isotopic constituents in the contemporary martian atmosphere, and have been interpreted, by a set of independent arguments, to indicate a possible higher pressure atmosphere in early martian history[6–8]. The most frequently cited estimates of total pressure are about 0.1 bar, but estimates range as high as 1 bar. Because of the low exosphere temperature, H_2 does not escape from Mars today significantly faster than it does from Earth, despite the larger gravitational acceleration of the latter.

The results indicate that if primitive Mars, like primitive Earth, had even a mildly reducing atmosphere, martian global temperatures a few times 10^9 yr ago may have been in the vicinity of the freezing point of seawater and, in many latitudes, the mean temperatures may have been above the freezing point. This result is of possible interest for the martian sinuous channels, many of which seem to be produced by aqueous fluvial erosion and which have been crudely dated by cratering statistics techniques as having been formed $1–4\times10^9$ yr ago[9–15]. Although the Viking imaging and microbiology experiments have so far yielded no unambiguous evidence for martian biology[16–20], the implication of this work—that in earlier martian history, temperatures and pressures may have been substantially higher in a reducing atmosphere and extensive bodies of liquid water present—certainly enhances significantly the *a priori* likelihood of the origin of life on early Mars. Of course, even if life arose, there is no guarantee that it survived subsequent inclemencies of martian history. Our results also imply, because of the increasing solar luminosity, a very clement martian epoch a few times 10^9 yr in the future (Fig. 2), when conditions on Earth will become—due to the inexorable nature of stellar evolution—less than ideal (Fig. 1).

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CARL SAGAN

Laboratory for Planetary Studies,
Cornell University,
Ithaca, New York 14853

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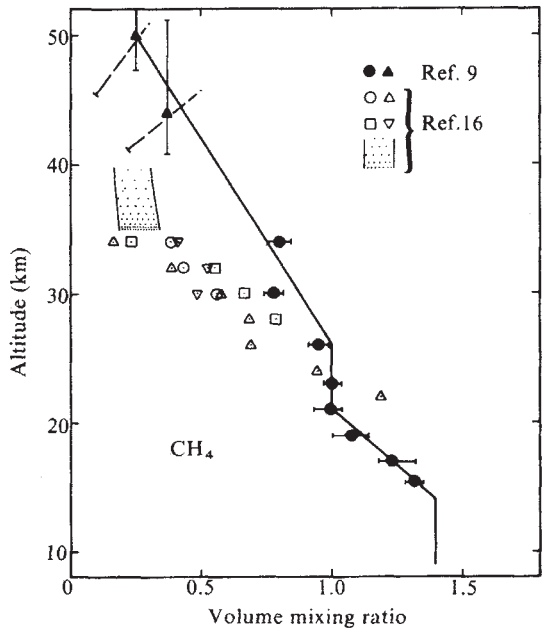

Fig. 1 Vertical distribution of the volume mixing ratio of methane in parts per million. The *in situ* sampling results[9] are shown with the values determined[16] by infrared spectrometry of the P_5 to P_8 multiplets of the 3.3-μm band. The solid curve represents the values used in model calculations[4]. The envelope above 35 km corresponds the methane absorptions at Zenith angle, χ, smaller than 90°.

Stratospheric CH_4, HCl and ClO and the chlorine–ozone cycle

SINCE it was suggested[1] that chlorine may influence stratospheric ozone balance, and that halocarbons can contribute significantly to the stratospheric chlorine content[2–4] much attention has been paid to the subject. We report here a new determination of atmospheric methane levels which gives a value lower than that often assumed by other workers. In model calculations this suggests that chlorine has a greater effect on the ozone balance than previously suspected.

In addition to atomic chlorine two main species of the chlorine–ozone cycle have been measured in the stratosphere—namely HCl (ref. 5) and ClO (ref. 6). The ratio of their abundances can be expressed by the relation[3]

$$n\mathrm{HCl}/n\mathrm{ClO} = (k_1 n\mathrm{CH_4} + k_2 n\mathrm{H_2} + k_3 n\mathrm{HO_2}) \times \times (k_4 n\mathrm{O} + k_5 n\mathrm{NO})/(k_6 n\mathrm{O_3} \times k_7 n\mathrm{OH}) \quad (1)$$

where nA represents the number density of species A and values of k expressed below in $\mathrm{cm^3\ mol^{-1}\ s^{-1}}$, represent the rate constants[7] of the reactions

$CH_4+Cl\rightarrow CH_3+HCl$	$k_1 = 5\times10^{-12}\,e^{-1114/T}$
$H_2+Cl\rightarrow H+HCl$	$k_2 = 5.6\times10^{-11}\,e^{-2250/T}$
$HO_2+Cl\rightarrow O_2+HCl$	$k_3 = 10^{-11}$
$ClO+O\rightarrow Cl+O_2$	$k_4 = 5.3\times10^{-11}$
$ClO+NO\rightarrow Cl+NO_2$	$k_5 = 1.7\times10^{-11}$
$Cl+O_3\rightarrow ClO+O_2$	$k_6 = 3.6\times10^{-11}\,e^{-318/T}$
$HCl+OH\rightarrow Cl+H_2O$	$k_7 = 3\times10^{-12}\,e^{-400/T}$

The $H_2O_2+Cl\rightarrow HCl+HO_2$ reaction has been neglected due to its low rate constant[8].

All species in very low stratospheric concentration (except HO_2 which has a minor role) intervening in relationship (1) have been measured—H_2 (ref. 9), NO (refs 10, 11), O (refs 12, 13) and OH (ref. 14). The abundance of ozone is known[15] and most studies have relied on CH_4 data obtained in the stratosphere by *in situ* sampling[9].

In the altitude range 32–36 km where data are available for computation the nHCl/nClO ratio is observed to be about 0.8 while values ranging from 4.5 to 3.5 result from model calculations[4].

We have performed a new determination[16] of CH_4 using infrared absorption spectrometry from a balloon platform to give methane mixing ratios over 25 km lower than currently used in stratospheric models. The results, shown in Fig. 1, were derived from spectra of the 3.3-μm CH_4 band obtained simultaneously with HCl absorption spectra[17]. They have been used in conjunction with all other measurements to evaluate the nHCl/nClO ratio from equation (1) in order to deduce the effect of these new data on the chlorine–ozone cycle. The

Table 1 Data used in the evaluation of nHCl/nClO and results

	Altitude (km)		
	32	34	36
nO_3 (ref. 15)	2.5×10^{12}	1.9×10^{12}	1.4×10^{12}
nCH_4 (ref. 16)	1.2×10^{11}	7.0×10^{10}	4.2×10^{10}
nH_2 (ref. 9)	2.0×10^{11}	1.4×10^{11}	1.0×10^{11}
nHO_2 (ref. 3)	2.2×10^{7}	1.9×10^{7}	1.5×10^{7}
nOH (ref. 4)	1.1×10^{7}	1.1×10^{7}	1.5×10^{7}
nO (ref. 13)	1.3×10^{8}	2.6×10^{8}	3.9×10^{8}
nNO (ref. 11)	1.3×10^{9}	1.1×10^{9}	7.0×10^{8}
T(K) (ref. 18)	228	234	239
nHCl (observed)[17]	4.2×10^{8}	3.0×10^{8}	2.4×10^{8}
nClO (observed)[6]	5×10^{8}	4×10^{8}	3×10^{8}
nHCl/nClO (equation (1))	1.2	1.2	0.8
nHCl/nClO (observed)	0.84	0.75	0.8
nHCl/nClO (model)[1]	4.5	3.9	3.5

number densities used in the computation are listed in Table 1 with the results. The computed values of the nHCl/nClO ratio seem to be in good agreement with observed values while the model calculated ratios are, especially at the lowest altitude, in marked disagreement. Part of this disagreement is due to the use in models of high methane concentrations which have already been considered as being surprisingly large by Wofsy and McElroy[19]. A similar opinion has been expressed by Rowland and Molina[3] who have considered the possibility of lower methane concentrations leading to an enhancement by a factor of 2 or 3 of the chlorine atom chain.

Thus introduction of high methane concentrations[9] into model calculations[4] has lead to a computed nHCl/nClO ratio, for the case considered here, 2.3 times higher than that obtained when using the lower level of methane reported here.

M. Ackerman

D. Frimout

C. Muller

Institut d'Aeronomie Spatiale de Belgique, 3, avenue Circulaire, B—1180—Brussels, Belgium

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Defects in natural type IB diamond

Natural type IB diamond has an anomalously low thermal conductivity. To investigate this we have carried out birefringence, infrared and ultraviolet absorption spectroscopy, electron spin resonance and transmission electron microscopy (TEM) experiments. We suggest here that the low IB thermal conductivity is due to the presence of previously unknown defects in this type of diamond. It is also suggested that these defects are related to the more common 'platelets' or planar faults which are found in type IA diamond.

The thermal conductivity of IB diamond (specimens C8 and C9 in Fig. 1) was first measured in 1972[1] and subsequent experiments[2,3] have produced similar results. It was found that the strength of the phonon scattering mechanisms which significantly reduced the IB conductivity as compared to purer IIA diamond, could not be explained solely by the presence of paramagnetic singly substitutional nitrogen atoms[1,4]. This has now been confirmed to be the case for six IB specimens. A satisfactory theoretical explanation of the original measurements on the basis of Rayleigh-type phonon scattering, could not be found[4] although the most recent results can be explained if the non-paramagnetic nitrogen (which in this case was more highly concentrated than is usual for type IB) was assumed to be in clusters of several atoms[3].

We chose for our investigations a transparent amber coloured African diamond (no. 2) from a batch provided by the Diamond Research Laboratory on the basis of extremely low birefringence. Electron spin resonance experiments were performed on this specimen using a Varian E-line spectrometer and a characteristic IB response was observed. Singly substitutional nitrogen atoms are responsible for this behaviour[5]. No attempt was made to calculate the spin density rigorously but it was estimated to be $\sim 10^{23}$ m^{-3}. Infrared and ultraviolet absorption spectroscopy confirmed that the specimen was a typical IB

Fig. 1 The thermal conductivity of two type IB diamonds, ■, C8 and ●, C9. It is impossible to compute the experimental IB thermal conductivity solely by the addition of a phonon point defect scattering term to that used to compute IIA conductivities.