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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References and Notes

1. D. M. Anderson, K. Biemann, L. E. Orgel, J. Oro, T. Owen, G. P. Shulman, P. Toulmin III, H. C. Urey, *Icarus* **16**, 111 (1972); K. Biemann, *Origins Life* **5**, 417 (1974).
2. T. Owen and K. Biemann, *Science* **193**, 801 (1976); K. Biemann, T. Owen, D. R. Rushneck, A. L. LaFleur, D. W. Howarth, *ibid.* **194**, 76 (1976).
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.
5. D. P. Lucero and F. C. Haley, *J. Gas Chromatogr.* **6**, 477 (1968); P. G. Simmonds, G. R. Shoemake, J. E. Lovelock, *Anal. Chem.* **42**, 881 (1970); W. D. Dencker, D. R. Rushneck, G. R. Shoemake, *ibid.* **44**, 1753 (1972).
6. This "effluent divider" can be preset in two different modes so as to provide maximum protection for the MS. In the hydrous mode, the assumption is that any overload is due to a very wide GC peak, for example, from water. In this mode, in order to avoid many rapid changes of state which would confuse data interpretation, a logical time filter count is utilized which inhibits changes of state to a lower state of division for longer periods of time than in the anhydrous mode. The following indicates the relationship of the four vent-ratios and the time filter count for changes to the next lower state in the hydrous mode with the count for the anhydrous mode in parentheses: 8000/1, 45 seconds (45 seconds); 400/1, 2 minutes (45 seconds); 20/1, 15 minutes (45 seconds); and 3/1, 15 minutes (45 seconds).
7. H. S. Hertz, R. A. Hites, K. Biemann, *Anal. Chem.* **43**, 681 (1971).
8. J. A. Biller and K. Biemann, in preparation.
9. R. W. Shorthill, R. E. Hutton, H. J. Moore, S. Liebes, R. F. Scott, C. R. Spitzer, *Science* **194**, 91 (1976).
10. L. O. Quam, Ed., *Research in the Antarctic* (AAAS, Washington, D.C., 1971), pp. 137–189; R. E. Cameron, J. King, C. N. David, *Soil Sci.* **109**, 110 (1970).
11. A. L. La Fleur, unpublished results.
12. J. S. Levine, *Icarus* **28**, 165 (1976), T. Owen, *ibid.*, p. 171; J. Oró, *Space Life Sci.* **13**, 507 (1972).
13. J. W. Morgan, in *Proceedings of the International Conference on Modern Trends in Activation Analysis 1976*, München, Germany.
14. L. A. Soderblom, C. D. Condit, R. A. West, B. M. Herman, T. J. Kreidler, *Icarus* **22**, 239 (1974).
15. F. P. Fanale, *ibid.* **28**, 179 (1976).
16. E. Anders and J. R. Arnold, *Science* **149**, 1494 (1965).
17. J. S. Hubbard, J. P. Hardy, G. E. Voecks, E. E. Golub, *J. Mol. Evol.* **2**, 149 (1973).
18. Calculations on the yield of photochemically induced organic compounds gives an upper limit of 100 nanomoles per gram of martian soil (J. S. Hubbard, personal communication). It is further estimated that about 20 percent is recoverable as an organic fraction with the approximate distribution: $HCOO^-M^+$, 20 nmole; CH_2O, 0.5 nmole; CH_3CHO, 0.25 nmole; $HOCH_2COOH$, 0.5 nmole. For the 100-mg sample used in our experiments this would correspond to concentrations of 920, 15, 11 and 38 ppb, respectively. Formate and glycolic acid would probably decompose during analysis; the high detection limit for formaldehyde has been discussed in the text. Acetaldehyde at a maximum concentration of 11 ppb is just below the minimum detection limit, provided most or all was admitted to the mass spectrometer, that is, at a low effluent MS, that is, at a low effluent divider state.
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.
20. M. Formenti, F. Juillet, P. Meriandeau, S. J. Teichner, *Chem. Technol.* **1**, 680 (1971).
21. N. H. Horowitz, A. J. Bauman, R. E. Cameron, P. J. Geiger, J. S. Hubbard, G. P. Shulman, P. G. Simmonds, K. Westberg, *Science* **164**, 1054 (1969).
22. H. P. Klein, N. H. Horowitz, 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, R. D. Johnson, *ibid.* **194**, 99 (1976).
23. T. A. Mutch, R. A. Arvidson, A. B. Binder, F. O. Huck, E. C. Levinthal, S. Liebes, Jr. E. C. Morris, D. Nummedal, J. B. Pollack, C. Sagan, *ibid.*, p. 87.
24. P. Toulmin III, B. C. Clark, A. K. Baird, H. J. Rose, Jr., K. Keil, *ibid.*, p. 81.
25. J. B. Pollack, D. Pitman, B. N. Khare, C. Sagan, *J. Geophys. Res.* **75**, 7480 (1970); J. B. Pollack, R. N. Wilson, G. G. Goles, *ibid.*, p. 7491.
26. D. M. Anderson, E. Goffney, P. F. Low, *Science* **155**, 319 (1967).
27. 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; A. La Fleur, J. Lavoi, and E. Ruiz who conducted and processed most of the tests on the laboratory instrument; our fellow team member T. Owen for his continuous interest and stimulation; D. Howarth, J. Rampacek, R. Williams, and C. Haag for their unfailing expert assistance before and during the mission, and finally L. Crafton without whose labor and prodding this manuscript could not have been produced. 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.

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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 sevenfold enrichment of minor constituents; the addition of nine more sampling and absorption cycles produced a final enrichment factor of 8.5.

Two excitation voltages were used to help discriminate among doubly and singly charged ions, and the enriched samples were always analyzed at both voltages. The first voltage given in Table 1 is that at which an instrumental background was also recorded.

The results derived from this series of experiments to date are summarized in Tables 2 and 3. The isotope ratios for carbon and oxygen in Table 2 are based on the relative intensities of $^{12}C^{16}O^{16}O$, $^{13}C^{16}O^{16}O$, and $^{12}C^{16}O^{18}O$ in the analyses of unaltered atmosphere; they show no significant departure from average terrestrial values. There is a definite enhancement of the abundance of ^{15}N relative to ^{14}N on Mars, but we are unable to be precise in our evaluation of the ratio of these isotopes because of possible interference at *m/e* 29 from ^{13}CO desorbed or formed in the instrument. (We cannot use *m/e* 15 as a check because of background interference.) $^{13}CO_2$ is introduced into the mass spectrometer in the organic analyses (*2*), and we can see its effects at *m/e* 29 in the analyses of unaltered atmosphere. We must therefore make a correction for the worst case of contamination on the assumption that this same contamination occurs in the mass spectra of the enriched samples, because all of the enriched samples were analyzed after an organic analysis had been performed. The range given in Table 2 reflects the value derived without correction ($^{15}N/^{14}N = 0.0064$, which is a 74 percent enhancement of ^{15}N) and the value obtained after correcting for the worst case of contamination described above ($^{15}N/^{14}N = 0.0050$, 36 percent enhancement of ^{15}N). Our results therefore just embrace the value derived by Nier *et al.* (*3*), who have discussed the significance of this finding.

We have detected ^{38}Ar in the martian atmosphere and we can evaluate its abundance relative to ^{36}Ar which we reported previously (*1*). Unfortunately, the instrumental background in this region has deteriorated and this, with the memory effects from the ion pump (release of previously buried argon), has prevented an accurate specification of the relative abundances of these two isotopes. The range given in Table 2 encompasses the terrestrial atmospheric value.

We have searched unsuccessfully for methane, neon, krypton, and xenon (Table 3). The methane limit is extremely high because of the substantial background in the instrument at the low masses. A global limit of 25 parts per billion of methane in the martian atmosphere has been established by infrared spectroscopy from Mariner 9 (*4*). Our upper limit for neon is set by the presence of doubly ionized ^{40}Ar at *m/e* 20 in the low voltage analyses. Thus, in contrast to the other noble gases, the enrichment process does not lower our previous limit. The other common isotope of neon at *m/e* 22 is expected to be on the order of one-tenth as abundant as ^{20}Ne and our maximum enrichment has not brought it above the threshold set by CO_2^{2+}.

The enrichment process considerably lowered the limits for krypton and xenon compared to those derived previously (*1*). The expected values for the krypton and xenon isotopes given in Table 3 are based on terrestrial abundances scaled from ^{36}Ar. It is evident that we have reached the level of sensitivity at which we would expect to detect krypton on Mars if it were present in the terrestrial abundance ratio.

These results place us in an interesting dilemma. The relatively low abundance of ^{36}Ar on Mars suggests that the total outgassing of the planet was perhaps as little as 1/100 the amount exhibited by Earth. But the enhancement of ^{15}N relative to ^{14}N implies that a large amount of nitrogen has escaped, which would indicate a much larger degree of total outgassing (*3*). However, these inferences are made by assuming that the original volatile inventory on Mars was essentially identical to that on Earth.

Table 1. Atmospheric analyses on Mars.

Date (August 1976)	Sample	Number of analyses	Excitation voltage (electron volts)
6 to 7	Unaltered	7	70
14	Enriched (10 cycles)	2	70 and 45
16	Same as above, reanalyzed	2	45 and 70
23	Enriched (19 cycles)	2	45 and 70

Table 2. Comparison of the isotope ratios in the martian and terrestrial atmospheres.

Species	Mars	Earth
$^{15}N/^{14}N$	0.0064 to 0.0050	0.00368
$^{13}C/^{12}C$	0.0118 ± 0.0012	0.0112
$^{18}O/^{16}O$	0.00189 ± 0.0002	0.00204
$^{36}Ar/^{38}Ar$	4 to 7	5.3

Table 3. Upper limits [expressed as parts per million (ppm)] of gases not detected in the martian atmosphere.

Species	Present upper limit (ppm)*	Expected value (ppm)
CH_4	<120	<25†
Ne	<10	5
Kr	< 0.3	0.3
Xe	< 1.5	0.02

*Based on calibration with pure gases of terrestrial isotope distribution. †Value for CH_4 expressed as parts per billion.

If, on the contrary, the martian volatile inventory was more primitive, that is, closer to that exhibited by the type 1 carbonaceous chondrites, one could accommodate an initial nitrogen abundance up to 30 times the present atmospheric value, while increasing the carbon dioxide abundance only by a factor of 10. This would be consistent with the previous low outgassing model in which the maximum surface pressure was on the order of 100 mbar (*1*).

Another possibility is that sweeping by the solar wind has drastically reduced the ^{36}Ar from an earlier amount that corresponded to a massive primitive atmosphere with terrestrial relative abundances. But this hypothesis would imply some enrichment of ^{84}Kr relative to ^{36}Ar in the present atmosphere, which we do not observe. On the other hand, an inventory of the C-1 type postulated above would predict a lower $^{84}Kr/^{36}Ar$ ratio on Mars than we find in the atmosphere of Earth. This seems to be the case.

It is too early to discriminate among these various possibilities. We anticipate that the mass spectrometer on Lander 2 will have better sensitivity for atmospheric analyses, based on calibrations before launching and on backgrounds obtained during cruise. We can also improve the enrichment factor at some risk to the instrument after completing all of the other types of analyses. We thus hope to be able to improve our existing precision on the isotope ratios and to lower still further the threshold for detecting trace constituents.

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References and Notes

1. T. Owen and K. Biemann, *Science* **193**, 801 (1976).
2. K. Biemann, J. Oro, P. Toulmin III, L. E. Orgel, A. O. Nier, D. M. Anderson, P. G. Simmonds, D. Flory, A. V. Diaz, D. R. Rushneck, J. A. Biller, *ibid.* **194**, 72 (1976).
3. A. O. Nier, M. B. McElroy, Y. L. Yung, *ibid.*, p. 68.
4. W. C. Maguire, *Icarus*, in press.

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Mars Climatology from Viking 1 After 20 Sols

Abstract. *The results from the meteorology instruments on the Viking 1 lander are presented for the first 20 sols of operation. The daily patterns of temperature, wind, and pressure have been highly consistent during the period. Hence, these have been assembled into 20-sol composites and analyzed harmonically. Maximum temperature was 241.8°K and minimum 187.2°K. The composite wind vector has a mean diurnal magnitude of 2.4 meters per second with prevailing wind from the south and counterclockwise diurnal rotation. Pressure exhibits diurnal and semidiurnal oscillations. The diurnal is ascribed to a combination of effects, and the semidiurnal appears to be the solar semidiurnal tide. Similarities to Earth are discussed. A major finding is a continual secular decrease in diurnal mean pressure. This is ascribed to carbon dioxide deposition at the south polar cap.*

We have previously published a brief report (*1*) on the results of the first 3 sols (*2*) of data returned by the meteorology experiment on the Viking 1 lander on the surface of Mars. We now expand that report to include the first 20 sols. The system continues to perform normally and, barring a mishap, we may expect ultimately to receive a very long series of data.

The high degree of consistency of the daily patterns of temperature, wind, and pressure described earlier (*1*) has persisted. In view of this consistency, we have assembled these 20 sols of data into a preliminary diurnal climatology of this site in summer (*3*).

A composite ambient temperature curve for the first 20 sols is given in Fig. 1. The curve was generated by least-squares fitting of the data to a fifth-order harmonic function for each 0.1-hour interval. According to the model the maximum temperature of 241.8°K occurs at 15:00 local lander time (L.L.T.), and the minimum of 187.2°K occurs at 05:00 L.L.T., shortly before sunrise. The fifth-order function does not fit the rather sharp temperature changes at dawn; the curve is, accordingly, dashed between 05:00 and 06:00.

A composite ambient temperature diurnal cycle for Earth is given in Fig. 2, in order to provide a general comparison. These and other data from Earth contained in this report are from China Lake, part of a broad, dry basin in the Mojave Desert, California (*4*). We produced the composite by averaging the hourly readings from ten early- to midsummer cloudless days. Day-to-day climatological variations at China Lake during this period are small. The period covered is analogous to the present season on Mars at the Viking 1 landing site. If we disregard the obviously warmer clime at China Lake, we note the marked similarity in the phase relationships. The times of temperature maximum and minimum are about the same at both sites. The similarity in times of maximum temperature can be explained by the fact that the dominant heating mechanism near the surface is convective transfer from the ground. The temperature maximum is reached when the ground temperature has cooled enough that convection effectively ceases. This occurs at about the same time (15:00 local) on both planets since the rate of convection and the atmospheric heat capacity are both proportional to air density. Thus, the time of maximum air temperature near the surface does not depend, to first order, on the air density. The minimum temperature at China Lake lags somewhat compared to the minimum at the Viking 1 site. This may result from the dominance of radiative transfer at this time of day. The atmosphere of Mars should respond more rapidly than Earth's to radiative forcing. The much larger temperature range and atmospheric heating rate at the Viking 1 site is a consequence of the large martian diurnal ground temperature range which itself is a result of the very low air density.

Table 1. First two pressure harmonics for the Viking 1 site and China Lake. Entries are the times of maximum (max) and minimum (min) and the peak-to-peak (PTP) amplitudes.

Max or min	Viking 1 site: Local time	Viking 1 site: PTP ampl. (mbar)	China Lake: Local time	China Lake: PTP ampl. (mbar)
		First harmonic		
Max	03:10		07:30	
		0.16		3.34
Min	15:30		19:30	
		Second harmonic		
Max	10:50 23:10		09:45 21:45	
		0.07		1.55
Min	04:40 17:00		03:45 15:45	

The diurnal pressure variation at the Viking 1 landing site is shown in Fig. 3. The composite curve includes only the first and second harmonics, the only two components having statistical significance at this stage of the analysis (*5*). Figure 4 shows the corresponding composite pressure data from China Lake, a fifth-order harmonic fit in which the first and second harmonics dominate the diurnal behavior. The local times of maxima and minima and peak-to-peak (PTP) amplitudes are given in Table 1. Also given are the corresponding values for China Lake. The amplitude ratios of the first (diurnal) to second (semidiurnal) harmonics are similar at the two locations. The phases of the semidiurnal component are also similar at the two locations, particularly when one adjusts for the somewhat longer martian solar day. The amplitudes of both martian pressure oscillations, expressed as a fraction of the mean pressure, are more than five times the amplitudes of their China Lake counterparts. Finally, the first harmonic maximum and minimum at China Lake occur about 4.5 hours later than at the Viking site.

The semidiurnal pressure oscillation at China Lake is a semidiurnal tide produced by the sun. This variation on Earth is the atmospheric response to the semidiurnal component of solar heating through a large depth of the atmosphere. Its dominant component is a westward-propagating mode with longitudinal wave number 2, the so-called S^2_2 mode (*6*). It is global in scale and insensitive to ocean-continent and topographic effects. The analogous mode is expected on Mars. The close phase agreement between the Viking 1 and China Lake semidiurnal pressure oscillations indicates that the martian semidiurnal oscillation is probably also predominantly the S^2_2 mode of the solar semidiurnal tide. If this identification is correct, Viking 2, planned for landing at about 47.5°N, should also see this harmonic, with a similar phase but a somewhat smaller amplitude.

The diurnal oscillations appear to be much more complicated. A consideration of the wind data should precede