tic extrusions associated with ridge systems interact with oxygenated seawater to form nontronitic clays (*20*). Ferroan clays are a common, if not abundant, result of hydrothermal alteration of mafic rocks (*17*).

Prior to the Viking mission, Huguenin (*21*) advanced theoretical arguments and experimental evidence for photochemical surface reactions with the potential for forming clay minerals from pyrogenic silicates in an environment similar to that on the surface of Mars. His reaction mechanism requires only the very low partial pressure of O_2 and H_2O known to be present in the present atmosphere of Mars. So far as we are aware, however, no clay minerals have yet been produced in the laboratory by such reactions. Furthermore, photochemical processes on mineral surfaces may be effective mostly on the very fine dust grains that are carried to high levels in the atmosphere, in which case some other agency for prior comminution must be sought. The sequential combination of argillization at or near the surface, and photochemical desiccation or oxidation (or both) of the resulting dust in the high atmosphere is one hypothesis consistent with these conditions.

Our mineralogic model has, therefore, two major requirements for petrogenesis on Mars. (i) There must be exposed on the surface of Mars abundant mafic parent materials for clay formation and, conversely, there cannot be large, exposed source areas providing alkali-rich granitic materials. (ii) There must be (or must have been) sufficient water or ice on Mars to interact with mafic rock material to form ferroan clays.

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References and Notes

1. T. A. Mutch, A. B. Binder, F. O. Huck, E. C. Levinthal, S. Liebes, Jr., E. C. Morris, W. R. Patterson, J. B. Pollack, C. Sagan, G. R. Taylor, *Science* **193**, 791 (1976).
2. The martian day (24 hours, 35 minutes, 39 seconds) has been designated a sol; sols are numbered consecutively from the day of landing of each lander.
3. R. W. Shorthill, H. J. Moore, II, R. F. Scott, R. E. Hutton, S. Liebes, Jr., C. R. Spitzer, *Science* **194**, 91 (1976).
4. R. W. Shorthill, H. J. Moore, II, R. E. Hutton, R. F. Scott, *ibid.*, p. 1309.
5. T. A. Mutch, R. E. 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.
6. P. Toulmin III, B. C. Clark, A. K. Baird, K. Keil, H. J. Rose, Jr., *Science* **194**, 81 (1976).
7. For efficiency, the data in most ground-based tests were taken via a multichannel analyzer rather than in the single-channel, step-scanning mode imposed by the flight unit.
8. B. C. Clark, A. K. Baird, H. J. Rose, Jr., P. Toulmin III, K. Keil, A. J. Castro, W. C. Kelliher, C. D. Rowe, P. H. Evans, *Science* **194**, 1283 (1976).
9. The Viking XRFS does not detect Na. We have assumed that the Na content of the Mars fines is very low, because (i) the analytical deficit (difference between sum of constituents determined and 100 percent) can be satisfactorily accounted for by other constituents with no, or very little, Na required; and (ii) the other alkali elements (K, Rb) are extremely low in all the Mars samples. Other assumptions are possible with regard to the analytical deficit; the model(s) proposed herein are based on our stated assumptions.
10. 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, *Science* **194**, 72 (1976).
11. R. B. Hargraves, D. W. Collinson, C. R. Spitzer, *ibid.*, p. 84.
12. T. Owen and K. Biemann, *ibid.* **193**, 801 (1976).
13. This material is an alteration product of a hedenbergite pyroxenite; we thank D. M. Morton, U.S. Geological Survey, for supplying the clay sample.
14. Bighorn bentonite, a commercial product.
15. The suggestion of nonisochemical weathering obviously raises the question of mass balance. Where and what are the compositional complements to the weathering products? This question can be addressed quantitatively only when compositional data on fresh rocks are available. Thus far we have not been successful in obtaining a sample of rocks from either Viking site, but this remains a high-priority goal for the extended mission.
16. R. E. Arvidson, personal communication.
17. J. Hower, personal communication.
18. C. S. Ross and E. V. Shannon, *Am. Ceram. Soc. J.* **9**, 77 (1926); H. M. Koster, *Beitr. Mineral. Petrogr.* **7**, 71 (1960); E. Bolter, *ibid.* **8**, 111 (1961).
19. C. S. Ross and S. B. Hendricks, *U.S. Geol. Surv. Prof. Pap. 205-B* (U.S. Government Printing Office, Washington, D.C., 1945).
20. E. Bonatti and O. Joensuu, *Science* **154**, 643 (1966); J. L. Bischoff, *Clays and Clay Minerals* **20**, 217 (1972); personal communication.
21. R. L. Huguenin, *J. Geophys. Res.* **79**, 3895 (1974).
22. We thank J. Hower (NSF) and J. Bischoff (U.S. Geological Survey) for sharing their extensive knowledge on terrestrial clay formation; the following members of the U.S. Geological Survey: R. R. Larson, J. M. Hammarstrom, C. S. Zen, J. Lindsay, P. Hearn, and J. Jensen for analytical aid; D. McIntyre, Pomona College, for a literature search of iron-bearing montmorillonites; N. Brosnahan, E. Hartman, and J. MacKay, of Pomona College for technical assistance; N. Nickle, of JPL, for assisting in the organization and operation of our x-ray laboratory; J. Gliozzi and the surface sampler team for their efforts in planning for and acquiring Mars surface samples for our experiment; R. Hargraves, E. Morris, A. Binder, and R. Arvidson for reviewing drafts of this report; R. R. Moore for providing needed calibration data through operation and maintenance of flightlike x-ray instruments. We thank S. Dwornik and G. J. Wasserburg for their help and encouragement with the x-ray experiments. Supported by NASA (Viking Program) grants NAS 1-11855, NAS 1-11858, L-9717, and NAS 1-9000.

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The Atmosphere of Mars: Detection of Krypton and Xenon

Abstract. *Krypton and xenon have been discovered in the martian atmosphere with the mass spectrometer on the second Viking lander. Krypton is more abundant than xenon. The relative abundances of the krypton isotopes appear normal, but the ratio of xenon-129 to xenon-132 is enhanced on Mars relative to the terrestrial value for this ratio. Some possible implications of these findings are discussed.*

We have previously reported the detection of ^{36}Ar and the establishment of upper limits on Ne, Kr, and Xe in the atmosphere of Mars, using the mass spectrometer on the first Viking lander (*1*). The upper limit on krypton was close to the value that would be predicted if the ^{36}Ar/Kr ratio on Mars were identical to that on Earth. It thus seemed important to try to increase the sensitivity of the experiment with the hope of actually detecting this important element.

The successful deployment of the second Viking lander (VL2) on Mars afforded us the opportunity to conduct this experiment. We had established from tests of the two instruments during the cruise from Earth to Mars that the background in the mass spectrometer on VL2 was much lower than that in the instrument on the first lander, making it a superior instrument for the detection of trace amounts of atmospheric gases. It was also clear from experience gained with the operation of VL1 that the best way to maintain this low instrumental background would be to perform the atmospheric analyses prior to any analyses of the martian soil. A delay in obtaining the first soil sample for our instrument with VL2 provided the opportunity to design an optimized enrichment sequence for detecting trace gases in the atmosphere.

The basic procedure has already been described (*1*). We use a chemical scrubber to remove over 99 percent of the CO and CO_2 in a given sample of martian atmosphere, admit a new sample, again remove CO_2, and repeat this procedure a preselected number of times to build up the concentration of trace constituents. The sample is exposed to a drying agent during each cycle to remove water gener-

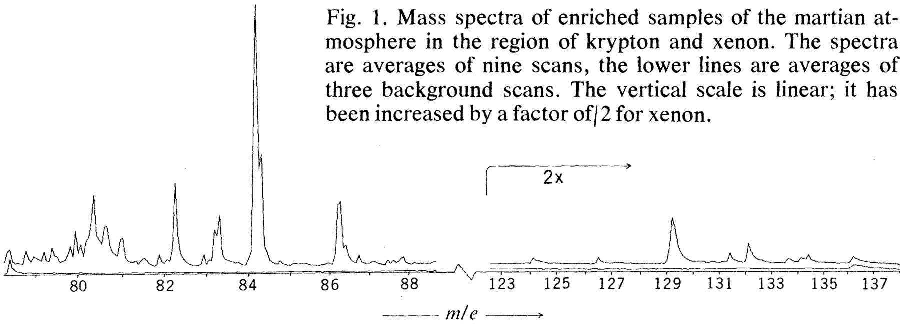

Fig. 1. Mass spectra of enriched samples of the martian atmosphere in the region of krypton and xenon. The spectra are averages of nine scans, the lower lines are averages of three background scans. The vertical scale is linear; it has been increased by a factor of 2 for xenon.

ated by the CO_2 scrubber. The sample is then admitted to the mass spectrometer through a molecular leak for analyses. Using sequences of five and ten cycles, we obtained enrichments of 4 and 6.3 over the yield from a single cycle. Mass spectra of the sample enriched 6.3 times showed an indication of krypton, but the identification was not conclusive. After evaluating the performance of the instrument, we changed the internal timing of the sequence and obtained a tenfold enrichment with 15 cycles. This sample was analyzed 16 times by the mass spectrometer with the electron multiplier gain increased by a factor 5.3 over its nominal value. These spectra gave clear evidence of the presence of krypton. The analysis was subsequently repeated after an additional 15 cycles with a multiplier gain of 28 times nominal.

The results are shown in Fig. 1, which indicates the appearance of the averaged mass spectrum in the vicinity of the krypton and xenon isotopes. The characteristic isotopic pattern of krypton is clearly evident; the broad peak at $m/e = 80$ is an artifact caused by the high partial pressure of argon in the instrument. In the case of xenon, ^{129}Xe is much more abundant relative to the other isotopes on Mars compared with the distribution in terrestrial atmospheric xenon. The absence of organic compounds of high molecular weight in the soil (*2*), the absence of spectroscopically active compounds of high molecular weight in the atmosphere (*3, 4*), and the clean instrumental background in this mass range make us quite confident that the peaks shown in this region of Fig. 1 are chiefly caused by xenon on Mars.

We plan to obtain additional data with both VL1 and VL2 ultimately using a more extreme enrichment sequence, which should lead to an additional gain in the concentration of trace gases by a factor between 1.5 and 2.0. Such a sequence involves some risk to the instrument, however, since the partial pressure of argon then becomes dangerously high for the capabilities of the ion pump. We will not, therefore, attempt this procedure until the postconjunction period, near the end of the extended mission.

It is not yet possible to compute accurate abundances for these two gases, or even to give precise values for the ratios of their isotopes. At this low level of detection, the instrumental response is noisy, nonlinear, and distorted by memory effects (degassing from the pump). There is, however, no question that ^{129}Xe is much more abundant than ^{132}Xe and ^{131}Xe, rather than almost equal to the other two isotopes as is the case on Earth. The mass spectrometer must be recalibrated in a manner that duplicates experimental conditions on Mars. Such tests are now being conducted with the third gas chromatograph–mass spectrometer (GCMS) that was built for this mission.

Meanwhile, we can point out some important consequences of this discovery, based on the available data. First, we can support our previous assertion that it is very unlikely that Mars had a massive, original atmosphere (produced, for example, by accretional heating) which subsequently was reduced to its present state by extensive solar wind sweeping. If that were the case, we would expect the ratio of ^{36}Ar to total krypton to be much lower than the value found in the earth's atmosphere or in the primordial gas in meteorites, since the argon would be swept off more efficiently than krypton in the upper atmosphere where diffusive separation occurs. The low total abundance of ^{36}Ar now in the martian atmosphere therefore implies the following possibilities: (i) that Mars was very depleted in volatiles at the time of its formation—an unlikely condition in view of its distance from the sun, (ii) that a large fraction of the primitive atmosphere was swept away in a manner that led to no mass discrimination, or (iii) that the planet has simply not outgassed as much as Earth—the conclusion we favor (*1, 5*).

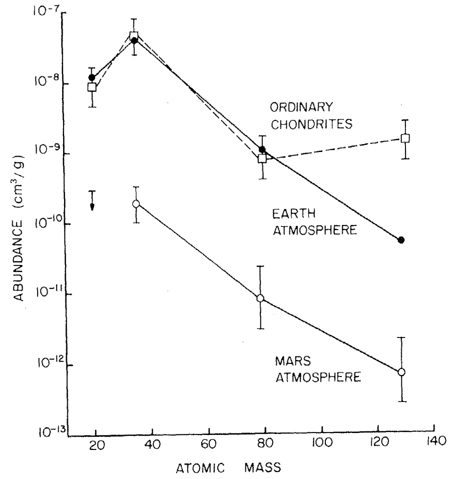

Fig. 2. The abundances of noble gases in ordinary chondrites and the atmospheres of Earth and Mars. Error bars are only approximate since systematic errors remain to be assessed.

The second consequence of this observation stems from there being, evidently, more krypton than xenon in the martian atmosphere. This result is important because the reverse is true in the primordial gas component of ordinary or carbonaceous chondrites (*6, 7*). The abundance pattern and the absolute abundances of noble gases in this primordial component closely match the abundances of the noble gases observed in the earth's atmosphere except for xenon (*8*), a fact that led to the prediction that this same pattern should exist in the martian atmosphere (*3, 5, 9*). This prediction was based on the assumption that the fractionation process that produced the primordial gas component in the meteorites must have occurred prior to the formation of the planets and thus must have affected the noble gas distribution in the accreting planetary material in the same way. Most meteorites come from the region of the asteroid belt, Mars is between Earth and the asteroids, hence it seemed reasonable that Mars should show the same type of noble gas abundance pattern.

However, in the earth's atmosphere, xenon is deficient compared with the primordial gas in meteorites, and this is exactly the situation we are now finding on Mars (Fig. 2). The xenon deficiency on Earth has been attributed to the preferential adsorption of xenon in shales and other sedimentary material after it was outgassed (*10*). One is thus led to the tentative conclusion that similar processes have been active on Mars, perhaps in association with the epochs of fluvial erosion that have left their imprint on the planet's surface. An alternative (or supplementary) suggestion is that some of the xenon could be absorbed in the regolith (*11*).

At this stage of our investigation of martian xenon, we can only be sure of the enhancement of ^{129}Xe. A determination of the relative abundances of the other isotopes requires additional analyses of enriched samples. It is generally agreed that ^{129}Xe anomalies in meteoritic and terrestrial gas samples result from the production of this isotope by decay of extinct ^{129}I (*12*). We find that the ratio of ^{129}Xe to ^{132}Xe is 2.5 (+ 2 or − 1); the terrestrial atmospheric value is 0.97, and in the carbonaceous and ordinary chondrites, values as high as 4.5 and 9.6 have been reported (*6, 7, 12*). There is a tendency for more ^{129}Xe in meteorites of types C-3 and C-4 than types C-1 or C-2, which may be attributable to the greater ability of the coarse-grained C-3 and C-4 types to retain the ^{129}Xe than the fine-grained C-1 and C-2 types, according to Mazor *et al.* (*7*). One might therefore conjecture that a planetary atmosphere derived from a partially degassed veneer enriched in material of type C-1 would show an enhancement of ^{129}Xe; but one might also expect such an enhancement in an atmosphere that had suffered massive losses at an appropriate interval after formation of the planet.

These are only two of several hypotheses that could explain the observations, however, and we shall study these problems in more detail after we have obtained results from the experiments planned for the end of the extended mission.

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References and Notes

1. 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).
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. E. Biller, *ibid.* **194**, 72 (1976).
3. T. Owen, *Comments Astrophys. Space Phys.* **5**, 175 (1974).
4. C. A. Barth, *Annu. Rev. Earth Planet. Sci.* **2**, 33 (1974).
5. One could argue that the noble gases were originally present on Mars in a "cosmic" ratio, in which case the ^{36}Ar/Kr ratio would be 2.5 × 10^3 and Kr/Xe ≈ 9 [A. G. W. Cameron, *Space Sci. Rev.* **15**, 121 (1973)]. The Ar/Kr ratio would then have been reduced to its present earthlike value coincidentally by solar wind sweeping. This seems to ask a lot both from coincidence and from the solar wind, but a definitive test would be the detection of neon, which may yet be possible. (The enhancement of ^{129}Xe also argues against a strictly cosmic noble gas inventory.)
6. P. Signer, in *The Origin and Evolution of Atmospheres and Oceans*, P. J. Brancazio and A. G. W. Cameron, Eds. (Wiley, New York, 1964), chap. 8.
7. E. Mazor, D. Heymann, E. Anders, *Geochim. Cosmochim. Acta* **34**, 781 (1970).
8. J. Wasson, *Nature (London)* **223**, 163 (1969).
9. F. Fanale, *Icarus* **15**, 279 (1971).
10. R. A. Canalas, E. C. Alexander, Jr., O. K. Manuel, *J. Geophys. Res.* **73**, 3331 (1968); F. R. Fanale and W. A. Cannon, *Earth Planet. Sci. Lett.* **11**, 362 (1971).
11. F. P. Fanale, private communication.
12. J. H. Reynolds, *J. Geophys. Res.* **68**, 2939 (1963); R. O. Pepin, in *The Origin and Evolution of Atmospheres and Oceans*, P. J. Brancazio and A. G. W. Cameron, Eds. (Wiley, New York, 1964), chap. 9.
13. We thank A. Tomassian and W. Dencker for optimizing the mass spectrometer and atmospheric filter assembly, respectively. We are indebted to A. V. Diaz, E. M. Ruiz, and R. Williams for their assistance. This work was supported by research contracts NAS 1-10493 and NAS 1-9684 from the National Aeronautics and Space Administration.

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Composition and Structure of the Martian Upper Atmosphere: Analysis of Results from Viking

Abstract. *Densities for carbon dioxide measured by the upper atmospheric mass spectrometers on Viking 1 and Viking 2 are analyzed to yield height profiles for the temperature of the martian atmosphere between 120 and 200 kilometers. Densities for nitrogen and argon are used to derive vertical profiles for the eddy diffusion coefficient over the same height range. The upper atmosphere of Mars is surprisingly cold with average temperatures for both Viking 1 and Viking 2 of less than 200°K, and there is significant vertical structure. Model calculations are presented and shown to be in good agreement with measured concentrations of carbon monoxide, oxygen, and nitric oxide.*

This report addresses a number of topics relevant to the composition and structure of the upper atmosphere of Mars. Densities of CO_2 as measured by the upper atmospheric mass spectrometers on Viking landers VL1 and VL2 (*1–3*) are used to determine profiles for temperature as a function of altitude. Temperatures derived in this manner are then used to analyze height profiles as measured for the concentrations of N_2 and Ar. This procedure gives information on the extent to which the composition of the upper atmosphere of Mars may be influenced by mass mixing, as measured here in terms of the parameter eddy diffusion (*4*). The general validity of the approach may be checked by applications

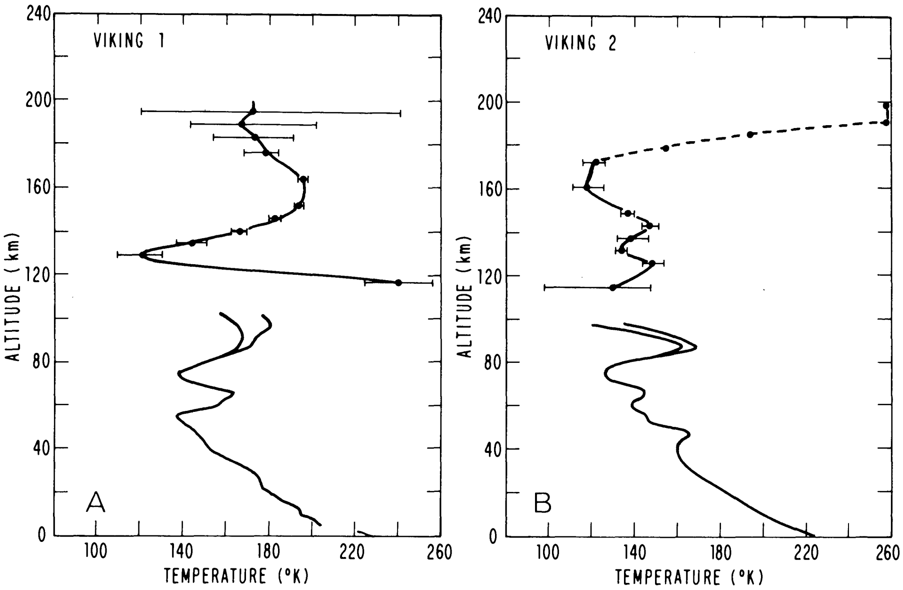

Fig. 1. (A) Temperatures for the martian atmosphere above 120 km obtained from an analysis of ion peaks at mass numbers 44, 22, and 12, as measured by VL1. Uncertainties implied by the spread in values obtained from the individual mass peaks are indicated by the error bars. Temperatures obtained by Seiff and his co-workers (*1, 5*) for the lower atmosphere are shown for comparison. (B) Same as (A) but for VL2. The dashed lines above 170 km indicate altitudes for which there are data only at mass number 44.