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## Seasonal Variability of Deuterium in the Upper Atmosphere of Mars

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Key Points:

1. Deuterium (D) emissions from the limb of Mars are analyzed to produce atomic abundances and escape rate estimates in the upper atmosphere.

2. D property variations are pronounced. Brightness and densities increase with Mars' proximity to the Sun and peak near southern summer solstice.

3. Variations of deuterium brightness, densities and escape rates suggest a seasonally varying D/H ratio at Mars.

39 **Abstract**

40

41 Measurements by multiple Mars Atmosphere and Volatile Evolution mission instruments,  
42 obtained between November 2014 and November 2017, are analyzed to produce deuterium  
43 properties in the upper atmosphere of Mars. We show here, for the first time, the seasonal  
44 distribution and variability of D densities, temperatures, and estimated Jeans escape rates at  
45 the exobase (200 km). Within the data constraints, it is found that the variations in D properties  
46 are similar for the northern and southern hemispheres, and peak near southern summer  
47 solstice. Trends in the D Lyman- $\alpha$  brightness, temperature, density, and escape rate are  
48 increasing during the beginning of the dust storm season, peak near southern summer solstice,  
49 and decrease toward the end of the dust storm season. This suggests that seasonal drivers at  
50 Mars cause deuterium in the upper atmosphere to become globally enhanced when Mars is  
51 closest to the Sun and during the martian dust season when water is provided to the upper  
52 atmosphere by subsurface, hydrological, and dust storm dynamics.

53

54

55

56 **1. Introduction**

57

58 Estimates of the ancient water content at Mars derived from surface mineralogy are  
59 presently debated [e.g., *Head et al.*, 2003; *Bibring et al.*, 2006]. Recent ground-based, orbital  
60 and in situ observations have been used to re-evaluate water reservoirs on the martian surface  
61 and in the lower atmosphere in order to better determine global water loss [*Smith et al.*, 2009;  
62 *Trokhimovskiy et al.*, 2015; *Mahaffy et al.*, 2015; *Villanueva et al.*, 2015, *Fedorova et al.*, 2018;  
63 *Orosei et al.*, 2018]. These determinations are made by constraining present epoch estimates  
64 that range from few to tens of meters to an integrated ancient reservoir of ~140 m global  
65 equivalent layer of water [e.g., *Jakosky et al.*, 2018].

66

67 The isotopic ratio of deuterium (D) to hydrogen (H) abundance at Mars has been useful  
68 for describing the planet's early formation [*Solomon et al.*, 2005; *Fisher*, 2007; *Horner et al.*,  
69 2009]. Directly measured and inferred ratios of D to H abundances (D/H) have been used to  
70 quantify water in the various ice and vapor reservoirs on the surface, within the subsurface, and  
71 throughout the lower atmosphere [*Owen*, 1992; *Kass and Yung*, 1999; *Krasnopolsky*, 2000;  
72 *Bertaux and Montmessin*, 2001; *Montmessin et al.*, 2005]. Derivations of the martian D/H ratio  
73 and comparisons with terrestrial values have been used to estimate the integrated loss rate of  
74 H, and subsequently to constrain water loss from Mars [e.g. *Yung et al.*, 1988; *Krasnopolsky*,  
75 2002; *Villanueva et al.*, 2015; *Jakosky et al.*, 2018 and references therein].

76

77 The upper atmosphere of Mars is the region where escape into outer space occurs [*Carr*,  
78 1986; *Lammer et al.*, 2013]. Determining the present escape rate of water and its variability in  
79 the upper atmosphere can therefore be used to extrapolate past values and to constrain  
80 estimates of primordial water abundance on the martian surface. To this purpose, roving and  
81 orbiting missions at Mars are being used to characterize the planet's climatology using a variety  
82 of techniques, such as determining the atmospheric abundance of species and their isotopes  
83 [*Jakosky et al.*, 1994; 2017; *Gillmann et al.*, 2011; *Ehlmann and Edwards*, 2014].

84

85 Atomic hydrogen in the upper atmosphere of Mars originates from photo-dissociated  
86 water lower in the atmosphere. Through chemical reactions and hydrological cycle dynamics,  
87 water-based atomic H and D are transported to the upper atmosphere where they can escape.  
88 Early theories set the timescale for this transport to be on the order of tens of years [*Hunten*  
89 *and McElroy*, 1970]. However, observations by the Hubble Space Telescope as well as Mars-  
90 orbiting spacecraft have shown the planet to have an extended H corona with properties that  
91 varied on shorter (seasonal) timescales than theoretically predicted [*Clarke et al.*, 2014; *Chaffin*  
92 *et al.*, 2014; 2015; *Chaufray et al.*, 2015; *Bhattacharyya et al.*, 2015, 2017b; *Halekas* 2017;  
93 *Chaffin et al.*, 2017; *Heavens et al.*, 2018; *Clarke*, 2018]. These variations in brightness are

94 consistent with variability in lower atmospheric water vapor and HDO observed at Mars  
95 [Villanueva *et al.*, 2015; Fedorova *et al.*, 2018].

96

97 Properties of H and D in the upper atmosphere of Mars can vary due to both external  
98 mechanisms such as space weather and solar activity as well as internal ones such as dust  
99 dynamics and atmospheric circulation [Mayyasi *et al.*, 2017b; 2018]. The timescales for these  
100 internal and external processes range from hours to months. Measuring properties of D and H  
101 over a baseline in time that exceeds the variability of individual physical processes is therefore  
102 fundamental to interpreting the dynamical nature of water escape where species are most  
103 volatile. The Mars Atmosphere and Volatile Evolution (MAVEN) mission has been in orbit about  
104 Mars since September 2014 [Jakosky, 2015]. MAVEN carries a high-resolution echelle channel,  
105 designed to resolve Lyman- $\alpha$  emissions from H and D at 121.567 and 121.534 nm, respectively,  
106 as well as other emissions [McClintock *et al.*, 2015; Clarke *et al.*, 2017; Mayyasi *et al.*, 2017a].

107

108 A comprehensive analysis of the properties of D in the upper atmosphere of Mars – the  
109 interface of loss to space – have so far been missing from the context of H variability and are  
110 critical in determining the D/H ratio. The MAVEN mission has been designed for such an  
111 analysis of D and H properties. In this work, 3 Earth years of echelle observations are used to  
112 map the properties of atmospheric D at Mars with unprecedented coverage. The optically thin  
113 D Lyman- $\alpha$  emission is analyzed and used with independent temperature derivations to provide  
114 modeled estimates of density and escape rates in order to provide insights into D/H and its  
115 variability.

116

117 A description of the MAVEN instruments used in this study is provided in Section 2. The  
118 models used to simulate the observations are described in Section 3. Resulting brightness  
119 values, derived densities, and escape rates for deuterium at Mars are shown in Section 4.  
120 Discussion and interpretation of the results is presented in Sections 5 and 6, respectively.  
121 Additional information showing consistent results for various modeling assumptions and  
122 observational details are provided in the Supplemental Material.

123

124

## 125 **2. Instruments and Observations**

126

127 Observations from three MAVEN instruments were used in this work: the remote  
128 sensing Imaging and Ultraviolet Spectrograph (IUVS), the in situ Neutral Gas and Ion Mass  
129 Spectrometer (NGIMS), and the Extreme Ultraviolet Monitor (EUVM) instruments.  
130 Measurements were separated into two seasonal epochs: aphelion (where solar longitude,  $L_s$ ,

131 varies between 0° and 120°) and perihelion (where  $L_s$  varies between 220° to 340°). Details on  
132 the observations are provided in the Supplemental Material.

133

134

## 135 2.1 IUVS

136

137 Observations early in the MAVEN mission defined the background noise threshold on  
138 the IUVS detector and showed that the few months around perihelion were optimal for  
139 observing faint emissions such as D [Mayyasi *et al.*, 2017a]. IUVS makes separate observations  
140 of the planet's disk, limb and corona with each orbit. The D emissions appear brightest at the  
141 sunlit limb-pointed line of sight due to limb brightening of the optically thin emission. We  
142 therefore concentrate exclusively on these limb observations for deriving a brightness profile  
143 for D. In order to obtain an altitude profile of deuterium emissions, only observations where  
144 the minimum ray height (MRH) was between the surface and 300 km were used. The deuterium  
145 signal above 300 km is too faint to be detected [Mayyasi *et al.*, 2017]. Resulting echelle spectra  
146 were reduced and calibrated at Lyman- $\alpha$  wavelengths to derive the D brightness in standard  
147 units of Rayleighs [Mayyasi *et al.*, 2017a].

148

## 149 2.2 NGIMS

150

151 NGIMS makes in situ measurements of neutral and ion densities [Mahaffy *et al.*, 2014].  
152 The neutral densities of species with masses ranging between 2 and 150 amu are measured in  
153 each nominal MAVEN orbit along inbound and outbound segments of the spacecraft track. Only  
154 inbound observations are used here due to adsorption of gas onto the walls of the  
155 spectrometer that affect measurements in the outbound orbital segments [e.g., Cui *et al.*,  
156 2009]. MAVEN periapsis altitudes reach ~150 km during nominal orbits and can drop to ~130  
157 km during select 'deep dip' campaigns [Benna *et al.*, 2015]. In the observations used here,  
158 nominal orbits were used. NGIMS data are used to derive neutral temperature values at the  
159 exobase (the altitude where the mean free path equals the scale height, taken here to be 200  
160 km). CO<sub>2</sub>, N<sub>2</sub>, and Ar are the most chemically stable species measured by NGIMS [Mahaffy *et*  
161 *al.*, 2015]. In this work, the neutral densities of CO<sub>2</sub> and Ar were used to calculate scale heights  
162 in order to provide a temperature in a given altitude range. The methodology for this derivation  
163 is described further in Section 3. Observations spanning aphelion and perihelion were used to  
164 constrain temperatures in the upper atmosphere of Mars.

165

## 166 2.3 EUVM

167

168           MAVEN carries an Extreme Ultraviolet Monitor (EUVM) instrument [Eparvier *et al.*,  
169 2015] that makes measurements of the solar energy incident at Mars using three wavelength  
170 channels. Two channels are dedicated to obtaining X-ray irradiances at 0.1-3 nm, and 0.1-7 nm  
171 wavelengths, and one channel is dedicated to isolating the solar Lyman- $\alpha$  line at 121.6 nm.  
172 EUVM measurements of the solar Lyman- $\alpha$  flux at Mars are used in the modeling component of  
173 this analysis, described below, to determine the concentrations of deuterium from the  
174 observed irradiances. EUVM observations that were made on the days of the echelle  
175 observations were used to provide the solar irradiance at Mars. In this work, observations from  
176 IUVS, NGIMS, and EUVM are averaged for relatively long periods of time, and span over 1.5  
177 Mars Years.

178  
179

### 180 **3. Models**

181

182           In order to derive physical properties from the observed D brightness, we use a single-  
183 scattering model, adapted for optically thin emissions [Bhattacharyya *et al.*, 2017a].  
184 Procedurally, these model simulations require constraining ambient atmospheric conditions at  
185 the times of the observed emissions in order to obtain the concentrations of the emitting  
186 species along a given line of sight. The single-scattering model utilized had previously assumed  
187 spherical symmetry for simplicity. To make model retrievals of the observations presented here  
188 more physically plausible, a spherically asymmetric background atmosphere is adopted, where  
189 the asymmetry is assumed to be due to variations in solar zenith angle (SZA) and martian  
190 season, denoted by solar longitude,  $L_s$ . SZA depends on both latitude as well as local time and is  
191 chosen as the single parameter to represent variations in planetographic observational  
192 conditions. Therefore, in this application, a single-scattering model is coupled to a 2D  
193 background atmospheric model, that includes empirically derived neutral densities and  
194 temperatures, to provide a global map of conditions that can be used to reproduce the  
195 observed emission brightness for D. Aphelion and perihelion scenarios were considered to  
196 account for seasonal variations at Mars.

197

198           Below 80 km, the predominantly CO<sub>2</sub> atmosphere of Mars absorbs almost all Lyman- $\alpha$   
199 emission, and no emissions are expected to be generated at those altitudes [Bhattacharyya *et*  
200 *al.*, 2017a]. At thermospheric altitudes (above 80 km), a global asymmetric background  
201 atmosphere is simulated using the following methodology: (1) Scale heights of CO<sub>2</sub> and Ar,  
202 obtained from NGIMS density profiles, are used to determine a neutral atmospheric  
203 temperature near exobase altitudes of  $\sim$ 200 km. (2) Empirically derived trends are used to  
204 account for variability in the exobase neutral temperature with SZA and season. (3) A  
205 mathematical representation is used to generate a temperature profile for remaining

206 thermospheric altitudes. (4) A CO<sub>2</sub> atmosphere is derived from the neutral temperature using  
207 an atmospheric model and constrained to NGIMS density observations, at overlapping  
208 altitudes, for consistency. (5) Finally, a single-scattering model uses the asymmetric background  
209 atmosphere, as well as IUVS observations, to simulate the D intensity for comparison with the  
210 IUVS observations to produce a best-fit exobase density.

211

212

### 213 *3.1.1 Obtaining Temperatures of the Martian Atmosphere at the Exobase*

214

215 In a horizontally stratified atmosphere, the altitude over which the density of a species  
216 decreases by e<sup>-1</sup> of its value at some reference altitude is defined as the scale height,  $H_n$ , and is  
217 defined as:

218

$$219 H_n = \frac{k_b T_n}{m_n g_r} \quad (1)$$

220

221 where,  $k_b$  is the Boltzmann constant,  $T_n$  is the neutral temperature,  $m_n$  is the mass of the  
222 neutral species  $n$ , and  $g_r$  is the gravity at the altitudes of the measurements.

223

224 For the observations used here, MAVEN spacecraft periapsis nominally ranged between  
225 ~150 km and 180 km. The slope of NGIMS CO<sub>2</sub> and Ar densities between 160 km and 200 km  
226 were used to derive a scale height for each species. In cases where the spacecraft periapsis was  
227 higher than 150 km, the slope of the densities between 180 km and 220 km was used. Using  
228 equation (1), the neutral temperature was calculated for each species. The temperatures  
229 derived using this method showed results similar to within ~10% for aphelion, and ~15% for  
230 perihelion, for each species. Since these differences were within the uncertainties in the  
231 measurements, an average temperature from the two species was adopted as a representative  
232 exobase temperature.

233

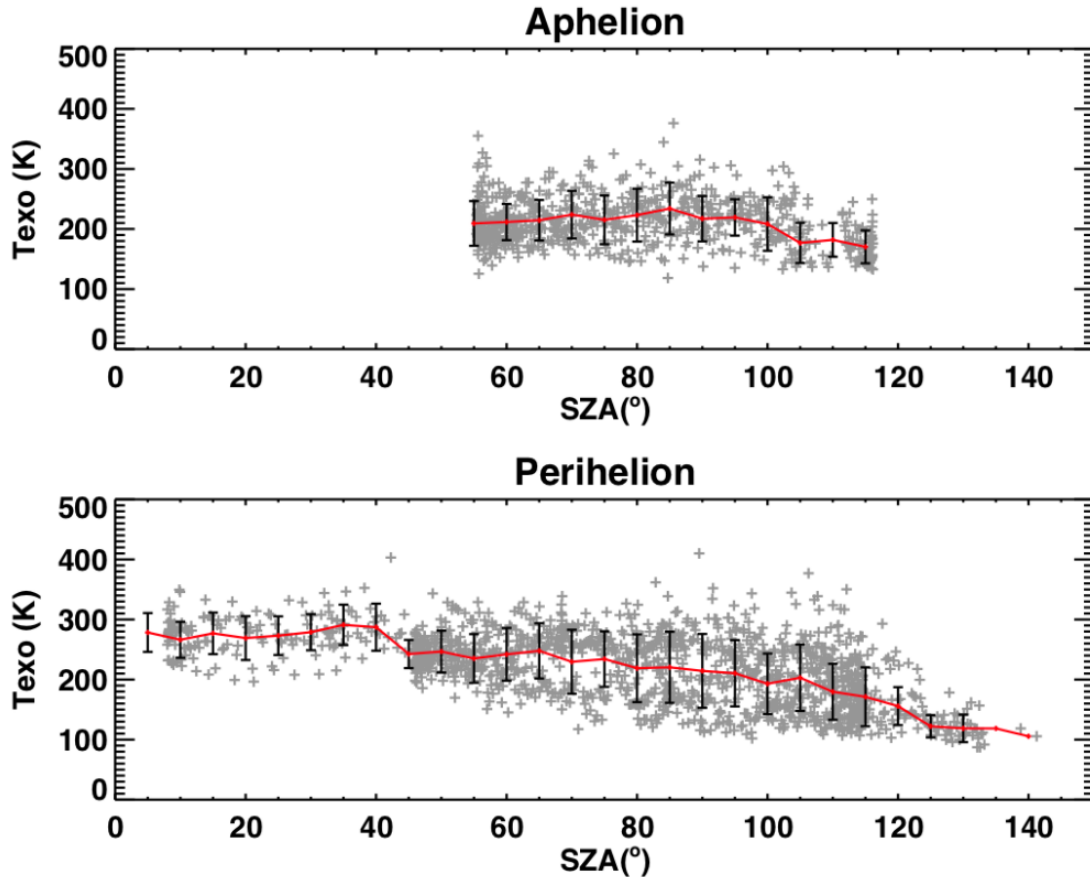
### 234 *3.1.2 Determining Seasonal and SZA Variations in Exobase Temperature*

235

236 The averaged CO<sub>2</sub> and Ar scale height derived temperatures are shown in Figure 1 for  
237 aphelion and perihelion seasons. During aphelion, NGIMS nominal in situ measurements  
238 spanned ~50° to 110° SZA. During both perihelion seasons observed by MAVEN to date, NGIMS  
239 measurements spanned ~5° to 140° in SZA. The red horizontal lines are the averages of values  
240 in 5° SZA bins, with their standard deviation in vertical black error bars. At the common SZA of  
241 50° for each season, aphelion and perihelion temperatures were ~210 ± 37 K and 235 ± 40 K,  
242 respectively.

243

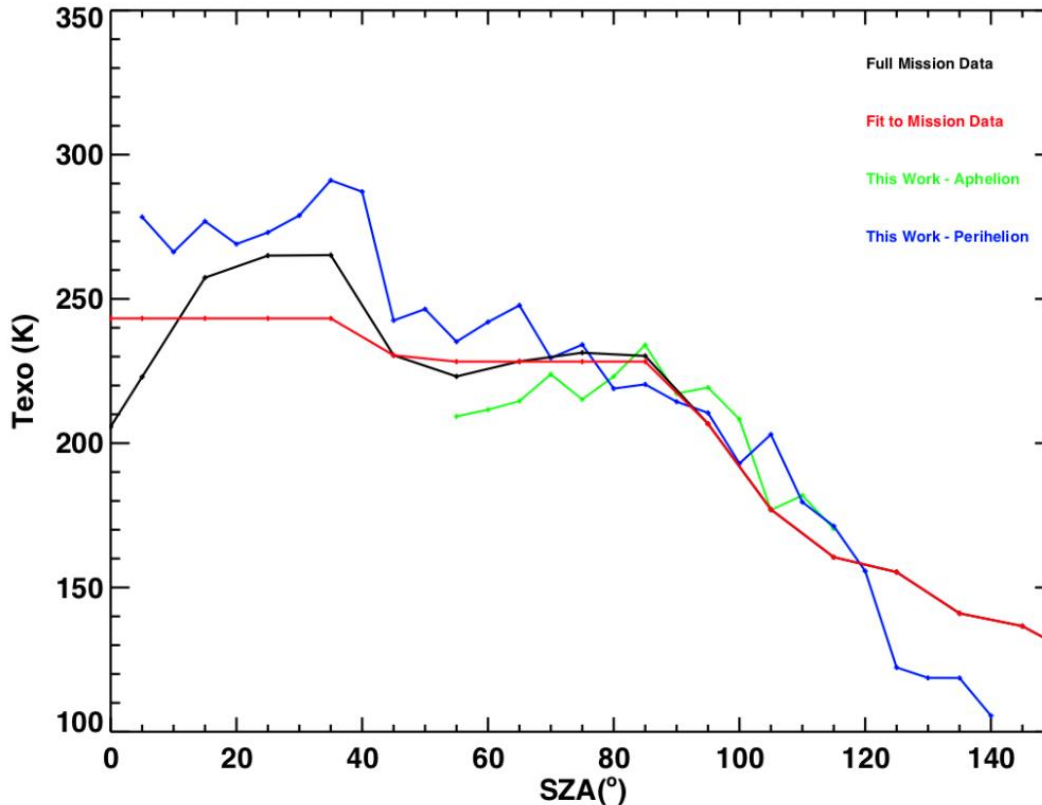




244  
 245 *Figure 1: Neutral temperatures derived from NGIMS observed scale heights for orbits at*  
 246 *aphelion (top) and perihelion (bottom) conditions. Individual orbit temperatures are shown as*  
 247 *grey plus symbols and span a range of SZAs. The red lines in each panel show trends from 5° SZA*  
 248 *bins. Black vertical lines represent the standard deviation within each bin.*

249  
 250 There have been ongoing efforts to characterize the neutral upper atmospheric  
 251 temperature at Mars [Stone et al., 2016, 2018; Bougher et al., 2017]. In order to get a broader  
 252 SZA representation of the neutral temperature variation at the exobase, the seasonal trends  
 253 obtained here from NGIMS-constrained scale heights are compared to trends of empirically  
 254 constrained MAVEN observations that span the whole mission and are shown in Figure 2. The  
 255 NGIMS measurements available at any time are for one location only. This necessitates  
 256 determining a time-averaged functional relationship for the global representation of  
 257 temperature variation with SZA. Local time variations in exobase neutral temperatures are  
 258 within the uncertainties of the mission-long averages and are not accounted for separately.

259  
 260



261  
 262 *Figure 2. A comparison of exobase temperature variability with SZA for specific seasons and for*  
 263 *all seasons across the MAVEN mission. NGIMS observations at aphelion are shown in green,*  
 264 *binned by 5° in SZA, and perihelion observations are shown in blue with similar SZA binning.*  
 265 *Observations from the first 1.75 years of the MAVEN mission are shown in black and fit to a*  
 266 *curve shown in red [Stone et al., 2018].*

267  
 268 The temperatures derived using the method described here are consistent with those  
 269 obtained independently and follow similar trends to observations across the MAVEN mission  
 270 [Stone et al., 2016; 2018]. The trend line fit to the full mission observations are used to  
 271 extrapolate the exobase temperatures to remaining SZAs not covered by NGIMS during the  
 272 IUVS observation times analyzed in this work. An additional temperature shift is done  
 273 (incremental for aphelion temperatures and decremental for perihelion temperatures) to the fit  
 274 trend line to account for seasonal variations in exobase temperatures. The resulting aphelion  
 275 and perihelion temperatures extracted from this interpolation and scaling are  $216 \pm 39$  K and  
 276  $255 \pm 29$  K, respectively, at the subsolar point ( $0^\circ$  SZA). Linear interpolations of these values  
 277 were used to constrain the exobase temperature of the martian atmosphere at  $0^\circ$  SZA  
 278 (overhead sun conditions) for other solar longitude observations.

279  
 280 **3.1.3 Determining Temperature Profiles with Altitude**

281

282 For the seasonal and SZA conditions of the observations, the neutral temperature,  
283 determined at the exobase was used to generate a profile at thermospheric altitudes. This was  
284 done using a mathematical representation [Krasnopolsky, 2002]:

285

$$286 \quad T(h) = T_{\infty} - (T_{\infty} - 125) \times \exp\left(-\frac{(h-90)^2}{11.4 \times T_{\infty}}\right) \quad (2)$$

287

288 where  $h$  is altitude (in km) between 90 and 400 km and  $T_{\infty}$  is the exospheric temperature (in  
289 degrees Kelvin) derived from the NGIMS neutral density scale heights. The neutral temperature  
290 is assumed to remain isothermal above the exobase (200 km) for a particular SZA.

291

### 292 *3.1.4 Generating a Consistent Neutral Atmosphere*

293

294  $\text{CO}_2$ , which is the dominant component of the martian atmosphere, absorbs Lyman- $\alpha$ ;  
295 therefore, a neutral background atmosphere consisting of  $\text{CO}_2$  as well as D densities is required  
296 as input to the single-scattering model. The  $\text{CO}_2$  abundance was generated from a volume  
297 mixing ratio at 80 km, and used the temperature provided by NGIMS measurements and  
298 molecular and eddy diffusion to account for interactions with other neutral species to provide a  
299 density profile for the altitudes of interest for the observing conditions [Matta et al., 2013].

300

301 The  $\text{CO}_2$  mixing ratios at 80 km are consistent with the relative abundances found in the  
302 Mars Climate Database for  $\text{CO}_2$  and did not show significant variability with SZA [Forget et al.,  
303 1999; Lewis et al., 1999]. However, the pressure of the neutral atmosphere is variable and can  
304 introduce variability not quantified by the mixing ratio used. The density of the atmosphere at  
305 80 km is a free parameter that was varied to constrain the modeled species with NGIMS-  
306 observed  $\text{CO}_2$  densities near spacecraft periapsis for aphelion and perihelion conditions  
307 [Mayyasi et al., 2018]. This methodology therefore provides an empirical density profile for  $\text{CO}_2$   
308 in the asymmetric background model that changes only with the neutral temperature.

309

310 Deuterium is a lighter species and varies differently with altitude than its heavier  
311 counterpart,  $\text{CO}_2$  [e.g., Krasnopolsky, 2002]. A density profile between the altitude limits where  
312 D emissions are most relevant (80 to 300 km), was needed for the single-scattering model  
313 input. Above the exobase altitude of 200 km, a modified Chamberlain approach, which  
314 accounts for the variation of temperature with SZA, was used [Vidal-Madjar and Bertaux,  
315 1972]. Between 120 and 200 km, a simple diffusion model was used [Chaufray et al., 2008]. At  
316 the exobase, the D density was considered to be a free parameter with a range of 6 values  
317 discussed in the next section. A mathematical formulation ( $nT^{5/2} = \text{constant}$ ; where  $n$  is density  
318 of a light species and  $T$  its temperature) first derived by [Hodges and Johnson, 1968] and

319 recently verified by Chaufray et al., [2018] for H atoms, was used to determine the SZA  
320 variability of D densities at the exobase. Below the assumed homopause at 120 km [Nagy et al.,  
321 2009; Mahaffy et al., 2015], a linear profile for D was used for simplicity, similar to that  
322 described in *Bhattacharyya et al.*, [2017a] and that was consistent with a diffusion-generated  
323 atmosphere.

324

### 325 *3.1.5 Simulating D Densities from Observed and Modeled Intensities*

326

327 A radiative transfer model described in *Bhattacharyya et al.*, [2017a], developed for  
328 interpreting the optically thick H Lyman- $\alpha$  observations was modified to simulate the optically  
329 thin D emission in order to interpret the IUVS deuterium observations. D Lyman- $\alpha$  emissions at  
330 Mars are optically thin along a given line of sight where only single-scattering is assumed. Since  
331 this D emission is due to solar resonant scattering, EUVM-measured solar Lyman- $\alpha$  flux is used  
332 to determine the intensity of the observed emission for a particular observation [*Thiemann et*  
333 *al.*, 2018]. The EUVM measurements of the line-integrated Lyman- $\alpha$  flux were converted to a  
334 line center flux in order to calculate the g value for the deuterium emission at Mars [*Emerich et*  
335 *al.*, 2005; *Chaufray et al.*, 2008]. The g values, ranging between  $4.93\text{--}12.1\times 10^{-4}$  photons  $\text{s}^{-1}$  for  
336 the data analyzed here. The g values were then multiplied by a line of sight column density in  
337 the single-scattering model to simulate the intensity for deuterium emission at Mars.

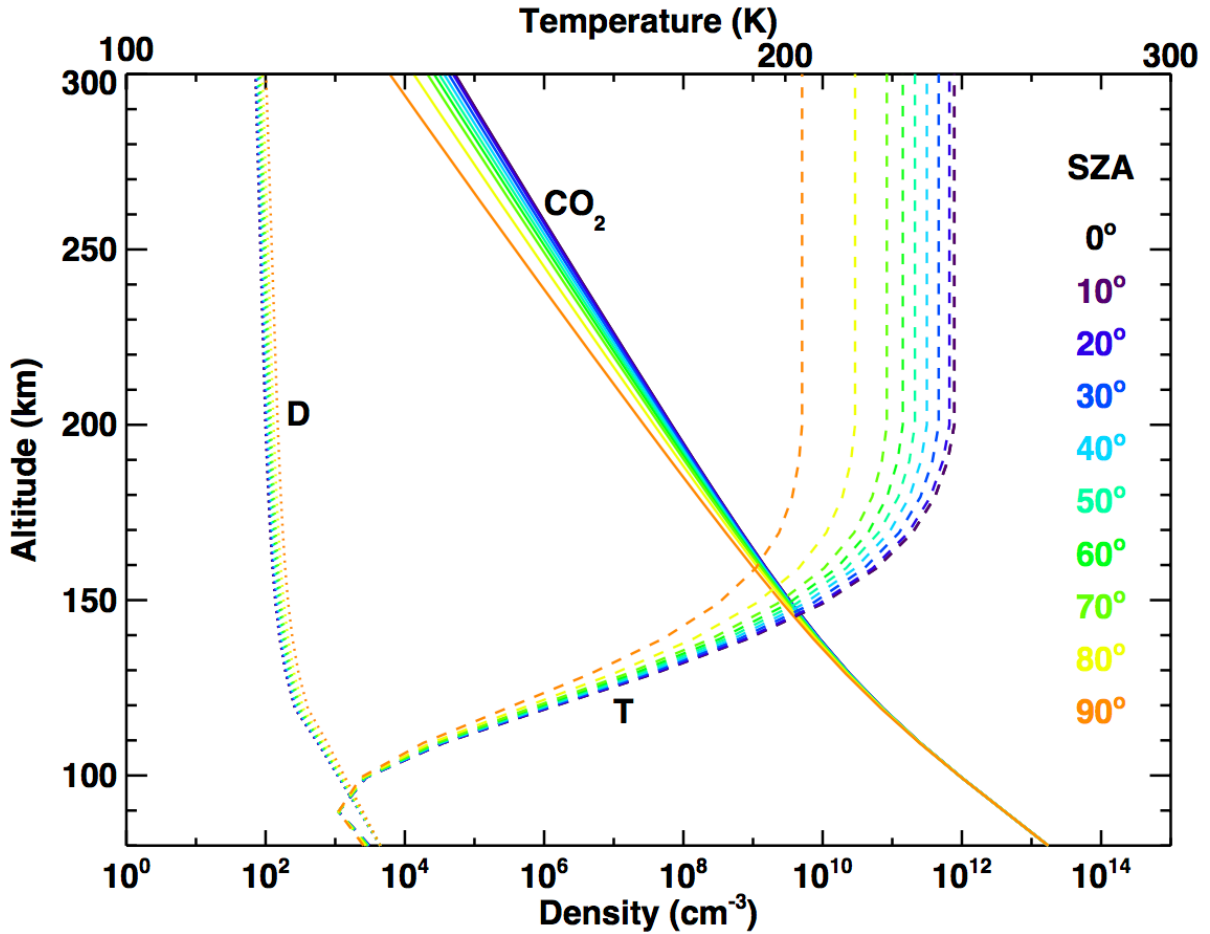
338

339 Six exobase D densities were used to generate the D background atmosphere for each  
340 of the observing conditions. These densities were chosen to be 100, 500, 1000, 3000, 5000, and  
341  $7000\text{ cm}^{-3}$ . Each of the six densities was used with the  $\text{CO}_2$  background and NGIMS-constrained  
342 temperatures to provide a library of atmospheres. The single-scattering model uses the solar  
343 flux measured at the time of each observation with this library of atmospheres to generate a  
344 set of emission profiles for each line of sight (LOS) in the observations. The exobase density that  
345 corresponds to the emission profile that best fits the data is determined by minimizing chi-  
346 squared deviations between data and model in a least squared fit. The uncertainty in the  
347 derived D density for a particular observation is determined by accounting for all modeled D  
348 densities that lie within the minimum chi-squared+1 range.

349

350 A sample neutral atmosphere generated as background for the single-scattering model  
351 is shown in Figure 3. The D and  $\text{CO}_2$  density profiles are adopted for an average temperature  
352 case at perihelion and use the  $100\text{ cm}^{-3}$  exobase density value for D.

353



354  
 355 *Figure 3. Background neutral atmosphere used in the single-scattering model to simulate D*  
 356 *Lyman- $\alpha$  emissions and derive D densities. This atmosphere is generated for the average neutral*  
 357 *temperature taken at perihelion derived from NGIMS observation for different SZA indicated by*  
 358 *line color. The CO<sub>2</sub> density is shown in solid lines, the D density is shown in dotted lines.*  
 359 *Temperatures follow the top x-axis scale and are shown in dashed lines.*

360  
 361

#### 362 4. Results

363

364 The D Lyman- $\alpha$  emission is faint in comparison to H Lyman- $\alpha$  [Bertaux *et al.*, 1984].  
 365 Therefore, only observations with a local SZA between 0° and 90° were considered to ensure  
 366 that the entire atmosphere was sunlit between the surface and 300 km. Over 20,000 echelle  
 367 image frames of the martian limb, measured across the observational time span used here, fit  
 368 the dayside criteria. Echelle spectra are averaged across the observational dataset in order to  
 369 optimize the signal to noise when retrieving the faint D signal.

370

371 The data were binned according to the LOS latitude, SZA, MRH altitude (hereafter  
372 referred to as altitude), and  $L_s$ . The bins considered include two in latitude, ranging between  
373  $90^\circ$  N and  $30^\circ$  N for northern hemisphere observations, and  $30^\circ$  S to  $90^\circ$  S for southern  
374 hemisphere observations. Three SZA bins were considered, ranging between  $30^\circ$  and  $75^\circ$  with  
375  $15^\circ$  spacing. Twenty-one bins in altitude were used ranging between 0 and 400 km with 20 km  
376 spacing. At the highest altitudes, D was too faint to be resolved and so only observations up to  
377 300 km were used in the analysis. At aphelion, one representative  $L_s$  bin was used ranging  
378 between  $0^\circ$  and  $120^\circ$  (described further next). At perihelion, six  $L_s$  bins were used ranging  
379 between  $220^\circ$  and  $340^\circ$  with  $20^\circ$  spacing. Observations made in each of the bins were spectrally  
380 aligned to account for differences in detector operational binning schemes before co-adding  
381 (see Table A1 in *Mayyasi et al.*, [2017b] for a description of detector binning schemes used  
382 throughout the MAVEN mission). Insufficient echelle observations were available at equatorial  
383 regions ( $30^\circ$  S to  $30^\circ$  N latitudes), lower SZAs ( $0^\circ$ - $30^\circ$ ), and  $L_s$  values beyond those considered  
384 here to build statistically significant brightness profiles due largely to the geometry of the  
385 MAVEN orbit. However, at the time of this writing, MAVEN continues to make echelle  
386 observations as Mars approaches perihelion. The next few months of observations would be  
387 used in future work to close existing observational gaps.

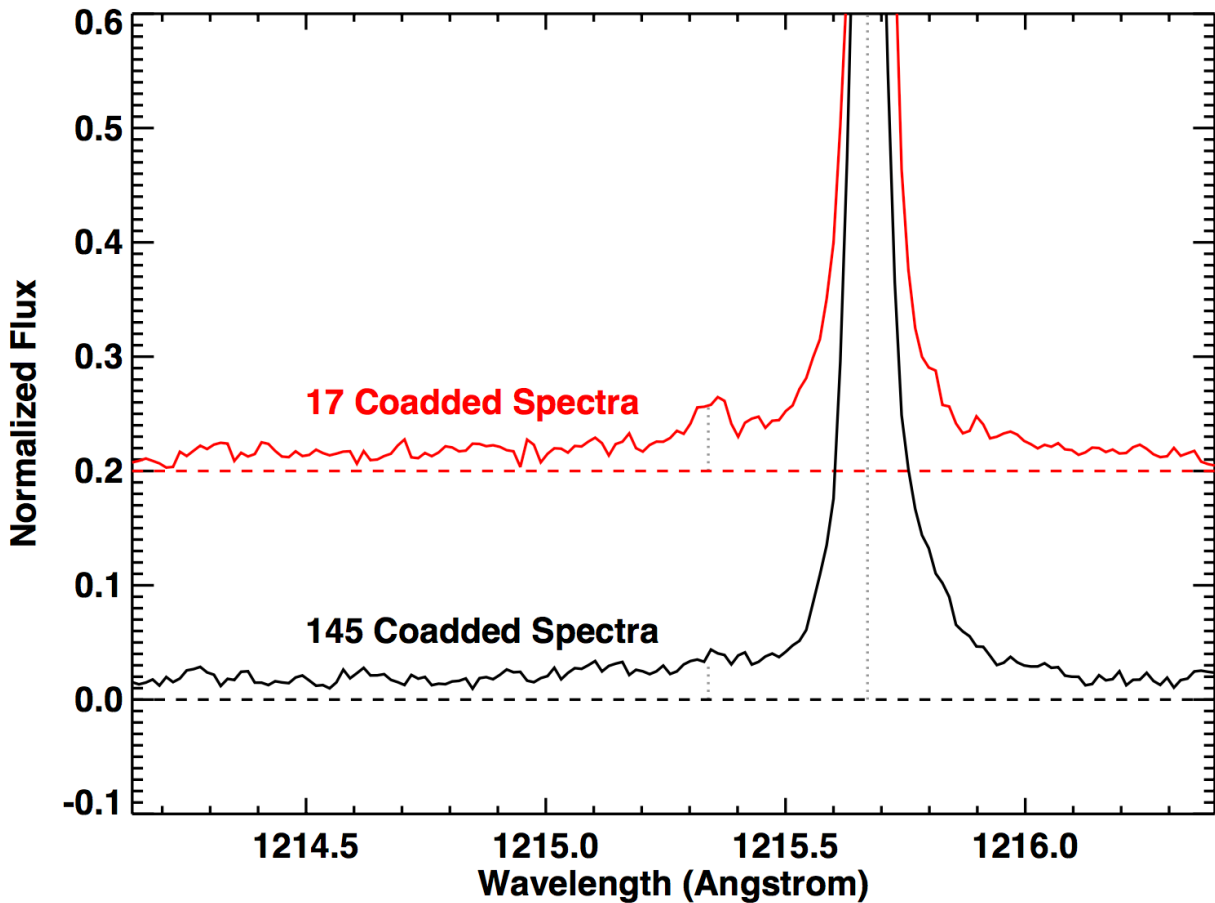
388

#### 389 4.1 Aphelion

390

391 The first detections of martian D emission based on Hubble Space Telescope (HST)  
392 observations showed Lyman- $\alpha$  brightness values of 30 Rayleigh [*Bertaux et al.*, 1993] and  $23 \pm 6$   
393 Rayleigh [*Krasnopolsky et al.*, 1998]. These observations occurred at times when Mars was at  
394  $63^\circ$  and  $67^\circ$   $L_s$ , respectively, and therefore close to Mars aphelion ( $71^\circ$   $L_s$ ). D and H Lyman- $\alpha$   
395 emissions observed by MAVEN were found to vary dramatically throughout a martian year and  
396 showed consistency with these previous detections [*Clarke et al.*, 2017; *Mayyasi et al.*, 2017b].  
397 Due to the faintness of the D signal near perihelion, and the limitations of the instrument, the D  
398 emission was not always attainable above the background detector noise. Aphelion  
399 observations between  $0^\circ$  and  $120^\circ$   $L_s$  were co-added to improve signal to noise yet still fell  
400 below the detection limits. An example is shown in Figure 4 for one line of sight bin for  
401 reference and demonstrates the resolvability of D emission above the blue-ward wing of the H  
402 emission. The D emission signal is comparable to the background when near aphelion and more  
403 clearly resolvable (with fewer individual observations) near perihelion. Co-added observations  
404 from all available dayside aphelion observations are therefore used to provide an upper limit  
405 for the simulated properties. Using the average aphelion exobase temperature of 216 K, the  
406 exobase density range and mean Jeans' escape rate for overhead Sun conditions are derived.  
407 The upper limits for the deuterium exobase density and escape rates at aphelion conditions are  
408 found to be  $2.3 \pm 2.3 \times 10^3 \text{ cm}^{-3}$  and  $\sim 3 \times 10^3 \text{ atoms cm}^{-2} \text{ s}^{-1}$ , respectively.

409  
410



411  
412 *Figure 4. Sample spectra from aphelion (black) and perihelion (red) that correspond to bins of*  
413 *60°–75° SZA and 120–140 km altitude obtained from observations of the northern hemisphere*  
414 *of Mars. The aphelion spectrum is obtained by averaging 145 available integrations obtained*  
415 *between 60° and 80° L<sub>s</sub>. The perihelion spectrum is obtained by averaging 17 available*  
416 *integrations between 220° and 240° L<sub>s</sub>. The vertical dotted lines represent the locations of the D*  
417 *and H Lyman- $\alpha$  emission wavelengths at 1215.34 and 1215.67 Å, respectively. Both spectra are*  
418 *normalized in flux and the perihelion spectrum is vertically offset by 0.2 to facilitate comparison*  
419 *of the relative brightness of the D emission at each seasonal epoch. The asymmetry in the*  
420 *aphelion (black) H profile is due to the interplanetary hydrogen emission that is shifted red ward*  
421 *of the Mars H emission for these observations.*

422  
423 4.2 Perihelion

424  
425 Mars perihelion occurs at 251° L<sub>s</sub>. Observations spanning a range of 220° to 340° L<sub>s</sub> were  
426 analyzed to provide D brightness profiles for near-perihelion conditions at the L<sub>s</sub> and SZA

427 binning scheme described previously. Only bins with at least 3 observed spectra and that  
428 resulted in profiles with data points in at least 5 altitude grids were used. The resulting D  
429 irradiance from co-added observations as well as the model best fits are shown in Figure 5 for  
430 the averaged perihelion derived temperature of 255 K, and are sorted by hemisphere,  $L_s$  and  
431 SZA. Data-model comparisons at the lower and higher temperature limits from the uncertainty  
432 in perihelion temperatures (226 K and 284 K), are shown in Figures S1 and S2, respectively, in  
433 the Supplemental Material, as are the number of observations used in each bin (Table S5).

434

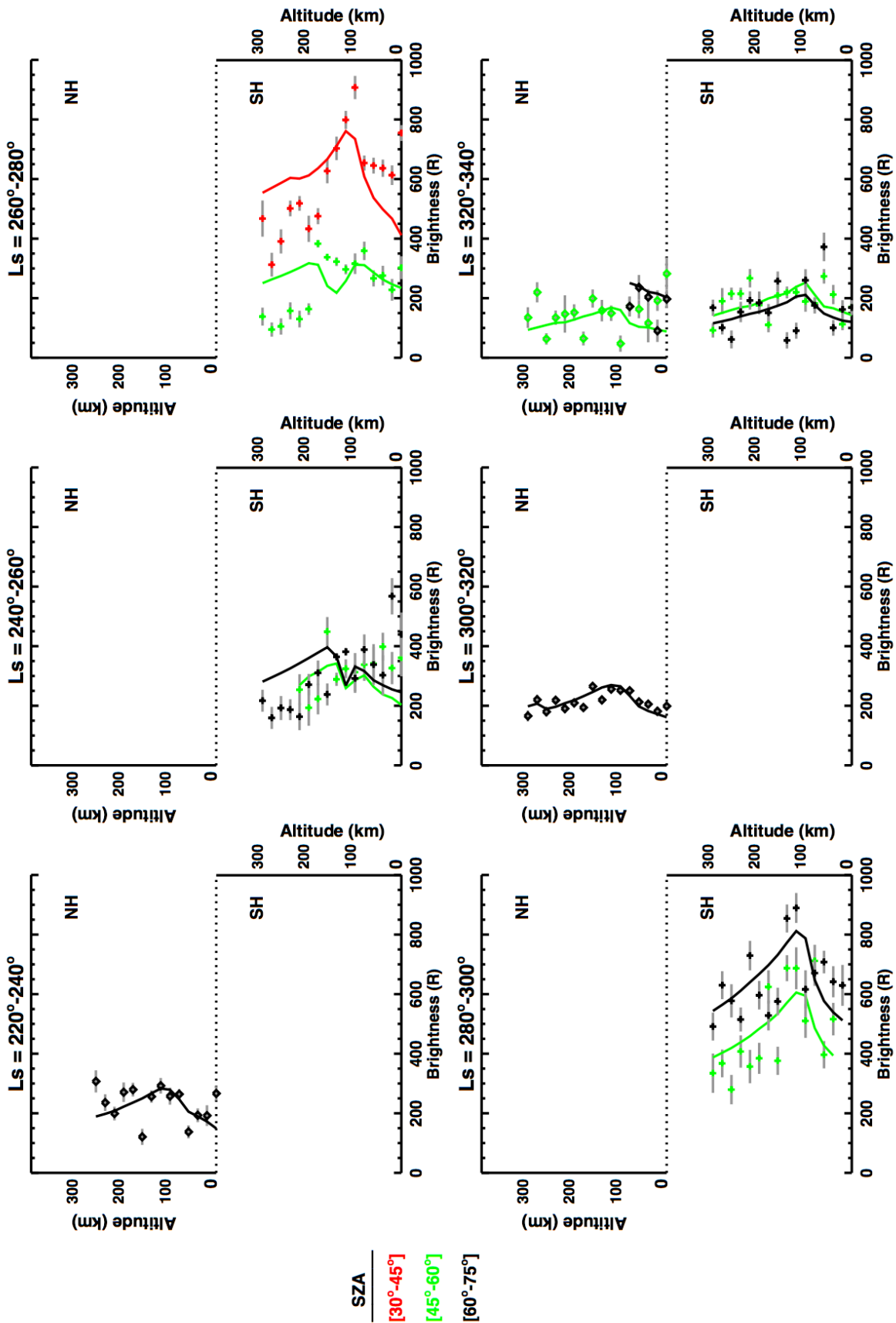
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440 *Figure 5. Deuterium brightness profiles derived from bin-specific co-added spectra, shown as a*  
441 *function of  $L_s$  (by panel), SZA (by color of profile), and adjacent hemispheres for comparison.*  
442 *Northern hemisphere (NH) profiles are shown on the top part of each panel as diamonds with*  
443 *an altitude scale on the top left of each panel. Southern hemisphere (SH) profiles are shown on*  
444 *the lower part of each panel as crosses with an altitude scale on the lower right of each panel.*  
445 *Season spans through perihelion with top rows covering 220°-240° (left), 240°-260°(middle) and*  
446 *260°-280° (right), respectively. Bottom row panels cover seasonal ranges of 280°-300° (left),*  
447 *300°-320° (middle), and 320°-340° (right), respectively. Data are shown in diamonds for SZAs*  
448 *spanning 30°-45° (red), 45°-60° (green), and 60°-75° (black). Uncertainties in the data points are*  
449 *shown in grey horizontal lines. Model fits to the data are shown as solid lines with the SZA-*  
450 *respective color code. In each panel, both NH and SH data and model plots follow the bottom*  
451 *scale for brightness in Rayleigh.*

452

453 The D densities at the exobase, derived by the single-scattering model from best fits to  
454 the irradiance data, and constrained to empirically-determined exobase temperatures are listed  
455 in Table 1. The data covers observations made over a range of SZA. Subsequently, the  
456 asymmetric model utilizes a range of neutral temperatures. The range of solar conditions  
457 applicable to the echelle observations in each bin contribute to the uncertainties in the model-  
458 determined densities. To facilitate comparisons, the exobase densities and temperatures  
459 derived for D from different SZAs are extrapolated to 0° SZA (overhead Sun conditions) and are  
460 also shown in Table 1. These results correspond to an asymmetric background model that  
461 adopts the average perihelion temperature of 255 K derived from NGIMS measurements.  
462 Similar results derived from the lower and higher perihelion temperature limits of 226 K and  
463 284 K are shown in Tables S1 and S2, respectively, in the Supplemental Material.

464

465 *Table 1: Modeled D number density at the exobase (200 km) for the observations shown in Fig.*  
466 *5, and extrapolated to subsolar point conditions (SZA,  $\chi=0^\circ$ ) using the averaged perihelion*  
467 *temperature of 255 K.*

$L_s$ Range	SZA Range	$T_{\text{exo}}$ (K)	$D_{\text{exo}}$ ( $\times 10^3 \text{ cm}^{-3}$ )	$\chi=0^\circ T_{\text{exo}}$ (K)	$\chi=0^\circ D_{\text{exo}}$ ( $\times 10^3 \text{ cm}^{-3}$ )
Northern Hemisphere					
220° - 240°	60° - 75°	232 ± 4	1.2 ± 0.18	248	1.0 ± 0.1
300° - 320°	60° - 75°	226 ± 6	1.5 ± 0.23	241	1.3 ± 0.1
320° - 340°	45° - 60°	227 ± 3	1.0 ± 0.26	237	0.8 ± 0.2
320° - 340°	60° - 75°	223 ± 4	2.4 ± 0.62	239	2.0 ± 0.4
Southern Hemisphere					
240° - 260°	45° - 60°	243 ± 3	1.0 ± 0.14	253	0.9 ± 0.1
240° - 260°	60° - 75°	237 ± 5	1.2 ± 0.19	253	1.0 ± 0.1

260° - 280°	30° - 45°	244 ± 3	2.3 ± 0.19	250	2.2 ± 0.1
260° - 280°	45° - 60°	241 ± 3	1.1 ± 0.16	251	1.0 ± 0.1
280° - 300°	45° - 60°	236 ± 2	2.4 ± 0.29	247	2.2 ± 0.2
280° - 300°	60° - 75°	230 ± 4	3.9 ± 0.54	246	3.3 ± 0.3
320° - 340°	45° - 60°	226 ± 3	1.5 ± 0.29	237	1.3 ± 0.2
320° - 340°	60° - 75°	221 ± 5	1.2 ± 0.33	238	1.0 ± 0.2

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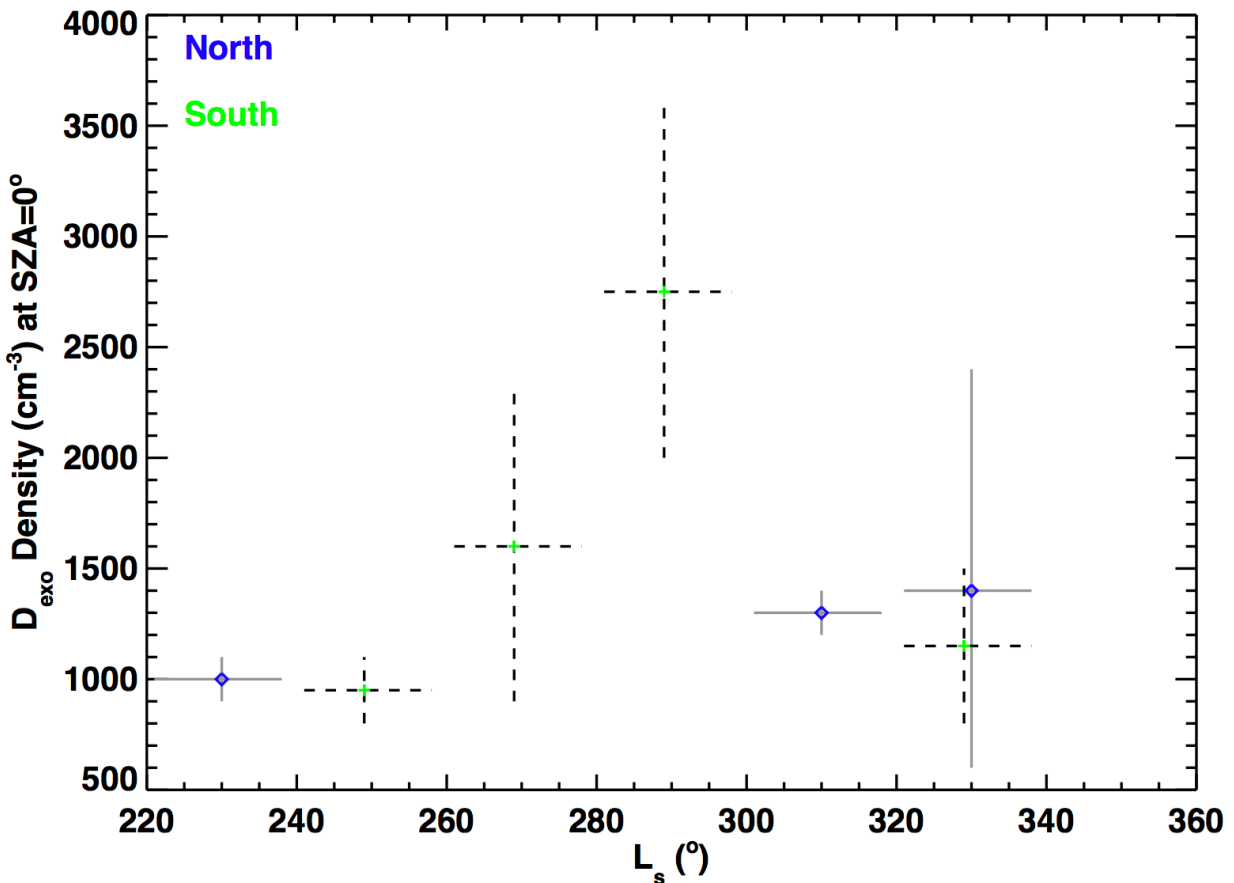
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477

The resulting D exobase densities, extrapolated to subsolar point conditions (SZA=0°) for perihelion observations are shown in Figure 6. The uncertainties in the modeled values stem from the ranges in the  $L_s$ , SZA, and altitude bins, and account for the range of results from model fits where more than one altitude profile (at different SZA bins) were available for interpolation to subsolar point conditions. Fig. 6 utilizes the averaged perihelion temperature of 255 K. Similar results corresponding to the low and high temperature ranges of 226 K and 284 K are shown in Figures S3 and S4, respectively, in the Supplemental Material.



478

479 Figure 6. Deuterium density at the exobase, extrapolated to 0° SZA, constrained by data and  
 480 model results at other SZA for perihelion conditions (220° to 340° L<sub>s</sub>). The northern hemisphere  
 481 data points (blue diamonds) and the southern hemisphere data points (green crosses) are  
 482 shown with their uncertainties in solid grey and dashed black lines, respectively. The modeled  
 483 results correspond to data averaged over a 20° range in L<sub>s</sub>, indicated by the length of the  
 484 horizontal uncertainties. The modeled density uncertainties (vertical lines) in each L<sub>s</sub> bin  
 485 correspond to the largest range of results from constraining the model to observed data at the  
 486 observation's SZA bins. Data points from the southern hemisphere are offset by one degree in L<sub>s</sub>  
 487 from center of bin for clarity when shown along overlapping northern hemisphere data points.  
 488

489 The averaged densities for each L<sub>s</sub> bin shown in Fig. 6 at subsolar conditions and the  
 490 corresponding empirical temperatures described in this work are used to generate the  
 491 estimated escape rates for deuterium [Jeans, 1925]. The resulting escape rates are listed in  
 492 Table 2 for the low, average, and high temperature cases of 226 K, 255 K, and 284 K,  
 493 respectively.  
 494  
 495  
 496  
 497

Table 2: Modeled Jeans escape rates at perihelion.

L <sub>s</sub> Range	$\chi=0^\circ$ Jeans Escape Rate (x 10 <sup>3</sup> atoms cm <sup>-2</sup> s <sup>-1</sup> )		
Northern Hemisphere			
	Low T Limit (226 K)	Average T (255 K)	High T Limit (284 K)
220° - 240°	1.1 ± 0.1	4.7 ± 0.5	16 ± 1.6
300° - 320°	0.9 ± 0.0	4.6 ± 0.4	15 ± 1.3
320° - 340°	0.8 ± 0.5	4.6 ± 2.7	17 ± 11
Southern Hemisphere			
	Low T Limit (226 K)	Average T (255 K)	High T Limit (284 K)
240° - 260°	1.6 ± 0.2	5.7 ± 0.9	16 ± 1.7
260° - 280°	2.2 ± 1.0	8.6 ± 3.8	25 ± 9.8
280° - 300°	2.9 ± 0.9	13 ± 3.6	37 ± 10
320° - 340°	0.6 ± 0.2	3.4 ± 1.0	12 ± 3.5

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## 5. Discussion

503 There is generally good agreement between observed and simulated D brightness  
 504 values at perihelion conditions, as shown in Fig. 5 (and Figs. S1 and S2). MAVEN arrived at Mars

505 in September 2014, during perihelion of Mars Year (MY) 32. In the early IUVS measurements,  
506 echelle observations were made with relatively short integration times (few seconds) that  
507 introduced higher uncertainties than longer-integration observations later in the mission (MY  
508 33 and beyond). A few cases in Fig. 5 show a model-data divergence at lower altitudes (namely,  
509 in the southern hemisphere,  $L_s=240^\circ\text{--}260^\circ$ ,  $\text{SZA}=45^\circ$  though  $75^\circ$  bins). The data from these bins  
510 are predominantly obtained from early mission data and the data-model discrepancy is likely  
511 associated with early echelle observational limitations [Mayyasi *et al.*, 2017b]. Additionally,  
512 model profiles agree better with the observations when temporally similar observations are  
513 used for co-adding. This is because there is less variability in the ambient atmosphere along the  
514 line of sight vector used to generate the background atmosphere as well as less variability in  
515 the input solar EUV flux.

516  
517 The D emission brightness increased as Mars approached perihelion and decreased as  
518 Mars moved further away from the Sun. These trends are similar in both hemispheres. When  
519 global data were available (in  $L_s$  bins  $280^\circ\text{--}300^\circ$  and  $320^\circ\text{--}340^\circ$ ), northern hemispheric D  
520 brightness observations were comparable to or brighter than southern hemispheric  
521 observations at similar seasonal epochs. In most of the subpanels in Fig. 5 with brightness  
522 profiles, more than one profile with SZA was available. The observed brightness profiles show  
523 increasing, constant, and decreasing trends with increasing SZA. Theoretical estimates of these  
524 trends predict an enhancement in D brightness with decreasing SZA. The present data coverage  
525 is too sparse to empirically analyze these trends, and so further interpretation of D brightness  
526 variability with SZA is deferred to future work once more observations near perihelion become  
527 available.

528  
529 The NGIMS temperatures at the exobase were derived with one-sigma uncertainties  
530 with lower and higher limits of 226 K and 284 K, respectively, at perihelion. A similar analysis  
531 was done at those temperature limits (with results shown in the Supplemental Material). The  
532 resulting trends in brightness profiles, model fits, exobase densities and escape rates for  
533 observational conditions as well as extrapolated subsolar conditions were consistent with the  
534 trends found at the average temperature of 255 K.

535  
536 Modeled values of D density at the exobase altitude of 200 km are derived for the  
537 binned observational conditions, with the caveat of having no hemispherical differences in the  
538 empirical background neutral atmosphere. These values are extrapolated to subsolar conditions  
539 for more direct comparisons by hemisphere, as shown in Fig. 6 (and Figs. S3 and S4). The  
540 exobase densities show similar trends in each hemisphere, with the northern hemisphere  
541 concentrations being comparable to and higher than concentrations in the southern  
542 hemisphere. Trends in the exobase density of both hemispheres peak near southern summer

543 solstice ( $L_s \sim 280^\circ\text{--}300^\circ$  range). Simulating the observed D brightness with different  
544 temperatures for the northern and southern hemispheres may produce different densities. 3D  
545 temperature models validated to ongoing observations of the upper atmosphere would be  
546 useful for making these determinations in future work. The temperature values derived for the  
547 observational conditions and their subsequent modeled densities at the exobase are shown in  
548 Table 1 (and Tables S1 and S2). These tables also include D exobase densities extrapolated for  
549 subsolar conditions. Southern hemisphere derived exobase temperatures do not vary from  
550 northern hemisphere temperatures, as expected from the atmospheric model assumptions.

551  
552 In averaging the results of this work from both hemispheres, the D density at the  
553 exobase varies from  $\sim 1 \times 10^3 \text{ cm}^{-3}$  at  $220^\circ L_s$  to  $\sim 3 \times 10^3 \text{ cm}^{-3}$  at  $280^\circ L_s$  and then decreases to  
554  $\sim 1 \times 10^3 \text{ cm}^{-3}$  at  $320^\circ L_s$  for the average exobase temperature of 255 K. No other existing  
555 measurements of D densities near perihelion have been published to date for comparison to  
556 these results; however, theoretical estimates have been made. Previous modeling work derived  
557 an exobase density of  $\sim 0.04 \times 10^3 \text{ cm}^{-3}$  at a higher temperature limit ( $\sim 350 \text{ K}$ ) than used here  
558 [Yung *et al.*, 1988]. A subsequent study derived a modeled exobase density of  $\sim 0.5 \times 10^3 \text{ cm}^{-3}$  for  
559 a temperature comparable to the average case here [Krasnopol'sky, 2002]. More recently, a  
560 theoretical model analyzing lower resolution (FUV) IUVS observations made during Dec 2014  
561 and Aug 2016 computed a D exobase density of  $\sim 2 \times 10^3 \text{ cm}^{-3}$  at  $L_s \sim 205^\circ$  for a temperature of  
562  $\sim 185 \text{ K}$ , and  $\sim 5 \times 10^3 \text{ cm}^{-3}$  at  $L_s \sim 255^\circ$  and temperature of  $\sim 265 \text{ K}$ , respectively [Chaffin *et al.*,  
563 2018]. These theoretical results compare favorably within the limits of the observations and  
564 simulations found in this work for the average temperature range and are consistent with the  
565 higher and lower limit temperature results shown in Supplemental Material Tables S1 and S2  
566 where the temperatures are closer to those modeled from FUV data.

567  
568 The Jeans escape rate was calculated for aphelion conditions (as an upper limit) and for  
569  $20^\circ$  seasonal bins at perihelion conditions. The trends in escape rate near perihelion follow  
570 those of D exobase density at  $0^\circ$  SZA and brightness at the observed conditions. The  
571 uncertainties in the escape rates are representative of those of the extrapolated densities at  
572 the assumed exobase temperatures described in Table 2. The D escape rate at the exobase for  
573 the average temperature conditions determined here varies seasonally within the range of  $\sim 2\text{--}$   
574  $19 \times 10^3 \text{ atoms cm}^{-2} \text{ s}^{-1}$  in the southern hemisphere. At the low temperature limit, these  
575 seasonal variations span  $\sim 0.5\text{--}4 \times 10^3 \text{ atoms cm}^{-2} \text{ s}^{-1}$ . At the high temperature limit, the  
576 southern hemisphere seasonal variations span  $\sim 9\text{--}47 \times 10^3 \text{ atoms cm}^{-2} \text{ s}^{-1}$ .

577  
578 Inter-hemispheric deuterium escape rate comparisons are limited by observations.  
579 There is insufficient coverage of northern hemisphere observations near perihelion at the time  
580 of this work to compare trends in escape rates, and from existing coverage, would seem to be

581 constant. Escape rates for the northern hemisphere vary from  $\sim 1$ , to  $\sim 4.5$ , to  $\sim 16 \times 10^3$  atoms  
582  $\text{cm}^{-2} \text{s}^{-1}$  for low, average and high temperature conditions, respectively, and seem relatively  
583 stable across the observed  $L_s$  ranges. The variation in escape rate across temperature limits and  
584 observed  $L_s$  range span an order of magnitude both hemispheres.

585

586 Previous theoretical models estimated a deuterium escape rate of  $\sim 8\text{--}15 \times 10^3$  atoms  
587  $\text{cm}^{-2} \text{s}^{-1}$  at temperature conditions similar to the average temperature adopted here  
588 [Krasnopolsky, 2002], and  $\sim 7 \times 10^3$  atoms  $\text{cm}^{-2} \text{s}^{-1}$  at higher temperatures than the high  
589 temperature limit obtained here [Yung *et al.*, 1988]. Analysis of ongoing and future MAVEN  
590 observations would enable further determinations of D abundances, escape rates, and their  
591 variability across hemispheres and seasonal coverage.

592

593

## 594 **6. Interpretation**

595

596 The simulated trends of D densities and escape rates are consistent with observed and  
597 theoretical expectations of Lyman- $\alpha$  brightness variations with martian season. The global  
598 mean temperature in the exosphere of Mars is higher at perihelion than at aphelion, and D  
599 irradiances were found to increase as Mars approaches the Sun in its orbit. It is plausible that  
600 seasonal drivers produce circulation patterns in the lower atmosphere that cause an upwelling  
601 of water and its deuterated constituents into higher altitudes when Mars is closer to the Sun.

602

603 The increasing and decreasing trends in D properties near perihelion occur during the  
604 dust season at Mars [ $L_s \sim 220^\circ\text{--}330^\circ$ ]. Type A and C dust storms originate in the northern  
605 hemisphere and migrate south [Fernández, 1998]. The dynamics of dust migration and  
606 circulation contribute to transporting water from the surface to higher altitudes [Heavens *et al.*,  
607 2018]. Additional weather circulation patterns distribute photo-dissociated water products  
608 from these altitudes into the upper atmosphere [e.g., Clarke, 2018], and may do so with varying  
609 efficiency in the hemisphere of dust storm origin. At the time of this writing, Mars is  
610 experiencing a planet encircling dust event. Analysis of MAVEN IUVS echelle observations for  
611 this time and over the subsequent few months would contribute to determining the effects of  
612 dust storms on the variability of D and H properties and their escape rates in the upper  
613 atmosphere of Mars.

614

615 These seasonal trends in D densities are global since they are consistent for both  
616 hemispheres. Similar trends have been found for properties of upper atmospheric hydrogen at  
617 Mars [Clarke *et al.*, 2014; 2017; Bhattacharyya *et al.*, 2015; Halekas, 2017]. Studies of water  
618 variability lower in the atmosphere, using spectral analysis of  $\text{H}_2\text{O}$  and HDO as well as using

619 simulations, have shown seasonal differences in the distribution of water and its isotopologues  
620 lower in the martian atmosphere [Montmessin et al., 2005; Krasnopolsky, 2015; Villanueva et  
621 al., 2015; Encrenaz et al., 2016; 2018; Fedorova et al., 2018]

622  
623 The surface in the northern hemisphere of Mars has been found to be as ancient as that  
624 in the southern hemisphere, estimated from underground crater detections [Watters et al.,  
625 2006]. Geological fluvial activity, attributed to covering up many of these craters in the  
626 northern hemisphere, is associated with an enhanced reservoir for subsurface H<sub>2</sub>O and HDO  
627 [Orosei et al., 2018]. The water cycle at Mars includes these reservoirs as sources for upper  
628 atmospheric deuterium [Bertaux and Montmessin, 2001]. Such a resource would plausibly  
629 contribute to asymmetric D abundances with hemisphere [Heavens et al., 2018].

630  
631 Seasonal processes that produce a near 3-fold brightening in deuterium emission on a  
632 planet-wide scale are inferred to produce factors of 3 enhancements in exobase densities and  
633 escape rates in the southern and northern hemispheres. Within the limitations of data  
634 coverage, these trends appear symmetric about southern summer solstice. The D densities and  
635 escape rates found here by analysis of the MAVEN IUVS echelle observations are comparable to  
636 previous theoretical estimates at similar seasonal times. At overhead Sun conditions, the D  
637 exobase density ranges between  $\sim 1\text{--}4 \times 10^3 \text{ cm}^{-3}$ . Extrapolating this density to lower altitudes  
638 using a simplified atmospheric model described in Matta [2013] produces a volume mixing ratio  
639 for deuterium that ranges between 4–22 parts per billion at 80 km for the average temperature  
640 conditions used here.

641  
642 Deriving H densities from these observations requires more comprehensive transfer  
643 modeling to account for the optically thick emission. Efforts are underway to do so in order to  
644 derive and interpret the D/H ratio and its variability in the upper atmosphere of Mars. Based  
645 on the results of this analysis, the properties of D and H are expected to vary with altitude from  
646 the surface to space as well as with season. The variations in D densities in the upper  
647 atmosphere presented in this work will complement derivations of the D/H ratio in the lower  
648 atmosphere of Mars (below 80 km) made by the Trace Gas Orbiter mission [Korablev et al.,  
649 2018; Vandaele et al., 2018]. As more perihelion observations become available, variations due  
650 to hemispherical processes may become more apparent. This variability would provide new  
651 insights into the hydrological cycle at Mars, the effects of dust activity on regional and global  
652 water escape and would be helpful in constraining primordial water content at the planet.

653  
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655



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661 <https://pds.nasa.gov/datasearch/subscription-service/SS-20180215.shtml> for release 12 of the  
662 IUVS level1a and level1c echelle dataset.

663

## 664 **References**

665

666 Anderson, D. and C. Hord (1971), Mariner 1 and 7 Ultraviolet Spectrometer Experiment:  
667 Analysis of Hydrogen Lyman-Alpha Data, *J. of Geophys. Res.*, 76 (28), p. 6666 – 6673.

668

669 Benna, M., P. R. Mahaffy, J. M. Grebowsky, J. L. Fox, R. V. Yelle, and B. M. Jakosky (2015), First  
670 measurements of composition and dynamics of the martian ionosphere by MAVEN's Neutral  
671 Gas and Ion Mass Spectrometer, *Geophys. Res. Lett.*, 42, 8958–8965, doi:10.1002/  
672 2015GL066146.

673

674 Bertaux, J. L., F. Goutail, E. Dimarellis, G. Kockarts, and E. Van Ransbeeck (1984), First optical  
675 detection of atomic deuterium in the upper atmosphere from Spacelab1, *Nature*, 309, 771-773.

676

677 Bertaux, J.L., J. Clarke, M. Mumma, T. Owen, and E. Quemerais (1993), A Search for the  
678 Deuterium Lyman-alpha Emission from the Atmosphere of Mars, in *Science with the Hubble*  
679 *Space Telescope*, ESO Proc. No. 44, 459

680

681 Bertaux, J.-L. and F. Montmessin (2001), Isotopic fractionation through water vapor  
682 condensation: The Deuteropause, a cold trap for deuterium in the atmosphere of Mars, *J.*  
683 *Geophys. Res.*, 106, E12, 32879-32884.

684

685 Bertaux, J.-L., et al. (2006), SPICAM on Mars Express: Observing modes and overview of UV  
686 spectrometer data and scientific results, *J. Geophys. Res.*, 111, E10S90,  
687 doi:10.1029/2006JE002690.

688

689 Bhattacharyya, D., J. T. Clarke, J.-L. Bertaux, J.-Y. Chaufray, and M. Mayyasi (2015), A strong  
690 seasonal dependence in the martian hydrogen exosphere, *Geophys. Res. Lett.*, 42, doi:10.1002/  
691 2015GL065804.

692

693    Bhattacharyya, D., J. Clarke, J.-L. Bertaux, J.-Y. Chaufray and M. Mayyasi (2017a), Analysis and  
694    modeling of remote observations of the martian hydrogen exosphere, *Icarus*, 281, 264-280,  
695    doi:10.1016/j.icarus.2016.08.034.  
696  
697    Bhattacharyya, D., J.T. Clarke, J. Y. Chaufray, M. Mayyasi, J. L. Bertaux, M. S. Chaffin, N. M.  
698    Schneider, G. L. Villanueva (2017b), Seasonal Changes in Hydrogen Escape from Mars Through  
699    Analysis of HST Observations of the Martian Exosphere near Perihelion, *J. Geophys. Res.*,  
700    doi:10.1002/2017JA024572  
701  
702    Bibring, J-P., Y. Langevin, J. Mustard, F. Poulet, R. Arvidson, A. Gendrin, B. Gondet, N. Mangold,  
703    P. Pinet, F. Forget and the OMEGA team (2006), Global Mineralogical and Aqueous Mars History  
704    Derived from OMEGA/Mars Express Data, *Science*, 312, doi:10.1126/science.1122659.  
705  
706    Bougher, S., D. Pawlowski, J. Bell, S. Nelli, T. McDunn, J. Murphy, M. Chizek, and A. Ridley  
707    (2015), Mars Global Ionosphere-Thermosphere Model (MGITM): Solar cycle, seasonal, and  
708    diurnal variations of the Mars upper atmosphere, *J. Geophys. Res. Planets*, 120, 311–342,  
709    doi:10.1002/2014JE004715.  
710  
711    Bougher, S. W., et al. (2017), The structure and variability of Mars dayside thermosphere from  
712    MAVEN NGIMS and IUVS measurements: Seasonal and solar activity trends in scale heights and  
713    temperatures, *J. Geophys. Res. Space Physics*, 122, doi:10.1002/2016JA023454.  
714  
715    Carr, M. (1986), Mars: A Water-Rich Planet?, *Icarus*, 68, 187-216.  
716  
717    Chaffin, M., J.-Y. Chaufray, I. Stewart, F. Montmessin, N. Schneider, J.-L. Bertaux (2014),  
718    Unexpected variability of Martian hydrogen escape, *Geophys. Res. Lett.*, 41 (2)  
719  
720    Chaffin, M., et al. (2015), Three-dimensional structure in the Mars H corona revealed by  
721    IUVS on MAVEN, *Geophys. Res. Lett.*, 42, 9001–9008, doi:10.1002/2015GL065287.  
722  
723    Chaffin, M., J. Deighan, N. Schneider & I. Stewart (2017), Elevated atmospheric escape of  
724    hydrogen from Mars induced by high-altitude water, *Nat. Geosci.*, 10, 174–178.  
725  
726    Chaffin, M., J.-Y. Chaufray, J. Deighan, N. Schneider, M. Mayyasi, J., Clarke, et al. (2018), Mars H  
727    escape rates derived from MAVEN/IUVS Lyman alpha brightness measurements and their  
728    dependence on model assumptions, *J. Geophys. Res.*, 123, 2192–2210,  
729    https://doi.org/10.1029/2018JE005574  
730

731 Chaufray, J.Y., Bertaux, J.L., LeBlanc, F., Quemerais, E., 2008. Observation of the hydrogen  
732 corona with SPICAM on Mars express. *Icarus* 195, 598–613.  
733

734 Chaufray, J.-Y., F. Gonzalez-Galindo, F. Forget, M. Lopes-Valverde, F. Leblanc, R. Modolo and S.  
735 Hess (2015), Variability of the hydrogen in the martian upper atmosphere as simulated by a 3D  
736 atmosphere-exosphere coupling, 245, p. 282 – 294.  
737

738 Chaufray, J.-Y., R. Yelle, F. Gonzalez-Galindo, F. Forget, M. Lopez-Valverde, F. LeBlanc, and R.  
739 Modolo (2018), Effect of lateral exospheric transport on the horizontal hydrogen distribution  
740 near the exobase of Mars, *J. Geophys. Res.*, doi:10.1002/2017JA025163.  
741

742

743 Clarke, J.T., Bertaux, J.-L., Chaufray, J.-Y., Gladstone, G.R., Quemerais, E., Wilson, J.K.,  
744 Bhattacharyya, D. (2014), A rapid decrease of the hydrogen corona of Mars, *Geophys. Res. Lett.*,  
745 41, 8013–8020. doi:10.1002/2014GL061803.  
746

747 Clarke, J. T., Mayyasi, M., Bhattacharyya, D., Schneider, N. M., McClintock, W. E., Deinghan, J. L.,  
748 ... Jakosky, B. M. (2017), Variability of D and H in the martian upper atmosphere observed with  
749 the MAVEN IUVS echelle channel. *Journal of Geophysical Research: Space Physics*, 122, 2336–  
750 2344, doi: 10.1002/2016JA023479  
751

752 Clarke, J. (2018), Dust-enhanced water escape, *Nature*, [https://doi.org/10.1038/s41550-018-](https://doi.org/10.1038/s41550-018-0383-6)  
753 0383-6  
754

755 Cui, J., R. Yelle, V. Vuitton, J. Waite, W. Kasprzak, D. Gell, H. Niemann, I. Müller-Wodarg, N.  
756 Borggren, G. Fletcher, E. Patrick, E. Raaen and B. Magee (2009), Analysis of Titan’s neutral  
757 upper atmosphere from Cassini Ion Neutral Mass Spectrometer measurements, *Icarus*, 200, 581  
758 – 615, doi: 10.1016/j.icarus.2008.12.005.  
759

760 Ehlmann, B. and C. Edwards (2014), Mineralogy of the Martian Surface, *Annu. Rev. Earth Planet.*  
761 *Sci.*, 42, 291 – 315, doi:10.1146/annurev-earth-060313-055024.  
762

763 Emerich, C., P. Lemaire, J.-C Vial, W. Curdt, U. Schuhle, W. Klaus (2005), A new relation between  
764 the central spectral solar H I Lyman  $\alpha$  irradiance and the line irradiance measured by  
765 SUMER/SOHO during the cycle 23, *Icarus*, 178, doi:10.1016/j.icarus.2005.05.002  
766

767 Encrenaz, T., C. DeWitt, M. Richter, T. Greathouse, T. Fouchet, F. Montmessin, F. Lefèvre, F.  
768 Forget, B. Bézard, S. Atreya, M. Case, and N. Ryde (2016), A map of D/H on Mars in the thermal  
769 infrared using EXES aboard SOFIA, *Astro. Astrophys.*, 586, A62, doi: 10.1051/0004-6361  
770 /201527018.

771  
772 Encrenaz, T., C. DeWitt, M. Richter, T. Greathouse, T. Fouchet, F. Montmessin, F. Lefèvre, B.  
773 Bézard, S. Atreya, S. Aoki, and H. Sagawa (2018), New measurements of D/H on Mars using  
774 EXES aboard SOFIA, *Astro. & Astroph.*, 612, A112, doi:10.1051/0004-6361/201732367.  
775  
776 Eparvier, F., Chamberlin, P., Woods, T., Thiemann, E. (2015), The solar extreme ultraviolet  
777 monitor for MAVEN, *Space Science Reviews*, 195(1-4), 293–301, doi:10.1007/s11214-015-0195-  
778 2  
779  
780 Fedorova, A., Bertaux, J.-L., Betsis, D., Montmessin, F., Korablev, O., Maltagliati, L., and Clarke, J.  
781 (2018), Water vapor in the middle atmosphere of Mars during the 2007 global dust storm,  
782 *Icarus*, 300, 440–457.  
783  
784 Fernández, W. (1998). Martian dust storms: A review, *Earth, Moon, and Planets*, 77, 19–46.  
785  
786 Fisher, D. A. (2007), Mars' water isotope (D/H) history in the strata of the North Polar Cap:  
787 Inferences about the water cycle, *Icarus*, 187, 430-441, doi:10.1016/j.icarus.2006.10.032.  
788  
789 Forget, F., F. Hourdin, R. Fournier, C. Hourdin, O. Talagrand, M. Collins, S. R. Lewis, P. L. Read,  
790 and J.-P. Huot (1999), Improved general circulation models of the martian atmosphere from the  
791 surface to above 80 km, *J. Geophys. Res.*, 104, 24155–24176.  
792  
793 Gillmann, C., P. Lognonné and M. Moreira (2011), Volatiles in the atmosphere of Mars: The  
794 effects of volcanism and escape constrained by isotopic data, *Earth Planet. Sci. Lett.*, 303, 299-  
795 309, doi:10.1016/j.epsl.2011.01.009.  
796  
797 Halekas, J. (2017), Seasonal variability of the hydrogen exosphere of Mars, *J. Geophys. Res.*,  
798 122, 901–911, doi:10.1002/2017JE005306.  
799  
800 Head, J., J. Mustard, M. Kreslavsky, R. Milliken and D. Marchant (2003), Recent ice ages on  
801 Mars. *Nature*, 426, 797-802, doi:10.1038/nature02114.  
802  
803 Heavens, N., A. Kleinböhl, M. Chaffin, J. Halekas, D. Kass, P. Hayne, D. McCleese, S. Piqueux, J.  
804 Shirley, and J. Schofield (2018), Hydrogen escape from Mars enhanced by deep convection in  
805 dust storms, *Nature*, 2, 126 – 132, doi: 10.1038/s41550-017-0353-4.  
806  
807 Hodges, R. and F. Johnson (1968), Lateral Transport in Planetary Exospheres, *J. Geophys. Res.*,  
808 73 (23), 7307–7317.  
809

810 Horner, J., O. Mousis, J.-M. Petit and B. Jones (2009), Differences between the impact regimes  
811 of the terrestrial planets: Implications for primordial D:H ratios, *Planet. Sp. Sci.*, 57, 1338-1345,  
812 doi:10.1016/j.pss.2009.06.006.  
813

814 Hunten, D. M., and M. B. McElroy (1970), Production and escape of hydrogen on Mars, *J.*  
815 *Geophys. Res.*, 75, 5989–6001, doi:10.1029/JA075i031p05989.  
816

817 Jakosky, B. (2015). MAVEN explores the martian upper atmosphere, *Science*, 350(6261), 643.  
818 <https://doi.org/10.1126/science.aad3443>  
819

820 Jakosky, B., R. Pepin, R. Johnson and J. Fox (1994), Mars Atmospheric Loss and Isotopic  
821 Fractionation by Solar-Wind-Induced Sputtering and Photochemical Escape, *Icarus*, 111, 271-  
822 288.  
823

824 Jakosky, B., M. Slipski, M. Benna, P. Mahaffy, M. Elrod, R. Yelle, S. Stone, and N. Alsaeed (2017),  
825 Mars' atmospheric history derived from upper-atmosphere measurements of  $^{38}\text{Ar}/^{36}\text{Ar}$ ,  
826 *Science*, 355, 1408-1410, doi:10.1126/science.aai7721.  
827

828 Jakosky et al. (2018), Loss of the Martian atmosphere to space: Present-day loss rates  
829 determined from MAVEN observations and integrated loss through time, *Icarus*, 315, 146 –  
830 157.  
831

832 Jeans, J. H. (1925), *The Dynamical Theory of Gases*, 4th ed., Cambridge Univ. Press,  
833 Cambridge, U. K.  
834

835 Kass, D. and Y. Yung (1999), Water on Mars: Isotopic constraints on exchange between the  
836 atmosphere and surface, *Geophys. Res. Lett.*, 26 (24), 3656-3656  
837

838 Korablev, O. et al (2018), The Atmospheric Chemistry Suite (ACS) of Three Spectrometers for  
839 the ExoMars 2016 Trace Gas Orbiter, *Sp. Sc. Rev.*, 214:7, doi:10.1007/s11214-017-0437-6  
840

841 Krasnopolsky, V., M. Mumma and G. Gladstone (1998), Detection of Atomic Deuterium in the  
842 Upper Atmosphere of Mars, *Science*, 280, 1576-1580, doi:10.1126/science.280.5369.1576.  
843

844 Krasnopolsky, V. (2000), On the Deuterium Abundance on Mars and Some Related Problems,  
845 *Icarus*, 148, 597-602, doi:10.1006/icar.2000.6534.  
846

847 Krasnopolsky, V. (2002), Mars' upper atmosphere and ionosphere at low, medium, and high  
848 solar activities: implications for evolution of water, *J. Geophys. Res.*, 107, 5128,  
849 doi:10.1029/2001JE001809.  
850

851 Krasnopolsky, V. (2015), Variations of the HDO/H<sub>2</sub>O ratio in the martian atmosphere and loss of  
852 water from Mars, *Icarus*, 257, 377-386, doi: 10.1016/j.icarus.2015.05.021.  
853

854 Lammer, H., E. Chassefière, Ö. Karatekin, A. Morschhauser, P. Niles, .... (2013), Outgassing  
855 History and Escape of the martian Atmosphere and Water Inventory, *Space Sc. Rev.*, 174, 113 –  
856 154, doi:10.1007/s11214-012-9943-8.  
857

858 Lee et al., 2018: Observations and Impacts of the 10 September 2017 Solar Events at Mars: An  
859 Overview and Synthesis of the Initial Results, *Geophys. Res. Lett.*, doi: 10.1029/2018gl079162  
860

861 Lewis, S. R., M. Collins, P. L. Read, F. Forget, F. Hourdin, R. Fournier, C. Hourdin, O. Talagrand,  
862 and J.-P. Huot (1999), A climate database for Mars, *J. Geophys. Res.*, 104, 24177–24194.  
863

864 Mahaffy, P., and 33 coauthors (2014), The Neutral Gas and Ion Mass Spectrometer on the Mars  
865 Atmosphere and Volatile Evolution Mission, *Space Sci. Rev.*, doi: 10.1007/s11214-014-0091-1.  
866

867 Mahaffy, P., Webster, C. R., Stern, J. C., Brunner, A. E., Atreya, S. K., Conrad, P. G., ... the MSL  
868 Science Team (2015), The imprint of atmospheric evolution in the D/H of Hesperian clay  
869 minerals on Mars, *Science*, 347(6220), 412–414, doi:10.1126/science.1260291.  
870

871 Mahaffy, P. R., M. Benna, M. Elrod, R. V. Yelle, S. W. Bougher, S. W. Stone, and B. M. Jakosky  
872 (2015), Structure and composition of the neutral upper atmosphere of Mars from the MAVEN  
873 NGIMS investigation, *Geophys. Res. Lett.*, 42, 8951–8957, doi:10.1002/2015GL065329.  
874

875 Matta, M. M. (2013), Modeling the Martian Ionosphere, PhD, Boston Univ., Boston, Mass.  
876

877 Matta, M., P. Withers, and M. Mendillo (2013), The composition of Mars' topside ionosphere:  
878 Effects of hydrogen, *J. Geophys. Res. Space Physics*, 118, 2681–2693, doi:10.1002/jgra.50104  
879

880 Mayyasi, M., Clarke, J., Quénerais, E., Katushkina, O., Bhattacharyya, D., Chaufray, J.-Y., ...  
881 Jakosky, B. (2017a). IUVS echelle-mode observations of interplanetary hydrogen: Standard for  
882 calibration and reference for cavity variations between Earth and Mars during MAVEN cruise.  
883 *Journal of Geophysical Research: Space Physics*, 122, doi:10.1002/2016JA023466  
884

885 Mayyasi, M., Clarke, J., Bhattacharyya, D., Deighan, J., Jain, S., Chaffin, M., ... Jakosky, B.  
886 (2017b). The variability of atmospheric deuterium brightness at Mars: Evidence for seasonal  
887 dependence. *Journal of Geophysical Research: Space Physics*, 122, doi:10.1002/2017JA024666  
888

889 Mayyasi, M., Bhattacharyya, D., Clarke, J., Catalano, A., Benna, M., Mahaffy, P., et al. (2018),  
890 Significant Space Weather Impact on the Escape of Hydrogen from Mars, *Geophys. Res. Let.*, 45,  
891 8844-8852, <https://doi.org/10.1029/2018GL077727>.  
892

893 McClintock, W., N. Schneider, G. Holsclaw, J. Clarke, A. Hoskins, I. Stewart, F. Montmessin, R.  
894 Yelle, J. Deighan (2015). The Imaging Ultraviolet Spectrograph (IUVS) for the MAVEN mission.  
895 *Space Science Reviews*, 195(1-4), 75–124. <https://doi.org/10.1007/s11214-014-0098-7>  
896

897 Montmessin, F., T. Fouchet and F. Forget (2005), Modeling the annual cycle of HDO in the  
898 martian atmosphere, *J. Geophys. Res.*, 110, E03006, doi:10.1029/2004JE002357.  
899

900 Nagy, A., A. Balogh, T. Cravens, M. Mendillo, I. Müller-Wodarg (Eds.), *Mars Aeronomy*, ISBN  
901 978-0-387-87824-9, published in January 2009.  
902

903 Orosei, R., et al. (2018), Radar evidence of subglacial liquid water on Mars, *Science*,  
904 10.1126/science.aar7268 (2018)  
905

906 Owen, T., (1992), The Composition and Early History of the Atmosphere of Mars, *Mars*, ed. H.  
907 Kieffer, B. Jakosky, C. Snyder and M. Matthews (Tucson: University of Arizona Press), 818 – 834.  
908

909 Smith, M., Wolff, M., Clancy, T., Murchi, S. (2009), Compact Reconnaissance Imaging  
910 Spectrometer observations of water vapor and carbon monoxide, *J. Geophys. Res.*, 114,  
911 E00D03, doi:10.1029/2008JE003288.  
912

913 Solomon, S., O. Aharonson, J. Aurnou, W. Banerdt, M. Carr, ... (2005), New Perspectives on  
914 Ancient Mars, *Science*, 307 (5713), 1214 – 1220, doi: 10.1136/science.1101812.  
915

916 Stone, S., R. Yelle, P. Mahaffy, M. Benna, M. Elrod, S. Bougher (2016), Temperature Variations in  
917 the Martian Upper Atmosphere from the MAVEN Neutral Gas and Ion Mass Spectrometer, AAS  
918 DPS meeting #48, id.303.08.  
919

920 Stone, S., R. Yelle, M. Benna, M. Elrod, P. Mahaffy (2018), Thermal structure of the martian  
921 upper atmosphere from MAVEN NGIMS, *J. Geophys. Res.*, doi: 10.1029/2018JE005559.  
922

923 Trokhimovskiy, A., A. Fedorova, O. Korablev, F. Montmessin, J-L. Bertaux, A. Rodin and M. Smith  
924 (2015), Mars' water vapor mapping by the SPICAM IR spectrometer: Five martian years of  
925 observations, *Icarus*, 251, p. 50 – 64, doi:10.1016/j.icarus.2014.10.007.  
926

927 Vandaele, A-C., (2018), NOMAD, an Integrated Suite of Three Spectrometers for the ExoMars  
928 Trace Gas Orbiter Mission: Technical Description, Science Objectives and Expected  
929 Performance, *Sp. Sci. Rev.*, 214:80, doi:10.1007/s11214-018-0517-2.  
930

931 Vidal-Madjar, A. and J.-L. Bertaux (1972), A calculated hydrogen distribution in the exosphere,  
932 *Planet. Sp. Sci.*, 20, p. 1147 – 1162.  
933

934 Villanueva, G., Mumma, M., Novak, R., Käufl, H., Hartogh, P., Encrenaz, T., ... Smith, M. (2015),  
935 Strong water isotopic anomalies in the martian atmosphere: Probing current and ancient  
936 reservoirs, *Science*, 348(6231), 218–221, doi:10.1126/science.aaa3630.  
937

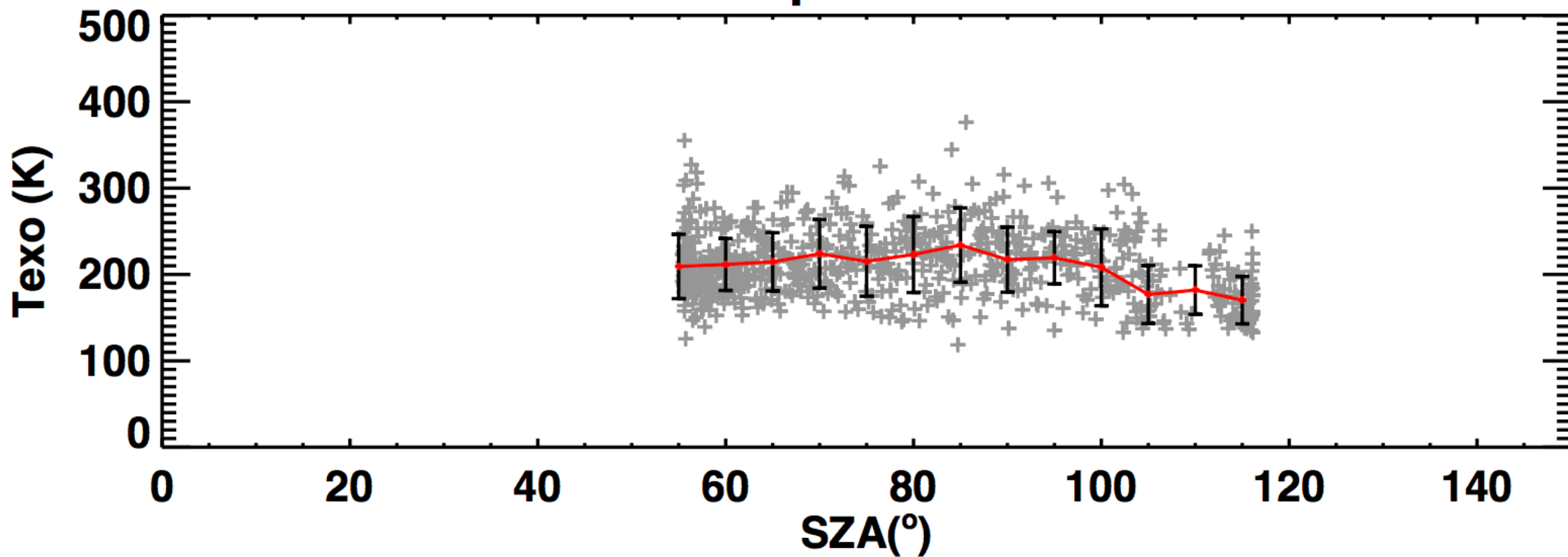
938 Watters, T., C. Leuschen, J. Plaut, G. Picardi, A. Safaenili, S. Clifford, W. Farrell, A. Ivanov, R.  
939 Phillips, and E. Stofan (2006), MARSIS radar sounder evidence of buried basins in the northern  
940 lowlands of Mars, *Nature*, 444, 905 – 908, doi: 10.1038/nature05356.  
941

942 Yung, Y., J.-S. Wen, J. Pinto, M. Allen, K. Pierce and S. Paulson (1988), HDO in the Martian  
943 Atmosphere: Implications for the Abundance of Crustal Water, *Icarus*, 76, 146 – 159.



Figure 1.

## Aphelion



## Perihelion

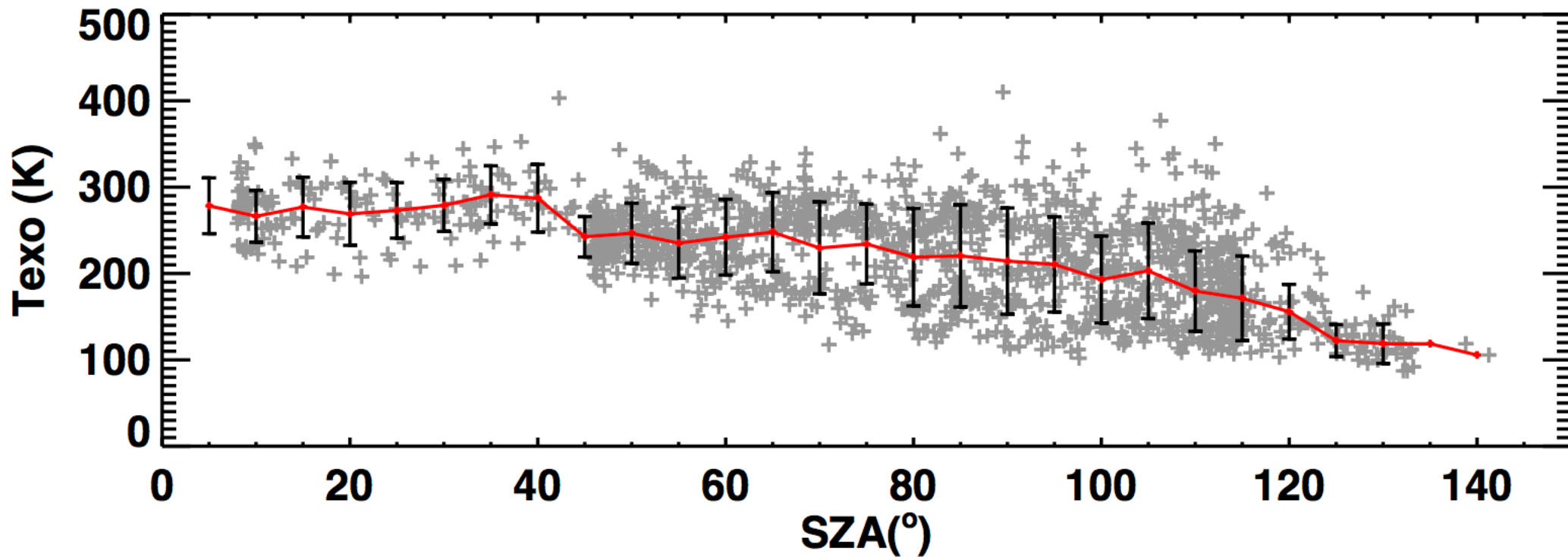


Figure 2.

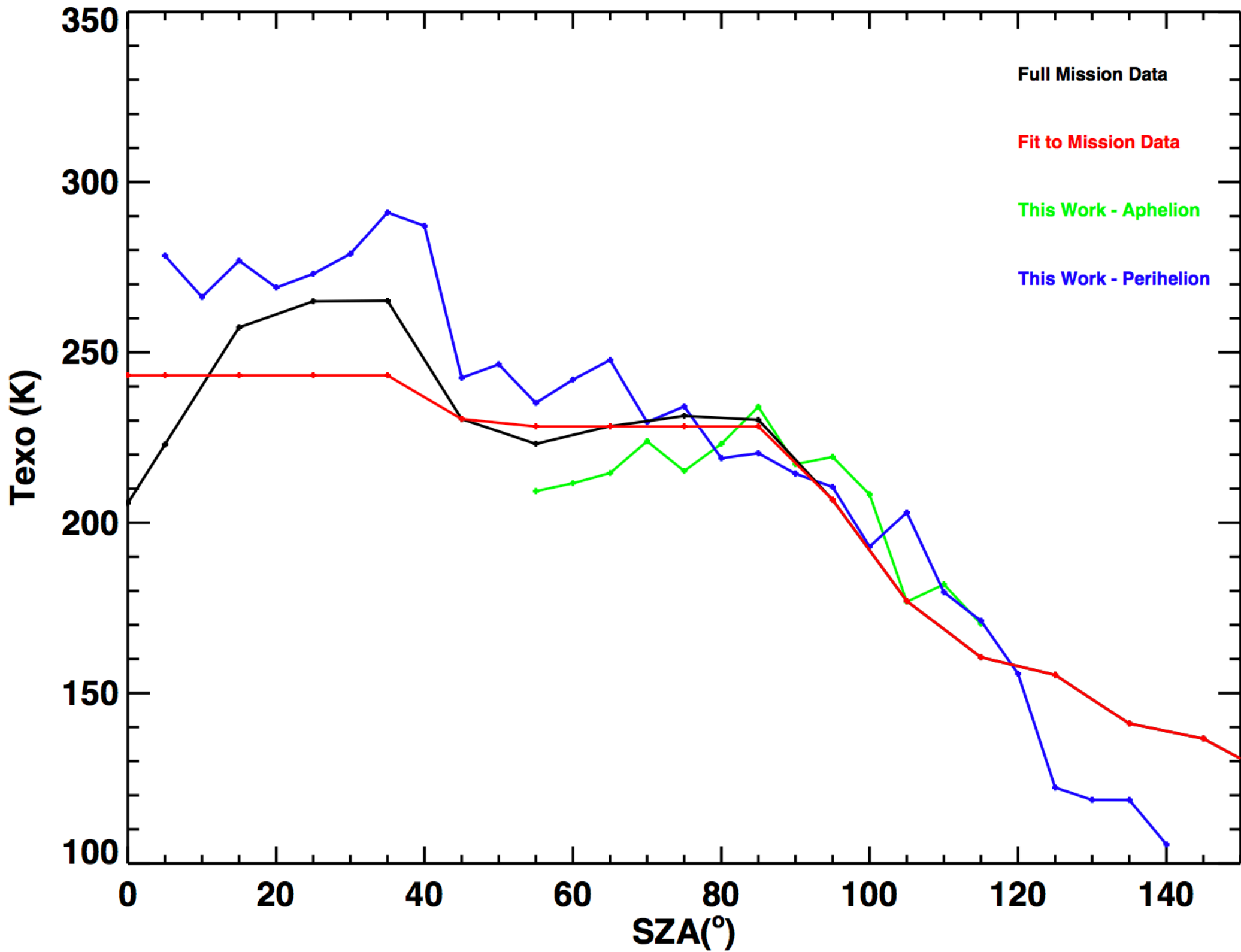
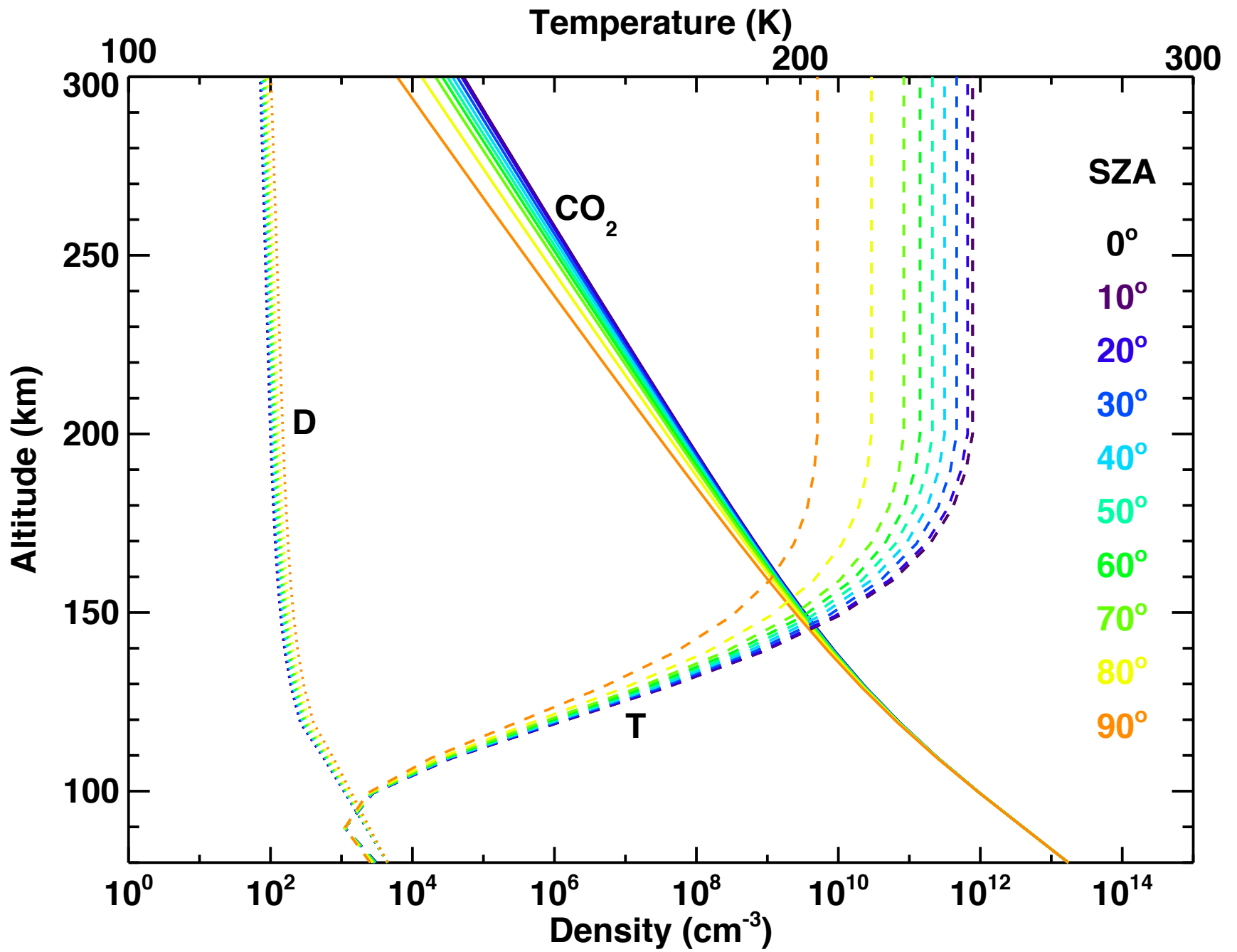


Figure 3.



**Figure 4.**

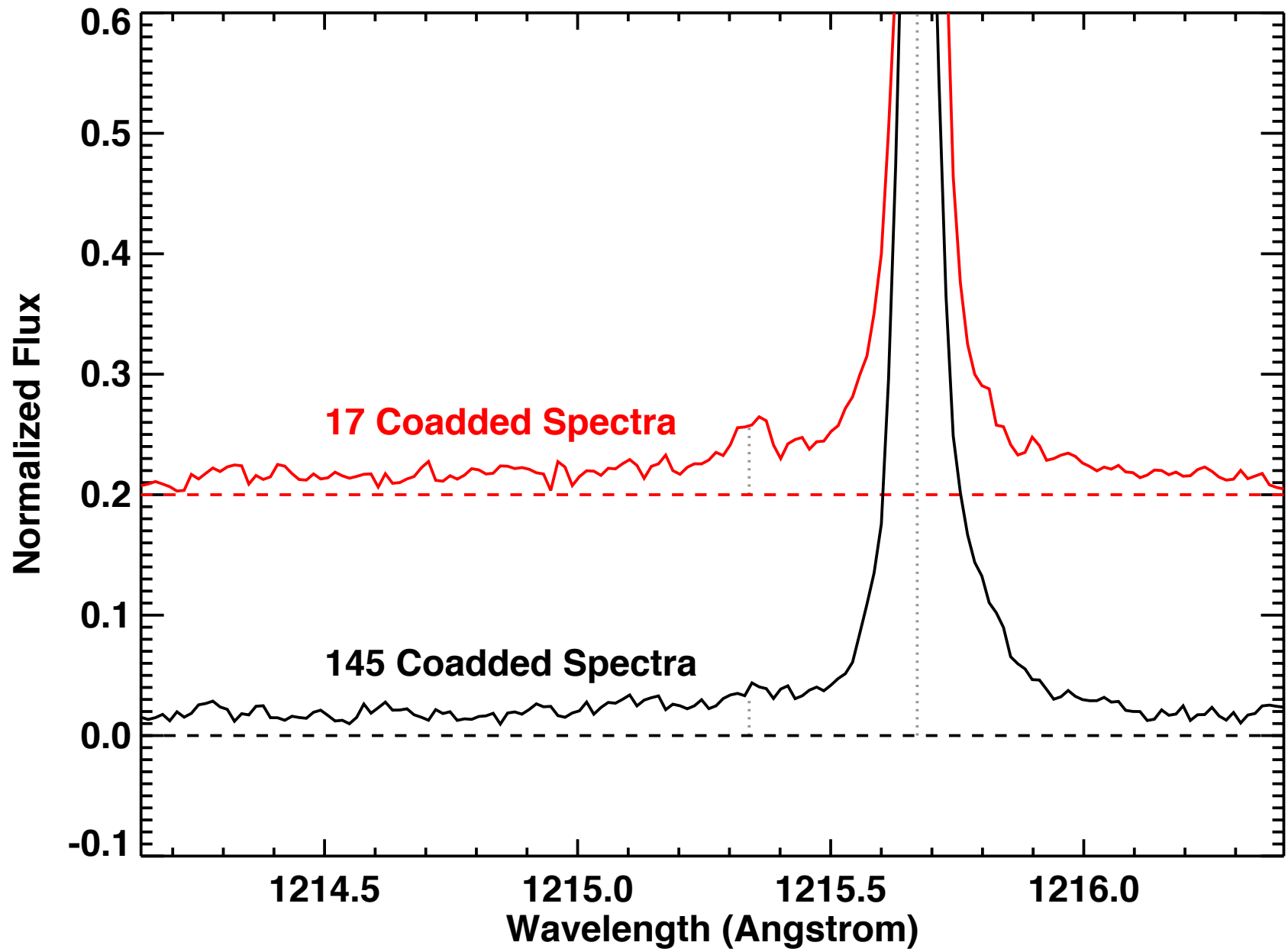




Figure 5.

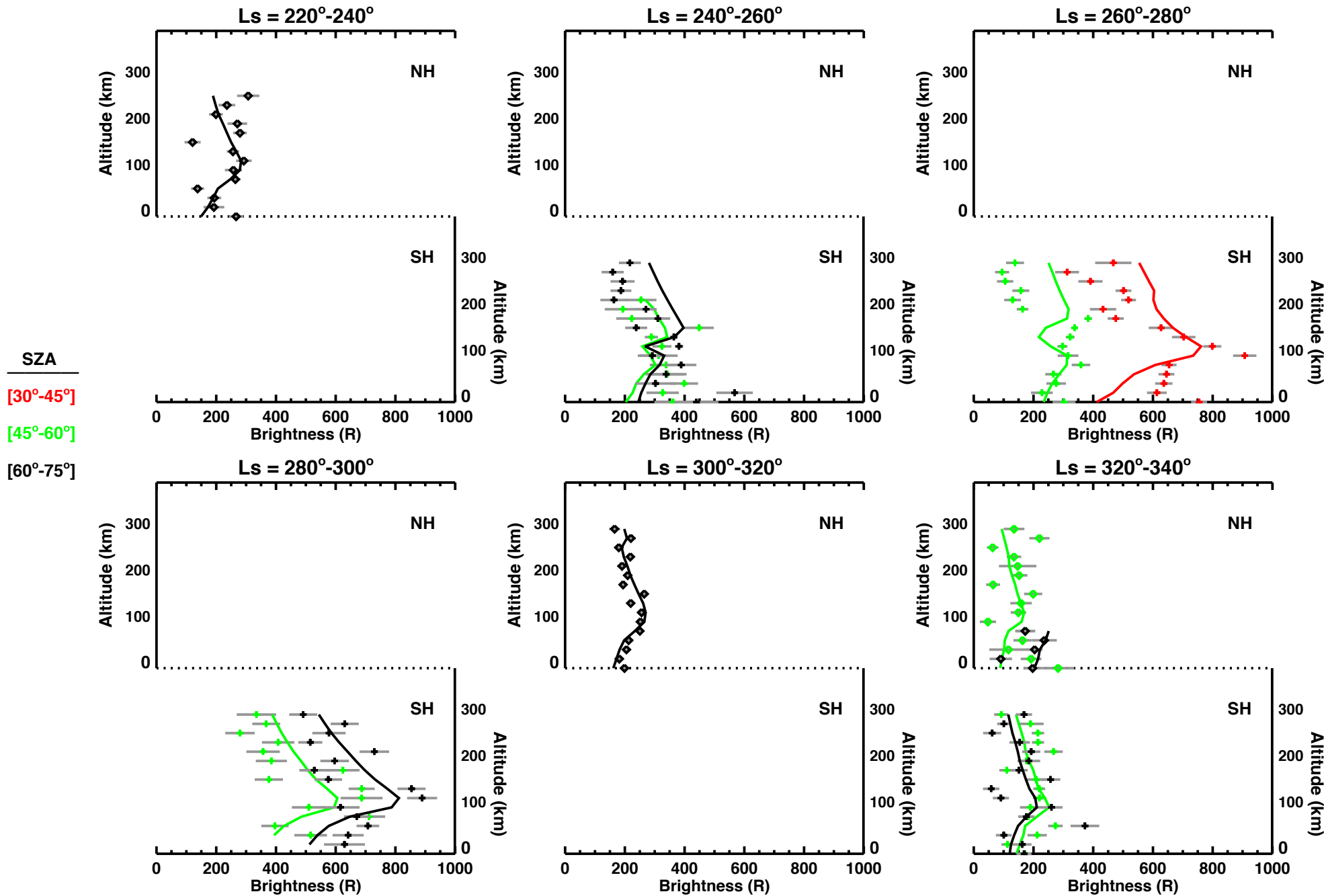


Figure 6.

