mosphere by irreversible heterogeneous processes at the surface (*4*). We assume that the concentration of atmospheric CO_2 remains constant with time and use the model described by McElroy and Yung (*10*) to evaluate the past evolutionary history of N_2. Results are shown in Fig. 1 for η, the efficiency with which escaping atoms may be formed by reaction 2, equal to 0.16, 0.032, and 0.016; that is, with the efficiency taken equal to the value given by Strobel (*9*) and reduced by factors of 5 and 10, respectively. This leads to predicted values for the enrichment of ^{15}N equal to 144, 90, and 63 percent, respectively; that is, the ratio $^{15}N/^{14}N$ exceeds the terrestrial value by factors of 2.44, 1.90, and 1.63, respectively. A model with an efficiency of 0.03 would be consistent with the Viking measurements. The initial concentration of N_2 would correspond to a partial pressure of about 5 mbar in this case. The contributions to the escape flux due to reactions 1 and 2 are comparable for an efficiency of 0.032.

Figure 2 shows results obtained with a model in which we allowed for incorporation of HNO_2 and HNO_3 into surface minerals, with the heterogeneous reaction coefficient, γ, taken equal to 3×10^{-2}, 1×10^{-2}, and 0 (*4*). For all cases shown in Fig. 2 we used the efficiency factor η given by Strobel (*9*). A reaction coefficient γ equal to 10^{-2} provides a satisfactory fit to the Viking data, and would imply an initial partial pressure of N_2 equal to about 30 mbar. The model requires a net integrated deposition of nitrogen in minerals of magnitude 2.5×10^{23} atoms (N) per square centimeter averaged over the martian surface. The escape rate for nitrogen is dominated by reaction 2 for all models shown here.

Figure 3 shows results obtained with a model in which we allow for a secular variation in the partial pressure of atmospheric CO_2, which might arise because of changes in the obliquity and orbital eccentricity of Mars if the atmospheric pressure were controlled by an equilibrium with the polar ice cap, as discussed for example by Ward *et al.* (*11*). Curve A is based on the assumption that the partial pressure of CO_2 was equal to 10 percent of the present value for approximately 30 percent of the time over the past 4.5×10^9 years. Curves B and C model the case for which the pressure might have been much higher in the past: the partial pressure of CO_2 is taken as 65 mbar, for 33 percent of the time in curve B and for as much as 10 percent of the time in curve C (*12*). For the model in Fig. 3 we assumed a passive surface, $\gamma = 0$, and $\eta = 0.032$. The initial partial pressure of N_2 for all three cases lies in the range 2 to 9 mbar.

The measurement of enriched ^{15}N on Mars provides a powerful diagnostic tool which may be used to derive invaluable data on the past history of Mars. The uncertainty indicated by the spread of results shown in Figs. 1 to 3 may be narrowed considerably by careful laboratory studies of the velocity distribution of atoms formed by electron impact dissociation of N_2. An appropriate laboratory investigation would clarify the role that heterogeneous processes might play in the chemistry of nitrogen on Mars and would permit a quantitative estimate of the rate at which nitrogen may have been incorporated in surface minerals over the past 4.5×10^9 years. It is difficult, in any event, to escape the conclusion that the abundance of atmospheric nitrogen on Mars must have been much higher in the past: the partial pressure of the gas may have been as high as 30 mbar, and was surely no less than about 2 mbar.

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7. We assume here that atoms are released isotropically. Half of the atoms formed will be emitted in the upward hemisphere and may escape to space without suffering further collisions. We use a model atmosphere given in (*4*) to describe mean martian conditions. The model has an exobase at 210 km. It is interesting to note that reaction 1 could provide a selective mechanism for escape of ^{14}N, although for most models considered here nitrogen is lost by reaction 2 rather than reaction 1, and one would not expect the escape efficiency for reaction 2 to depend critically on isotopic composition. Moreover, the temperature assumed here for ions may be conservative on the low side, which would further reduce the dependence of the escape flux on the isotopic composition of N_2. We shall assume that ^{15}N and ^{14}N should escape with equal probability from the exobase. Clearly this matter should be reexamined as further data become available on the detailed kinetics for reactions 1 and 2, and as further measurements are made to define the temperature of Mars' high-altitude ionosphere. If we were to neglect the escape flux due to reaction 2 and if we were to further postulate that reaction 1 should favor escape of ^{14}N by a factor of 2, the initial pressure of N_2 would be 0.56 mbar and the enrichment for ^{15}N would be about 110 percent for a passive surface. If we were to reduce the escape efficiency for reaction 2 to a value $\eta = 0.008$, and again assume that reaction 1 favors reduction of fast ^{14}N by a factor of 2, the enrichment for ^{15}N would be about 140 percent, and the initial N_2 pressure would have a value of 1.1 mbar, for models similar to Fig. 1.
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Search for Organic and Volatile Inorganic Compounds in Two Surface Samples from the Chryse Planitia Region of Mars

Abstract. *Two surface samples collected from the Chryse Planitia region of Mars were heated to temperatures up to 500°C, and the volatiles that they evolved were analyzed with a gas chromatograph–mass spectrometer. Only water and carbon dioxide were detected. This implies that organic compounds have not accumulated to the extent that individual components could be detected at levels of a few parts in 10^9 by weight in our samples. Proposed mechanisms for the accumulation and destruction of organic compounds are discussed in the light of this limit.*

The objective of the Viking molecular analysis experiment is to analyze periodically the composition of the atmosphere at the surface of Mars and to search for organic compounds and certain inorganic volatiles in the surface material at the landing site. The principal instrument used for both investigations is a mass spectrometer (MS). It is used in conjunction with a gas chromatograph (GC) for the organic analyses. The objective of the entire system have been described previously (*1*), as have the results of the atmospheric analyses (*2*).

A gas chromatograph–mass spectrometer (GCMS) was chosen for the search for organic compounds chiefly because of its sensitivity and versatility. A number of mechanisms could contribute to the contemporary accumulation of organic compounds on Mars, for example, photochemical or biological processes and meteoritic infall. It is also possible that fossil organic compounds are present in the soil which reflect synthesis under conditions which existed on Mars long ago. The MS could analyze mixtures formed in any of these ways, and it was hoped that the details of the analyses would help to elucidate the mechanisms of synthesis.

Because the experiment involves the expulsion of the volatile or pyrolyzable constituents of the surface sample, one obtains, incidentally, information about volatiles such as water or CO_2 that might be released from the mineral matrix.

Experimental details. The instrument and some of the performance data have been described previously (*1*). Briefly, the instrument consists of a set of three small ovens in which a crushed surface sample (particle size < 300 μm) can be heated for 30 seconds to any of three temperatures (200°, 350°, or 500°C) to expel volatile substances and pyrolysis products. These substances are then swept onto the GC column (*3*) by a stream of $^{13}CO_2$ (*4*), and eluted from the column with H_2 being used as a carrier gas.

The GC column temperature is held at 50°C for the first 10 minutes, then linearly increased to 200°C in 18 minutes and held at this temperature for another 18, 36, or 54 minutes as desired. (Any of these three time periods can be selected by ground command.) The carrier gas is removed by passage through a palladium separator (*5*), and the eluting components enter the MS.

To protect the MS from an excess of material that could harm the ion source or pump, the latter automatically controls an effluent divider which reduces in steps the fraction of the effluent that enters the separator, and vents the remainder of the effluent to the atmosphere (*1*, *6*). The use of the effluent divider to protect the instrument results in a decrease of sensitivity in each segment of the chromatogram, this sensitivity being inversely proportional to the split ratio of the effluent divider operative in that segment.

The MS repetitively and continuously scans from *m/e* 12 to 200 in 10 seconds and has a dynamic range of 1 : 10^7. Each spectrum is recorded as 3840 digital data points, each one representing an ion current value encoded to 9 bits on a log scale. All these data, together with various other operating parameters, are telemetered back to Earth (about 1.4 to 1.8×10^7 bits per experiment). The data are processed on the ground by means of computer techniques that were developed previously (*7*) and were adapted specifically for the particular application discussed here (*8*).

Table 1. Acquisition sites and conditions of analysis for the two martian samples.

Date of analysis	Temperature (°C)	Mode	Time held at temperature (minutes)
Sample 1 [*GCMS-1* (*9*)] *subsurface; acquired on sol 8 (29 July 1976)*			
Sol 17 (7 August)	200°	Hydrous	18
Sol 23 (13 August)	500°	Anhydrous	36
Sample 3 [*GCMS-2* (*9*)] *surface; acquired on sol 31 (21 August 1976)*			
Sol 32 (22 August)	350°	Hydrous	54
Sol 37 (27 August)	500°	Hydrous	54
Sol 43 (2 September)	500°	Hydrous	36

After the Viking 1 spacecraft was launched on 20 August 1975, the instrument was tested during the Earth to Mars cruise from November 1975 to January 1976. One of the more important tests consisted of a complete "blank" experiment during which one of the sample ovens was heated to 500°C. The data (504 mass spectra and all associated engineering data) were returned to Earth and analyzed. They confirmed the presence of a few homologous oligomers of fluoropropyleneoxide (Freon-E type) in addition to residual adsorbed water. The level of contamination was sufficiently low that it did not cause concern. In fact, the impurities, fortuitously, provide an excellent mass standard.

After the successful landing of Viking 1, three separate samples of the martian surface were acquired by the surface sampler on sol 8 (GCMS-1), sol 14 (GCMS-2), and sol 31 (GCMS-3). The sol 8 acquisition was predominantly a fine-grained subsurface sample (from a depth of 4 to 6 cm) mixed with, at most, 10 percent of surface material. This sample was not immediately analyzed as planned, because the processor and distribution assembly (PDA) failed to indicate a full sample cavity. However, in view of the small amount of material required (< 200 mg) to fill one of the ovens, the decision was made to command the GCMS to proceed with the first analysis of the sol 8 sample at 200°C, while attempting to acquire a second sample.

The next sample, acquired on sol 14, was also a subsurface sample and was collected directly adjacent to the sol 8 site. The sol 14 (GCMS-2) sample was never analyzed but was discarded in favor of a sample from a very different site. The sol 31 (GCMS-3) sample was acquired in an area about 3 m from the sol 8 sites and was primarily a surface sample, composed of a coarse cohesionless granular material. A more complete description of the sites and the physical properties of the surface material are given elsewhere (*9*). The sample sites, times of acquisition, and conditions of analysis for the two samples from the Chryse Planitia region are summarized in Table 1.

Results. During the analysis of the first sample, traces of methylchloride and perfluoroethers of the Freon-E type were detected. These are contaminants previously encountered in preflight and cruise tests. Their detection as sharp gas chromatographic peaks producing the proper mass spectra demonstrates the correct functioning of all parts of the instrument. None of the five gas chromatograms obtained in the experiments listed in Table 1 showed any indication of the presence of organic compounds indigenous to the two samples. However, at 350° and 500°C considerable quantities of water were evolved (Table 2).

In experiments with the second sample we did not detect methylchloride or perfluoroether contaminants. Water eluting from the column, and accumulated water background in the instrument kept the effluent divider in a higher ratio than previously, thus obscuring the small amounts of these compounds that were present.

The absence of evidence for organic compounds in the data derived from these two samples from the surface at Chryse Planitia should be discussed. Obviously, compounds that are not transmitted by the GC column (*3*) or its interface with the MS cannot be detected. The detection limit for compounds that are transmitted can be calculated from the mass spectral data obtained in these experiments. Since the retention behavior of any compound can be predicted, we examined the signal observed at the proper retention time in the mass chromatogram (*7*) and used the intensity of the most diagnostic, intense ion signal of the compound in question to estimate its abundance. In no case of interest was there a maximum in the mass chromatogram; this indicates the absence of all the compounds which we have searched for as yet, at the level corresponding to the background ion current. Table 3 lists the upper limits for a few typical compounds. A range is given because the sen-

Table 2. Results of the molecular analysis experiments.

Material	Quantity (temperatures in degrees Celsius)
I. Inorganic	
Carbon dioxide	Some in all experiments (quantitation not yet available)
Water	Sample 1: at 200°, much less than 0.1% at 500°, 0.1 to 1.0% Sample 2: at 350°, 0.1 to 1.0% at 500°, somewhat less than at 350°
II. Organic	None detected (see Table 3 for detection limits)
III. Terrestrial contaminants	
Methyl chloride	~ 15 ppb
Fluoroethers	1 to 50 ppb

sitivity differs from run to run due to the variability of the effluent divider state. It should be noted that our estimates represent upper limits at the present state of data reduction, and do not imply that we believe that the substances referred to in Table 3 are present at that or a lower level. They were selected solely as examples because they have been detected at a level of 0.01 to 10 parts per million (ppm) in other relevant materials, for example, a terrestrial soil from the Antarctic (*10*) and the Murchison meteorite, by means of an instrument virtually identical with that operating on the surface of Mars (*11*).

There are a number of small molecules of intrinsic interest in relation to nonbiological as well as biological chemistry for which it is difficult to set a detection limit because of (i) the way in which the instrument was operated, (ii) the relatively large amount of water that was evolved at temperatures higher than 200°C, and (iii) the use of $^{13}CO_2$ to flush the vaporized material out of the sample oven and onto the GC column. For this reason, compounds like CH_4, C_2H_2, C_2H_4, C_2H_6, and probably NH_3 would have been completely obscured. For other very volatile materials such as CH_3OH, CH_2O, HCN, $(CN)_2$, and C_3H_{4-8} the detectability is limited by the split ratio of the effluent divider in the relevant part of the chromatogram, particularly where CO_2 and H_2O elute. The limit of detection estimated for these compounds is in the tens of parts per million for most experiments. One exception is the 200°C experiment with sample 1, where the split ratio in this region of the gas chromatogram was much more favorable (3 : 1, that is, 25 percent of the effluent admitted to the MS), in which case this group would have been detected at levels of tens of parts per billion.

In view of the results obtained by Viking 1 it is planned to modify the strategy of the experiments to be conducted with the instrument on Viking lander 2 in such a manner as to eliminate the contributions of the $^{13}CO_2$ to the obscuration of the most volatile components that might evolve from the sample upon heating.

We have not been able to detect SO_2, free sulfur, or H_2S. While traces of H_2S would have been vented with the CO_2, thus escaping detection, any appreciable quantities of either S or H_2S entering the palladium separator would have substantially decreased its efficiency or even inactivated it completely. The efficient operation of the separator provides indirect evidence that these two substances were not evolved at levels corresponding to a few parts per million in the samples.

Discussion. The failure to find organic compounds at the detection limit of our instrument in the two Viking lander 1 sampling sites is an important observation that must be carefully evaluated. It has implications concerning the composition of the planet in the Chryse Planitia region, the fate of organic compounds from nonmartian sources falling on the planet's surface, and the steady-state concentration of any organic compounds which are being synthesized by photochemical processes. It also provides an upper limit to the amount of biologically maintained organic material in the samples.

Cosmochemical considerations, and studies on the volatiles of Mars (*12*), indicate that substantial quantities of CO_2 must have been derived from more reduced forms of carbon during the planet's history. The fact that such carbon compounds are not present in detectable levels in the Chryse Planitia region does not necessarily preclude their existence in less disturbed areas of the planet's surface or interior, where they may have been protected from oxidation, photodestruction, and other degradative processes.

The contribution of organic compounds to the martian regolith from nonmartian sources (mainly meteoritic matter) can be calculated from estimates of their influx rate on Mars relative to that on the moon. It is estimated that after mixing in a regolith that has a mean thickness of 4.6 m, meteoritic input at three Apollo sites on the moon contributes an amount of material equivalent to 1.1 percent of type 1 carbonaceous chondrites (or C-1 equivalent component) to the regolith (*13*). The infall of meteorites on Mars has been estimated by some authors to be approximately twice that on the moon (*14*). The martian regolith is considered to be approximately 2 km deep (*15*), that is, several orders of magnitude larger than the regolith on the moon. Thorough mixing with the regolith would cause substantial dilution of the meteoritic input of organic compounds, and their concentrations would be reduced to an equivalent of about 0.005 percent of material from type 1 carbonaceous chondrites. Therefore, an organic compound, such as naphthalene, detected in the Murchison meteorite at the level of 1 ppm with the laboratory version of the Viking lander 1 instrument (*11*) would, according to these estimates, be diluted in the martian regolith to 0.05 part per billion (part per 10^9).

However, some authors suggest a higher meteoritic infall rate on Mars (*16*), and a mixed regolith layer of only about 100 m. If this were correct the abundance of naphthalene in the martian soil would be about 10 ppb, which would be detectable by the instrument on Mars. The fact that we have not found naphthalene at this level argues against such a model unless the meteoritic organic compounds have been destroyed to a large extent.

Contemporary synthesis of organic compounds on the surface of Mars, or on dust particles suspended in its atmosphere, represents another source of such substances. Hubbard *et al.* (*17*) have demonstrated the synthesis of organic compounds by an ultraviolet light-induced reaction of CO with water adsorbed on inorganic matrices under simulated martian conditions. The steady-state concentrations of the primary products of this process are just below our detection limit (*18*). The fact that we have not found organic compounds implies that the accumulation of stable products by further condensation reactions of the primary photochemical products has not been a major process.

Finally, the implications of our results on the interpretation of direct life-detection experiments should be discussed. The Viking GCMS was not intended to be an instrument for the detection of life. However, if organic compounds were found in the martian soil, such a finding could be considered under certain circumstances supportive of the positive identification of biological processes on Mars. The reverse is not necessarily true, however. It is possible to have a small population of microorganisms in a sample without being able to detect the organic compounds evolved from their biomass (*19*).

Substantial amounts of residual organic matter are usually found associated even with small numbers of microorganisms on Earth. More than 20 organic compounds were identified, at the level of 0.01 to 1 ppm, in a 100-mg sample of Antarctic soil (*11*) that was supposed to contain less than 10^4 microorganisms per gram (*10*). If substantial numbers of organisms were present in our sample they would have to be much more efficient than terrestrial organisms as scavengers of biological debris.

Having discussed the possible sources of organic materials we should also mention potential degradative processes which could cause their disappearance. It is difficult to estimate the degree to which oxidation and other degradative processes might reduce the abundance of organic compounds in the martian regolith. Possible destructive agents include ultraviolet radiation, oxygen, and such oxidants as nitrates and metal oxides, acting independently or synergistically. Certainly, continuous exposure to shortwave ultraviolet light, in the presence of oxygen, will cause rapid photolysis of most organic compounds. Even ultraviolet light of longer wavelength is known to photooxidize many organic compounds on the surface of certain metal oxide catalysts (for example, FeO, Fe_2O_3, and TiO_2) (*20*).

The destructive oxidation of organic compounds by nitrate, either in situ or during the heating of the martian sample in the GCMS oven, should also be considered. However, limited experiments with terrestrial soils (*21*) indicate that only a fraction of the organic matter is oxidized when samples are heated to 500°C in the presence of excess nitrate.

The presence of highly oxidizing inorganic constituents in the martian surface material has been inferred from some of the data generated by two of the Viking biology experiments (*22*). For a number of reasons, we tend to rule out the possibility that such agents, if present, have destroyed organic material in our sample during the 30-second heating period. First, the oxygen evolution, 725 nmole of O_2 per cubic centimeter of surface sample, would at most oxidize the equivalent of 6 μg of reduced carbon, if the oxidation were quantitative; second, the evolution of water, even at 200°C, is sufficient to convert the oxidizing material to O_2; and third, the observation of CH_3Cl in one of the experiments seems to demonstrate that organic compounds are not oxidized to the extent that they would escape detection.

Table 3. Upper limits of selected organic compounds which would be detected if present, in the two samples from the Chryse Planitia region of Mars.

Compound	Range of detection limits (parts per 10^9)
Aliphatic hydrocarbons	
Butene	< 1 to 10
Hexane	< 1 to 10
Octane	< 1 to 10
Aromatic hydrocarbons	
Benzene	< 0.5 to 5
Toluene	< 0.5 to 5
Naphthalene	< 0.05 to 0.5
Oxygen-containing compounds	
Acetone	<10 to 50
Furan	< 0.1 to 1
Methylfuran	< 0.2 to 2
Nitrogen-containing compounds	
Acetonitrile	< 1 to 10
Benzonitrile	< 0.2 to 2
Sulfur-containing compounds	
Thiophene	< 0.1 to 0.5
Methylthiophene	< 0.1 to 0.5

Mineralogical implications. The data of particular interest from a mineralogical point of view are those dealing with the evolution of volatiles produced by thermal destruction of minerals such as hydrates or hydroxides, carbonates, sulfates, and nitrates. Data of the lander imagery (*23*) and inorganic chemical (*24*) investigations strongly suggest the presence of fine-grained ferric oxide or hydroxide in the material sampled, but do not definitely discriminate between anhydrous ferric oxide (presumably hematite) and hydrated forms, the commonest of which, at least terrestrially, is goethite, FeOOH. The data presented here indicate that most of the water is evolved at 350°C or below; additional water detected at 500°C after the 350°C heating of the second sample presumably includes some contribution from minerals incompletely decomposed in the 350°C heating. This behavior seems likely to reflect the presence of some hydrate other than goethite. Direct experimental data on decomposition of minerals at the heating rates and durations used in the present experiments are scanty, and the dehydration temperature of goethite is known to depend on many factors, such as degree of crystallinity, which cannot be determined in this instance. Calculations from kinetic data (*25*) indicate, however, that the characteristic (e^{-1}) time for dehydration of goethite should be tens of days at 200°C, tens of minutes at 350°C, and a few seconds at 500°C. If these figures are of the correct order, the H_2O evolved from the martian samples could not have been derived from goethite. Hydrated sulfates may be present in the martian surface material (*24*), and could possibly be the sources of the H_2O evolved between 200° and 350°C.

Most terrestrial clay minerals lose their lattice H_2O at temperatures above 500°C; physically adsorbed or loosely bound H_2O, if present, would not have been detected as it would have been desorbed between sample acquisition and analysis (*26*). Thus clay minerals should not have contributed to the water which we detected. Detailed testing of various materials on the laboratory GCMS may permit more confident identification of the hydrates in our samples.

The very low upper limit on evolved sulfur corresponds to partial pressures of the order of 10^{-4} atm (maximum) in the oven at 500°C. This value does not preclude a priori the existence of mineral sulfides in the sample. On the other hand, terrestrial soils containing sulfide minerals have evolved detectable amounts of reduced sulfur species in the laboratory instrument, and we, therefore, regard the presence of sulfides (other than extremely refractory ones, for example, troilite) as very unlikely.

The data also suggest that the sample evolved CO_2 during heating, but complexities in the dynamics of flow within the instrument make interpretation difficult at this time. More detailed analysis of the data, and testing on the laboratory instrument, may enable us to make better estimates of the amounts of CO_2 evolved, and hence better understand the nature of the carbonates present in the samples.

Conclusions. Our preliminary results obtained from two samples of the surface of Mars in the Chryse Planitia region indicate that the material releases only 0.1 to 1 percent of water when it is heated to 350° or 500°C. This water is presumably present in mineral hydrates which release water at these high temperatures. The samples do not contain organic compounds more complex than, for example, propane or methanol, at the level of a part per 10^9. Such low-molecular-weight compounds were not found at detection limits in the range of 1 part per 10^5. These results seem to exclude the existence of any efficient contemporary process that produced organic compounds. It also makes it unlikely that there are low-efficiency processes occurring over a long period, which slowly accumulate organic compounds stable in the martian environment. It has to be reiterated that these findings relate to only two samples at one landing site, and care has to be taken in extrapolating our conclusions to other parts of the planet. It is hoped that the results soon to be obtained from the Viking lander 2 will add another dimension to our knowledge.

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3. The GC column is filled with a liquid-modified organic adsorbent consisting of 60- to 80-mesh Tenax-GC (2,6 diphenyl-*p*-phenylene oxide) coated with polymetaphenoxylene. This specific packing was developed to (i) maximize the separation of H_2O and CO_2 from organic compounds, (ii) transmit efficiently most compound classes at the low nanogram level, (iii) have exceptional thermal stability, and (iv) have mechanical strength compatible with the rigors of space flight [M. Novotny, J. M. Hayes, F. Bruner, P. G. Simmonds, *Science* **189**, 215 (1975)].
4. The use of $^{13}CO_2$ for flushing the oven during the heating period was a late change in design. It was necessitated by the observation that some compounds were reduced by the hydrogen previously used in this step. Isotopically labeled CO_2 was chosen in order to distinguish it from any CO_2 evolved from the sample upon heating. Furthermore, it would make it possible to detect incorporation of CO_2 into organic compounds during the heating or pyrolysis.
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19. The average detection limit (Table 2) of the GCMS for a single compound is 1 ppb (10^{-9} g per gram of soil). If we assume that the efficiency of pyrolysis is 10 percent, then 10^{-7} g of organic matter would be required for the detection of a major component that represented 10 percent of the total pyrolyzate-volatile fraction. Furthermore, if the dry weight of a typical prokaryotic cell were taken as 10^{-13} g, then 10^6 organisms would be required to yield 10^{-7} g of organic matter.
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The Atmosphere of Mars near the Surface: Isotope Ratios and Upper Limits on Noble Gases

Abstract. *Several new analyses of the martian atmosphere have been carried out with the mass spectrometer in the molecular analysis experiment. The ratios of abundant isotopes of carbon and oxygen are within 10 percent of terrestrial values, whereas nitrogen-15 is considerably enriched on Mars. We have detected argon-38 and set new limits on abundances of krypton and xenon. The limit on krypton is sufficiently low to suggest that the inventories of volatile substances on Mars and on Earth may be distinctly different.*

We have obtained new data on the composition of the martian atmosphere using the mass spectrometer of the molecular analysis experiment (*1*). The purpose of this set of investigations was to determine the relative abundances of the isotopes of argon, carbon, oxygen, and nitrogen and to search for trace constituents, especially the other noble gases. Analysis of these results and the acquisition of additional data are continuing.

A summary of the analyses carried out is given in Table 1. Atmospheric gases were accumulated in the sample chamber (i) as unaltered atmosphere for direct analysis, or (ii) as enriched atmosphere in which progressively admitted samples of the atmosphere were subjected to treatment, with Ag_2O and LiOH [as described in (*1*)] to absorb the CO and CO_2, and $Mg(ClO_4)_2$ to remove the resulting water, so that the partial pressures of the trace gases would be increased before the contents of the sample chamber were analyzed. In this way, the cycling and chemical scrubbing of ten samples of martian atmosphere admitted progressively to the analytical chamber led to a