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► To cite this version:

N. Yoshida, H. Nakagawa, N. Terada, J.S Evans, N. M. Schneider, et al.. Seasonal and latitudinal variations of dayside N₂/CO₂ ratio in the Martian thermosphere derived from MAVEN IUVS observations. *Journal of Geophysical Research. Planets*, 2020, 125 (12), pp.e2020JE006378. 10.1029/2020JE006378 . insu-03005617

HAL Id: insu-03005617

<https://insu.hal.science/insu-03005617>

Submitted on 8 Dec 2020

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1 **Seasonal and latitudinal variations of dayside N₂/CO₂ ratio in the Martian**
2 **thermosphere derived from MAVEN IUVS observations**

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5 N. Yoshida¹, H. Nakagawa¹, N. Terada¹, J. S. Evans², N. M. Schneider³, S. K. Jain³, T.
6 Imamura⁴, J.-Y. Chaufray⁵, H. Fujiwara⁶, J. Deighan³, and B. M. Jakosky³

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8
9 ¹ Graduate School of Science, Tohoku University, Sendai, Japan

10 ² Computational Physics Inc., Springfield, Virginia, USA

11 ³ Laboratory for Atmospheric and Space Physics, University of Colorado, Boulder, Colorado,
12 USA

13 ⁴ Graduate School of Frontier Science, The University of Tokyo, Chiba, Japan

14 ⁵ Laboratoire Atmosphères, Milieux, Observations Spatiales (LATMOS), CNRS, Guyancourt,
15 France

16 ⁶ Faculty of Science and Technology, Seikei University, Tokyo, Japan

17
18 Corresponding author: Nao Yoshida (n.yoshida@pat.gp.tohoku.ac.jp)

19
20 **Key Points:**

- 21 • IUVS limb scan observations show significant variations of N₂/CO₂ at 140 km, with
22 both seasonal sinusoidal and latitudinal trends.
- 23 • Seasonal change of inferred dayside homopause is suggested to be mainly controlled by
24 inflation and contraction of the lower atmosphere.
- 25 • Latitudinal dependences of homopause altitudes are, for the first time, suggested by
26 observed latitudinal dependences of N₂/CO₂.
- 27

28 Abstract

29 The dayside N_2/CO_2 at 140 km altitude in the Martian thermosphere has been
30 investigated by the Imaging UltraViolet Spectrograph (IUVS) aboard the Mars Atmosphere
31 and Volatile Evolution (MAVEN) spacecraft during the period from October 2014 to May
32 2018. We find that N_2/CO_2 at 140 km altitude varies significantly in the range of 0.02 to 0.20
33 and shows a seasonal sinusoidal trend. The higher value appears during aphelion and the
34 lower value during perihelion. Variations of observed N_2/CO_2 ratio at 140 km are mainly
35 associated with CO_2 number density. Thus, while we found that N_2/CO_2 varies at a given
36 altitude, we could not identify variations at a given pressure level. In order to reveal the
37 drivers of N_2/CO_2 variations at 140 km, we examine the effects of surface N_2/CO_2 ,
38 thermospheric temperature, and homopause altitude. The variations of homopause altitude
39 could be the dominant driver of changes in N_2/CO_2 . Inferred dayside homopause altitudes
40 derived from IUVS observations show an anti-correlation with the trend of N_2/CO_2 at 140 km.
41 Distributions of CO_2 density at the inferred homopause altitudes suggest that dayside
42 homopause altitude is mainly controlled by inflation and contraction of the lower atmosphere.
43 Additionally, N_2/CO_2 shows a clear latitudinal dependence for $L_s = 80^\circ - 100^\circ$. Higher
44 N_2/CO_2 values appear in the southern winter hemisphere, corresponding to lower homopause
45 altitude by ~ 30 km. Meanwhile, the latitudinal dependence of both N_2/CO_2 and homopause
46 altitude disappears for $L_s = 340^\circ - 360^\circ$.

47

48 Plain Language Summary

49

50 Changes of atmospheric composition in the upper atmosphere could be a source of
51 variation of gas species escaping to space. We report the seasonal and latitudinal variations of
52 dayside N_2/CO_2 ratios at 140 km altitude by a remote-sensing instrument aboard the Mars
53 Atmosphere and Volatile Evolution spacecraft. Our observations showed that changes in
54 N_2/CO_2 could be caused by the variations of homopause altitude. Distributions of CO_2
55 density at the inferred homopause altitudes suggest that dayside homopause altitude is mainly
56 controlled by inflation and contraction of the lower atmosphere.

57

58 1 Introduction

59

60 Planetary atmospheres are generally characterized by a compositional boundary,
called the homopause, below which gases are well-mixed by eddy diffusion (homosphere)

61 and above which gases are diffusively separated according to their own scale heights by
62 molecular diffusion (heterosphere). In the heterosphere, the mixing ratio of lighter species is
63 expected to increase with altitude above the homopause. The location of the homopause
64 altitude influences the thermospheric composition and thereby the escape of species to space.
65 In addition, the fractionation between the homopause and the exobase determines the relative
66 abundance of species that escape to space and the total atmospheric loss from the isotope
67 record (Jakosky et al., 1994, 2017; Lammer & Bauer, 2003; Chassefière & Leblanc, 2004;
68 Slipski & Jakosky, 2016).

69 Early measurements of atmospheric composition in the Martian thermosphere were
70 performed by the neutral mass spectrometers mounted on the aeroshell of Viking 1 and 2
71 landers (Nier & McElroy, 1977). Viking observed vertical profiles of CO₂, N₂, Ar, CO, and
72 O₂ in the range between 120 and 200 km. The Viking observations showed that the relative
73 abundance of lighter species increases with altitude due to diffusive separation. After the
74 Viking observations, the Mars Atmosphere and Volatile Evolution (MAVEN) spacecraft
75 measures atmospheric composition in detail in the thermosphere using in-situ and
76 remote-sensing instruments; e.g., the Neutral Gas and Ion Spectrometer (NGIMS) (Mahaffy,
77 Benna, King et al., 2015) and the Imaging UltraViolet Spectrograph (IUVS) (McClintock et
78 al., 2014). In the beginning of MAVEN mission, vertical profiles of several species observed
79 by both the NGIMS and IUVS instruments confirmed diffusive separation in the
80 thermosphere (Mahaffy, Benna, Elrod et al., 2015; Withers et al., 2015; Evans et al., 2015).
81 Vertical profiles between the Viking and MAVEN observations are different in both scale
82 heights and background temperature. The scale heights of CO₂ are larger in the MAVEN
83 NGIMS measurements (15 km) than from Viking (10 km), with corresponding temperatures
84 of 270 K and 180 K, respectively (Withers et al., 2015). Withers et al. (2015) mentioned that
85 the warmer temperature observed by MAVEN is due to the Sun-Mars distance and the solar
86 cycle. Vertical profiles of N₂/CO₂ observed by the Viking probes and MAVEN/IUVS are
87 compared in Evans et al. (2015). Diffusive separation of the two species is more effective in
88 the Viking observations and the difference with IUVS observations is obvious above 140 km
89 altitude. It is noted that the comparison of atmospheric composition by Evans et al. (2015)
90 was conducted in the beginning of the MAVEN mission. The vertical profile measurements
91 by IUVS aboard MAVEN have now been taken for over three Martian Years, allowing an
92 investigation into compositional distribution and variation of N₂ and CO₂ densities in the
93 thermosphere of Mars.

94 The Martian homopause altitude was considered to be located around 120 and 130

95 km from observations by the Viking landers (Nier & McElroy, 1977). However, numerical
96 simulations after this suggested that the Martian homopause altitude varies due to the
97 atmospheric global circulation (González-Galindo et al., 2009), and the saturation of
98 small-scale gravity waves, planetary-scale waves, and thermal tides (Imamura et al., 2016;
99 Leovy, 1982). Recently, Jakosky et al. (2017) and Slipski et al. (2018) reported substantial
100 variations of the homopause altitude by using vertical profiles of $N_2/^{40}Ar$ observed by
101 NGIMS. The inferred homopause altitudes are located between 60 and 140 km. Slipski et al.
102 (2018) demonstrated the possibility of a seasonal change in homopause altitude at noon by
103 ~ 30 km, with the largest values observed between $L_s = 240^\circ$ and 360° and the smallest values
104 between $\sim 50^\circ$ and 180° . Slipski et al. (2018) also showed the latitudinal dependence of
105 homopause altitudes, but a clear latitudinal dependence predicted in González-Galindo et al.
106 (2009) was not obtained because latitudinal and local time effects could not be distinguished
107 due to the NGIMS observing geometry.

108 In addition to homopause altitude variations, it is noted that Mars' thermospheric
109 temperature is variable because solar extreme ultraviolet (EUV) irradiance changes with time
110 and it is absorbed above ~ 100 km altitude. Gröller et al. (2018) showed diurnal temperature
111 variations for a pressure level of 3×10^{-5} Pa (around 130 km) and for latitudes below 50° over
112 one Martian year in their Figure 19. The average temperature between 12:00 and 16:00 local
113 time (LT) is ~ 170 K, but observed temperatures showed broad variability between ~ 150 and
114 ~ 200 K. Gröller et al. (2018) mentioned that the relatively large variability could be due to
115 variations with latitude and season. Bougher et al. (2017) implied that long-term variations of
116 temperature in the Martian dayside upper thermosphere correlate with solar EUV irradiance
117 at Mars. The observed temperature range corresponding to scale heights over 150 - 180 km in
118 Bougher et al. (2017) is 170 to 240 K. Thiemann et al. (2018) also showed the correlation
119 between thermospheric temperature and solar EUV irradiance using solar occultations of
120 EUV irradiance at Mars. The thermospheric temperature has an impact on vertical profiles of
121 atmospheric composition because each gas has its own scale height above the homopause
122 altitude, $H = kT/mg$, where k is the Boltzmann constant, T is temperature, m is molecular mass
123 according to species, and g is gravity. Therefore, the atmospheric composition above the
124 homopause can be affected by the thermospheric temperature.

125 In addition, the atmospheric composition at the homopause would vary associated
126 with variations of mixing ratio near the surface. Due to the tilt of the rotation axis, Mars poles
127 become cold enough for CO_2 to condense out during local fall and winter, with CO_2
128 subliming from the poles during local spring and summer. The change in atmospheric mass

129 results in variations of surface pressure with two peaks at $L_s \sim 60^\circ$ and $L_s \sim 270^\circ$ each year,
130 corresponding to times when the greatest amount of CO_2 is in the atmosphere (Hess et al.,
131 1980). Both of two Viking landers observations showed a similar variation in pressure at the
132 surface, although an absolute value of pressure is different due to their locations. Similar
133 seasonal peaks of surface pressure were obtained by Mars Pathfinder lander, Phoenix lander,
134 and Mars Science Laboratory (MSL) (Martínez et al., 2017; Ordonez-Etxeberria et al., 2017).
135 When the main atmospheric constituent condenses out, trace gases that do not condense out
136 with the CO_2 , such as Ar and N_2 , are relatively enhanced (i.e., their mixing ratio increases).
137 Mixing ratio of N_2 at Gale crater was measured by MSL (Trainer et al., 2019). A maximum
138 mixing ratio of N_2 appears when the surface pressure is minimum. The seasonal variation of
139 mixing ratio of N_2 at the surface is about $\pm 10\%$ (Trainer et al., 2019). Note that the mixing
140 ratio of trace gases varies with location and time, due to transport by advection and mixing. A
141 strong depletion of mixing ratio of trace gases, such as CO and Ar, occurs in the summertime
142 polar regions, associated with sublimation of CO_2 polar caps (e.g., Smith et al., 2018;
143 Sprague et al., 2007). Around the winter polar region, an enhancement of mixing ratio of
144 trace gases is expected. Such variations might affect the atmospheric composition above the
145 homopause.

146 In this study, we aim to investigate variations of atmospheric composition in the
147 thermosphere and to reveal drivers of the variations. We use remote-sensing data for this
148 study, which enables us to distinguish geophysical and geometrical effects owing to a wider
149 coverage than in-situ observations, for better understanding the drivers of the variations in the
150 thermosphere.

151 The outline of this paper is as follows. In Section 2, we describe the dataset used in
152 this study. The seasonal, local time, and latitudinal variations of N_2/CO_2 are shown in Section
153 3. We discuss the drivers of N_2/CO_2 variation, inferred homopause altitudes from IUVS
154 observations, and comparisons with model predictions in Section 4. Finally, our conclusions
155 are summarized in Section 5.

156 2 MAVEN IUVS

157 We use limb observations from IUVS aboard MAVEN. The MAVEN orbit is
158 elliptical with apoapsis near 6000 km and periapsis near 160 km altitude, with a 4.5-hour
159 period. IUVS limb measurements are taken near periapsis below 500 km altitude for dayglow
160 observations in the far and mid-UV regime (115 - 340 nm) (Jain et al., 2015). Dayglow

161 emissions of CO₂⁺ Ultraviolet Doublet (UVD) at 288 - 289 nm (Jain et al., 2015; Evans et al.,
162 2015) and N₂ Vegard-Kaplan bands (VK) at 258.0 - 287.5 nm (Stevens et al., 2015) are used
163 to retrieve CO₂ and N₂ densities, respectively from 100 to 200 km with an altitude resolution
164 of 5 km (Evans et al., 2015; Stevens et al., 2015). To understand variations of atmospheric
165 composition in the thermosphere, it is better to use non-reactive species that do not vary
166 spatially and temporally. N₂ is weak in photochemical reactivity and non-condensable. The
167 CO₂ density can vary due to photochemistry and meteorology of the condensation as CO₂ ice
168 clouds, but these effects should be negligible because CO₂ is the dominant species in Mars'
169 atmosphere. Since the effect of sublimation and condensation from the polar ice caps is well
170 understood as the variation of surface pressure, CO₂ variations can be corrected using a
171 knowledge of surface pressure. Thus, we analyze the number densities of CO₂ and N₂ to
172 investigate the mixing ratio in the thermosphere. It is noted that Evans et al. (2015) adopted
173 an upper limit of 60° for Solar Zenith Angle (SZA) over concerns that the retrievals may be
174 biased at larger SZA values due to anisotropy effects (i.e. variation in solar illumination along
175 the slant path). The upper limit has since been raised to 75° because no evidence of a bias has
176 been seen in retrievals for SZAs up to this revised limit. This is not surprising, since CO₂⁺
177 UVD and N₂ VK are optically thin such that most of the airglow signal originates from within
178 a few scale heights of the tangent point, or the airglow peak, whichever is larger. In general,
179 contributions along the slant path within two scale heights of a tangent point of 130 km will
180 have an SZA within ~ 6° of the SZA at the tangent point. We use the dataset of level 2
181 version 13 revision 1 provided in the Planetary Data System (PDS).

182 In the level 2 dataset, CO₂ densities are provided at fixed altitude bins centered at
183 130, 140, 150, and 170 km, whereas N₂ densities are provided at 125, 137, 153, and 173 km.
184 The uncertainties of CO₂ densities are small (less than 10%) whereas those of N₂ densities are
185 relatively large, typically up to 40% below 140 km and above 160 km. Below 140 km
186 altitude, there is a possibility of contamination by solar stray light in the N₂ VK emission
187 bands. On the other hand, above 160 km, the intensity of N₂ VK emission becomes dimmer,
188 resulting in a reduced signal-to-noise ratio in the N₂ VK emission and corresponding
189 increased uncertainties of retrieved N₂ densities. In this study, we confine our analysis to
190 ~140 km where the densities have the smallest uncertainties. We interpolate the N₂ density
191 between 137 and 153 km onto the CO₂ altitude grid and evaluate the mixing ratio at 140 km.
192 Data we applied in this study have uncertainties in N₂/CO₂ less than 50%. Under the given
193 constraint, uncertainties of N₂/CO₂ at 140 km used for this study are in the range of 15% to
194 50% with a mean value of 37%.

195 We analyzed CO₂ and N₂ densities derived from IUVS limb scan observations from
196 October 2014 to May 2018, which correspond to 9258 profiles. The tangential footprints of
197 IUVS limb observation included in the analysis are shown in Figure 1. The dayside
198 measurements by IUVS have been performed in several groups of orbits during different
199 seasons throughout the MAVEN mission. Local time is limited from 7:00 to 19:00 except for
200 observations around the southern polar region. SZA is in the range from 0° to 75°. IUVS limb
201 observations over the time period considered here provide good coverage in longitude,
202 latitude, local time, and season.

203 3 Results

204 Time variations of IUVS observations vs. L_s are shown in Figure 2. Figure 2(a)
205 provides the Sun-Mars distance (blue line) and the orbit averaged solar EUV irradiance at 17
206 - 22 nm observed by the Extreme UltraViolet Monitor (EUVM) (Eparvier et al., 2015) aboard
207 MAVEN (black line). Figures 2(b)-2(d) show the observed CO₂ density, N₂ density, and N₂/
208 CO₂ at 140 km, respectively. Colors correspond to the observed local time. Uncertainties
209 are shown by gray bars. The dayside N₂/CO₂ varies from 0.02 to 0.20, but variations of CO₂
210 density, N₂ density, and N₂/CO₂ shown in Figure 2 include effects of season, local time, and
211 latitude. A short-term variation of N₂/CO₂ during L_s = 30° - 70° in Martian Year (MY) 33, L_s
212 = 120° - 160° in MY 33, and L_s = 340° - 40° through MY 33 to MY 34, which correspond to
213 orbits around 1800 - 2200, 2900 - 3500, and 4800 - 5500, respectively, is seen in Figure 2(d).
214 These variations are explained below.

215 3.1 Seasonal variation

216 Figure 3 demonstrates a seasonal trend of the CO₂, N₂ number densities, and
217 N₂/CO₂ ratio at 140 km. Each color represents a specific local time bin, including 8:00 -
218 10:00, 12:00 - 14:00, and 16:00 - 18:00, and symbols represent observed MYs. Figures 3(a)
219 and 3(b) demonstrate that CO₂ and N₂ densities, distinguished by local time, vary with L_s.
220 Higher number densities of CO₂ and N₂ appear around perihelion (L_s ~ 250°). Lower number
221 densities appear around aphelion (L_s ~ 70°). This seasonal variation of CO₂ density obtained
222 in this study agrees well with that found by Mars Express (MEx) Spectroscopy for
223 Investigation of Characteristics of the Atmosphere Mars (SPICAM) observations of CO₂
224 density in the lower thermosphere (Forget et al., 2009). Although each profile's density
225 depends on the combinations of local time, latitude, and local season, the variations in CO₂
226 and N₂ densities at 140 km observed by IUVS limb show predominately a seasonal sinusoidal

227 trend. Those variations correspond to the inflation and contraction of the lower atmosphere. It
 228 is noteworthy that variations in CO₂ densities have a larger amplitude than variations in N₂
 229 densities and this affects the variation of N₂/CO₂. The seasonal N₂/CO₂ variations, which in
 230 the local time bin of 12:00 - 14:00 become ~0.063 on average during aphelion (between 50°
 231 and 90° in L_s) and ~0.031 on average during perihelion (between 230° and 270° in L_s), show
 232 an anti-correlation with the variations of CO₂ and N₂ densities. The other local time bins also
 233 demonstrate a clear seasonal variation.

234 3.2 Local time variation

235 Figure 4 shows the short-term variations of IUVS observations vs. local time
 236 during three seasons. We selected three groups L_s = 30° - 70° in MY 33, L_s = 120° - 160° in
 237 MY 33, and L_s = 340° - 40° in MY 33 to 34 because those well cover the range from morning
 238 terminator to evening. In all three groups, local time of IUVS observation varies from
 239 evening to morning for each period as shown in Figure 1. We have to note that data taken
 240 during L_s = 240° - 300° in MY 33 have wide local time coverage, however, we didn't select
 241 this group since observation during this period included data at high southern latitudes (>
 242 ~65°S) which are sunlit throughout the sol (i.e. there is no night). The results presented in
 243 Figure 4 represent the combination of local time and seasonal variations, thus caution must be
 244 taken. Data taken during L_s = 120°- 160° in MY 33, the second column in Figure 4,
 245 correspond to an increasing of number density with season. Meanwhile, data taken during L_s
 246 = 30°- 70° in MY 33 and L_s = 340°- 40° in MY 33 to 34, the first and the third columns in
 247 Figure 4, correspond to a decreasing of number density with season.

248 In Figures 4(d) and 4(e), observed CO₂ and N₂ densities have their maximum
 249 around noon. That would be a result of local time variation. A similar local time variation of
 250 Ar density is found in the upper thermosphere (Gupta et al., 2019). On the other hand, CO₂
 251 and N₂ densities in Figures 4(a), 4(b), 4(g), and 4(h) don't have any clear peaks around noon.
 252 It could be that the effects of season and local time on number density cannot be
 253 distinguished from these datasets. Nevertheless, Figures 4(c), 4(f), and 4(i) show that N₂/CO₂
 254 become minimum around noon and increase toward the dawn side. N₂/CO₂ around dawn is
 255 larger than that at noon by a factor of 1.6 on average. This suggests that N₂/CO₂ at 140 km
 256 has a local time variation. In order to verify the local time effect on CO₂, and N₂ densities and
 257 N₂/CO₂ ratio, additional data are needed.

258 3.3 Latitudinal variation

259 Additionally, we have investigated latitudinal dependences of CO₂, N₂, and N₂/CO₂.
 260 To constrain the local time effects found in Figure 4, local time is limited from 10:00 to 14:00.
 261 We selected the datasets that cover more than 60 degrees in latitude. Latitudinal dependences
 262 are investigated for observation in $L_s = 80^\circ - 100^\circ$ and $L_s = 340^\circ - 360^\circ$. In Figure 5, plots of
 263 densities vs. latitude and N₂/CO₂ vs. latitude in the northern summer ($L_s = 80^\circ - 100^\circ$) are
 264 shown in Figures 5(a) through 5(c), and in the northern spring ($L_s = 340^\circ - 360^\circ$) are shown
 265 in Figures 5(d) through 5(f), respectively. It is noted that the latitudinal variation observed in
 266 the northern spring contains observations during both MY 32 and MY 33. MYs in the
 267 northern spring are distinguished by color in Figure 5. Uncertainties are shown by gray bars.
 268 In the northern summer, CO₂ densities become larger toward the northern polar region, which
 269 are $3.4 \times 10^9 \text{ cm}^{-3}$ around 45°S on average and $8.6 \times 10^9 \text{ cm}^{-3}$ around 25°N on average.
 270 Although N₂ densities have relatively large uncertainties, N₂ densities slightly increase
 271 toward the northern polar region, which are $3.5 \times 10^8 \text{ cm}^{-3}$ around 45°S on average and
 272 $4.3 \times 10^8 \text{ cm}^{-3}$ around 25°N on average. A larger amplitude of CO₂ density variations than that
 273 of N₂ density drives the latitudinal dependence of N₂/CO₂. The dayside N₂/CO₂ ratio in the
 274 northern summer is larger in the southern hemisphere (~0.11 around 45°S on average) and
 275 smaller in the northern hemisphere (~0.05 around 25°N on average). On the other hand, in
 276 the northern spring, these latitudinal dependences disappear. Because both CO₂ and N₂
 277 densities have a similar latitudinal variation, N₂/CO₂ is almost constant with latitude. On the
 278 other hand, it is noteworthy that both CO₂ and N₂ densities in the southern hemisphere
 279 observed in MY 32 (red dots) are slightly higher than those in MY 33 (black dots). Higher
 280 densities in MY 32 might be associated with inflation at the upper atmosphere due to solar
 281 EUV heating in MY 32, for which EUV irradiance is about two times larger as seen in Figure
 282 2(a). Our observation suggests that the latitudinal variation of N₂/CO₂ in the thermosphere
 283 has a strong seasonal dependence.

284 4 Discussion

285 4.1 Drivers of seasonal variation

286 In order to reveal drivers of the seasonal variations of N₂/CO₂ at 140 km, we have
 287 examined seasonal variations of surface N₂/CO₂, thermospheric temperature, and homopause
 288 altitude. To infer the effects of these parameters on N₂/CO₂ at 140 km, we use the same
 289 method described in Mahaffy, Benna, Elrod et al. (2015), Jakosky et al. (2017), and Slipski et
 290 al. (2018). Under assumptions of isothermal atmosphere and hydrostatic equilibrium, we can

291 estimate vertical profiles of CO₂ and N₂ densities using observed densities at 140 km and
292 thermospheric temperature. A vertical profile of mixing ratio is obtained from the CO₂ and N₂
293 profiles, which is expected to match the mixing ratio in the homosphere at the homopause
294 altitude. The mixing ratio in the homosphere is assumed to be the mixing ratio at the surface.
295 Therefore, densities of CO₂ and N₂ at 140 km observed from IUVS are functions of the
296 surface N₂/CO₂, thermospheric temperature, and homopause altitude. For the sake of
297 simplicity, a plausible range of these parameters to explain the observed N₂/CO₂ at 140 km is
298 evaluated under the assumption that the other two parameters are fixed. We constrain the
299 geometry from 10:00 to 14:00 in LT and from 45°S to 45°N in latitude to derive these
300 parameters. Under the given constraints, mean values of N₂/CO₂ at 140 km derived from
301 IUVS are 0.033 near perihelion (between L_s = 230° and 270°) and 0.056 near aphelion
302 (between L_s = 50° and 90°), respectively. The results of our parameter study are summarized
303 in Table 1.

304 We find that the surface N₂/CO₂ is required to vary by ~70% between 0.016 and 0.027
305 with season in order to explain the observed variation of N₂/CO₂ at 140 km between 0.033
306 and 0.056 if we assume an isothermal temperature of 180 K and a constant homopause
307 altitude of 120 km. The seasonal variation of inferred surface N₂/CO₂ shows a similar trend
308 with observed variation of N₂/CO₂ at 140 km, with a minimum value near perihelion and a
309 maximum value near aphelion. In contrast, the typical surface value of mean N₂/CO₂ ratio is
310 0.0272 and surface N₂ mixing ratio has a seasonal variation in ±10%, which are measured by
311 MSL (Trainer et al., 2019). Since we restricted the data between 45°S to 45°N here, an
312 enhancement and a depletion of mixing ratio of trace gases around the polar region are out of
313 scope. Trainer et al. (2019) showed that N₂ mixing ratio has its maximum at L_s ~ 160° and a
314 second maxima-at L_s ~ 0°, responding to the condensation of the CO₂ polar cap (Hess et al.,
315 1980; Ordóñez-Etxeberria et al., 2017; Martínez et al., 2017). However, two peaks of N₂
316 mixing ratio shown in Trainer et al. (2019) do not agree with the timing and magnitude of
317 seasonal variation of inferred surface N₂/CO₂ from this study. For these reasons, the seasonal
318 variation of surface N₂/CO₂ cannot explain the observed N₂/CO₂ variation at 140 km.

319 It is also found that a plausible range of the variation of thermospheric temperature
320 cannot explain the observed N₂/CO₂ variation when we assume a constant surface mixing
321 ratio to be 0.020 (Mahaffy et al., 2013) and two cases of homopause altitudes (110 and 120
322 km). In the case of an assumed homopause altitude at 110 km (120 km), the thermospheric
323 temperature is required to vary between 193 and 403 K (129 and 269 K), a difference of 210
324 K (140 K), due to the variation of N₂/CO₂ at 140 km. However, previous observations

325 suggested that the dayside upper thermospheric temperature varies by ~ 70 K in the range
326 from 170 to 240 K due to the effects of changing heliocentric distance and solar cycle
327 (Bougher et al., 2017). In addition, Bougher et al. (2000; 2015) determined the seasonal
328 variation of the exobase temperature to be ~ 40 K under the solar moderate condition ($F_{10.7} =$
329 130) using numerical modeling. In addition to the upper thermosphere, temperature in the
330 lower thermosphere around ~ 130 km observed in Gröller et al. (2018) varies between ~ 150
331 and ~ 200 K. The inferred range of thermospheric temperatures (210 K and 140 K) are clearly
332 out of the plausible range reported by these previous studies and not sufficient to explain the
333 observed seasonal variation of N_2/CO_2 at 140 km.

334 Thus, we propose that variations in homopause altitudes are most likely needed to
335 reproduce the observed seasonal variation of N_2/CO_2 at 140 km altitude. Under the
336 assumption of a constant surface mixing ratio of 0.020 and two cases of isothermal
337 temperatures (150 and 200 K), inferred homopause altitudes are estimated between ~ 110 and
338 ~ 130 km. Analysis of observations by MAVEN/NGIMS suggested that homopause altitudes
339 on the dayside are located between ~ 100 and 140 km (Slipski et al., 2018). Their inferred
340 homopause altitudes have seasonal differences of ~ 30 km. Inferred homopause altitudes in
341 this study show a reasonable agreement with the results reported by Slipski et al. (2018).
342 Consequently, we conclude that variations of the homopause altitude could be the dominant
343 driver of changes in N_2/CO_2 in the thermosphere.

344 4.2 Estimation of homopause altitude

345 Hereafter, we determine homopause altitudes considering the variations of surface
346 N_2/CO_2 and thermospheric temperature. Here, we use the N_2/CO_2 ratio at 50 km altitude, in
347 the homosphere, predicted by Mars Climate Database (MCD) version 5.3 (Millour et al.,
348 2018) instead of the surface N_2/CO_2 . As the input for the MCD, IUVS observation geometries
349 shown in Figure 1 are applied, and an average condition of solar EUV flux and a typical dust
350 climatology are used. The mean mixing ratio of N_2 in the MCD is designed to match the
351 observational result by MSL/SAM (Mahaffy et al., 2013). N_2/CO_2 reported in Mahaffy et al.
352 (2013) is ~ 0.020 at $L_s = 187.5^\circ$. Figures 6(a) and 6(b) show N_2/CO_2 in the homosphere
353 derived from the MCD and temperature at 175 km observed from IUVS, respectively, which
354 are used to infer homopause altitudes. The MCD predicts N_2/CO_2 values within the range
355 between 0.012 and 0.022. The MCD N_2/CO_2 obtained around $L_s = 270^\circ$ in MY 33 (orbits
356 near 4000) are remarkably low because N_2/CO_2 has a gradient toward the higher latitude in
357 the MCD. Roughly speaking, the MCD predictions of N_2/CO_2 in the homosphere except for

358 the data in the polar region are well matched with the observation of surface N_2/CO_2 from
359 MSL in Mahaffy et al. (2013). Temperatures corresponding to an altitude of 175 km are
360 determined from Chapman fits to CO_2^+ UVD brightness profiles observed by IUVS (Lo et al.,
361 2015; Bougher et al., 2017). We have applied the 8607 profiles whose temperatures are valid.
362 We assume an isothermal atmosphere and thus the temperature at 175 km is applied at all
363 altitudes. The standard deviation of derived temperatures is ~ 50 K, which reflects a
364 combination of atmospheric phenomena, such as nonmigrating tides (e.g., Lo et al., 2015)
365 and thermal tides (e.g., Stevens et al., 2017). A temperature deviation of ~ 50 K corresponds
366 to a deviation of ~ 10 km in the inferred homopause altitudes. Values of observed N_2/CO_2 at
367 140 km would not be expected to be lower than N_2/CO_2 in the homosphere based on an
368 assumption of a well-mixed homosphere, thus we exclude these values from the ensemble
369 data when inferring homopause altitudes. Although the number of excluded profiles is 17,
370 that is negligible compared with the total number of profiles (9258). Inferred homopause
371 altitudes, shown in Figure 6(c), are located between ~ 60 and 140 km. The uncertainty of
372 inferred homopause altitudes is $\pm \sim 8$ km based on the uncertainty of N_2/CO_2 at 140 km by
373 IUVS, which is $\sim 37\%$ on average. The inferred homopause altitudes clearly have an
374 anti-correlation with the variations of N_2/CO_2 at 140 km.

375 To evaluate the effect of an isothermal atmospheric assumption on the inferred
376 homopause altitudes, we assume a constant gradient of temperature below 140 km but still an
377 isothermal atmosphere above that altitude. The constant gradient of temperature is
378 determined such that the temperature at 100 km should be 130 K (cf. Gröller et al., 2018;
379 Forget et al., 2009). In this case, the inferred homopause altitudes are located between 105
380 and 140 km. It should be noted that the impacts of assuming a non-isothermal atmosphere on
381 the inferred homopause altitude is strong below 105 km, where the inferred altitude increases
382 by up to ~ 45 km and by ~ 19 km on average. However, even when the non-isothermal
383 atmosphere is assumed, a seasonal variation similar to Figure 6(c) is obtained.

384 Recently, Franz et al. (2017) revised the volume mixing ratio of both N_2 and CO_2
385 measured by MSL, which suggests that the surface N_2/CO_2 value is higher by a factor of ~ 1.5
386 than that measured by Mahaffy et al. (2013) and used by the MCD. We find that a factor of
387 1.5 increase in the surface mixing ratio uniformly increases the inferred homopause altitude
388 by ~ 10 km.

389 Figure 7 shows time variations of pressure at 140 km as in Figure 2. As the pressure,
390 CO_2 partial pressure derived from CO_2 density and temperature is applied. We assume an
391 isothermal atmosphere; i.e., the temperature at 175 km derived from IUVS observations are

392 used. Uncertainties of pressure are calculated from both that of CO₂ density and temperature,
 393 shown as gray bars. Pressure changes between $\sim 4 \times 10^{-6}$ and $\sim 3 \times 10^{-4}$ Pa and shows a seasonal
 394 sinusoidal trend; higher pressure appears around perihelion and lower pressure around
 395 aphelion. A similarity of seasonal trend between N₂/CO₂ and pressure would suggest that
 396 N₂/CO₂ variation at 140 km is mainly caused by variation of background pressure due to the
 397 inflation and contraction of the lower atmosphere. While we found that seasonal N₂/CO₂ ratio
 398 varies at a given altitude, we could not identify the seasonal variation at a given pressure
 399 level. It is noted that the N₂/CO₂ variation from MY 33 L_s = 340° to MY 34 L_s = ~30° is
 400 somewhat different to the pressure variation over the same period. This might imply that
 401 N₂/CO₂ could also change slightly via other mechanisms.

402 The CO₂ density at the inferred homopause altitude, extrapolated from the CO₂
 403 density at 140 km, is shown in Figure 8, which are extrapolated from CO₂ density at 140 km
 404 altitude. The average value is 2.6×10^{11} cm⁻³ but it deviates between 10^{10} and $\sim 10^{13}$ cm⁻³.
 405 Distributions of CO₂ density at the inferred homopause altitude suggest that dayside
 406 homopause altitude changes would be generated by two factors: (1) the inflation and
 407 contraction of the lower atmosphere due to changing of solar irradiance that changes the
 408 homopause altitude at a fixed pressure level, (2) eddy diffusion via turbulence related to
 409 atmospheric wave activity as reported by Slipski et al. (2018) that changes the pressure level
 410 at the homopause. Although our study doesn't include dust storm events, the atmospheric
 411 heating due to the dust loading in the lower atmosphere, which absorbs the solar irradiation,
 412 could cause the change in homopause altitude and N₂/CO₂ variation in the upper atmosphere.

413 We have also inferred the latitudinal dependence of homopause altitudes. In Figure
 414 9, plots of inferred homopause altitude vs. latitude are shown for the same seasons as in
 415 Figure 5. In Figure 9(a), the inferred homopause altitudes in the northern summer decrease
 416 toward the southern winter polar region. The difference in altitudes between northern and
 417 southern hemispheres is about ~30 km. In Figure 9(b), the latitudinal dependence of inferred
 418 homopause altitudes in the northern spring disappears. This is the first observational evidence
 419 of a latitudinal dependence of dayside homopause altitudes, which matches well with model
 420 predictions by González-Galindo et al. (2009). In their model, homopause altitude is defined
 421 where mixing ratio of CO₂ equals to 0.9. They mentioned that lower homopause altitudes in
 422 southern winter indicate a relative depletion of CO₂ in the upper atmosphere. Certainly, our
 423 observations showed that relative depletion of CO₂ in the southern hemisphere.
 424 González-Galindo et al. (2009) indicated that the depletion of CO₂ could result from the
 425 condensation of CO₂ due to colder temperatures or the meridional transportation of CO₂-poor

426 air from the upper thermosphere. Latitudinal asymmetrical heating in the lower atmosphere
427 due to its season would also be a potential driver of the latitudinal dependence of homopause
428 altitude. The driver of the latitudinal dependence of homopause altitudes, however, cannot be
429 fully constrained by our study.

430 4.3 Comparison of densities and composition with Mars Climate Database 431 predictions

432 Figure 10 shows a comparison of densities of CO₂ and N₂, and N₂/CO₂ derived
433 from IUVS observations with those predicted by the MCD using an average solar EUV input
434 and a typical dust climatology for the corresponding geometries of the IUVS observations.
435 IUVS observations are shown as black dots. The gray bars represent uncertainties of IUVS
436 observations. The MCD predictions are shown as red dots. The MCD well reproduces the
437 seasonal variation of N₂/CO₂ derived from IUVS observations throughout the observation
438 period. However, the MCD overestimates the N₂/CO₂ value at 140 km by a factor of two. The
439 possible reason for this discrepancy is that the homopause altitude is too low in the MCD. As
440 can be seen in Figure 10, the MCD shows large discrepancies of N₂ densities between L_s =
441 30° and L_s = 70° in MY 33 with an opposite trend in the N₂ densities between L_s = 340° and
442 L_s = ~40° in MY 33 to 34. The opposite trend found in this study suggests that the treatment
443 of minor species in the model is not perfect, and further investigation is required to explain
444 the contradiction with the observations reported here (private communication with F.
445 González-Galindo, E. Millour, & F. Forget). Further studies of discrepancies between the
446 model and observations offer opportunities to improve our understanding of atmospheric
447 composition in the upper atmosphere.

448 5 Conclusions

449 In this paper, we have investigated dayside N₂/CO₂ at 140 km using MAVEN/IUVS
450 limb scan observations from October 2014 to May 2018. We find that N₂/CO₂ at 140 km
451 significantly varies in the range of 0.02 to 0.20 and clearly exhibits seasonal and latitudinal
452 dependences. Seasonal dependence is observed throughout the MAVEN mission, which
453 shows a sinusoidal trend that N₂/CO₂ is largest near aphelion (~0.063 on average between 50°
454 and 90° in L_s) and smallest near perihelion (~0.031 on average between 230° and 270° in L_s).
455 A latitudinal dependence of N₂/CO₂ is found in the northern summer. N₂/CO₂ increases
456 toward the southern winter hemisphere by a factor of two (between latitude 45°S and 25°N).
457 Meanwhile, the latitudinal dependence of N₂/CO₂ disappears in the northern spring.

458 In order to reveal the drivers of seasonal variations of N₂/CO₂ at 140 km, we have

459 examined the effects of surface N_2/CO_2 , thermospheric temperature, and homopause altitude.
460 Homopause altitudes inferred from IUVS under the assumption of an isothermal atmosphere
461 and a fixed surface N_2/CO_2 are estimated to vary between 100 and 130 km. The altitudes of
462 inferred homopause and seasonal trends agree reasonably well with Slipski et al. (2018). The
463 variations of the homopause altitude could be the dominant driver of changes in N_2/CO_2
464 ratios in the thermosphere. In addition, we inferred homopause altitudes by considering the
465 variations of both surface N_2/CO_2 and thermospheric temperature by combining the MCD
466 predictions with IUVS observations. Our inferred homopause altitudes vary between ~60 and
467 140 km altitude throughout the MAVEN mission and exhibit an anti-correlation with a
468 seasonal sinusoidal trend of N_2/CO_2 at 140 km. Distributions of CO_2 density at the inferred
469 homopause altitude suggest that dayside homopause is mainly controlled by inflation and
470 contraction of the lower atmosphere. Variations of observed N_2/CO_2 ratio at 140 km are
471 associated with CO_2 number density, namely pressure, at 140 km. Thus, we suggest that
472 inflation of the lower atmosphere near perihelion causes an increase in the dayside
473 homopause altitude and a decrease in the mixing ratio of N_2 in the upper atmosphere. Our
474 results show, for the first time, the clear evidence for a latitudinal dependence of homopause
475 altitudes in the northern summer. The inferred homopause altitudes in the northern summer
476 decrease toward the southern winter polar region. The difference in altitudes between
477 northern and southern hemispheres is about ~30 km. On the other hand, the latitudinal
478 dependence of inferred homopause altitudes in the northern spring disappears.

479 We have compared IUVS observational results with model predictions of N_2/CO_2
480 from MCD v5.3. The MCD well reproduces the seasonal variation of N_2/CO_2 derived from
481 IUVS observations throughout the MAVEN mission. However, the MCD overestimates
482 IUVS N_2/CO_2 values by a factor of two. A possible reason for this discrepancy is that the
483 homopause altitude is systematically low in the MCD. The observation of the N_2 mixing ratio
484 at 140 km by MAVEN/IUVS offers a source for improvements to atmospheric composition in
485 global circulation models.

486 IUVS observations imply significant impacts to the variations of the homopause
487 altitude on atmospheric composition in Mars' upper thermosphere. Our results support the
488 idea that atmospheric composition in the exosphere varies with the homopause altitude.
489 Understanding the influence of the homopause altitude on the escape of minor species should
490 be clarified in future work.

491 **Data Availability Statement**

492 MAVEN/IUVS limb level 2 version 13 revision 1 data used in this study are
493 available through the NASA Planetary Data System (PDS) at
494 https://atmos.nmsu.edu/data_and_services/atmospheres_data/MAVEN/limb.html. (Schneider,
495 N. et al., MAVEN IUVS Derived-level Data product Bundle,
496 urn:nasa:pds:maven.iuvs.processed 2015). MAVEN/EUVM level 2 version 11 revision 4 data
497 are available through the NASA PDS at <https://pds-ppi.igpp.ucla.edu>. (Eparvier, F. G.,
498 MAVEN EUV calibrated irradiances Data Collection,
499 urn:nasa:pds:maven.euv.calibrated:data.bands 2020) The full version of MCD v5.3 was
500 provided from E. Millour. The results retrieved from the IUVS limb observation and
501 extracted from the MCD used in this article are available at
502 <https://scholar.colorado.edu/concern/datasets/q237ht027>, (Yoshida et al., 2020).
503

504 **Acknowledgments**

505 This study was supported by Grant-in-Aids for Scientific Research (C) No.
506 19K03943 and No. 18H04453 and for Scientific Research (A) No. 19H00707 and No.
507 16H02229 from JSPS. The MAVEN project is supported by NASA through the Mars
508 Exploration Program. This work was conducted under NASA's MAVEN Participating
509 Scientist Program (proposal #12-MAVENPS12-0017, PI: K. Seki). YN is supported by The
510 international Joint Graduate Program in Earth and Environmental Sciences, Tohoku
511 University (GP-EES). YN would like to acknowledge F. González-Galindo, E. Millour, and F.
512 Forget for their assistance and fruitful comments with the results of the MCD in this paper.
513 YN highly appreciates constructive comments and feedback from anonymous reviewers and
514 Editor, and B. Johnston's kind proofreading.

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694 **Figure 1.** The tangential footprint of IUVS limb observation analyzed in this paper. (a) Solar
 695 longitude (L_s ; deg), (b) local time (hours), (c) SZA (deg), and (d) latitude (deg). The horizontal
 696 axis shows orbit number (bottom) and corresponding Earth date (top).

697 **Figure 2.** Time variations of (a) solar EUV irradiance (mW m^{-2} ; black), the Sun-Mars distance
 698 (AU; blue), number densities (cm^{-3}) of (b) CO_2 , (c) N_2 , and (d) N_2/CO_2 at 140 km altitude.
 699 Uncertainties are shown by gray bars in (b, c, d). Colors in (b, c, d) represent the local time
 700 (hours) of observation. The lower horizontal axis shows L_s and Mars Year (MY) and that of top
 701 shows corresponding Earth date.

702 **Figure 3.** The variations of (a) CO_2 and (b) N_2 density, and (c) N_2/CO_2 at 140 km altitude as a
 703 function of L_s . IUVS observations are constrained at specific local time bins, including 8:00 -
 704 10:00 (purple), 12:00 - 14:00 (light blue), and 16:00 - 18:00 (yellow). Data obtained in MY 32,
 705 33, and 34 are indicated with triangles, diamonds, and squares, respectively.

706 **Figure 4.** Local time variations of CO_2 , N_2 , and N_2/CO_2 at 140 km altitude. Uncertainties are
 707 shown by gray bars. Data shown are constrained to three seasons. (a, b, c) Observations from L_s
 708 30° to 70° in MY 33, which correspond with orbits around 1800 - 2200. (d, e, f) Observations
 709 from L_s 120° to 160° in MY 33, which correspond with orbits around 2900 - 3500. (g, h, i)
 710 Observations from L_s 340° to 40° in MY 33 through 34, which correspond with orbits around
 711 4800 - 5500.

712 **Figure 5.** Latitudinal variations of CO_2 , N_2 , and N_2/CO_2 at 140 km altitude. Uncertainties are
 713 shown by gray bars. Local time is limited from 10:00 to 14:00. (a, c, e) L_s is limited between
 714 80° and 100° , which corresponds to the northern summer. (b, d, f) L_s is between 340° and 360° ,
 715 which corresponds to the northern spring. MYs observed between 340° and 360° are
 716 distinguished by colors; red is MY 32 and black is MY 33.

717 **Figure 6.** Time variations of (a) N_2/CO_2 at 50 km, in the homosphere, predicted by the MCD,
 718 (b) temperature (K) at 175 km observed by IUVS, and (c) inferred homopause altitude (km)
 719 considering the effect of variations of N_2/CO_2 in homosphere, isothermal thermospheric
 720 temperature, and N_2/CO_2 at 140 km.

721 **Figure 7.** The same as Figure 2 (b) but CO_2 partial pressure at 140 km altitude is shown.
 722 Corresponding CO_2 partial pressure is calculated to be based on IUVS observations both CO_2
 723 density at 140 km and temperature at 175 km under the assumption for isothermal atmosphere.

724 **Figure 8.** Time variations of CO₂ density at inferred homopause altitude shown in Figure 6.
 725 CO₂ density is extrapolated from the IUVS observation.

726 **Figure 9.** (a, b) Latitudinal variations of homopause altitude inferred from IUVS observation.
 727 (a) L_s is limited between 80° and 100°. (b) L_s is between 340° and 360°. The limitation in local
 728 time is the same as in Figure 3.

729 **Figure 10.** Comparisons between IUVS observations and the MCD prediction. (a) CO₂ density
 730 (cm⁻³) at 140 km, (b) N₂ density (cm⁻³) at 140 km, and (c) N₂/CO₂ at 140 km. IUVS is shown as
 731 black dots and the MCD as red dots. Uncertainties of IUVS observations are represented by
 732 gray bars. The MCD prediction is for average solar EUV and climatology dust conditions. The
 733 geometries of the MCD input are provided by the footprints of IUVS observations shown in
 734 Fig. 1.

735 **Table 1.** The results of the parameter study. Typical values required to explain N₂/CO₂ at 140
 736 km observed by MAVEN/IUVS are shown. Among three parameters considered (surface
 737 N₂/CO₂, thermospheric temperature, and homopause altitude), a plausible value for the
 738 parameter of interest in each case is evaluated while the other two parameters are fixed.

Case	Object parameter	Season	Fixed parameters		Result
1	Surface N ₂ /CO ₂ ratio	Perihelion	Temperature; 180 [K]	Homopause altitude: 120 [km]	0.016
2	Surface N ₂ /CO ₂ ratio	Aphelion	Temperature; 180 [K]	Homopause altitude: 120 [km]	0.027
3	Temperature	Perihelion	Surface N ₂ /CO ₂ ; 0.02	Homopause altitude: 110 [km]	403 [K]
4	Temperature	Perihelion	Surface N ₂ /CO ₂ ; 0.02	Homopause altitude: 120 [km]	269 [K]
5	Temperature	Aphelion	Surface N ₂ /CO ₂ ; 0.02	Homopause altitude: 110 [km]	193 [K]
6	Temperature	Aphelion	Surface N ₂ /CO ₂ ; 0.02	Homopause altitude: 120 [km]	129 [K]
7	Homopause altitude	Perihelion	Surface N ₂ /CO ₂ ; 0.02	Temperature; 150 [K]	129 [km]
8	Homopause altitude	Perihelion	Surface N ₂ /CO ₂ ; 0.02	Temperature; 200 [K]	126 [km]

9	Homopause altitude	Aphelion	Surface N ₂ /CO ₂ : 0.02	Temperature; 150 [K]	117 [km]
10	Homopause altitude	Aphelion	Surface N ₂ /CO ₂ : 0.02	Temperature; 200 [K]	109 [km]