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1 Photochemistry on Mars reduces the abundance of heavy isotopes in atmospheric 2 CO and their escape efficiency to space

3
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16 Abstract

17
18 The atmosphere of Mars is enriched in heavy isotopes with respect to Earth as a result of
19 the escape of the atmosphere to space over billions of years. Estimating the enrichment in
20 heavy isotopes due to atmospheric escape requires a rigorous understanding of all
21 atmospheric processes that contribute to the evolution of isotopic ratios between the lower
22 and upper atmosphere, where escape processes take place. Using a combination of vertical
23 profiles from the Atmospheric Chemistry Suite (ExoMars Trace Gas Orbiter) with the
24 predictions of a photochemical model, we provide evidence for a new process of
25 photochemistry-induced fractionation that depletes the heavy isotopes of C and O in CO.
26 Accounting for this new source of fractionation, we find that only a fraction of $\approx 12\%$ of the
27 atmosphere needs to have been lost to space through CO photochemical escape to explain
28 the enrichment of $^{13}\text{C}/^{12}\text{C}$ in CO_2 measured by the Curiosity Rover.

30 1. Main text

31
32 Numerous lines of geomorphological and mineralogical evidence suggest that liquid water
33 was once abundant on Mars' surface (e.g., Baker (2001); Carr & Clow (1981); Head et al.
34 (1999); Murchie et al. (2009)), but it remains unclear what climatic conditions enabled this, or
35 what drove the transition in the climate to the dry, low pressure atmosphere we observe
36 today. Enrichment in the heavy isotopes of several species such as Ar, N and H suggests
37 that atmospheric escape has been an important mechanism shaping the climate and
38 composition of the atmosphere throughout history (e.g., McElroy et al. (1976); Owen (1982);
39 Owen et al. (1988)). Combining measured atmospheric isotope ratios with evolution models
40 allows the estimation of the abundance of species in the atmosphere of early Mars, which
41 demonstrates the value of a thorough understanding of the atmospheric isotope composition
42 (Hu et al., 2015; Hu & Thomas, 2022; Jakosky et al., 2017; Scheller et al., 2021).

43
44 Accurate estimations of the long-term evolution of the atmosphere from its isotope
45 composition rely on two important quantities: measurements of the past and present isotopic
46 ratios, and the net escape fractionation factor, which determines the efficiency of the heavy-
47 isotope enrichment as the atmosphere escapes to space (e.g., Krasnopolsky et al. (1998);
48 Yung et al. (1988)). The most accurate measurements of the isotopic composition of C and
49 O in the atmosphere of Mars were made by the Curiosity Rover, which showed an
50 enrichment in the heavy isotopes in CO_2 with respect to Earth-like standards ($^{13}\text{C}/^{12}\text{C} = 1.046$
51 ± 0.004 VPDB and $^{18}\text{O}/^{16}\text{O} = 1.048 \pm 0.005$ VSMOW, see Methods for definition of

standards), consistent with the hypothesis of substantial atmospheric loss (Mahaffy et al., 2013; Webster et al., 2013). On the other hand, while the fractionation factor of several escape processes of C and O has been estimated before (Fox & Hać, 1999; Fox & Hać, 2010; Hu et al., 2015), the net escape fractionation factor, accounting for all processes from the lower atmosphere to the upper atmosphere as well, remains undetermined.

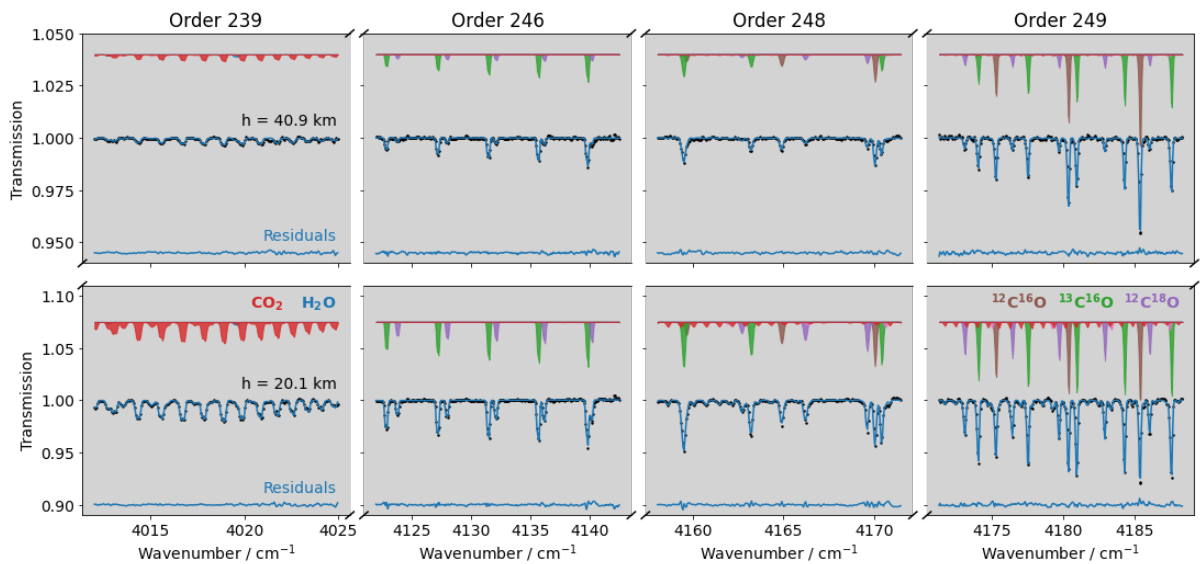
By applying this methodology to the C isotopes, the density of CO₂ in the atmosphere of early Mars has been estimated (Hu et al., 2015; Jakosky, 2019). The escape of C at present is suggested to occur mostly in the form of hot C produced by a number of different photochemical reactions, such as the direct photodissociation of CO₂ and CO or the dissociative recombination of CO⁺ (Cui et al., 2019; Gröller et al., 2014; Lo et al., 2021; McElroy, 1972). Hu et al. (2015) showed that the photodissociation of CO efficiently enriches the atmosphere in ¹³C as it escapes to space, and whose contribution is an important factor for explaining the current enrichment in ¹³C in CO₂ measured by the Curiosity Rover. However, whilst CO therefore seems to be an important species for understanding the isotopic evolution of C in the atmosphere of Mars, its present-day isotopic composition has not yet been determined.

Carbon isotopic ratios can also reveal the nature of surface-atmosphere interaction processes and mineral formation. Recently, carbon isotopic measurements by the Curiosity Rover revealed anomalously large depletions in ¹³C (¹³C/¹²C ≈ 0.86-0.93 VPDB) on sedimentary organics potentially associated with a possible paleosurface (House et al., 2022). One of the possible explanations suggested to produce ¹³C-depleted organic material is the photochemical reduction of CO₂ into formaldehyde (CH₂O) with CO as an intermediate. In this production, the abundance of ¹³C in CO is suggested to be lower than that in CO₂ as a result of the differential photolysis of ¹²CO₂ and ¹³CO₂ (Schmidt et al., 2013), transferring its isotopic signature into formaldehyde and other organics that accumulated on the surface of Gale Crater (House et al., 2022). Direct measurements of the ¹³C/¹²C in CO may therefore provide constraints on whether the photoreduction of CO₂ is the responsible mechanism for the depletion of ¹³C on the surface organics.

The reactions that determine the abundance of CO in the atmosphere of Mars are the same as the ones controlling the long-term stability of CO₂: the photolysis of CO₂ into CO, and the posterior recombination of CO back into CO₂. The stability of CO₂ in Mars' atmosphere was at first not well understood since the photodissociation of CO₂ molecules (CO₂ + hv → CO + O) is much faster than the recombination of the products (CO + O + M → CO₂ + M). It was later realised that the stability of CO₂ is instead controlled by catalytic reactions with odd-hydrogen species (CO + OH → CO₂ + H), which can convert CO into CO₂ at a much faster rate (McElroy & Donahue, 1972; Parkinson & Hunten, 1972). This reaction network not only determines the relative abundances of CO₂ and CO in the atmosphere of Mars, but also controls the relative isotopic fractionation of C and O in these species.

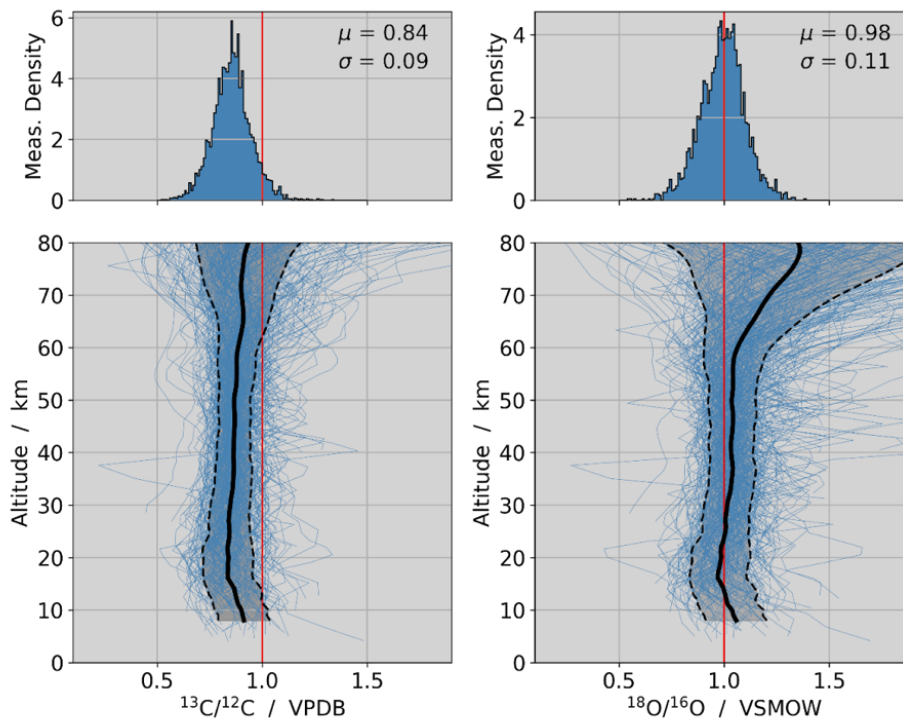
Here, we investigate the isotopic composition of C and O in CO using solar occultation measurements by the Atmospheric Chemistry Suite (ACS) onboard the ExoMars Trace Gas Orbiter (TGO) (Korablev et al., 2018). ACS includes three spectrometers dedicated to investigate the atmosphere using different spectral ranges: the near-infrared channel (NIR), which operates between 0.7-1.7 μm; the mid-infrared channel (MIR) operating between 2.3-4.2 μm; and the thermal infrared channel (TIRVIM), which samples the atmosphere between 0.7-17 μm. In this study, we use observations from the MIR channel, which is dedicated to solar occultation observations. For these observations, the instrument's boresight is pointed towards the Sun as it rises or sets from behind the Mars disk. By making measurements every 2.1 s, the instrument's line-of-sight crosses the atmosphere at different tangent altitudes above the surface, allowing the reconstruction of the atmospheric vertical profiles.

106 ACS observations have been previously used to measure for the first time the vertical
 107 distribution of CO and its seasonal variations in the atmosphere of Mars (Fedorova et al.,
 108 2022; Olsen et al., 2021). Here, we use the MIR data employed by Fedorova et al., but
 109 studying the relative abundances of $^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$. In particular, we use the
 110 ACS MIR measurements obtained using the secondary grating position 6, which includes
 111 fourteen diffraction orders (236-249) encompassing a spectral range between 3950-4193
 112 cm^{-1} . We perform the retrievals in four spectral windows in diffraction orders 239 (4012-4025
 113 cm^{-1}), 246 (4122-4142 cm^{-1}), 248 (4158-4171 cm^{-1}) and 249 (4171-4188 cm^{-1}) (see Figure
 114 1), to retrieve the pressure, temperature and volume mixing ratios of H_2O and the
 115 aforementioned CO isotopes (see Methods). The retrieved dataset in this study comprises
 116 all ACS MIR secondary grating position 6 observations where the four presented diffraction
 117 orders were measured, which includes 242 vertical profiles mainly measured in the second
 118 halves of Martian Year (MY) 34 ($L_s = 166^\circ$ - 349°) and MY35 ($L_s = 141^\circ$ - 366°). This large
 119 range of observing conditions in terms of season, local time, location and dust-activity allows
 120 a better characterisation of any potential variability in the isotopic ratios, as well as to derive
 121 more reliable estimates of the measurement uncertainties.
 122
 123
 124



125
 126 *Figure 1: Example of ACS MIR spectra from secondary grating position 6 made during orbit*
 127 *1896 (Latitude = 83.8° ; Longitude = 170.5° ; $L_s = 166^\circ$; Local time = 22.5 h). The panels show*
 128 *the measured transmission spectra in four diffraction orders (black dots) and best fit (blue*
 129 *lines) at 20 (bottom) and 40 km (top). The residuals between the measurement and best fit*
 130 *in each diffraction order are shown in each panel, together with the contribution from each*
 131 *gas to each spectrum, adding a constant offset in both to improve the visibility of the figure.*
 132

133
 134 Figure 2 shows a summary of all $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ isotopic ratios in CO measured in this
 135 dataset. We observe the $^{13}\text{C}/^{12}\text{C}$ ratio to be systematically depleted in the heavy isotopes
 136 with respect to the Earth-like standard with a weighted averaged value of $^{13}\text{C}/^{12}\text{C} = 0.84 \pm$
 137 0.09 VPDB, where the uncertainties correspond to the standard deviation of the
 138 measurements. Comparing this value to that measured in CO_2 by the Curiosity Rover, it
 139 corresponds to a depletion of $^{13}\text{C}/^{12}\text{C}$ in CO of approximately 20%. On the other hand, the
 140 $^{18}\text{O}/^{16}\text{O}$ ratio is consistent at all altitudes with the Earth-like fractionation. The distribution of
 141 measured values in this case yields a weighted average isotopic ratio of $^{18}\text{O}/^{16}\text{O} = 0.98 \pm$
 142 0.11 VSMOW, which compared to the isotopic ratio measured in CO_2 by the Curiosity Rover
 143 corresponds to a depletion of the O isotopic ratio in CO of 6%.



145
 146 *Figure 2: Vertical profiles of the C and O isotopic ratios in CO in the atmosphere of Mars.*
 147 *The top panels show the histogram of all measured $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ ratios in standard*
 148 *units with uncertainties lower than 0.4. The lower panels show the 242 measured vertical*
 149 *profiles of the isotopic ratios in this dataset (blue thin lines), as well as the weighted average*
 150 *(black line) and the standard deviation of the profiles (shaded areas). The red lines indicate*
 151 *the Earth-like standards given by Vienna Pee Dee Belemnite (VPDB) and Vienna Standard*
 152 *Mean Ocean Water (VSMOW).*

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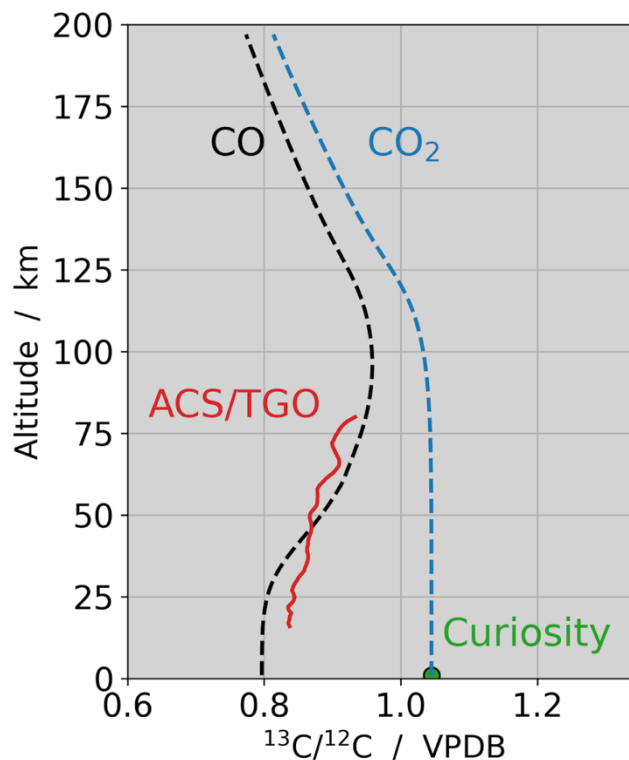
155 In order to understand the physical and chemical processes that give rise to the depletion of
 156 the C and O isotopic ratios measured in CO, we constructed a 1D photochemical model to
 157 simulate the isotopic fractionation between CO and CO₂. In particular, we include isotope-
 158 specific rates for the two most important reactions relating these two species: the photolysis
 159 of CO₂ into CO + O, and the recombination of CO + OH back into CO₂. The photolysis cross-
 160 sections for $^{12}\text{C}^{16}\text{O}_2$, $^{13}\text{C}^{16}\text{O}_2$ and $^{18}\text{O}^{12}\text{C}^{16}\text{O}$ are taken from Schmidt et al. (2013), while the
 161 fractionation during the recombination of CO into CO₂ is modelled using the data from the
 162 laboratory measurements by Stevens et al. (1980) (see Methods). This photochemical
 163 model extends from the surface up to an altitude of 200 km and is set to represent martian
 164 mean dayside conditions (i.e., solar zenith angle equal to 60° and Sun-Mars distance of 1.52
 165 AU (Krasnopolsky, 2010)). The isotopic ratios in the model are initialised assuming Earth-
 166 like fractionation at all altitudes, and the model is then run for approximately 20 years, the
 167 time by which the isotopic ratios in CO and CO₂ have converged to a steady-state solution
 168 (see Extended Data Figure 2).

169

170

171 Figure 3 shows the derived C isotopic abundances from the photochemical model scaled to
 172 the isotopic composition of the atmosphere of Mars measured by the Curiosity Rover,
 173 together with the measured values from the ACS observations. The C isotopic ratios in both
 174 CO and CO₂ show a similar altitudinal trend above approximately 100 km, where they
 175 continuously decrease with increasing altitude due to diffusive separation: above the
 176 homopause, where molecular diffusion dominates, species are mixed according to their own

177 mass-dependent scale height. As a result of this, the isotopic ratios steadily decrease with
 178 altitude, with the decrease in $^{13}\text{C}/^{12}\text{C}$ being approximately half of $^{18}\text{O}/^{16}\text{O}$ (Alday et al., 2021)
 179 (see Extended Data Figure 2). While the isotopic ratios in CO_2 below the homopause altitude
 180 are approximately constant, those in CO are depleted in the heavy isotopes due to
 181 photochemistry-induced fractionation, mainly due to the preferential photolysis of $^{12}\text{C}^{16}\text{O}_2$
 182 over $^{13}\text{C}^{16}\text{O}_2$ and $^{18}\text{O}^{12}\text{C}^{16}\text{O}$ (see Extended Data Figures 3 and 4). In particular, the
 183 photochemical model suggests that below 30 km the C isotopic ratio in CO is approximately
 184 24% lower than in CO_2 , increasing to about 9% at 100 km. The effect of the photochemistry
 185 has a smaller impact in the O isotope ratios, with the depletion of the heavy isotopes near
 186 the surface being approximately 9%. The lower value of the $^{13}\text{C}/^{12}\text{C}$ ratio in CO than that in
 187 $^{18}\text{O}/^{16}\text{O}$ predicted by the photochemical model is consistent with the ACS measurements
 188 presented in this study.
 189



190
 191 *Figure 3: Photochemistry-induced fractionation of the C isotopes in the atmosphere of Mars.*
 192 *The ACS measurements (red) reveal a decrease of the $^{13}\text{C}/^{12}\text{C}$ isotope ratio in CO with*
 193 *respect to that in CO_2 measured by the Curiosity Rover at the surface (green). The*
 194 *predictions from the 1D photochemical model suggest that this decrease is produced by the*
 195 *chemistry of the martian atmosphere, which preferentially favours the transfer of ^{13}C from*
 196 *CO (black dashed line) to CO_2 (blue dashed line). The isotope ratio in CO in the upper*
 197 *atmosphere, responsible for a substantial fraction of the C escape to space, is substantially*
 198 *lower than that of the bulk CO_2 atmosphere, suggesting a lower escape fractionation factor*
 199 *than previously thought.*

200
 201 Both the ACS measurements and the predictions from the model suggest that the
 202 photochemistry of the atmosphere of Mars produces a depletion of the heavy C and O
 203 isotopes in CO , which represents the first direct detection of this effect in the atmosphere of
 204 Mars. Isotopic fractionation also occurs during the photolysis of other species such as H_2O ,
 205 whose effect in the martian atmosphere has been extensively studied (Cheng et al., 1999;
 206 Vladimir A. Krasnopolsky, 2002). The photolysis-induced fractionation in H_2O is responsible
 207 for fractionating the D/H ratio in water, molecular hydrogen, and finally the escaping

208 products, giving rise to an efficient enrichment in D/H as the atmosphere escapes to space
209 (e.g., Cangi et al. (2020); Krasnopolsky (2002)).

210

211 Since CO contributes a substantial fraction of the C escape from Mars, this new source of
212 fractionation has to be accounted for when estimating the net escape fractionation factor.
213 The escape of C from the atmosphere of Mars due to CO photodissociation and
214 photoionisation is most efficient at altitudes above 150 km (Cui et al., 2019; Lo et al., 2021).
215 At these altitudes, the isotopic composition of CO is affected by both the chemistry and
216 diffusive separation. Our model suggests that at 200 km, the $^{13}\text{C}/^{12}\text{C}$ isotopic ratio in CO is
217 ≈ 0.74 times lower than that of the bulk atmosphere, which combined with the fractionation
218 factor due to escape by CO photodissociation ($\alpha \approx 0.6$, Hu et al. (2015)) yields a net escape
219 fractionation factor of ≈ 0.44 for this reaction. This lower fractionation factor indicates that the
220 C escape through CO photodissociation enriches the atmosphere in ^{13}C more efficiently than
221 previously thought. In particular, considering a primordial isotopic ratio of $^{13}\text{C}/^{12}\text{C} = 0.975$
222 VPDB (Wright et al., 1986), and a long-term enrichment of the isotopic ratio through
223 Rayleigh distillation, we estimate that only a loss of 12% of the atmosphere is required to
224 have escaped to space through this mechanism to explain the enrichment of the heavy
225 isotopes measured by the Curiosity Rover. While the total density of C on early Mars is also
226 subject to other processes such as carbonate formation or outgassing from the surface (Hu
227 et al., 2015), our results highlight the efficient role of this mechanism to enrich the
228 atmosphere in the heavy isotopes, suggesting that C escape may have been less important
229 than previously thought.

230

231 Since the atmospheric mass of ^{12}C and ^{13}C is conserved, the chemistry-induced fractionation
232 also implies a preferential transfer of ^{13}C from CO to CO_2 , which yields an enrichment in the
233 $^{13}\text{C}/^{12}\text{C}$ ratio in CO_2 . The near-surface isotopic ratio in CO_2 is found to be $\approx 3 \times 10^{-5}$ times
234 higher than that in the initial atmosphere, which corresponds to an enrichment of $\delta^{13}\text{C} \approx$
235 0.03 ‰ . This value is much smaller than the enrichment in the heavy isotopes observed by
236 the Curiosity Rover ($\delta^{13}\text{C} = 46 \pm 4 \text{ ‰}$, Webster et al. (2013)), which suggests that
237 atmospheric escape remains as the preferred process contributing to the enrichment of ^{13}C
238 in the atmosphere of Mars.

239

240 The depletion of ^{13}C in CO observed with the ACS measurements and predicted by the
241 photochemical model is in line with the measurements of the $^{13}\text{C}/^{12}\text{C}$ ratio in Martian
242 organics made by the Curiosity Rover (House et al., 2022). While other suggested formation
243 mechanisms such as the photolysis of CH_4 released from the subsurface or the deposition of
244 cosmic dust cannot be ruled out as responsible for the production of ^{13}C -depleted organics
245 on Mars, our results confirm that the photolysis of CO_2 can produce strong depletions of the
246 $^{13}\text{C}/^{12}\text{C}$ ratio in CO, an isotopic signature that can be transferred to formaldehyde or other
247 organics that might accumulate on the surface of Mars.

248

249 The photochemical model also predicts a relative depletion of the $^{18}\text{O}/^{16}\text{O}$ isotopic ratio in
250 CO with respect to CO_2 , although to a lesser extent than for the C isotopes. The implications
251 of this new source of fractionation to the long-term evolution of the O isotopes are
252 nevertheless more complicated due to the much more complex O chemistry in the
253 atmosphere of Mars. The dissociative recombination of O_2^+ , responsible for most of the O
254 escape from Mars (Jakosky et al., 2018), also efficiently enriches the atmosphere in ^{18}O as
255 escape occurs (Fox & Hać, 2010). However, the overall escape fractionation factor will be
256 subject to the $^{18}\text{O}/^{16}\text{O}$ ratio in O_2^+ and the source species of these ions (i.e., O, O^+ , CO_2 ,
257 CO_2^+ , (Fox & Hać, 2009)), which will likely be affected by the isotope photochemistry. Based
258 on the isotope-specific photolysis cross-sections included in this study, while the O isotopic
259 ratios of CO_2 in the ionosphere will mostly be affected by the diffusive separation above the
260 homopause, the isotopic composition of atomic O will be affected by the preferential
261 photolysis of $^{12}\text{C}^{16}\text{O}_2$ over $^{18}\text{O}^{12}\text{C}^{16}\text{O}$, similar to the observed depletion of $^{18}\text{O}/^{16}\text{O}$ in CO.

262 However, since atomic O is produced and lost in several other chemical reactions, a
263 comprehensive analysis of the O isotopic composition in the upper atmosphere requires a
264 model accounting for ^{18}O in other species, which is planned but beyond the scope of the
265 work presented here.

266
267 The results from this study highlight the important role of photochemistry in fractionating the
268 C and O isotopic composition of the atmosphere of Mars. Future measurements of the
269 isotopic ratios in different species may not only provide key information about the
270 photochemical cycles in the atmosphere of Mars, but also provide accurate estimations of
271 the fractionation between the lower and upper atmospheres, which has important
272 implications to our understanding of the long-term evolution of Mars' climate.

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305 2. Methods

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307 2.1 Retrieval scheme

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309 The inversion of the spectra is performed using the NEMESIS algorithm (Irwin et al., 2008),
310 applying the same two-step methodology as in Alday et al. (2021). First, the pressure and
311 temperature profiles are determined using the CO₂ absorption features in diffraction order
312 239 (see Figure 1). Secondly, the pressure and temperature are fixed, and the abundances
313 of the trace gases (i.e., H₂O, ¹²C¹⁶O, ¹³C¹⁶O and ¹²C¹⁸O) are retrieved using all diffraction
314 orders. All gaseous absorption in this study is modelled using pre-computed line-by-line
315 look-up tables generated using the spectroscopic parameters from the 2020 edition of the
316 HITRAN database (Gordon et al., 2022). Apart from the retrieval of the atmospheric
317 parameters, the instrument line shape (ILS) is also fitted in each occultation using a double
318 Gaussian parameterisation (Alday et al., 2019).

319

320 The pressure and temperature profiles are retrieved under the assumption of an atmosphere
321 in hydrostatic equilibrium and a known CO₂ volume mixing ratio. This approach has been
322 widely used in the past to determine the thermal structure of the atmosphere of Mars from
323 solar occultation observations (Forget et al., 2009; Montmessin et al., 2006; Quémerais et
324 al., 2006). The retrieval scheme from the NEMESIS algorithm works using the optimal
325 estimation framework, which aims to find an optimal solution that is consistent with the
326 observed spectra subject to a minimal departure from the *a priori*. Given that the absorption
327 features of CO₂ measured in ACS MIR secondary grating position 6 typically disappear at
328 lower tangent altitudes than the CO ones, we use temperature profiles from simultaneous
329 observations by ACS NIR (Fedorova et al., 2022) as the *a priori* in our retrievals, which
330 ensures an accurate description of the temperature field at all altitudes. The use of accurate
331 measurements of temperature is crucial to derive precise measurements of the CO isotopic
332 ratios, which are highly sensitive to this parameter (see Supplementary Material).

333

334 Once the pressure and temperature profiles are determined, these are fixed, and the
335 gaseous abundances of the CO isotopes and H₂O are retrieved. In this case, the *a priori*
336 information is taken from the OpenMARS reanalysis dataset (Holmes et al., 2020), which
337 assimilates the temperature profiles and dust opacities measured by the Mars Climate
338 Sounder onboard the Mars Reconnaissance Orbiter into the General Circulation Model. The
339 *a priori* isotopic composition is assumed to follow that of Earth-like conditions given by the
340 Vienna Pee Dee Belemnite (¹³C/¹²C = 1 VPDB = 0.0112372) and the Vienna Standard Mean
341 Ocean Water (¹⁸O/¹⁶O = 1 VSMOW = 0.0020052). Given that the sensitivity of the retrieval to
342 the CO isotopes can be different at different altitudes (i.e., the ¹²C¹⁸O absorption lines
343 typically disappear at lower tangent heights than the ¹²C¹⁶O), the influence of the *a priori*
344 guess in the retrieval of the isotopologues might also be different. Therefore, in order to
345 ensure no biases from the *a priori* are introduced into the derivations of the isotopic ratios,
346 the retrievals are run twice, the second time using the retrieved ¹²C¹⁶O abundances from the
347 previous iteration as the *a priori* and scaling the abundances of the minor isotopes with the
348 same Earth-like isotopic ratios.

349

350 In each acquisition made by ACS MIR, the observed diffraction orders encompass about 20
351 detector rows, which correspond to the instantaneous field-of-view of the instrument, with
352 each row sampling slightly different tangent heights ($\Delta z \approx 150$ m per row). In addition, the
353 ILS varies from row to row, which can introduce systematic uncertainties in the retrievals. In
354 order to increase the confidence of the retrievals and better understand the uncertainties
355 arising from the ILS fitting, we apply the retrieval scheme to seven detector rows. The
356 retrieved profiles from each row are then combined using a weighted average. The
357 uncertainties are calculated considering both the error of the mean, and the standard
358 deviation of the profiles (Alday et al., 2021). We consider this method for calculating the

359 uncertainties to provide a more accurate representation of the true uncertainty of the
 360 retrieval in which not only the random uncertainties, but also the systematic ones are
 361 captured.

362
 363 A detailed validation of the retrievals presented in this study is provided in the
 364 Supplementary Material.

366 2.2 Photochemical model

367 The 1D photochemical model aims to solve the continuity equation given by

$$370 \quad \frac{\partial n_i}{\partial t} = P_i - L_i - \frac{\partial \phi_i}{\partial z},$$

371
 372 where n_i is the number density of a given species, P_i and L_i represent the production and
 373 loss of density due to the photochemical reactions, and the last term represents the diffusion
 374 between layers, where ϕ is the flux. The flux is calculated considering both Eddy and
 375 molecular diffusion and is given by

$$377 \quad \phi_i = -(K + D_i) \frac{\partial n_i}{\partial z} - n_i \left[K \left(\frac{1}{H_0} + \frac{1}{T} \frac{\partial T}{\partial z} \right) + D_i \left(\frac{1}{H_i} + \frac{(1 + \alpha)}{T} \frac{\partial T}{\partial z} \right) \right],$$

378
 379 where K and D_i are the Eddy and molecular diffusion coefficients, H_0 is the mean scale
 380 height, H_i is the gas-dependent scale height, α is the thermal diffusion coefficient, and T is
 381 the temperature.

382
 383 The diffusion term is calculated by finite differences, using an approach similar to
 384 Krasnopolsky (1993), which yields

$$386 \quad \frac{\partial \phi_{i,j}}{\partial z} \sim -(k_j + d_{i,j}) \cdot n_{i,j+1} + (kl_j + dl_{i,j} + k_{j-1} + d_{i,j-1}) \cdot n_{i,j} - (kl_{j-1} + dl_{i,j-1}) \cdot n_{i,j-1}$$

387
 388 where the subscripts i and j represent the gas and layer, respectively. The coefficients in the
 389 finite differences approximation are given by

$$391 \quad k_j = \frac{K_{j+1/2}}{\Delta z^2},$$

$$392 \quad d_{i,j} = \frac{D_{i,j+1/2}}{\Delta z^2},$$

$$393 \quad kl_j = k_j \cdot \left(1 - \frac{\Delta z}{H_{0_{j+1/2}}} - \frac{T_{j+1} - T_j}{T_{j+1/2}} \right),$$

$$394 \quad dl_{i,j} = d_{i,j} \cdot \left(1 - \frac{\Delta z}{H_{i,j+1/2}} - (1 + \alpha) \cdot \frac{T_{j+1} - T_j}{T_{j+1/2}} \right),$$

395
 396
 397 where Δz is the altitude of each layer.

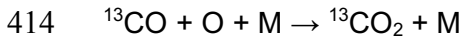
398
 399 The production and loss terms are calculated using the latest version of the photochemical
 400 scheme from the Mars Planetary Climate Model (PCM) , which has been extensively used to

401 model the photochemical cycles in the atmosphere of Mars (Cariolle et al., 2017; Lefèvre et
 402 al., 2021; Lefèvre et al., 2004). This scheme includes 14 chemical species and 39 chemical
 403 reactions to model the photochemistry of H, C and O in the atmosphere of Mars. Here, we
 404 introduce four new species ($^{13}\text{C}^{16}\text{O}_2$, $^{13}\text{C}^{16}\text{O}$, $^{18}\text{O}^{12}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$) and ten chemical
 405 reactions to model the isotopic fractionation between CO_2 and CO . The reaction rates are
 406 calculated assuming mean dayside conditions with a constant solar zenith angle of 60° and
 407 a constant Sun-Mars distance of 1.52 AU.

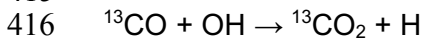
408
 409 The reactions included to model the ^{13}C chemistry are:



413



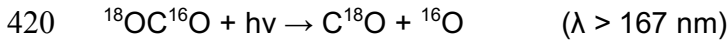
415



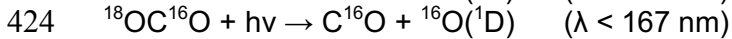
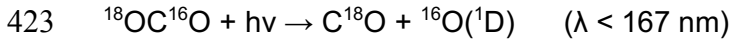
417

418 The reactions included to model the O fractionation between CO_2 and CO are:

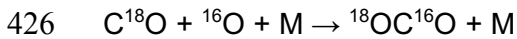
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422



425



427



429

430 It must be noted that in the version for the ^{18}O chemistry the total mass is not conserved, as
 431 we do not include ^{18}O or $^{18}\text{O}(^1\text{D})$ in the chemistry scheme. These species, together with the
 432 definition of the ^{18}O isotopologues in other O-bearing species are necessary to model the
 433 complete chemistry of ^{18}O in the atmosphere of Mars. Here, we just aim to model the relative
 434 fractionation of the $^{18}\text{O}/^{16}\text{O}$ isotopic ratio between CO_2 and CO , which is not expected to be
 435 affected by this simplification, since CO molecules are solely produced by the photolysis of
 436 CO_2 , which is included in the scheme.

437

438 The continuity equation is solved using a second-order Rosenbrock algorithm (Hobbs et al.,
 439 2019; Verwer et al., 1999). The density at the next time step is calculated following

440

441
$$n^{t+1} = n^t + 1.5\Delta t \cdot g_1 + 0.5\Delta t \cdot g_2,$$

442
$$(I - \gamma\Delta t J)g_1 = f(n^t),$$

443
$$(I - \gamma\Delta t J)g_2 = f(n^t - \Delta t g_1) - 2g_1,$$

444

445 Where $\gamma = 1 + 1/\sqrt{2}$, Δt is the time step, $f(n)$ is the right-hand side of the differential
 446 equation (i.e., the chemistry and transport terms evaluated at the density n) and J is the
 447 Jacobian matrix of the combined chemistry-transport system. Since the densities of a given
 448 species at a given layer are only influenced by the densities of the other gases in the same
 449 layer (i.e., chemistry) and the densities of the same gas in the adjacent layers (i.e.,
 450 diffusion), the Jacobian matrix takes the form of a block tridiagonal matrix, which is efficiently
 451 inverted using the Thomas algorithm (Hu et al., 2012).

452

453 The choice of the time step is made based on the maximum local error, which is estimated
 454 by the difference between the first-order and second-order solutions, following

455
 456
$$\varepsilon = n^{t+1} - n_1^{t+1} = (n^t + 1.5\Delta t \cdot g_1 + 0.5\Delta t \cdot g_2) - (n^t + \Delta t \cdot g_1).$$

 457

458 The timestep is self-adjusted by $\Delta t^{t+1} \sim \Delta t^t / \sqrt{\varepsilon_{max}}$, which ensures that the convergence of
 459 the system to a steady-state solution will capture the orders-of-magnitude difference in the
 460 chemical and diffusion timescales while optimising the computational time.

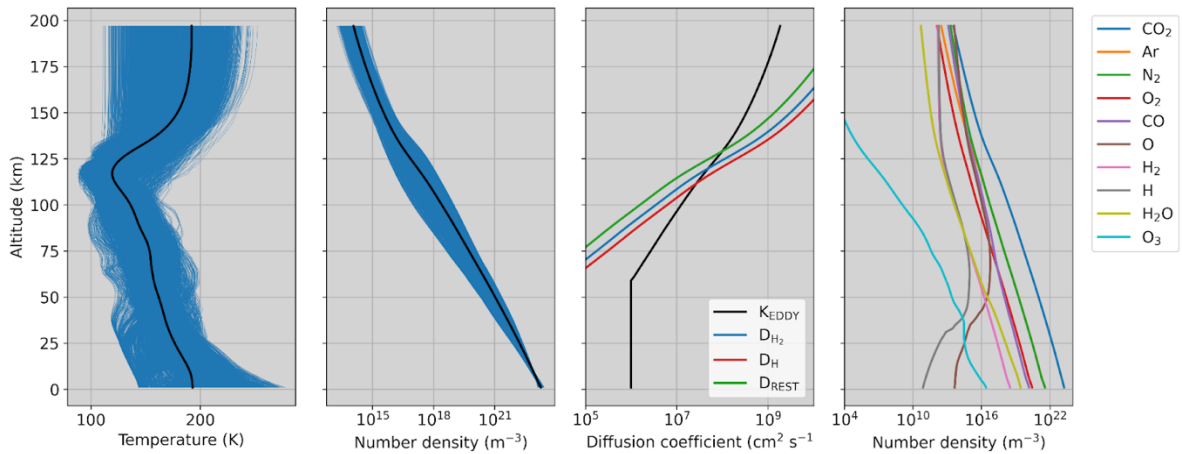
461
 462 The 1D photochemical model requires several inputs to represent the composition and
 463 mixing of the atmosphere of Mars. The initial temperature and density profiles are derived
 464 using an average of vertical profiles generated from the Mars Climate Database (Forget et
 465 al., 1999) at different times and locations. In particular, we generate vertical profiles of
 466 temperature, number density and volume mixing ratios from 0 to 200 km in a grid of
 467 latitudes, local times and solar longitude L_S . The latitudes expand from -80° to 80° with a
 468 step of 20° . The local time expands from 0 to 24 hours with a two-hour step. The L_S expands
 469 the whole year, with a step of 10° . The calculated profiles are then averaged using the
 470 atmospheric density as a weight (see Extended Data Figure 1). The abundances of CO_2 and
 471 CO from the Mars Climate Database are then divided into the different isotopologues by
 472 assuming a given isotopic ratio, and using

473
 474
$$[^{12}\text{C}^{16}\text{O}_2] = [\text{CO}_2] / (1 + R)$$

 475
$$[^{13}\text{C}^{16}\text{O}_2] = [^{12}\text{C}^{16}\text{O}_2] \times R$$

 476

477 where the bracketed quantities represent the abundances of the different species, and R is
 478 the assumed Earth-like isotopic ratio (i.e., $^{13}\text{C}/^{12}\text{C} = 1$ VPDB and $^{18}\text{O}/^{16}\text{O} = 1$ VSMOW).
 479



480
 481 *Extended Data Figure 1: Overview of the main inputs for the photochemical model. The*
 482 *initial profiles for the temperature, total number density and partial number density are*
 483 *calculated by averaging profiles from the Mars Climate Database throughout different*
 484 *seasons, locations and local time. The Eddy and molecular diffusion coefficients are*
 485 *calculated from Krasnopolsky (1993) and using the coefficients from Hunten (1973),*
 486 *respectively.*

487
 488 The diffusion coefficients assumed in our Mars 1D photochemical model are the same as
 489 those used by Chaffin et al. (2017) and Cangi et al. (2020), which were taken from other
 490 previous studies (e.g., Hunten (1973); Krasnopolsky (1993)). In particular, the Eddy diffusion
 491 coefficient is given by

492

493 $K(z < 60 \text{ km}) = 10^6 \text{ cm}^2 \text{ s}^{-1}$,
494 $K(z < 60 \text{ km}) = 2 \cdot 10^{13} \cdot n(z)^{-1/2} \text{ cm}^2 \text{ s}^{-1}$,

495

496 as shown in Extended Data Figure 1. The molecular diffusion coefficient is given by

497

$$D(z) = \frac{AT(z)^s}{n(z)}.$$

498

499

500 The coefficients A and s for H_2 and H are given by Hunten, (1973), which are equal to $A_{\text{H}} =$
501 8.4×10^{17} , $s_{\text{H}} = 0.597$, $A_{\text{H}_2} = 2.23 \times 10^{17}$, $s_{\text{H}_2} = 0.75$. For the rest of the species, we adopt $A =$
502 10^{17} and $s = 0.75$ (see Extended Data Figure 1).

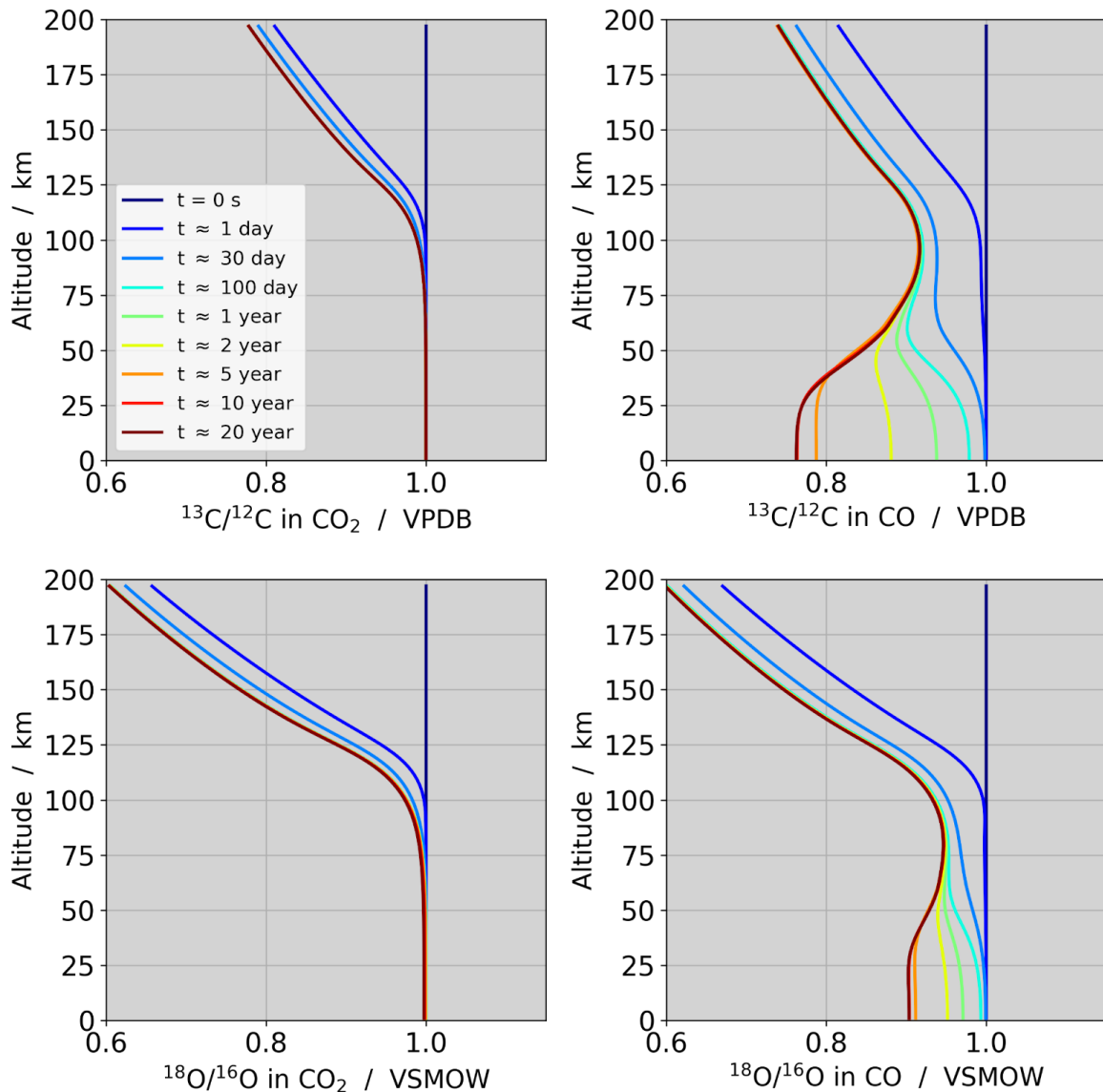
503

504 The boundary conditions are similar to those used in Chaffin et al. (2017). We consider the
505 top boundary conditions to be a zero flux for all species but for H_2 , H and O . For H_2 and H ,
506 we fix their escaping velocities to be $v_{\text{H}_2} = 3.4 \times 10^1 \text{ cm s}^{-1}$ and $v_{\text{H}} = 3.1 \times 10^3 \text{ cm s}^{-1}$, while
507 for O we fix the escaping flux to be $\phi_{\text{O}} = 1.2 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$. For the lower boundary
508 conditions, we set a zero flux for all species, but for H_2O , whose density is assumed to be
509 fixed below 50 km.

510

511 Using these inputs and the presented model setup, we run a simulation for 20 years, the
512 time by which the O and C isotopic ratios in both CO and CO_2 have converged to a steady-
513 state solution, as it is shown in Extended Data Figure 2.

514

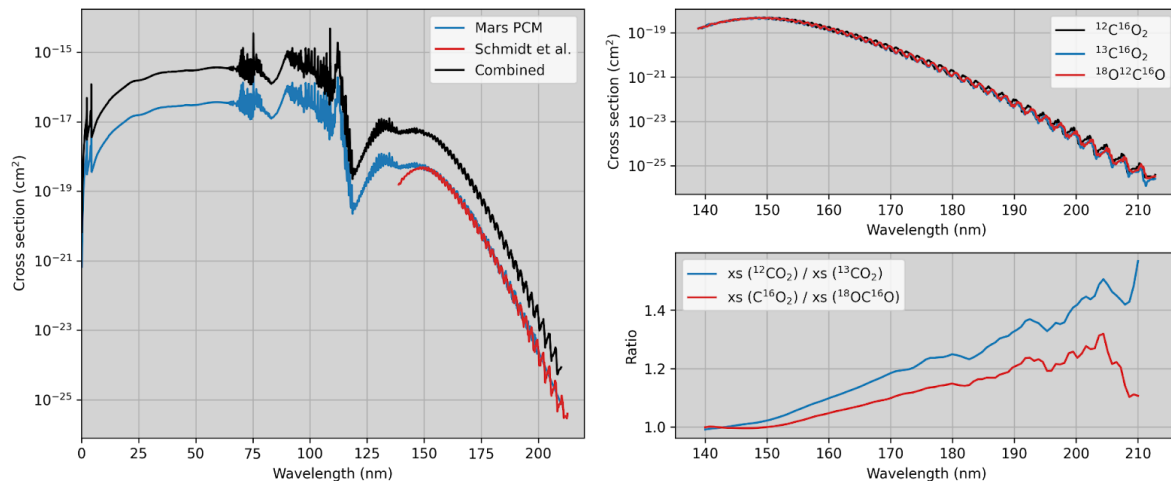


515
 516 *Extended Data Figure 2: Evolution of the isotopic ratios in the 1D photochemical model. The*
 517 *four panels show the carbon (top) and oxygen (bottom) isotopic ratios in CO₂ (left) and CO*
 518 *(right) as a function of time as the simulation from the photochemical model progresses. The*
 519 *isotopic ratios in CO₂ converge rapidly, as they are mostly affected by diffusive separation,*
 520 *which produces a decrease of the isotopic ratios above the homopause according to their*
 521 *own mass-dependent scale heights. The isotopic ratios in CO are affected by both diffusive*
 522 *separation and by the photochemistry-induced fractionation. The photochemistry of the*
 523 *atmosphere produces a depletion in the ¹³C/¹²C and ¹⁸O/¹⁶O ratios, whose effect is stronger*
 524 *for the former of the two, consistent with the ACS observations.*
 525

526 **2.3 Fractionation during the photolysis of CO₂**

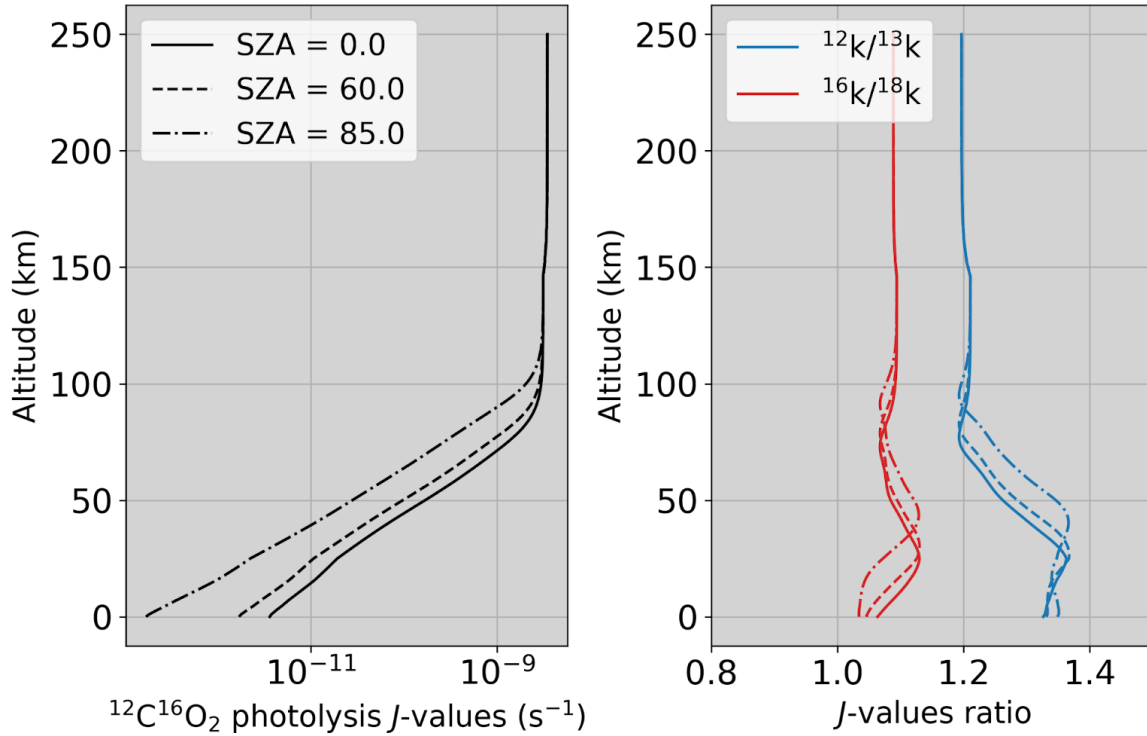
527
 528 The photolysis cross sections of CO₂ used in the chemistry scheme of the LMD Mars PCM
 529 are a composite of different laboratory measurements in different spectral ranges (Huestis &
 530 Berkowitz, 2010; Lewis & Carver, 1983; Parkinson et al., 2003; Stark et al., 2007; Yoshino et
 531 al., 1996) and tabulated at temperatures of 195, 295 and 370 K (Lefèvre et al., 2021). In
 532 order to model the fractionation factor of this reaction, we use the photolysis cross sections
 533 calculated by Schmidt et al. (2013) for ¹²C¹⁶O₂, ¹³C¹⁶O₂ and ¹⁸O¹²C¹⁶O between 150-210 nm,
 534 which are combined with the Mars PCM reference for <150nm at 195, 295 and 370 K.

535 Extended Data Figure 3 shows how the calculated cross sections for $^{12}\text{C}^{16}\text{O}_2$ compare with
 536 those tabulated in the chemistry scheme, together with a comparison between the cross
 537 sections calculated for the different isotopologues. These results suggest that the photolysis
 538 cross sections of $^{12}\text{C}^{16}\text{O}_2$ are larger than those of the minor isotopes (i.e., $^{13}\text{C}^{16}\text{O}_2$ and
 539 $^{18}\text{O}^{12}\text{C}^{16}\text{O}$) by a factor of 1.0-1.5 and 1.0-1.3, respectively. The ratio between the cross
 540 sections of $^{12}\text{C}^{16}\text{O}_2$ and those of the minor isotopes also depends on the temperature, with
 541 that at 195 K being on average 5% larger than that at 295 K.
 542



543
 544 *Extended Data Figure 3: Summary of the photolysis cross sections used in this study. The*
 545 *left plot shows a comparison between the cross sections tabulated in the Mars PCM (blue*
 546 *line) and those calculated by Schmidt et al. (2013) (red line) at 295 K. In addition, the*
 547 *combined cross sections used in this study are shown with a x10 offset. The top right plot*
 548 *shows the cross sections calculated by Schmidt et al. (2013) for the different isotopologues.*
 549 *The bottom right plot shows the ratio between the cross sections of the major and minor*
 550 *isotopes, convolved with a Gaussian function with a FWHM of 2.5nm to smooth out high*
 551 *frequency variations.*
 552

553 It is important to note that the cross sections for the minor isotopes are only available for a
 554 limited spectral range (>150 nm), and these are lower than the cross sections elsewhere
 555 (<150 nm), where we assume that they are equal for all isotopes. In order to evaluate where
 556 the cross sections >150 nm are most effective in the photolysis of CO_2 molecules in the
 557 atmosphere of Mars, we calculate the photolysis J -values as a function of altitude (see
 558 Extended Data Figure 4). These results show that the J -values are approximately constant
 559 above ≈ 100 km, where the atmosphere is optically thin. Below this altitude, the atmosphere
 560 becomes optically thick for wavelengths lower than 150 nm, and the J -values decrease with
 561 decreasing altitude as the atmosphere also becomes optically thick for wavelengths >150
 562 nm. Therefore, while the cross sections <150 nm are important above 100 km, their effect
 563 becomes negligible below 100 km, the region where the ACS observations can measure the
 564 isotopic fractionation between CO_2 and CO .
 565



566
 567 *Extended Data Figure 4: Photolysis J-values of $^{12}\text{C}^{16}\text{O}_2$ and the isotope effect. The left-hand*
 568 *panel shows the calculated photolysis J-values of the $^{12}\text{C}^{16}\text{O}_2$ at three different solar zenith*
 569 *angles. The right-hand panel shows the ratio between the photolysis rates of $^{12}\text{C}^{16}\text{O}_2$ over*
 570 *those of $^{13}\text{C}^{16}\text{O}_2$ and $^{18}\text{O}^{12}\text{C}^{16}\text{O}$.*

571
 572 The right-hand panel of Extended Data Figure 4 shows the ratio between the photolysis
 573 rates of $^{12}\text{C}^{16}\text{O}_2$ over those of $^{13}\text{C}^{16}\text{O}_2$ and $^{18}\text{O}^{12}\text{C}^{16}\text{O}$, which is higher than one at all
 574 altitudes. These results suggest that the photolysis of $^{12}\text{C}^{16}\text{O}_2$ is faster than that of the minor
 575 isotopes, meaning that $^{12}\text{C}^{16}\text{O}$ will be more efficiently produced than $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$. The
 576 net effect of this process is to produce a depletion of the $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ ratios in CO
 577 with respect to those in CO_2 , and the magnitude of this effect is larger for the C isotopes
 578 than the O ones.

579
 580 **2.4 Fractionation during the recombination of CO + OH**

581
 582 The recombination of CO with the hydroxyl radical OH is an important reaction in the
 583 chemistry of the atmosphere of Mars, which is responsible for the stability of CO_2 (McElroy &
 584 Donahue, 1972; Parkinson & Hunten, 1972). In order to model the isotopic fractionation of
 585 the C and O isotopes in this reaction, we use the data derived from laboratory
 586 measurements by Stevens et al. (1980). These measurements determined the kinetic
 587 isotope effect at a range of pressures from 0.2 to 1.35 atm (see Extended Data Figure 5). In
 588 order to extrapolate the measurements to the low pressure of the martian atmosphere, we fit
 589 this dependence using a second-order polynomial function. The fitted polynomial functions
 590 for the C and O isotopes are respectively

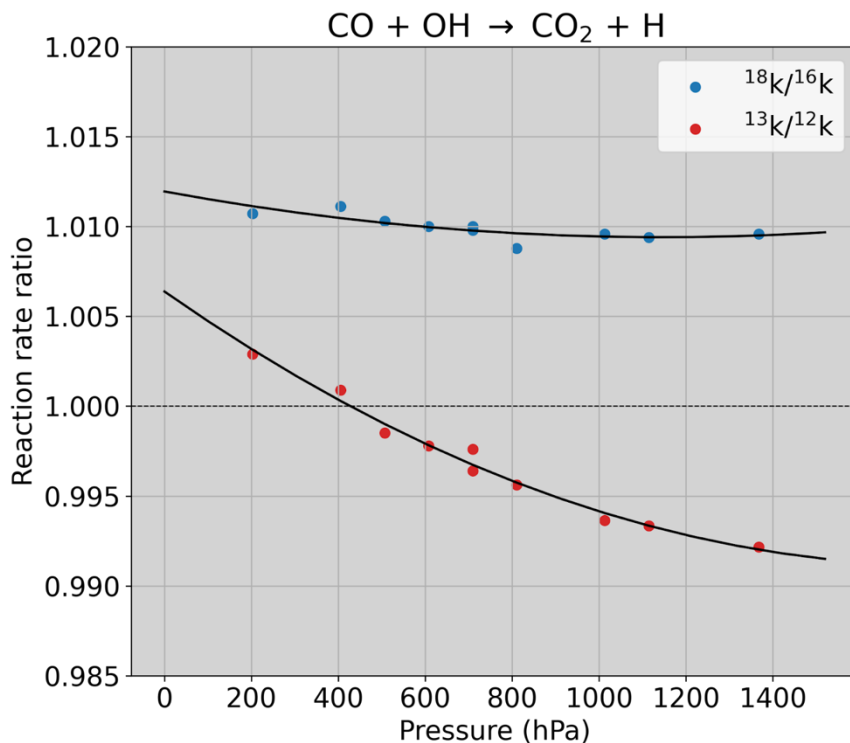
591
 592
$$k^{13}/k_{12} = 1.00638 - 1.69300 \times 10^{-7} \cdot p + 4.69677 \times 10^{-13} \cdot p^2,$$

 593
$$k^{18}/k_{12} = 1.01195 - 4.44340 \times 10^{-7} \cdot p + 1.93835 \times 10^{-13} \cdot p^2,$$

594

595 where the ratios $^{13}\text{k}/^{12}\text{k}$ and $^{18}\text{k}/^{16}\text{k}$ represent the ratio between the reaction rates of the
596 minor isotopes (i.e., ^{13}CO and C^{18}O) with respect to that of the major one (i.e., $^{12}\text{C}^{16}\text{O}$) and p
597 is the pressure in Pascals.

598
599 At the low pressures of the martian atmosphere, this reaction is faster for the minor isotopes,
600 which yields a preferential transfer of ^{13}C and ^{18}O over ^{12}C and ^{16}O from CO to CO_2 .
601 Therefore, the net effect of this reaction is to produce a depletion of the $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$
602 isotopic ratios in CO with respect to CO_2 . However, given the small magnitude of this
603 fractionation factor with respect to that produced by the photolysis of CO_2 , this process is
604 expected to have a much minor effect in the overall fractionation between CO_2 and CO .



605
606 *Extended Data Figure 5: Isotopic fractionation during the recombination of CO and OH into*
607 *CO_2 and H . The blue and red dots represent the ratio between the reaction rates of*
608 *$\text{C}^{18}\text{O}/\text{C}^{16}\text{O}$ and $^{13}\text{CO}/^{12}\text{CO}$, measured by Stevens et al. (1988). The black lines are a*
609 *second-order polynomial fit used to capture the pressure dependence of this fractionation*
610 *effect.*

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