The Search for Organic Substances and Inorganic Volatile Compounds in the Surface of Mars

K. BIEMANN,[1] J. ORO,[2] P. TOULMIN III,[3] L. E. ORGEL,[4] A. O. NIER,[5] D. M. ANDERSON,[6] P. G. SIMMONDS,[7] D. FLORY,[8] A. V. DIAZ,[9] D. R. RUSHNECK,[10] J. E. BILLER,[1] AND A. L. LAFLEUR[1]

A total of four Martian samples, one surface and one subsurface sample at each of the two Viking landing sites, Chryse Planitia and Utopia Planitia, have been analyzed for organic compounds by a gas chromatograph–mass spectrometer. In none of these experiments could organic material of Martian origin be detected at detection limits generally of the order of parts per billion and for a few substances closer to parts per million. The evolution of water and carbon dioxide, but not of other inorganic gases, was observed upon heating the sample to temperatures of up to 500°C. The absence of organic compounds seems to preclude their production on the planet at rates that exceed the rate of their destruction. It also makes it unlikely that living systems that behave in a manner similar to terrestrial biota exist, at least at the two Viking landing sites.

1. INTRODUCTION

One of the major goals of the Viking mission was to find out whether or not organic compounds exist on the surface of the planet Mars and, if they do exist, to determine their structures and measure their abundances. This seemed important because we hoped that the nature of Martian organic molecules would provide a sensitive indicator of the chemical and physical environment in which they were formed. Furthermore, we hoped that the details of their structures would indicate which of many possible biotic and abiotic syntheses are occurring on Mars. The relatively simple compounds expected from the photochemical reaction of the components of the atmosphere [*Hubbard et al.*, 1973] differ greatly, for example, from the organic compounds found in carbonaceous chondrites [*Oro*, 1972; *Nagy*, 1975] and which in turn differ greatly from the complex and highly ordered structurally specific substances produced by living cells. Furthermore, since much is known about the degradation of organic compounds under the influence of high temperature, pressure, irradiation, etc. [*Miller et al.*, 1976], the absence of organic compounds above a certain limit of detection might eliminate certain sets of conditions that otherwise could be postulated to exist or to have existed at the surface.

To achieve our goal, a sensitive technique of high structural specificity and broad applicability was required. A gas chromatograph coupled to a mass spectrometer was chosen [*Anderson et al.*, 1972] in order to combine the sensitivity and the structural specificity of electron impact mass spectrometry with the separation power of gas chromatography. An obvious approach would have been to mimic terrestrial laboratory procedures by digesting the surface material to be analyzed by wet chemical methods, followed by solvent extraction and possibly chemical separation. However, the automation and the miniaturization of such a system, which has to be of the utmost reliability, was clearly beyond the technical and economic resources available for the experiment and was certainly far outside the weight and power allocations. In the task at hand, where nothing at all is known about the organic chemistry of the Martian surface, a general or group identification is a major advance, should one encounter a very complex mixture. This is in contrast to terrestrial investigations, where much more specific information is required and can be achieved.

For these reasons, thermal volatilization (without or with thermal degradation) of the organic compounds from the surface material was selected as the simplest and most reliable approach. It was expected that the nature of the thermal degradation products (pyrolyzate) would lead to the identification of the set of parent compounds originally present in the sample.

The original plans [*Anderson et al.*, 1972] also included a sample oven which was directly monitored by the mass spectrometer, thus making it possible to detect more complex and less volatile substances which would not pass through the gas chromatograph and associated interfaces. However, this part was eliminated during the design and test phase to simplify the final instrument package [*Biemann*, 1974]. At the same time the number of sample ovens connected to the gas chromatograph was reduced from eight to three. Since each oven could utilize only one soil sample, the flexibility of the experiment was considerably reduced. In addition, during interplanetary cruise it was found that one oven in each instrument was not operable. Fortunately, the excellent data transmission quality and quantity throughout the mission and the seemingly uniform surface composition made this reduction in the number of samples less damaging than might have been anticipated. The loss of the direct input oven which could be heated slowly and continuously was, in retrospect, more regrettable because it could have been used to obtain more information concerning the mineralogy of the surface material.

2. INSTRUMENTATION

The instrument has, in principle, been described previously [*Anderson et al.*, 1972; *Biemann*, 1974], but the final flight hardware differed in some of the parameters. It is therefore

[1] Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.
[2] Department of Biophysical Sciences, University of Houston, Houston, Texas 77004.
[3] U.S. Geological Survey, Reston, Virginia 22092.
[4] Salk Institute for Biological Studies, San Diego, California 92102.
[5] School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota 55455.
[6] Division of Polar Programs, National Science Foundation, Washington, D. C. 20550.
[7] Organic Geochemistry Unit, School of Chemistry, University of Bristol, Bristol, England.
[8] Spectrix Corporation, Houston, Texas 77054.
[9] NASA Langley Research Center, Hampton, Virginia 23665.
[10] Interface, Inc., Fort Collins, Colorado 80522.

Paper number 7S0556.

necessary to describe here briefly the final version and its mode of operation. Figure 1 illustrates the major features of the instrument. It consists of the sample ovens with their associated valves, the gas chromatograph, an effluent divider which protects the mass spectrometer from excessive gas pressure, the carrier gas separator, the mass spectrometer, and the associated electronics and logic system.

The sample ovens (ceramic, 2-mm inside diameter, 19 mm long) are mounted in a circular holder that can be positioned in a preset sequence upon a command from the instrument's internal logic system, but this sequence in turn can be modified (within limits) by ground command if the experimental results call for a change.

There are two positions to which any of the ovens can be moved in any sequence. The 'load position' is directly under the sampling system, which delivers about 1–2 cm^3 of surface material that after having been ground is passed through a 0.3-mm sieve. A mechanical poker pushes the material through a funnel into the oven. This operation is timed in such a manner that the filling of the oven is complete with any of the terrestrial test soils (including finely ground basalt, commonly referred to as 'lunar nominal'). However, there is no sensor measuring the final level or completeness of the filling operation. Thus one has to assume that the oven is filled to capacity, i.e., approximately 60 mm^3 of surface material is being analyzed. The oven is then moved by rotation of the circular holder to the 'analysis position,' where the lines leading to valves V1 and V3 are clamped onto both ends of the oven. A gas-tight seal is achieved by pressing the circular knife edges, into which the gas lines terminate, into gold rings attached to each end of the oven. In the normal use of an oven this seal is established only once. It had been shown in a series of tests that the seal can be reestablished more than a dozen times without leaking because the precision of the positioning mechanism is such that the knife edge always hits the groove made in the first sealing operation.

Each oven can be heated to 50°, 200°, 350°, or 500°C in 1–8 s (depending on the temperature selected) and held there until a total of 30 s has elapsed. Valves V1 and V3 are opened for 30 s prior to the heating of the oven and are closed immediately after the heating period. Any volatile material that emerges from the sample is swept onto the gas chromatographic column with about 2–3 ml of ^{13}C-labeled carbon dioxide (99+%

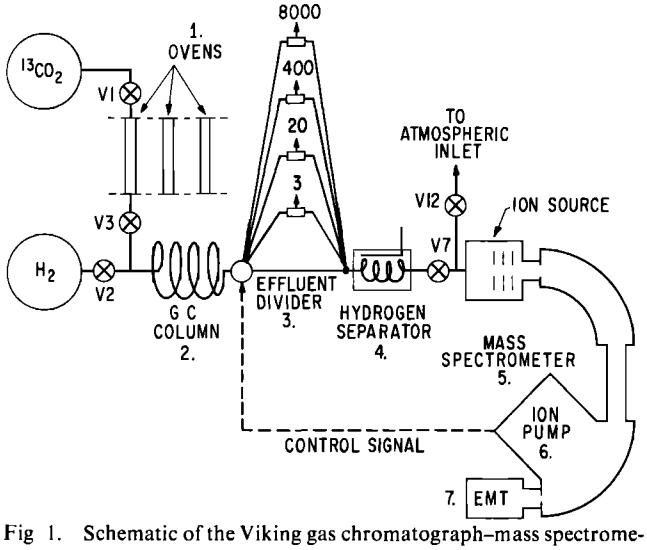

Fig 1. Schematic of the Viking gas chromatograph–mass spectrometer.

isotopic purity, Mound Laboratories). The use of CO_2 rather than H_2, which is the carrier gas for the gas chromatograph, avoids catalytic or thermally induced reduction of the organic material possibly present in the sample. It causes certain complications, however, which will be discussed later in connection with the operation of the so-called effluent divider.

At this point it should be noted that during the 50 min preceding the heating of the sample the entire instrument is turned on in the following sequence: the 'thermal zone' (which contains the effluent divider with valves V4, V4A, V5, and V6; the hydrogen separator; and valves V7 and V12) and the ion source of the mass spectrometer are heated; then the tubing leading to the oven and to the column are heated; finally, the mass spectrometer is energized. The recording of data begins just prior to the first opening of valves V1 and V3. Valve V7 opens 1 min later; thus six scans of the mass spectrometer background are obtained just prior to the analysis.

Simultaneously with the closing of valves V1 and V3, valve V2, which connects the hydrogen tank (initial pressure of ~750 psi (52 bars)) to the gas chromatograph, is opened, thus starting the gas chromatographic phase of the experiment.

The gas chromatographic 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 maximize the separation of water and CO_2 from organic compounds, to transmit efficiently most compound classes at the low nanogram level, to have exceptional thermal stability, and to have mechanical strength compatible with the rigors of space flight [*Novotny et al.*, 1975]. The column consists of a stainless steel tube of 0.76-mm inside diameter 2 m in length. Initially, the temperature of the gas chromatographic column is held at 50° for 12 min, followed by a linear increase to 200° over a period of 18 min, and then held at this temperature for 18, 36, or 54 min. The holding period can be selected by commands previously sent from earth. This permits control of the amount of data produced to avoid filling valuable tape recorder space with data not containing useful information. There were a number of additional commands which allowed one to manipulate the volume of data recorded during each experiment, but they were rarely used during the mission.

The restrictor at the hydrogen tank was adjusted to give a flow rate of about 2.5 ml/min for the first experiment. It slowly decreased in each additional run because of decreasing tank pressure. The amount of hydrogen carried along was such that one could expect to perform a large number of experiments (prelaunch and postlaunch tests and experiments on the Martian surface) before the flow rate falls below 1.5 ml/min, which was still deemed to be an acceptable value.

The interface between the gas chromatograph and the mass spectrometer includes a network of valves and restrictors (the 'effluent divider'). These are designed to prevent the entry into the mass spectrometer of large quantities of gases which would raise the pressure above the capacity of the small ion pump, which would then cease to function. Such an event would permanently disable the spectrometer and thus the entire instrument, including its capability to perform atmospheric analyses. To protect itself from such a catastrophe, the ion pump controls the flow rate of material into the spectrometer by causing the effluent divider to vent to the Martian atmosphere such a fraction of the gas chromatographic effluent that the remainder which enters the spectrometer can be pumped efficiently. This is accomplished by a control loop in which the magnitude of the ion pump current, in combination with its

rate of rise, controls the valves between the exit of the gas chromatographic column and the hydrogen separator. Four such valves are employed, each of which contains a restrictor. The restrictors are of such a conductance that they produce nominal split ratios (parts entering the mass spectrometer to parts vented) of 1:3, 1:20, 1:400, and 1:8000. Naturally, this causes a decrease of total system sensitivity by the same ratio, but the higher split ratios are reached only when very large amounts of material emerge from the column. It was expected that this would only be water or carbon dioxide from decomposing minerals and the $^{13}CO_2$, all of which appear at the very beginning of the gas chromatogram. If the ion pump current exceeds a predetermined value, value V7 (the one just ahead of the mass spectrometer) closes, affording final protection. The reversal of these steps is controlled both by the ion pump current falling below a certain level and by the time elapsed since the last action to avoid valve 'chatter' (rapid changing of the split ratio back and forth). There are two modes of operation that can be selected by ground command, each involving different sets of lapse times. One is termed the 'hydrous' mode and requires 45 s before the effluent divider switches from 1:8000 to 1:400, 2 min for the next step (1:400 to 1:20), and 15 min each for the third and fourth steps (1:20 to 1:3 to 1:0). Although the gas chromatographic column was designed [*Novotny et al.*, 1975] to elute water early as a sharp peak, it is not reasonable to expect the pump current to decrease from maximum to 1:20 of its value in less than 45 s and to 1:400 in less than 2 min 45 s, etc. Since this large overload was expected only from water expelled upon heating the sample, the term hydrous was adopted for this operating mode. For situations where it is reasonable to assume that negligible quantities of water are produced (i.e., if it turned out that the Martian surface material is free of thermally labile water or hydrates), another mode, termed 'anhydrous,' is available upon command; in that case the maximum waiting period is 15 s between each step. If the pressure falls below a predetermined level, the waiting period becomes 10 s in either mode.

The hydrogen separator [*Dencker et al.*, 1972] consists of a 60-cm-long silver-palladium tube of 0.15-mm inside diameter surrounded by a sodium hydroxide–water eutectic which melts at about 160° and is operated at 220°C. The Ag-Pd tube forms the anode, and another larger tube placed within the electrolyte but opening to the atmosphere forms the cathode of an electrolytic cell ($\Delta V = 0.7V$). The separator removes more than 99.99995% of the hydrogen carrier gas and thus prolongs the life of the ion pump and keeps the ion pump current well below the threshold at which the effluent divider network starts to operate. In the organic analysis mode the ion source of the mass spectrometer is held at 225°C, the filament is operated at 70 eV, and the accelerating voltage is scanned from 2350 V ($\approx m/e$ 11.5) to 125 V ($\approx m/e$ 215) every 10.24 s during the entire experiment. The electron multiplier is set to a gain of about 10^3 but specifically to such a value that the ion currents for CO_2 in the atmospheric mode are equal for both the Viking lander 1 (VL-1) and the Viking lander 2 (VL-2) instruments, which have inlet leaks of slightly different conductance. There are two higher gains that can be selected by ground command, but these were not used during the mission except for the atmospheric analysis [*Owen et al.*, 1977].

During each scan, 3840 samples of the output of the electron multiplier amplifier were taken after conversion to a log value and were encoded to 9 bit. The original plans for handling the data had called for peak selection and mass assignment at that point and perhaps even further compression of the data. However, when an on-board tape recorder with high capacity became available and the predicted data rate for transmission from lander to orbiter and from orbiter to earth increased to 16 kbit/s and 4 kbit/s, respectively, the transmission of all raw data (about 17 Mbit per analysis) became possible. Thus all the data processing to mass spectra and chromatograms, mass scale calibration, noise spike recognition, averaging of data, etc., was done on earth, either at the Jet Propulsion Laboratory (JPL) or at the Massachusetts Institute of Technology (MIT) by using algorithms previously developed in the latter laboratory [*Hertz et al.*, 1971; *Biller and Biemann*, 1974; *Biller et al.*, 1977]. The final data were recorded on 16-mm microfilm and displayed on a film reader for inspection and interpretation. For the immediate first-order processing of the data during the mission these programs were adapted by R. Williams for use on the JPL computer system.

The performance of the instrument will be demonstrated by the results obtained with a laboratory version. It corresponds almost exactly to the flight instrument with the exception of the associated test equipment and the capability of reusing a single sample oven which is filled manually. A sample of Antarctic soil (sample 638 [*Cameron et al.*, 1970]) was heated to 200° and 500°C and was analyzed as described above. The gas chromatogram (as total ion current plot) is shown in Figure 2. The interpretation of the mass spectral data led to the identification of a large number of compounds, the more abundant of which are marked in the figure and listed in the following tabulation.

Code in Figure 2	Compound
AR-1	benzene
AR-2	toluene
AR-3	xylene (benzene-C_2)
AR-5	benzene-C_3
AR-9	naphthalene
AR-10	methyl naphthalene
AR-11	biphenyl
O-1	furan
O-2	acetone
O-4	methyl vinyl ketone
O-5	methyl furan
O-6	furane-C_2
O-7	benzofuran
O-8	phenol
O-10	dibenzofuran
N-1	acetonitrile
N-2	propionitrile
N-3	pyridine
N-4	benzonitrile
N-5	toluonitrile
S-1	thiophene
S-2	methylthiophene
S-3	thiophene-C_2
S-4	benzthiophene
S-5	sulfur dioxide
HC-1	cyclohexene

Code 'AR' stands for aromatic hydrocarbons; 'O,' for oxygen-containing compounds; 'N,' for nitrogen-containing compounds; 'S,' for sulfur-containing compounds; and 'HC,' for aliphatic hydrocarbons. The compounds detected range in size from acetonitrile to dibenzofuran. Although the latter does not give rise to a discernible peak in the gas chromatogram, a well-developed peak is displayed in the mass chromatogram of the m/e 168, the molecular ion of dibenzofuran. As a measure of sensitivity the quantities represented by the peaks representing benzonitrile and benzofuran were calculated and found to correspond to 150 and 43 ppb, respectively. In fact, acetoni-

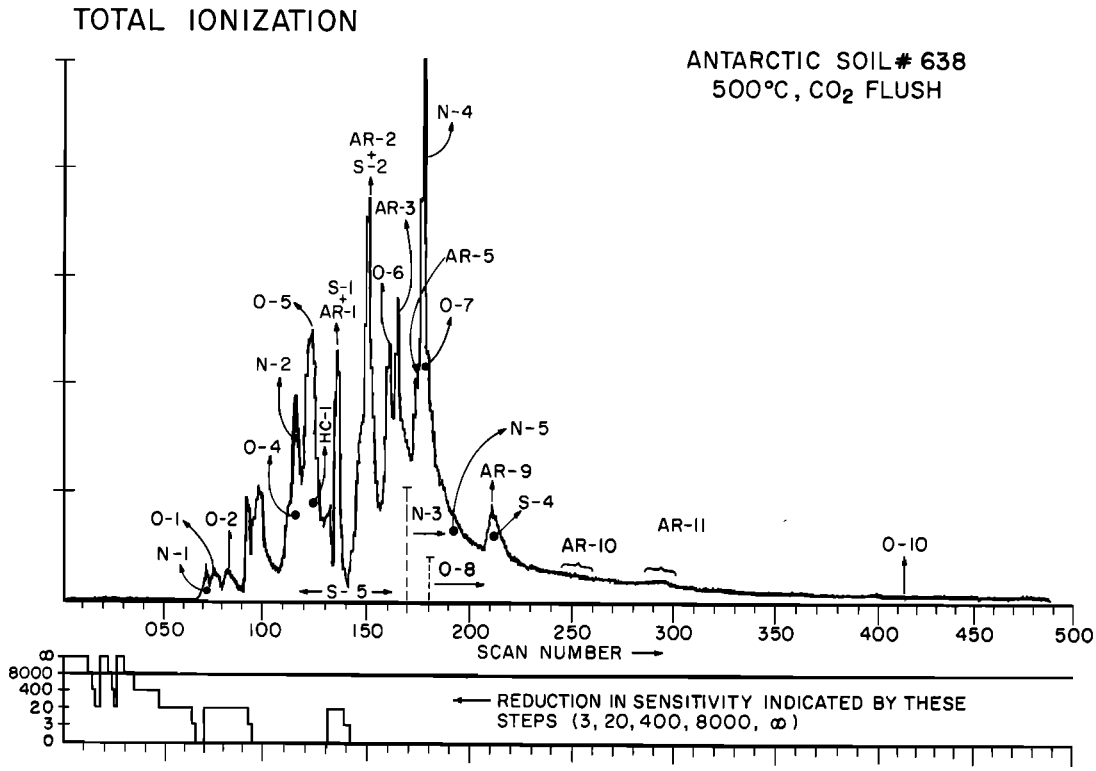

Fig. 2. Gas chromatogram (plot of the sum of intensities above *m/e* 47) obtained with a sample of Antarctic soil. The identifying codes for the various components are listed in the tabulation in section 2 of the text. Components N-3 (pyridine) and O-8 (phenol) appear (as judged from the mass chromatograms of their molecular ions) as tailing peaks with a sharp front represented by the vertical dashed lines at scans 170 and 180, respectively. The abscissa represents scan numbers of the consecutive mass spectral scans of 10.24 s each; each tick mark thus corresponds to 102.4 s of elapsed time of the gas chromatogram. The ordinate is linear, with the largest peak plotted to full scale.

trile and benzene are major components that cause the effluent divider to switch into the 20:1 state. Compounds eluting before acetonitrile are obscured by the large water peak which causes the venting of most or all of the material emerging from the gas chromatograph.

TABLE 1. Acquisition Sites and Analysis Conditions for the Four Martian Samples

Identification Number*	Date of Analysis	Oven Temperature, °C	Mode	Oven Purge Gas	Time Column Held at 200°, min	Oven
VL-1 Sample 1 (Subsurface), Acquired on Sol 8						
10015	sol 17	200	hydrous	$^{13}CO_2$	18	1
10018	sol 23	500	anhydrous	$^{13}CO_2$	36	1
VL-1 Sample 2 (Surface), Acquired on Sol 31						
10023	sol 32	350	hydrous	$^{13}CO_2$	54	2
10024	sol 37	500	hydrous	$^{13}CO_2$	54	2
10025	sol 43	500	hydrous	$^{13}CO_2$	36	2
VL-2 Sample 1 (Bonneville Duracrust), Acquired on Sol 21						
10032	sol 24	200	hydrous	H_2	36	2
10033	sol 26	350	hydrous	H_2	36	2
10034	sol 35	500	hydrous	H_2	36	2
10035	sol 37	500	hydrous	$^{13}CO_2$	36	2
VL-2 Sample 2 (Under Badger Rock), Acquired on Sol 37						
10036	sol 41	50	hydrous	H_2	36	3
10037	sol 43	200	hydrous	H_2	36	3
10038	sol 45	350	hydrous	H_2	36	3
10039	sol 47	500	hydrous	H_2	36	3
10041	sol 61	500	hydrous	$^{13}CO_2$	36	3

*This number is a data processing code listed here to facilitate correlation of data in this table with the figures in the text.

3. RESULTS

Altogether, four samples of Martian surface and subsurface materials were analyzed for organic compounds and inorganic volatiles. Two samples were obtained at each landing site, Chryse Planitia (VL-1) and Utopia Planitia (VL-2). The results of the former have been summarized previously [*Biemann et al.*, 1976] and will be discussed here in more detail. The VL-2 data, which gave essentially the same results, have not been described before and thus will require more discussion.

Table 1 lists all samples, including dates and conditions, that were analyzed during the prime mission (before conjunction) at both landing sites. Two major changes were made for the experiments at the second site. First, the $^{13}CO_2$ purge mode was replaced in the first few analyses of each sample by the 'hydrogen expansion mode,' in which the opening of valve V1 was replaced by the opening of valve V2 just before the heating of the sample. In this way the effect which the large amount of carbon dioxide has on the effluent divider (which remains in the 1:8000 mode for a relatively long time and even closes valve V7) is eliminated because the oven becomes filled with hydrogen at relatively high pressure (about 0.5 atm), which during the heating of the sample expands back into the carrier gas stream. In addition, this mode replaces the gas in all the void areas between valves V1 and V3 by hydrogen, thus allowing more reliable detection of CO_2 which may evolve from the sample in subsequent heating cycles.

The second change that is evident from Table 1 is the fact that more consecutive analyses were performed on the samples

from Utopia than from Chryse. Confidence in the communication system had substantially increased since the beginning of the first mission. New data could therefore be transmitted in place of the automatic retransmission of each set of data (as was done previously to avoid accidental loss of any of the irretrievable information).

The results are summarized in Figure 3, in which the gas chromatograms of all VL-1 experiments are plotted at the same scale. These chromatograms are shown as the summed intensity of all ions above *m/e* 47 (to eliminate the effect of H_2O and CO_2) in each scan versus scan number along the abscissa. The gas chromatogram shown at the top is the blank experiment performed during cruise (oven 2 at 500°C).

As is discussed in the preliminary report [*Biemann et al.*, 1976], the sharp peak in the very first gas chromatogram (identification number 10015, 'Sandy Flats' site, 200°) returned to earth from Mars was identified as methyl chloride. This identification was based on the mass spectrum recorded at that point and the fact that the mass chromatograms of all ions characteristic for CH_3Cl showed the same sharp maximum. As an example the mass chromatogram of *m/e* 50 ($CH_3{}^{35}Cl$) is shown in Figure 4. The calculation of the abundance of this compound is based on the integrated intensity of this ion, corrected for the effluent divider state. The sensitivity of the mass spectrometer for this or any compound can be determined from the signal obtained from the *m/e* 44 ion during the analysis of the Martian atmosphere [*Owen and Biemann*, 1976] combined with the known atmospheric pressure, 7.65 mbar at that time [*Hess et al.*, 1976], the conductance of the leak in the atmospheric inlet system, and the relative intensities of *m/e* 44 for CO_2 and of any chosen peak in the compound of interest. These relative intensities can be taken from the *American Petroleum Institute* [1955] collection of mass spectral data. This method had been chosen because it would have been impossible to calibrate the flight instrument with many compounds without severely contaminating it. For this reason, and owing to the uncertainty in the amount of surface material contained in the oven (see the discussion in section 2), all values for abundances may deviate from the actual values by a factor of 2 or even more, but this is quite sufficient for the purpose at hand. Needless to say, the relative abundance ratios could be determined more accurately by reconstituting the appropriate mixture and analyzing it on the spare flight instrument, but this has not been necessary because no complex mixtures of organic compounds were encountered.

On the basis of such a calculation the amount of methyl chloride represented by the peak centered around scan 27 in the first gas chromatogram from Mars (identification number 10015) was found to represent about 15 ppb with respect to the sample. Comparisons of all the gas chromatograms from the VL-1 samples (Figure 3) indicates that this is the only clearly identifiable gas chromatographic peak. All other changes in signal correspond to changes in effluent divider status (plotted in the top part of each chromatogram) and thus to changes in the amount of material which slowly and continuously elutes from the gas chromatographic column (column bleed) and enters the mass spectrometer. This should be noted particularly for the pattern of the 500° analysis of sample 1 (third from the top in Figure 3), which has the appearance of a series of peaks. This experiment was run in the anhydrous mode (see the discussion in section 2), but the unexpectedly large amount of water evolved at 500° kept the residual ion pump current at such a level as to cause the effluent divider to cycle between the 0:1 state (no venting) and the 20:1 split rate. Since the gas chromatogram is plotted as the sum of all ions above *m/e* 47, these fluctuations are due not to the ion current of H_2O but to the above-mentioned traces of material continuously eluted from the column and inner surfaces of the interfaces which are attenuated by the valve switching. For this reason all further experiments were conducted in the hydrous mode.

From the sharpness of the peak for methyl chloride and its height, which corresponds to only 15 ppb, it is evident that there is no other compound observable that is of this magnitude or larger, except possibly for those regions of the gas chromatograms where the effluent divider is in a state where a large portion of the material is vented. This occurs mostly at the very beginning of the chromatogram, when $^{13}CO_2$ and H_2O emerge. The only other identifiable compounds were fluorocarbons of the freon-E type (polyperfluoropropylene oxides), which can be detected on the basis of the mass chromatograms of their characteristic ions at *m/e* 69, 97, 101, 119, 147, etc. The small peaks in the region from scan 50 to scan 150 in the cruise test (top of Figure 3) are due to a series of oligomers of this type. A typical spectrum is shown in Figure 5. It corresponds well with that of any of these oligomers, which all give very similar spectra in this mass region. The ions at *m/e* 47 (CFO), 97 (C_2F_3O), and 147 (C_3F_5O) are characteristic for these oxygen-containing fluorocarbons; so are ions at *m/e* 51 (CF_2H) and 101 (C_2F_4H) because the oligomers contain one hydrogen atom per unit.

Traces of freon-E and methyl chloride had been detected in previous tests on earth. There is no doubt that all the freon-E is of terrestrial origin. The low level, a few tens of parts per billion, did not interfere with the experiment; in fact, it provided a welcome calibration of the mass scale of the instrument. The methyl chloride, or part of it, could conceivably be indigenous to Mars. However, if it were, one would expect that other related compounds like ethyl chloride or methyl bromide would also be formed, but none were detected. The abundance ratio of *m/e* 50 to *n/e* 52 was about 3:1, corresponding to the terrestrial isotope ratio of chlorine; but this does not necessarily confirm its origin, because there is no reason to predict a different ratio for Martian chlorine. Considering all these facts, we tend to believe that all the methyl chloride is from terrestrial sources (chlorinated solvents or from adsorbed traces of methanol and HCl).

Using the abundance calculation for the methyl chloride as an example, one can then proceed to search for the presence of any compound by inspection of the mass chromatogram of a characteristic ion in the region of the determined or the predicted retention time (the retention behavior of a sufficient number of compounds had been determined on the laboratory version of the instrument or on a gas chromatograph fitted with a flight column). Such searches were carried out for quite a number of compounds, particularly those encountered in the Antarctic soil discussed in section 2 and in a sample of Murchison meteorite analyzed on the laboratory version of the Viking gas chromatograph–mass spectrometer. For none of these compounds could a peak be observed in the mass chromatograms of the VL-1 experiments, thus demonstrating their absence below the detection limit of the instrument. This detection limit was determined by calculating the amount of material that would correspond to the background signal integrated over 10 scans in the region of the appropriate retention time and assuming that that amount, when present in addition to the background signal, would have produced an observable peak in the mass chromatogram. Some of these detection limits for a few typical compounds are listed in Table

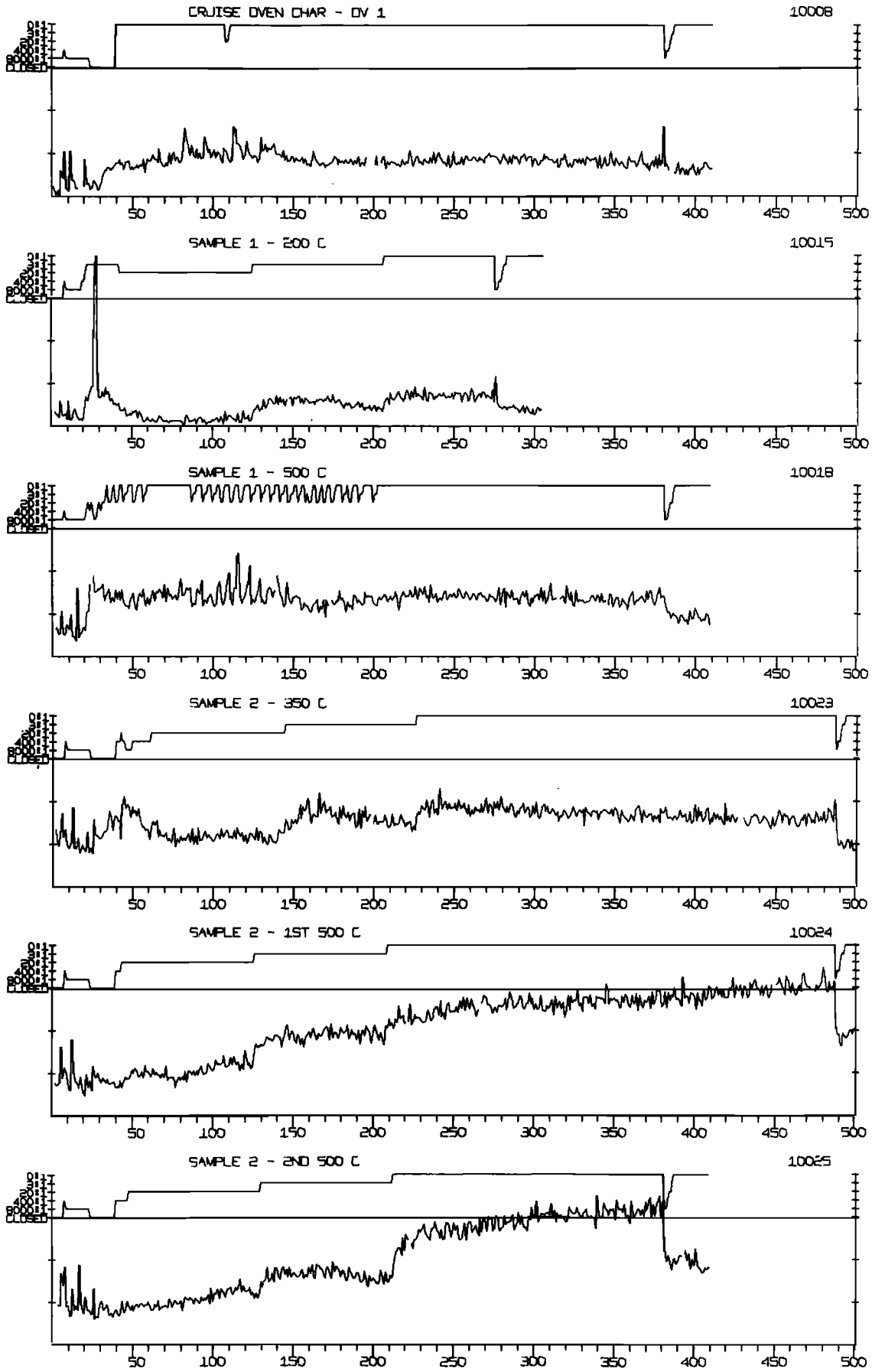

Fig. 3. Gas chromatograms of cruise blank and five VL-1 experiments, plotted as sums of all ions above m/e 47. All are plotted at the same scale for comparison. The upper quarter of each plot indicates the effluent divider status during each experiment (also in Figures 7 and 8).

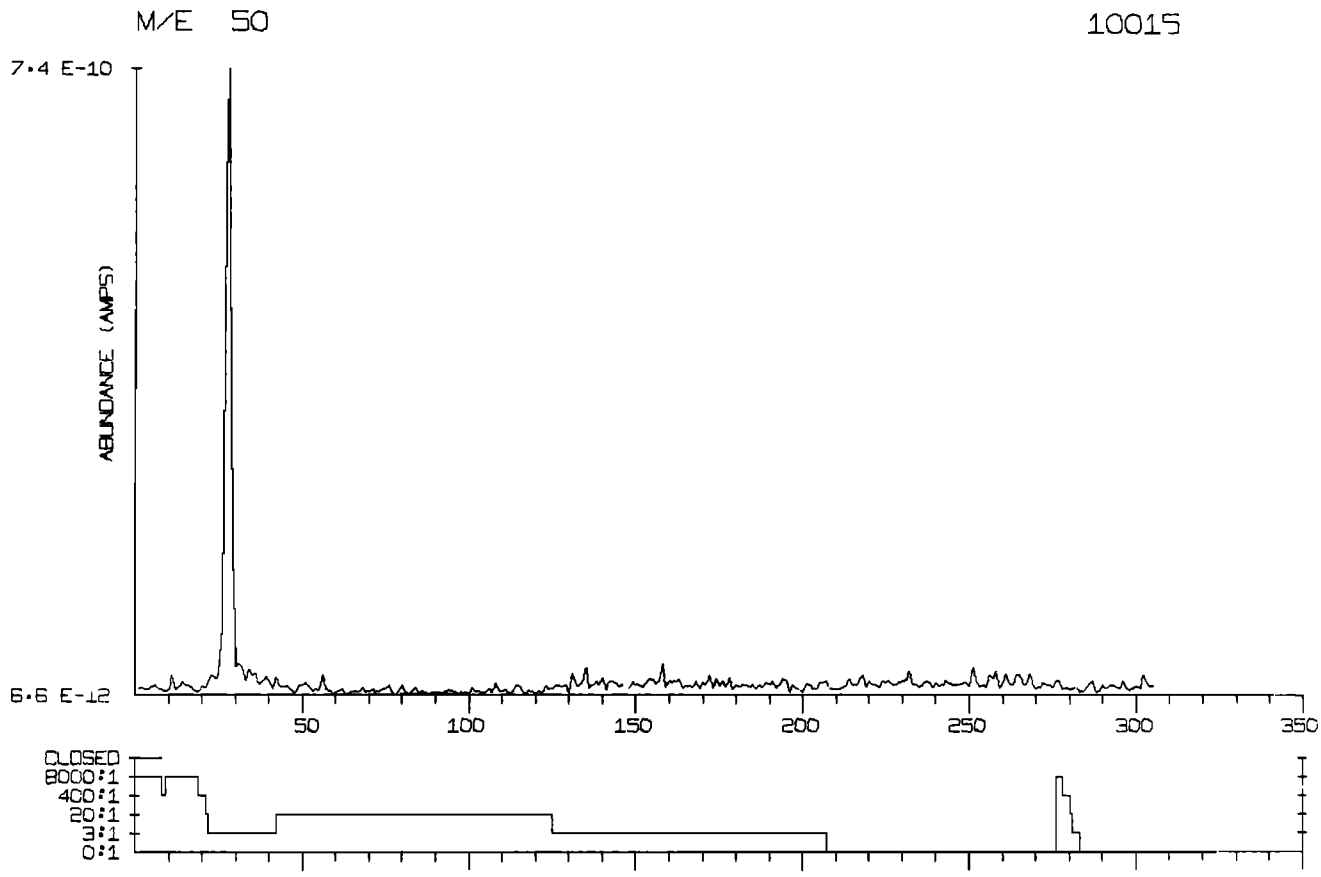

Fig. 4. Mass chromatogram of m/e 50 from the 200° experiment of the first VL-1 sample. In this figure and in Figures 6 and 9 the effluent divider status is plotted underneath the graph (the horizontal line indicates the 1:8000 level, and the step function represents the effluent divider status).

2. The mass chromatograms of two typical examples are shown in Figure 6, where m/e 58 is chosen as being representative of acetone and m/e 128 of naphthalene. These compounds are expected to emerge in the regions around scans 90 (acetone) and 200 (naphthalene). It will be noted that there are no maxima in these regions, and the signal is around 1×10^{-11} A for m/e 58 and about 2×10^{-13} A for m/e 128. Furthermore, the split ratio of the effluent divider is 20:1 where acetone would emerge, while it is 3:1 in the naphthalene region. Therefore the detection limits quoted in Table 2 for these two compounds differ by about 2 orders of magnitude.

As was the case on the instrument on Viking lander 1, the one on Viking lander 2 had also been shown probably to contain one inoperable oven and thus to limit the experiments to the collection and analysis of two rather than three samples. While the mass spectrometer on this instrument displayed a much lower background than that on VL-1 and was thus particularly suitable for the analysis of the Martian atmosphere at a trace level, those subsystems involved in the soil analysis, namely, the sample ovens and the tubing and valving prior to and possibly after the gas chromatographic column, were less clean. For this reason the interpretation of the soil

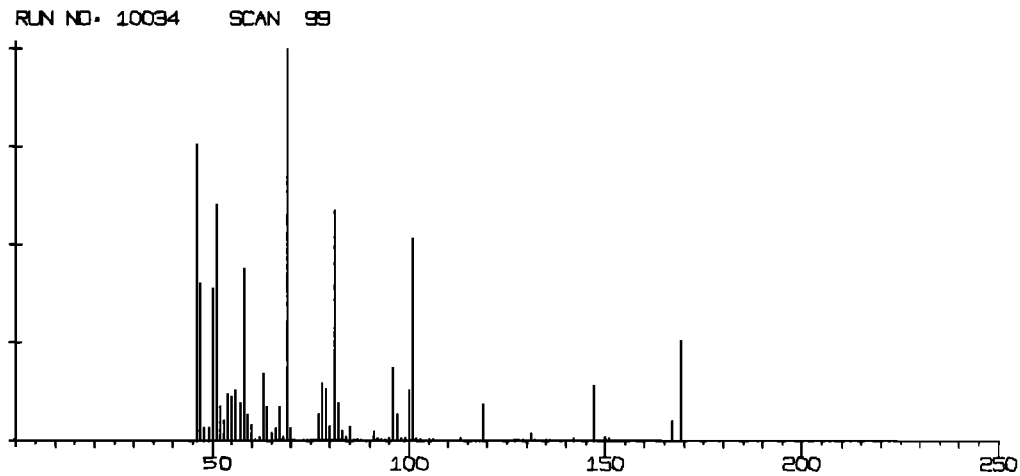

Fig. 5. Typical mass spectrum of the freon-E contaminants. Peaks in the region below m/e 46 have been deleted to avoid distortion of the plot due to contributions of H_2O and CO_2.

TABLE 2. Upper Limits of Selected Organic Compounds Which Would Be Detected If Present in the Martian Soil Samples

Compound	Range of Detection Limits, parts per 10^9	
	Lander 1 (Chryse Planitia)	Lander 2 (Utopia Planitia)
Simple Molecules		
Methanol	*	<300–3000†
Ethanol	*	<9–90
Formaldehyde	*	<1200–12,000‡
Ethane	*	<1200–12,000‡
Propane	*	<3–30
Aliphatic Hydrocarbons		
Butane	<1–10	<3–30
Hexane	<1–10	<0.5–5
Octane	<1–10	<0.15–1.5
Aromatic Hydrocarbons		
Benzene	<0.5–5	<8–80
Toluene	<0.5–5	<3–30
Naphthalene	<0.05–0.5	<0.0015–0.015
Oxygen-Containing Compounds		
Acetone	<10–50	<250–2500
Furan	<0.1–1	<0.05–0.5
Methylfuran	<0.2–2	<0.15–1.5
Nitrogen-Containing Compounds		
Acetonitrile	<1–10	<0.5–5
Benzonitrile	<0.2–2	<0.015–0.15
Sulfur-Containing Compounds		
Thiophene	<0.1–0.5	<0.015–0.15
Methylthiophene	<0.1–0.5	<0.015–0.15

*The limit of detection estimated for these compounds is of the order of tens of parts per million for most of these experiments because the eluting $^{13}CO_2$ keeps the effluent divider in the 8000:1 state or even closes valve V7.

†Effluent divider in 400:1 split ratio.

‡Effluent divider in 8000:1 split ratio.

analysis data requires the subtraction in a qualitative and a quantitative sense of the background data acquired during a complete blank run performed during cruise. This blank was obtained on oven 2 and therefore holds strictly for that oven, and the use of these background data with the data obtained with oven 3 is based on the assumption that the contamination level of the two ovens would be similar.

In the region of Utopia Planitia, two samples were analyzed for volatile materials. The first was collected from the area named Bonneville and was thought to represent duracrust-type material; the second was obtained from underneath a rock (Badger). These were the two regions in the accessible area from which a sample could be obtained and which were believed to be possibly different from the region of the exposed surface area [*Shorthill et al.*, 1976]. Exposed regolith had been analyzed on VL-1 as well as by the biology experiment on VL-2, which indicated that it may not substantially differ from the VL-1 material. For this reason it was decided to reserve the two samples which could be analyzed by the gas chromatograph–mass spectrometer for the most different materials within the VL-2 region.

In an effort to lower the detection limit for the most volatile components that could be expected the experiments on VL-2 were run in the so-called hydrogen expansion mode with the exception of the last experiment on each sample, which was performed in the normal mode (see Table 1). The gas chromatograms obtained in the cruise blank experiment and the first four sample experiments are summarized in Figure 7. It should be noted that the gas chromatogram from the blank experiment (top) has been corrected for a small difference in the behavior of the gas chromatographs between cruise and surface experiments. Inspection of the column temperature engineering data revealed that it stayed rather constant during the cruise test but always increased slowly to about 70° in the sample runs on the surface of Mars. This speeds up the elution of acetone and at the same time broadens its gas chromatographic peak. Simulation of this column temperature shift before plotting the cruise data resulted in a gas chromatogram which is practically identical with that of the 200° Bonneville experiment (identification number 10032). Thus there is no difference in the nature of the materials eluted in these two experiments except that there is only half as much in run 10032. Table 3 represents a semiquantitative evaluation of the major components observed in the experiments run on the VL-2 instrument. (Rather than labeling all the peaks in all chromatograms, which would greatly confuse the figures, only the middle peak in Figure 7, i.e., Bonneville, 350°, is labeled.) It is obvious that with the exception of methylene chloride all other compounds are identical with those detected in the cruise experiment. Their quantities vary while always remaining in the same order of magnitude as those in the blank experiment. This is to be expected because of the difference in the temperature regime to which each sample was heated and the fact that some of the impurities deplete (like the more volatile acetone) or are lower at the lowest temperatures and higher at higher temperatures.

The only still puzzling peak is the one always eluting around scan 110 and labeled 'methyl fluorosiloxane.' Its mass spectrum, which was equally prominent in the cruise experiment and was observed to a much lesser extent in the VL-1 data also, is dominated by a peak of *m/e* 81 and also shows, among others, an ion of *m/e* 96. A group of peaks at *m/e* 207–209 also maximizes in intensity at that same point. While the spectrum from *m/e* 96 on down is very similar to that of dimethyldifluoro-silane, $(CH_3)_2SiF_2$, this compound is ruled out by the gas chromatographic behavior (it elutes much earlier). The best interpretation of the spectra, at present, also involves the peak at *m/e* 207, which is typical for polymeric dimethyl siloxanes (common silicones). Thus a compound like $F[Si(CH_2)_2\text{-}O]_nSi(CH_3)_2F$, which may arise from a reaction of a silicone with HF or another fluoride, could give rise to the observed mass spectrum by a fluorine transfer, accompanied by cyclization of the dimethyl siloxane portion after ionization in the mass spectrometer. (The mass spectra of dimethyl silicones have been discussed by *Biemann* [1962].) This interpretation is still to be verified in laboratory simulations.

The second and last sample analyzed from the Utopia Planitia region was collected from underneath so-called 'Badger Rocks.' Great care was taken to assure that the collected material was entirely from the area which the rock protected from ultraviolet radiation. In an effort to determine the amount of carbon dioxide that is released from the sample upon heating and to differentiate it from that which was merely due to the occluded atmosphere sealed into the oven with a sample, the first experiment was run without appreciable heating of the sample. This is accomplished in the 50° mode, where the sample is heated to that temperature or the ambient temperature of the sample oven, whichever is higher. Thus the sample from underneath the rock was analyzed five times, namely, at 50°, 200°, 350°, and 500° in the hydrogen

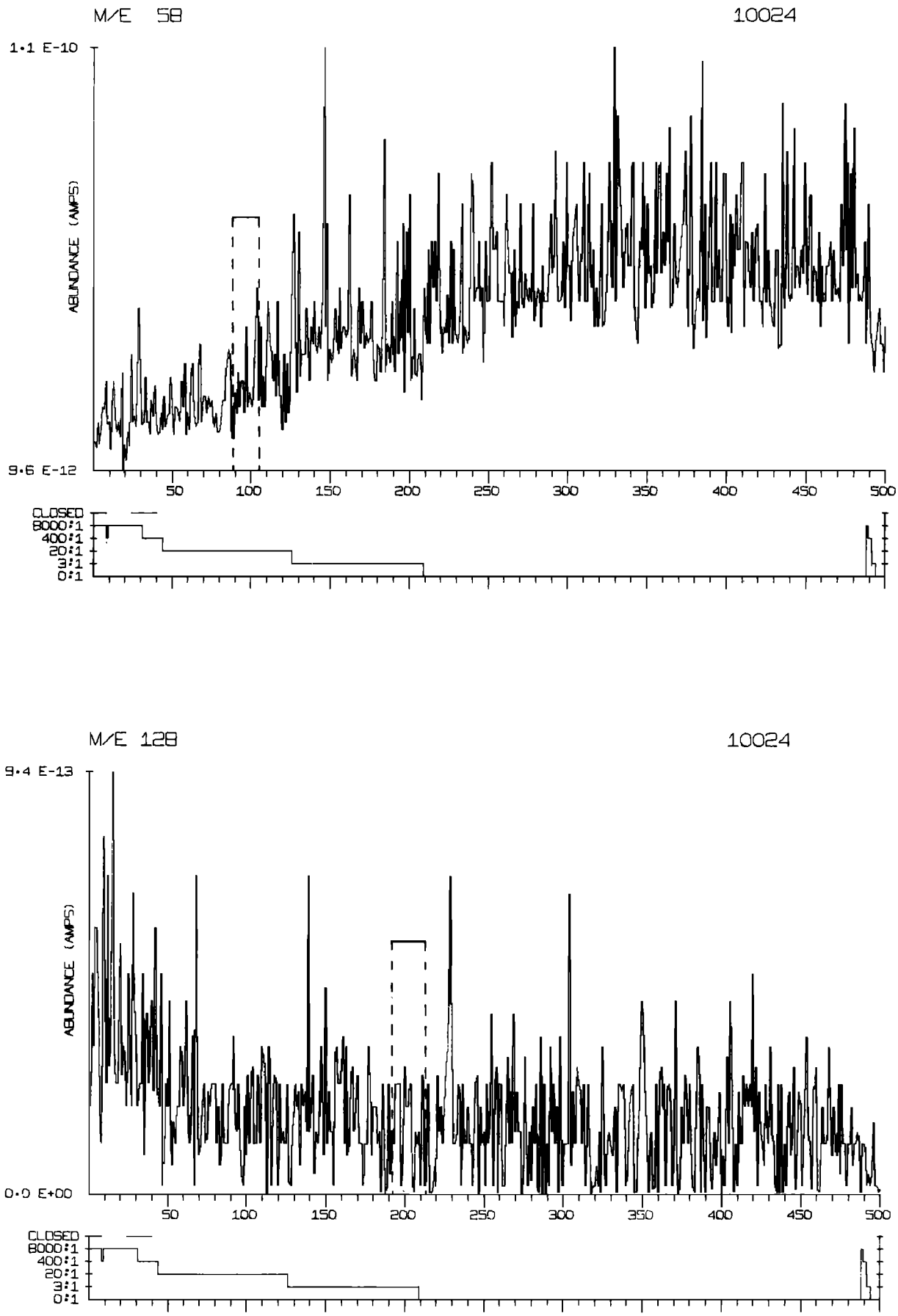

Fig. 6. Mass chromatograms of (top) *m/e* 58 and (bottom) *m/e* 128 to illustrate the method of establishing the detection limits listed in Table 2. The dashed lines bracket the retention times of (top) acetone and (bottom) naphthalene.

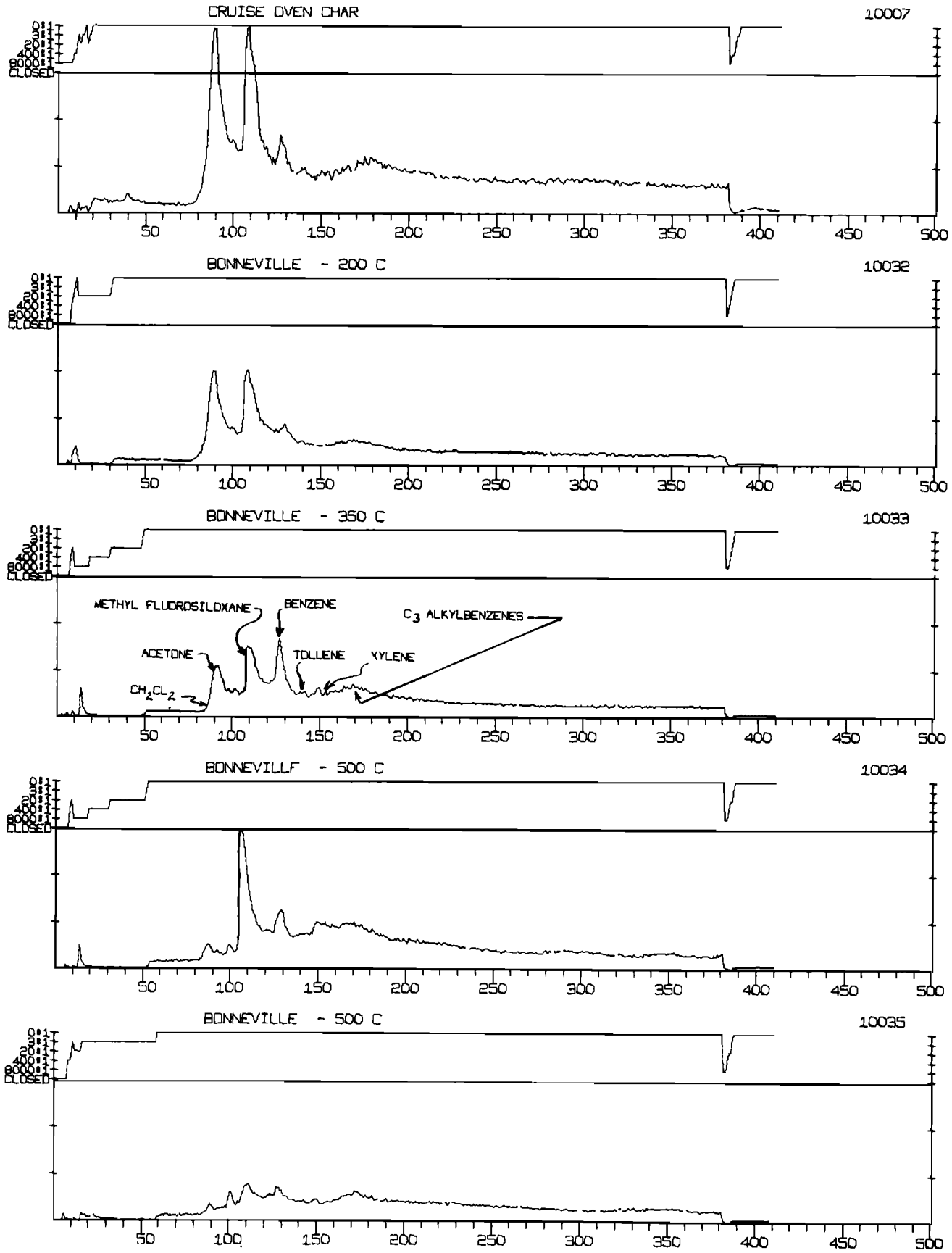

Fig. 7. Gas chromatograms of the cruise blank and four experiments with the first VL-2 sample (Bonneville). For details, see the Figure 3 legend.

TABLE 3. Terrestrial Contaminants Identified in VL-2 Samples

Sample	Temperature, °C	Mode	Methylene Chloride (89)	Acetone (92)	Freons (40, 105, 130)	Methyl Fluoro-Siloxane (110)	Benzene (129)	Toluene (140)	Xylene (150)	C_3 Alkyl Benzene (162)
Blank (oven 2)	500	CO_2	ND	120–240	10–20	60–120	4–8	1–2	0 6–1.4	0.6–1.0
Bonneville	200	H_2	ND	60–120	6–10	100–200	1–2	2–3	0.3–0.5	0.1–0.3
(oven 2)	350	H_2	6–14	40–70	10–20	70–130	3–6	2–3	0.3–0.5	0.09–0.16
	500	H_2	6–14	10–20	10–20	160–320	3–6	0.8–1.6	0.4–0.8	0.1–0.2
	500	CO_2	2–6	1–2	10–20	35–70	2–4	0.6–1.4	1–3	0.04–0.08
Under Badger	50	H_2	ND	ND	ND	20–40	0.2–0.4	0.1–0.3	ND	ND
Rock	200	H_2	0.04–0.08	200–400	4–8	40–85	0.6–1.4	0.4–0.8	0.3–0.5	0.8–1 6
(oven 3)	350	H_2	10–20	30–60	2–4	30–55	0.6–1.4	0.3–0.5	ND	0.04–0.08
	500	H_2	<4	<5	0.04–0.08	140–280	1–2	0.04–0.08	ND	ND
	500	CO_2	20–40	5–10	5–10	50–90	0.75–1.75	1–1.5	0.1–0.2	ND

Text

Values are in parts per billion, 100-mg samples being assumed.
Numbers in parentheses indicate the approximate scan numbers where components elute.
ND, not detected.

expansion mode and again at 500° in the CO_2 purge mode. Figure 8 again summarizes the five chromatograms obtained in this series of experiments headed by the plot of the cruise experiment (which is, of course, the same experiment as that shown at the top of Figure 7). It is clear that very little is evolved in the 50° experiment and that a rather large amount of acetone (see Table 3) is produced in the 200° experiment. This would imply that there was more residual acetone in oven 3 than there was in oven 2.

It should be noted, however, that in the chromatograms obtained from the subrock sample, as in all the previous experiments, no new materials were observed in addition to those detected in the blank run performed during cruise. Therefore none of the gas chromatographic peaks observed are deemed to be due to compounds indigenous to the Martian soil sample. As was the case with the Bonneville sample, traces of methylene chloride were produced from the second sample as well, but since this was a common laboratory solvent which had been used in the cleaning of the oven–gas chromatograph subsystem, it was considered a terrestrial contaminant although it had not been detected at those levels in the blank run.

There is one peak which appears to be new in the 500° hydrogen expansion experiment (second from the bottom, Figures 7 and 8). It appears at scan 130, and an inspection of the mass spectrum corresponding to this gas chromatographic peak suggests that it is most likely due to gas chromatographic column bleed that is pushed through the column by the water which evolves upon heating of the sample to 500°. Because the Tenax column transmits water very quickly [*Novotny et al.*, 1975], this peak emerges only after the water peak trails off (it should be noted that all of these gas chromatograms are generated by summing the ion intensities above mass 47 and therefore do not show the contributions of water which otherwise would completely dominate the gas chromatograms).

The appearance of the last gas chromatogram (500° CO_2 purge) is somewhat unusual because it shows a blank region from scan 100 to scan 135. A similar effect is noted, but less clearly, in the 500° hydrogen expansion experiment between scan 70 and scan 106. As is noted in the effluent divider status plot at the top of each gas chromatogram, this is a region where the effluent divider is in the 1:20 mode. A detailed assessment of the mass spectral intensities before and after the switch from 1:3 to 1:20 and vice versa indicates that the 1:20 divide ratio is not true for the VL-2 instrument. It is most likely due to blockage of the corresponding restrictor. Blockage of this restrictor would result in an effluent divide mode that corresponds to the next step, in this case, 1:400. Thus in the two regions mentioned the sensitivity of the instrument is decreased by a factor of 400 instead of 20, leading to the apparent blocking of this region.

The level of these contaminants, while clearly recognizable, is still within or not much above the instrument specifications, which called for no more than 1 ppm total organic contaminants. While this value may seem high, one has to keep in mind how difficult it is to manufacture such a complex instrument and still keep organic materials completely out. Because of the greater than expected sensitivity of the instrument, they are very noticeable but would not severely hamper the detection of other substances not present in the cruise blank. The major disadvantage of the presence of these impurities is that they greatly increase the detection limits of these compounds in the Martian soil, as is evident from Table 2. However, their presence demonstrates that both the gas chromatograph and the mass spectrometer operated reliably and reproducibly and that compounds of this type are not readily oxidized by the Martian soil under the conditions of the experiment. In this connection it should be noted that the relatively sharp gas chromatographic peaks demonstrate that the impurities evolve during the heating of the oven and must be there, rather than elsewhere in the system.

In summary, one can state that the two samples analyzed in the Utopia Planitia region do not contain any detectable amounts of organics. Furthermore, the hydrogen expansion mode (in which most of these experiments were conducted) did not reveal any of the small organic molecules that could have escaped detection in the VL-1 experiments.

4. DISCUSSION

Mechanisms for the Production and Destruction of Organic Molecules on Mars

The data outlined in section 3 demonstrate that if organic materials are present in the samples analyzed, they must be there at extremely low levels. This is an important finding as such. At present, it is impossible to provide a unique, detailed interpretation that would lead to a single set of circumstances responsible for the apparent absence of organic substances. It is only possible to outline a number of processes that could lead to the accumulation of organic molecules on Mars and a second set of processes that could destroy these organic molecules. We know very little about the rates at which the various

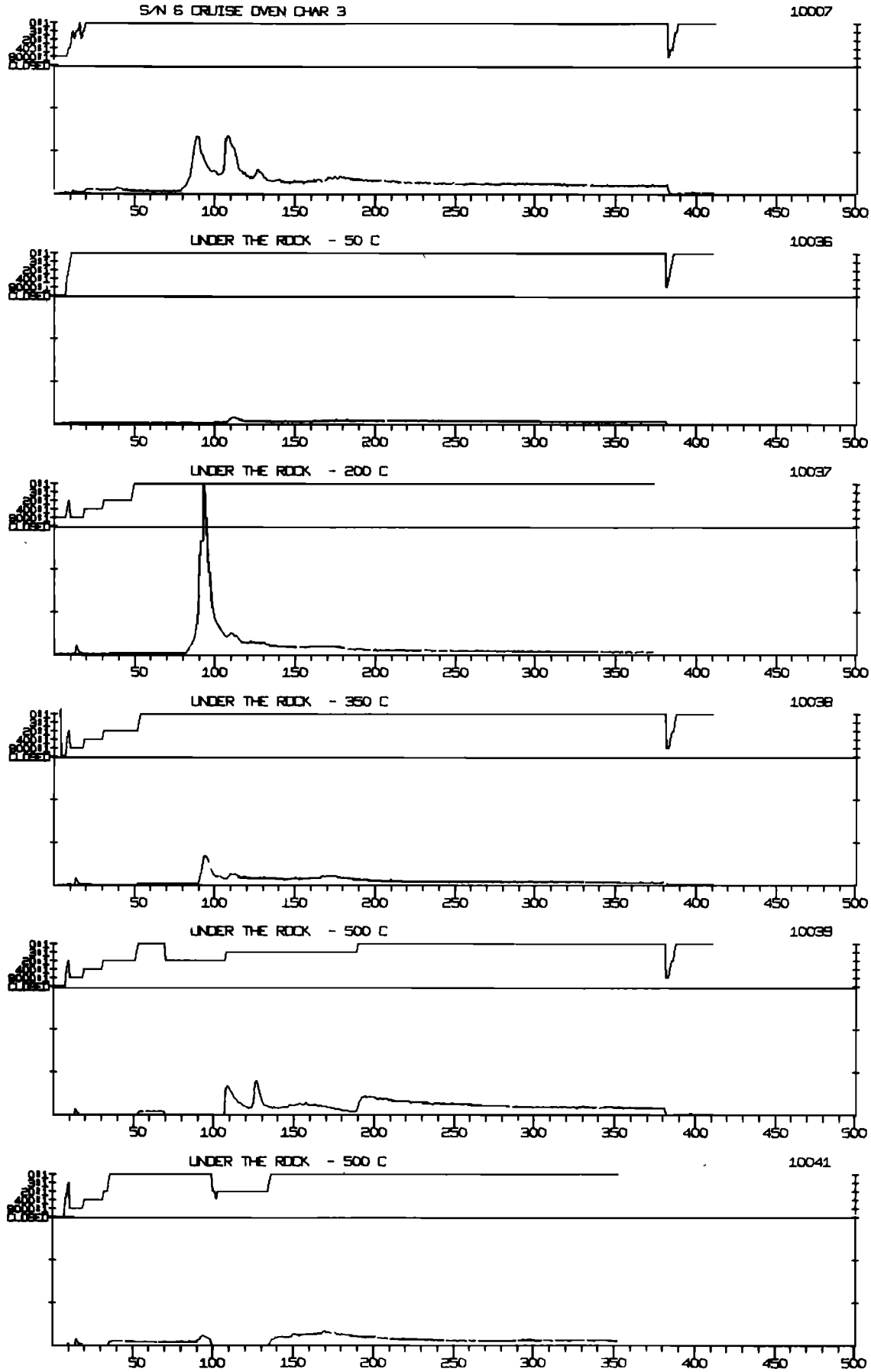

Fig. 8. Gas chromatograms of the cruise blank and five experiments with the second VL-2 sample (from under Badger Rock). For details, see the Figure 3 legend.

processes are presently occurring or about the rates at which they occurred in the past. Consequently, the conclusions drawn must be largely qualitative.

While one could postulate that neither now nor in the past has there existed a process that leads to the formation of organic compounds at the surface or in the atmosphere of the planet and that none of the organic compounds possibly present in the material from which the planet accreted has survived, one must admit that organic molecules present in meteoritic material must be arriving at the Martian surface. As on the moon [*Anders et al.*, 1973; *Morgan*, 1976], type 1 carbonaceous chondrites and micrometeorites of similar composition would be expected to make up a significant fraction of the meteoritic material reaching the surface of Mars. On the moon this material is more or less uniformly distributed over the entire lunar surface and comprises about 1.1% of well-exposed lunar maria soils at three Apollo sites [*Morgan*, 1976]. It is also known that type 1 carbonaceous chondrites contain on the average 3–5% carbon in the form of organic matter [*Mason*, 1971; *Wasson*, 1974]. Thus if the Martian surface contained unmodified meteoritic material in substantial amounts, the organic material contained therein should be detectable by the Viking gas chromatograph–mass spectrometer.

One approach to the estimation of the meteoritic input again utilizes data from the moon. The average micrometeoritic and carbonaceous chondrite input at the three Apollo sites is equivalent to a layer of meteoritic debris from type 1 carbonaceous chondrites about 5 cm deep. This material has been diluted into a regolith about 4.6 m deep, on the average. The input of meteorites on Mars has been estimated by some authors to be only twice as great as that on the moon [*Soderblom et al.*, 1974] and the depth of the regolith to be as much as 2 km [*Fanale*, 1976]. If these rather extreme estimates are used, the meteoritic material would be much more 'dilute' in the Martian regolith than on the moon and would be equivalent to a 0.005% contribution of material from type 1 carbonaceous chondrites. Typical organic compounds found in meteorites, for example, naphthalene, are detected in type 1 carbonaceous chondrites at levels of about 1 ppm by using a laboratory version of the Viking gas chromatograph–mass spectrometer. Thus if the above estimates are correct, they should not be detected in the Martian surface material, since the anticipated abundance would be about 0.05 ppb for naphthalene, which is below our detection limit (see Table 2).

However, other authors have made very different estimates, both of the rate of meteoritic input on Mars and of the depth of the regolith. If one supposes that the regolith is only 100 m deep on the basis of arguments involving the adsorption of xenon onto the regolith (T. Owen, private communication, 1976) and accepts a value for the meteoritic input that is 25 times higher than that on the moon [*Anders and Arnold*, 1965], the expected abundance for naphthalene would be as high as 12.5 ppb, a value well above the detection limit of this experiment (Table 2).

A second, much less likely, exogenous source of organic material on Mars is the solar wind. Here the situation is quite unlike that on the moon because carbon-containing ions in the solar wind would be unlikely to penetrate the Martian atmosphere. Furthermore, any of those reaching the surface would be extensively diluted into the regolith when the surface is disturbed by winds, etc. Thus one can safely exclude the solar wind as a contributor to organic material deposited at the surface of Mars.

There is one process known that must be producing organic molecules on the surface of the planet at the present time, and that is the photochemical reduction of carbon monoxide (and possibly also carbon dioxide) at the interface between solid particles and the atmosphere. Recent studies by *Hubbard et al.* [1973] have established that formic acid, glycolic acid, formaldehyde, acetaldehyde, etc., are produced when a number of solids, including Vycor and volcanic ash, are irradiated under a simulated Martian atmosphere with ultraviolet light corresponding to the solar spectrum incident on Mars. The organics are derived from carbon monoxide rather than carbon dioxide.

The biology experiments on the two Viking spacecraft have given perplexing results. However, the pyrolytic release experiment suggests that the surface material on Mars is more active than the samples studied by *Hubbard et al.* [1973] in bringing about the photochemical fixation of CO when irradiated at relatively long wavelengths. On the other hand, very recent terrestrial experiments have shown that darkly colored iron-containing materials are less effective than the lightly colored samples previously studied when irradiated at shorter wavelengths (J. S. Hubbard, private communication, 1976). Thus it is hard to estimate whether the total rate of production on Mars is greater or less than that originally suggested on the basis of these experiments.

The steady state concentration of primary products found in the terrestrial experiments, when the sample was thoroughly mixed throughout the irradiation, was not very much below the detection limits of the Viking gas chromatograph–mass spectrometer [*Biemann et al.*, 1976, footnote 18]. However, when the samples were left undisturbed during the irradiation, the steady state yields were much lower. The Martian samples which were analyzed for their organic content had not been disturbed for a substantial time before their acquisition. Thus it is not necessary to postulate special destructive mechanisms on Mars to explain the failure to detect in these samples organic molecules that could have been produced by the above mechanism because the amounts would be too low.

A number of energy sources are effective in producing organic molecules when they act on reducing gas mixtures [*Miller and Orgel*, 1974]. These processes could not be taking place to any great extent on the bulk of the Martian surface at the present time, since the only reducing form of carbon that has been detected in the atmosphere, carbon monoxide, is present at very low levels. However, they might occur at special sites, for example, where volcanic gases are vented. Also, they may have been important at an earlier stage in the history of the planet if the Martian atmosphere was ever more reducing.

Finally, organic molecules could be formed by biological processes if there were living organisms on Mars. Vast quantities of CO_2 are fixed on the earth by photosynthetic mechanisms. There is no overriding reason why similar processes, or possibly nonphotochemical fixation, should not occur on Mars. However, it should be emphasized that at the present time there is no persuasive evidence for the existence of organisms on Mars.

Prior to the Viking mission it was anticipated that the lifetime of organic molecules at the surface of Mars, although limited by destructive photochemical processes, would still be long enough to permit some compounds to accumulate. The situation is changed by the discovery that Martian surface material has the capacity to oxidize organic compounds. Under these circumstances is is not possible to estimate the half-life of typical organics in the environment from which the Viking samples were obtained.

Short-wavelength ultraviolet radiation would destroy most organic compounds sooner or later. In the presence of oxygen, hydrogen peroxide, certain metal oxides, and many other oxidizing agents this radiation would remove organic compounds very much faster. Some oxidizing agents which might be present on Mars, for example, hydrogen peroxide [*McElroy and Kong*, 1976], would be destructive even in the dark. It is clear, then, that a number of different destructive mechanisms are operating on Mars. One knows little about the detailed mechanisms of oxidation and nothing about the rates of destruction for different classes of organic molecules under Martian conditions.

As was mentioned in section 3, it is unlikely that the failure to detect organics is due to their destruction in the ovens of the gas chromatograph–mass spectrometer by the oxidizing components of the Martian surface material because the terrestrial contaminants that were detected survived, thus ruling out the total destruction of all organic compounds. Furthermore, it must be recalled that the material in the surface which generates oxygen must be present in very small amounts. The oxygen (about 1 μmol) evolved in the gas exchange experiment [*Klein et al.*, 1976] is equivalent to only about 6 μg of reduced carbon per gram of surface material. The efficiency of oxidation is unlikely to be very high, and thus the total amount of organic carbon that could be oxidized must be far below the parts per million level. Finally, the amount of water present in the sample as mineral hydrate would be ample to convert the oxidizing agent, whatever it is, to O_2. Molecular oxygen would hardly have much effect on the organic material under the pyrolytic conditions of the experiment (30 s at temperatures of up to 500°C), particularly at such a low abundance.

Given all the uncertainties discussed above, it does not seem to be useful to elaborate specific models in great detail. The fact remains that the samples, when heated, did not evolve organic compounds at detectable levels. One cannot be certain that organic materials are transported to or synthesized at the Martian surface in quantities large enough to be detected by this instrument. It is reasonable to assume that if they were, they would be photooxidized so quickly that the steady state concentrations would still remain below the detection limit as discussed earlier.

Intuitively, it appears unlikely that organic compounds will be found in substantial amounts in the red iron-containing material that covers much of the Martian surface. It would be interesting to examine subsurface material taken from as great a depth as possible at the Viking landing sites or elsewhere. Material taken from very different sites, for example, the polar regions, where organic substances may have been cold trapped, would be of much greater interest. Nothing that has been learned about Mars at this point rules out the possibility that organic compounds have concentrated at favored sites on the surface of the planet.

Implications for Biology

The Viking gas chromatograph–mass spectrometer was not designed to search for life on Mars. Consequently, the demonstration that very little, if any, organic material is present does not exclude the existence of living organisms in the samples analyzed and certainly does not rule out the possibility of a rich biota out of range of the Viking landing sites. However, at the very least the results of this experiment demonstrate the absence of a widely distributed Martian biota which, like that on earth, has left its mark almost everywhere.

In an extensive study of soils collected in the Antarctic and ranging from practically sterile to highly populated with microorganisms, *Cameron et al.* [1970] have shown that there is on an average at least 10^4 times more organic carbon in these soils than there is in the bacteria present in them. Thus the organic material that was detected in the Antarctic soil sample discussed at the close of section 2 must be due to the organic debris derived from a long period of biological activity rather than from the microorganisms themselves present in the soil sample (this particular soil sample discussed in section 2 is believed to have contained about 100 bacteria and few algae per gram).

In view of the low detection limits for organic compounds (see Table 2) it is difficult to maintain the possibility that living organisms based on the familiar carbon-hydrogen-nitrogen-oxygen chemistry are present in appreciable numbers in the samples analyzed, unless one postulates that they differ in one important respect from terrestrial organisms: they must be much more efficient in scavenging organic carbon. It is hard to know whether this is a severe requirement, since one knows so little about the potential of living organisms to deal with a limitation of this kind. Alternatively one could postulate that organisms are present and that the absence of organic carbon is due to the unusual oxidizing properties of the soil rather than the peculiarity of the organisms. We think this to be unlikely.

In summary, the results of the organic analysis experiment do not rule out completely the possibility that there are living organisms in the samples analyzed, but they should not give encouragement to those who hope to find life on Mars.

Mineralogical Interpretations

A subsidiary goal of these experiments is to derive mineralogical constraints on the constitution of the surface materials by detection and measurement of inorganic volatiles evolved from the samples on heating and comparison of the results with the thermal decomposition behavior of appropriate mineral phases [*Anderson et al.*, 1972]. Inorganic volatiles of particular interest in this regard include H_2O, CO_2, sulfur-containing species, and oxides of nitrogen. Of these, only the first two were detected at levels regarded as possibly of mineralogical significance (see Table 4).

The results of other investigations [*Toulmin et al.*, 1977] have led to mineralogical models for the Martian surface materials incorporating hydrous silicates such as iron-rich montmorillonitic clays; hydrates and hydrated oxides, chiefly of iron; sulfates, possibly hydrated; and carbonates. The high level of sulfur reported by the inorganic chemical investigation [*Clark et al.*, 1977] implies the abundance of minerals containing major amounts of sulfur; both reduced (sulfide) and oxidized (sulfate) forms of this element occur in such minerals on earth. Rather wide variations exist in the thermal stability of mineral sulfides and sulfates; information with respect to the evolution of sulfur species from the Martian surface material on heating should therefore be relevant to the interpretation of the mineralogical occurrence of the element.

Several factors severely complicate the determination of the amount of water evolved upon heating Martian soils. The principal obstacle is the operation of the effluent divider network because the sample flow dynamics resulting when it changes state rapidly make quantitative determinations very difficult. Under these conditions it is impossible to determine the ratio of sample introduced into the mass spectrometer to sample vented by the effluent divider. It is only when the effluent divider is in a given split ratio for the complete dura-

tion of a gas chromatographic peak that a reliable determination can be made. Water emerges quite early (in approximately 100 s) as a relatively sharp peak at a time when the effluent divider is allowing greater and greater quantities of sample to flow into the mass spectrometer. This often results in the closing of valve V7 for a significant length of time (up to 44.5 s), and when this is the case, the mass spectrometer does not generate useful data for a large fraction of the time during which the water peak emerges from the gas chromatograph.

To obtain more reliable values for the amount of water evolved in a particular experiment on Mars, we carried out simulations on the earth-based laboratory instrument. Although it is impossible to duplicate exactly test results from such complex instruments involving highly complex modes of operation, a reasonable simulation of the data can be achieved by injection of known quantities of water into the laboratory instrument while key parameters such as effluent divider status, ion pump current, and resolved ion current as a function of time are recorded. A series of tests were carried out to narrow the range down to a 'best' value. The results shown in Figure 9 were obtained by the injection of 0.2 mg of water into the laboratory instrument. The shapes of the two curves (mass chromatograms of *m/e* 17, which was used because *m/e* 18 would be off scale in one of them) are nearly identical, as is the effluent divider behavior. Other parameters which were recorded, such as the ion pump current, also give credence to the assumption that the two sets of data correspond to nearly identical quantities of water. The ion intensity obtained was much higher in the Martian data than in the laboratory result mainly because the sensitivity of the laboratory instrument had degraded through constant use. The problems of duplicating the Martian results were further complicated by the fact that one of the flow restrictors (20 1) in the lander 2 gas chromatograph–mass spectrometer effluent divider was found to have been blocked almost completely. This condition was simulated as closely as possible in the laboratory tests.

The results of the simulation tests lead us to the conclusion that the amount of water evolved in the experiment on sol 43 (identification number 10037) is equivalent to approximately 0.2 mg (which in the very worst case could be off by a factor of 5). This corresponds to 0.2% by weight based on a 100-mg soil sample. Values estimated for the other experiments are listed in Table 4.

Inspection of the data in Table 4 shows that most samples lost little H_2O at 200°, but all evolved significant and generally similar amounts at 350° and 500°. Samples from areas of surface crustification (Bonneville, Rocky Flats) seem to evolve decreasing amounts of H_2O on successive heatings. This is not so apparent for other samples. However, it must be noted that the VL-1 H_2O data are much more ambiguous because the use of $^{13}CO_2$ as a purge gas further complicates the behavior of the effluent divider.

The most distinctive difference among the samples was the increased evolution of both H_2O and CO_2 at 200° from the sample taken under Badger Rock. Considerably more H_2O and CO_2 was driven off at this temperature than from other comparable samples; results at 350° and 500° were not distinctively different from other samples. The CO_2 values listed in Table 4 are still very uncertain at the present state of data analysis.

The CO_2 evolved upon heating the samples presumably is partly desorbed from mineral surfaces and partly derived by partial decomposition of carbonate minerals. Table 5 shows approximate values of partial pressure of CO_2 in equilibrium

TABLE 4. Water and Carbon Dioxide

Sample	Temperature, °C	Mode	Water, wt %	CO_2, ppm
		*VL-1**		
Oven 1 (cruise)	500	$^{13}CO_2$	<0.1	
Sandy Flats	200	$^{13}CO_2$	<0.1	
	500	$^{13}CO_2$	0.1–1.0	
Rocky Flats	350	$^{13}CO_2$	0.1–1.0	
	500	$^{13}CO_2$	0.1–1.0	
	500	$^{13}CO_2$	0.1–1.0	
		VL-2		
Bonneville	200	H_2	0.05	<50
	350	H_2	0.3	50–500
	500	H_2	1.0	50–500
	500	$^{13}CO_2$	0.25	
Under Badger Rock	50	H_2	<0.01	<50
	200	H_2	0.2	50–500
	350	H_2	0.3	40–400
	500	H_2	0.8	70–700
	500	$^{13}CO_2$	0.6	

*Values for water are much less precise for VL-1 than for VL-2 because of experimental conditions ($^{13}CO_2$ mode).

with some common carbonate minerals at the temperature to which the samples are heated, calculated from the data of *Robie and Waldbaum* [1968]. It is hardly likely that gas-solid equilibrium is attained or even closely approached in the short time the samples are heated (30 s), but the equilibrium values presumably are upper limits, and their relative values give some indication of the pattern of thermal evolution of CO_2 to be expected. Although one can make only approximate estimates of the partial pressure of CO_2 in the oven from the abundance data, it would seem that thermal decomposition of calcite alone is inadequate to explain the amount of CO_2 evolved from the Martian samples. The relative importance of adsorbed CO_2 and CO_2 evolved from more labile carbonates is very difficult to assess without more specific kinetic data.

Interpretation of the data on the evolution of H_2O in terms of presumed mineral phases is more difficult both because of the greater variety of possible sources and because of the uncertainties attached to the analytical results. Other than adsorbed H_2O on mineral grain surfaces, the sources for evolved H_2O suggested by the most widely proposed mineralogical models include clays, goethite, and hydrated sulfates. Thermal studies of iron-rich montmorillonitic clays generally support the conclusion that most dehydroxylation occurs above 200° and may take place progressively over a temperature range of several hundred degrees [*MacKenzie and Rogers*, 1977]. Thermal dehydration of a nontronite from Riverside, California, whose major element composition is appropriate for a major constituent of the Martian surface samples showed a maximum dehydroxylation rate at about 350° in an inert gas atmosphere. Goethite varies widely in its dehydration

TABLE 5. Equilibrium Vapor Pressure P_{CO_2} Over Some Carbonate Minerals, Calculated From Data of *Robie and Waldbaum* [1968]

	P_{CO_2}, atm		
	200°C	350°C	500°C
Calcite ($CaCO_3$)	5×10^{-12}	2×10^{-7}	1.3×10^{-4}
Dolomite ($CaMg(CO_3)_2$)	9×10^{-6}	2×10^{-2}	2.4
Magnesite ($MgCO_3$)	1.4×10^{-4}	0.2	10

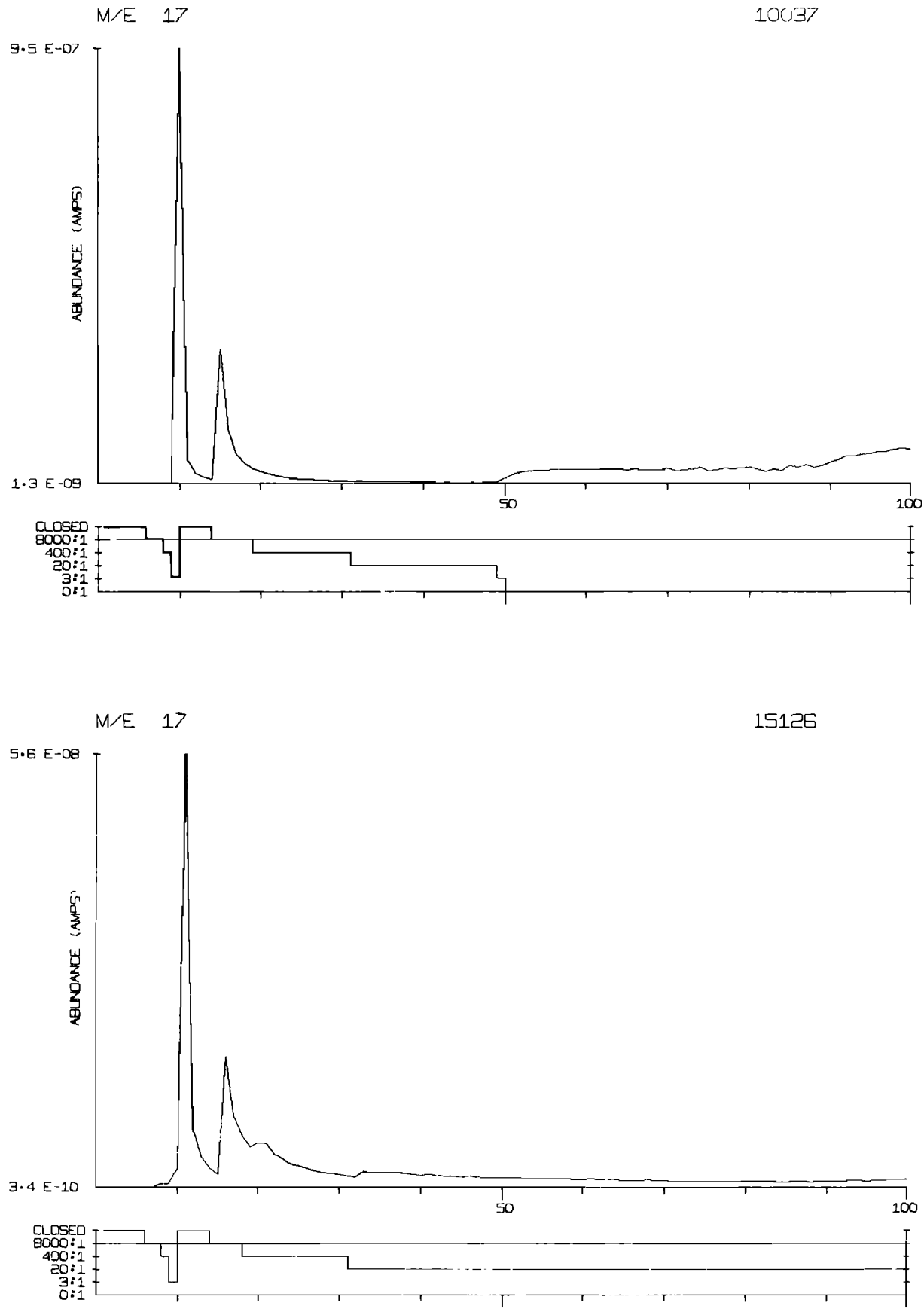

Fig. 9. Comparison of the mass chromatograms of *m/e* 17 (fragment ion of H_2O) and the effluent divider behavior between the 200° experiment on the second VL-2 sample and an injection of 0.2 mg of H_2O into the laboratory version of the flight instrument.

TABLE 6. Equilibrium Vapor Pressures in Inert Atmospheres (P_{S_2}) and in 1 atm H_2 (P_{H_2S}) Over Iron Sulfide Minerals, From Data of *Toulmin and Barton* [1964] and *Barton and Skinner* [1977]

	Equilibrium Vapor Pressure, atm		
	200°C	350°C	500°C
	Troilite (FeS)		
P_{S_2}	2×10^{-28}	2×10^{-20}	2×10^{-15}
P_{H_2S}	8×10^{-14}	2×10^{-10}	2×10^{-8}
	Pyrite (FeS_2)		
P_{S_2}	5×10^{-18}	4×10^{-10}	3×10^{-5}
P_{H_2S}	2×10^{-3}	3	370

rate and temperature range; crystallinity and particle size are especially important parameters. A well-crystallized specimen, ground to a fine powder, dehydrated mostly over the range 290°–410°, with the maximum rate (0.9–1.4% min^{-1}) at 360°–380° (heating rate 10° min^{-1}). Both these materials are being studied in a simulated flight instrument at MIT in order to elucidate their behavior under Vikinglike conditions. Similar experiments on hydrated sulfates are contemplated.

The absence of any indication of sulfur-containing species in our data is of interest in view of the rather high content of that element in the surface materials, as was shown by the inorganic analysis experiment. This result is consistent with the supposition that the sulfur occurs as a thermally stable sulfate, with a low vapor pressure (at least with respect to sulfur-containing species) below 500°. Table 6 shows the partial pressure of S_2 and H_2S (the latter in the presence of 1 atm H_2) in equilibrium with two common iron sulfides at the temperatures of interest [*Toulmin and Barton,* 1964; *Barton and Skinner,* 1977]. Common terrestrial pyrrhotites are solid solutions, $Fe_{1-x}S$, and have equilibrium sulfur pressures intermediate between pyrite (FeS_2) and troilite (FeS). Although the prima facie implication of these data is that the presence of pyrite and probably most pyrrhotites is inconsistent with the lack of detectable sulfur species in the evolved gases, caution is indicated until the appropriate simulations on the laboratory instrument have been carried out. Because of the danger to the laboratory instrument (copious amounts of sulfur or hydrogen sulfide in the gas stream poisons the H_2 separator) this experiment must be delayed until all other contemplated experiments have been completed.

Acknowledgments. We are indebted to all of the many individuals whose efforts and talents have contributed to this work. We thank specifically H. C. Urey, G. A. Shulman, and R. A. Hites for their contributions at the earlier phases of the Viking activities; our fellow team member T. Owen for his continuous interest and stimulation; D. Howarth, R. Rampacek, and C. Haag for their expert assistance before and during the mission; R. Williams and E. Ruiz through whose dedication and efforts the necessary software was developed at JPL and MIT; J. Lavoie, who helped in running the many tests on the laboratory instrument at MIT; and the Viking Surface Sampler Team for their successful efforts to acquire the samples needed for the experiments. Above all, the authors are indebted to those individuals at JPL who were involved in the design of the entire instrument, particularly C. E. Griffin, who was instrumental in the design of the mass spectrometer, and to Litton Industries, Perkin Elmer Aerospace Division, and Beckman Instruments, who constructed the flight hardware. Finally, our gratitude goes to the entire Viking Flight Team, whose dedication and expertise made possible the successful conduct of our experiments. This work was supported by NASA research contract NAS 1-9684 and many other related ones. P.G.S. is a research fellow at the University of Bristol.

REFERENCES

American Petroleum Institute, *Catalog of Mass Spectral Data, Res. Proj. 44,* New York, 1955.

Anders, E., and J. Arnold, Age of craters on Mars, *Science, 149,* 1494–1496, 1965.

Anders, E., R. Ganapathy, U. Krahenbuhl, and J. W. Morgan, Meteoritic material on the moon, *Moon, 8,* 3–24, 1973.

Anderson, D. M., K. Biemann, L. E. Orgel, J. Oro, T. Owen, G. P. Shulman, P. Toulmin III, and H. C. Urey, Mass spectrometric analysis of organic compounds, water, and volitile constituents in the atmosphere and surface of Mars: The Viking Mars lander, *Icarus, 16,* 111–138, 1972.

Barton, P. B., Jr., and B. J. Skinner, Sulfide mineral stabilities, in *Geochemistry of Hydrothermal Ore Deposits,* 2nd ed., edited by H. L. Barnes, John Wiley, New York, in press, 1977.

Biemann, K., *Mass Spectrometry: Organic Chemical Applications,* pp. 171–172, McGraw-Hill, New York, 1962.

Biemann, K., Test results on the Viking gas chromatograph–mass spectrometer experiment, *Origins Life, 5,* 417–430, 1974.

Biemann, K., J. Oro, P. Toulmin III, L. E. Orgel, A. O. Nier, D. M. Anderson, P. B. Simmonds, D. Flory, A. V. Diaz, D. R. Rushneck, and J. E. Biller, Search for organic and volatile inorganic compounds in two surface samples from the Chryse Planitia region of Mars, *Science, 194,* 72–76, 1976.

Biller, J. E., and K. Biemann, Reconstructed mass spectra, a novel approach for the utilization of gas chromatograph–mass spectrometer data, *Anal. Lett., 7*(7), 515–528, 1974.

Biller, J. E., W. C. Herlihy, and K. Biemann, Identification of the components of complex mixtures by GCMS, in *Computer Assisted Structure Elucidation,* edited by D. H. Smith, American Chemical Society, Washington, D. C., in press, 1977.

Cameron, R. E., J. King, and C. N. David, *Soil Sci., 109,* 110–120, 1970.

Clark, B. C., III, A. K. Baird, H. J. Rose, Jr., P. Toulmin III, R. P. Christian, W. C. Kelliher, C. D. Castro, K. Keil, and G. R. Huss, The Viking X ray fluorescence experiment: Analytical methods and early results, *J. Geophys. Res., 82,* this issue, 1977.

Dencker, W. D., D. R. Rushneck, and G. R. Shoemaker, Electrochemical cell as a gas chromatograph–mass spectrometer interface, *Anal. Chem., 44,* 1753–1758, 1972.

Fanale, E. P., Martian volatiles: Their degassing history and geochemical fate, *Icarus, 28,* 179–202, 1976.

Hertz, H. S., R. A. Hites, and K. Biemann, Identification of mass spectra by computer-searching a file of known spectra, *Anal. Chem., 43,* 681–691, 1971.

Hess, S. L., R. M. Henry, C. B. Leovy, J. A. Ryan, J. E. Tillman, T. E. Chamberlain, H. L. Cole, R. G. Dutton, G. C. Greene, W. E. Simon, and J. L. Mitchell, Preliminary meteorological results on Mars from the Viking I lander, *Science, 193,* 788–791, 1976.

Hubbard, J. S., J. Hardy, G. E. Voecks, and E. E. Golub, Photocatalytic synthesis of organic compounds from CO and water: Involvement of surfaces in the formation and stabilization of products, *J. Mol. Evol., 2,* 149–166, 1973.

Klein, H. P., G. V. Levin, V. I. Oyama, J. Lederberg, A. Rich, J. S. Hubbard, G. L. Hobby, P. A. Straat, B. J. Berdahl, G. C. Carle, F. S. Brown, and R. D. Johnson, The Viking biological investigation: Preliminary results, *Science, 194,* 99–105, 1976.

MacKenzie, K. J. D., and D. E. Rogers, Thermal and Mossbauer studies of iron-containing hydrous silicates, I, Nontronite, *Thermochim. Acta, 18,* 177–196, 1977.

Mason, B. (Ed.), *Handbook of Elemental Abundances in Meteorites,* Gordon and Breach, New York, 1971.

McElroy, M. B., and T. Y. Kong, Oxidation of the Martian surface: Constraints due to chemical processes in the atmosphere, *Geophys. Res. Lett., 3,* 569–572, 1976.

Miller, S. L., and L. E. Orgel, The formation of the solar system, in *The Origins of Life on the Earth,* edited by W. D. McElroy and C. P. Swanson, pp. 5–15, Prentice-Hall, Englewood Cliffs, N. J., 1974.

Miller, S. L., H. C. Urey, and J. Oro, Origin of organic compounds on the primitive earth and in meteorites, *J. Mol. Evol., 9,* 59–72, 1976.

Morgan, J. W., Chemical fractionation in the solar system, in *Proceedings of the International Conference on Modern Trends in Activation Analysis,* Munich, Germany, 1976.

Nagy, B., *Carbonaceous Meteorites,* Elsevier, New York, 1975.

Novotny, M., J. M. Hayes, F. Bruner, and P. G. Simmonds, Gas

chromatographic column for the Viking 1975 molecular analysis experiment, *Science, 189,* 215–216, 1975.
Oro, J., Extraterrestrial organic analysis, *Space Life Sci., 3,* 507–550, 1972.
Owen, T., and K. Biemann, Composition of the atmosphere at the surface of Mars: Detection of argon-36 and preliminary analysis, *Science, 193,* 801–803, 1976.
Owen, T., K. Biemann, D R. Rushneck, J. E. Biller, D. W. Howarth, and A. L. Lafleur, The Atmosphere of Mars: Detection of krypton and xenon, *Science, 194,* 1293–1295, 1976.
Robie, R. A., and D. R. Waldbaum, Thermodynamic properties of minerals and related substances at 298.15 K (25.0 C) and one atmosphere (1.013 bars) pressure and at higher temperatures, *U.S. Geol. Surv. Bull., 1259,* 256, 1968.
Shorthill, R. W., H. J. Moore II, R. E. Hutton, R. F. Scott, and C. R. Spitzer, The environs of Viking 2 lander, *Science, 194,* 1309–1318, 1976.
Soderblom, L. A., C. D. Condit, R. A. West, B. M. Herman, and T. J. Kreidler, Martian planet-wide crater distribution implications for geologic history and surface processes, *Icarus, 22,* 239–263, 1974.
Toulmin, P., III, and P. B. Barton, Jr., A thermodynamic study of pyrite and pyrrhortite, *Geochim. Cosmochim. Acta, 28,* 641–671, 1964.
Toulmin, P., III, A. K. Baird, B. C. Clark, K. Keil, H. J. Rose, Jr., R. P. Christian, P. H Evans, and W. C. Kelliher, Geochemical and mineralogical results, *J. Geophys. Res., 82,* this issue, 1977.
Wasson, J. T., *Meteorites: Classification and Properties,* Springer, New York, 1974.

(Received June 1, 1977;
revised June 15, 1977;
accepted June 15, 1977.)