

# Observations of the isotopic composition of vapor and condensed water in the tropical tropopause layer

Harvard ICOS/HOxotope

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Harvard H<sub>2</sub>O

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SPARC general assembly

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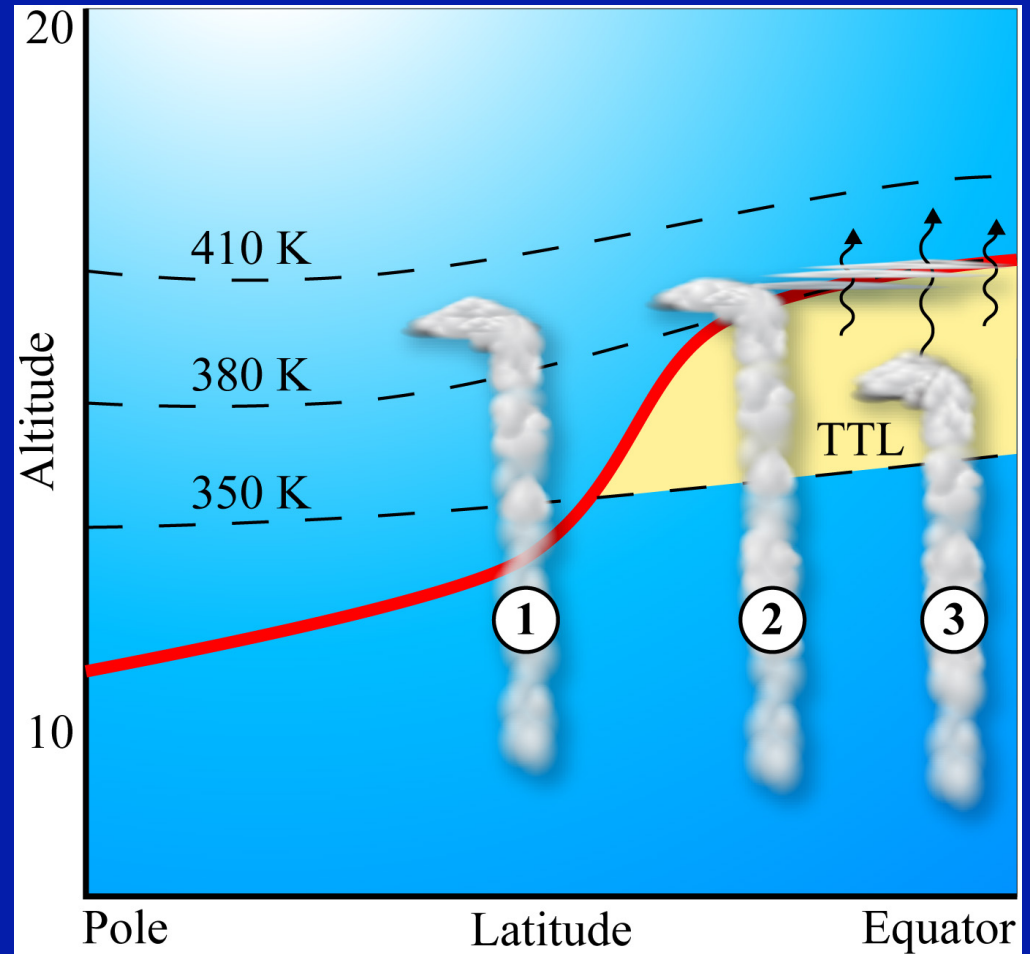
## Hydration pathways

H<sub>2</sub>O and H<sub>2</sub>O isotopes observations can be used to quantify:

- 1) Ice lofting and convective outflow above 380 K in mid-lats
- 2) Ice lofting into the tropical stratosphere
- 3) Convective influence in the TTL

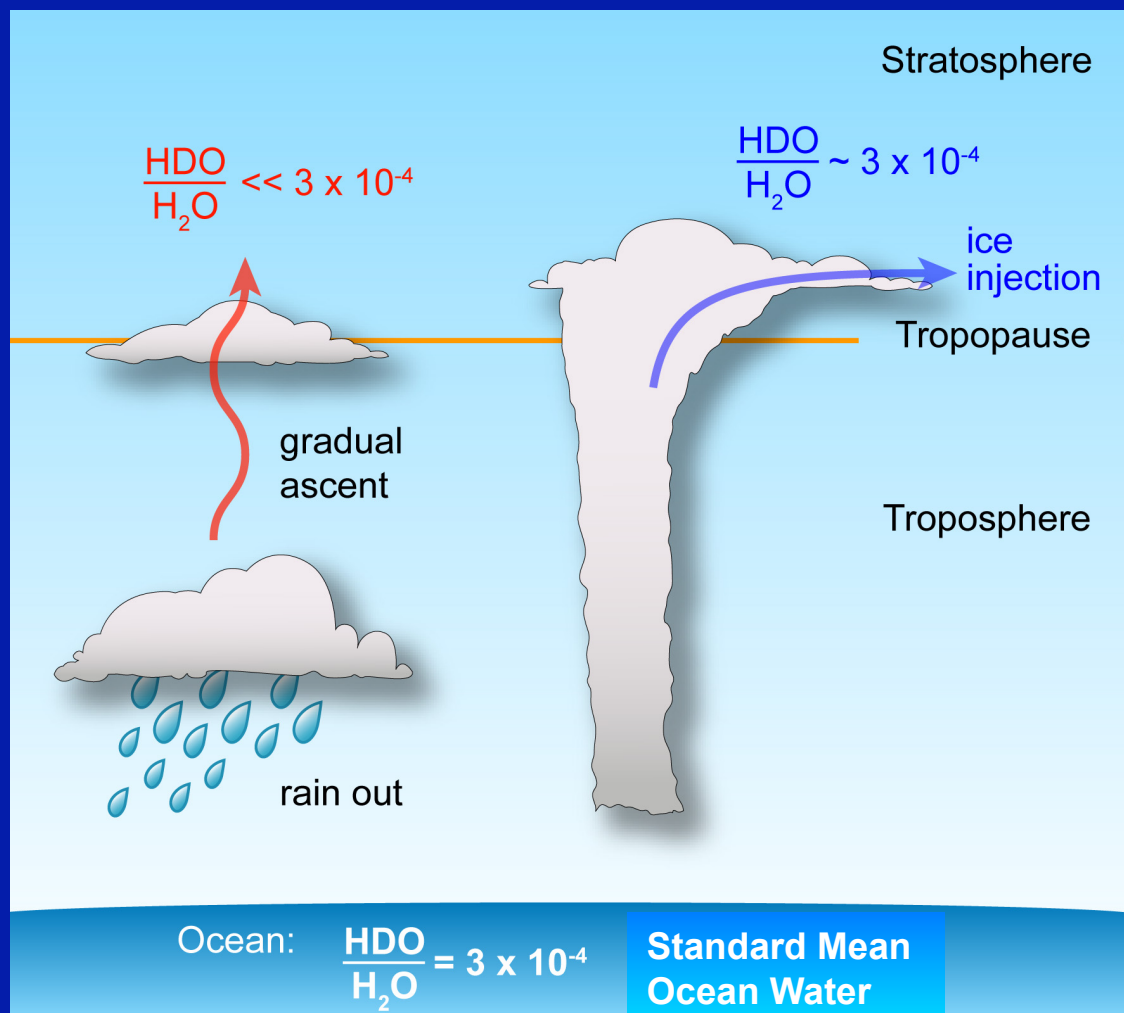
The isotopically heavy stratosphere indicates that the sum of 1 – 3 is significant.

What is the relative contribution of these pathways?



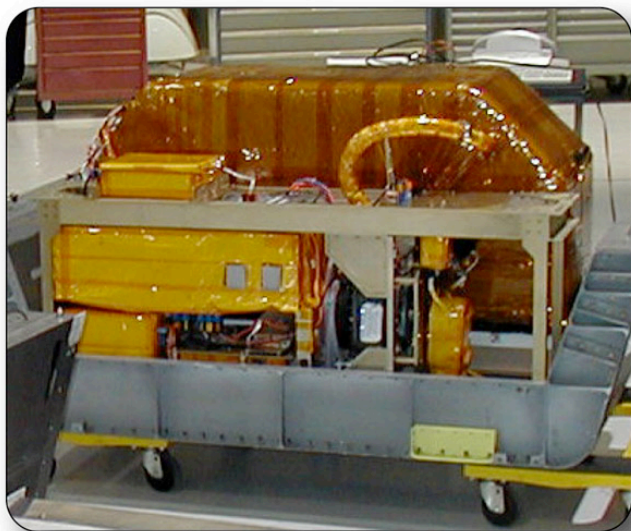
## Water isotopes as tracers of Convection

- HDO condenses more readily than H<sub>2</sub>O
- Rainout leads to HDO depletion
- Ice injection can make the stratosphere “Heavy”
- *In situ* water isotope measurements can offer a tracer for the condensation history of air parcels



$$\delta\text{D} = 1000 \left( \frac{\text{HDO}}{\text{H}_2\text{O}} / \text{SMOW} - 1 \right)$$

## ICOS Isotope Instrument



- Mid-IR absorption spectroscopy using new cavity-based technique
- (*Integrated cavity output spectroscopy*)
- Enhanced sensitivity (x 40) because of 4 km optical path
- Multiple species ( $\text{H}_2\text{O}$ , HDO,  $\text{H}_2^{18}\text{O}$ ,  $\text{H}_2^{17}\text{O}$ ,  $\text{CH}_4$ )

**D.S. Sayres, et al., in prep.**

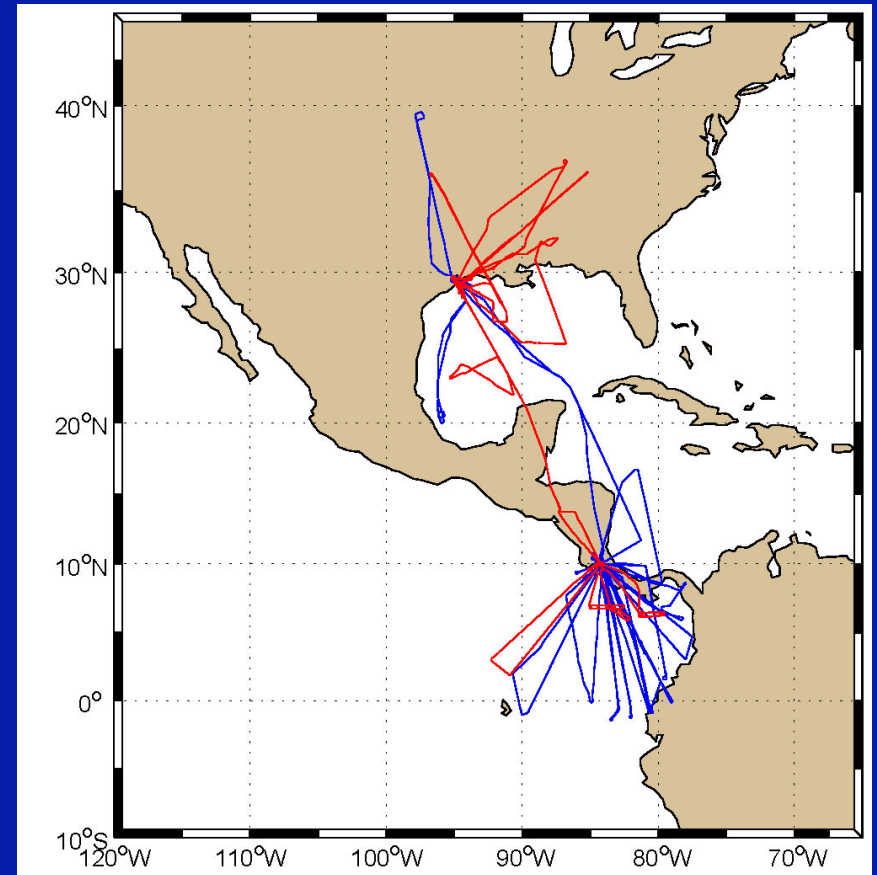
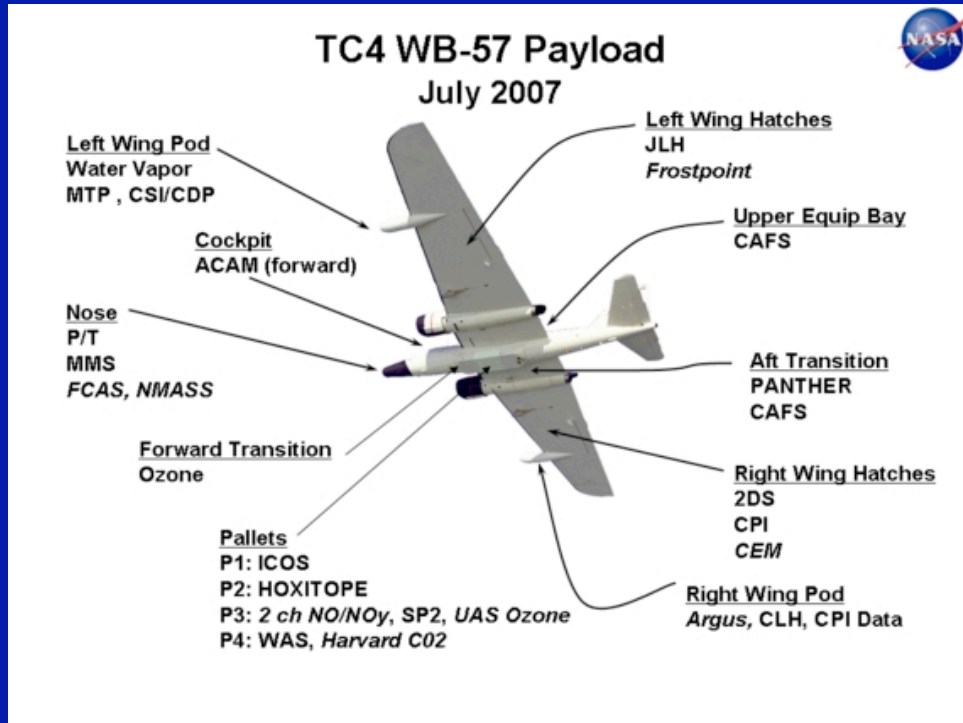
## Hoxtope total water isotope instrument



- Photofragment laser-induced fluorescence of OH and OD
- (*Heritage of Harvard HOx instrument*)
- Contamination-free sampling ( $\text{HO}_x$  radicals lost on wall contact)
- Improved sensitivity (x 2-10) over conventional techniques

**J. M. St.Clair, et al., *Rev. Sci. Instrum.*, 2008**

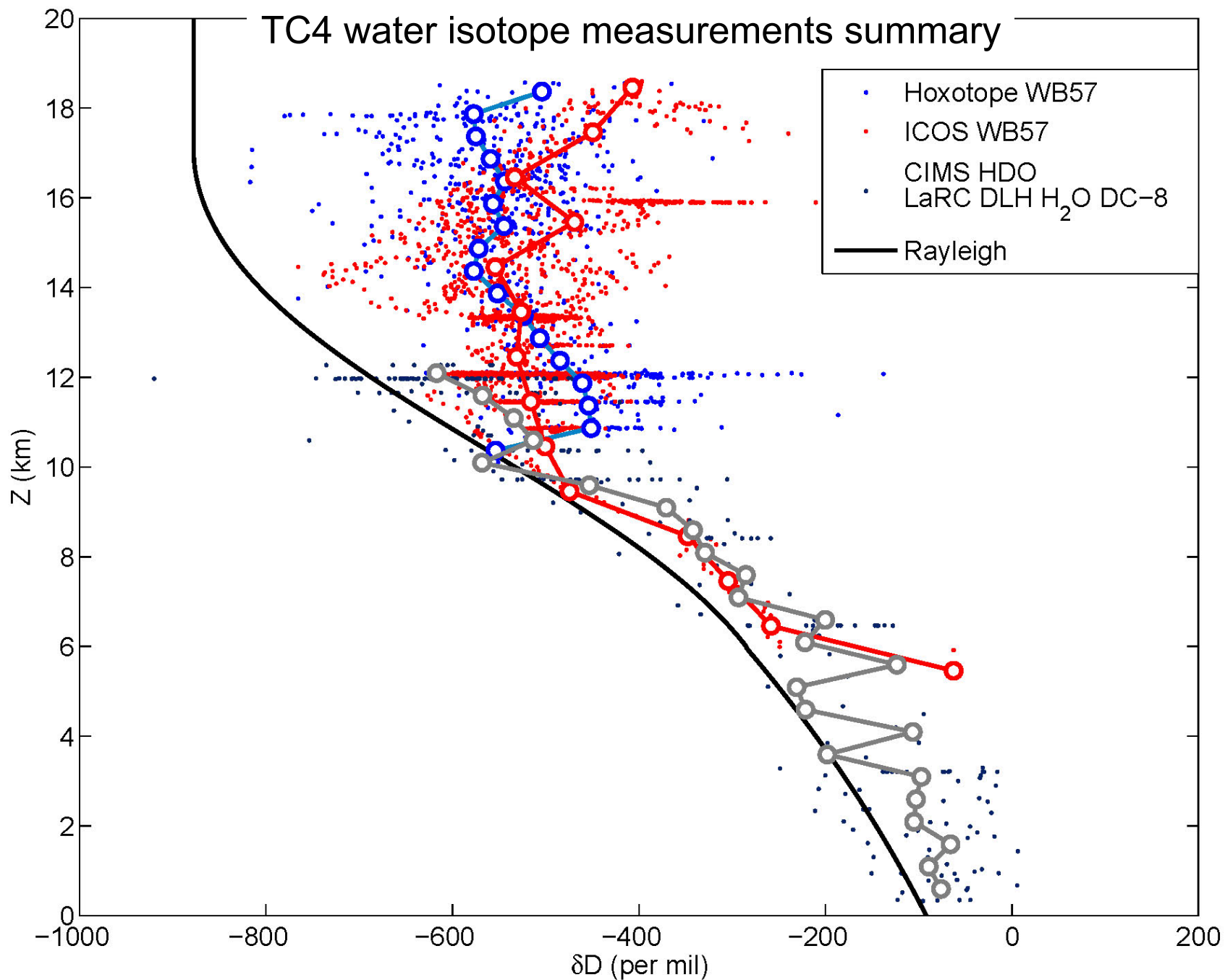
# AVE\_WIIF, CR\_AVE, TC4



Blue Lines: CR-AVE Winter 2006

Red Lines: AVE-WIIF, TC4 Summer 2005 and 2007

# TC4 water isotope measurements summary



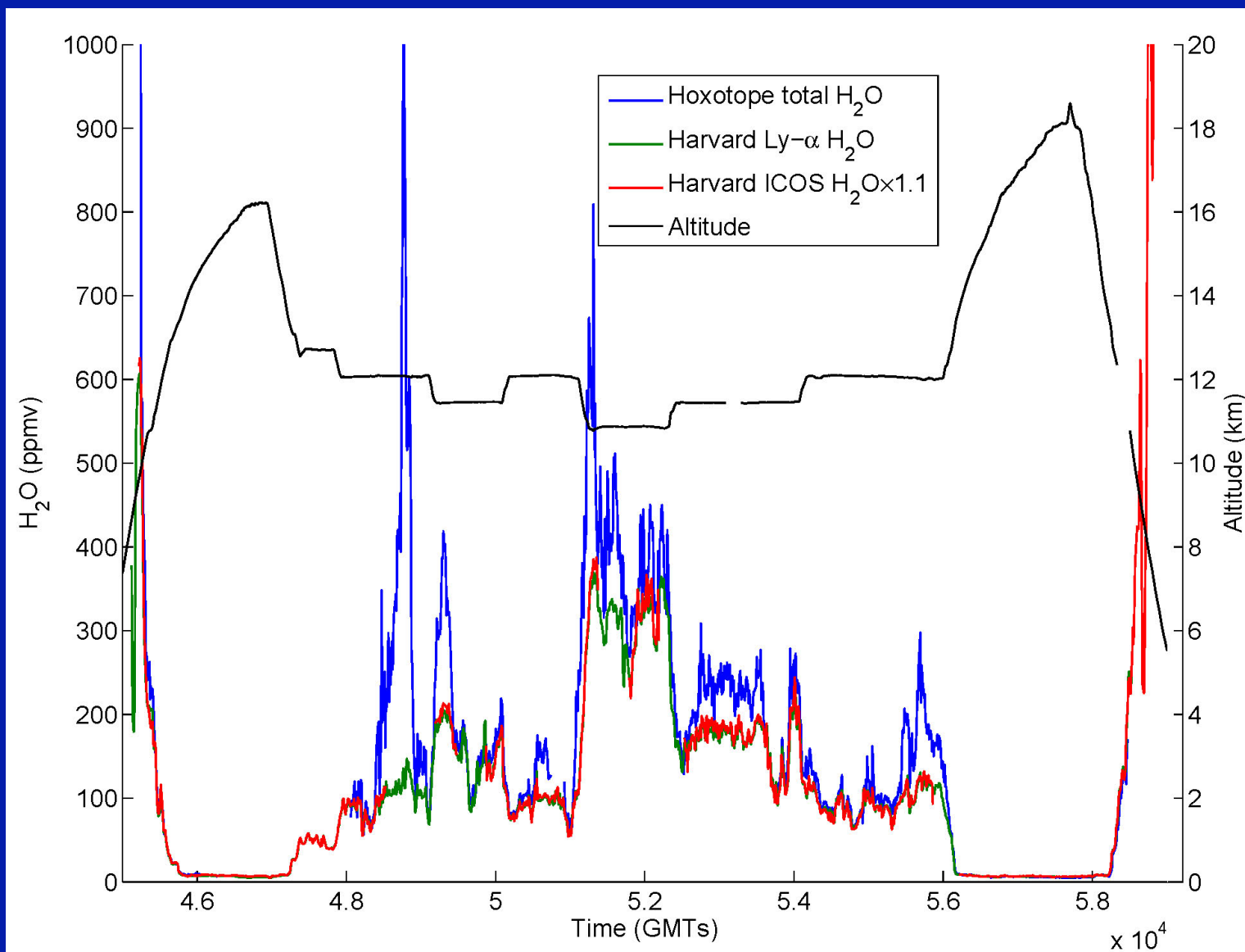


## Ice water isotopes

What is the source of water vapor in convective outflow in the base of the TTL?

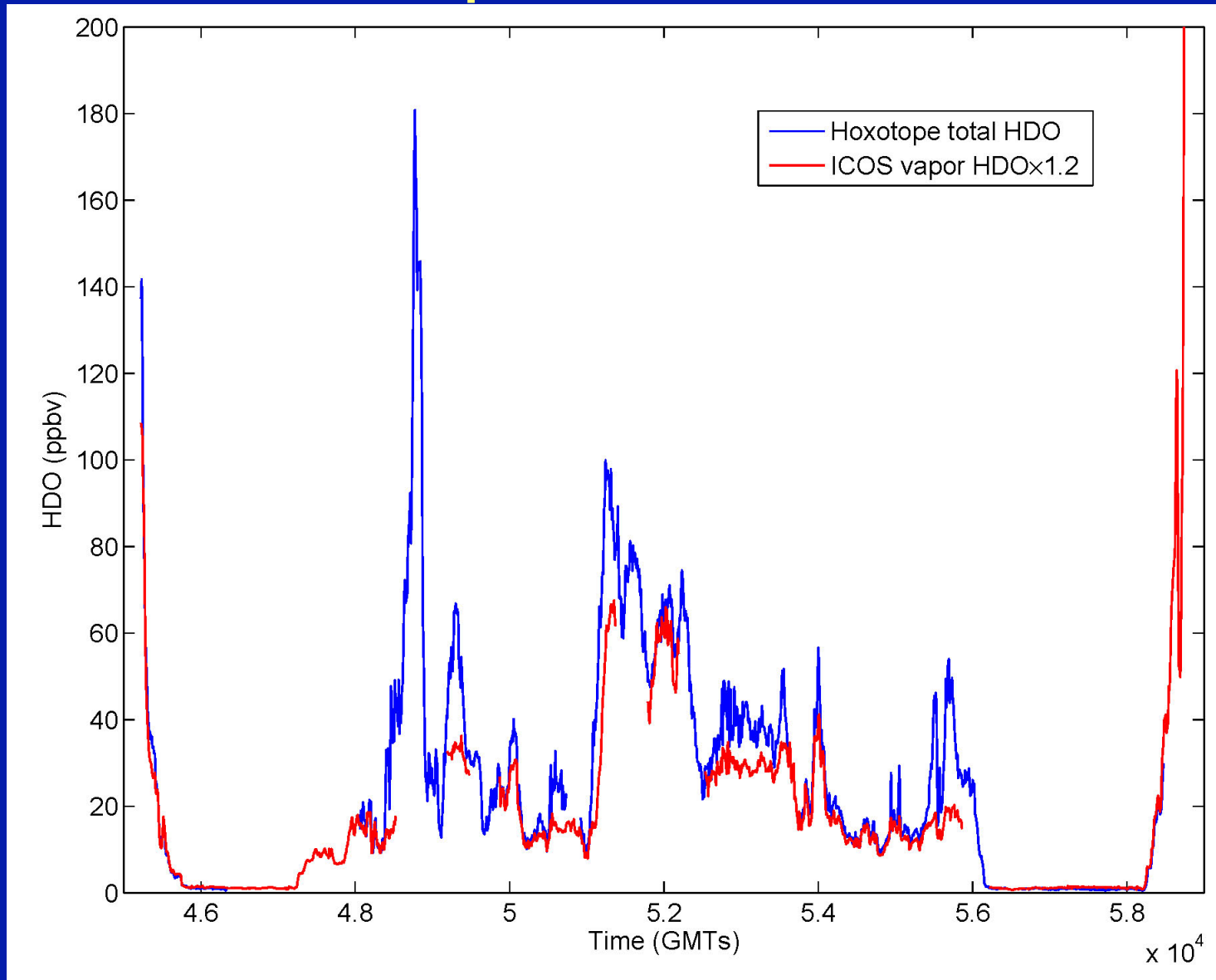
Hoxotope total water isotopes and ICOS water vapor isotopes used to derive ice water isotope ratios

# 20070808 Pacific Convection Total and vapor H<sub>2</sub>O measurements

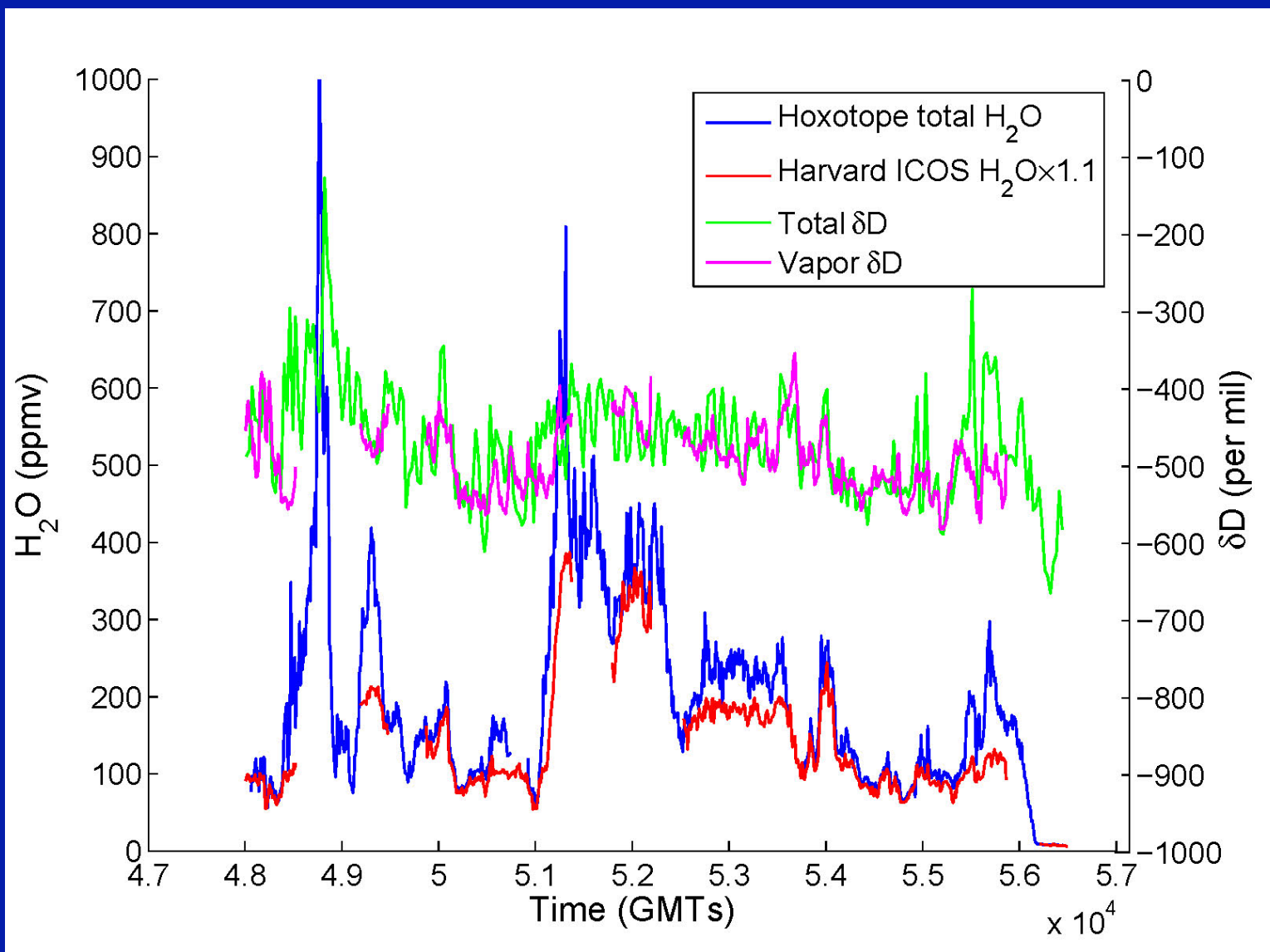




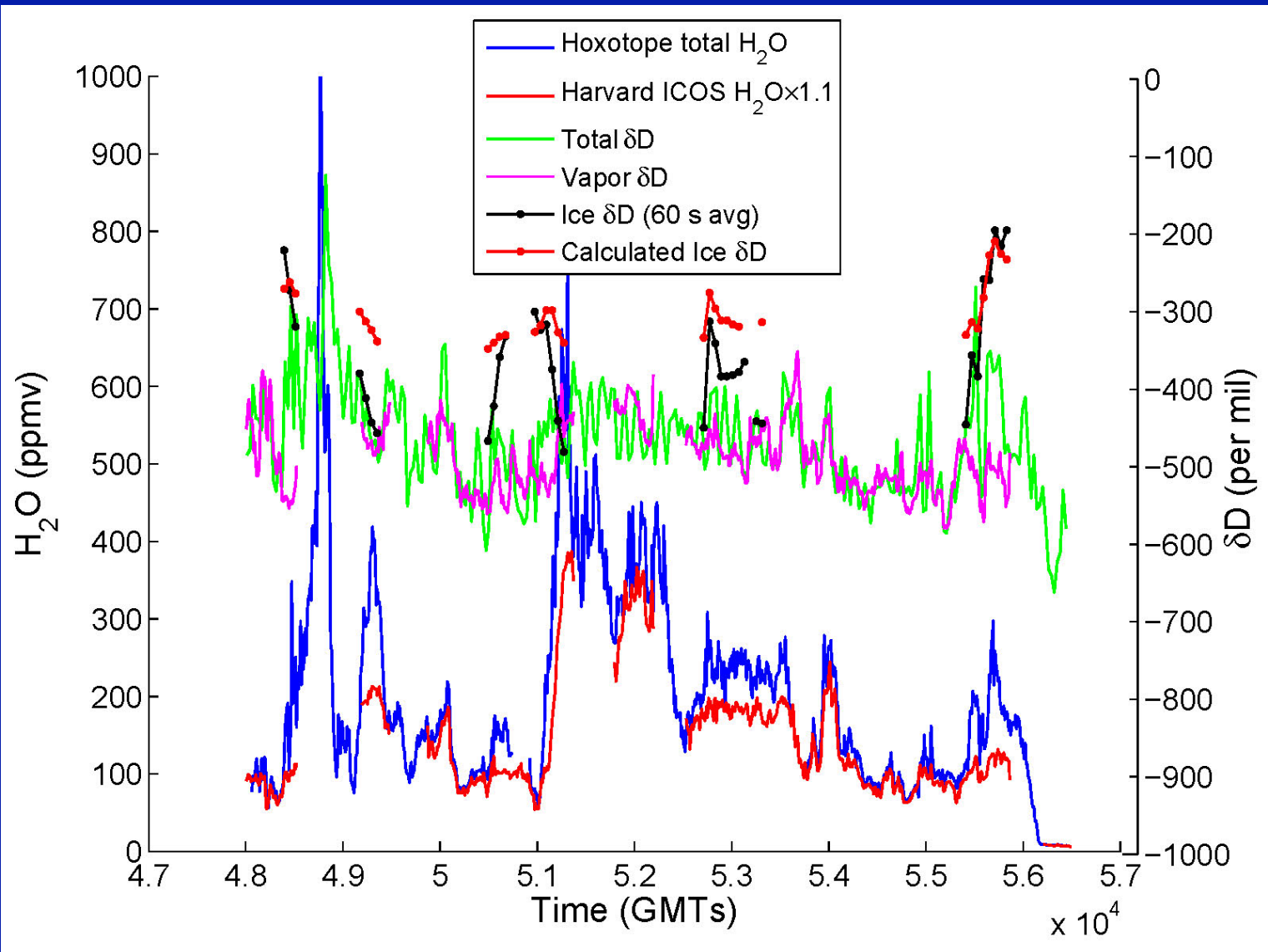
# 20070808 Pacific Convection Total and vapor HDO measurements



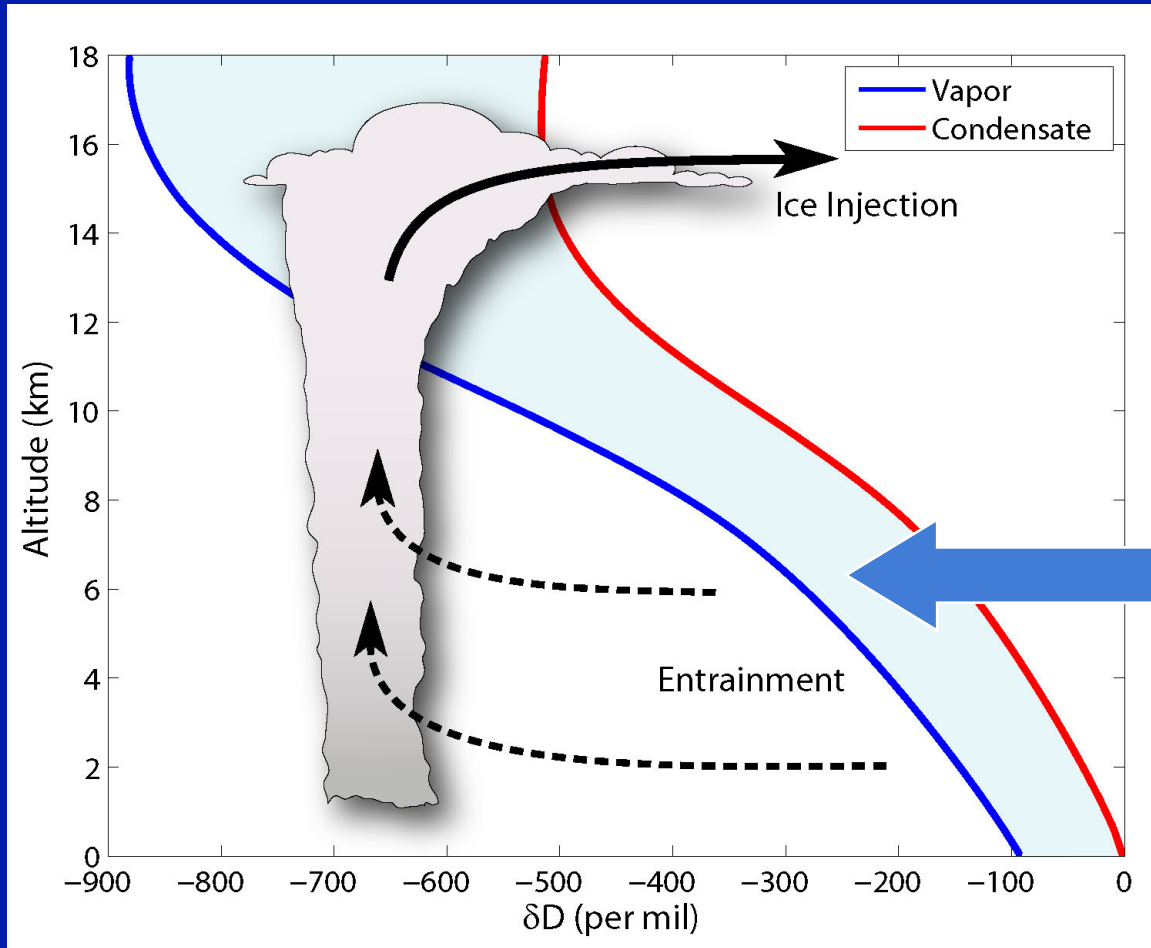
## 20070808 Pacific Convection Total and vapor $\delta D$ measurements



# 20070808 Pacific Convection Ice $\delta D$ measurements



## Ice water isotope ratio summary

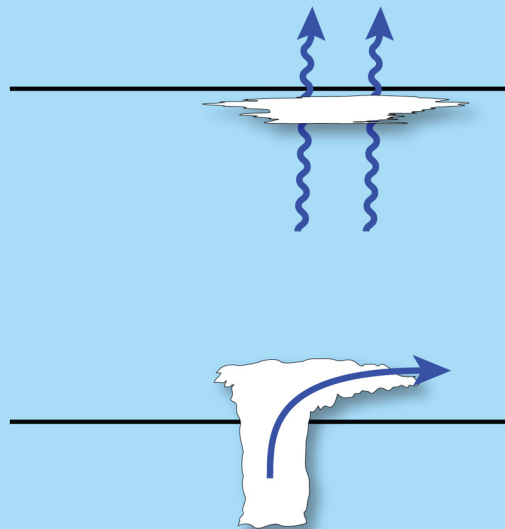


Condensed  
phased water  
isotope  
measurements  
indicate  
entrainment from  
6 – 8 km

# TTL convection and water isotopologues

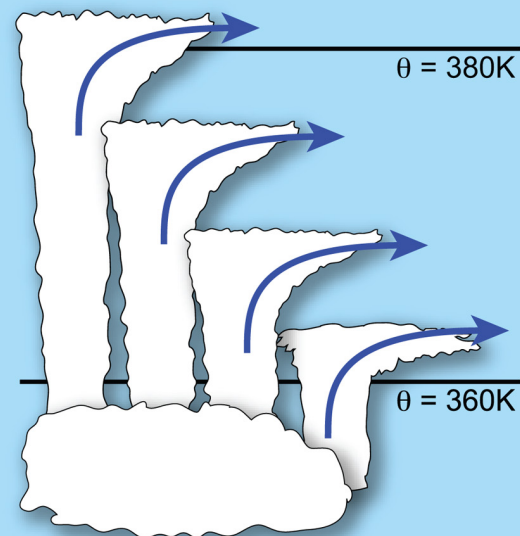
1) Temperature control

Large depletion in HDO  
 $\delta D = -900 \text{ ‰}$



2) Convective influence

Less depletion in HDO  
 $\delta D \gg -900 \text{ ‰}$

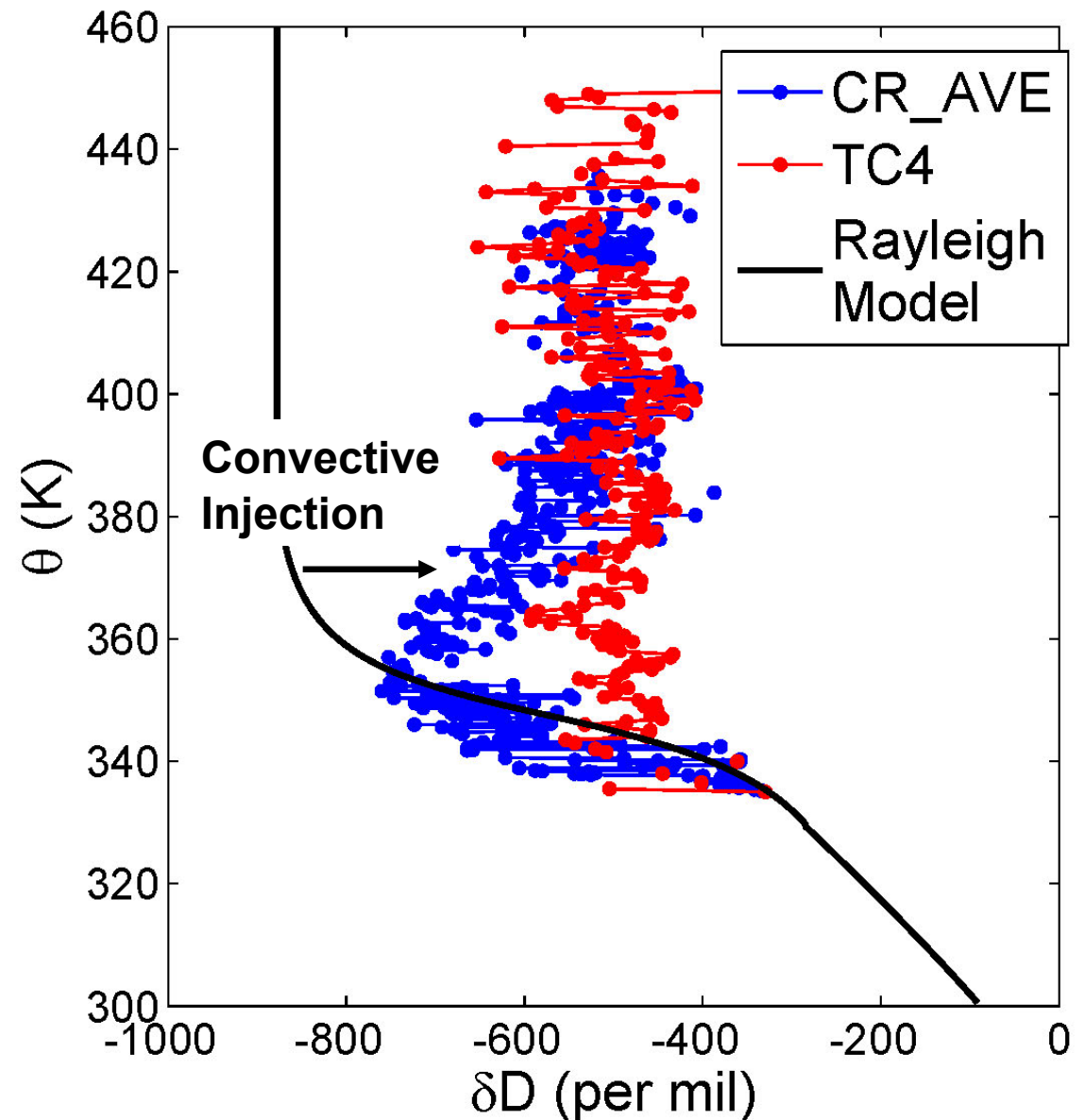


## In situ profiles of $\delta D$ indicate convective input

We expect  $\delta D$  to follow the Rayleigh curve in an atmosphere where  $H_2O$  is removed with increasing altitude

Departure from the Rayleigh curve indicates rehydration by the evaporation of ice

How much ice evaporates?



## Conceptual model

Consider an airmass rising in the TTL, slowly dries as T drops.

Inject isotopically heavy water (eg. ice)

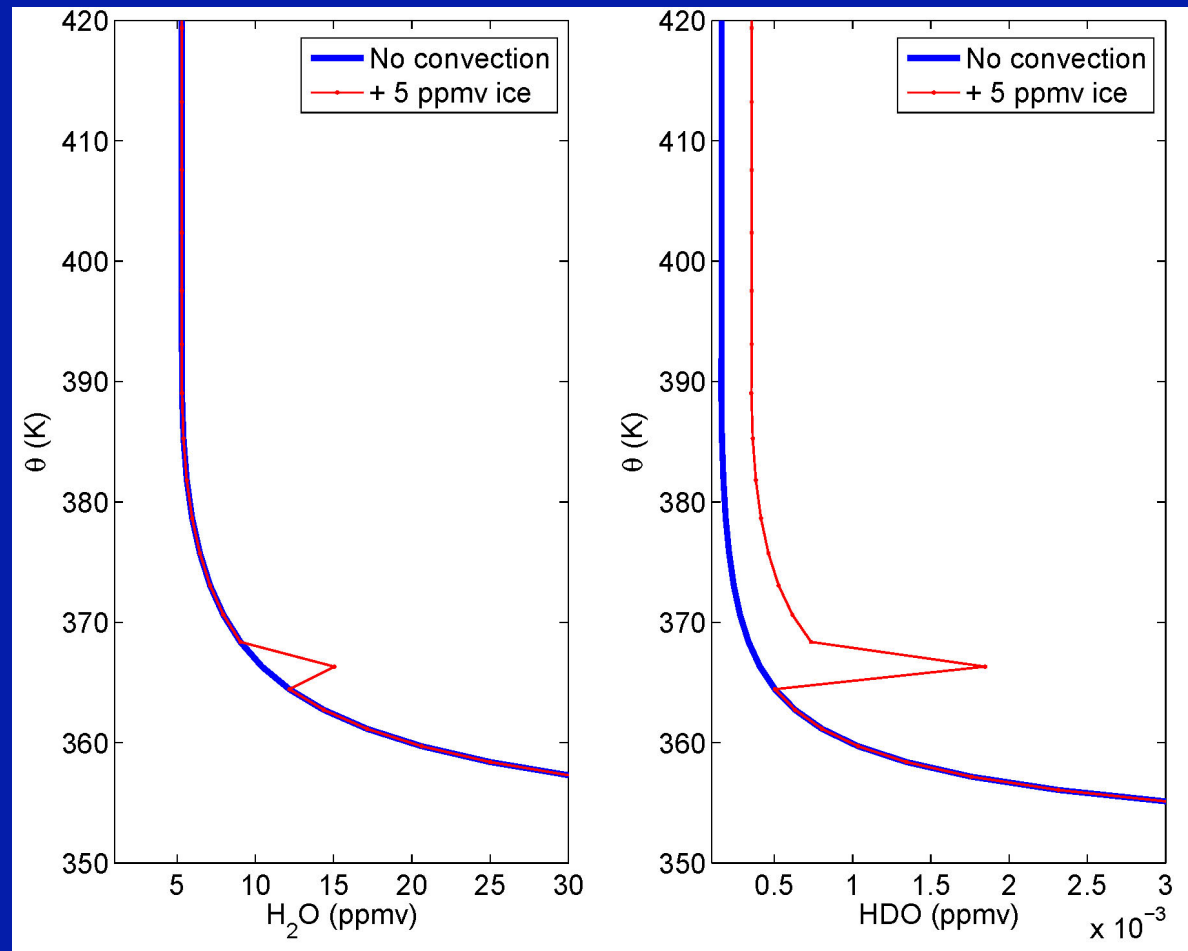
Assume that T fluctuates enough to support ice evaporation but H<sub>2</sub>O and HDO are still defined by ice saturation (ie  $T_{min}$ ).

H<sub>2</sub>O abundance is not changed:

$$H_2O = H2O_{sat}(T,P)$$

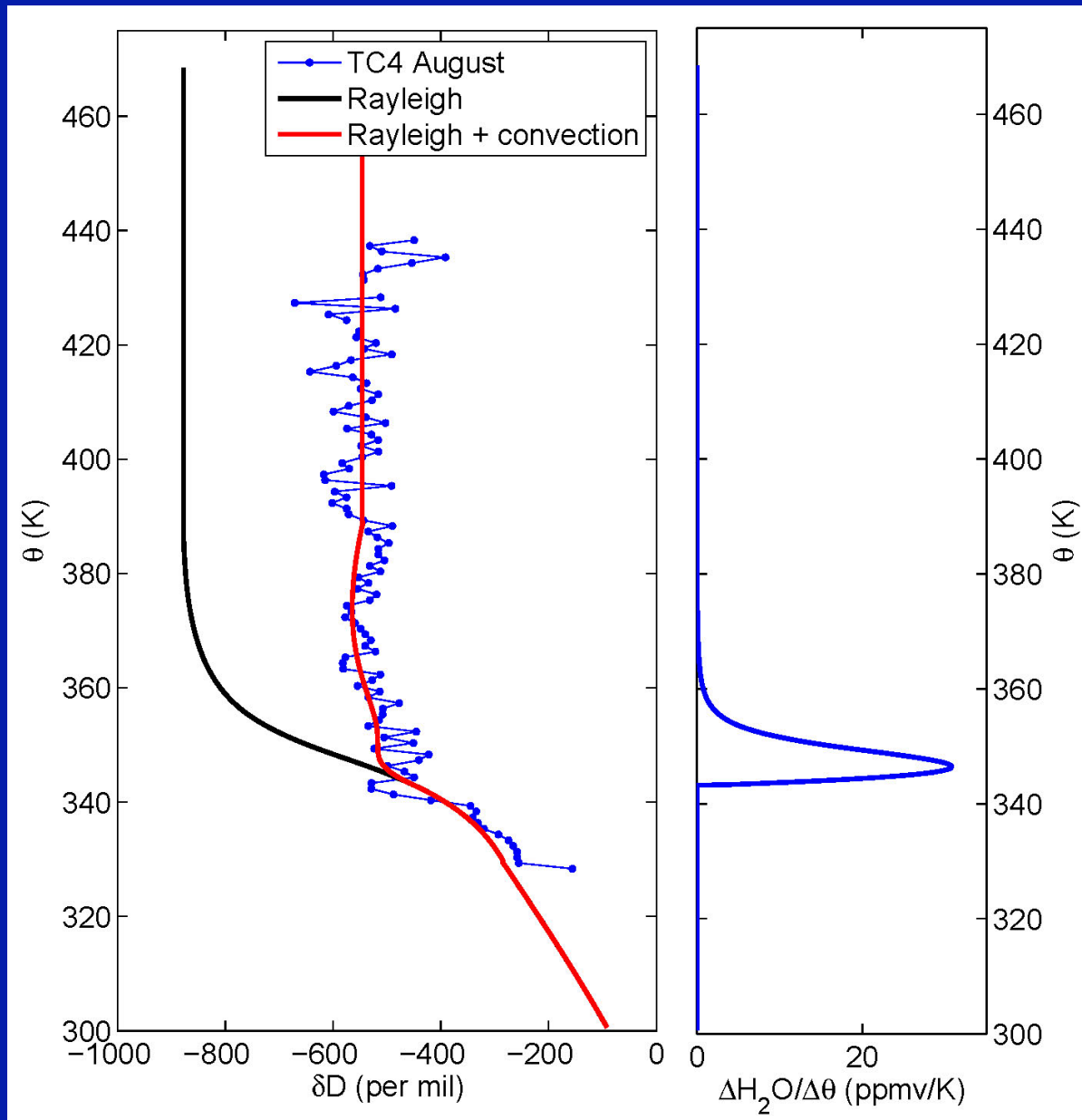
HDO abundance is changed:

$$HDO = H2O_{sat}(HDO/H_2O, T)$$

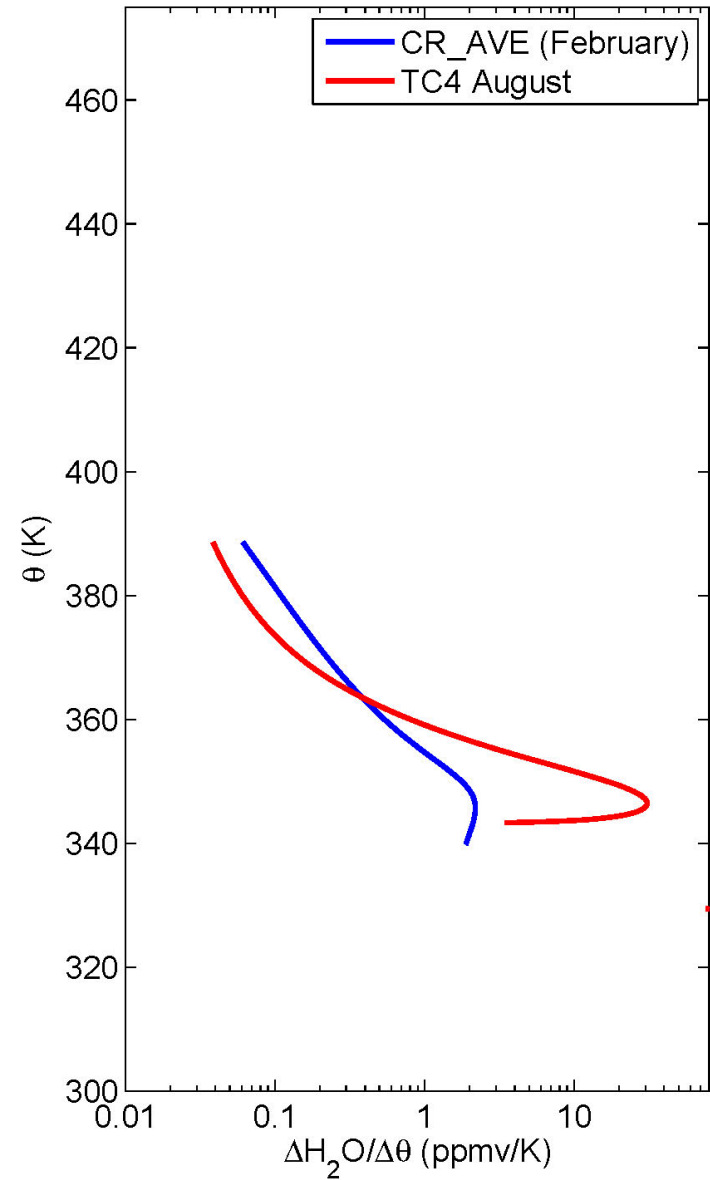
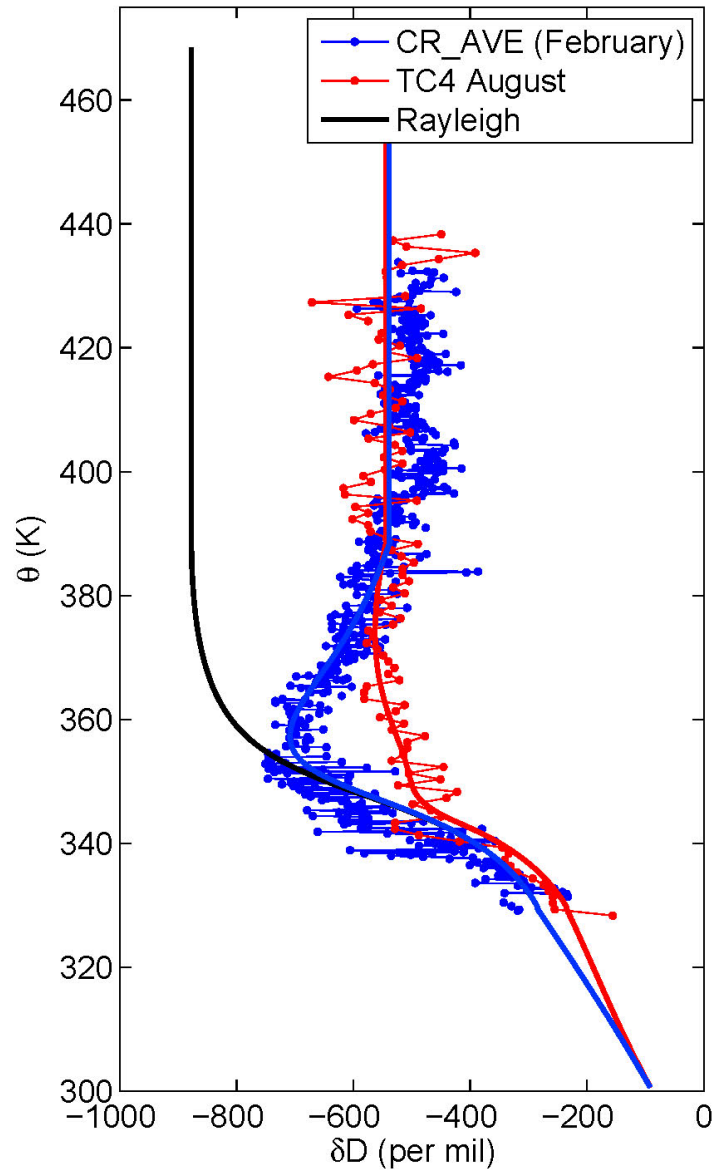




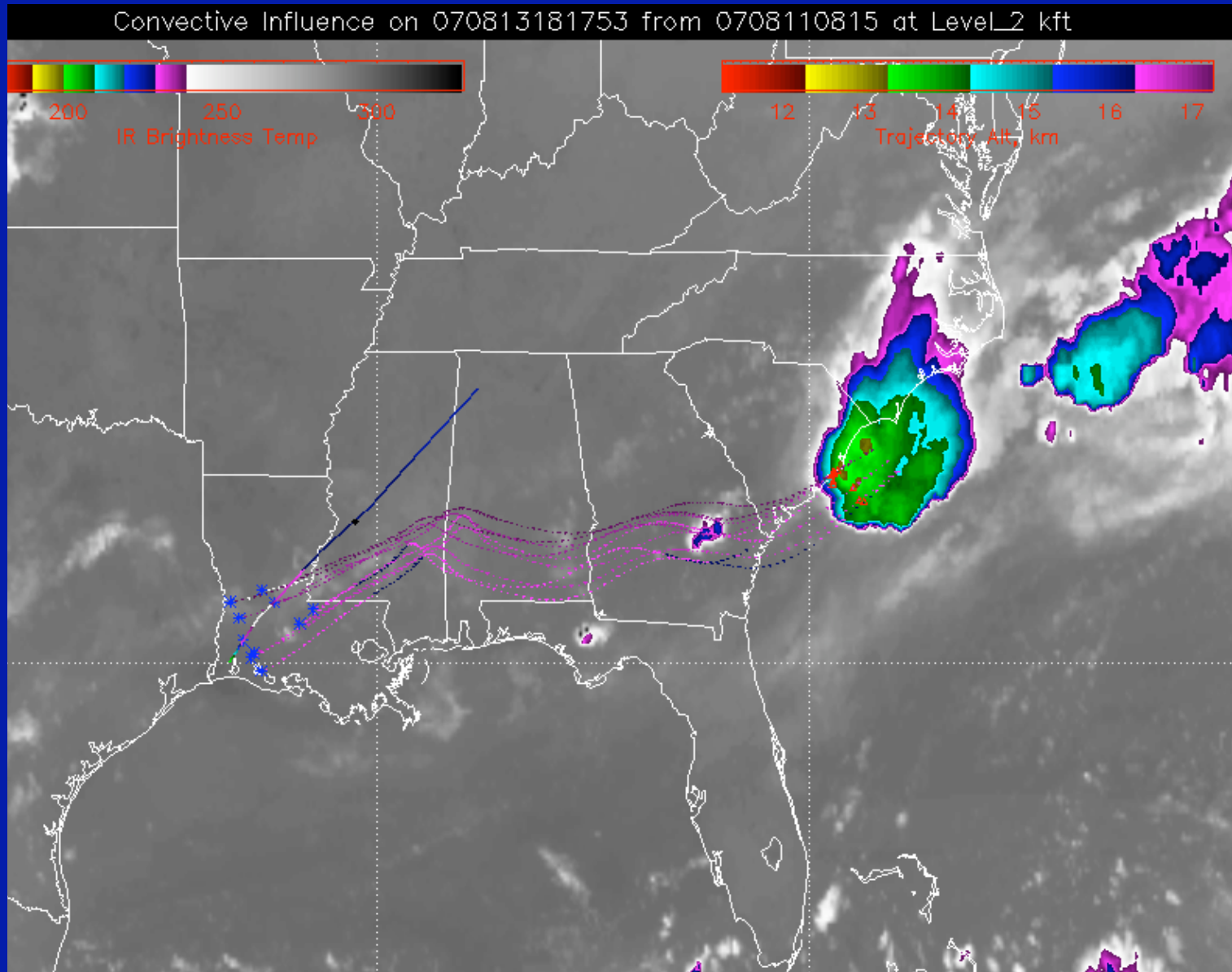
# Modeled convective influence



# TTL seasonal comparison

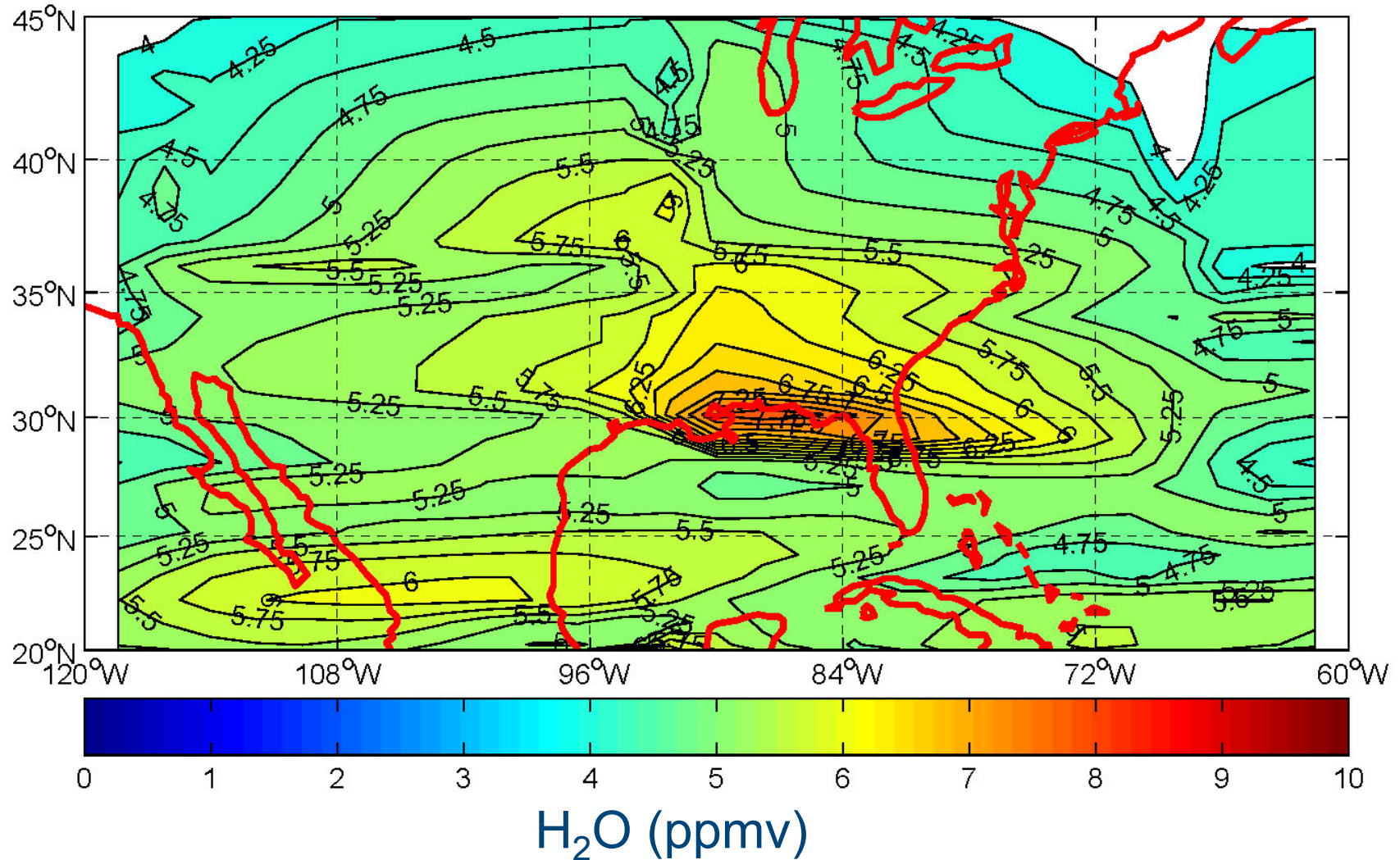


# Extra Tropical Convection

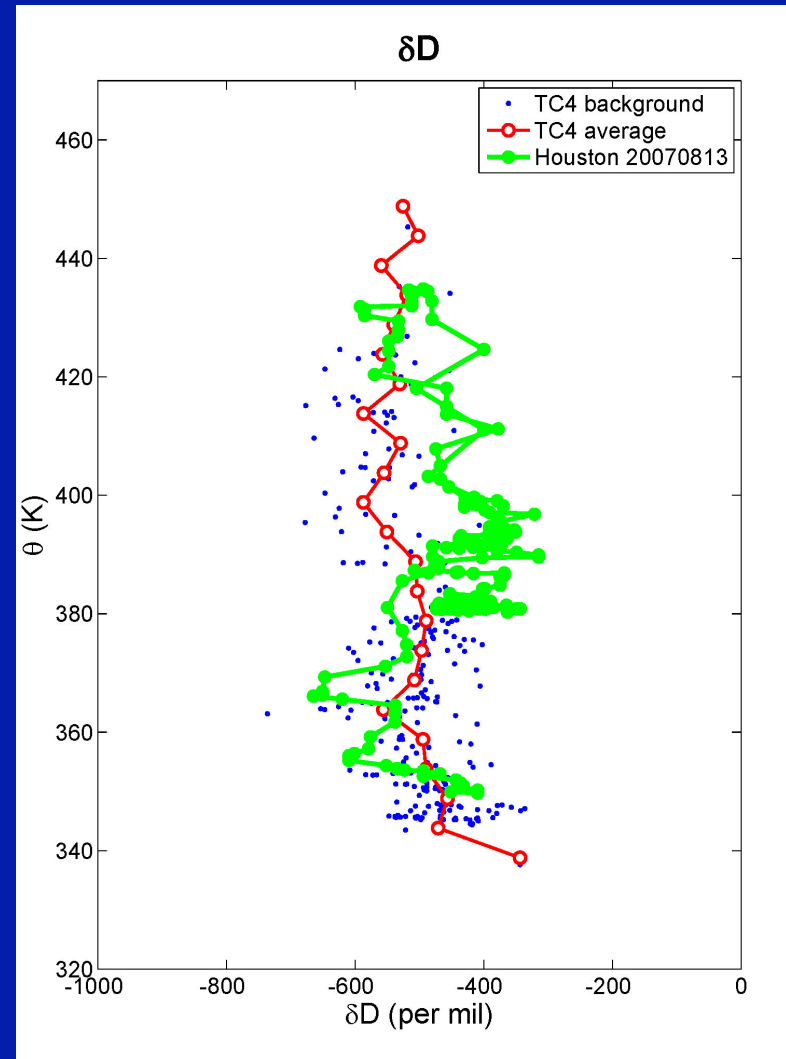
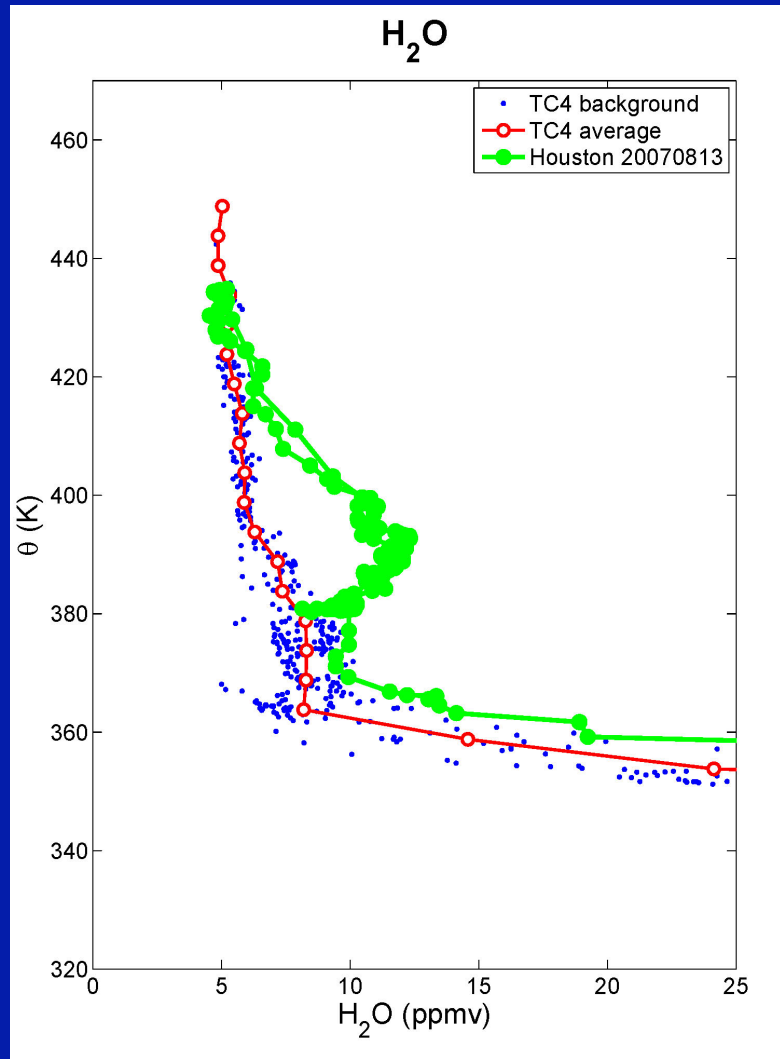


# AURA MLS

20080812 P = 82 mbar, Z = 17.5 km  $\theta = 400$  K



## Extra tropical H<sub>2</sub>O and δD



We continue to see the influence of deep convection on mid-latitude and tropical stratospheric water vapor.

## Summary

H<sub>2</sub>O and H<sub>2</sub>O isotopes observations indicate:

- Ice lofting significantly perturbs the water isotope ratio via path 3.
- H<sub>2</sub>O abundance is not significantly perturbed by deep convection in the TTL by path 3, but HDO is.
- Convective influence on stratospheric water isotopes by path 2 is small and yet to be determined in the tropics.
- Pathway 1 is significant and frequently observed, but not yet quantified.

