Photolysis controls the isotopic composition of water products escaping Mars' atmosphere

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1 **Photolysis controls the isotopic composition of water products escaping**

2 **Mars' atmosphere**

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30 **Abstract**

31 The current Martian atmosphere is about five times more enriched in deuterium than Earth's,
32 providing a direct testimony that Mars hosted several times more water in its early youth than
33 nowadays. Estimates of the total amount of water lost to space from the current mean D/H
34 value depend on a rigorous appraisal of the relative escape between deuterated and
35 non-deuterated water. The transport of water to the upper atmosphere, from whence it may
36 escape to space, has been assumed to be controlled by water condensation and photolysis,
37 both of which affect the isotope composition of the escaping hydrogen. Their respective role
38 in influencing the relative proportion of escaping D and H atom populations in the upper
39 atmosphere has remained speculative. Here we report HDO and H₂O profiles observed by the
40 Atmospheric Chemistry Suite (ExoMars Trace Gas Orbiter) in orbit around Mars that, once
41 combined with expected photolysis rates, reveal that the ultraviolet dissociation of water not
42 only governs the production of atomic hydrogen, prevailing over the ion chemistry
43 mechanism, but also dominates the production of H relative to D atoms, disrupting the old
44 paradigm of atmospheric condensation being the main process differentiating D and H in the
45 upper atmosphere.

46 **Main text**

47 The isotope composition of the Martian atmosphere has often been used as a means to
48 understand its evolution¹. Assuming that Earth and Mars were assembled out of the same
49 material, the relative enrichment of heavy isotopes in Martian atmospheric water vapour with
50 respect to Earth suggests that the escape of water throughout the Martian history has been
51 substantial^{2–11}, consistent with the geomorphological and mineralogical imprints on the

52 surface, which require the presence of liquid water on ancient Mars^{12,13}. Although these clues
53 indicate that water was abundant in the past, the amount that existed remains uncertain.
54 Estimations of the size of the ancient water reservoir on Mars from its isotope composition
55 depend not only on the present-day atmospheric ratio, but also on the net escape fractionation
56 factor, f . This factor relates the efficiency of escape of D with respect to H, including all
57 fractionation processes occurring along the physical and chemical pathways by which the
58 initial H₂O and HDO molecules are decomposed and ultimately escape to space by either
59 thermal or non-thermal means¹⁴⁻¹⁷.

60 The initial part of the process by which water escapes to space comprises the production of
61 atomic H and D from water vapour. For a long time, this production was assumed to be
62 sourced by long-lived molecular hydrogen, which is formed as a by-product of the catalytic
63 recombination of carbon dioxide with odd-hydrogen (H, OH, HO₂) produced in the
64 dissociation of H₂O¹⁵. However, observations of atomic hydrogen in the upper atmosphere
65 reveal variations not consistent with the sole production by molecular hydrogen¹⁸, which
66 might be produced by the direct photodissociation of water vapour in the middle
67 atmosphere^{19,20}. In both of these scenarios, two factors can fractionate the production of
68 deuterium relative to hydrogen: 1) the preferential photolysis of H₂O molecules relative to
69 HDO depletes the dissociation products in deuterium²¹; 2) the preferential condensation of
70 HDO in water ice clouds²³ leaves the atmosphere depleted in the heavy isotopes above the
71 condensation level, which can impact the supply of D/H to the upper atmosphere, if
72 photolysis occurs above the cloud deck^{24,25}. Both of these mechanisms are expected to
73 fractionate the isotopic composition of atomic hydrogen, although the effectiveness of each
74 of these remains unknown.

75 We investigate the vertical distribution of the isotope composition (D/H and $^{18}O/^{16}O$) of water
76 vapour in the Martian atmosphere using solar occultation measurements made by the
77 mid-infrared (MIR) channel of the Atmospheric Chemistry Suite (ACS)²⁶ onboard the
78 ExoMars Trace Gas Orbiter (TGO). ACS MIR is an echelle cross dispersion spectrometer
79 dedicated to solar occultation measurements in a spectral range between 2.2 and 4.4 μm . Its
80 novel design allows the simultaneous selection of 9 to 25 contiguous diffraction orders within
81 the entire spectral range of the instrument, achieving high resolving power ($\lambda/\Delta\lambda \sim 30,000$) in
82 a wide instantaneous spectral range (0.15-0.3 μm). The dataset assembled for this study
83 includes all available ACS MIR solar occultation observations made using secondary grating
84 position 4, which allows the selection of ten diffraction orders (215-224) in a spectral range
85 between 2.65-2.77 μm (3600 – 3770 cm^{-1}), encompassing absorption bands of several
86 isotopologues of carbon dioxide and water vapour (see Supplementary Methods). To date,
87 there are 549 secondary grating position 4 solar occultations, which account for
88 approximately 14% of all available ACS MIR observations, covering more than a full
89 Martian year of observations and including more than half of Martian Year 34 (MY34) ($L_s =$
90 160-360°) and of MY35 ($L_s = 0$ -290°). The observational coverage used in this dataset
91 allows the analysis of the variations of the D/H ratio in three dimensions, including the
92 vertical, latitudinal, and seasonal effects.

93 The analysis of the data and the retrieval of the atmospheric vertical profiles is performed
94 using the NEMESIS (Nonlinear optimal Estimator for MultivariatE spectral analySIS)
95 algorithm²⁷, which utilises the optimal estimation framework²⁸. In particular, the retrieval
96 scheme is performed in two steps. First, vertical profiles of pressure and temperature are
97 retrieved from CO_2 absorption, along with the vertical distribution of the $H_2^{16}O$ volume

98 mixing ratio. Secondly, the pressure and temperature profiles are fixed, and the retrieved
99 H_2^{16}O volume mixing ratio is used as an *a priori* estimate to retrieve the volume mixing ratios
100 of H_2^{16}O , H_2^{18}O and HD^{16}O , assuming an *a priori* isotopic composition of $^{18}\text{O}/^{16}\text{O} = 1$ and
101 $\text{D}/\text{H} = 5$ with respect to the Vienna Standard Mean Ocean Water (VSMOW; $\text{D}/\text{H} = 1.6 \times 10^{-4}$
102 and $^{18}\text{O}/^{16}\text{O} = 2.0 \times 10^{-3}$), and using a spectral window suitable for the derivation of the
103 isotopic ratios (see Fig. 1). More details describing the retrieval scheme and its validation are
104 given in the Supplementary Methods.

105

106 Figure 2 shows a summary of the climatology of the retrieved parameters from the spectra.
107 During the observed period, both temperature and H_2O volume mixing ratio profiles show
108 drastic seasonal and latitudinal changes. During the Southern Hemisphere (SH) spring and
109 summer seasons ($L_s = 180^\circ$ and $L_s = 270^\circ$) in both MY34 and MY35, Mars is close to
110 perihelion ($L_s = 251^\circ$), and the greater dust heating and proximity to the Sun intensify the
111 Hadley circulation²⁹, allowing warmer temperatures to expand to the middle atmosphere in
112 both the northern and southern hemispheres. These greater temperatures move the
113 hygropause (i.e. level at which water vapour saturates) upwards to higher altitudes, allowing
114 water vapour to migrate to the middle and upper atmospheres, and reaching values greater
115 than 50 ppmv as high as 100 km. On the other hand, during the Northern Hemisphere (NH)
116 spring and summer seasons ($L_s = 0^\circ$ and $L_s = 90^\circ$), although high water vapour abundances ($>$
117 150 ppmv) are observed in the NH, these are confined to altitudes below ~ 20 km. At high
118 southern latitudes ($> 60^\circ\text{S}$), during this time, very low water vapour abundances (< 1 ppmv)
119 and temperatures (< 150 K) are observed. These seasonal trends are in agreement with other

120 observations^{30–33} and with the expectations from the simulations of a General Circulation
121 Model (GCM)³⁴.

122 The measurements also depict a very dynamic behaviour of the D/H ratio, varying from 1 to
123 6 VSMOW, with an isotopic ratio representative of the present-day Martian atmosphere of 5
124 ± 0.4 VSMOW (see Supplementary Methods). During the SH summer, H₂O and HDO in both
125 hemispheres expand into the middle atmosphere, exhibiting isotopic ratios between 4–6
126 VSMOW up to 40–60 km, until they reach the saturation level. Above this level, the D/H
127 ratio starts to decrease down to values between 1–3 VSMOW, as predicted by the preferential
128 condensation of HDO over H₂O during the formation of water ice clouds^{22,25}. The presence of
129 isotopic fractionation in condensation processes is even clearer during the NH summer, which
130 shows a steady decrease of the D/H ratio from 4–5 VSMOW at 10 km down to 2–3 VSMOW
131 at 20–30 km, due to a lower altitude of the hygropause (see Figs. 2 and S8).

132

133 The variations in the D/H ratio are found to be positively correlated with those in the water
134 vapour volume mixing ratio (see Fig. S9). A logarithmic relation between D/H and water
135 vapour abundance is predicted by the isotope fractionation during condensation²⁵, which
136 appears therefore responsible for the observed variations. Similarly, the observed variations
137 of the D/H ratio appear to be related to the atmospheric temperature: while the higher values
138 of the D/H ratio (> 4 VSMOW) are found in a wide range of temperatures (170–210 K), low
139 values of D/H (< 3 VSMOW) are only measured for $T < 180$ K. This correlation corroborates
140 the hypothesis of the prominent role of condensation-induced fractionation, which is
141 predicted to increase with decreasing temperatures^{4,5,22,35}.

142

143 The $^{18}\text{O}/^{16}\text{O}$ is found to be much less variable than the D/H ratio. The value representative of
144 the present-day atmospheric ratio is found to be 1.14 ± 0.08 VSMOW, which is in line with
145 values reported in previous studies^{3,11}. We observe variations ranging between 0.9 and 1.3
146 VSMOW, although this level of variability is in the same range as the typical measurement
147 uncertainty, which makes it difficult to disentangle potential variations of the isotopic ratios
148 from statistical noise (see Supplementary Methods). Expectations from isotopic fractionation
149 in condensation processes predict a preferential condensation of H_2^{18}O over H_2^{16}O , similar
150 than for the D/H ratio, but with a lower magnitude^{22,23,36}. The absence of measured variability
151 does not rule out the presence of fractionation processes though, since they might be smaller
152 than, and therefore masked by the measurement uncertainty (see Fig. S9).

153

154 Estimations of how H_2O and HDO molecules are fractionated as they are photodissociated
155 into lighter molecules ($\text{OH} + \text{H}$) are made with the photolysis code of the LMD-GCM^{21,37} (see
156 Supplementary Methods). These calculations are combined with ACS MIR water vapour
157 density vertical profiles to estimate the dissociation rates, which reveal the perihelion season
158 to be dominant in the dissociation of water vapour, with rates approximately 100 times
159 greater than those found close to aphelion (see Fig. 3A). This result is consistent with
160 measurements of the H and D Lyman- α brightness, representative of atomic H and D
161 atmospheric densities, which show peak values around perihelion^{38–40}. Our calculations
162 indicate column-integrated photodissociation rates of at least $10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ during the
163 perihelion season, which are between one and two orders of magnitude higher than those
164 predicted by the formation of atomic hydrogen from ion chemistry⁴¹, evidencing the prevalent
165 role of photolysis in the production of atomic hydrogen.

166

167 We calculated the fractionation factor relating the D/H ratio in the photolysis products with
168 respect to the mean D/H ratio representative of water in the lower atmosphere ($F =$
169 $(D/H)_{\text{bulk}}/(D/H)_{\text{products}}$), taking into account the impact of both photolysis-induced fractionation
170 F_p (i.e., fractionation due to the difference in the photolysis cross sections of HDO and H₂O)
171 and condensation-induced fractionation F_c (i.e., fractionation due to the depletion in D/H of
172 the parent water molecules with respect to the average D/H ratio of water in the lower
173 atmosphere). More details about how these calculations are performed are given in the
174 Supplementary Methods. Our calculations suggest that, while the dissociation products are
175 expected to have a D/H ratio about 2-2.5 times lower than the average D/H ratio in the lower
176 atmosphere ($D/H_{\text{bulk}} = 5 \pm 0.4$ VSMOW) during perihelion, the fractionation factor F would
177 increase up to 5-6 during aphelion (see Fig. 3B). However, the dissociation rates during the
178 aphelion season are between one and two orders of magnitude lower than during perihelion
179 and are therefore expected to have a minor contribution to the annual average (see Fig. 3B).
180 Consequently, the annual average D/H fractionation factor F is heavily weighted towards
181 perihelion, which is in agreement with the measurement of the D/H ratio in molecular
182 hydrogen, which was found to be approximately 2.5 times smaller than the D/H ratio in
183 water¹⁵.

184

185 While condensation-induced fractionation appears to be the main driver of the variations of
186 the D/H ratio in atmospheric water vapour, it has a minor influence on shaping the isotopic
187 composition of the dissociation products as compared to photolysis-induced fractionation.
188 During perihelion, at the altitudes at which photolysis is more efficient (40-50 km), while

189 water vapour is still not affected by condensation ($F_{cond} \sim 1$), the photolysis-induced
190 fractionation factor is expected to be about $F_{photo} \sim 2.0\text{--}2.5$ (see Fig. S11). During aphelion,
191 the role of condensation-induced fractionation increases with respect to perihelion ($F_{cond} \sim$
192 $1.5\text{--}2.0$), but so does the role of photolysis-induced fractionation ($F_{photo} \sim 1.5\text{--}2.0$) (see Fig.
193 S12). Besides, as previously mentioned, the role of the aphelion season in the dissociation of
194 water vapour is expected to be negligible with respect to perihelion. Our results provide new
195 insights for resolving the old paradigm regarding the role of the different mechanisms to
196 fractionate the D/H ratio of water vapour in the lower atmosphere and that of its dissociation
197 products, leading to the enrichment of D/H in the atmosphere as it escapes into space^{21,24,42}.

198

199 Similarly, as for HDO, the H_2^{18}O molecules are expected to have a different UV absorption
200 cross-section than the H_2^{16}O ones, which can impact the isotope composition of the
201 dissociation products of water vapour and the efficiency of ^{18}O to reach the upper
202 atmosphere⁴³. We estimate that, while the dissociation products are expected to be about 2-2.5
203 times depleted in D/H with respect to the ratio in water vapour in the lower atmosphere, this
204 factor would just be 1.08-1.10 for the $^{18}\text{O}/^{16}\text{O}$ ratio, revealing a much higher efficiency of ^{18}O
205 to be transferred to the dissociation products with respect to D (see Supplementary Methods).
206 This might explain the dichotomy between the large enrichment in the heavy isotope of the
207 D/H ratio (~ 5 VSMOW) as opposed to the mild enrichment in the $^{18}\text{O}/^{16}\text{O}$ ratio (~ 1.14
208 VSMOW): while ^{18}O is efficiently transferred to the photolysis products of water vapour,
209 HDO molecules are less efficiently photolyzed, decreasing the D/H ratio of the lighter species
210 that ultimately the escape to space. Therefore, as H and O escape from the Martian
211 atmosphere, they will enrich more efficiently the D/H ratio than the $^{18}\text{O}/^{16}\text{O}$ ratio.

212 Nevertheless, it must also be noted that, while the O isotopic composition of the atmosphere
 213 may be buffered by interactions with the O in the surface, atmospheric-surface interactions
 214 are expected to have a lower influence on the H isotopic composition of the atmosphere^{1,16,44}.

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346

347

348 Figures

350 **Figure 1: Example of ACS MIR spectra and summary of the retrieval scheme.** ACS MIR spectra shown in this
 351 figure was obtained in orbit 4409 (Latitude = 42°S, $L_s = 291^\circ$, Local time = 19h). In step 1 of the retrieval
 352 scheme, pressure and temperature based on the absorption of CO₂, and H₂¹⁶O volume mixing ratio profiles are
 353 retrieved from one detector row in diffraction orders 223 and 224. In step 2, spectra from five different detector
 354 rows are independently used to retrieve the volume mixing ratios of H₂¹⁶O, H₂¹⁸O and HD¹⁶O from the spectral
 355 window in diffraction order 224, which allow the derivation of the D/H and ¹⁸O/¹⁶O isotope ratios.

361 **Figure 2: Climatology of the retrieved atmospheric parameters.** The panels show the values of the retrieved
 362 parameters as a function of altitude and solar longitude for the northern (left) and southern (right) hemispheres.
 363 A) Distribution of ACS MIR solar occultation observations, with the local time represented by the colour bar. B)
 364 Atmospheric temperature. C) Water vapour volume mixing ratio. E) D/H ratio in water vapour with
 365 uncertainties lower than 1 VSMOW.

Figure 3: Seasonal evolution of the isotopic fractionation of D/H during the photodissociation of water vapour. A) The column-integrated photolysis rate of water vapour exhibits large seasonal variations, revealing the perihelion season to be dominant in the production of OH and H. B) The estimated fractionation factor between the value representative of the lower atmosphere ($D/H = 5$ VSMOW) and its photodissociation products ($(D/H)_{\text{bulk}}/(D/H)_{\text{products}}$) (red curve) is anti-correlated with the photolysis of water vapour, peaking near aphelion. Also plotted is the contribution index (normalised photolysis rate of H_2O - black line) of each point to the annual average of the D/H fractionation factor, showing the prevalence of the perihelion season on the global scale. The contribution of condensation-induced (F'_{cond}) and photolysis-induced fractionation (F'_{photo}) (shaded polygons) to the total D/H fractionation factor (B, shaded polygons) demonstrate the prevalence of the latter in shaping the isotopic composition of the escaping hydrogen.

380 **Methods**

381 **ACS instrument and measurements**

382 ACS is a combination of three different infrared spectrometers: a spectrometer combining an
383 acousto-optic tunable filter (AOTF) with an echelle grating in the near infrared (NIR), an
384 echelle cross dispersion spectrometer in the middle infrared (MIR), and a Fourier Transform
385 spectrometer for the thermal infrared (TIRVIM), covering a total spectral range from 0.7 to
386 $17\ \mu\text{m}^{26}$. ACS MIR, used in this study, counts with a novel design that allows the
387 simultaneous selection of 9 to 25 diffraction orders, achieving high resolving power
388 ($\lambda/\Delta\lambda\sim 30,000$) in a wide instantaneous spectral range (0.15-0.3 μm). The selected diffraction
389 orders are projected onto a 640×512 pixel detector frame, creating a two-dimensional image
390 such that the horizontal dimension represents the spectral coordinate, while the vertical axis
391 comprises the projection of the slit for the different diffraction orders⁴⁵. The projection of the
392 slit on the detector covers between 10 and 20 pixels and represents the instantaneous
393 field-of-view of the instrument (1×14 arcmin), with a vertical resolution of approximately
394 150 m per pixel (see Fig. S1).

395

396 In each ACS MIR solar occultation, the Sun is observed from an altitude of 270 km until it is
397 concealed by the surface, accumulating the detector frames every 2.1 s, which allows the
398 reconstruction of vertical profiles with a sampling of approximately 1-2 km, although the
399 effective vertical resolution can be increased by combining different rows from the detector.
400 The reference solar spectrum used to derive the transmission spectra is estimated from the
401 acquisitions above 190 km, while the observations beneath the Martian surface are used to
402 estimate the dark signal. Calibration of the transmission spectra includes the removal of the
403 dark signal, straylight and hot pixels, as well as a correction for the sub-pixel drift occurring

404 due to the slightly varying thermal state of the instrument. Spectral calibration of the
405 measurements is performed using a comparison of the solar lines with the ACE-FTS solar
406 atlas ⁴⁶, and then further refined using absorption lines of H₂O and CO₂.

407

408 Comparison between the measured and modelled transmission spectra depicted a doubling of
409 the absorption lines ¹¹, which later on was revealed to be the result of a doubled image of the
410 detector frame. The cause of this doubled-image is unknown, although it is presumably the
411 result of a partial fracture in one of the lenses broken during launch. The nature and
412 magnitude of the double image is complex, varying throughout the detector array, and
413 making a potential rectification of the fault difficult. Fig. S1 shows the spectra acquired by
414 ACS MIR when using secondary grating position 4 in different diffraction orders, situated in
415 the upper and lower parts of the detector, and in two different rows within the diffraction
416 orders. In diffraction order 217, which is situated in the upper part of the detector, the
417 spectrum measured at the stripe centre shows absorption lines with two peaks, caused by the
418 doubling of the image. At the slit edge, the spectrum shows single peaks for each absorption
419 line instead. On the other hand, the impact of the doubling is milder for the lower part of the
420 detector frame. While the measured spectra show clear differences between the doubling at
421 the slit centre and edge in diffraction order 217, these differences are milder for diffraction
422 order 223, which is situated at the bottom part of the detector frame.

423

424 The dataset assembled for this study includes spectra measured in diffraction orders 223 and
425 224, which are both situated at the lower part of the detector frame. Although the impact of
426 the doubled-image is expected to be small in this portion of the detector, it is accounted for in

the analysis of the data, considering an instrument line shape (ILS) consisting of a superposition of two Gaussian functions¹¹. In particular, the following assumptions are made to create a model to fit the ILS: 1) The full-width at half-maximum (FWHM) of the two Gaussian functions is the same, and constant in wavelength units; 2) The relative offset of the two Gaussians is constant along the selected spectral range; 3) The relative depth of the two Gaussians is linearly dependent with wavenumber. 4) The same ILS parameters apply to all acquisitions made within the same solar occultation measurement.

Selection of spectral range

The design of the ACS MIR instrument allows the simultaneous observation of 9 to 25 diffraction orders with a spectral width ranging between 0.15-0.3 μm , within the total spectral range covered by the instrument (2.2-4.4 μm). The first step of the study relies on selecting the spectral range most suitable for the measurements of isotopic ratios in Martian water vapour, taking into account the characteristics of ACS MIR.

Figure S2 shows a synthetic spectrum of the Martian atmosphere covering the full spectral range of ACS MIR, showing the absorption by CO_2 and several isotopologues of H_2O . In addition, the instantaneous spectral range covered by ACS MIR when using different secondary grating positions is shown. This figure shows secondary grating positions 4, 5, 10 and 11 to be the most suitable for the measurement of water vapour isotopes. However, all these spectral ranges have both advantages and disadvantages:

- Secondary grating position 10 (2529-2761 cm^{-1}): Absorption by HD^{16}O is measurable and the absorption is not contaminated by other species. However, the absence of measurable lines of H_2^{16}O impedes the derivation of the D/H ratio (see Fig. S3).

- 449 • Secondary grating position 11 (2713-2996 cm^{-1}): Absorption by HD^{16}O is measurable
450 in several diffraction orders and not contaminated by other species. H_2^{16}O lines are
451 observable in diffraction order 175, allowing the derivation of the D/H. However, the
452 H_2^{16}O lines are weaker than those from HD^{16}O and disappear at lower altitudes,
453 limiting the vertical extent of the retrievals.
- 454 • Secondary grating position 4 (3604-3769 cm^{-1}): Absorption by H_2^{16}O , H_2^{18}O , H_2^{17}O
455 and HD^{16}O is measurable within the spectral range, enabling the derivation of the H
456 and O isotope ratios. Most of the absorption lines are masked by the CO_2 absorption,
457 making diffraction order 224 the only suitable for isotopic studies.
- 458 • Secondary grating position 5 (3789-3987 cm^{-1}): Absorption by H_2^{16}O , H_2^{18}O , H_2^{17}O
459 and HD^{16}O is measurable within the spectral range in several diffraction orders,
460 enabling the derivation of the H and O isotope ratios. Nevertheless, the HD^{16}O
461 absorption lines are weaker than those found in the other positions, limiting the
462 accuracy and detectability of the D/H ratio¹¹.

463 From this analysis, we select the ACS MIR measurements made with secondary grating
464 position 4 to perform the retrievals. The availability of HD^{16}O and H_2^{18}O lines is more limited
465 than when observing using other positions, but the lines are among the strongest within ACS
466 MIR's spectral range, and observed within the same diffraction order, which reduces the
467 impact of potential systematic uncertainties from the data. In addition, this position allows the
468 simultaneous characterisation of the pressure and temperature fields, which is essential for
469 the correct characterisation of the spectroscopic parameters and the interpretation of the
470 results.

471 Retrieval scheme

472 The retrieval scheme is performed in two steps. First of all, the pressure and temperature
473 profiles are retrieved from the CO₂ absorption in diffraction order 223, while the vertical
474 profile of H₂¹⁶O volume mixing ratio is retrieved from diffraction order 224. Secondly, the
475 pressure and temperature profiles are fixed, and the retrieved H₂¹⁶O volume mixing ratio is
476 used as an *a priori* estimate to retrieve the volume mixing ratios of H₂¹⁶O, H₂¹⁸O and HD¹⁶O
477 in diffraction order 224, assuming an *a priori* isotopic composition of ¹⁸O/¹⁶O = 1 and D/H =
478 5 with respect to VSMOW, and using a spectral window suitable for the derivation of the
479 isotopic ratios. All gaseous absorption is modelled using pre-computed look-up tables using
480 line-by-line modelling. The absorption of CO₂ is modelled using the spectroscopic parameters
481 listed in the 2016 edition of the HITRAN database ⁴⁷. In the case of H₂O we use
482 spectroscopic parameters suitable for a CO₂-rich atmosphere ⁴⁸⁻⁵¹.

483

484 Pressure and temperature profiles are retrieved from the CO₂ absorption under the
485 assumptions of a known CO₂ volume mixing ratio, which is obtained from the Mars Climate
486 Database (MCD) ⁵², and an atmosphere in hydrostatic equilibrium. Traditionally, this retrieval
487 technique consisted on retrieving a density profile from CO₂ absorption, and deriving the
488 pressure and temperature profiles from the hydrostatic and ideal gas laws ^{53,54}. In this study,
489 the same assumptions are made, but retrieving a continuous profile of temperature and the
490 pressure at a given tangent height. The rest of the pressure levels are re-computed based on
491 the hydrostatic equation given by

$$492 \quad p(z) = p(z_r) \cdot \exp\left(-\int_{z_r}^z \frac{g(\bar{z}) \cdot M(\bar{z})}{T(\bar{z}) \cdot k_B} d\bar{z}\right),$$

493 where $g(z)$ is the gravity, $M(z)$ is the molecular mass and k_B is the Boltzmann constant (
494 $k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$). This retrieval procedure has the advantage of updating the
495 temperatures in each iteration, and consequently updating the temperature dependence of the
496 strength of the different absorption lines. In order to perform these retrievals, a spectral
497 window in diffraction order 223 between 3741 and 3753 cm^{-1} is selected, choosing a row
498 from the detector frame corresponding to maximum intensity, which yields the highest
499 signal-to-noise ratio (SNR).

500

501 The initial retrieval of the vertical distribution of H_2^{16}O volume mixing ratio is also
502 performed using the maximum-intensity row, but using a spectral window between 3759.5
503 and 3767 cm^{-1} in diffraction order 224, which encompasses strong lines of H_2^{16}O visible up to
504 high altitudes ($>100 \text{ km}$). Comparison of the retrieved H_2^{16}O with those derived from
505 simultaneous measurements by ACS NIR ³¹ in 1.38 μm band revealed a bias between the
506 retrieved water vapour abundance using both datasets when observing high water vapour
507 densities (see Fig. S4). This bias is presumably related to the saturation of the water vapour
508 absorption lines, which impact the sensitivity of the line along the line-of-sight. In order to
509 reconcile the retrievals from both datasets, we select a smaller spectral window (3763-3765.4
510 cm^{-1}) including weaker absorption lines of H_2^{16}O . In this case, the retrievals are in good
511 agreement with those retrieved from ACS NIR spectra at low altitudes (see Fig. S4).

512

513 The retrieval of the D/H and $^{18}\text{O}/^{16}\text{O}$ isotope ratios is performed using the spectral window
514 between 3763 and 3765.4 cm^{-1} in diffraction order 224. However, in this case, given the
515 smaller number and strength of the absorption lines, five different rows from the detector

516 frame are independently retrieved and later combined, increasing the effective vertical
 517 resolution of the measurements, as well as the confidence of the retrievals. The independent
 518 retrieved profiles of $H_2^{16}O$, $H_2^{18}O$ and $HD^{16}O$ volume mixing ratio are combined using a
 519 weighted average, in which the weights are given by the inverse of the retrieved variance at
 520 each altitude ($\sigma(z)^{-2}$), after applying a correction to mitigate the effect of the *a priori*
 521 uncertainty in the retrieval errors^{11,55}. The uncertainty of the weighted-average profiles is
 522 calculated considering not only the retrieved uncertainties of each independent retrieval, but
 523 also the dispersion of each of the independent retrieved profiles, which is considered to
 524 provide a more accurate representation of the true uncertainty of the retrieval (see Fig. S5).
 525

526 Once the vertical profiles of the $H_2^{16}O$, $H_2^{18}O$ and $HD^{16}O$ mixing ratios are calculated, it is
 527 possible to derive the D/H and $^{18}O/^{16}O$ isotopic ratios following

$$528 \quad D/H = \frac{1}{2} \frac{[HD^{16}O]}{[H_2^{16}O]} \quad \text{and} \quad ^{18}O/^{16}O = \frac{[H_2^{18}O]}{[H_2^{16}O]},$$

529 which are then normalised using the Vienna Standard Mean Ocean Water (VSMOW; D/H =
 530 1.6×10^{-4} and $^{18}O/^{16}O = 2.0 \times 10^{-3}$). The uncertainties in the isotope ratios are then calculated
 531 using

$$532 \quad \sigma_{D/H} = D/H \cdot \sqrt{\left(\frac{\sigma_{HD^{16}O}}{[HD^{16}O]}\right)^2 + \left(\frac{\sigma_{H_2^{16}O}}{[H_2^{16}O]}\right)^2} \quad \text{and}$$

$$533 \quad \sigma_{^{18}O/^{16}O} = ^{18}O/^{16}O \cdot \sqrt{\left(\frac{\sigma_{H_2^{18}O}}{[H_2^{18}O]}\right)^2 + \left(\frac{\sigma_{H_2^{16}O}}{[H_2^{16}O]}\right)^2}.$$

534 **Validation of measurements and methods**

535 From the start of the science mission, comparisons between the simultaneous observations
 536 made by the MIR and NIR channels have been used to validate the measurements and

537 methods. Here, we validate the ACS MIR position 4 vertical profiles of temperature and
538 water vapour volume mixing ratio against those measured by ACS NIR, which constrain the
539 pressure and temperature profiles from the CO₂ absorption band at 1.57 μm and the water
540 vapour mixing ratio from the absorption band at 1.38 μm ³¹. As shown in Fig. S6, both
541 analyses are found to be in good agreement, increasing the confidence in the retrieved
542 profiles from both datasets.

543

544 Unfortunately, the ACS NIR channel does not include any absorption bands of the minor
545 water isotopologues (i.e. H₂¹⁸O and HD¹⁶O), and the retrievals of the isotope ratios cannot be
546 validated with simultaneous measurements. In order to validate these, we perform retrievals
547 of the D/H ratio using secondary grating position 11, using the pressure and temperature
548 fields retrieved by ACS NIR. In particular, we retrieve the H₂¹⁶O and HD¹⁶O mixing ratios
549 from diffraction orders 175 and 162 (see Fig. S3), using spectral windows between 2932 and
550 2938 cm⁻¹, and 2719 and 2725 cm⁻¹, respectively. The derived vertical profiles of D/H ratio
551 from both spectral ranges show similar behaviours, confirming and validating the retrievals
552 from secondary grating position 4 (see Fig. S7).

553 **Estimation of the average D/H and ¹⁸O/¹⁶O isotopic ratios**

554 Understanding the variability of the isotopic ratios is essential to disentangle the values
555 inferred from localised measurements, which are subject to fractionating processes, and the
556 isotopic ratio representative of the Martian atmosphere. Figure S9 shows a histogram of the
557 measured values with uncertainties lower than 0.8 VSMOW for the D/H ratio, and 0.12
558 VSMOW for the ¹⁸O/¹⁶O isotope ratio, as well as their relation to other atmospheric
559 parameters.

560

561 The observed values of the D/H ratio show a large range of variability, varying from values as
562 low as 1-2 to 5-6 VSMOW, with uncertainties typically lying within 0.3-0.5 VSMOW. The
563 estimation of the D/H ratio representative of the present-day Martian atmosphere requires the
564 subtraction of climatological effects that impact the isotopic composition at certain times and
565 locations. Climatological fractionation effects are expected to be minimum when observing
566 high temperatures and water vapour abundances, when water is fully vaporised and free from
567 condensation⁴. Under these conditions, most of the observations yield D/H ratios between 4
568 and 5 VSMOW. Larger values of the D/H ratio (5-6 VSMOW) are observed in certain
569 instances, although this may simply be an artefact due to the intrinsic uncertainty of the
570 measurements ($\sigma \sim 0.4$ VSMOW), as shown in Figure 4. Therefore, we estimate the value
571 representative of the present-day atmosphere to be $D/H = 5.0 \pm 0.4$ VSMOW.

572

573 In the case of the $^{18}\text{O}/^{16}\text{O}$ isotope ratio, the observed variations are smaller than those
574 observed in D/H, ranging from approximately 0.9 to 1.3 VSMOW, and showing no apparent
575 correlation with water abundance or temperature (see Fig. S9). With typical uncertainties
576 lying between 0.08 and 0.12 VSMOW, it is not possible to disentangle potential variations of
577 the $^{18}\text{O}/^{16}\text{O}$ isotope ratio in the Martian atmosphere from the statistical noise of the
578 instrument. From the measured $^{18}\text{O}/^{16}\text{O}$ isotope ratios throughout more than one Martian year,
579 we estimate that the $^{18}\text{O}/^{16}\text{O}$ isotope ratio representative of the Martian atmosphere is found to
580 be 1.14 ± 0.08 VSMOW, where the uncertainty corresponds to the lower bound of the typical
581 measured uncertainties. Within the observed variations, our results are consistent with the
582 measurement made with the Sample Analysis at Mars (SAM) instrument on the Curiosity

583 Rover, which revealed an enrichment of the $^{18}\text{O}/^{16}\text{O}$ isotope ratio of 1.084 ± 0.01 VSMOW³,
 584 and with previous solar occultation measurements made with ACS MIR secondary grating
 585 position 5, which yielded a value of 1.20 ± 0.08 VSMOW¹¹.

586

587 **Estimation of the fractionation factor between water vapour and its photolysis** 588 **products**

589 Accurate estimations of the total amount of water vapour lost throughout Martian history
 590 from isotopic measurements require an understanding of the relative efficiency of the
 591 different isotopologues to escape into space. This relative efficiency is represented by the
 592 fractionation factor, f , which includes all fractionating processes from the start as H_2O
 593 molecules, until they escape into space by either thermal or non-thermal means^{14,15,17}. The
 594 escape fractionation factor is defined as

$$595 \quad f = \frac{(D/H)_{\text{escape}}}{(D/H)_{\text{bulk}}} = \frac{\phi_D/\phi_H}{([HDO]/2[H_2O])_{\text{bulk}}} ,$$

596 where $(D/H)_{\text{escape}}$ represents the ratio of escaping fluxes for deuterium (ϕ_D) and hydrogen
 597 (ϕ_H), and $(D/H)_{\text{bulk}}$ represents the value of the D/H ratio representative of the Martian lower
 598 atmosphere, which we estimate to be $(D/H)_{\text{bulk}} = 5.0 \pm 0.4$ VSMOW. The first part of this
 599 escape process includes the photolysis of H_2O , giving rise to OH and H. The D/H ratio of the
 600 photolysis products may be estimated using

$$601 \quad (D/H)_{\text{products}}(z) = (D/H)_{\text{parent}}(z) \cdot \frac{J_{HDO}(z)}{J_{H_2O}(z)}$$

602 where $(D/H)_{parent}$ represents the D/H ratio of the parent H₂O molecules and J_{HDO} and J_{H_2O} are
 603 the photolysis rates of HDO and H₂O in s⁻¹, respectively. Note that the D/H ratio of the parent
 604 molecules being photolyzed might be different from the D/H ratio of the bulk of the
 605 atmosphere if water vapour is fractionated in the lower atmosphere, leading to a localised
 606 enrichment or depletion with respect to the average lower atmosphere value. Therefore, the
 607 fractionation factor between the isotopic composition of the photolysis products and that of
 608 the bulk of the atmosphere can be calculated as

$$609 \quad f'(z) = \frac{(D/H)_{products}}{(D/H)_{bulk}}(z) = \frac{(D/H)_{parent}}{(D/H)_{bulk}}(z) \cdot \frac{J_{HDO}}{J_{H_2O}}(z) .$$

610 Therefore, it is the combination of two factors:

- 611 • The fractionation between the D/H ratio of the atmospheric bulk representative of the
 612 Martian lower atmosphere, and the D/H ratio of the parent H₂O molecules, which
 613 might be subject to fractionation processes occurring in the lower atmosphere. Given
 614 that the observed variations in the D/H ratio in H₂O appear to be consistent with the
 615 expectations from condensation-induced fractionation, this factor represents the effect
 616 that condensation processes have in fractionating the isotopic composition between
 617 the bulk and the photolysis products, and is given by

$$618 \quad f'_{cond}(z) = \frac{(D/H)_{parent}}{(D/H)_{bulk}}(z) .$$

- 619 • The fractionation inherent in the photolysis of H₂O, which differentiates between the
 620 H₂O and HDO because of their different ultraviolet cross sections²¹ (see Fig. S10).
 621 Therefore, the fractionation factor inherent in the photolysis mechanism is given by

622

$$f'_{photo} = \frac{J_{HDO}}{J_{H_2O}}(z) .$$

623 Similarly, one may estimate the ratio of the D/H representative of the atmospheric bulk and
 624 the D/H ratio in the photolysis products using

625

$$F'(z) = \frac{(D/H)_{bulk}}{(D/H)_{products}} = \frac{1}{f'(z)} = F'_{cond}(z) \cdot F'_{photo}(z) = \frac{(D/H)_{bulk}}{(D/H)_{parent}}(z) \cdot \frac{J_{H_2O}}{J_{HDO}}(z) .$$

626 In order to estimate the efficiency of these processes to fractionate the isotopes during their
 627 photodissociation, the absorption cross-sections of H₂O and HDO are implemented in the
 628 photolysis model of the LMD-GCM^{17,39}. The middle panel in Fig. S10 shows the photolysis
 629 rates of H₂O and HDO calculated for four solar zenith angles (SZA = 0°, 30°, 60°, 85°), and
 630 at a Sun-Mars distance of 1.52 astronomical units (AU). At high altitudes, the photolysis rates
 631 of HDO and H₂O are dominated by the absorption at wavelengths $\lambda < 180$ nm, which exhibit
 632 similar cross-sections, leading to little fractionation. At lower altitudes, the absorption by CO₂
 633 becomes important, impeding photons with $\lambda < 180$ nm to penetrate to the lower altitudes.
 634 Instead, the photolysis of H₂O and HDO at lower altitudes is driven by photons with $\lambda > 180$
 635 nm, which yield lower photolysis rates due the lower absorption cross-section at these
 636 wavelengths, but higher fractionation between the two isotopologues.

637 In order to get an insight into the importance of seasonal effects on the photolysis of water
 638 and its isotopic fractionation, the photolysis rates from the model at SZA = 60°, are scaled to
 639 the relevant Sun-Mars distance, and multiplied by the water vapour number densities
 640 retrieved from the ACS MIR spectra during the summer seasons in the southern and northern
 641 hemispheres (see upper panels in Fig. S11). These estimated dissociation rates show very
 642 different seasonal behaviours. During the SH summer, the stronger Hadley circulation allows

643 water to expand into the middle atmosphere in both hemispheres, where photolysis increases,
644 reaching a maximum of H₂O dissociation rates at approximately 50 km in the SH (10^4 - 10^5
645 $\text{cm}^{-3} \text{s}^{-1}$), and at about 40 km in the NH (10^3 - $10^4 \text{cm}^{-3} \text{s}^{-1}$). On the other hand, during the NH
646 summer, the lower altitude of the hygropause confines water vapour to the near-surface,
647 where photolysis is very inefficient, yielding maximum dissociation rates at 10 km (10^3cm^{-3}
648 s^{-1}). The column-integrated photolysis rates are shown in the top panels of Figure S12 for the
649 perihelion and aphelion seasons observed with ACS MIR. These calculations evidence the
650 prevalence of the perihelion season for the dissociation of water, with rates between 10 and
651 100 times higher than those found during aphelion.

652 The lower panels in Figure S11 show the fractionation factors F' associated with
653 condensation-induced and photolysis-induced fractionation. It is shown that during the
654 perihelion season, condensation-induced fractionation is not effective at 50 km ($F'_{cond} \sim 1$),
655 where the dissociation rates peak. At this altitude, the photolysis-induced fractionation factor
656 (F'_{photo}) is between 2 and 2.5, meaning that the photolysis products will be depleted in D/H
657 by a factor of 2-2.5 with respect to the average D/H of water vapour in the lower atmosphere.
658 During the aphelion season, photodissociation of water vapour peaks closer to the surface,
659 and both condensation-induced and photolysis-induced fractionation become more important.

660 Similarly, the lower panels in Figure S11 show the fractionation factors integrated over the
661 column. However, while the calculation of the photolysis-induced column-integrated
662 fractionation factor can be performed using all altitudes, the condensation-induced
663 fractionation factor can just be calculated using the altitudes at which the measurements are
664 sensitive to HDO, and missing part of the column. Therefore, the condensation-induced

fractionation factor is just shown when the column-integrated photolysis rates where the measurements are sensitive to HDO (yellow points in top panels of Fig. S12) are at least 75% of those using all altitudes (black points in top panels of Fig. S12). The results show a higher fractionation factor during the aphelion season by both photolysis-induced and condensation-induced fractionation, as compared to the perihelion season. However, even during aphelion, when the role of condensation-induced fractionation becomes more important, it does not exceed the role of photolysis-induced fractionation. Besides, when taking into account that the contribution of each data point to the annual average is proportional to the photolysis rate (see Fig. 3B), it is clear that the annual average fractionation factor F' will be heavily weighted towards the perihelion season, when most of the photodissociation of water vapour molecules occurs.

In order to calculate the seasonal evolution of the column-integrated photolysis rates and fractionation factor (see Fig. 3), these are binned in L_s with a step of 10° . In order to obtain averages of the fractionation factor over latitude, we calculate a contribution index (CI), which is equivalent to the photolysis rate, but multiplied by a normalising factor to match its maximum with unity. The averages of the fractionation factors are then calculated using the contribution index as a weight. In order to visualise the relative role of photolysis-induced fractionation and condensation-induced fractionation in Figure 3, we shade the areas in each L_s bin corresponding to

$$CI_{photo} = CI \cdot \frac{(F'_{photo} - 1)}{(F'_{photo} + F'_{cond} - 2)} \text{ and } CI_{cond} = CI \cdot \frac{(F'_{cond} - 1)}{(F'_{photo} + F'_{cond} - 2)} .$$

686 Similarly, as for HDO, the H_2^{18}O molecules are expected to have a different UV absorption
687 cross-section than the H_2^{16}O ones, which can impact the isotope composition of the
688 dissociation products of water vapour and the efficiency of ^{18}O to reach the upper
689 atmosphere. To our knowledge, there are no available cross-sections for H_2^{18}O . However,
690 theoretical methods⁴³ to quantify the photo-induced isotopic fractionation predict most
691 noticeable differences in the absorption cross-sections of H_2^{18}O and H_2^{16}O for wavelengths λ
692 > 180 nm, similar to the H_2O -HDO dichotomies (see Fig. S10). However, while the
693 cross-section of H_2O is about 60% higher than that of HDO for $\lambda > 180$ nm, it is only about
694 2.5% higher than that of H_2^{18}O . If considering that most of the dissociation of water occurs
695 during the perihelion season between 40-60 km, while H_2^{16}O molecules are about 2-2.5 times
696 more efficiently dissociated than the HD^{16}O ones, they will be just about 1.08-1.10 times
697 more efficiently dissociated than the H_2^{18}O ones. This means that the efficiency of ^{18}O to be
698 transferred to lighter molecules is about 24 times higher than that of deuterium.

699

Supplementary Figures

Figure S1: ACS MIR data and impact of doubled image to the spectra. The left panels show the measured detector frames highlighting the rows corresponding to the maximum intensity (blue) and the slit edge (red) in diffraction orders 217 and 223, whose corresponding spectrum is shown in the right panels.

Figure S2: Synthetic transmission spectrum of the Martian atmosphere within the spectral range of ACS MIR. The spectra was calculated using an instrument lineshape described by a Gaussian function with FWHM of 0.15 cm^{-1} , and shows the instantaneous spectral range covered by ACS MIR when using different secondary grating positions. The contribution by CO_2 and different isotopologues of H_2O is shown in different colours, following the legend.

Figure S3: Synthetic transmission spectrum of the Martian atmosphere within the instantaneous spectral range covered by ACS MIR when observing with secondary grating positions 4, 5 and 11. The spectra was calculated using an instrument lineshape described by a Gaussian function with FWHM of 0.15 cm^{-1} , and shows the spectral range of the different diffraction orders acquired by ACS MIR when observing with secondary grating positions 4, 5 and 11. The contribution by CO_2 and different isotopologues of H_2O is shown in different colours, following the legend.

Figure S4: Characterising biases in the retrievals by comparing with simultaneous ACS NIR measurements.

The top panel shows an ACS MIR transmission spectrum (black dots), the best fit to the data (red line), as well as the contribution from different gases to the spectra, following the different colours shown on the legend. The lower three panels show the retrieved profiles from ACS NIR spectra (black dashed lines - Fedorova et al.³¹), as well as the retrieved profiles from ACS MIR when using the whole spectral window shown in the top panel (blue lines) and the spectral range shown between the black dashed lines in the top panel (orange lines). The three observations shown here correspond to the observations made during orbits 3418 (Lat = 50°N, L_s = 240°, Local time = 16h), 4124 (Lat = 49°N, L_s = 276°, Local time = 8h) and 4517 (Lat = 55°N, L_s = 296°, Local time = 8h).

Figure S5: Calculation of the averaged profiles and uncertainties in the combination from several detector rows. The different panels show the vertical profiles of $H_2^{16}O$, $H_2^{18}O$ and $HD^{16}O$ retrieved independently from several detector rows. The uncertainties in the weighted-averaged profiles (black lines) are calculated using the maximum between the propagation of errors from the different profiles and the dispersion from the independent profiles from the mean. The profiles on the top panels correspond to the observation made in orbit 4124 ($Lat = 49^\circ N$, $L_s = 276^\circ$, Local time = 8h) and the ones at the bottom to the observation made in orbit 8856 ($Lat = 66^\circ N$, $L_s = 108^\circ$, Local time = 0h).

738 **Figure S6: Validation of the retrieved vertical profiles of temperature and water vapour mixing ratio from**
 739 **ACS MIR and ACS NIR.** The different panels show the retrieved profiles of temperature and water vapour
 740 volume mixing ratio from simultaneous observations made by ACS MIR (solid lines - this study) and ACS NIR
 741 (dashed lines - Fedorova et al.³¹) in different latitudes and seasons.

Figure S7: Validation of the retrieved vertical profiles of D/H using ACS MIR observations with secondary grating positions 4 and 11. The different panels show the retrieved profiles of water vapour mixing ratio and D/H ratio for observations taken during the perihelion season of MY34 and the aphelion season of MY35 when observing with secondary grating positions 4 (green) and 11 (purple).

749 **Figure S8: Evolution of the water vapour mixing ratio and the D/H and $^{18}O/^{16}O$ isotopic ratios in the**
 750 **perihelion and aphelion seasons of MY34 and MY35. The different panels show the retrieved profiles**
 751 **separated in different seasons, with the colour of the lines representing the latitude of the observations. For the**
 752 **clarity of the figure, only the points with uncertainties of $D/H < 1$ VSMOW and $^{18}O/^{16}O < 0.13$ VSMOW are**
 753 **shown.**

Figure S9: Histogram of the measured D/H and ¹⁸O/¹⁶O isotope ratios, as well as their relation with the water vapour mixing ratio and temperature. Only the points with uncertainties of D/H < 1 VSMOW and ¹⁸O/¹⁶O < 0.13 VSMOW are shown. The black dashed lines on the histogram plots represent typical measurement uncertainties, centred at D/H = 5 ± 0.4 VSMOW and ¹⁸O/¹⁶O = 1.14 ± 0.11 VSMOW. The colour of the points on the plots in the middle and right columns represents the density of measured points.

762 **Figure S10: Calculation of the H_2O and HDO photolysis rates with the photolysis code of the LMD-GCM³⁷.**
 763 Left) UV absorption cross-sections of H_2O and HDO . Middle) Photolysis rates of H_2O (solid) and HDO
 764 (dashed) in s^{-1} at different solar zenith angles (SZA), calculated at a Sun-Mars distance of 1.52 AU. Right)
 765 Ratio of the $\text{H}_2\text{O}/\text{HDO}$ photolysis rates as a function of SZA.

767 **Figure S11: Comparison of the estimated impact of fractionation during photolysis for the perihelion and**
 768 **aphelion seasons during MY34 and MY35.** The top panels show the estimated H_2O dissociation rates, with the
 769 colour of the lines representing the latitude of the observations. The bottom panels show the fractionation factor
 770 between the D/H ratio representative of water vapour in the lower atmosphere and that of the photolysis
 771 products for the cases of photolysis-induced fractionation $F'_{photo} = J_{H_2O}/J_{HDO}$ (black line) and
 772 condensation-induced fractionation $F'_{cond} = (D/H)_{bulk}/(D/H)_{parent}$ (colour-coded lines).

775 **Figure S12: Column-integrated water vapour photolysis rates and D/H fractionation factors for the**
 776 **perihelion and aphelion seasons during MY34 and MY35.** The top panels show the column-integrated
 777 photolysis rates (black dots) as a function of latitude. The yellow dots represent the column-integrated
 778 photolysis rates when using the part of the column in which the measurements are sensitive to HDO. The bottom
 779 panels show the fractionation factors between the D/H ratio representative of the lower atmosphere and that of
 780 the photolysis products ($F = (D/H)_{\text{bulk}} / (D/H)_{\text{products}}$) for the cases of photolysis-induced fractionation (blue dots)
 781 and condensation-induced fractionation (orange dots). The condensation-induced fractionation factor is only
 782 plotted if the column-integrated photolysis rate using the part of the column in which the measurements are
 783 sensitive to HDO (yellow dots in top panels) is at least 75% of that calculated when using the whole column
 784 (black dots in top panels).

Figures

Figure 1

Example of ACS MIR spectra and summary of the retrieval scheme. A CS MIR spectra shown in this figure was obtained in orbit 4409 (Latitude = 42°S , $\text{Ls} = 291^\circ$, Local time = 19h). In step 1 of the retrieval scheme, pressure and temperature based on the absorption of CO_2 , and H_2O volume mixing ratio profiles are retrieved from one detector row in diffraction orders 223 and 224. In step 2, spectra from five different detector rows are independently used to retrieve the volume mixing ratios of H_2O , H_2^{18}O and HD^{16}O from the spectral window in diffraction order 224, which allow the derivation of the D/H and $^{18}\text{O}/^{16}\text{O}$ isotope ratios.

Figure 2

Climatology of the retrieved atmospheric parameters. The panels show the values of the retrieved parameters as a function of altitude and solar longitude for the northern (left) and southern (right) hemispheres. A) Distribution of ACS MIR solar occultation observations, with the local time represented by the colour bar. B) Atmospheric temperature. C) Water vapour volume mixing ratio. E) D/H ratio in water vapour with uncertainties lower than 1 VSMOW.

Figure 3

Seasonal evolution of the isotopic fractionation of D/H during the photodissociation of water vapour. A) The column-integrated photolysis rate of water vapour exhibits large seasonal variations, revealing the perihelion season to be dominant in the production of OH and H. B) The estimated fractionation factor between the value representative of the lower atmosphere ($\text{D}/\text{H} = 5 \text{ VSMOW}$) and its photodissociation products ($(\text{D}/\text{H})_{\text{bulk}} / (\text{D}/\text{H})_{\text{products}}$) (red curve) is anti-correlated with the photolysis of water vapour, peaking near aphelion. Also plotted is the contribution index (normalised photolysis rate of H_2O - black line) of each point to the annual average of the D/H fractionation factor, showing the prevalence of the perihelion season on the global scale. The contribution of condensation-induced (F_{cond}) and photolysis-induced fractionation (F_{photo}) (shaded polygons) to the total D/H fractionation factor (B, shaded polygons) demonstrate the prevalence of the latter in shaping the isotopic composition of the escaping hydrogen.