$ is equal to the minimum SMR seen by an ascending parcel, precisely the converse of what has commonly been assumed. The likely mechanism for hydration is the lofting of hydrometeors through the tropopause into the lower stratosphere where they evaporate in the undersaturated air. Lofting may be accomplished either in cumulonimbus associated with deep convection or in thin cirrus associated with large-scale uplift.

To sharpen the discussion, we sketch two mechanistic scenarios for T-STE, "convective" or "gradual". In convective T-STE, we assume that convective events penetrate the tropopause. Air entering the stratosphere in convective events is cooler than the mean tropopause, so the SMR is below its mean tropopause value. The moisture budget is balanced by evaporation of hydrometeors lofted into the stratosphere.

In gradual T-STE we assume very little convection above ~150 hPa. Net upward mass flux above ~150 hPa is driven by nonlocal forcing. Uplift causes saturation and the formation of thin cirrus. Gravitational settling accomplishes dehydration of the air to the approximate saturation mixing ratio of the tropopause.

2. Isotopic Constraints on T-STE

Two processes fractionate water isotopes in the troposphere. The lower vapor pressure of HDO and $H_2{}^{18}O$ relative to H_2O is of primary importance; it produces fractionation between phases (e.g., vapor and liquid) in equilibrium. Of lesser importance is the "kinetic effect" due to the low diffusivity of the heavy isotopes that causes fractionation in diffusion-limited, nonequilibrium processes, such as condensation in supersaturated conditions. Fractionation is typically measured as deviation from standard mean ocean water (SMOW)

in parts per thousand (‰), denoted by δD or $\delta^{18}O$. Equilibrium fractionation in HDO is ~8 times larger than in $H_2{}^{18}O$, while their diffusivities are almost equal. Thus fractionation of $H_2{}^{18}O$ is more sensitive to nonequilibrium processes than is fractionation of HDO.

2.1. Model

If we assume that deep convection lofts air from cloud base to the tropopause without significant mixing, then the fractionation of water vapor may be simply modeled. Omission of mixing between cloud base and the detrainment level at cloud top is plausible because we are only interested in parcels that reach the top of the troposphere. In the tropics, θ_e has approximately equal maxima at the sea surface and the tropopause, with a mimimum in the middle troposphere. This temperature structure is evident in Figure 1, in which the moist adiabat is warmer than the mean sounding in the middle troposphere. During convection, air parcels that mix with environmental air at intermediate levels will therefore not have sufficient buoyancy to reach the tropopause (see the discussion of buoyancy sorting by *Emanuel* [1991]).

In the absence of mixing or particle evaporation, we may construct a one-dimensional isotopic model that predicts the isotopic composition of vapor during ascent along a specified temperature profile. If no isotopic equilibration is allowed between vapor and condensate, then we integrate

$$d\ln R_v = (\alpha(T)-1)\,d\ln q \qquad (1)$$

to find R_v, the isotopic mixing ratio in vapor, as a function of height. Where q is the specific humidity and α is the temperature-dependent fractionation factor between vapor and condensate: $R_{condensate} = \alpha(T) R_{vapor}$. If we allow complete isotopic equilibration, then R_v is given by

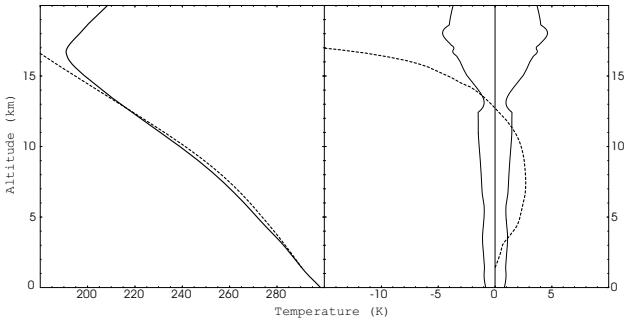

Figure 1. Temperature structure of the tropical atmosphere. (left) The heavy solid curve is a mean sounding from Menado and the dashed curve is a moist adiabat tied to the sounding at 850 hPa (see the end of section 2.1). (right) The deviation of the moist adiabat from the mean sounding is shown. Note the increasing stability above ~13 km where the adiabat becomes increasingly cooler than the sounding, suggesting a decreasing influence of convection in the upper troposphere. The thin lines bracketing the zero temperature axis indicate one standard deviation of temperature variance in the soundings. Note the increase in temperature variability with altitude.

$$R_v = \frac{R_{v0}}{(f(\alpha-1)+1)}, \qquad (2)$$

where f is the fraction of original vapor which has been condensed and R_{v0} is the initial isotopic fractionation of the vapor. There is no equilibration between ice and vapor, but significant equilibration may occur between vapor and liquid cloud droplets. As a reference case we switch between complete (equation (2)) and zero (equation (1)) equilibration at 0°C and then vary the altitude of the switch to gauge the magnitude of this uncertainty (see Table 1).

Standard equilibrium fractionation factors are used [*Majoube*, 1970, 1971; *Merlivat and Nief*, 1967]. Kinetic effects are included by adjusting α as a function of the saturation S of vapor relative to the condensate according to

$$\alpha_{kinetic} = \frac{\alpha S}{(\alpha D(S-1)+1)}, \qquad (3)$$

where D is the diffusivity of the isotope relative to H_2O [*Jouzel and Merlivat*, 1984].

Finally, we assume that the fractionation of vapor at cloud base is equal to that of vapor evaporating from the sea surface.

The equations of the resulting one-dimensional model were solved using a combination of analytic methods and numerical integration in the Mathematica software environment (Wolfram Research, Champaign, Illinois). Use of the Mathematica high-accuracy numerical integration algorithms ensures that numerical errors play an insignificant role.

Two temperature profiles are used in the analysis, one a mean sounding from Menado (124º E, 1º N), and the other a moist adiabat tied to the sounding at 850 hPa. The Menado sounding is a November through February mean. For the analysis presented here it is a good proxy for the tropical mean profile, because its minimum SMR of 3.9 ppmv (at 98 hPa) is very close to the observed tropical mean minimum SMR of 3.8±0.3 ppmv [*Dessler*, 1998]. The moist adiabat is the temperature of a parcel lifted pseudoadiabatically (specific heat of the condensate is ignored) from 850 hPa; we assume that this temperature profile is followed by a parcel undergoing deep convection. Figure 1 shows the temperature profiles and the standard deviation of the soundings.

2.2. The Stratospheric HDO Puzzle

If T-STE occurs in convective clouds that penetrate the stratosphere, and if cloud ice falls back to the troposphere without significant evaporation [*Danielsen*, 1982], then we may estimate the isotopic fractionation of vapor by integrating the model along the moist adiabat from cloud base to 100 hPa. The resulting δD is less than -900‰, as seen in Table 1 and in the thick line of Figure 3. This prediction is wrong. Stratospheric HDO has been measured by several investigators. Using a balloon-borne infrared spectrometer measuring thermal emission, *Johnson et al.* [1995] have estimated the mean δD of air entering the stratosphere as -650±24‰ based on several years of data [*Johnson et al.,* 1998]. This is consistent with an earlier value of -670±80‰, obtained by spaced-based atmospheric absorption measurements using the

Table 1. Sensitivity of Fractionation to Model Parameters

		δD		$\delta^{18}O$	
	Value	500 hPa	100 hPa	500 hPa	100 hPa
Reference case		-164	-956	-20	-247
Equilibration switch	-10°C	-149	-950	-18	-241
	+10°C	-191	-956	-24	-250
Saturation (*S*)	1.1	-154	-935	-17	-206
	1.2	-146	-910	-15	-169
Climatological profile		-162	-886	-20	-191

The reference case uses the moist adiabatic profile, an equilibration switch at 0°C, and *S*=1.0. "Equilibration switch" is the temperature of the switch between complete and zero vapor-to-condensate equilibration. The effect of using a climatological temperature profile is shown last.

Atmopheric Trace Molecule Spectroscpy Experiment (ATMOS) instrument [*Moyer et al.*, 1996].

To resolve the puzzle, we first consider the possibility that our model prediction is wrong due to the simplistic representation or omission of processes known to be important in the lower troposphere, such as evaporation from the sea surface, mixing of subcloud air with isotopically lighter air descending into the boundary layer, or the partial equilibration between cloud vapor and precipitation falling from above. Isotopic models have incorporated substantial cloud microphysics to study convection and several general circulation models (GCMs) have incorporated sophisticated treatments of isotopic fractionation. Why use a simple model? Because the complex models described above have aimed to understand the isotopic content of precipitation and so have focused on processes in the lower troposphere. While the isotopic GCMs do include a stratosphere, they have insufficient vertical resolution to resolve the tropical tropopause and have not been integrated long enough to allow the isotopic composition of the stratosphere to attain equilibrium (G. Hoffmann, personal communication, 1998).

The modeled isotopic depletion of water at 100 hPa is dominated by fractionation occurring at altitudes above 500 hPa. Fractionation is stronger in the upper troposphere because both terms in equation (1), the equilibrium fractionation $(\alpha - 1)$ and the magnitude of $d \ln q / dz$, increase with increasing altitude. The model is therefore insensitive to uncertainties in the lower troposphere, such as the altitude at which equilibration between condensate and vapor becomes negligible, or the isotopic fractionation between sea surface and cloud base (Table 1). Note that even use of the warm mean sounding rather than the moist adiabatic temperature profile is unable to make the model match observations (Table 1).

We conclude that the model's failure to predict the observed isotopic depletion of HDO entering the stratosphere is not due to the omission of mixing processes that might be included in a GCM, nor to simplistic treatment of isotopic exchange processes in the lower troposphere. This is the stratospheric HDO puzzle.

There are three plausible causes of the discrepancy between model and observations: (1) rapid ascent in convecting clouds generates large supersaturation that reduces fractionation due to kinetic effects, (2) the fractionation factors are incorrect, or (3) fractionation is reduced by lofting and evaporation of isotopically heavy ice.

2.3. Kinetic Effects

Moyer et al. [1996] considered two explanations for the discrepancy between measured δD and that predicted by the foregoing assumptions. Either condensation takes place under strongly supersaturated conditions, or lofting and later reevaporation of isotopically heavy condensate reduces the fractionation. Moyer et al. calculated that cloud relative humidity (RH) of >150% is required to match observed stratospheric δD and argued that such large supersaturation is possible in rapidly ascending cumuli. Owing to the differing importance of kinetic effects, supersaturation would cause a relatively larger decrease in $-\delta^{18}O$ than in -δD. Thus observation of $\delta D/\delta^{18}O$ would constrain estimates of supersaturation.

Observations of stratospheric $\delta^{18}O$ have been inconsistent.

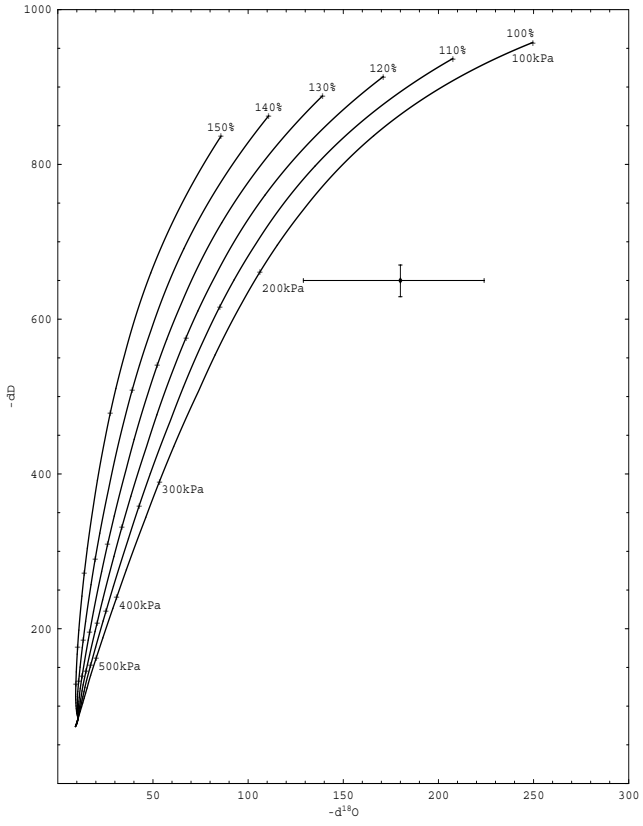

Figure 2. Plots of δD versus $\delta^{18}O$ for cloud vapor during ascent along a moist adiabat. The five curves show the effect of supersaturations from 100% to 150% as shown by the labels at the top. Pluses are placed along each curve every 100 hPa from 500 to 100 hPa. The data point is from *Johnson* [1998] as described in section 2.3.

Early results [*Carli and Park*, 1988] showed substantial enhancement of $H_2{}^{18}O$. *Kaye* [1990] analyzed the possibility that ^{18}O content of water was enriched by exchange with O_3 which is known to be enriched in ^{18}O, and concluded that such exchange was unlikely. Recent observations [*Johnson et al.*, 1998] arguably provide the first robust measurement of $\delta^{18}O$ in the stratospheric overworld and find a value of -180±50‰.

Figure 2 shows modeled δD versus $\delta^{18}O$ for various supersaturations. Without a $\delta^{18}O$ constraint, a δD of -650‰ can be explained by assuming a supersaturation of ~150% and an effective termination of fractionation at ~150 hPa (in agreement with *Moyer et al.* [1996]). New measurements of $\delta^{18}O$ are plotted in Figure 2. If correct, the measurements rule out the kinetic effect as an explanation for the stratospheric HDO puzzle. Note that equilibration of oxygen between $H_2{}^{18}O$ and O_3 would make $\delta^{18}O$ larger (less fractionated). If oxygen equilibration had affected the $\delta^{18}O$ of lower stratospheric water vapor, then the $\delta^{18}O$ water vapor entering the stratosphere must have been lower (more fractionated) to account for the observed $\delta^{18}O$. Thus the (unlikely) influence of oxygen equilibration would only strengthen the conclusion that kinetic effects in the troposphere cannot be significant.

2.4. Uncertainty in Isotopic Physics

Could the isotopic physics expressed in the equilibrium and kinetic fractionation factors be significantly in error? The standard equilibrium isotopic fractionation factors between ice and vapor are based on laboratory measurements above 240 K [*Majoube*, 1970; *Merlivat and Nief*, 1967]. It is plausible that the formula for α is significantly in error at the colder temperatures of interest here. To test the impact of errors in the equilibrium fractionation factor for HDO, we integrate the model using a modified α derived by fitting a line to the formula given by Merlivat and Nief over the range of temperatures at which α was measured (-33º to 5º C). The modified α has a value of 1.30 at 200 K, where the original formula has a value of 1.37. The modified α reduces the predicted -δD of ~900‰ at 100 hPa by ~30‰. Applying the same test to $H_2{}^{18}O$, we find α reduced from 1.031 to 1.029 at 200 K, only half the relative reduction in $(\alpha - 1)$ as in the case of HDO. The kinetic fractionation factors may also be in error, both because of errors in the relative diffusivities, and because the kinetic fractionation factors depend on assumptions about ice particle geometry.

Our cursory examination of the effects of plausible errors in standard fractionation factors at low temperatures suggests that such errors are relevant to predictions of isotopic fractionation in the tropopause region. However, it seems unlikely that errors in the isotopic physics are of sufficient magnitude to resolve the HDO puzzle. We thus consider the third explanation for the discrepancy between models and observations, ice lofting.

2.5. Ice Lofting

The lofting and subsequent evaporation of isotopically heavy ice provides a resolution of the HDO puzzle that is consistent with the emerging understanding of the stratospheric water budget. We now return to the two scenarios (convective and gradual) for T-STE and demonstrate that either scenario can (with appropriate parameter choices) simultaneously balance stratospheric H_2O and HDO budgets.

Air that reaches the tropical tropopause in convective T-STE is colder than the mean tropopause because the lapse rate of the upper ~100 hPa of the troposphere is subadiabatic. The minimum temperature of the mean sounding is 191 K at 98 hPa with corresponding SMR of 3.9 ppmv. At the same pressure the moist adiabat is 179 K with an SMR of only 0.4 ppmv. If most air entered the stratosphere in convective events at temperatures corresponding to adiabatic ascent, then about 3.5 ppmv of cloud ice would need to evaporate in the stratosphere to match the observed $[H_2O]_e$ of ~4 ppmv. In order to match the stratospheric δD of -650‰, a substantial component of lofted ice would need to originate from ~12.5 km or below, where 12.5 km is the altitude at which the δD of vapor in a convective event has a value of approximately -650‰ (Figure 3).

Gradual T-STE occurs in two steps. First, convection supplies moisture (ice and vapor) to the upper troposphere where the outflow from convection mixes horizontally and begins to

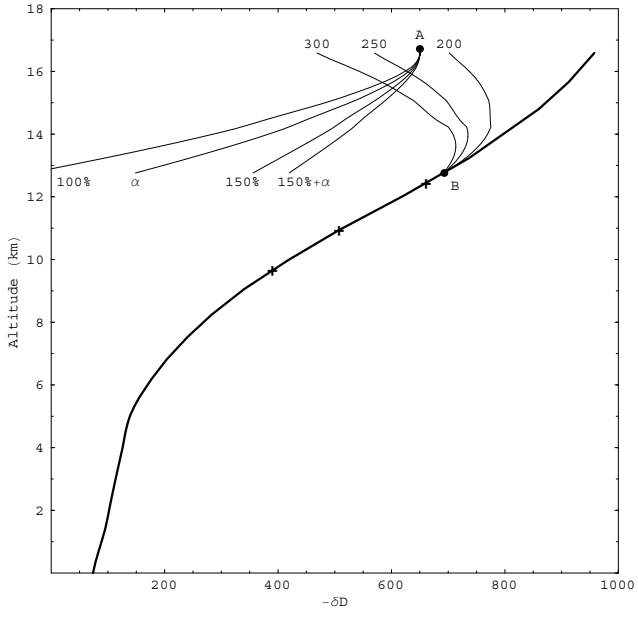

Figure 3. Plots of δD versus height. The solid curve is -δD of vapor for the reference conditions of Table 1. Point A marks the altitude of the tropopause and a δD of -650‰. The curves descending from point A show the fractionation at a given altitude that is required to produce $\delta D = -650‰$ at the tropopause. The four curves show the effects of 100% or 150% supersaturation and of standard or modified fractionation factor, where the modified α is indicated with an α. The curves ascending from point B show the fractionation of vapor obtained after sufficient ice has evaporated to achieve saturation at the mean sounding temperature given that the ice is lofted from 200, 250, or 300 hPa. The three plusses on the solid curve mark these three source altitudes.

sink due to radiative cooing. Lofted ice evaporates in the outflow, hydrating the tropical upper troposphere and decreasing the isotopic fractionation of the vapor. The second step of gradual T-STE occurs when air is lofted from the upper troposphere through the tropopause. Upward motion of saturated air will cause the formation of thin cirrus clouds from which excess moisture is removed by sedimentation of large ice particles [*Jensen et al.*, 1996]. Radiative heating in the cirrus may then help to drive uplift. Both gravity waves and larger-scale vertical motions have been proposed as local mechanisms that could trigger upward motion [*Jensen et al.*, 1996].

We may explore the isotopic fractionation due to this two-step process as follows. The fractionation of air in the outflow from convection is modeled by assuming maximum possible evaporation of cloud ice, that is, by assuming that sufficient ice evaporates to saturate the air at the temperature of the mean environment (the mean sounding in Figure 1). For outflow at a given altitude the isotopic fractionation of the outflow vapor is determined by the two reference temperature profiles (mean and moist adiabatic) and the isotopic fractionation of the ice particles. We may crudely estimate the isotopic fractionation of the ice particles by assuming they are formed from vapor at a single altitude. The fractionation of ice is then given by the modeled fractionation of vapor at that altitude. The thin curves in Figure 3 that originate at ~13 km show the predicted fractionation of vapor in the outflow for various altitudes of ice origin. Below ~13 km the model is inapplicable as the temperature of the moist adiabat is warmer than that of the mean sounding (Figure 1).

Fractionation in the second step of gradual T-STE may be explored by computing the required fractionation of source vapor necessary to produce the known stratospheric δD assuming that vapor is fractionated during ascent along the mean temperature profile with removal of ice particles by sedimentation. This is accomplished by integrating equation (1) downward from the stratospheric boundary conditions. Results are shown in Figure 3 for three cases: 100% saturation and standard fractionation factor α, 150% saturation, and the modified (linear fit) α described above. Although substantial kinetic fractionation appears to be ruled out by the stratospheric $\delta^{18}O$, it seems relevant to examine the effects of supersaturation here because there is reason to expect supersaturation in thin cirrus formed by homogeneous nucleation [*Jensen et al.*, 1996; *Tabazadeh et al.*, 1997].

The limited overlap between two families of curves in Figure 3, the δD of vapor in the outflow from convection and the δD required to produce a stratospheric δD of -650‰ during gradual ascent, shows that it is difficult to match observations given the foregoing assumptions. If we assume that an air parcel first descends after convection, prior to beginning its gradual ascent, then more ice can evaporate, further decreasing the fractionation of the vapor. Simple models of two-step gradual T-STE that permit descent prior to ascent can match the observations, but require several free parameters.

3. Summary

Data on the mean isotopic composition of water vapor entering the stratospheric overworld cannot immediately resolve the key questions regarding the mechanisms of T-STE. For example, sufficient free parameters exist (principally the altitude from which cloud ice is lofted) in both the gradual and convective scenarios analyzed in section 2.5 that it proves little to demonstrate agreement with the observed isotopic content of air entering the stratosphere.

Analysis of new observations of stratospheric $\delta^{18}O$ [*Johnson et al.*, 1998] shows that kinetic (nonequilibrium) effects cannot play a substantial role in the fractionation of water vapor entering the stratosphere. The elimination of kinetic effects as a means of reducing the depletion of HDO reaching the stratosphere permits us to infer that transport of water vapor through the tropical tropopause involves a substantial contribution from the evaporation of lofted cloud ice [*Moyer et al.*, 1996]. However, data on stratospheric isotopic fractionation cannot determine if the ice was lofted through the tropopause by convection or if it evaporated in the upper troposphere to provide a source of HDO-enriched moisture for subsequent transport into the stratosphere. Observations of isotopic fractionation in the top ~100 hPa of the tropopause should discriminate between these mechanisms.

Data and analysis presented here eliminate the model of T-STE in which the dominant flux of moisture into the tropical stratosphere is vapor injected by convection [*Danielsen*, 1982]. The isotopic data confirm the result from analysis of water vapor alone, that $[H_2O]_e$ is too large to be explained by the convective overshoot and dehydration mechanism proposed by Danielsen. T-STE may by dominated by convective events, but if so, then enough lofted ice must evaporate in the stratosphere to balance the water vapor and HDO budgets.

Acknowledgments. I thank D. G. Johnson for kindly providing unpublished analysis of stratospheric $\delta^{18}O$ and δD, and J. A. Anderson, D. B. Kirk-Davidoff, A. E. Dessler, E. J. Hintsa, E. J. Moyer, R. B. Smith, R. Spackman, and E. M. Weinstock for their intellectual and/or editorial insight.

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