

1 Photochemistry on the bottom side of the mesospheric Na layer

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## 8 **Abstract**

9 Lidar observations of the mesospheric Na layer have revealed considerable diurnal variations  
10 particularly on the bottom side of the layer where more than an order-of-magnitude increase of Na  
11 density has been observed below 80 km after sunrise. In this paper, multi-year Na lidar observations over  
12 a full diurnal cycle at Utah State University (USU) (41.8°N, 111.8°W) and a global atmospheric model of  
13 Na with 0.5 km vertical resolution in the mesosphere and lower thermosphere (WACCM-Na) are utilized  
14 to explore the dramatic changes of Na density on the layer bottom side. Photolysis of the principal  
15 reservoir NaHCO<sub>3</sub> is shown to be primarily responsible for the increase in Na after sunrise, amplified by  
16 the increased rate of reaction of NaHCO<sub>3</sub> with atomic H, which is mainly produced from the photolysis  
17 of H<sub>2</sub>O and the reaction of OH with O<sub>3</sub>. This finding is further supported by Na lidar observation at USU  
18 during the solar eclipse (> 96% totality) event on August 21<sup>st</sup>, 2017, when a decrease and recovery of the  
19 Na density on the bottom side of the layer were observed. Lastly, the model simulation shows that the Fe  
20 density below around 80 km increases more strongly and earlier than observed Na changes during sunrise  
21 because of the considerably faster photolysis rate of its major reservoir FeOH.

## 22 **1. Introduction**

23 The layer of Na atoms in the upper mesosphere and lower thermosphere (MLT, ~ 80-105 km in  
24 altitude), is formed naturally by meteoric ablation along with other metallic layers such as Fe, Mg, Ca  
25 and K [Plane et al., 2015]. The climatological variations of this Na layer are known to be mainly  
26 controlled by a series of chemical reactions and dynamics, including tides, gravity waves and the mean  
27 circulation in the MLT [Plane, 2004, Marsh et al., 2013]. Mesospheric Na atoms are an important tracer  
28 in the MLT, where they are observed by resonance fluorescence, either by the lidar technique [Krueger et

29 al., 2015] or solar-pumped dayglow from space [Fan et al., 2007]. The Na lidar technique has enabled  
30 high temporal and spatial resolution measurements of the mesospheric Na layer since the 1970s  
31 [Sandford and Gibson, 1970]. In addition to Na density observations, Na temperature/wind lidars can  
32 measure the atmospheric temperature and wind fields over the full diurnal cycle by observing Doppler  
33 broadening and shifting of the hyperfine structure of one of the Na D lines [Krueger et al., 2015].  
34 Atmospheric observations have been complemented by laboratory kinetic studies of the important  
35 reactions which control both the neutral and ion-molecule chemistry of Na in the MLT [Plane, 1999;  
36 2004; Plane et al., 2015], and the development of atmospheric models which satisfactorily reproduce  
37 seasonal observations over most latitudes [Plane, 2004; Marsh et al., 2013; Li et al., 2018]

38         However, less detailed work has been done to investigate the diurnal variations in Na density,  
39 especially on the bottom side of the layer where neutral chemistry dominates. Advances in lidar  
40 technology have enabled Na density observations over a full diurnal cycle [Chen et al., 1996; States and  
41 Gardner, 1999; Clemesha et al., 2002; Yuan et al., 2012]. Utilizing multi-year observations, Yuan et al.  
42 [2012] investigated the diurnal variation and tidal period perturbations of the Na density. These tidal Na  
43 perturbations were then used to estimate the tidal vertical wind perturbations [Yuan et al., 2014], showing  
44 that, although closely correlated with tidal waves and dominated by tidal wave modulations in the lower  
45 thermosphere, the Na diurnal and semidiurnal variations cannot be induced by tidal modulations alone.  
46 This is especially the case on the bottom side of the layer below  $\sim 90$  km, where tidal wave amplitudes  
47 are relatively small (see Figure 5a and 5b in Yuan et al., 2012), implying that other mechanisms make a  
48 significant contribution to the diurnal variation of the Na layer bottom side.

49         Plane et al. [1999] recognized the important role of photochemical reactions for characterizing the  
50 bottom side of the Na layer, and then measured the photolysis cross sections of several Na-containing  
51 molecules – NaO, NaO<sub>2</sub>, NaOH and NaHCO<sub>3</sub>, which models show to be significant mesospheric  
52 reservoir species [Self and Plane, 2002, Marsh et al., 2013]. These cross sections, measured at  
53 temperatures appropriate to the MLT, were then used to calculate mesospheric photolysis rates:

|    |                                                              |                                     |    |
|----|--------------------------------------------------------------|-------------------------------------|----|
| 54 | $\text{NaO} + h\nu \rightarrow \text{Na} + \text{O}$         | $5.5 \times 10^{-2} \text{ s}^{-1}$ | R1 |
| 55 | $\text{NaO}_2 + h\nu \rightarrow \text{Na} + \text{O}_2$     | $1.9 \times 10^{-2} \text{ s}^{-1}$ | R2 |
| 56 | $\text{NaOH} + h\nu \rightarrow \text{Na} + \text{OH}$       | $1.8 \times 10^{-2} \text{ s}^{-1}$ | R3 |
| 57 | $\text{NaHCO}_3 + h\nu \rightarrow \text{Na} + \text{HCO}_3$ | $1.3 \times 10^{-4} \text{ s}^{-1}$ | R4 |

58           These *direct* photochemical reactions release atomic Na during daytime. Furthermore, *indirect*  
59 photochemistry also plays a role. The photolysis of O<sub>2</sub>, O<sub>3</sub> and H<sub>2</sub>O [Brasseur and Solomon, 2005] lead  
60 to the production of H and O (R5 – R8), increasing their concentrations by more than 1 order of  
61 magnitude during daytime at an altitude around 80 km [Plane, 2003]. The daily variation of H is further  
62 facilitated by the reactions between HO<sub>2</sub> and O/O<sub>3</sub>, which has strong diurnal variations.

|    |                                                                           |  |    |
|----|---------------------------------------------------------------------------|--|----|
| 63 | $\text{O}_2 + h\nu \rightarrow 2\text{O}$                                 |  | R5 |
| 64 | $\text{O}_3 + h\nu \rightarrow \text{O} + \text{O}_2$                     |  | R6 |
| 65 | $\text{H}_2\text{O} + h\nu \rightarrow \text{H} + \text{OH}$              |  | R7 |
| 66 | $\text{OH} + \text{O} \rightarrow \text{H} + \text{O}_2$                  |  | R8 |
| 67 | $\text{NaHCO}_3 + \text{H} \rightarrow \text{Na} + \text{H}_2\text{CO}_3$ |  | R9 |

68 Thus, H and O reduce these Na compounds listed above to atomic Na [Plane, 2004].

69           To demonstrate the effect of solar radiation on mesospheric Na layer, including R1-R8, Figure 1  
70 shows the averaged Na density variation in the layer between 75 km and 105 km during a 6-hour period  
71 that straddles sunrise (from 3 hours before to 3 hours after sunrise) in the fall season (from August 20 to  
72 September 30). The results are based on 50 days of Na lidar observations at USU (41.8°N, 111.8°W)  
73 between 2011 and 2016. Figure 1 also includes the ratio profile between the Na density 3 hours after  
74 sunrise to that 3 hours before sunrise. The lidar observations clearly show that, while there is an overall  
75 Na density increase after sunrise below ~ 92 km, the increase at and below 80 km is much larger than

76 closer to the layer peak: the Na density increases by a factor of  $\sim 6$  at 80 km and  $\sim 40$  near 78 km,  
77 whereas it is almost unchanged around  $\sim 95$  km. The dramatic oscillation of the ratio below 78 km is due  
78 to very low Na density before sunrise (usually below  $1 \text{ cm}^{-3}$ ). Note that this ratio calculation for Na  
79 density profiles 1 hour before and 1 hour after sunrise generates a similar ratio profile, which  
80 demonstrated even larger ratio near 80 km, a factor of  $\sim 20$ . This implies very quick Na density  
81 enhancement during the process of sunrise. This analysis therefore provides strong evidence for the  
82 impact of photochemistry on the bottom side of the Na layer.

83 In this paper we compare the USU Na lidar diurnal cycle observations of the mesospheric Na  
84 layer during a continuous 7-day campaign in fall 2012 with the Na density variation simulated by  
85 NCAR's Whole Atmosphere Community Climate Model with Na chemistry (WACCM-Na) [Marsh et al.,  
86 2013] for the USU location during the same period, in order to investigate quantitatively the role of  
87 photochemistry on the Na layer. In addition, Fe density variation by the latest WACCM-Fe [Feng et al.,  
88 2017] due to photolysis is also discussed to show the distinct feature of the Fe in the bottom side of the  
89 main layer. The Na Lidar measurements made during the solar eclipse on August 21, 2017 in North  
90 America are then used as a further robust test of the role of photolysis.

## 91 **2. Instrument and Model description**

92 The USU Na Temperature/Wind lidar system, originally developed at Colorado State University, has  
93 been operating at the USU main campus since summer 2010. In addition to Na density observations,  
94 neutral temperature and winds are also measured for the mesopause region ( $\sim 80$ - $110$  km) [Krueger et al.,  
95 2015]. The lidar return signals can be recorded in 150 m bins in the line-of-sight direction, and saved  
96 every minute. Facilitated by a pair of customized Faraday filters deployed at its receiver [Harrell et al.,  
97 2009], this advanced lidar system can also reject the sky background significantly during daytime, while  
98 receiving the Na echo with minimum loss. This technique provides robust measurements of these  
99 important atmospheric parameters under sunlight condition, thereby enabling this investigation of Na  
100 photochemistry. In this study, we focus on two sets of Na lidar data: Na density data taken between UT

101 Day 271 (September 27) and UT Day 277 (October 3) of 2012 and lidar observations during the solar  
102 eclipse on August 21, 2017. The lidar observations presented here are processed with 2-km vertical  
103 resolution, and 10-minute and 30-minute temporal resolution for nighttime and daytime data,  
104 respectively, to achieve appropriate signal to noise (S/N) for studying the bottom side of the layer  
105 between 75 and 80 km, where the Na density is low ( $<100 \text{ cm}^{-3}$ ). The lidar observations during the solar  
106 eclipse are processed with 10-minute resolution to investigate the potential eclipse-induced perturbations  
107 in detail.

108 WACCM-Na is a global meteoric Na model which satisfactorily reproduces lidar and satellite  
109 measurements of the Na layer [e.g., Marsh et al., 2013; Dunker et al., 2015; Plane et al., 2015; Langowski  
110 et al., 2017; Dawkins et al., 2016; Feng et al., 2017]. WACCM-Na uses the Community Earth System  
111 Model (version 1) framework [e.g., Hurrell et al., 2013], which includes detailed physical processes as  
112 described in the Community Atmosphere Model, version 4 (CAM4) [Neale et al., 2012], and has the fully  
113 interactive chemistry described in Kinnison et al. [2007]. The current configuration for WACCM is based  
114 on a finite volume dynamical core [Lin, 2004] for tracer advection. Water vapor in WACCM is  
115 prognostic and includes the source in the stratosphere from methane oxidation. The approximate water  
116 vapor concentration at the USU Na lidar site between 75 and 80 km on the day of the eclipse is  $1\text{-}3 \times 10^9$   
117  $\text{cm}^{-3}$  (equivalent to 3-5 ppmv). For the present study, we used a specific dynamics (SD) version of  
118 WACCM, in which winds and temperatures below 50-60 km are nudged towards NASA's Modern-Era  
119 Retrospective Analysis for Research and Applications (MERRA) [Lamarque et al., 2012]. The horizontal  
120 resolution is  $1.9^\circ$  latitude  $\times$   $2.5^\circ$  longitude. For this study we performed model experiments using two  
121 different vertical resolutions: 88 and 144 vertical model levels (termed as lev88 and lev144), both have  
122 the same 62 vertical levels from surface to 0.42 Pa (below  $\sim 50$  km) as MERRA with different vertical  
123 resolutions above 0.42 Pa. Basically, lev88, which has been used as a standard SD-WACCM, gives a  
124 coarse height resolution from  $\sim 1.9$  to  $\sim 3.5$  km above the upper stratosphere to MLT, while lev144  
125 increases the resolution from 1.9 km down to around 500 m in MLT [Merkel et al., 2009; Viehl et al.,  
126 2016]. The Na reaction scheme described in Plane et al. (2015) is updated with the results of recent

127 laboratory studies [Gomez-Martin et al., 2016; 2017], and the meteoric input function (MIF) of Na from  
128 Cárriillo-Sanchez et al. (2016) is used. Note that the absolute Na MIF used in this paper is the same as in  
129 Li et al. (2018) and Plane et al. (2018); i.e., it has been divided by a factor of 5 from the MIF in Cárriillo-  
130 Sanchez et al. [2016], to match the observations. In order to contrast the photochemical behavior of the  
131 Na layer bottom side with that of the Fe layer, a WACCM-Fe simulation was also performed. The model  
132 output was sampled over USU (41.8°N, 111.8°W) every thirty minutes (the model time step) then  
133 interpolated to the same observational period for the available lidar daytime measurements for direct  
134 comparisons (note that the modelled nighttime outputs use the same temporal resolution as that of the  
135 daytime results because the model time step is every 30 minutes, while the lidar nighttime measurement  
136 is every 10 minutes).

### 137 **3. Comparison of the Na lidar observations with WACCM-Na**

138 The averaged Na density diurnal variation calculated from the intensive 7-day USU Na lidar  
139 campaign is presented as the top plot in Figure 2. During the campaign, the time of sunrise in the MLT is  
140 around 06:56 local time (LT) based on solar elevation angle ( $-5^\circ$  represents sunrise in the MLT); the noon  
141 and sunset times are 13:45 LT and 20:35 LT, respectively. The observations reveal strong variations  
142 within the layer during the day. Close to the layer peak there are three minima at around 20:00 LT  
143 (evening), 04:00 LT (right before dawn) and 16:00 LT (afternoon), where the Na density falls to  $\sim$   
144  $3000/\text{cm}^3$ . These are separated by two significant maxima near 91 km: the stronger one occurs right after  
145 sunrise and lasts almost the whole morning with a peak density more than  $4400/\text{cm}^3$ ; the other maximum  
146 occurs near 22:00 LT (shortly before midnight), and has a much shorter lifetime ( $\sim 1$  hour) with peak  
147 density slightly above  $4100/\text{cm}^3$ . Similar to Figure 1, on the bottom side of the main layer there is clear  
148 evidence of an increase of Na density after sunrise.

149 Compared with the lidar observations, Figure 2 (middle panel) shows that the relatively coarse  
150 resolution WACCM-Na produces a reasonable Na layer in terms of a peak Na density close to  $4500 \text{ cm}^{-3}$ .  
151 However, in contrast to the lidar observations, three distinct features are observed: first, the maxima and

152 minima around the layer peak are much less obvious; second, the peak height of the simulated Na layer is  
153 near 87 km, about 3-4 km lower than the lidar observations, partly due to a few km lower mesopause in  
154 SD-WACCM [Feng et al., 2013]; third, the absolute value of Na density vertical gradient below the layer  
155 peak is much larger than observed. For instance, the modeled Na density decreases from near  $4500 \text{ cm}^{-3}$   
156 at 87 km to  $\sim 2000 \text{ cm}^{-3}$  around 82 km, while a similar density decrease is observed by the lidar to occur  
157 between about 95 km and 82 km. Of course, the second and third differences are probably related. In  
158 contrast, Figure 2 (bottom panel) shows that the WACCM-Na high resolution (lev144) output does  
159 capture the three-minima at the layer peak during a diurnal cycle, as observed (Figure 2, top panel).  
160 Although the Na density near the first minimum ( $\sim 4500 \text{ cm}^{-3}$ ) is higher than observed, the times of the  
161 minima, which are close to 20:00 LT, 05:00 LT and 14:00 LT, are in good accord with the lidar  
162 observations. However, the Na peak density ( $> 5500/\text{cm}^3$ ), along with the overall Na column abundance,  
163 is considerably higher than measured by the lidar, and the differences in peak height and vertical density  
164 gradient still persist.

165 In order to examine the density variation on the bottom side of the layer in greater detail, Figure 3  
166 compares the time-resolved variation of the partial Vertical Column Density (VCD) below 80 km, where  
167 the magnitude of variations is the largest, from the 7-day lidar observations in September 2012 and the  
168 two WACCM-Na simulations. The variation of solar zenith angle is also plotted. Here, due to the  
169 differences of absolute density among the data sets, each VCD is normalized to its maximum so that all  
170 can fit in one plot. There is excellent agreement between the measured and modeled rates of change in Na  
171 VCD around sunrise and sunset. The VCD reaches a maximum around midday and is then fairly constant  
172 in the afternoon. This is because, contrary to the scenario in troposphere, the solar intensity in the  
173 mesosphere is pretty constant during the day. During the night, the Na VCD gradually decays to a  
174 minimum immediately before sunrise. The WACCM lev144 simulation also captures better the observed  
175 rate of decrease of Na immediately after sunset. Note also that the rate of decrease after sunset is faster  
176 than the increase following sunrise. This is caused by the rapid decrease in the concentrations of O and H

177 at sunset, compared with their slower photochemical buildup (R5-R8) and the photolysis of Na reservoir  
178 species (R1-R4) after sunrise.

179 An interesting contrast can be made with the behavior of the bottom side of the mesospheric Fe layer,  
180 where considerable density variations due to photolysis have also been observed by Fe lidars within the  
181 similar altitude range [Yu et al., 2012; Viehl et al., 2016]. Also included in Figure 3 is the modeled  
182 variation of the Fe VCD between 75 and 80 km, using a lev144 simulation with WACCM-Fe, which has  
183 been validated against Fe lidar observations [Viehl et al., 2016]. Note that although the rate of decrease of  
184 the Fe VCD around sunset is almost identical to that of Na (because both species correlate with the  
185 falling O and H concentrations after sunset) the rate of increase at sunrise is significantly faster. The Fe  
186 VCD reaches 70% of its daytime maximum within about 1 hour, whereas the Na VCD takes more than 4  
187 hours to reach the same percentage of its maximum.

#### 188 **4. Na variation during solar eclipse**

189 During the solar eclipse on August 21 2017, the USU Na lidar conducted a special campaign to  
190 observe its potential impact on the MLT. The lidar beam was pointed to the north, 30° off zenith, and  
191 operated between 09:45 LT and 15:00 LT. Although this campaign was limited by poor sky conditions in  
192 the early morning and afternoon, it was able to cover the complete course of the solar eclipse and observe  
193 the MLT at the peak of the eclipse with more than 96% of totality at 11:34 LT. To our knowledge, these  
194 are the first lidar observation in the MLT during an eclipse.

195 The lidar-observed mesospheric Na density variations during the event are shown in Figure 4, and the  
196 temporal resolution is 10-minute. The averaged return signal between 200 and 220 km altitude per lidar  
197 Line-of-Sight (LOS) binning range (150 m) is treated as the sky background, which is also shown in  
198 Figure 4. The background variation indicates that at the USU location the eclipse began at 10:25 LT,  
199 peaked at 11:34 LT, and ended just before 13:00 LT. The high background before 10:00 LT was due to  
200 hazy sky condition in the early morning, similar to after 15:00 when it became cloudy. During the course  
201 of this event, the mesospheric Na layer weakened with decreasing peak density. In particular, Na density

202 variation was more evident below 85 km. As Figure 4 shows, before the eclipse the constant density lines  
203 on the bottom side of the layer were moving downwards (i.e. increasing density at each altitude). As the  
204 eclipse unfolded, these constant density lines started to move towards higher altitudes (the density  
205 decreased at each altitude). During the recovery phase of the eclipse, the Na density began to increase  
206 again. By  $\sim 13:00$  LT, the Na layer was fully recovered, and no significant change was observed on the  
207 bottom side of the layer. For example, the density line of  $450 \text{ cm}^{-3}$  was near 80 km right before the eclipse  
208 started. It moved upward to near 81.5 km at the culmination of the event, before it went back and stayed  
209 near 80 km at the end of the event. A similar behavior can be seen in all constant density lines below 85  
210 km. Further calculation of the lidar measured bottom side Na VCD (75-85 km) shows that it decreased by  
211 about 40% between 10:25 LT and 11:35 LT.

212 The simultaneous temperature and horizontal wind measurements during the eclipse, however, do not  
213 reveal apparent variations that can be associated with the event (not shown). For instance, the measured  
214 temperature change is within the daytime lidar measurement uncertainty ( $\sim 5\text{K}$  with 20-minute and 4 km  
215 smoothing). The temperature change during the solar eclipse is expected to be that small when  
216 considering the general energy budget in the MLT. When the short-wave heating that dominates the  
217 daytime budget (mainly exothermic heating from atomic O recombination is turned off [Brasseur and  
218 Solomon, 2005], infrared cooling due to  $\text{CO}_2$  emission would lead to net cooling in the mesopause  
219 region. However, the magnitude of this cooling is only about 1 K/hour [Roble, 1995]. Thus, for a solar  
220 eclipse that only lasts for two hours with just a few minutes of totality, a noticeable temperature change  
221 should not occur. This result is consistent with a recent simulation of the eclipse using the WACCM-X  
222 model, which concluded that the temperature variation in the mesosphere would have been no more than  
223 4 K [McInerney et al., 2018]. Furthermore, the variation of temperature within this range will not have a  
224 significant impact on the Na reaction kinetics and hence the Na atom density [Plane et al., 1999].

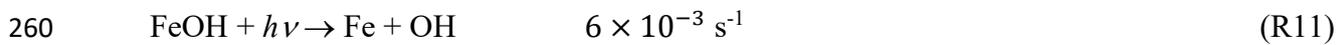
## 225 5. Discussion

226 The major reservoir for Na on the bottom side of the layer is NaHCO<sub>3</sub>, which forms by three steps  
227 from Na atoms: oxidation of Na by O<sub>3</sub> to NaO; reaction with H<sub>2</sub>O or H<sub>2</sub> to form NaOH; and  
228 recombination of NaOH with CO<sub>2</sub> [Plane et al., 2015; Gomez-Martin et al., 2017]. NaHCO<sub>3</sub> is converted  
229 back to Na either by photolysis (reaction R4), or by reaction with atom H in R9. The rate coefficient for  
230 this reaction, R9, is  $k_9 = 1.84 \times 10^{-13} T^{0.78} \exp(-1014/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [Cox et al., 2001], which is  $7.1$   
231  $\times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The typical daytime H concentration between 75 and 80 km is around  $5 \times 10^7$   
232  $\text{cm}^{-3}$  [Plane et al., 2015], so the first-order rate of this reaction is  $\sim 4 \times 10^{-6} \text{ s}^{-1}$ , which is about 40 times  
233 slower than R4. Thus, photolysis of NaHCO<sub>3</sub>, which has built up during the night, is responsible for  
234  $\sim 98\%$  of the increase in the Na VCD after sunrise (Figure 3). The excellent agreement between the  
235 laboratory-measured photolysis rate of NaHCO<sub>3</sub> [Self and Plane, 2002], and the observed increase of the  
236 Na VCD is strong evidence that NaHCO<sub>3</sub> is indeed the major Na reservoir on the bottom side of the Na  
237 layer. Indeed, as shown in Figure 5, the WACCM\_Na simulated variations of Na, H and O, between  
238 local midnight and noon, are highly correlated in the upper mesosphere in the same 144-level run.  
239 Within the same region, the NaHCO<sub>3</sub> density decreases above 78 km after sunrise due to photolysis and  
240 the increases in H and O. Below this altitude, the change in NaHCO<sub>3</sub> is much smaller because the  
241 concentrations of O and H, despite increasing after sunrise, are too small to prevent any Na produced  
242 being rapidly converted back to NaHCO<sub>3</sub>. This is because the initial oxidation step – the recombination  
243 reaction of Na with O<sub>2</sub> (which is a pressure-dependent) – becomes very fast below 78 km.

244 Based on the above discussion, a decrease of Na on the bottom side of the layer would be expected  
245 during the eclipse, because of the reduction in the photolysis rates (R1-R4) and atomic O and H. As  
246 shown in Figure 4, a decrease in the Na density below 85 km was indeed observed by the lidar during this  
247 period. However, the decrease in Na is relatively small when compared with the natural variability  
248 measured with the USU Na lidar during the morning hours (observed over 50 days of lidar data between  
249 August 20 and September 30 in 2011-2016), which can be as much as 60% between 75 and 85 km and is  
250 mostly driven by atmospheric gravity wave modulations [Shelton et al., 1980]. The effect of the eclipse  
251 was modeled by driving a 1D model of the Na layer (0.5 km vertical resolution, 5 min time resolution)

252 [Plane, 2004] with the background atmospheric species (O<sub>3</sub>, O, H etc.) from the WACCM-X simulation  
 253 of the eclipse [McInerney et al., 2018]. As shown in Figure 6, the modeled decrease in Na around 80 km  
 254 is within the natural variability and much less than the diurnal change in the layer bottom side because  
 255 the time when photolysis is significantly reduced during the eclipse is too short.

256 In terms of the mesospheric Fe layer, the major Fe reservoir in this region is most likely FeOH [Self  
 257 and Plane 2003; Plane 2004; Plane et al., 2015]. Similar to Na, the dominant Fe production processes  
 258 within the bottom half of the layer involve reaction with H and photolysis:



261 The rate coefficients of both these reactions are considerably higher than those of the analogous Na  
 262 reactions, particularly R11 which is faster than R4 by more than two orders of magnitude [Viehl et al.,  
 263 2016]. It is this feature which controls the more rapid appearance of Fe around 80 km after sunrise, as  
 264 shown in Figure 4. Note that this rapid increase has been previously observed by lidar [Viehl et al., 2016;  
 265 Yu et al., 2012].

## 266 **6. Conclusions**

267 Observations of the full diurnal cycle of the bottom side of the mesospheric Na layer reveal  
 268 substantial changes in Na density near and below 80 km, with more than an order-of-magnitude increase  
 269 after sunrise, while the change of Na density above 90 km during the same process is relatively slow. In  
 270 this study we show that this diurnal variation is largely driven by the photochemistry of the major  
 271 reservoir species NaHCO<sub>3</sub>. This result is established by demonstrating reasonable agreement between  
 272 USU lidar observations of the Na layer below 80 km, and a whole atmosphere chemistry-climate model  
 273 which includes a comprehensive Na chemistry module (WACCM-Na). Indirect photochemistry, where  
 274 atomic H and O are produced by the photolysis of O<sub>3</sub>, O<sub>2</sub> and H<sub>2</sub>O, and these atoms then reduce Na  
 275 compounds (NaHCO<sub>3</sub>, NaOH, NaO and NaO<sub>2</sub>) back to Na, also plays an important role in the diurnal  
 276 variability. The more rapid increase of atomic Fe after sunrise, which has been observed in several

277 locations [Viehl et al., 2016; Yu et al., 2012], is consistent with the much faster rate of photolysis of  
278 FeOH compared with NaHCO<sub>3</sub>. Lidar observations made during the solar eclipse on August 21, 2017 (at  
279 a location with 96% totality) did not reveal significant changes in either temperature or Na density that  
280 were larger than the natural variability around 80 km. This is consistent with a recent study using  
281 WACCM-X [McInerney et al., 2018] and the Na model results presented here.

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287 at: <http://madrigal.physics.colostate.edu/htdocs/>. The National Center for Atmospheric Research is  
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395

396 **Figure Captions:**

397 Figure 1. The Na density ( $\text{cm}^{-3}$ ) variation between 75 km and 105 km in MLT during sunrise between  
398 August 20<sup>th</sup> and September 30<sup>th</sup> (contour plot) in 2011-2016. Zero hour marks time of the sunrise at the  
399 mesopause (bottom abscissa). The solid black profile is the ratio between the Na density 3 hours after  
400 sunrise to that 3 hours before sunrise (its tick marks is plotted in top abscissa).

401 Figure 2. The averaged lidar measured Na density variation during the 7-day Na lidar campaign between  
402 September 27 and October 3, 2012 (top); the Na density variations at USU location during the same time  
403 frame simulated by WACCM\_Na 88-level (middle) and 144-level (bottom).

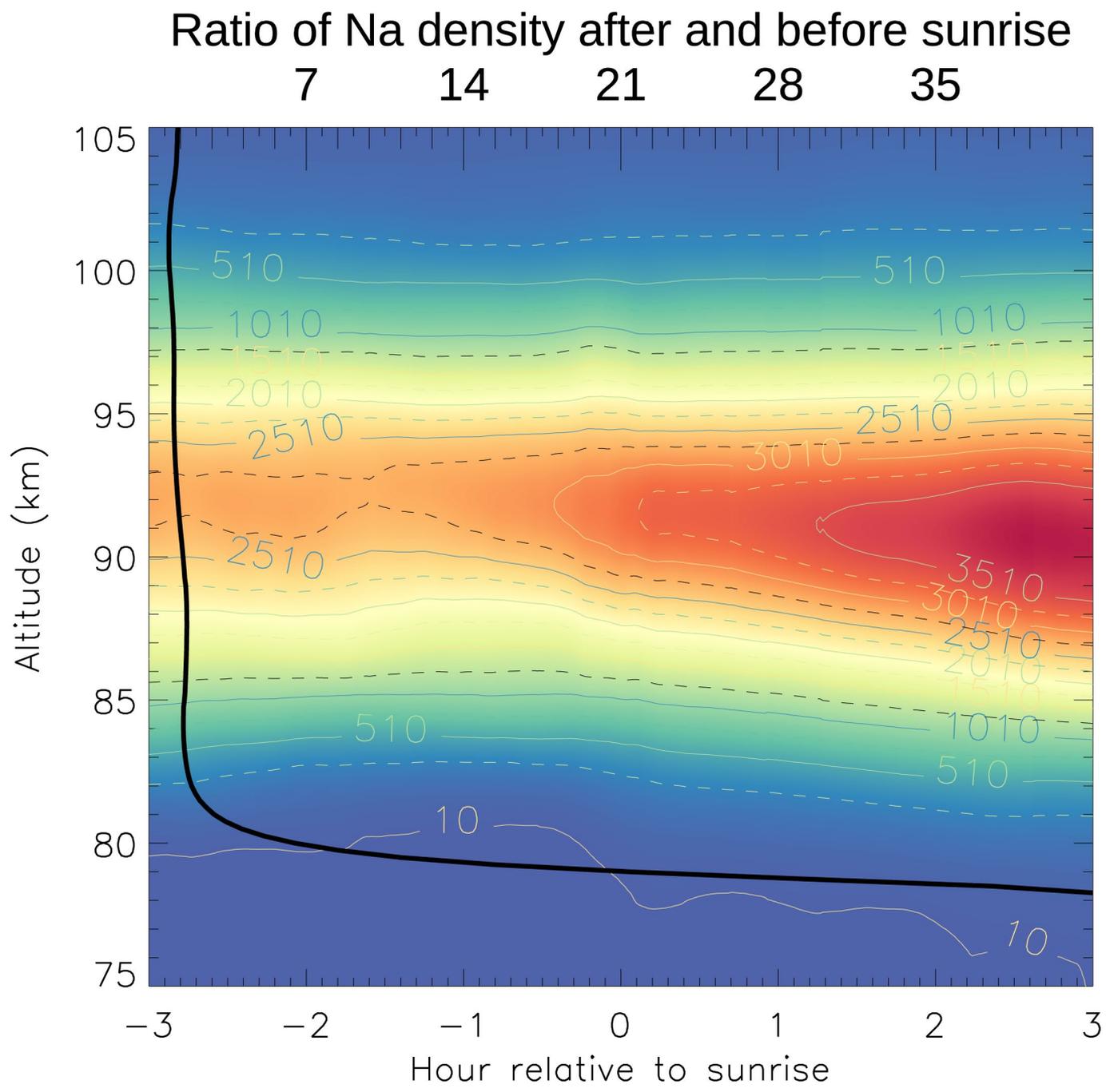
404 Figure 3. The variations of Na VCD (75-80 km) measured the USU Na lidar during the 7-day Na lidar  
405 campaign (asterisks), simulated by WACCM\_Na 88-level run (orange dotted line) and 144-level run  
406 (orange dashed line) and solar zenith angle (black long-dashed line), along with Fe VCD (75-80 km)  
407 simulated by WACCM\_Fe 144-level run (blue solid line).

408 Figure 4. The mesospheric Na density variation during the solar eclipse on August 21, 2017, observed by  
409 the Na lidar at Utah State University. The yellow solid line represents the lidar-detected sky background.  
410 The unit for the lidar background measurement is #photon/bin/minute.

411 Figure 5. The variations of Na (a), NaHCO<sub>3</sub>(b), H(c) and O(d) in the bottom side of the mesospheric Na  
412 layer, simulated by WACCM\_Na\_144-level run.

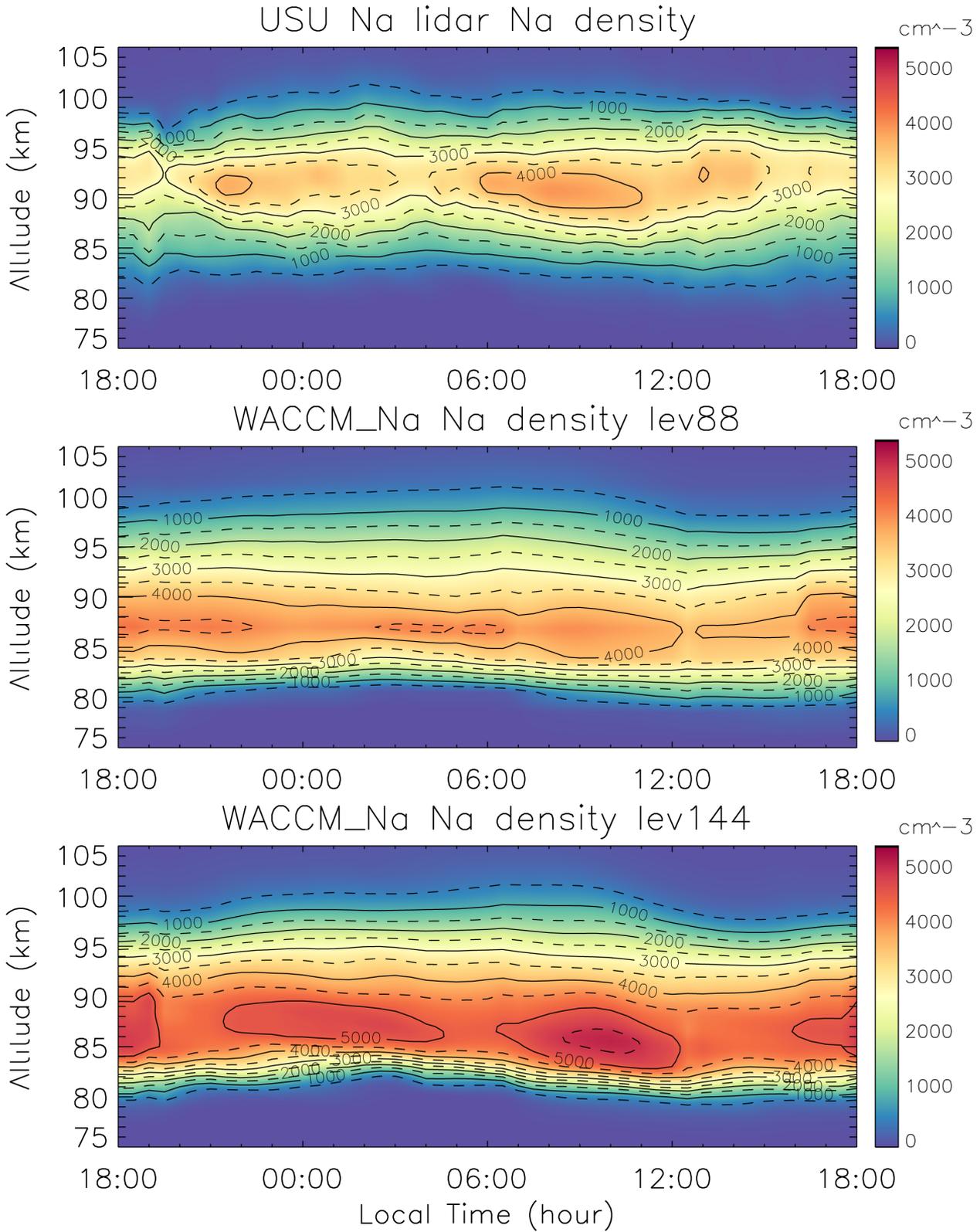
413 Figure 6. A 1D model simulation of the Na layer variation during the solar eclipse between 18:00 LT on  
 414 August 20 and 18:00 LT on August 21 in 2017. The solar eclipse at the USU Na lidar location peaked at  
 415 11:34 on August 21 (marked by the solid arrow). The background atmospheric species ( $O_3$ , O, H etc.) are  
 416 based on the outputs of WACCM-X eclipse simulation.

417



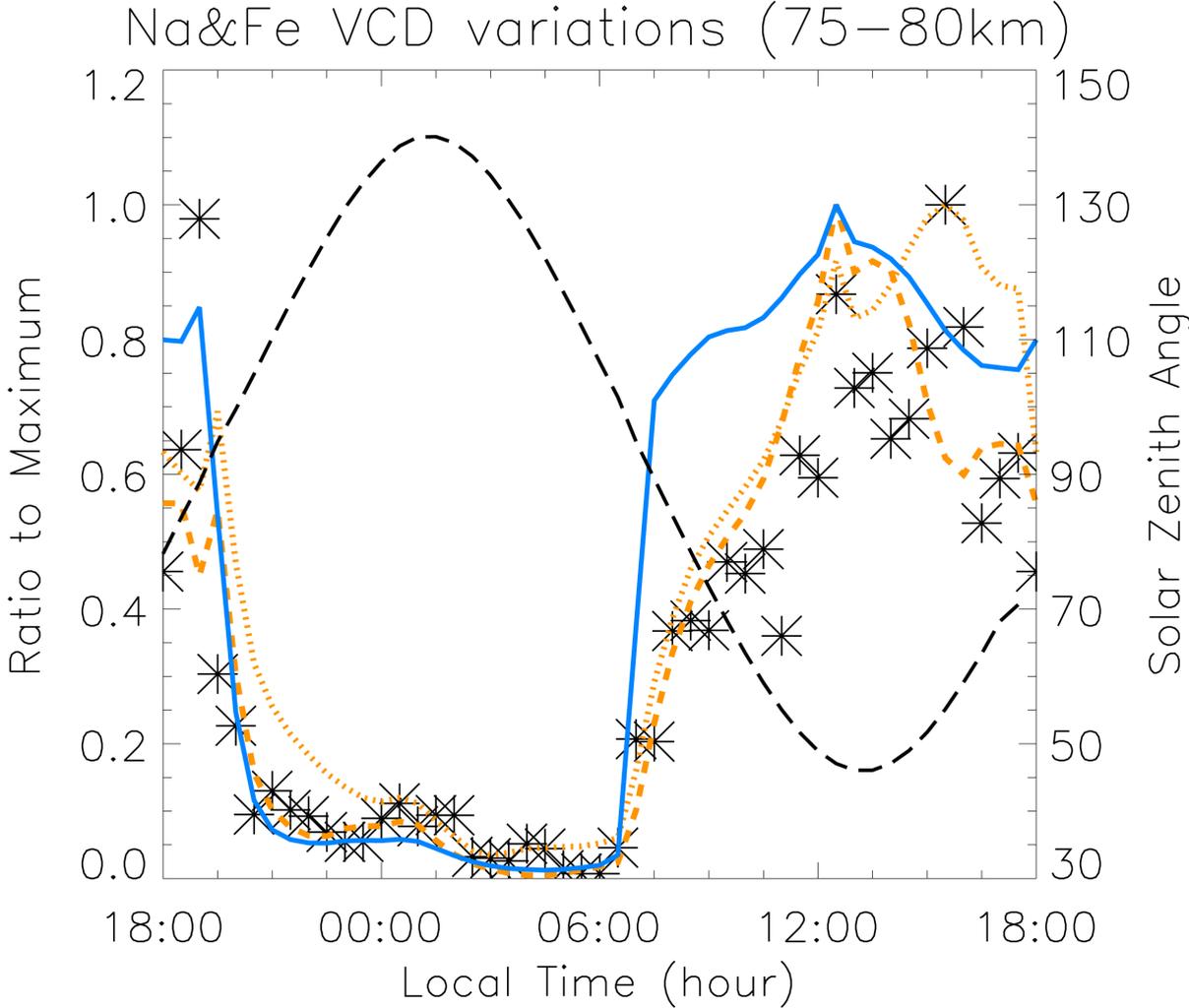
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421 mesopause (bottom abscissa). The solid black profile is the ratio between the Na density 3 hours after  
422 sunrise to that 3 hours before sunrise (its tick marks is plotted in top abscissa).

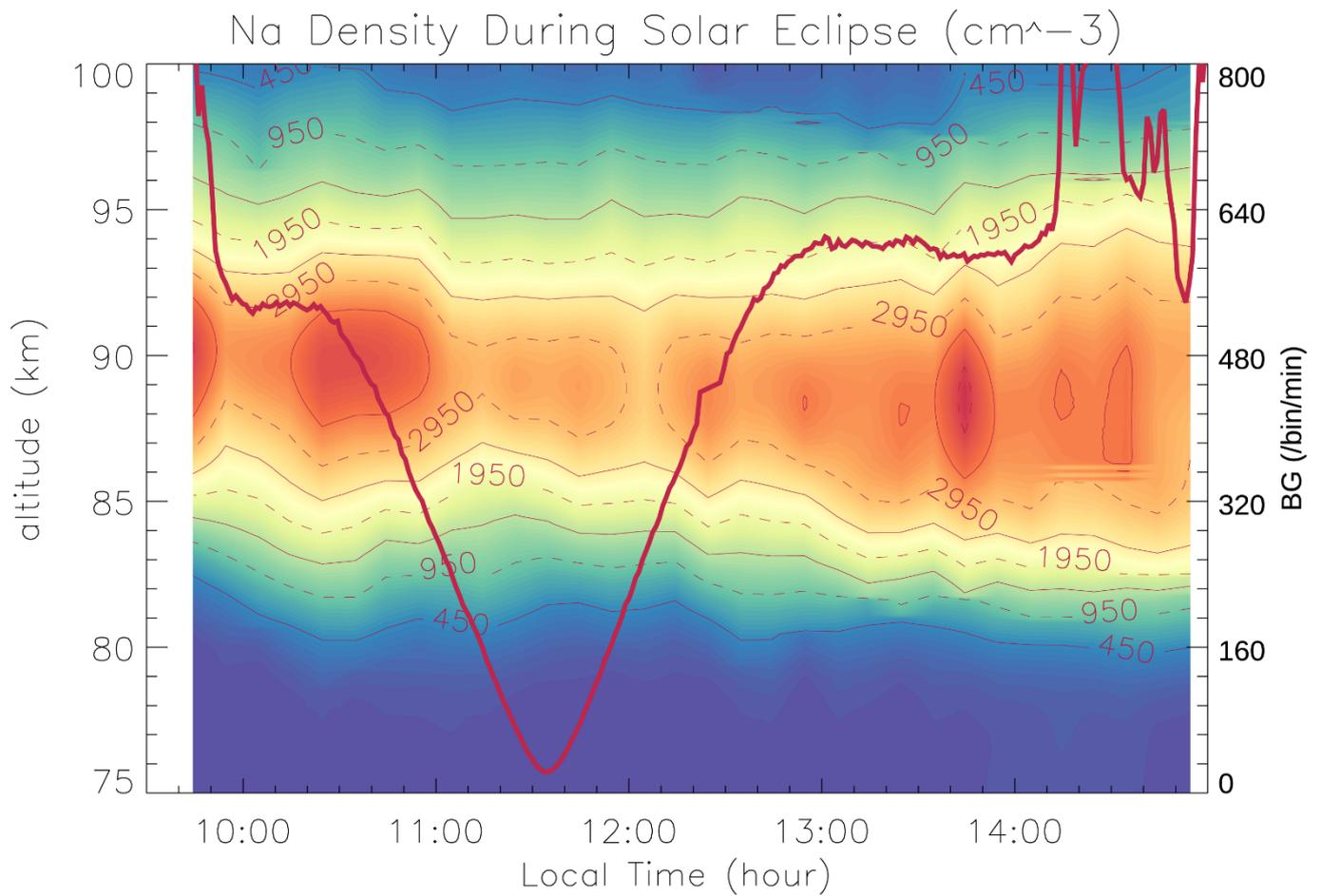


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 427



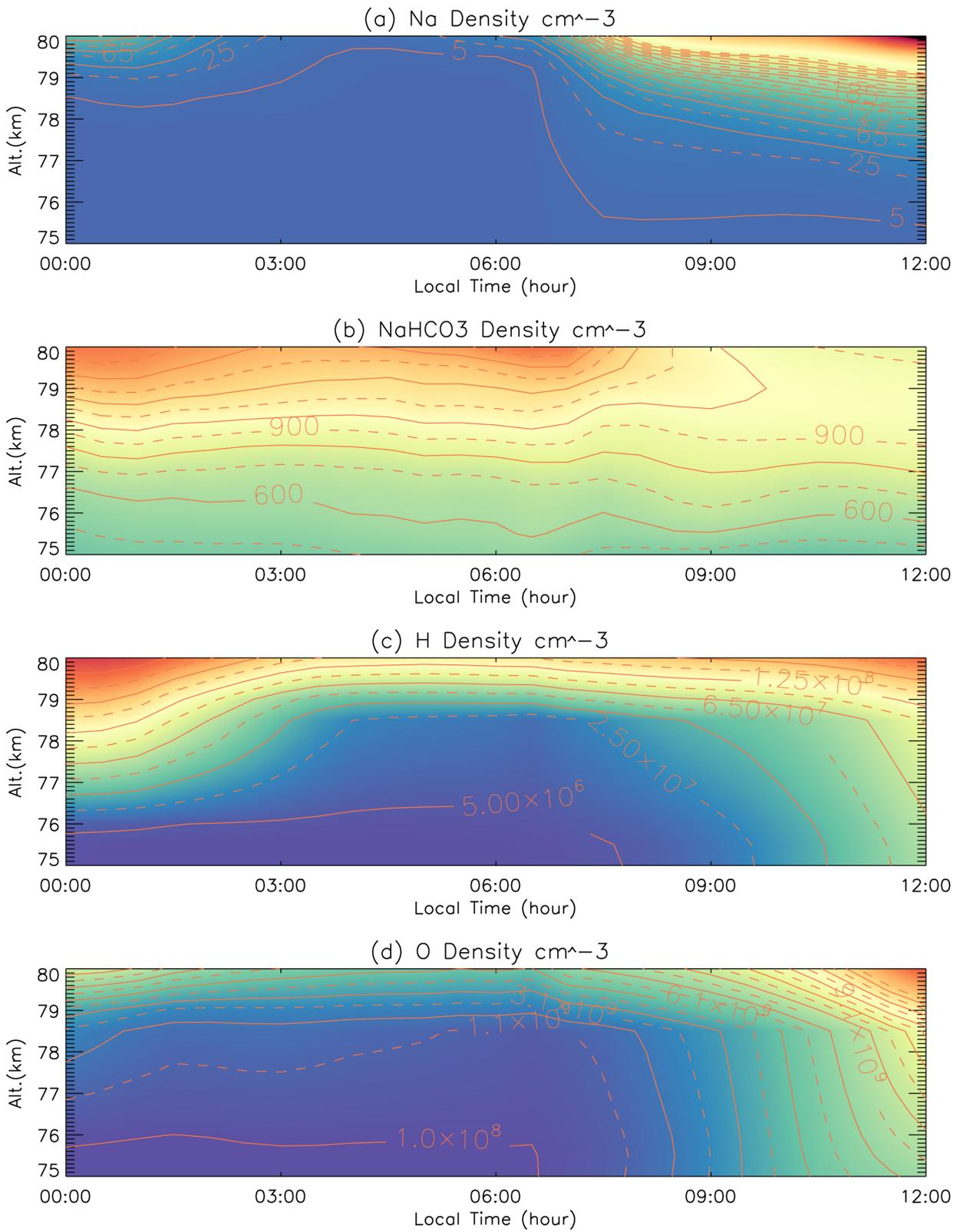
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433

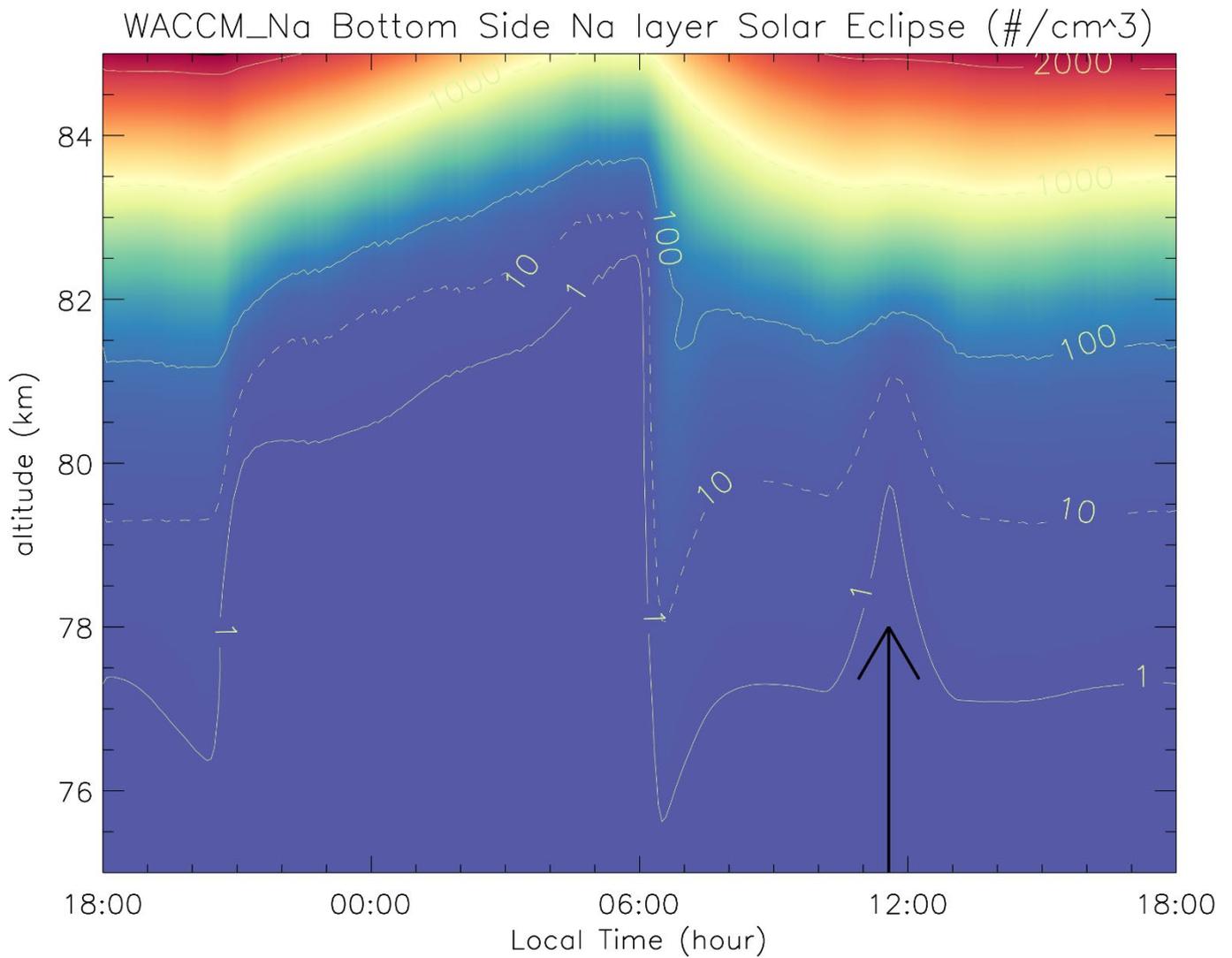
434 Figure 4. The mesospheric Na density variation during the solar eclipse on August 2, 2017, observed by  
 435 the Na lidar at Utah State University. The red solid line represents the lidar-detected sky background. The  
 436 unit for the lidar background measurement is #photon/bin/minute.

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439 Figure 5. The variations of Na (a),  $\text{NaHCO}_3$ (b), H(c) and O(d) in the bottom side of the mesospheric Na  
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446