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Abstract: We present the seasonal variation of the HDO/H₂O ratio caused by sublimation-condensation processes in a global view of the Martian water cycle. The HDO/H₂O ratio was retrieved from ground-based observations using high-dispersion echelle spectroscopy of the Infrared Camera and Spectrograph (IRCS) of the Subaru telescope. Coordinated joint observations were made by the Planetary Fourier Spectrometer (PFS) onboard Mars Express (MEX). The observations were performed during the middle of northern spring ($L_s = 52^\circ$) and at the beginning of summer ($L_s = 96^\circ$) in Mars Year 31. The retrieved latitudinal mean HDO/H₂O ratios are 4.1 ± 1.4 ($L_s = 52^\circ$) and 4.4 ± 1.0 ($L_s = 96^\circ$) times larger than the terrestrial Vienna Standard Mean Ocean Water (VSMOW). The HDO/H₂O ratio shows a large seasonal variation at high latitudes. The HDO/H₂O ratio significantly increases from 2.4 ± 0.6 wrt VSMOW at $L_s = 52^\circ$ to 5.5 ± 1.1 wrt VSMOW at $L_s = 96^\circ$ over the latitude range between 70°N and 80°N . This can be explained by preferential condensation of HDO vapor during the northern fall, winter, and spring and sublimation of the seasonal polar cap in the northern summer. In addition, we investigated the geographical distribution of the HDO/H₂O ratio over low latitudes at the northern spring in the longitudinal range between 220°W and 360°W , including different local times from 10 h to 17 h. We found the HDO/H₂O ratio has no significant variation (5.1 ± 1.2 wrt VSMOW) over the entire range. Our observations suggest that the HDO/H₂O distribution in the northern spring and summer seasons is mainly controlled by condensation-induced fractionation between the seasonal northern polar cap and the atmosphere.

This paper presents HDO/H₂O distribution on Mars at the northern spring and summer. We performed ground-based observations using high-dispersion echelle spectroscopy. We found seasonal increase of the HDO/H₂O ratio at the polar region (70–80°N). The seasonal variation of HDO/H₂O ratio can be explained by phase change.

1 **Seasonal variation of the HDO/H₂O ratio in the atmosphere of Mars at the middle of**
2 **northern spring and beginning of northern summer**

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1 **Abstract**

2 We present the seasonal variation of the HDO/H₂O ratio caused by sublimation–condensation
3 processes in a global view of the Martian water cycle. The HDO/H₂O ratio was retrieved from
4 ground-based observations using high-dispersion echelle spectroscopy of the Infrared Camera and
5 Spectrograph (IRCS) of the Subaru telescope. Coordinated joint observations were made by the
6 Planetary Fourier Spectrometer (PFS) onboard Mars Express (MEX). The observations were
7 performed during the middle of northern spring ($L_s = 52^\circ$) and at the beginning of summer ($L_s =$
8 96°) in Mars Year 31. The retrieved latitudinal mean HDO/H₂O ratios are 4.1 ± 1.4 ($L_s = 52^\circ$) and
9 4.4 ± 1.0 ($L_s = 96^\circ$) times larger than the terrestrial Vienna Standard Mean Ocean Water
10 (VSMOW) The HDO/H₂O ratio shows a large seasonal variation at high latitudes. The HDO/H₂O
11 ratio significantly increases from 2.4 ± 0.6 wrt VSMOW at $L_s = 52^\circ$ to 5.5 ± 1.1 wrt VSMOW at
12 $L_s = 96^\circ$ over the latitude range between 70°N and 80°N . This can be explained by preferential
13 condensation of HDO vapor during the northern fall, winter, and spring and sublimation of the
14 seasonal polar cap in the northern summer. In addition, we investigated the geographical
15 distribution of the HDO/H₂O ratio over low latitudes at the northern spring in the longitudinal
16 range between 220°W and 360°W , including different local times from 10 h to 17 h. We found the
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1 observations suggest that the HDO/H₂O distribution in the northern spring and summer seasons is
2 mainly controlled by condensation-induced fractionation between the seasonal northern polar cap
3 and the atmosphere.

4

5 **1. Introduction**

6 Since the first discovery of water vapor in the Martian atmosphere using ground-based
7 observations (Spinrad et al., 1963), the investigation of the water cycle on Mars has been one of
8 the central topics of Martian planetary science. Space-borne observations have revealed that the
9 global and seasonal distribution of water vapor is mainly controlled by dynamics and
10 sublimation–condensation process between the atmosphere and the polar caps. Sublimation of
11 water ice from the northern polar cap during spring and summer provides water vapor to the whole
12 planet, and the water vapor re-condenses to the polar cap in fall and winter (e.g., Farmer et al.,
13 1977; Smith, 2002; Fedorova et al., 2006; Fouchet et al., 2007; Maltagliati et al., 2008; Smith et al.,
14 2009a). In addition to the polar latitudes, the observations have revealed the geographical
15 distribution of water vapor at the low–middle latitudes. Two local maxima of the water vapor
16 amount located over Tharsis (~120°W) and Arabia Terra (~330°W) were identified at middle
17 latitudes. The maxima could be caused by atmospheric dynamics or possible release of water from

1 the subsurface. In addition to the presence of water vapor, water ice clouds form when water vapor
2 in the atmosphere is saturated. Thus far, two major distributions of water ice clouds have been
3 identified (e.g., Montmessin et al., 2004). One is observed at particular low-latitude regions and is
4 called as the “equatorial cloud belt (ECB).” This is where the air is cooled in the ascending branch
5 of the Hadley cell during the northern spring–summer season (e.g., Smith, 2004). The other major
6 distribution of water ice clouds occurs at middle–high latitudes and is referred to as the “polar
7 hood clouds”. These appear during the fall and spring seasons (e.g., Benson et al., 2011). In
8 addition to the ice clouds in the atmosphere, the Gamma Ray Spectrometer (GRS) onboard Mars
9 Odyssey discovered signals associated with subsurface water ice **in the upper ~1-2 m of soil** (e.g.,
10 Boyton et al., 2002; Feldman et al., 2004). Hydrogen-rich deposits (between 20 % and 100 %
11 water-equivalent by mass) were found at high latitudes ($>50^\circ$). It suggests that there are large
12 underground water reservoirs at high latitudes. In fact, Phoenix uncovered a shallow ice table at the
13 landing site (68.22°N) (Smith et al., 2009b). Moreover, the hydrogen-rich deposits were found not
14 only at high latitudes, but also in low-latitude regions. The water content in low-latitude regions
15 never drops below ~2% water-equivalent hydrogen by mass and can be as high as 8–10% around
16 330°W and 175°W . It implies that the subsurface water ice may present at low-latitude regions.

1 Water on Mars exists as vapor in the atmosphere, ice in the form of ice clouds, surface ice, and
2 subsurface ice. The phase change between vapor and ice occurs via a sublimation–condensation
3 process. Spatial and temporal variation of water vapor on Mars should be inseparably connected
4 with this sublimation–condensation process. However, from the currently available observations of
5 atmospheric H₂O on Mars, we cannot discriminate between several different physical mechanisms,
6 e.g., atmospheric dynamics circulation, sublimation from and condensation to polar cap ice or ice
7 clouds, and exchange with the subsurface reservoir. Mapping of the HDO/H₂O ratio allows us to
8 infer the sublimation–condensation process. In the terrestrial case, global mapping of the
9 HDO/H₂O ratio from a space satellite identified regions of strong evapotranspiration and
10 condensation of water vapor (e.g., Frankenberg et al., 2009). Similar mapping of isotopic
11 fractionation in water vapor is expected to provide deeper insight into the physical processes of the
12 water cycle on Mars. The key theory is that the condensation process induces isotopic fractionation
13 of water vapor due to the difference in vapor pressure. Heavier HDO vapor preferentially
14 condensates compared to lighter H₂O vapor (e.g., Fouchet and Lellouch, 2000). Montmessin et al.
15 (2005) calculated seasonal variations of the HDO/H₂O ratio using the General Circulation Model
16 (GCM). They predicted that the HDO/H₂O ratio changes by a factor of 2 owing to
17 condensation-induced fractionation in the polar region. On the other hand, no isotopic fractionation

1 has been expected during sublimation owing very slow molecular rate of diffusion within ice.
2 However, a recent experimental study reported that the HDO/H₂O ratio of the sublimated gas is
3 decreased from the bulk ratio when mineral dust present in the water ice such as the Martian polar
4 caps (Moores et al., 2012). Thus, it is still an open question whether isotopic fractionation occurs
5 or not during sublimation of the polar caps on Mars.

6 HDO/H₂O ratio also has been used as a proxy to understand of the atmospheric evolution of Mars.

7 Previous observations showed that the mean HDO/H₂O ratio in the current Martian atmosphere is

8 5-6 times larger than the terrestrial standard (Vienna Standard Mean Ocean Water, VSMOW;

9 HDO/H₂O = 3.11×10^{-4}). This is probably due to atmospheric evolution, i.e., preferential escape of

10 H atoms from the atmosphere into space for an extended period of time (e.g., Owen et al., 1988;

11 Krasnopolsky et al., 1997; Webster et al., 2013). Understanding of the current water isotope

12 variations in time and space can help to reveal the water history of Mars, because such variations

13 can constrain the distribution of water reservoirs on Mars (e.g., Fisher, 2007).

14 So far, the distribution of the HDO/H₂O ratio has been investigated using only a few ground-based

15 observations (e.g., Fisher et al., 2008; Novak et al., 2011). Fisher et al. (2008) showed that the

16 HDO/H₂O ratio was not uniform but it varied within a range between 2 and 10 wrt VSMOW

17 depending on latitude and season using the data by Mumma et al. (2003). Novak et al. (2011)

1 found latitudinal gradients of the HDO/H₂O ratio at $L_s=50^\circ$ (northern middle spring). Relatively
2 low ratios at high latitudes were interpreted as the effect of condensation of HDO vapor over high
3 latitudes at the middle of the northern spring. Recently, Villanueva et al. (2015) reported global
4 maps of HDO/H₂O ratio at $L_s=335^\circ$ (northern late winter), $L_s=50^\circ$ (northern middle spring), and
5 $L_s=80^\circ$ and 83° (northern late spring). They claimed that the averaged HDO/H₂O ratio is ~7 wrt
6 VSMOW, which is larger than the previous observations by Owen et al. (1988) and Krasnopolsky
7 et al. (1997). Moreover, they found correlation among HDO/H₂O ratio, atmospheric temperature,
8 and H₂O column abundance, and possible anti-correlation between HDO/H₂O ratio and surface
9 altitude. In addition, they found very low HDO/H₂O ratio (1-3 wrt VSMOW) at the winter
10 hemisphere. Isotopic fractionation induced by sublimation-condensation process could explain
11 some of the latitudinal variability, however, the phase change fractionation could not explain the
12 reported non-uniform distribution. It might imply existence of multiple ice reservoirs having
13 different HDO/H₂O ratios depending on their size, accessibility, and location (Fisher, 2007).
14 To improve our observational knowledge of this topic, we investigated the HDO/H₂O ratio during
15 two different seasons, the northern spring ($L_s = 52^\circ$) and summer ($L_s = 96^\circ$), to reveal the seasonal
16 variation. The comparison of two different seasons is expected to assist in the identification of the
17 physical processes that cause the non-uniform distribution of HDO/H₂O. We performed

1 ground-based observations using high-dispersion echelle spectroscopy ($\lambda/\Delta\lambda\sim 20,000$) of the
2 Infrared Camera and Spectrograph (IRCS) of the Subaru telescope (8.2 m) at the Mauna Kea
3 observatory and coordinated joint observations with the Planetary Fourier Spectrometer (PFS)
4 onboard the Mars Express (MEX).

5

6 **2. Observations**

7 2.1. Ground-based observations with Subaru/IRCS

8 Our ground-based observations by Subaru/IRCS were performed on January 4–5, 2012 and April
9 13, 2012. **Table 1** summarizes the observation conditions. The observed seasons on Mars
10 correspond to spring ($L_s = 52.4^\circ$ and $L_s = 52.9^\circ$) and summer ($L_s = 96.2^\circ$) in the northern
11 hemisphere of Mars for January 2012 and April 2012, respectively. The observational diameters of
12 Mars were 9.3–9.4 and 11.5 arcsec on January 4–5 and on April 13, respectively. Doppler shift
13 between Mars and Earth was -15 km/s on January 4–5 and +11 km/s on April 13. During these
14 observations, the longitude of the sub-earth point varied from 256°W to 302°W at 23.6°N on
15 January 4, from 237°W to 294°W at 23.6°N on January 5, and from 34°W to 60°W at 22.3°N on
16 April 13. The longitude of the sub-solar point varied from 292°W to 339°W at 19.7°N on January

1 4, from 273°W to 330°W at 19.8°N on January 5, and from 344°W to 19°W at 25.0°N on April 13,
2 2012.

3 IRCS is designed to deliver diffraction-limited images at 2–5 μm , as well as to provide
4 spectroscopy with grisms and a cross-dispersed echelle (Kobayashi et al., 2000). We used the
5 high-dispersion echelle mode in L-band (2.85–4.16 μm) and the camera with a J-band filter ($1.25 \pm$
6 $0.16 \mu\text{m}$) as a slit viewer. IRCS has a 1024×1024 pixel InSb array detector with a pixel size of
7 0.055 arcsec (slit length direction) \times 0.068 arcsec (slit width direction). The longest and narrowest
8 slit ($6.69 \text{ arcsec} \times 0.14 \text{ arcsec}$) was used to maximize the spatial coverage and spectral resolving
9 power that features an instrumental resolving power of $\sim 20,000$ with a sampling rate of $\sim 40,000$.

10 The high spectral resolution of IRCS is essential for this study because the lines of Martian HDO
11 and H_2O are quite narrow (line width $\sim 0.005 \text{ cm}^{-1}$).

12 The slit was placed along the north–south direction to investigate latitudinal distribution covering
13 the northern pole during the observations on January 5 and April 13. The slit was fixed at the
14 sub-earth longitude that advances at a rate of about 15° in Martian longitude per hour **local time**
15 (due to planetary rotation of Mars). During the observation on January 4, however, the slit was
16 oriented along the east–west direction to investigate longitudinal distribution. For this latter case,

1 we obtained the spectra at 15 latitudes from 0°N to 40°N by manually setting the slit on different
2 positions.

3 We nodded the telescope along the slit observing Mars and sky in the A and B positions,
4 respectively, with a difference of 30 arcsec. Subtraction of (A–B) removes the telluric emissions
5 and other instrumental features. Flat field was obtained immediately before and after the
6 observations. In addition, we performed standard star (*Denebola* on January 4–5 and *Regulus* on
7 April 13) measurements at the beginning, middle, and end of each observation and Ar lamp
8 measurements in order to investigate the instrumental line shape of IRCS.

9 An example of the spectrum measured by IRCS is shown in **Fig. 1**. Owing to the cross-dispersion,
10 we could measure the following five spectral bands simultaneously: 2.94–3.01 μm (Order-19 of the
11 IRCS grating), 3.01–3.18 μm (Order-18), 3.28–3.36 μm (Order-17), 3.49–3.57 μm (Order-16), and
12 3.72–3.81 μm (Order-15). The observed spectra exhibit strong absorption lines of CO₂ (627), CO₂
13 (628), and HDO at Order-15, CO₂ (626) at Order-16, CH₄ at Order-16 and 17, and H₂O at Order-17,
14 18, and 19. The wide spectral coverage of IRCS allows us to observe H₂O and HDO features
15 simultaneously. The spatial resolution of our measurements is mainly restricted by the atmospheric
16 seeing on the observation dates, ~0.8 arcsec on January 4–5 and ~0.5 arcsec on April 13. For the
17 H₂O and HDO analysis, the measured spectra were binned over 10 pixels (~0.55 arcsec) along the

1 slit to increase signal to noise ratio.

2

3 2.2. Coordinated joint observation by MEX/PFS

4 PFS is a double-pendulum interferometer mainly designed for atmospheric analyses, such as

5 measuring the 3-D temperature field in the lower atmosphere, the variations of minor constituents,

6 and the optical properties of aerosols (Formisano et al., 2005). It has two spectral channels, one is

7 the Short Wavelength Channel (SWC) and the other is the Long Wavelength Channel (LWC). The

8 SWC covers the spectral range between 1750 and 8200 cm^{-1} and the LWC covers the spectral

9 range between 250 and 1700 cm^{-1} , both with a sampling step of 1.0 cm^{-1} . The spectral resolution is

10 1.3 cm^{-1} without apodization and 2 cm^{-1} when a Hamming function is applied to the interferograms.

11 One of the advantages of PFS is its wide spectral coverage combined with relatively high spectral

12 resolution.

13 We planned and performed coordinated joint measurements by MEX/PFS from April 10 to 16

14 (within ± 3 days from the Subaru/IRCS observation). The original purpose of this joint observation

15 was to compare H_2O retrievals between IRCS and PFS. However, the abundances of H_2O could not

16 be retrieved from the IRCS data because of the high terrestrial humidity during the joint

17 observation. Therefore, the PFS measurements were used to retrieve H_2O abundances and were

1 subsequently coupled with the HDO data from Subaru/IRCS to derive the HDO/H₂O ratio (there
2 was no problem retrieving both H₂O and HDO from Subaru/IRCS data for the other observations
3 carried out in January 2012). During the planned period (April 10 to 16) of the coordinated
4 observations, PFS observations were performed in 26 orbits across Mars (MEX orbit
5 #10541–10567). Unfortunately, PFS had some problems with the motion of the double-pendulum
6 during this period of simultaneous observation with the Subaru/IRCS. However, PFS worked
7 nominally in the 4 orbits listed in **Table 2** and these observations have been successfully included
8 in this work (as quasi simultaneous observations).

9

10 **3. Method of analysis**

11 3.1. Retrieval of H₂O and HDO abundances from Subaru/IRCS data

12 We retrieved H₂O abundances from the absorption lines at 3035.78356 cm⁻¹ (3.29 μm, Order-17)
13 and 3216.52218 cm⁻¹ (3.10 μm, Order-18) and HDO abundances from the lines at 2672.59294 cm⁻¹
14 and 2677.71967 cm⁻¹ (both around 3.74 μm, Order-19). We performed retrievals for each line
15 independently in order to evaluate the accuracy of our retrievals. **Table 3** describes the line
16 parameters obtained from the HITRAN 2008 database (Rothman et al., 2009). As shown in **Fig. 1**,
17 there are multiple H₂O and HDO lines in the measured spectral range. However, most of the H₂O

1 lines are saturated or not strong enough, and CO₂ isotopic lines under the finite spectral resolution
2 of IRCS contaminate most of the HDO lines on the measured spectra. We carefully selected the
3 absorption lines to be used in this work. The selected lines satisfy the following conditions: strong
4 enough (i.e., line strength is order of 10⁻²² for H₂O and 10⁻²⁴ for HDO), not saturated, minimal
5 instrumental effect (i.e., line center is stable within ~1 pixel along the slit), and minimal
6 contamination from the other lines (i.e., the other terrestrial [O₃, N₂O, CH₄, and H₂O isotopes],
7 Martian CO₂, and solar lines).

8 Since the Martian H₂O and HDO lines appear on the wings of the deep terrestrial ones (the Martian
9 lines are shifted ~2 pixels from the terrestrial lines due to the Doppler shift), the contribution from
10 the terrestrial atmosphere should be separated in order to extract the Martian lines. The extraction
11 requires special considerations of the narrowness of the Martian lines (~1/10 of the IRCS spectral
12 resolution) and of the intrinsic (anamorphic) optical properties of IRCS that lead to an irregular
13 mapping of the spatial and spectral dimensions on to the detector array. For removal of telluric
14 absorptions, co-measured spectra of nearby reference stars are often used in ground-based
15 observations. However, extrapolating the reference star (point-source) signal to an extended object
16 introduces systematic errors. In addition, since the method with standard stars requires atmospheric
17 stability and the same observed air mass between the target and reference stars, it does not always

1 guarantee the quality of the calibration. To solve these problems, we numerically synthesized the
 2 terrestrial atmospheric opacity by developing a dedicated line-by-line radiative transfer model and
 3 fitted it to the measurement spectra to obtain the telluric absorptions during our observations.

4 Our model is based on clear-sky atmosphere model and takes into account the atmospheric
 5 opacities due to terrestrial lines of H₂O, HDO, and O₃, Martian lines of H₂O, HDO, and CO₂
 6 isotopologues (626, 627, 638), solar lines, and the instrumental line shape of IRCS. The line
 7 parameters were obtained from the HITRAN 2008 spectroscopic database (Rothman et al., 2009).

8 Isotopic ratios of CO₂ (627) and CO₂ (638) were obtained from recent results by Curiosity/TLS
 9 (Webster et al., 2013; reported isotopic ratios of CO₂ (627) and CO₂ (638) are 7.618×10^{-4} and
 10 4.928×10^{-5} , respectively). The expected signal intensity $I(x_0)$ at pixel-point x_0 was calculated as

11 follows:

$$12 \quad I(x_0) = [(ax + b) \times t_{solar}(x) \times \exp(-\tau_E(x) - \tau_M(x))] \otimes ILS(x_0 - x, w_{ILS}),$$

13 where x is pixel-point with a sampling rate of ten milli-pixels (x_0 and x are a function of
 14 wavelength), a and b are the scaling factors for continuum, t_{solar} is the transmittance of the solar
 15 lines, τ_E is the total optical depth of the terrestrial lines, τ_M is the total optical depth of the Martian
 16 lines, and ILS is the instrumental line shape of IRCS. The transmittance of the solar spectrum was
 17 obtained from the database of the high-spectral-resolution observation performed by the ACE/FTS

1 (Hase et al., 2010). The instrumental line shape of IRCS was retrieved from Ar lamp
 2 measurements. Since this analysis is sensitive to the line shape and especially to its wing, accurate
 3 characterization of the ILS is indispensable to retrieve the Martian H₂O and HDO abundances
 4 correctly. We found that the instrumental line shape can be expressed as a function of one
 5 parameter (its width W_{ILS}) depending on pixel position over the detector, and this function can be
 6 defined by a combination of two Gaussian functions (see *Appendix A* in detail). For calculations of
 7 the terrestrial lines, we considered 32 atmospheric layers from 4 km to 50 km. The vertical profiles
 8 of temperature, pressure, water vapor, and O₃ in the terrestrial atmosphere were obtained from US
 9 standard atmosphere. Since the line shapes of the terrestrial atmosphere are dominated by
 10 molecular collisions, we considered the collisional line width at each atmospheric layer and
 11 summed the optical depths along the 32 atmospheric layers:

$$12 \quad \tau_E(x) = \sum_j \frac{\eta N_j S(T_j) \alpha_L(T_j, P_j) / dw}{\pi [(x - x_0)^2 + (\alpha_L(T_j, P_j) / dw)^2]} \times z_j,$$

13 where $\tau_E(x)$ is the total optical depth at x pixel-point, η is the telluric air mass, N_j is the column
 14 abundance of the gas at the j -th layer, T_j is the temperature at the i -th atmospheric layer, $S(T_j)$ is the
 15 line strength at T_j K, α_L is the collisional line width, dw is the dispersion of the IRCS echelle mode
 16 in L-band (0.763 \square /pixel at order18, 0.809 \square /pixel at order-17, and 0.914 \square /pixel at order-15), x_0
 17 is the central pixel-point of the terrestrial line, and z_j is the thickness of the layer. The temperature

1 correction of the line intensity is referred to Rothman et al. (1998) by using the total internal
 2 partition sum from Gamache et al. (2000).

3 Line width of H₂O and HDO in the Martian atmosphere is dominated by the Doppler line width
 4 (e.g., Krasnopolsky et al., 2004), because the pressure in the atmosphere is relatively low.

5 Therefore, we computed the optical depth considering the Doppler line widths:

$$6 \quad \tau_M(x) = \sum_j \frac{\mu N_j S(T_j)}{\sqrt{\pi} \alpha_D(T_j) / dw} \exp\left(-\left[\frac{(x - x_0 + ds/dw)}{\alpha_D(T_j) / dw}\right]^2\right) \times z_j,$$

7 where $\tau_M(x)$ is the total optical depth at x pixel-point, μ is the total air mass on Mars, α_D is the
 8 Doppler line width, and ds is Doppler shift. For the Martian atmosphere, we considered 10
 9 atmospheric layers from 0 km to 20 km, and the vertical profiles of temperature, pressure, and
 10 water vapor were derived from Mars Climate Database ver 4.3
 11 (<http://www-mars.lmd.jussieu.fr/mars/access.html>). We assumed the effects of dust and ice
 12 aerosols to be negligible at this wavelength; accordingly, these were not included in the radiative
 13 transfer calculation.

14 The measured signals include both solar radiation reflected at the Martian surface (2-way path in
 15 the Martian atmosphere: Sun–Mars–Earth) and the thermal radiation of the Martian surface (1-way
 16 path: Mars–Earth). Thus, the total air mass μ is given by

$$17 \quad \mu = r_s(\mu_s + \mu_e) + (1 - r_s)\mu_e,$$

1 where r_s is the rate of solar radiation, $(1-r_s)$ represents the rate of the thermal radiation, μ_s is the
2 Sun-to-surface air mass, and μ_e is the surface-earth air mass. Our radiative transfer model showed
3 that the contribution of thermal radiation from the Martian surface is negligible (i.e., $r_s = 1.0$) at the
4 H₂O spectral range. Conversely, at the HDO spectral range, the contribution of thermal radiation
5 must be taken into account. The rate r_s was retrieved using a strong solar line at 2669.7849 cm⁻¹ by
6 comparing the observed spectrum with the synthetic spectrum of the solar line. **Fig. 2** shows the
7 retrieved rate of surface radiation $(1-r_s)$ retrieved from the IRCS data. The rates are variable
8 depending on surface albedo and temperature. The enhancement of surface radiation rate $(1-r_s)$ at
9 280-320°W and 0-20°N appeared in the January data can be explained by low surface albedo
10 (Christensen et al., 2001), and the latitudinal gradient appeared in the April data can be explained
11 by decrease of surface temperature toward polar region. The relatively high rate at high-latitude
12 region (>70°N) found in January data is probably caused by high surface albedo due to the
13 presence of the seasonal polar cap on the ground.

14 For retrieval, the synthetic spectra were calculated in the limited spectral range of ± 7 pixels ($\sim \pm 0.5$
15 cm⁻¹) from the line center for each H₂O line, and ± 5 pixels ($\sim \pm 0.3$ cm⁻¹) from the line center for
16 each HDO line. We retrieved the following five parameters: scaling factor for the continuum (a
17 and b), center pixel-point of the deep terrestrial line x_0 , width of instrumental line shape w_{ILS} , total

1 column density of the terrestrial water vapor, and total column density of the Martian water vapor.

2 We set the spectral resolution as an unknown parameter because it varies along the slit and

3 dispersion direction. The total column density of the terrestrial water vapor was assumed as a

4 constant value along the slit. The retrieval was performed by setting a parameter domain for the

5 column density of Martian water vapor from 0 pr- μm to 25 pr- μm with intervals of 1 pr- μm for

6 H_2O and 0 pr-nm to 100 pr-nm with intervals of 1 pr-nm for HDO. Then, for each condition of

7 Martian H_2O and HDO abundances, we retrieved the other 5 parameters using

8 Levenberg–Marquardt non-linear minimization algorithm. Finally, we derived the Martian H_2O

9 and HDO column densities that provide the minimum values for chi-squares. To check our

10 retrieval scheme, we applied the retrieval algorithm to standard star data as well as Mars

11 observations. **Figures 3** and **4** show examples of the fitting analysis in the H_2O and HDO spectral

12 ranges, respectively. No residual signal is present from the standard star observation, as expected.

13 This indicates that the signal derived from Mars data represents the real Martian contribution.

14 There are two sources of error in the retrieved Martian H_2O and HDO abundances: instrumental

15 noise and uncertainty in the forward (radiative transfer and IRCS instrumental) model. The

16 instrumental noise was estimated from standard deviation (1-sigma) of the residuals between IRCS

17 data and best-fit synthetic spectrum. Regarding the forward model error, the dominant factor is

1 uncertainty in the temperature profile obtained from the Mars Climate Database, whose uncertainty
2 is expected to be ~5% (Sindoni et al., 2011). This uncertainty propagates to the errors of ~7% and
3 ~1% in the retrieved H₂O abundances from 3035 cm⁻¹ and 3216 cm⁻¹ and ~5% and ~4% in the
4 retrieved HDO abundances, respectively. Finally, the uncertainties in the retrieved H₂O or HDO
5 abundances σ were given by

6
$$\sigma = \sqrt{\sigma_n^2 + \sigma_m^2},$$

7 where σ_n is error due to instrumental noise, and σ_m represents error due to the model.

8 After the errors were evaluated, the H₂O abundances retrieved from the absorption lines at 3035
9 cm⁻¹ and 3216 cm⁻¹ and the HDO abundances from the lines at 2672 cm⁻¹ and 2677 cm⁻¹ were
10 compared, respectively. We excluded results of the two retrieved values (H₂O or HDO
11 abundances) that were inconsistent beyond 2σ as “low confidence” results. Note that the
12 inconsistent results were less than 15% of the whole data set. Lastly, the derived H₂O abundances,
13 HDO abundances, and their errors were calculated from the weighted averages:

14
$$y = \frac{w_a y_a + w_b y_b}{w_a + w_b},$$

$$\sigma = \frac{1}{\sqrt{w_a + w_b}},$$

15 where y represents the derived H₂O or HDO abundance, y_a and y_b are the values retrieved from
16 each of the lines, and w_a and w_b are given by

$$w_a = \frac{1}{\sigma_a^2},$$
$$w_b = \frac{1}{\sigma_b^2},$$

1

2 where σ_a and σ_b are the errors retrieved from each of the lines.

3

4 3.2. Retrieval of H₂O abundances from MEX/PFS data

5 We retrieved H₂O abundances from PFS observations listed in **Table 2**. For the H₂O retrievals, the

6 absorption band from 3780 to 3950 cm⁻¹ at the Short Wavelength Channel (SWC) was used

7 (Tschimmel et al., 2008; Sindoni et al., 2011). We averaged 9 consecutive spectra with a sampling

8 rate of every two spectra in order to improve the SNR and the accuracy of the retrieved H₂O

9 abundances. **Figure 5** shows an example of averaged PFS spectrum in the considered spectral

10 range, and the best-fit synthetic spectrum. We retrieved H₂O abundances using a fast radiative

11 transfer model developed for PFS data processing (Ignatiev et al., 2005) and least-squares method.

12 The details of the retrieval algorithm can be found in Sindoni et al. (2011). The uncertainty in the

13 retrieved H₂O mixing ratio is about 19% total (Sindoni et al., 2011).

14

15 **4. Latitudinal distribution at $L_s = 52^\circ$ (northern spring)**

16 **Figure 6** shows latitudinal distribution of column-integrated H₂O and HDO abundances retrieved

1 from Subaru/IRCS observations carried on January 5, 2012 ($L_s = 52^\circ$) and the H₂O abundances
2 taken from Mars Climate Database (MCD) ver-5.0
3 (<http://www-mars.lmd.jussieu.fr/mars/access.html>) for comparison. Different colors indicate the
4 observed longitudes. These values have been normalized by surface pressure in order to remove
5 the effect of topography. The retrieved H₂O abundances range from 4 pr- μm to 15 pr- μm (1 pr- μm
6 = $3.34 \times 10^{18} \text{ cm}^{-2}$), and exhibit maximum values around 60–70°N. On the other hand, the H₂O
7 abundances predicted by MCD range from 5 pr- μm to 15 pr- μm , and show a maximum value
8 around 60°N. Our observed H₂O abundances show general agreement with those from the MCD in
9 terms of absolute values and latitudinal distribution. In addition, the longitudinal trend at the edge
10 of Arabia Terra (over 302°W and 298°W at middle latitudes) appears both in the observation and
11 model.

12 In the northern spring season ($L_s = 52^\circ$), the edge of the northern polar cap is expected to be
13 around 70°N, according to the observations by near-infrared spectroscopy (e.g., Appéré et al.,
14 2011). Since surface temperature exceeds water condensation temperature at the edge of the polar
15 cap, sublimation of the water ice cap would occur there. Indeed, the previous observations of water
16 vapor during this season exhibit its enhancement at the edge of polar cap (e.g., Fouchet et al.,
17 2007; Pankine et al., 2010). Thus, the enhancement of H₂O shown in our observations is likely due

1 to sublimation of water ice.

2 The latitudinal distribution of HDO appears slightly different to that of H₂O. The retrieved HDO
3 abundances range from 3 pr-nm to 17 pr-nm (1 pr-nm = $3.34 \times 10^{15} \text{ cm}^{-2}$) and have a maximum
4 value around 30–40°N. The difference between H₂O and HDO produces latitudinal gradients in the
5 HDO/H₂O ratio. **Fig. 7** shows the latitudinal distribution of the HDO/H₂O ratio retrieved from the
6 Subaru/IRCS observation (left panel), their mean values averaged over the faced longitude
7 (256–302°W), and values predicted by the GCM model of Montmessin et al. (2005) (right panel).
8 The derived mean HDO/H₂O ratio ranges between 5.0 ± 0.9 wrt VSMOW (at 30°N) and 2.4 ± 0.6
9 wrt VSMOW (at 80°N). The global mean value of the HDO/H₂O ratio and its standard deviation
10 are 4.1 ± 1.4 wrt VSMOW. The distribution exhibits a maximum around sub-solar latitudes
11 (20–40°N) and decreases at high latitudes (>60°N). As shown in **Fig. 7**, such a latitudinal gradient
12 was also predicted by the GCM model based on condensation-induced fractionation (Montmessin
13 et al., 2005). The model predicted that the HDO/H₂O ratio would decrease from 5 wrt VSMOW to
14 2 wrt VSMOW owing to preferential condensation of HDO vapor at high latitudes. We consider
15 this depletion of HDO around 50–80°N is mainly due to the condensation of water vapor on the
16 polar cap. In fact, the previous observation of surface composition detected the formation of a
17 water ice cap over the polar cap at 70–90°N (e.g., Appéré et al., 2011) and the GCM suggested the

1 formation of polar hood clouds at 50–90°N (Montmessin et al., 2004).

2

3 **5. Latitudinal distribution at $L_s = 96^\circ$ (northern summer)**

4 We retrieved the latitudinal distribution of the HDO/H₂O ratio during the northern summer ($L_s =$
5 96°) using HDO abundance obtained by Subaru/IRCS data and H₂O abundances retrieved from
6 MEX/PFS data in order to investigate seasonal variation. HDO could not be detected from IRCS
7 data with enough accuracy below 40°N owing to the high terrestrial humidity during the
8 ground-based observation. **Fig. 8** shows the latitudinal distribution of the H₂O column density
9 retrieved from PFS/SWC data (left panel) and the HDO column density retrieved from
10 Subaru/IRCS data (right panel). These values have been normalized by surface pressure to remove
11 the effect of topography. We found that both H₂O and HDO column densities have a large value in
12 the polar region during the northern summer ($L_s = 96^\circ$).

13 In order to derive the HDO/H₂O ratio from these data, we calculated the mean profile of H₂O
14 column density retrieved by PFS with the latitudinal grid of the SUBARU observation. For that,
15 the H₂O column densities within the latitudinal footprint of SUBARU observation (i.e.,
16 atmospheric seeing during the observation) were averaged. The red curve in the left panel of **Fig. 8**
17 shows the mean profile of H₂O column density. The black points shown in **Fig. 9** represent the

1 HDO/H₂O ratio calculated by the profiles, and the red curve shown in **Fig. 9** is the averaged
2 HDO/H₂O ratio in order to compare with that of $L_s=52^\circ$ (the blue curve shown in **Fig. 9**). The
3 mean value (averaged over all observed longitudes and latitudes) of the HDO/H₂O ratio at $L_s = 96^\circ$
4 and its standard deviation are 4.4 ± 1.0 wrt VSMOW. Although the error values are relatively large
5 (mainly owing to the standard deviation of the H₂O column density from PFS data and longitudinal
6 variability), the latitudinal distribution of HDO/H₂O ratio at $L_s=96^\circ$ is more uniform profile than
7 the one observed at $L_s=52^\circ$. An interesting result from **Fig. 9** is the seasonal variation of HDO/H₂O
8 ratio over the latitude range between 70°N and 80°N . We found that the HDO/H₂O ratio increased
9 from 2.4 ± 0.6 wrt VSMOW ($L_s = 52^\circ$) to 5.5 ± 1.1 wrt VSMOW ($L_s = 96^\circ$) at the high latitude.
10 As described in Section 4, the relatively low value of the HDO/H₂O ratio at $L_s = 52^\circ$ can be
11 explained by condensation of water vapor. Since the water vapor abundances in the polar region
12 exhibit a drastic increase from $L_s = 52^\circ$ to $L_s = 96^\circ$, the seasonal increase of the HDO/H₂O ratio
13 from $L_s = 52^\circ$ to $L_s = 96^\circ$ can be considered to be due to sublimation of the polar water ice cap.
14 Moreover, this relatively uniform latitudinal distribution of HDO/H₂O ratio $L_s = 96^\circ$ implies that
15 the isotopic fractionation during sublimation is small and is beyond the sensitivity of this analysis.
16 The observed seasonal variation suggests that the sublimation–condensation process can induce a
17 change in the isotopic fractionation by a factor of 2.

1 Note that the IRCS and PFS measurements were taken at different local times on Mars (IRCS:
2 9-10h, PFS: 16h). This may cause systematic error in the retrieved HDO/H₂O ratio. However,
3 Phoenix measurements showed no significant difference in H₂O abundance between 9h and 16h
4 (Smith et al., 2009b). Moreover, recent remote-sensing studies by MEX/SPICAM and MGS/TES
5 show that local time variation of total H₂O column is small at this season (e.g., Pankine and
6 Tamppari, 2015; Trokhimovskiy et al., 2015). The systematic error in the HDO/H₂O ratio can be
7 estimated to be less than ~10%. Therefore, we assume that the systematic error in the HDO/H₂O
8 ratio due to using the different local time observations by IRCS and PFS can be less than ~10%.
9 The seasonal increase of HDO/H₂O ratio over the latitude range between 70°N and 80°N is still
10 significant even if the systematic error is taken into account.

11

12 **6. Geographical distribution over low latitudes at $L_s = 52^\circ$ (northern spring)**

13 We investigated the geographical distribution of the HDO/H₂O ratio over low latitudes at the
14 northern spring ($L_s = 52^\circ$) in the longitudinal range between 220°W and 360°W, including various
15 local times from 10 h to 17 h. **Fig. 10** shows the longitudinal distribution of column-integrated
16 H₂O and HDO abundances retrieved from the Subaru/IRCS observations carried out on January 4,
17 2012. These values have been normalized by surface pressure in order to remove the effect of

1 topography. The retrieved H₂O abundances are distributed in the range from 4 pr- μ m to 18 pr- μ m,
2 and the HDO abundances range from 5 pr-nm to 19 pr-nm. The retrieved H₂O abundances are
3 consistent with the typical abundance during this season reported by the space-borne observations.
4 For example, MGS/TES and Viking/MAWD results determined that the longitudinal mean
5 abundances at this season are between 10 pr- μ m and 15 pr- μ m (e.g., Smith, 2002). The retrieved
6 longitudinal distribution of water vapor exhibits a local maximum over Arabia Terra (~330°W),
7 according to both H₂O and HDO abundances. **Fig. 11** illustrates the longitudinal distribution of the
8 HDO/H₂O ratio retrieved from the Subaru/IRCS observations (top panel) and the value averaged
9 over all latitudes (bottom panel). The global mean value of the derived HDO/H₂O ratio and its
10 standard deviation are 5.1 ± 1.2 wrt VSMOW. The local enhancement of water vapor abundances
11 over Arabia Terra has been depicted in a seasonal-averaged map of water vapor using
12 spacecraft-borne measurements with MGS/TES (Smith, 2002) and MEX/PFS (Fouchet et al.,
13 2007; Tschimmel et al., 2008; Sindoni et al., 2011). On the other hand, as shown in **Fig. 11**, there is
14 no significant longitudinal variation in the HDO/H₂O ratio. Although the results cannot constrain
15 the sources of local enhancement, i.e., atmospheric dynamics or sublimation from subsurface ice,
16 we have demonstrated that there is no significant longitudinal distribution over Arabia Terra.
17 These observations also covered different local times ranging from 10 h to 17 h, although not for

1 the same longitudes. **Fig. 12** shows the local time distribution of H₂O and HDO abundances
2 normalized by surface pressure. The retrieved water vapor exhibits a local maximum around 12–13
3 h that corresponds to Arabia Terra (~330° W). **Fig. 13** represents the local time dependence of the
4 HDO/H₂O ratio retrieved from the Subaru/IRCS observation. It shows that the distribution of
5 HDO/H₂O is no significant variation (5.1 ± 1.2 with respect to VSMOW) in the local time range
6 between 10 h and 17 h. Note that recent observations reveal a significant depletion of HDO at
7 dawn that may be explained by condensation-induced fractionation due to cloud formation
8 (Villanueva et al., 2008; Villanueva et al., 2013; Novak et al., 2014). Further observation is needed
9 to address this issue, because the dawn side was not covered by our observations.

10

11 **7. Comparison with the previous observations**

12 The latitudinal mean HDO/H₂O ratios retrieved from our observations are 4.1 ± 1.4 ($L_s = 52^\circ$) and
13 4.4 ± 1.0 ($L_s = 96^\circ$) wrt VSMOW, which agrees with the global mean values reported by previous
14 ground-based observations by Owen et al. (1988) [6 ± 3 wrt VSMOW] and Krasnopolsky et al.
15 (1997) [5.5 ± 2.0 wrt VSMOW] but smaller than the value reported by Villanueva et al. (2015) [\sim
16 7 wrt VSMOW]. One possible explanation for this discrepancy is temporal variation of the
17 HDO/H₂O ratio (seasonal, localtime, or inter-annual variation). The other possible explanation is

1 due to systematic error in the analysis. For instance, in this analysis, the effect of dust and water
2 ice was not taken into account. This may give an impact the retrieved HDO abundance (see SOM
3 of Villanueva et al., 2015). The implementation of the aerosol effect in our retrieval is one of the
4 future works.

5 As shown in **Fig. 7**, we found that the retrieved latitudinal distribution at $L_s = 52^\circ$ exhibits a
6 maximum around sub-solar latitudes ($20\text{--}40^\circ\text{N}$) and decreases at high latitudes ($>60^\circ\text{N}$), which
7 was also found by Novak et al. (2011). The observation by Novak et al. (2011) was performed in
8 the same season ($L_s=50^\circ$) as our observation but for a different Martian year (MY 29), longitude
9 (153°W), and local time (9:40) by the IRTF/CSHELL. The HDO/H₂O ratio retrieved by Novak et
10 al. (2011) peaks at 6.9 ± 0.2 wrt VSMOW in the sub-solar region and decreases to 3.8 ± 0.3
11 towards the pole. Although our values are smaller than those obtained by Novak et al. (2011), the
12 two observations have a similar distribution that peaks near the sub-solar latitude and decreases
13 toward the pole. Moreover, Villanueva et al. (2015) reported the map of HDO/H₂O ratio taken by
14 the IRTF/CSHELL in the same season ($L_s=50^\circ$), the same Martian year (MY 29), and including
15 same longitude (153°W) of the observation by Novak et al. (2011). However, the map by
16 Villanueva et al. (2015) does not show the depletion of HDO at the high latitudes region.
17 Villanueva et al. (2015) also revealed correlation between HDO/H₂O ratio and H₂O column

1 abundance. The positive correlation is agreed with the concept of the Rayleigh distillation
2 considered in the GCM model (Montmessin et al., 2005). On the other hand, Fisher et al. (2008)
3 reported that the HDO/H₂O ratio is very large when the atmosphere's water vapor column is small
4 from the data by Mumma et al. (2003). The anti-correlation between H₂O column density and
5 HDO/H₂O ratio was interpreted as the possible effect of existence of multiple ice reservoirs having
6 different HDO/H₂O ratios depending on their size, accessibility, and location. **Fig. 14** shows the
7 relationship between H₂O column density and HDO/H₂O ratio from our results. Our result at
8 $L_s=52^\circ$ also suggests the anti-correlation. Further observations are necessary to constrain these
9 issues. Furthermore, Villanueva et al. (2015) reported possible anti-correlation between HDO/H₂O
10 ratio and surface altitude. Although possible regionalism could be seen in our results, we cannot
11 make sure if it is real variation since the error values are large. Regionalism of HDO/H₂O is
12 beyond the scope of this paper.

13 As shown in **Fig. 11**, we found that the HDO/H₂O ratio was no significant variation (5.1 ± 1.2 wrt
14 VSMOW) in the longitudinal range between 220°W and 360°W at $L_s=52.4^\circ$. Novak et al. (2014,
15 conference proceeding) reported the longitudinal distribution of HDO/H₂O ratio over the same area
16 but at different season ($L_s=72.5^\circ$). The HDO/H₂O ratio at $L_s=72.5^\circ$ reported by Novak et al.
17 (2014) is distributed between 2 to 5 wrt VSMOW (see the **Fig. 3B** of Novak et al. (2014)). The

1 HDO/H₂O values are lower than those of our results at $L_s=52.4^\circ$. Although the reason is not clear
2 at the moment, the seasonal variation of HDO/H₂O ratio at low latitudes could be related with the
3 fact that Villanueva et al. (2015) found very low HDO/H₂O ratio (1-3 wrt VSMOW) at the winter
4 hemisphere. Similar seasonal decrease of the HDO/H₂O ratio at the low-latitude region also can be
5 seen in the maps (at $L_s=50^\circ$ and 80°) reported by Villanueva et al. (2015).

6

7 **8. Summary**

8 In this study, seasonal variation of HDO/H₂O distributions by latitude during the northern spring
9 ($L_s = 52^\circ$) and summer ($L_s = 96^\circ$) was investigated. The derived seasonal variation of the
10 HDO/H₂O ratio and global view of the water cycle on Mars inferred from our observations is
11 summarized in **Fig. 15**. We found seasonal increase of the HDO/H₂O ratio at the polar region
12 ($70\text{--}80^\circ\text{N}$), from 2.4 ± 0.6 wrt VSMOW ($L_s = 52^\circ$) to 5.1 ± 0.7 wrt VSMOW ($L_s = 96^\circ$). The
13 seasonal increase can be explained by the interaction between the atmosphere and the north polar
14 cap: condensation of water vapor occurs as polar hood clouds and/or the seasonal polar cap form in
15 the northern spring ($L_s = 52^\circ$), and sublimation of the polar water ice cap occurs in the northern
16 summer ($L_s = 96^\circ$). On the other hand, the latitudinal mean HDO/H₂O ratios do not show a
17 significant seasonal variation, with values of 4.1 ± 1.4 ($L_s = 52^\circ$) and 4.6 ± 0.7 ($L_s = 96^\circ$). We

1 found the HDO/H₂O ratio has no significant variation (5.1 ± 1.2 wrt VSMOW) over low latitudes
2 during the northern spring in the longitudinal range between 220°W and 360°W for different local
3 times from 10 h to 17 h. As shown in **Fig. 15**, we did not take into account the effects of
4 subsurface-atmosphere interaction in the interpretation of the results since it is still unknown that
5 how much the ground ice interacts with atmospheric water vapor and how much they induce
6 isotopic fractionations. However, our results suggest that HDO/H₂O distribution in the atmosphere
7 is mainly controlled by condensation-induced fractionation between the northern polar cap and the
8 atmosphere.

9 Still, further observations are necessary to conduct open issues. For example, relationship between
10 H₂O column density and HDO/H₂O ratio and its interpretation are not fully understood. Very low
11 HDO/H₂O ratio (1-3 wrt VSMOW) at the winter hemisphere reported by Villanueva et al. (2015)
12 might be related to subsurface-atmosphere interaction. In order to increase data set, we plan to
13 investigate the HDO/H₂O ratio by comparing between the HDO map observed by IRTF/TEXES
14 (e.g., Encrenaz et al., 2010) and the H₂O map retrieved from MEX/PFS. In addition, Nadir and
15 Occultation for Mars Discovery (NOMAD) onboard ExoMars Trace Gas Orbiter (Vandaele et al.,
16 2011) will perform to measure maps of HDO/H₂O ratio and its vertical profile are obtained from
17 the Mars Orbiter. It will allow us to obtain a complete picture of its geographical and seasonal

1 distributions.

2

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15

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7

8 **Appendices**

9 **Appendix A. Retrieval of Instrumental line shape of IRCS**

10 Since line widths of the Martian H₂O and HDO lines are ~10 times smaller than the spectral
11 resolution of IRCS, the observed line shapes reflect the instrumental line shape (ILS) of IRCS.
12 Therefore, characterization of the ILS is important to perform retrieval accurately. Here, we
13 retrieved the ILS using Ar lamp measurements carried out in a similar configuration to the Mars
14 observation. The lamp measurements were performed for 2.5 h in order to obtain sufficient signal
15 to noise ratio. Line widths of Ar lamps are so narrow (~0.02 cm⁻¹, Engleman et al., 2003) that the
16 observed line shapes represent the ILS of IRCS. There are five independent lines in the measured
17 spectral ranges (3016.7336 cm⁻¹, 3023.0817 cm⁻¹, 3040.5647 cm⁻¹, 3191.5201 cm⁻¹, and 3272.9622

1 cm^{-1}), and we used lines at $3040.5647 \text{ cm}^{-1}$, $3191.5201 \text{ cm}^{-1}$, and $3272.9622 \text{ cm}^{-1}$ for retrieval of
 2 the ILS. **Figure A-1** shows all the measurements for the three lines. We found that full width at
 3 half maximum (FWHM) of the ILS is not constant but depends on pixel position on the detector.

4 We attempted to retrieve the ILS as a function of FWHM. As the first attempt, Gaussian and
 5 sinc-squared functions were applied to fit these data since these functions are well known as a line
 6 shape of eschelle spectroscopy. However, as shown in **Fig. A-2**, both functions could not reproduce
 7 the observed line shape, especially in the wings. Therefore, we assumed that the ILS is a
 8 combination of two functions, one for line center and the other for wings. We tested the six cases
 9 listed in **Table A-1** and determined the most accurate one by using the least squares method. We
 10 derived the switching spectral point of the two functions and the relationship between their
 11 FWHMs in the retrieval process.

12 As shown in **Table A-1**, the combination of two Gaussian functions is most accurate for the ILS of
 13 IRCS. The retrieved ILS of IRCS is given by

$$14 \quad ILS(x) = \begin{cases} F_1(x) & (|x - x_0| \leq 1.9 \text{ pixels}) \\ F_2(x) & (|x - x_0| > 1.9 \text{ pixels}) \end{cases},$$

15

16 where

$$17 \quad F_1(x) = \exp\left(-\frac{(x - x_0)^2}{w_{ILS}}\right) / 2, \quad F_2(x) = \beta \times \exp\left(-\frac{(x - x_0)^2}{w'_{ILS}}\right) / 2,$$

1 $w'_{ILS} = w_{ILS} \times 1.72, \beta = F_1(1.9) / \exp(-(1.9/w_{ILS})^2 / 2).$

2 w_{ILS} and w'_{ILS} are FWHM of the Gaussian functions. The FWHM of the second function (for line
3 wing) is 1.72 times larger than that of the first function (for line center). The two functions are
4 switched at the 1.9 pixel far from the observed wavelength. **Figure A-3** shows the Ar lamp
5 measurements and the retrieved ILS. The IRCS could reproduce the wings of the lamp spectra
6 much better than simple Gaussian or sinc-squared function (**Fig. A-2**).

7

8 **Figure captions**

9 **Figure 1.** Example of a spectrum obtained by IRCS. Five spectral bands can be observed
10 simultaneously: 2.94–3.01 μm (order-19), 3.01–3.18 μm (order-18), 3.28–3.36 μm (order-17),
11 3.49–3.57 μm (order-16), and 3.72–3.81 μm (order-15). The spectrum was observed on January 5
12 with 5-min integration and without binning. Circular symbols in (c) represent CH_4 lines and the
13 other features in Order-17 are H_2O lines. Triangle symbols in (e) represent the HDO lines. The
14 gray boxes represent the spectral ranges used in this analysis.

15

16 **Figure 2.** Rate of surface radiation in the observed IRCS signals at HDO spectral range.
17 Differences in colors show the observing latitudes or longitudes.

1

2 **Figure 3.** Examples of the fitting analysis with Mars (top) and standard star (bottom) H₂O lines. In
3 the upper spectra at each panel, the IRCS data are shown in black and the best-fit synthetic spectra
4 with and without Martian contributions are in red and blue, respectively. The bottom spectra show
5 residual spectra after removing the terrestrial contributions (Black: IRCS data, Red: the best-fit
6 spectra). The Martian spectra were measured on January 5, 2012 over the latitude 35°N. Retrieved
7 column densities of Martian H₂O are 8 (±2) pr-μm from 3035 cm⁻¹ ranges and 11 (±1) pr-μm from
8 3216 cm⁻¹ ranges (1 pr-μm equals 3.34 × 10¹⁸ molecules/cm²).

9

10 **Figure 4.** Same as Fig. 3, but for HDO lines. Retrieved column densities of Martian HDO are 16
11 (±4) pr-nm from 2677 cm⁻¹ ranges and 12 (±3) pr-nm from 2672 cm⁻¹ ranges.

12

13 **Figure 5.** An example of retrieval of H₂O abundance from PFS/SWC data at 13.3°N. The black
14 curve shows the averaged PFS spectrum and the red one represents the best-fit synthetic spectrum.
15 The retrieved H₂O mixing ratio is 150 ± 28 ppm. The uncertainty in the retrieved H₂O mixing ratio
16 is about 19% total (Sindoni et al., 2011).

17

1 **Figure 6.** (Left) Latitudinal distribution of H₂O abundances measured by Subaru/IRCS. (Middle)
2 Latitudinal distribution of H₂O abundances predicted by the Mars Climate Database (ver5.0).
3 (Right) Latitudinal distribution of HDO abundances measured by Subaru/IRCS. Differences in
4 colors show the observing longitudes. The values are divided by ($P_{surf}/6.1$) to remove the effect of
5 topography, where P_{surf} is surface pressure in mbar. The horizontal bars show the estimated error
6 values and the vertical bars represent the latitudinal footprints of the binned 10 pixels.

7
8 **Figure 7.** (Left) Latitudinal distribution of the HDO/H₂O ratio (relative value to VSMOW)
9 measured by Subaru/IRCS. Differences in color represent the observed longitudes. The horizontal
10 bars show the estimated error values and the vertical bars represent the latitudinal footprints of the
11 binned 10 pixels. (Right) Latitudinal mean values of the HDO/H₂O ratios are shown in the top
12 panel. The error bars correspond to standard deviations. The triangle symbols show the predicted
13 values by GCM of Montmessin et al. (2005). The values are extracted from the zonal averaged
14 map of the HDO/H₂O ratio shown in **Fig. 2** of Montmessin et al. (2005).

15
16 **Figure 8:** (Left) Latitudinal distribution of the H₂O column density retrieved from
17 MEX/PFS–SWC observations. The light blue, blue, yellow, and green curves represent orbit10542

1 (16°W, 10/April), orbit10547 (167°W, 12/April), orbit10542 (162°W, 14/April), and orbit10542
2 (109°W, 14/April), respectively. The red curve corresponds to the longitudinal mean profile and the
3 error bars represent standard deviation. The black points show the H₂O column density at $L_s = 52^\circ$
4 (northern spring) retrieved by Subaru/IRCS. (Right) Latitudinal distribution of the HDO column
5 density retrieved from Subaru/IRCS observations. The red and black points represent the values at
6 $L_s = 96^\circ$ (northern summer) and $L_s = 52^\circ$ (northern spring), respectively. The blue curve denotes
7 the longitudinal mean profile of the retrieved HDO column density at $L_s = 96^\circ$ and the error bars
8 represent standard deviation. These values have been normalized by surface pressure in order to
9 remove the effect of topography.

10

11 **Figure 9:** Seasonal variation of the HDO/H₂O ratio (relative to VSMOW). The red curve
12 represents the distribution observed at $L_s = 96^\circ$ and the black curve indicates the distribution at L_s
13 $= 52^\circ$ (similar to the right panel of **Fig. 7**). The error values of the HDO/H₂O ratio at $L_s = 96^\circ$ are
14 estimated from standard deviations of both H₂O and HDO mixing ratios. ~~The values are extracted~~
15 ~~from the zonal-averaged map of the HDO/H₂O ratio shown in Fig. 2 of Montmessin et al. (2005).~~

16

17 **Figure 10.** (Top) Longitudinal distribution of H₂O column abundances. (Bottom) Longitudinal

1 distribution of HDO column abundances. Differences in colors represent the observing latitudes.
2 The values are divided by $(P_{surf}/6.1)$ to remove the effect of topography, where P_{surf} is surface
3 pressure in mbar. The vertical bars denote the estimated error values and the horizontal bars
4 represent the longitudinal footprints of the binned 10 pixels.

5

6 **Figure 11.** (Top) Longitudinal distribution of the HDO/H₂O ratio (relative value to VSMOW;
7 HDO/H₂O = 3.11×10^{-4}). Differences in colors signify the observing latitudes. The vertical bars
8 show the estimated error values and the horizontal bars represent the longitudinal footprints of the
9 binned 10 pixels. (Bottom) Latitudinal-mean values of the HDO/H₂O ratios shown in the top panel.
10 The error bars correspond to their standard deviations.

11

12 **Figure 12.** (Top) Local time distribution of H₂O column abundances. (Bottom) Local time
13 distribution of HDO column abundances. Differences in colors represent the observing latitudes.

14

15 **Figure 13.** (Top) Local time distribution of the HDO/H₂O ratio. Differences in colors denote the
16 observing latitudes. (Bottom) Latitudinal mean values of the HDO/H₂O ratios shown in the top
17 panel. The error bars correspond to their standard deviations.

1

2 **Figure 14.** HDO/H₂O ratio with H₂O column density from our measurements at $L_s=96^\circ$ (left) and
3 $L_s=52^\circ$ (right).

4

5 **Figure 15.** Sublimation–condensation process in the Martian water cycle and the HDO/H₂O ratio
6 in water vapor during the northern spring ($L_s = 52^\circ$) and summer ($L_s = 96^\circ$), inferred from our
7 observations

8

9 **Figure A-1.** Ar lamp spectra measured by IRCS at 3049.5647 cm^{-1} (left), 3191.5201 cm^{-1} (center),
10 and 3272.9622 cm^{-1} (right). All observed data (all pixels in the slit) are shown together.

11

12 **Figure A-2.** Ar lamp spectra shown in Figure A-1 and their best-fit spectra with Gaussian function
13 (red curves) and Sinc-squared function (blue curves).

14

15 **Figure A-3.** Ar lamp spectra shown in Figure A-1 and the retrieved ILS by combination of two
16 Gaussian functions (red curves).

Tables

Table 1 Parameters of Mars observations with Subaru/IRCS

Date and time (UT)	L_s ($^\circ$)	MY	Doppler shift (km/s)	Diameter ($''$)	Airmass	Slit direction	Observing areas ($^\circ$)	Local Time
4/January/2012 13:12–16:26	52.4	31	-15	9.3	1.14–1.09	E–W	0N–40N	10–17
5/January/2012 12:34–16:28	52.9	31	-15	9.4	1.25–1.10	N–S	256W–302W	13–15
13/April/2012 8:24–10:49	96.2	31	+11	11.5	1.05–1.56	N–S	34W–60W	9–10

Table 2 PFS orbits used for the joint observation with Subaru/IRCS

Orbit number	Date (UT)	Longitude	Local time
#10542	10/April/2012 12:21–13:20	16 $^\circ$ W	16 h
#10547	11/Aprli/2012 23:08–24:06	167 $^\circ$ W	16 h
#10554	13/April/2012 23:47–25:14	162 $^\circ$ W	16 h
#10557	14/April/2012 20:45–22:12	109 $^\circ$ W	16 h

Table 3 Parameters of HDO and H₂O lines used in this study. The values are taken from the HITRAN 2008 spectroscopic database (Rothman et al., 2009).

Molecular	H ₂ O	H ₂ O	HDO	HDO
Wavenumber [cm^{-1}]	3035.78356	3216.52218	2672.59294	2677.71967
Intensity [cm] (for 296 K)	3.219×10^{-22}	2.848×10^{-22}	7.463×10^{-24}	9.117×10^{-24}
Lower state Energy [cm^{-1}]	446.6966	222.0528	116.4613	91.3302

Air-broadened half-width [cm⁻¹ atm⁻¹] (for modeling of terrestrial lines)	0.0702	0.1080	0.0969	0.0975
Temperature-dependence exponent for the half-width	0.32	0.76	0.77	0.77

Table A1. List of combinations tested in retrieval of the ILS

	1 st function (for line center)	2 nd function (for line wing)	Chi-square (relative values)
Case-1	Gauss	Gauss	1.00
Case-2	Lorenz	Lorenz	5.19
Case-3	Gauss	Lorenz	1.38
Case-4	Lorenz	Gauss	5.17
Case-5	Sinc	Gauss	2.31
Case-6	Sinc	Lorenz	2.43

Figure 1

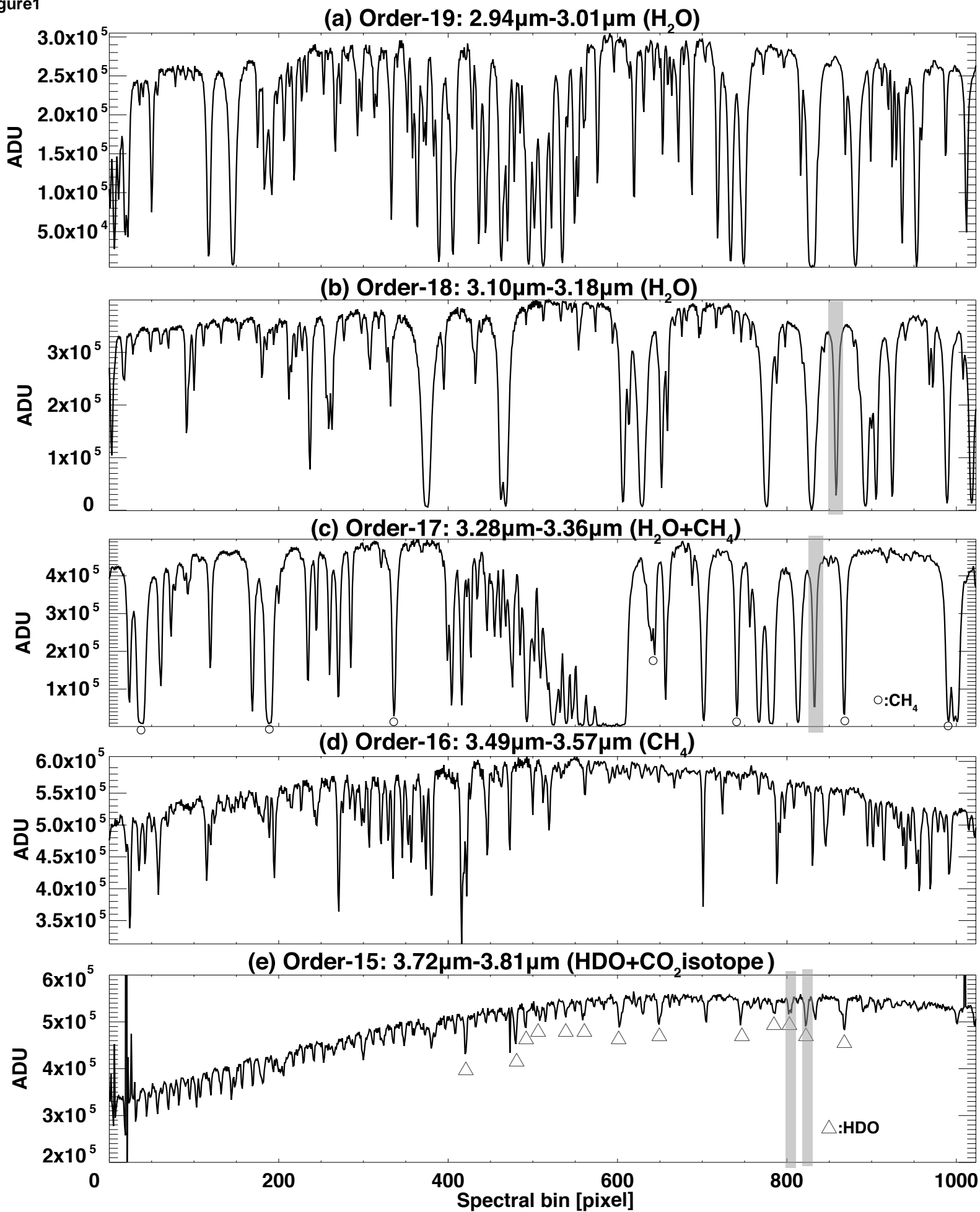
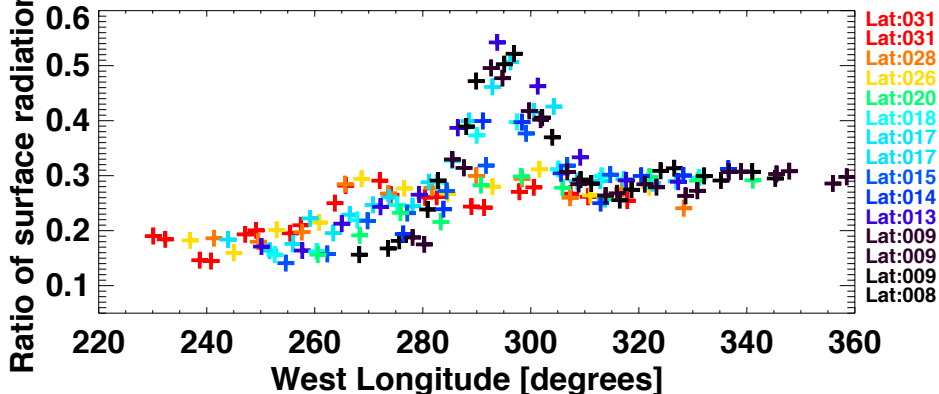
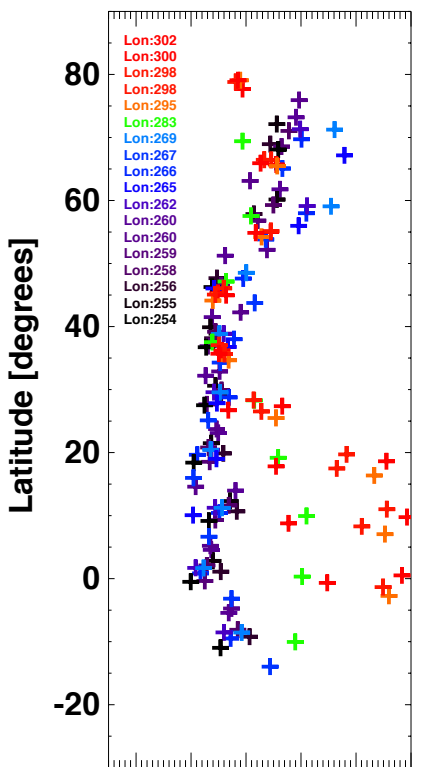


Figure2

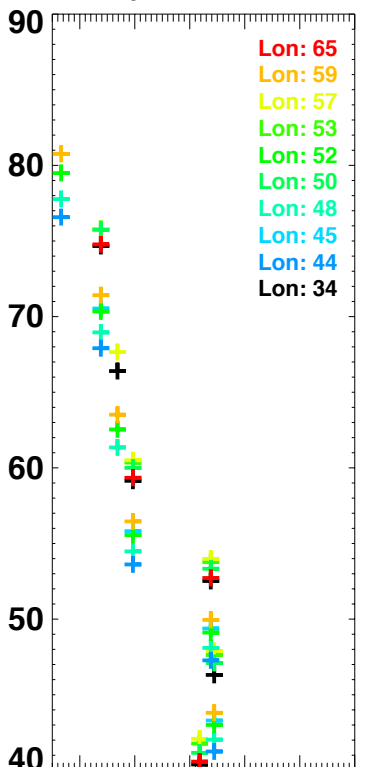
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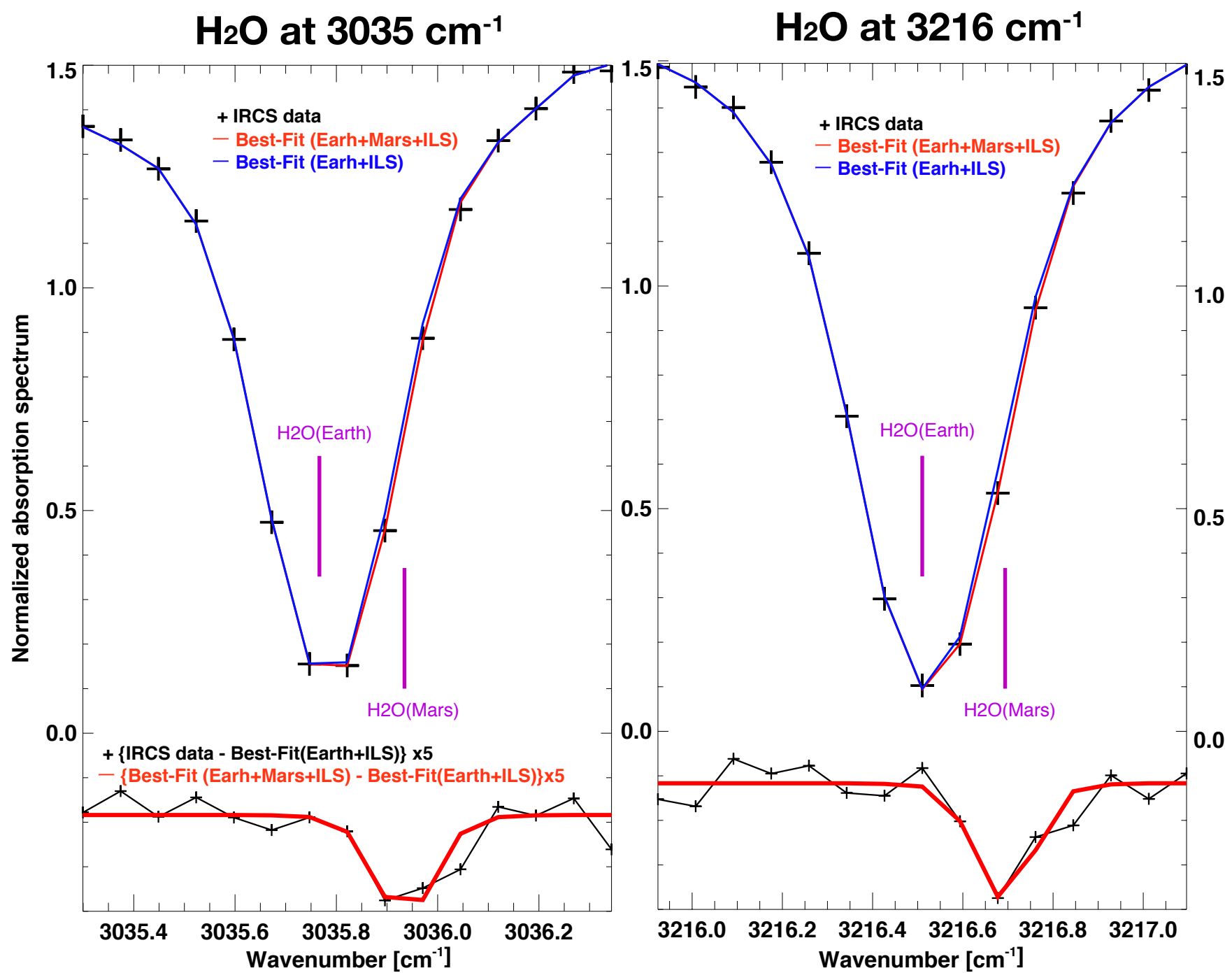
5-Jan Observation



13-April Observation



Mars



Star

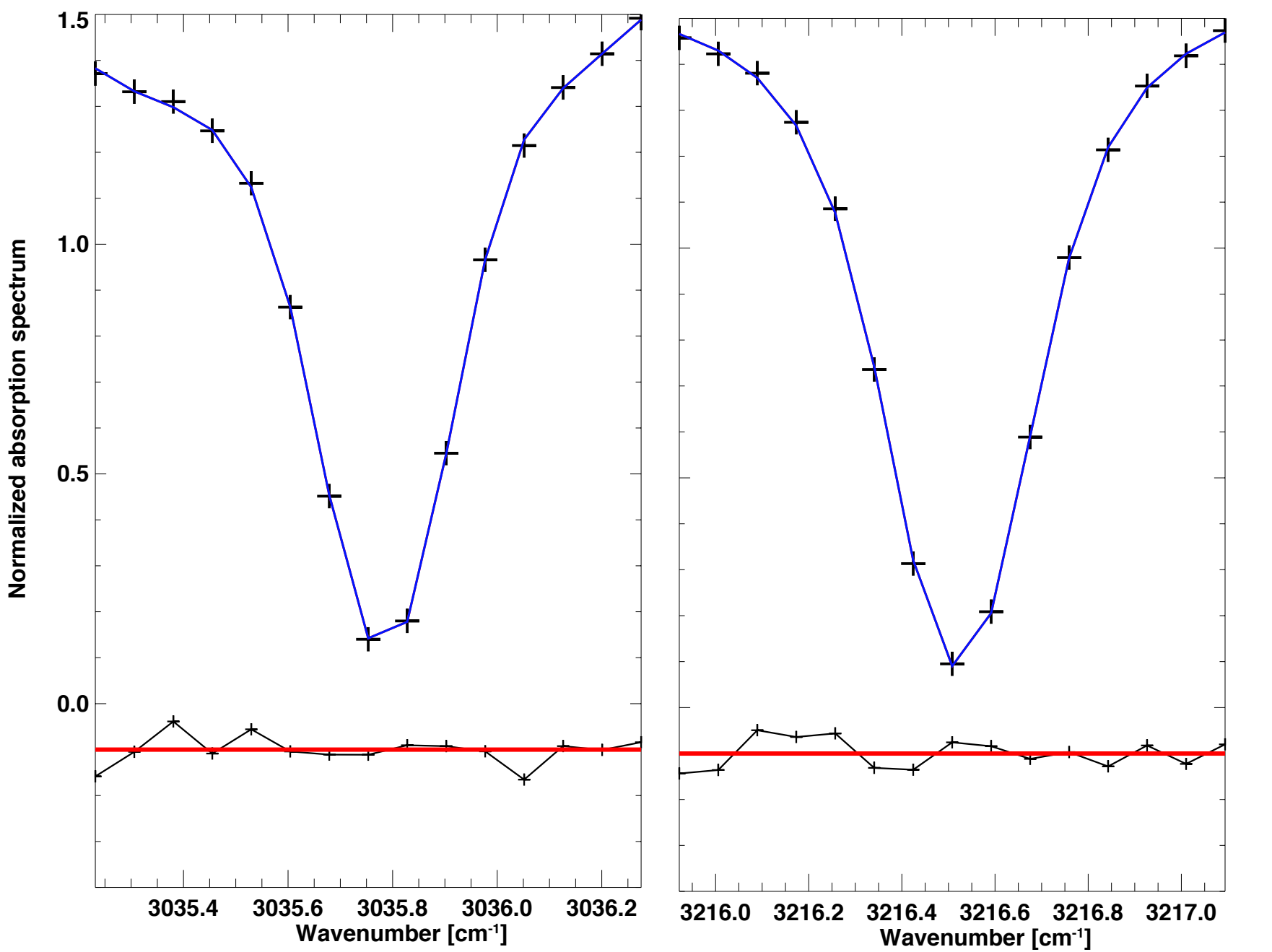
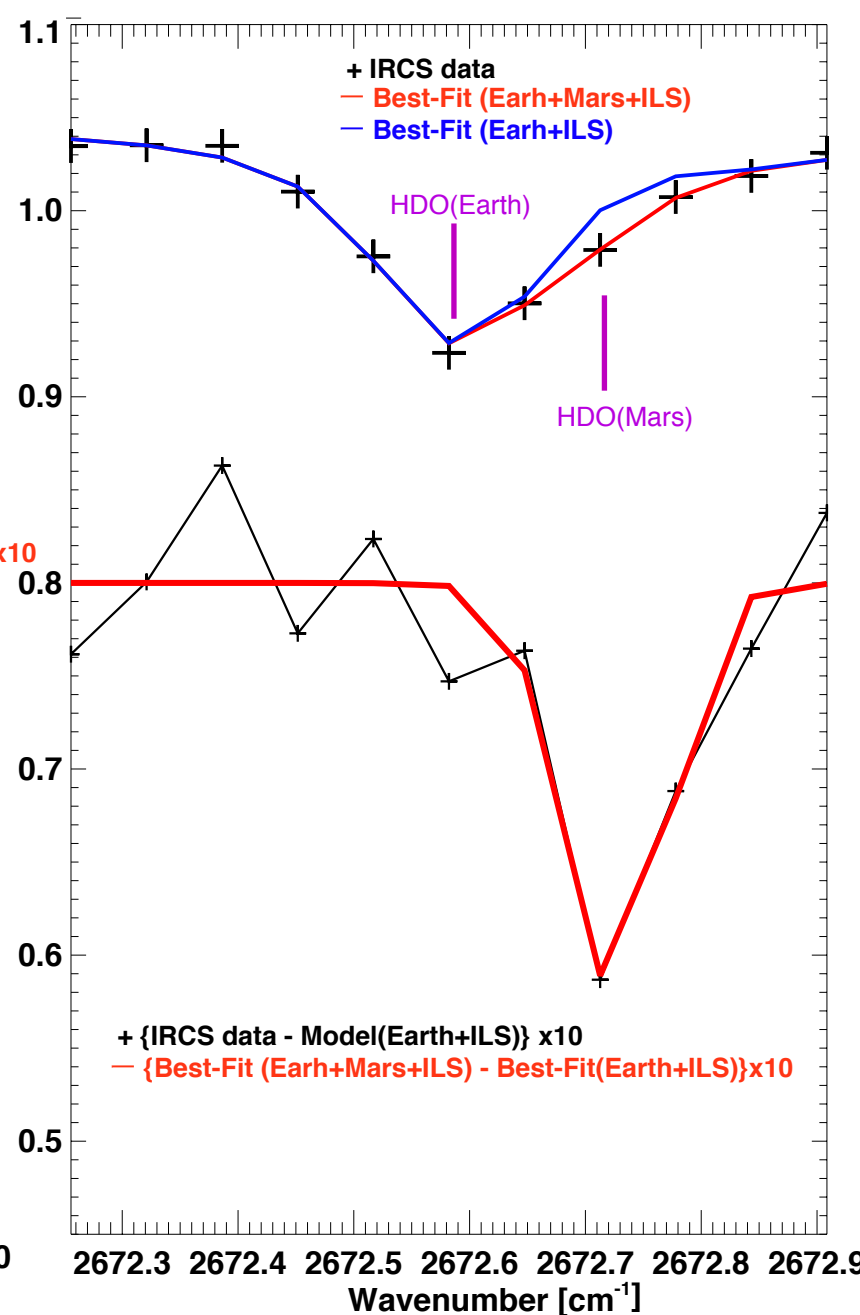
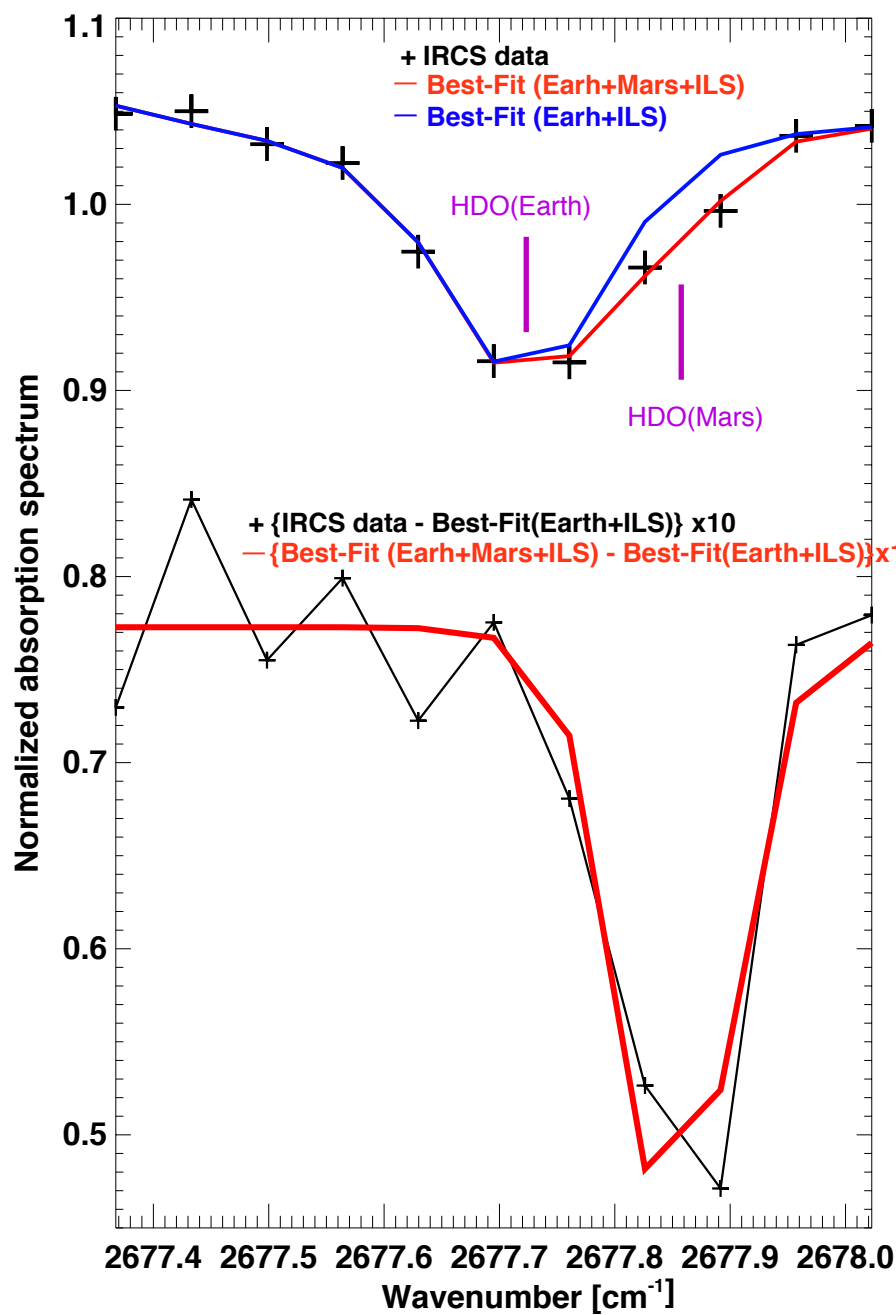
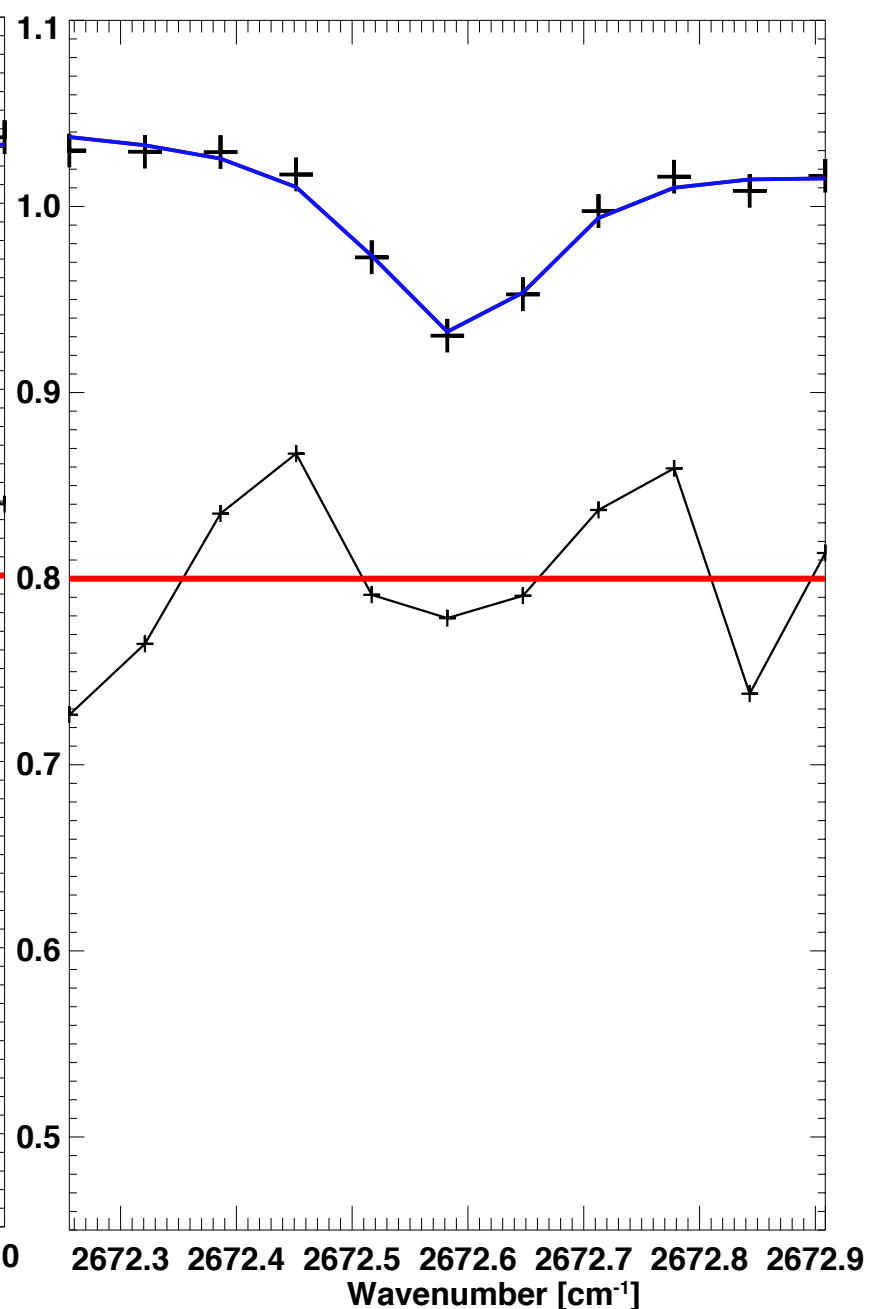
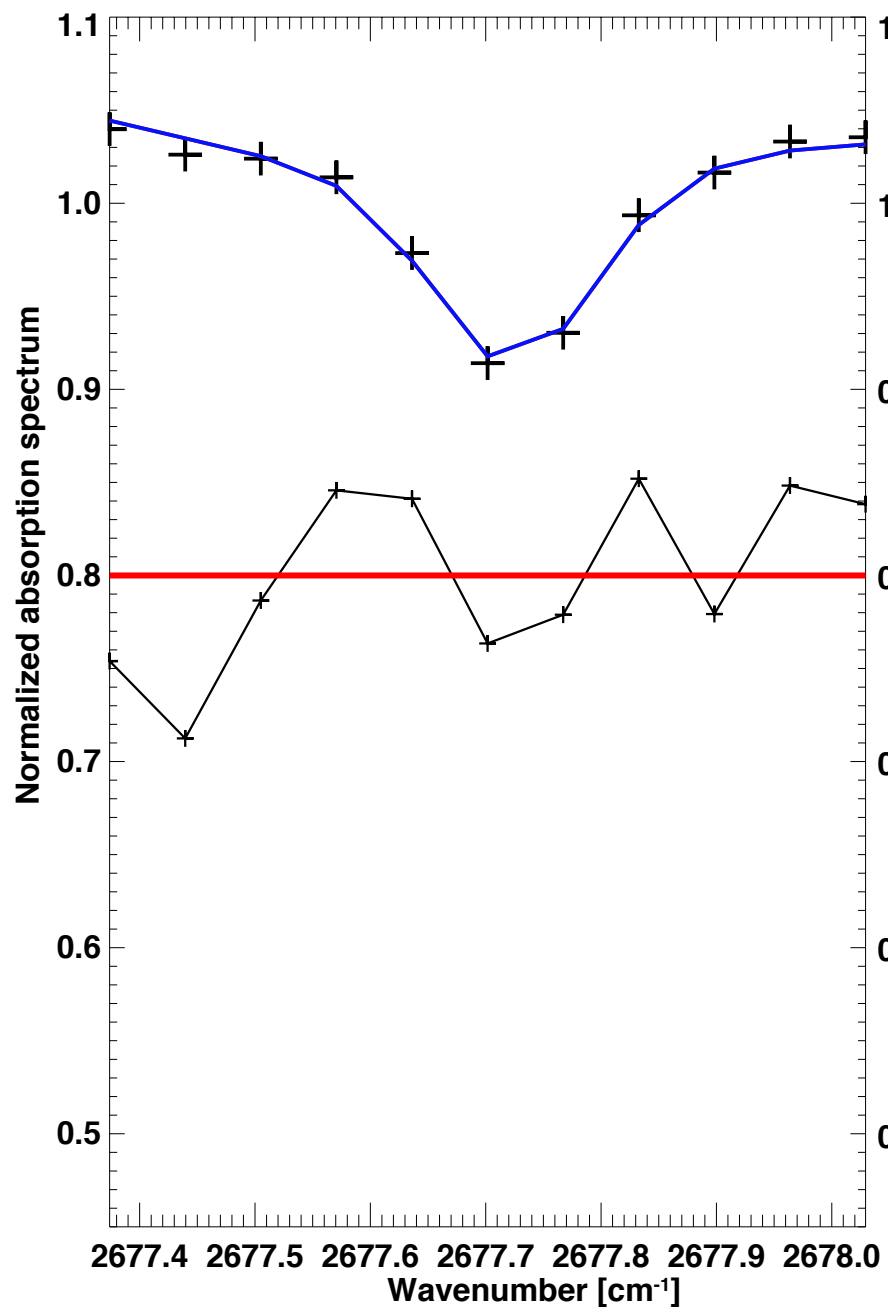


Figure 4

HDO at 2677 cm⁻¹HDO at 2672 cm⁻¹

Mars



Star

Figure5

[Click here to download high resolution image](#)

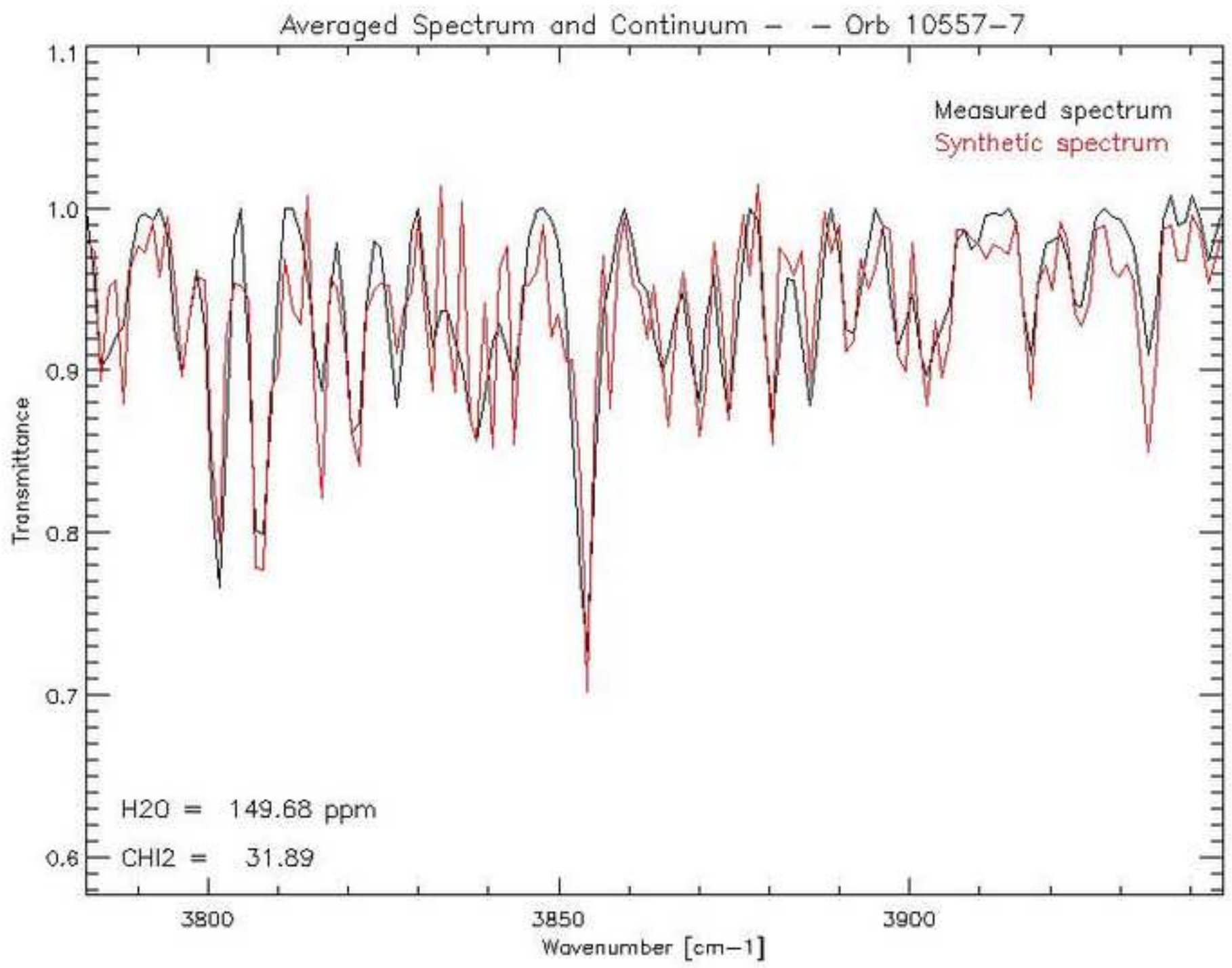


Figure 6

 H_2O (Obs.) H_2O (Model)

HDO

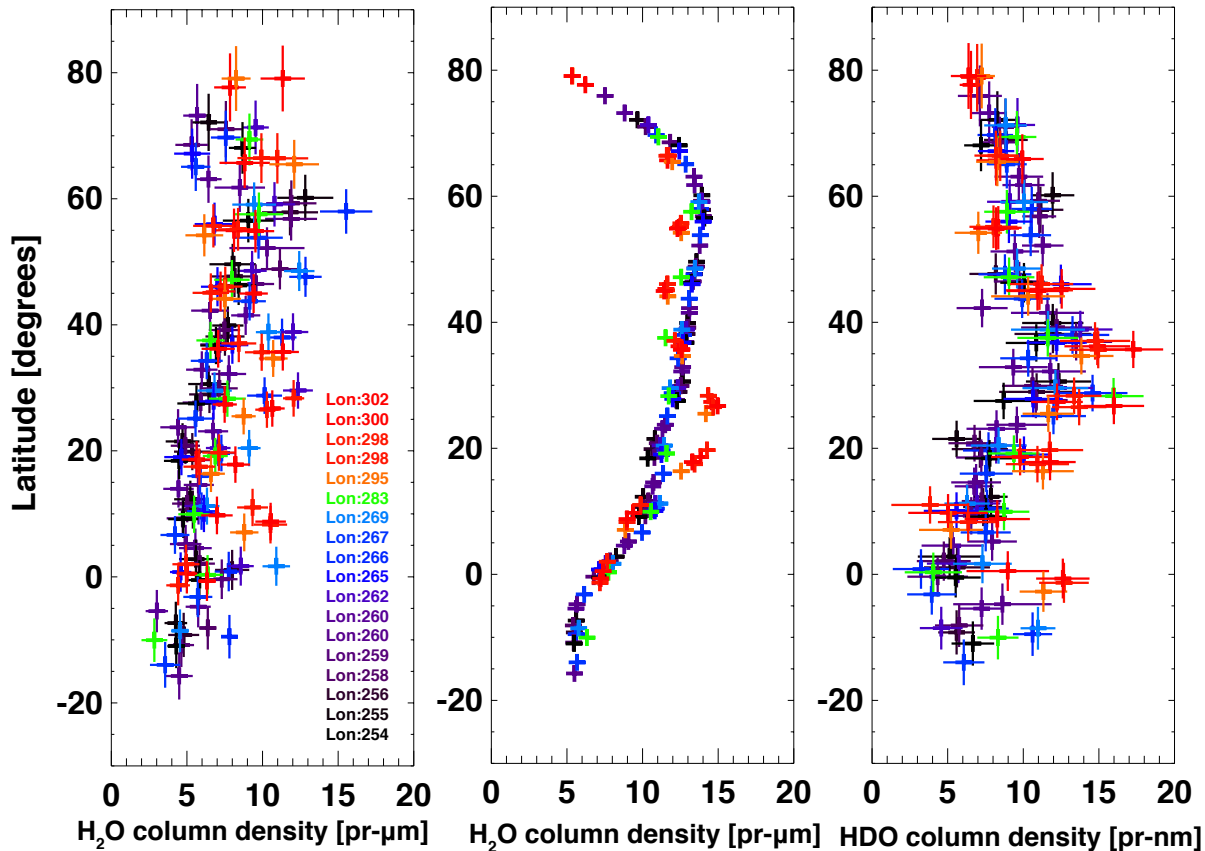


Figure 7

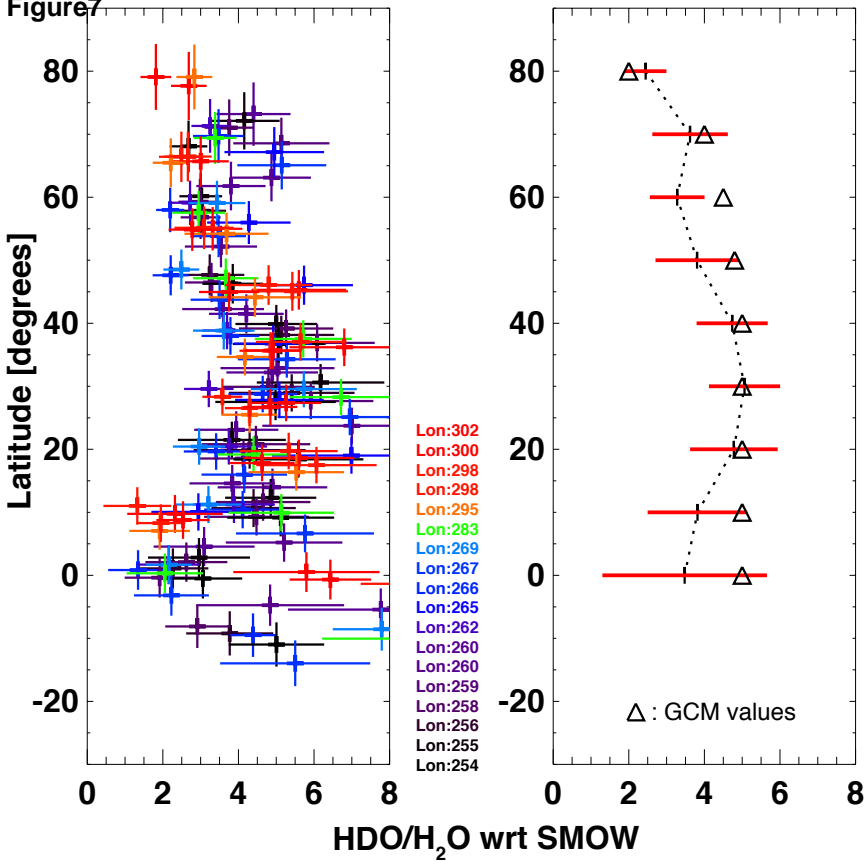


Figure8

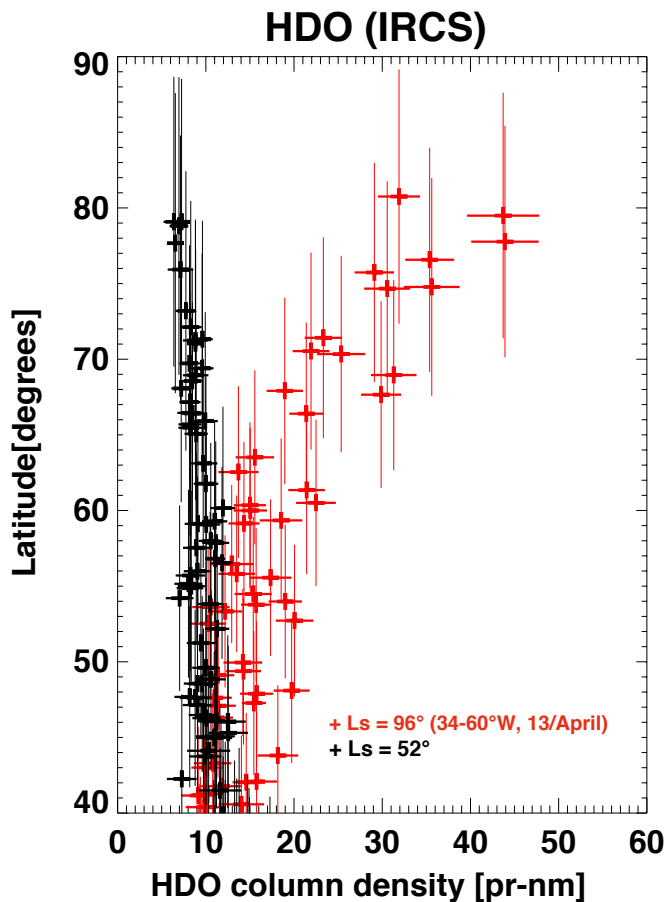
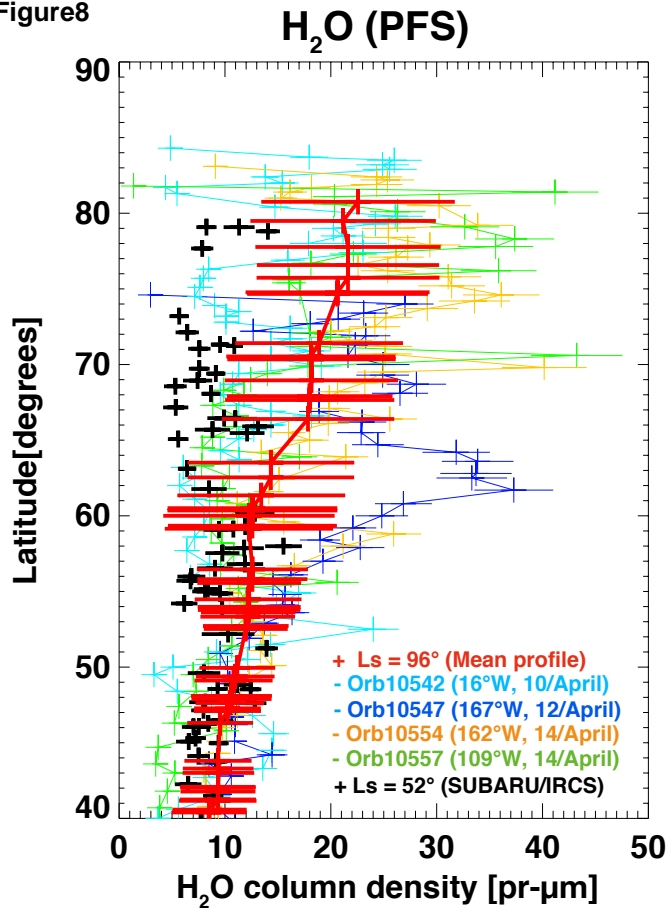


Figure 9

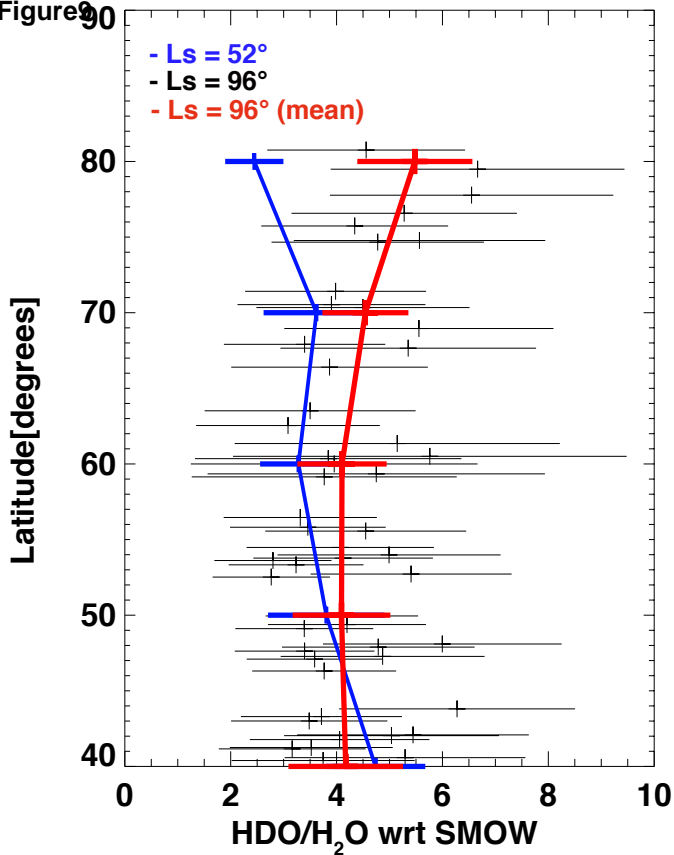


Figure 10 Column-integral abundances (divided by $P_s/6.1$)

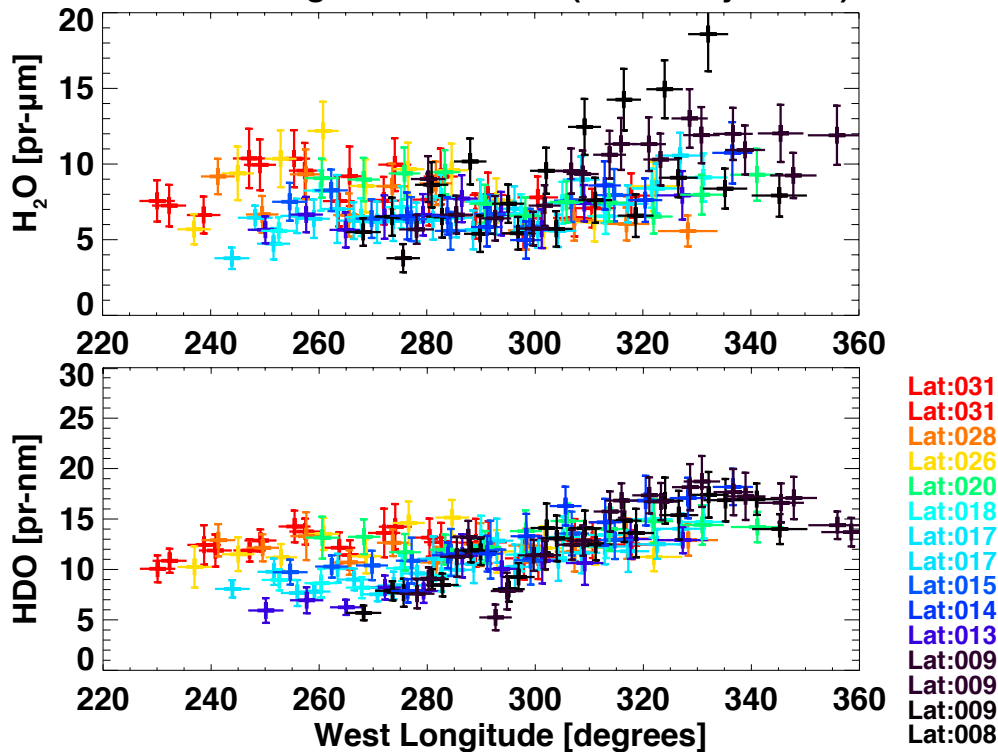


Figure 11

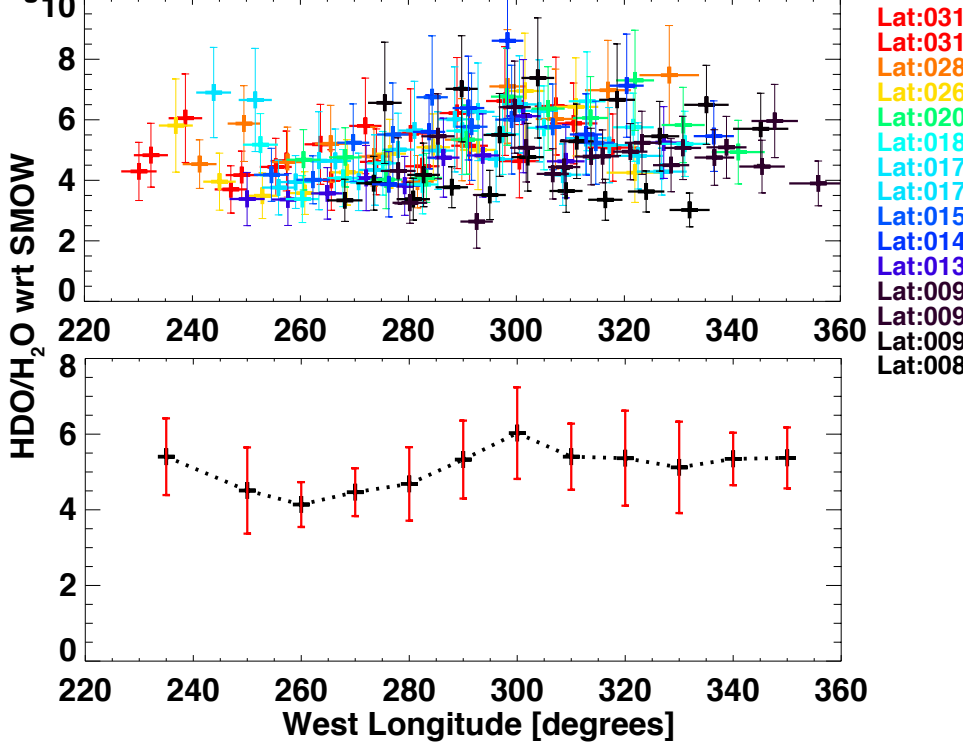


Figure12

Column-integral abundances (divided by Ps/6.1)

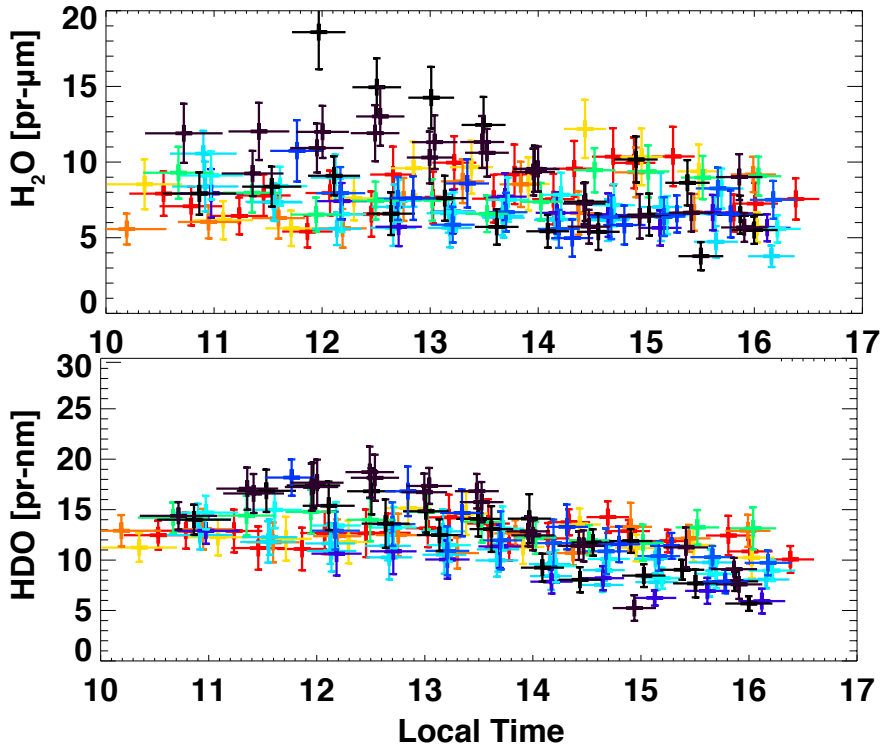


Figure 13

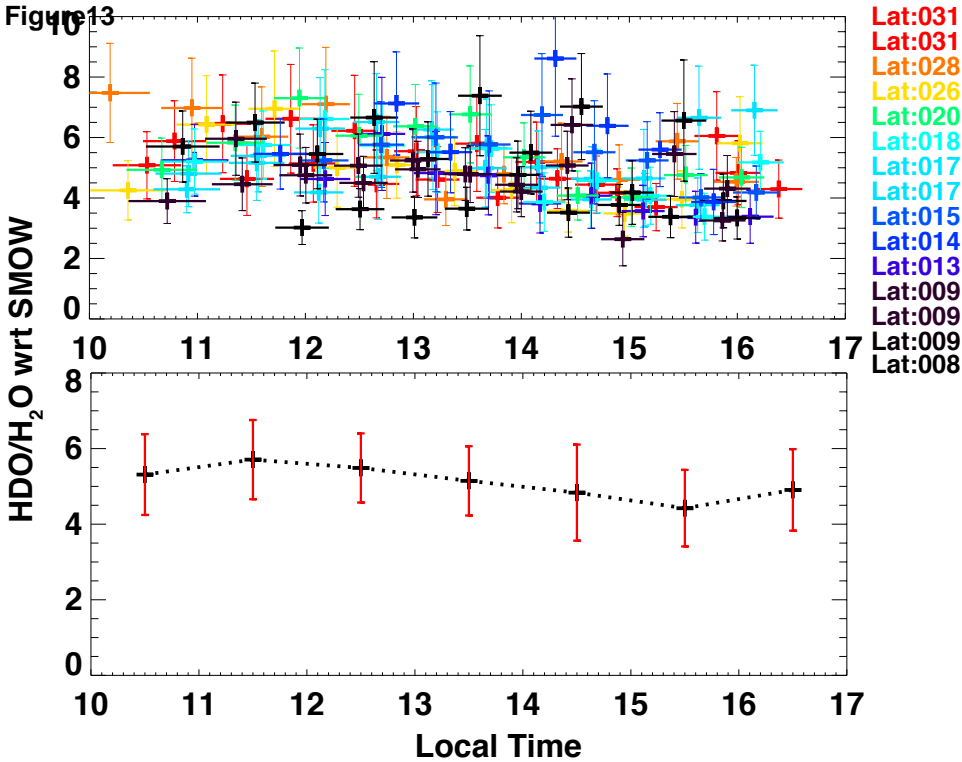
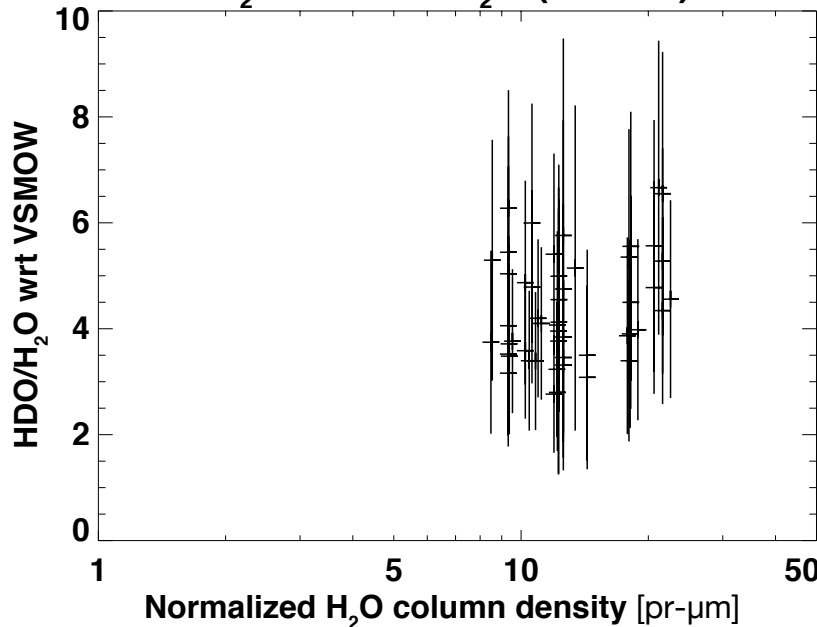
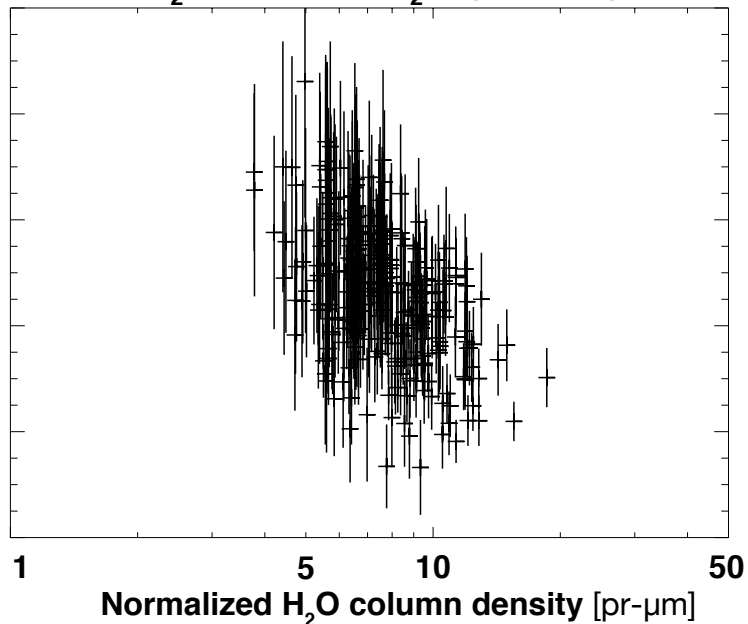
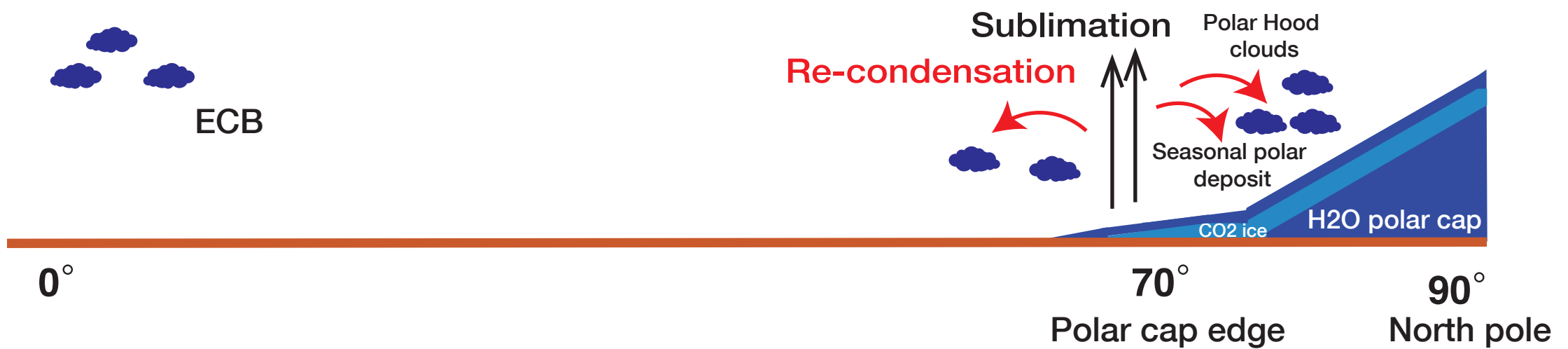
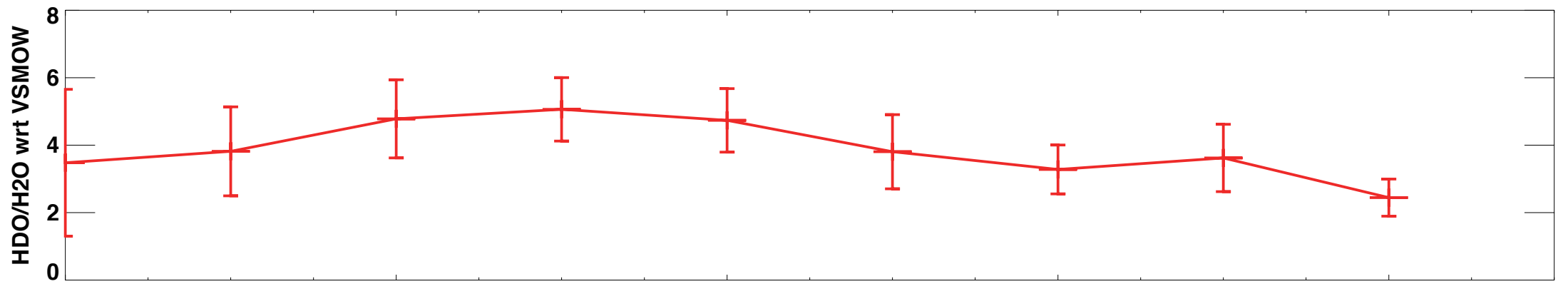


Figure 14

 H_2O vs $\text{HDO}/\text{H}_2\text{O}$ ($L_s=96^\circ$) H_2O vs $\text{HDO}/\text{H}_2\text{O}$ ($L_s=52^\circ$)

Northern spring (Ls=52°)



Northern summer (Ls=96°)

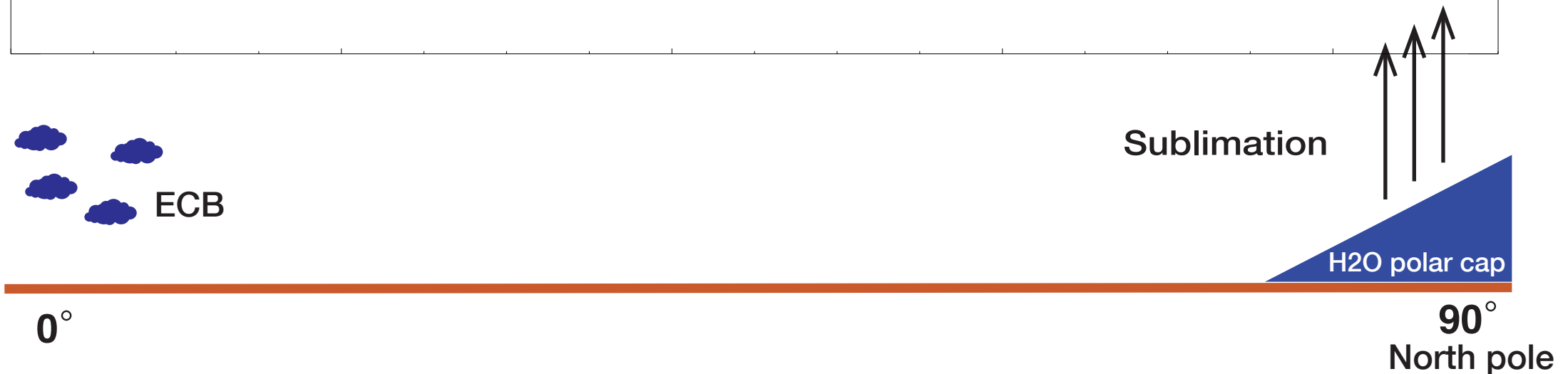
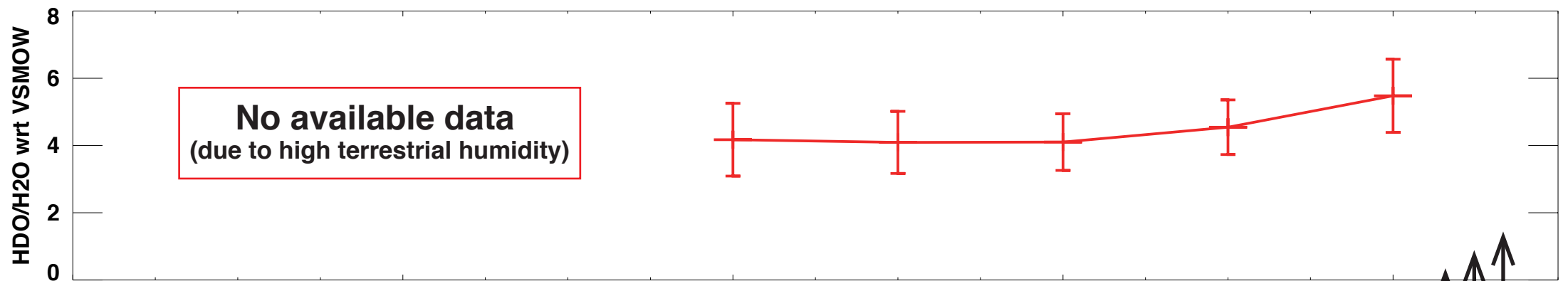
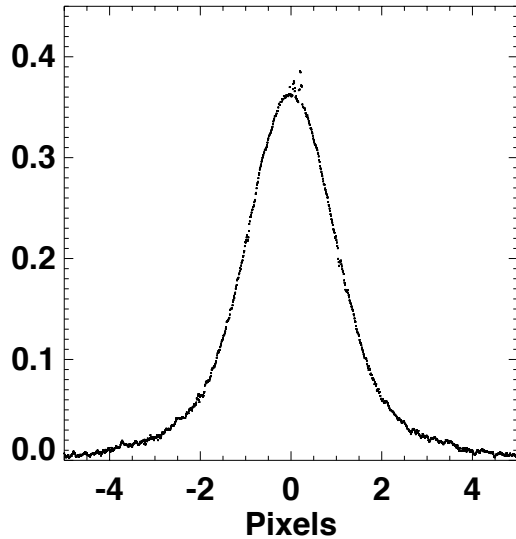
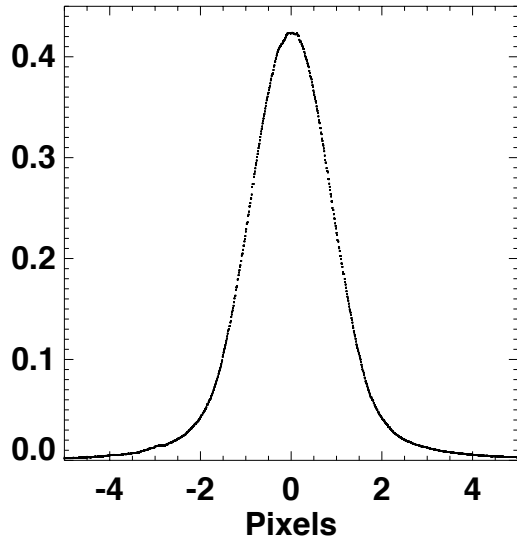


Figure A1 **Ar: 3040.5647 cm⁻¹**



Ar: 3191.5201 cm⁻¹



Ar: 3272.9622 cm⁻¹

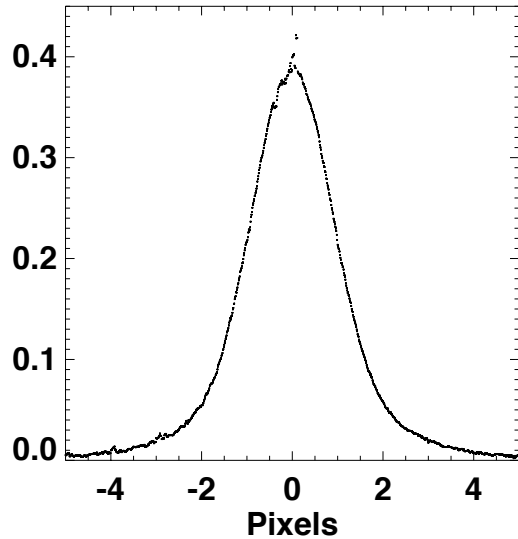
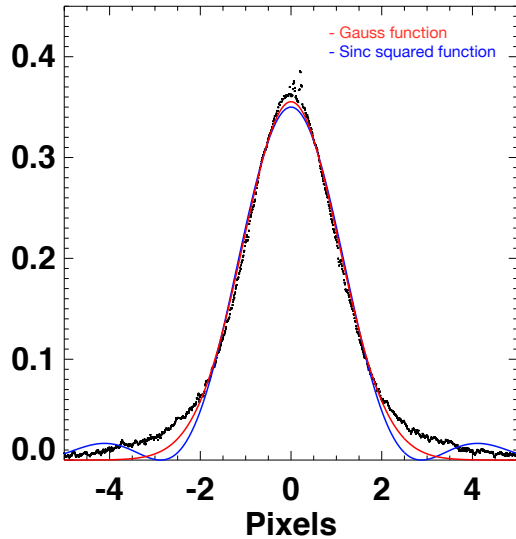
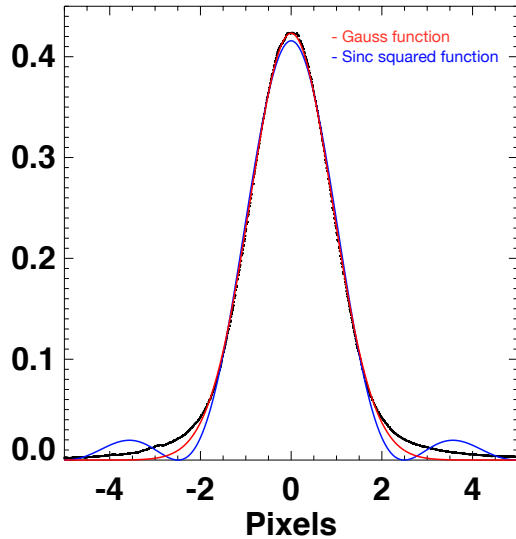


Figure A2 **Ar: 3040.5647 cm⁻¹**



Ar: 3191.5201 cm⁻¹



Ar: 3272.9622 cm⁻¹

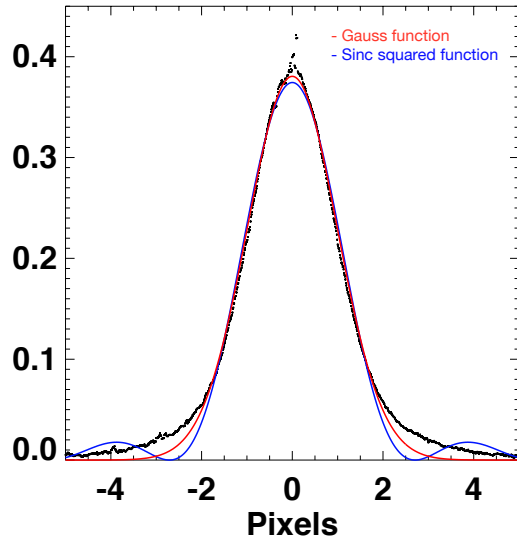
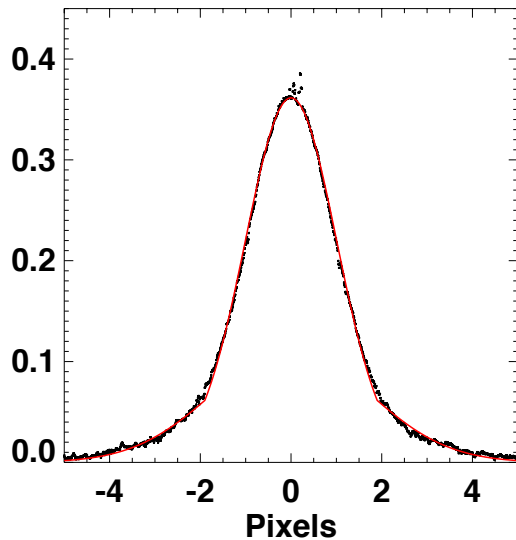
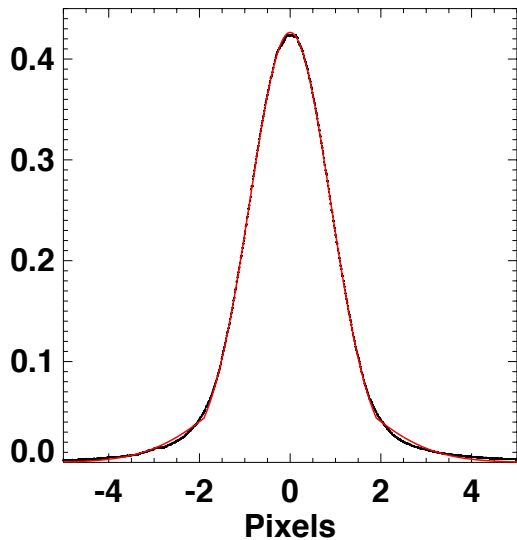


Figure A3

Ar: 3040.5647 cm^{-1} Ar: 3191.5201 cm^{-1} Ar: 3272.9622 cm^{-1} 