CHEMISTRY RELATED TO POSSIBLE OUTGASSING SOURCES ON MARS. A. S. Wong, S. K. Atreya and N. O. Renno, Department of Atmospheric, Oceanic and Space Sciences, University of Michigan, Ann Arbor, MI 48109-2143 (aswong@umich.edu).

Introduction: An earlier paper, "Chemical markers of possible hot spots on Mars" by A. S. Wong, S. K. Atreya and Th. Encrenaz [1], explored the modification of the atmosphere of Mars following an influx of methane, sulfur dioxide and hydrogen sulfide (CH_4, SO_2, H_2S) from any outgassing sources which are referred to as hot spots. The feasibility of detection of the new species by Planetary Fourier Spectrometer on Mars Express is reported in a subsequent paper, "Atmospheric photochemistry above possible martian hot spots" by A. S. Wong, S. K. Atreya, V. Formisano, Th. Encrenaz and N. Ignatiev [2]. This abstract is a follow-up on the previous two papers. Here we treat the effect of any outgassed halogens rigorously. We also make estimates of dilution factors relative to the source location following convection and meridional transport.

The typical terrestrial outgassing species include H_2O, CO_2, SO_2, H_2S, CH_4, and small amounts of halogens. None of the sulfur, hydrocarbon and halogen species have yet been detected in large-scale surveys of the martian atmosphere. Any localized and transient sources, if present, are likely to go undetected in such observations due to dilution following transport away from source and the relatively short photochemical lifetimes of the species. With the above in mind, and due to considerable interest in the question of extinct or extant life on Mars, we have developed a one-dimensional photochemical model, considering the possibility that SO_2, H_2S, CH_4, and HCl from any outgassing sources may be introduced into the martian atmosphere. From this model we predict the abundances of the various new molecules that are expected to be formed in the ensuing atmospheric chemistry. The hot spot photochemical model is based on a globally averaged standard martian atmosphere model which includes all common atmospheric species including nitrogen species, found between the ground and 220 km. A detailed discussion of the model can be found in [1].

Sulfur Chemistry: The presence of SO_2 and H_2S in the atmosphere of Mars has been speculated previously [3, 4]. The upper limits of SO_2 and H_2S are 0.1 ppm each for globally averaged observations [5]. In our model, we have both gases outgassing from the surface together, and we vary the concentration of each from 0.1 ppm to 100 ppm. The principal reaction pathways are shown in Figure 1. Only for the purpose of illustration, we present the result of one case in

which the surface mixing ratio of each outgassed species is set to 100 ppm (Figure 2). The resulting mixing ratios and column abundances of SO_2, H_2S, and SO are summarized in Table 1. All sulfur species scale more or less proportionally with the amount of outgassing species.
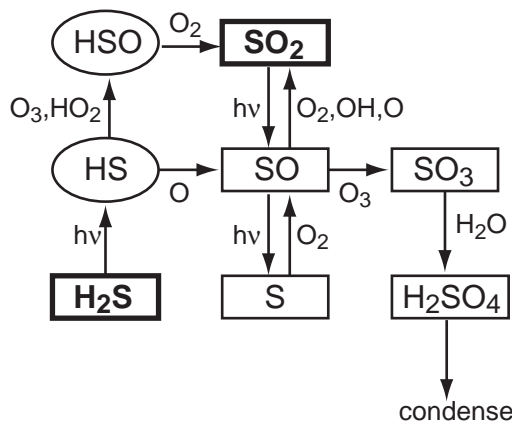
Figure 1. Important reaction pathways for sulfur species in the martian atmosphere.
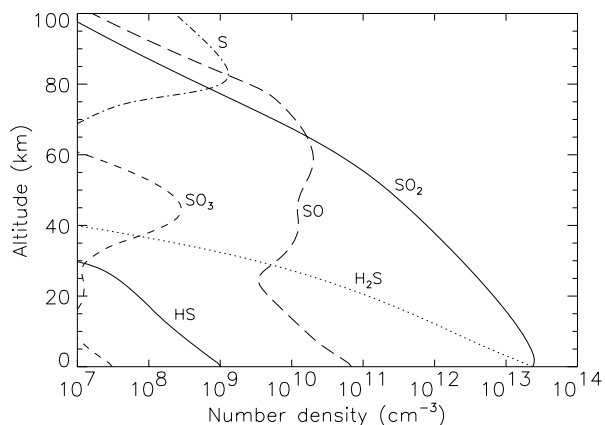
Figure 2. Calculated number density profiles of important sulfur species, assuming 100 ppm each of H_2S and SO_2 is outgassed at the surface of Mars.

Once in the atmosphere, SO_2 will be photodissociated to produce SO. The reaction of SO with O_2 or OH recycles some SO_2, while the reaction with O_3 forms SO_3, which quickly combines with water vapor to form H_2SO_4 and subsequently condenses in the lower atmosphere. Outgassed H_2S is rapidly converted to SO_2 and the reactions follow that of SO_2 (see Figure

1). The photochemical lifetime of SO_2 is 160 days, and that of H_2S is 9 days.

Table 1. Summary of possible detectable species from martian hot spots, their mixing ratios (at 10 km), column abundances (above 10 km), and photochemical lifetimes, assuming 100 ppm of SO_2, H_2S and CH_4, and 1 ppm of HCl are outgassed from the surface of Mars.

| Species	Mixing ratio at 10 km	Column abundance (cm^{-2})	Photo-chemical lifetime
SO_2	1.7×10^{-4}	1.8×10^{19}	180 days
H_2S	1.8×10^{-5}	7.4×10^{17}	9 days
SO	1.7×10^{-7}	7.8×10^{16}	4.6 hours
CH_4	1.0×10^{-4}	1.0×10^{19}	670 years
CH_2O	2.8×10^{-11}	1.6×10^{13}	7.5 hours
CH_3OH	4.3×10^{-12}	8.2×10^{11}	74 days
C_2H_6	6.4×10^{-12}	9.6×10^{11}	25 days
HCl	1.0×10^{-5}	1.0×10^{17}	5.7 years

Hydrocarbon Chemistry: If present, methane could be of geochemical or biological origin. The present upper limit of CH_4 from global surveys is 0.02 ppm [5]. Our model calculates the abundances of new species that get formed upon the introduction of CH_4 into the martian atmosphere by outgassing, and the important pathways are shown in Figure 3. For the purpose of illustration, the result for a case with 100 ppm CH_4 is shown in Figure 4. The most abundant species are CH_4, CH_2O, CH_3OH, and C_2H_6, and the resulting mixing ratios and column abundances are summarized in Table 1.

At altitudes above 80 km, CH_4 is photodissociated into CH, $^3CH_2$, $^1CH_2$ and CH_3, and its oxidation by $O(^1D)$ forms CH_3. $^3CH_2$ reacts with CO_2 to form CH_2O. At the low altitudes, the oxidation of methane by OH forms CH_3. CH_3 reacts with O to form CH_2O, reacts with OH to form CH_3OH, and recombines to form C_2H_6. The abundances of hydrocarbons derived from the methane photochemistry are very low even when the concentration of methane is relatively large in the atmosphere. The reason is that CH_4 does not dissociate efficiently to start the hydrocarbon chemistry. Photolysis of CH_4 is largely shielded by the much more abundant CO_2 whose absorption cross section overlaps that of CH_4. In the lower atmosphere, the most effective way to break down methane is by reaction with OH, which is quickly removed by CO and O. The photochemical lifetime of CH_4 is about 670 years, which is the longest amongst the principal hydrocarbon species. Therefore, CH_4 may be easier to detect even far from the source region, provided that its source flux is reasonably large. On the other hand, CH_2O has a relatively short lifetime of several hours. Therefore, if the previous tentative detection of CH_2O (0.5 ppm, [6]) is confirmed by future observations, it would imply a nearly continuous supply of methane to the atmosphere. Moreover, the amount of methane required would have to be much greater than the "global" upper limit of 20 ppb, since the models produce only 30 ppt of CH_2O with 100 ppm of CH_4. On the other hand, CH_2O itself could also be outgassed from the interior, or formed in surface reactions.
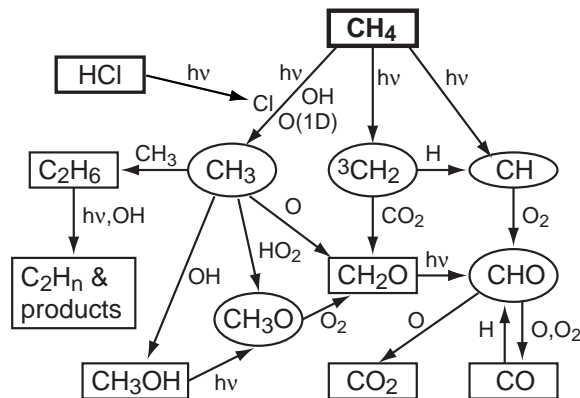
Figure 3. Important reaction pathways of hydrocarbon and halogen chemistry in the martian atmosphere.
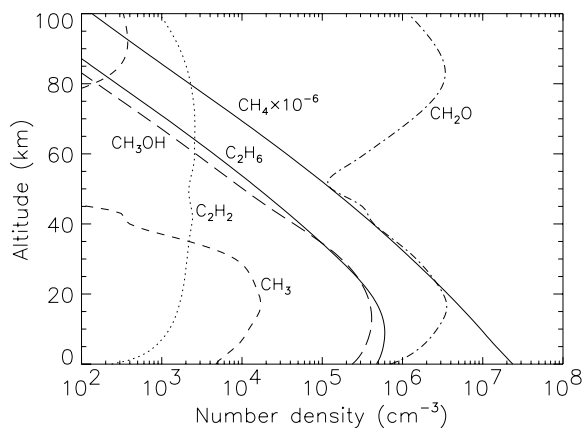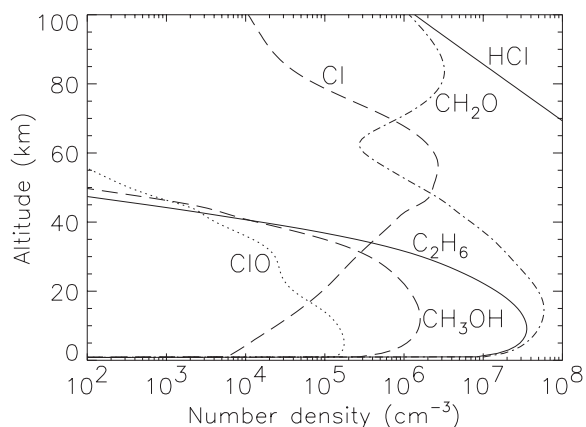

Figure 4. Calculated number density profiles of important hydrocarbon species, assuming 100 ppm of CH_4 is outgassed at the surface of Mars.

Halogen Chemistry: In terrestrial outgassing, only a very small amount of halogens (HCl, Cl_2, etc.) are released from outgassing processes. The total amount of halogens comprises a small fraction, about 1%, of SO_2, mostly in the form of HCl [7]. On Mars, the present global upper limit of HCl is 2×10^{-9} [8], which is presumably the most abundant halogen. Our model finds that with up to 1 ppm of HCl outgassing,

the direct effect of halogens on the "standard" atmosphere, as well as on sulfur chemistry, is negligible.

We investigate the effect of halogens on hydrocarbon chemistry. When HCl is released into the atmosphere together with methane, it is broken down by the solar ultraviolet photons at $\lambda \leq 230$ nm and OH radicals to form the atomic chlorine. Chlorine reacts in a similar way to OH, enhancing the breakdown of methane into CH_3 (Figure 3) and subsequently increasing the production of other hydrocarbons. Our model shows, with 1 ppm of HCl outgassing alongside with 100 ppm of CH_4, the column abundances of CH_2O, CH_3OH, and C_2H_6 are increased by 6, 2 and 3 times, respectively, compared to the case of no HCl outgassing (Figure 5). The overall effect on CH_4 is minimal. The lifetime of HCl is calculated to be 5.7 years.

Figure 5. Calculated number density profiles of important hydrocarbon and halogen species, assuming 100 ppm of CH_4 and 1 ppm of HCl are outgassed at the surface of Mars. This figure illustrates the effects of halogens on hydrocarbon chemistry.

Conclusion and Discussions: We have shown that if outgassing is taking place somewhere on Mars today, only a handful of new species with significant abundance would be formed as a result of photochemical processes involving the products of outgassing. In particular, the outgassed H_2S and SO_2 would produce significant amounts of only SO in the gas phase. Similarly, photochemistry of any outgassed CH_4 would produce appreciable amounts of only CH_2O and CH_3OH, but the hydrocarbon photochemical products would be much less abundant than CH_4. Thus, the best candidates for the chemical markers of any hot spots on Mars are SO_2, H_2S, CH_4, possibly HCl, SO, CH_2O, and CH_3OH. The largest source of methane in the earth's atmosphere is methanogenic bacteria living in anaerobic soils in tropical forests, swamps and rice paddies and in the guts of cattle and other grass eating animals, with smaller contributions from fossilized

matter. Methane and its products could serve as possible biomarkers in the martian atmosphere as well. Halogens would probably outgas in very small amounts, and their only noticeable effect on the atmosphere and outgassing chemistry is the slight increase of hydrocarbon photoproducts.

In the relatively short time-scale of about an hour, ordinary convective processes alone can reduce the mixing ratios of outgassed species by factors of 10^4–10^5, spreading the outgassed species over distances of up to 50 km away from the source. In addition, the time-scale for spreading the outgassed species over the entire planet (with corresponding dilution factor of $\sim 10^8$) would be approximately one year. In view of these time scales and the relatively short photochemical lifetimes of the species, detection of any sulfur or hydrocarbon species would indicate presence of currently active hot spot/s in close proximity of the observation. Unless the source flux is extremely large, detection far from a transient source would be unlikely due to dilution. The best conditions for detecting any possible hot spots would be over valleys, between early and mid mornings. At this time period, any outgassed species would be trapped between the surface and the top of the thermal inversion created by the nocturnal radiative cooling of the surface and lower atmosphere. Thus, the near surface concentration of outgassed species would be the highest. As the depth of the convective layer increases during the morning, this concentrated layer gradually grows, up to values larger than the atmospheric scale height (about 10 km). During the cold season, convection is inhibited, the thermal inversions are stronger, and the convective layers shallower. Therefore, morning limb observations during winter are ideal for detecting any possible martian hot spots. The best locations to find hot spots include martian high latitudes where most of the signs of recent water seepage and ground water runoff have been seen, and calderas of volcanoes in the Tharsis.

References: [1] Wong A. S. et al. (2003) *JGR, 108(E4),* 5026, doi:10.1029/2002JE002003. [2] Wong A. S. et al. (2003) *Adv. Space Res.,* in press. [3] Farquhar J. et al. (2000) *Nature, 404,* 50–52. [4] Wänke H. and Dreibus G. (1994) *Phil. Trans. Phys. Sci. Eng., 349,* 285–293. [5] Maguire W. S. (1977) *Icarus, 32,* 85–97. [6] Korablev O. I. et al. (1993) *PSS, 41,* 441–451. [7] Walker J. C. G. (1977) *Evolution of the atmosphere*, p. 205, Macmillan. [8] Krasnopolsky V. A. et al. (1997) *JGR 102*, 6526–6534.