

We thank P. Morrison, B. Marsden, B. Goldstein and D. Pingree for helpful discussions, and A. I. Sabra for his clarifications of the translation and for help in interpreting the Arabic text.

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Received 5 April; accepted 17 April 1978.

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Primitive atmosphere and implications for the formation of channels on Mars

THE channels on Mars^{1,2} suggest that a flowing fluid has been present on the surface of the planet. It seems natural to assume that this fluid was water. The major difficulty, however, is that water freezes in climatic conditions like those now^{3,4} on Mars. It has been suggested⁵⁻⁷ that primitive Mars had a reducing atmosphere, composed mainly of methane. Such an atmosphere, as we show here, could be polymerised by solar ultraviolet radiation to produce higher hydrocarbons. These compounds are low viscosity liquids at today's temperature on Mars, and could contribute to the formation of channels.

We adopt a simple model of the early martian atmosphere similar to Sagan's⁵ and Pollack's⁷, except for ammonia. The total pressure equals 100 mbar, with CH₄, H₂ and N₂ as major components in proportions 60:6:1 by volume. The thermal structure of this atmosphere is similar to that given by Yung *et al.*⁸ The amount of water vapour is then determined by assuming 50% relative humidity. The physical parameters of our model closely resemble those on Mars today. Ammonia was included in Sagan's model mainly to provide a greenhouse effect, but we omit for simplicity. Ultraviolet light dissociates CH₄ directly or indirectly by



and



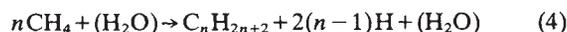
where the radical OH is derived from



Reaction (1) occurs primarily in the upper atmosphere,

followed by reactions similar to those in the jovian atmosphere⁹. Reaction (2) provides the driving force for photochemistry in the lower atmosphere. Every dissociation of a water molecule, equation (3) brings about the dissociation of a hydrocarbon molecule.

The subsequent reactions leading to the formation of higher hydrocarbons are described in Table 1 and can be summarised by



where H₂O plays the part of a catalyst. The system is analogous to that studied by Lasaga, Holland and Dwyer¹⁰ in connection with a primordial oil slick on Earth but differs in one major aspect. We use the photolysis of water, which is much larger than that of methane to drive the alkane photochemistry in the lower atmosphere, where associative reactions of alkyl radicals are efficient. The results of a steady state calculation are shown in Fig. 1. Comparison with Table 2 shows that the alkanes beyond C₇H₁₆ would condense into a liquid. Using the production rates of alkanes in our model, we estimate that a major fraction of the atmosphere could be polymerised in less than 10 Myr giving rise to a layer of liquid alkanes as thick as 1 m if uniformly spread over the planet's surface. If we had started with 1 bar of methane, the amount of liquid would be 10 m.

Escape of hydrogen plays a crucial part in the evolution of a methane dominated atmosphere. With equation (1) as a high altitude source of hydrogen atoms the escape rate would be of order 10¹⁰ atoms cm⁻²s⁻¹, or about 100 times higher than the present escape rate¹¹. The loss of hydrogen leaves a surplus of carbon atoms and the system must evolve towards a state with lower H:C ratio by converting methane into higher hydrocarbons. It is now clear that given an initial methane atmosphere on a small planet like Mars, hydrogen escape and polymerisation are inevitable. Upon completion of polymerisation,

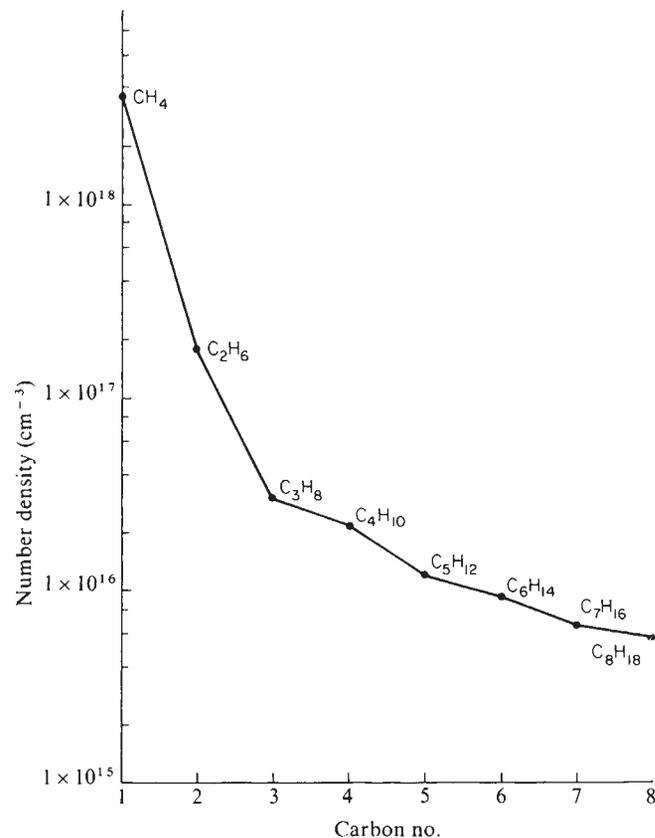


Fig. 1 Number densities of the lighter alkanes in the lower atmosphere of Mars. The total atmospheric pressure equals 100 mbar. The surface temperature is 220 K, and the adiabatic lapse rate = 1.9 K km⁻¹.

Table 1 Major reactions in the early martian atmosphere

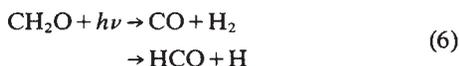
$H_2O + h\nu \rightarrow H + OH$	<i>J</i>	Ref. 8
$CH_4 + h\nu \rightarrow CH_2 + H_2$	<i>J</i>	9
$\rightarrow CH + H_2 + H$		
$C_2H_6 + h\nu \rightarrow C_2H_2 + 2H_2$	<i>J</i>	9,16
$\rightarrow C_2H_4 + 2H$		
$C_nH_{2n+2} + h\nu \rightarrow \text{Products}$	<i>J</i>	18
$CH_2 + H_2 \rightarrow CH_3 + H$	$k = 5.0 \times 10^{-14}$	9
$OH + H_2 \rightarrow H_2O + H$	$k = 3.6 \times 10^{-11} \exp(-2590/T)$	17
$H + H \xrightarrow{M} H_2$	$k = 1.0 \times 10^{-32}M$	9
$C_2H_2 + H \xrightarrow{M} C_2H_3$	$k = 5.0 \times 10^{-29} \exp(-1213/T)M$	19
$C_2H_3 + H \rightarrow C_2H_2 + H_2$	$k = 1.5 \times 10^{-11}$	20
$CH_4 + OH \rightarrow CH_3 + H_2O$	$k = 2.4 \times 10^{-12} \exp(-1710/T)$	17
$CH_3 + H \xrightarrow{M} CH_4$	$k = 1.0 \times 10^{-10}$	21
$CH_3 + CH_3 \xrightarrow{M} C_2H_6$	$k = 4.0 \times 10^{-11}$	9,22
$C_2H_6 + OH \rightarrow C_2H_5 + H_2O$	$k = 1.9 \times 10^{-11} \exp(-1230/T)$	17
$C_2H_5 + CH_3 \xrightarrow{M} C_3H_8$	$k \approx 4.0 \times 10^{-11}$	9,22
$C_2H_5 + C_2H_5 \xrightarrow{M} C_4H_{10}$	$k \approx 4.0 \times 10^{-11}$	9,22
$C_nH_{2n+2} + OH \rightarrow C_nH_{2n+1} + H_2O$	$k = (2n + 2) \times 10^{-12} \exp(-820/T) (n \geq 3)$	17
$C_nH_{2n+1} + C_mH_{2m+1} \xrightarrow{M} C_{m+n}H_{2(m+n)+2}$	$k \approx 4.0 \times 10^{-11}$	9,22

The units for photolysis rates (*J*) and two body reaction rates (*k*) are s⁻¹ and cm³ s⁻¹ respectively. *M* denotes number density of a third body (in units of cm⁻³). Where *M* does not explicitly appear in a three body reaction rate *k* is taken to be the two body rate at high pressure.

the initial resource of hydrogen by equation (4) is exhausted, and further escape of hydrogen must be supplied from water, with production of oxygen. Oxygen will now oxidise the alkyl radicals by reactions such as:



followed by



The appearance of CO initiates a catalytic cycle that competes with equation (2) for OH:



While equations (2) and (3) form a closed loop for H₂O, equations (3), (8) and (9) result in releasing more oxygen atoms for

reactions such as equation (5). Thus, all the alkanes could be destroyed in perhaps as short a time as it had taken to make them.

The channels on Mars are a complex phenomenon and probably no single explanation would suffice. Our photochemical model provides a modest amount of fluid (1–10 m) for a brief interval of time (10–100 Myr). The existence of liquid alkanes complements rather than competes with other mechanisms for the formation of channels. A preliminary investigation suggests that the alkanes do not contribute significantly to greenhouse effects but their associated products such as C₄H₆O and C₃H₇N may. Also compounds like CH₃OH that can depress the freezing point of water may be present. We shall include these compounds in an extended study.

Two crucial aspects of this theory can be tested by suitable measurements. The assumption of an early massive reducing atmosphere is based on Holland's¹² work on the evolution of the Earth's atmosphere. There is more evidence from an analysis of D/H ratio¹³ to support this hypothesis. A similar measurement of D/H ratio of water on Mars would yield

Table 2 Properties of simple alkanes

	C ₅ H ₁₂	C ₆ H ₁₄	C ₇ H ₁₆	C ₈ H ₁₈	H ₂ O	
Freezing point (K)	143	178	182	216	273	
Viscosity (cP)	0.29	0.41	0.52	0.71	1.8	
Heat of fusion (cal g ⁻¹)	28	36	34	43	80	
Heat of vaporisation (cal g ⁻¹)	92	89	89	81	540	
Number density of saturated vapour (cm ⁻³)	160 K	1.8 × 10 ¹⁵	1.2 × 10 ¹⁴	6.9 × 10 ¹²	1.2 × 10 ¹²	3.2 × 10 ¹⁰
	180 K	1.6 × 10 ¹⁶	1.5 × 10 ¹⁵	1.4 × 10 ¹⁴	2.7 × 10 ¹³	2.1 × 10 ¹²
	200 K	9.2 × 10 ¹⁶	1.2 × 10 ¹⁶	1.5 × 10 ¹⁵	3.1 × 10 ¹⁴	5.8 × 10 ¹³
	220 K	3.8 × 10 ¹⁸	6.0 × 10 ¹⁶	1.1 × 10 ¹⁶	2.4 × 10 ¹⁵	8.7 × 10 ¹⁴

Water is included for comparison. Viscosity is taken at 0°C, but it is not a strong function of temperature. Data come from ref. 23.

valuable information on the amount of hydrogen that has escaped. The evolution of a methane atmosphere can best be tested on Titan¹⁴, whose atmosphere bears striking similarities to our model of the primitive martian atmosphere, especially in view of a measurement¹⁵ of a surface temperature in excess of 200 K. The detection of higher alkanes or carbon monoxide on the satellite would be expected on the basis of our photochemical model.

Y.L.Y. thanks Professor M. B. McElroy for valuable insights on atmospheric evolution, hydrogen escape and isotopic ratio and J. B. Pollack and O. B. Toon for discussion of present and past climates on Mars. This research was supported by Ames Research Center under NASA contract NSG-2283. J.P.P. acknowledges support by NASA grant NSG-5163 to Columbia.

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Received 6 February; accepted 3 May 1978.

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Meteor radar rates, geomagnetic activity and solar wind sector structure

THERE is evidence which indicates^{1–4} that the occurrence rate of meteor radar echoes varies inversely with solar cycle activity, this phenomenon can be explained^{5–6} by a long-term variation in the atmospheric density gradient at the meteor ablation level. Inferred changes in the atmospheric properties are attributed to a long-term variation in the solar EUV radiation. Although the long-term, solar cycle changes in radar-determined meteor rates show an inverse correlation with sunspot numbers and other measures of solar activity, such correspondence is not readily evident in the day-to-day meteor radar data. One reason for this is the inability of most solar activity indices to measure the relevant solar parameters involved in short-term solar-terrestrial effects. The study of solar-influenced meteor rate changes on a time scale of days has, therefore, not received adequate attention. Evidence for a short-term dependence of meteor radar rates on geomagnetic activity and solar corpuscular radiation is presented here.

This investigation is based on the long series of radar observations of meteors made at the Onsala Space Observatory in Sweden. These were carried out during pre-selected time periods in August and September, with occasional runs in

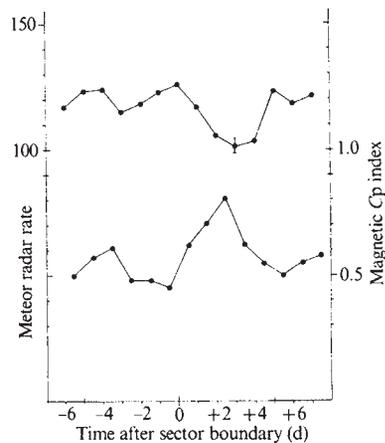


Fig. 1 Variation of meteor radar rates and geomagnetic activity with time measured from the passage of a solar magnetic sector boundary past the Earth. Superimposed-epoch analysis of all meteor radar data August–November 1953–74. Top curve: radar-determined meteor hourly rate (left scale); lower curve: geomagnetic C_p index for days of radar recordings (right scale). Radar rates are referred to the nearest 00 UT, geomagnetic activity to the nearest 12 UT. Sector boundaries as given by Svalgaard are referred to the nearest 00 UT. Each datum point in Fig. 1 represents the mean of 35–49 individual measurements of the radar rate. The s.e.m. varies from 4.4 to 8.0 units. A vertical bar indicates the standard error of the mean for epoch day +3.

October and November. Our radar equipment operated at 32.6 MHz and recorded meteor echoes of duration >0.02 s corresponding to visual meteors brighter than about fifth zenithal magnitude. The experimental technique has been described elsewhere⁷. Here we analyse night-time recordings (2100–0300 UT) made between 1953 and 1974 and daytime recordings (0700–1300 UT) made between 1960 and 1974. The original echo rate data are available on a 1-h basis. In the present study 6-h averaged total meteor rates for a night or day-period are analysed.

The short-term response of meteor radar echo rates to geomagnetic activity and solar corpuscular radiation was investigated with the technique of superimposed epochs. This technique has been used for many years in the study of solar-terrestrial relationships, and recently several meteorological and geophysical phenomena have been correlated with the solar wind sector structure^{8–10}. In our study, we therefore investigated whether meteor radar echo rates and geomagnetic activity were influenced by the passage time of the solar wind sector boundary. The atlas of well-defined sector boundaries prepared by Svalgaard¹¹ was used to define the key day (zero day) in the superimposed epoch analysis. An advantage of the superimposed epoch technique is that variations unrelated to the sector structure—such as meteor rate changes of an astronomical nature—will tend to cancel out in the superimposition process.

The results of our analysis are shown in Figs 1–4. In each case, the top curve depicts the variation of the mean hourly rate of meteor radar echoes as the solar sector structure is carried past the Earth by the solar wind. The lower curve shows the corresponding variation of the geomagnetic C_p index.

An analysis of all available meteor data 1953–74 is given in Fig. 1. The following features are evident: an increase in geomagnetic activity begins after sector boundary passage, with a maximum occurring about 2.5 d later. A broad minimum in meteor radar echo rates begins after passage of the sector boundary and is most pronounced near epoch day +3. A secondary maximum in geomagnetic activity and a secondary minimum in radar rates are seen a few days before sector boundary passage. Although the latter features are not very prominent in Fig. 1 they are also observed when the data are grouped in other ways (Figs 2–4).