

References and Notes

1. S. L. Hess, 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, J. L. Mitchell, *Science* **193**, 788 (1976).
 2. The term "sol" refers to the martian day of 24.660 hours and is used to avoid confusion with the terrestrial day.
 3. The best present estimate of the location of the Viking 1 lander is 22.48°N, 48.00°W. These differ slightly from the preliminary coordinates (1). The season is summer. Sols 1 to 20 correspond to L_s ranging from 98° to 108°, where L_s is the areocentric longitude of the sun with 90° being northern hemisphere summer solstice.
 4. These data were collected by personnel of the China Lake Naval Weapons Center and compiled in computerized form, together with data from other stations in the American Southwest, for general distribution by the Aerospace Corporation, El Segundo, California. China Lake is located at 35.7°N, 117.7°W.
 5. The pressure sensor has an intrinsic reproducibility (as determined by calibration) of at least 0.02 mbar. The data are returned with a digitization increment of about 0.08 mbar. During the period reported here, four samples of pressure were obtained during each of the approximately 14 modules per sol of the other meteorological data. The four samples have only rarely differed from one another by as much as one digital count, which indicates the stability of the instrument and the absence of significant dynamic effects of wind on the pressure at the inlet port.
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We have indications from a comparison of the sensor values during entry and just after touchdown that there may have been a zero-level shift, which would cause uncertainty about the absolute pressure of one or two digital counts. There is no comparable uncertainty about the slope of the calibration curve. The diurnal variation of pressure, and its secular trend also given in this report, depend on the slope of the calibration curve and not on the absolute value.

6. S. Chapman and R. S. Lindzen, *Atmospheric Tides* (Gordon & Breach, New York, 1970).
7. E. Euler and F. Hopper, personal communication.
8. J. M. Wallace and F. R. Hartranft, *Mon. Weather Rev.* **96**, 446 (1969).
9. W. S. Hering and T. R. Borden, *J. Atmos. Sci.* **19**, 81 (1962).
10. R. W. Zurek, *ibid.* **33**, 321 (1976).
11. H. H. Kieffer, S. C. Chase, Jr., E. D. Miner, F. D. Palluconi, G. Münch, G. Neugebauer, T. Z. Martin, *Science* **193**, 776 (1976).
12. G. A. Briggs, *Icarus* **23**, 167 (1974).
13. J. B. Pollack, C. B. Leovy, Y. H. Mintz, W. Van Camp, *Geophys. Res. Lett.*, in press.
14. D. Dzurisin and A. P. Ingersoll, *Icarus* **26**, 437 (1975).
15. We thank S. Albers, who assisted with data reduction, and R. W. Zurek for helpful comments. This research was supported by the National Aeronautics and Space Administration under contracts NAS1 9693, NAS1 11854, and NAS1 9694.

by a 16.5-cm forward extension in the same trench. The material was delivered by sieving through the 2-mm screen in the sampler head. The acquisitions for the x-ray instrument were made between 10:35 and 12:06, and analysis began at 23:00 L.L.T. During the period of sample acquisition and delivery, the winds were blowing from a SE to SSW direction at 4 to 17 m sec⁻¹ (5). Based on tests conducted in a reduced-pressure wind tunnel, it is unlikely that any serious distortion of the sample composition occurred as a result of aeolian winnowing during delivery.

The material delivered is apparently quite fine-grained and very cohesive, allowing very steep and sharp trench walls to be maintained [for images and detailed discussions, see (6)]. The disturbed material in the walls of the trench appears darker than the adjacent undisturbed surface, but colorimetric comparison studies suggest that there is little, if any, difference in actual color (7). Also, what appears to be a weakly cemented, thin surface crust may be seen in some images. The sample delivered to the x-ray fluorescence spectrometer was acquired at a depth of 4 to 6 cm below the martian surface. The possibility that some admixture of shallower material occurred cannot be excluded.

Instrument calibration and operation on Mars. The instrument can be calibrated on Mars to determine instrument gain and to verify overall performance by three independent techniques: (i) by measuring x-ray fluorescent emissions from calibration "plaques" exposed when no sample is present in the analysis cavity; (ii) by determining the mean channel of the backscatter peak from the sample; and (iii) by activating a solenoid which positions an Al and Ca calibration target, or "flag," between the sample and the ⁵⁵Fe source. Plaque calibrations were performed 32 hours prior to landing and again 7 hours after landing. Gain in each proportional counter (PC) had changed by less than 4 percent from that at the time of delivery of the flight unit to the Viking lander (January 1975). In addition, flag calibrations were performed six times on sol 25, which verified that the resolution functions of PC-1 and PC-2 were equal to or even slightly superior to the values prior to the flight.

Initially, all data on Mars were taken over all 128 channels and in the rapid mode, with a dwell time of 7.7 seconds per channel for the scanning single-channel analyzer. This provides a large body of repeated spectral measurements from which instrument precision can be evaluated. As expected, both temperature-dependent and time-dependent (secular drift) gain changes are evident in the

Preliminary Results from the Viking X-ray Fluorescence Experiment: The First Sample from Chryse Planitia, Mars

Abstract. Iron, calcium, aluminum, silicon, and sulfur are major elements in the first surface sample of Mars that has been analyzed by the Viking x-ray fluorescence spectrometer. Titanium is present in minor quantities. This is consistent with the sample being a mixture of fine silicate and oxide mineral grains, with a significant proportion of sulfates, possibly hydrated. Ferric oxide is regarded as the red pigmenting agent on the martian surface, but if it coats silicate grains, the coatings must be very thin (≤ 2 micrometers) or discontinuous. A high abundance of Fe, relatively low abundances of Al, Rb, Sr, and Zr, and a high Ca/K ratio are distinctive features of the spectra. Preliminary determinations indicate the following abundances (as percentages by weight): Fe, 14 ± 2 ; Ti < 1; S, 2 to 5; the Ca/K ratio by weight is greater than 5.

The x-ray fluorescence spectrometer on board the Viking 1 lander (1) is designed to determine the abundances of elements with $Z \geq 12$ and thus is capable of detecting most of the geochemically significant major elements and some minor elements, provided that they occur in sufficient concentrations (2). On sol 0 (the day of landing on Mars), the instrument was operated for calibration purposes, and an upper limit of argon in the martian atmosphere was established (3). Here, we present preliminary data on the composition of the first sample of martian surface fines, delivered on sol 8 and analyzed on sols 8 to 30.

Sample acquisition and description. Imagery obtained on the first few days after landing led to recognition of a safer sampling site than the one that had been preprogrammed. High-resolution stereoscopic imagery and detailed microtopographic profiles showed that this area, in front and to the left of the center of the lander's general field of view, was visibly free of rocks large enough to pose a threat to the surface sampler's safety

and seemed to consist of a fairly uniform, fine-grained material. The surface is smooth and slopes gently to the right and toward the lander. It apparently forms part of a patch of wind-driven material, whose source is unknown.

It is important to note that while the sample collected may be representative of this geologic unit, one cannot regard it as representative of the overall composition at this site or over any larger region. A diversity of materials appears to exist in the landing site area; at least two types of fine-grained material and fragments of several rock types have been recognized (4).

At 6:54 lander local time (L.L.T.) on sol 8 the Viking surface sampler began the series of operations that provided a sample to the x-ray fluorescence spectrometer. After one sample was delivered to the biology instrument and two acquisitions in the same trench were made for organic analysis [combined gas chromatographer and mass spectrometer (GCMS) instrument], a double acquisition for the x-ray instrument was made

data. These do not affect the determinations of most of the major elements, but both factors will require detailed analyses in order to realize the full potential of the technique for the determination of light, minor, and trace elements.

Modification of the compamp table for instrument operation from sol 18 onward provided a fourfold increase in counting times for selected areas of spectra, including the trace element and Mg and Al regions. After appropriate corrections are made, it will be possible to pool all data taken on this first sample over the 22-sol period from sol 8 to 30, so as to obtain composite spectra statistically equivalent to accumulations of 2500, 2100, 420, and 2000 seconds per channel for PC-1 through PC-4, respectively.

Data reduction. For several reasons (limited resolution of the detectors, lack of a multichannel analyzer, and lack of sample preparation), quantitative analysis of spectra obtained with the Viking x-ray fluorescence spectrometer is a complex undertaking. Element concentra-

tions are derived from the data by two techniques. First, a mathematical model encompassing the physics of x-ray production in the sample and instrument response is used to calculate concentrations which give the best fit to the experimental results (8). Second, geological analogs (rock powders, soils, mixtures) are measured in the laboratory in a flight-like instrument. Both techniques have been employed to date and will be used to refine the analyses. Of the hundreds of samples for which spectra were taken during studies prior to the mission, none matches in all respects the results obtained with the first sample from Chryse Planitia. Nowhere is this more apparent than in the P-S-Cl region of the PC-2 spectrum (Fig. 1). As an example, we have shown for comparison the spectrum of our reference standard 8087 (9), which approximates the martian results for certain elements, especially Si and Ca, and to a lesser extent K and Ti. Normalizing to the intensity of the backscattered ^{55}Fe peak and subtracting, we pro-

duce a difference spectrum indicating lesser amounts of K and Ti in Mars surface fines relative to this material, and the presence of significant amounts of S. Other comparisons are the lower proportion of Al and the much higher content of Fe in the Mars sample (Figs. 2 and 3).

Summary of results. The results of our preliminary analysis of the x-ray spectra may be summarized as follows.

1) Three well-defined peaks representing, respectively, the combined effects of the elements Al and Si, K and Ca (PC-2, Fig. 1), and Mg and Al (PC-1, Fig. 2), prove the presence of silicate materials in the martian surface fines and show that these fines are not composed of pure iron oxides or hydroxides, carbonates, or other nonsilicate minerals. The following elements have been unambiguously detected: Al, Si, S, Ca, Ti, and Fe.

2) A strong peak at the Fe $K\alpha$ position gives a value of 14 ± 2 for the percentage of Fe by weight in the sample. This supports the inference that ferric oxide or oxyhydroxide is the pigmenting

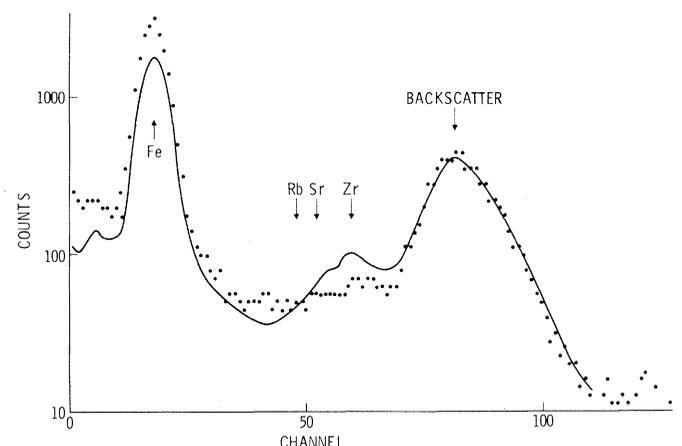
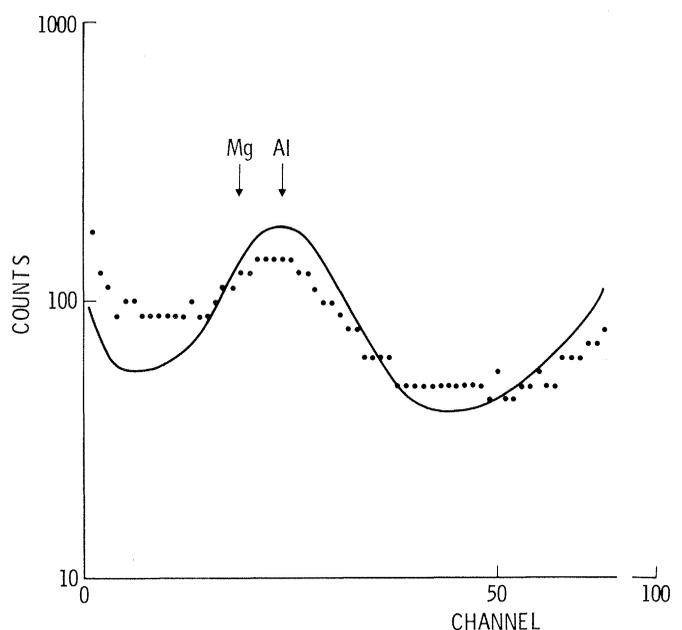
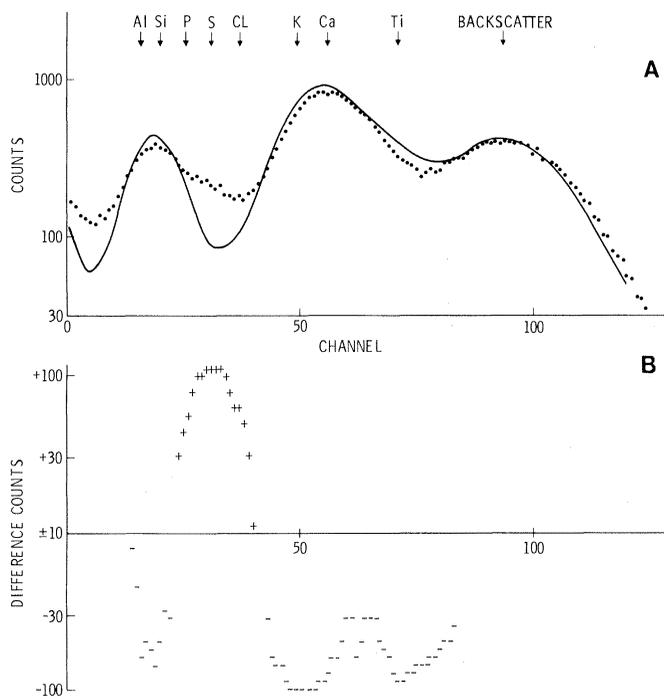


Fig. 1 (top left). (A) Uncorrected pool of PC-2 spectra from sols 13 through 16 (dots) compared with reference material 8087 (solid line). All data have been normalized to a 30-second count period. (B) The subtraction spectrum emphasizes the elements for which the two materials are dissimilar, that is, the higher S and lower Si, K, and Ti in the Mars sample. Fig. 2 (top right). Pooled and normalized PC-1 spectra (dots) overlaid with reference spectrum 8087. The Al content of the Mars sample is distinctly lower than that of the reference material. Analysis for Mg requires meticulous examination of the leading edge of the Mg-Al composite peak. Fig. 3 (bottom right). Pooled and normalized PC-4 spectra (dots) overlaid with reference spectrum 8087. The lack of well-defined Sr, Zr, or Rb peaks in the martian surface fines is unusual compared with most terrestrial igneous rocks. Note the high Fe content of the Mars sample.

agent of the martian surface fines, although much of the Fe may be present in silicate, oxide, or other materials. The inferred ferric oxide may be present as particles mixed with silicate mineral grains or as coatings on silicate particles. In the latter case, however, the coatings must be extremely thin, discontinuous, or present only on some grains; because Fe strongly absorbs the soft x-rays produced by Si and Al, continuous coatings thicker than 1 to 2 μm would not have allowed the peaks corresponding to these elements to have been detected. The degree of hydration of the inferred ferric oxide and its mineralogical identity (for example, hematite, goethite, lepidocrocite, amorphous material, or some other form) cannot be determined from the data of this experiment alone. Data from the Viking organic analysis experiment may contribute to the solution of this problem, inasmuch as calculations based on kinetic data (10) predict that goethite will decompose, with the evolution of copious water vapor, under the conditions of the organic analysis experiment at 500°C, but not at the next lower operating temperature of 350°C. The temperature of dehydration of terrestrial goethite and limonite, as determined in laboratory heating experiments, depends on a variety of instrumental and sample-related factors, however, and full interpretation of the organic analysis experiment will require experimental tests with the GCMS instrument (11).

3) An important characteristic of the martian sample is the high Ca/K ratio implied by the sharp rise of the low-energy flank of the composite peak (Fig. 1). Although the limits are wide at the present stage of data reduction, the ratio may well be 10 or higher, and almost certainly is not less than 5.0. This implies that the sample does not contain a large fraction of granitic or other alkali-rich material, nor is it likely to have developed from such material.

4) Another feature of the spectra is the low count rate for the trace elements Sr, Rb, and Zr (Fig. 3) by comparison with most terrestrial igneous rocks. Rock classes exhibiting this characteristic are ultramafic igneous rocks, meteorites, and certain terrestrial weathering products. The martian sample may represent, at least in part, the product of weathering processes. The deficiency in the trace elements may therefore reflect either the weathering process or the original composition of the parent rocks. The planned analysis of samples containing rock fragments should help answer this question, unless such fragments are themselves weathered or uniformly and

thickly coated with weathering products.

5) The Ti content of the sample is less than 1 percent.

6) The relatively high count rate in the spectral region corresponding to P, S, and Cl is important (Fig. 1). The bulk of the counts corresponds to sulfur, although minor amounts of phosphorus and chlorine may be present. Spectral comparison, obtained by subtracting a spectrum of a terrestrial material from the Mars spectrum, reveals a difference peak clearly located at the S K α energy (Fig. 1). Preliminary analysis of the PC-2 spectrum suggests a total S content in the range of 2 to 5 percent by weight. It is important to know the mode of occurrence and especially the valence state of the S. The highly oxidized appearance of the fine-grained fraction of the martian surface materials in the sampled area suggests that the S may be present largely as sulfates. Independent evidence from the Viking biology investigation (12) also suggests that the surface materials are highly oxidizing (though not necessarily of high oxidizing capacity). Furthermore, the absence of reduced S species in the organic analysis experiment at 500°C (11) suggests a low level or absence of S as sulfide. The soil-water model of Farmer (13), which involves diurnal cycling of H₂O between the lower atmosphere and the surface, where the H₂O occurs as adsorbed intergranular films with a transient existence in the liquid phase, might be expected to lead to the leaching of soluble ions from the rock particles, and their subsequent fixation as water-soluble salts. Sulfates of Ca, Mg, Fe, or the alkali metals (14) are plausible candidates; these may exist as crystalline phases in various degrees of hydration, each of which loses its water of hydration at a characteristic temperature. Further analysis and comparison with the results of the GCMS may eventually permit more definite identification of the sulfate minerals here postulated.

Despite the preceding discussion, it is important to recognize that no data in hand absolutely preclude the existence of sulfide minerals in the martian surface material. There is evidence for a range of degrees of oxidation and weathering, both from color imagery and the magnetic properties experiment (15). Thus, even though marked disequilibrium among the phases is implied, the coexistence of highly oxidized and reduced forms of S cannot now be excluded.

7) The quantitative determination of the elements Mg, Al, and Si, because their low-energy x-rays are especially subject to matrix and absorption effects and because their low fluorescent yields

produce lower count rates, requires more detailed and elaborate data analysis than has yet been possible. Nonetheless, we can state with some confidence that Al is significantly less abundant in the martian sample than in basaltic rocks, both absolutely and in relation to Si. Data analysis leading to the determination of Mg is continuing.

8) The data on the composition of the martian surface fines in the present state of analysis permit a wide range of mineralogical and lithologic models. These range between such extremes as an ultramafic igneous rock (with some admixture of ferric oxide) on the one hand, and the products of extensive chemical weathering, for example, Fe-rich clay minerals, sulfates, iron oxides, carbonates, and possibly free silica, on the other. Distinctions among these models will depend on our further refining the data on the numerical abundances, especially of Mg and the other light elements.

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References and Notes

1. P. Toulmin III, A. K. Baird, B. C. Clark, K. Keil, H. J. Rose, Jr., *Icarus* **20**, 153 (1973).
2. B. C. Clark and A. K. Baird, *Earth Planet. Sci. Lett.* **19**, 359 (1973).
3. B. C. Clark, P. Toulmin III, A. K. Baird, K. Keil, H. J. Rose, Jr., *Science* **193**, 804 (1976).
4. A. Binder, personal communication.
5. Viking Meteorology Team, personal communication.
6. R. W. Shorthill, R. E. Hutton, H. J. Moore, S. Liebes, R. F. Scott, C. R. Spitzer, *Science* **194**, 91 (1976).
7. S. Saunders, personal communication.
8. B. C. Clark, *Adv. X-Ray Anal.* **17**, 238 (1974).
9. Reference sample 8087 is tephra from the 1970 eruption of Hekla Volcano, Iceland, supplied by R. B. Hargraves.
10. J. B. Pollack, D. Pitman, B. N. Khane, C. Sagan, *J. Geophys. Res.* **75**, 7480 (1970); J. B. Pollack, R. N. Wilson, G. G. Goles, *ibid.*, p. 7491.
11. 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).
12. H. P. Klein, *ibid.*, p. 99.
13. C. B. Farmer, *Icarus* **28**, 279 (1976).
14. Sodium is not determined directly by the x-ray fluorescence spectrometer, so the possible occurrence of sodium sulfates cannot be suggested on the basis of our data. Ultimately, a rough upper limit for Na will be established by subtracting the sum of the percentages of the directly determined elements from 100 percent. The K content of the sample is low, so potassium salts are not likely to be major constituents.

15. R. B. Hargraves, D. W. Collinson, C. R. Spitzer, *Science* **194**, 84 (1976).
16. The planning and coordination of the mission operations that have made possible the successful operation of this experiment would have been impossible without the devoted and capable attention of A. Castro, whose engineering skills, moreover, are in large part responsible for the construction and excellent performance of the x-ray instrument. W. Kelliher's contributions to these activities and to the general oversight of the instrument building process were

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Viking Magnetic Properties Investigation: Preliminary Results

Abstract. *Three permanent magnet arrays are aboard the Viking lander. By sol 35, one array, fixed on a photometric reference test chart on top of the lander, has clearly attracted magnetic particles from airborne dust; two other magnet arrays, one strong and one weak, incorporated in the backhoe of the surface sampler, have both extracted considerable magnetic mineral from the surface as a result of nine insertions associated with sample acquisition. The loose martian surface material around the landing site is judged to contain 3 to 7 percent highly magnetic mineral which, pending spectrophotometric study, is thought to be mainly magnetite.*

This investigation (1) is designed to detect magnetic particles, and their composition and abundance if present, in the martian surface material around the Viking landing sites. The experiment is simple, employing a series of permanent magnet arrays that are either inserted directly into the surface material or passively exposed to windblown particles. The magnets are periodically viewed with the lander imaging system, the resulting pictures being the primary data on which conclusions are based. A 4× magnifying mirror will eventually be employed to enhance particle resolution. Plans also call for the eventual use of a magnet cleaning brush to allow for more controlled experiments.

Magnet arrays. The shape and dimensions of the samarium cobalt permanent

magnets (1) are illustrated in Fig. 1. The center and ring magnets are magnetized parallel to their axes, but in opposite directions.

One of these annular arrays is mounted on the central photometric reference test chart (RTC) (2) atop the lander, the other two being incorporated in the backhoe of the surface sampler. These latter (Fig. 2) are fitted so that where the surface of one array is approximately 0.5 mm from the surface, the adjacent array is sunk 3 mm below, which provides two levels of attractive force. The weak array on one side of the backhoe is the strong array on the other, and vice versa. The effective magnetic field and field gradient at the surface of a strong array (including the magnet on the photometric target) are 2500 gauss and

10,000 gauss/cm; for a weak array these values are 700 gauss and 3000 gauss/cm, respectively. The magnetic attractive force provided by the strong and weak magnet arrays is in the approximate ratio 12 : 1.

The images of the magnets which had been taken at the time of writing are listed in Table 1. The results are summarized and interpreted below.

Reference test chart magnet. Survey mode images (lower resolution) of this magnet were received immediately after touchdown and again on sol 3 (Table 1). In both there is evidence of material adhering to the magnet. On sol 15 and again on sol 31, high-resolution images of the RTC magnet revealed an unmistakable bull's-eye pattern, indicating a significant and substantially increased amount of material on the magnet array (Fig. 3).

Three possible sources of these magnetic particles are (i) dust elevated into the atmosphere by the rocket exhausts on landing, (ii) dust generated in connection with sample acquisition and delivery, and (iii) dust particles normally suspended in the atmosphere.

The pink sky on Mars is attributed to the presence of reddish dust particles of the order of 1 μm in diameter (3) and in an amount equivalent to about ten particles per cubic centimeter (4). Such particles, if of hematite or goethite, would be attracted to the RTC magnet. We have calculated that a wind of 5 m/sec blowing such atmosphere over the magnets could in 15 days result in a layer on the magnets 10 μm thick if the extraction efficiency is assumed to be 5 percent. If the layer were to grow thicker than 100 μm a strong wind (>20 m/sec) might tend to remove such particles. We await data that will indicate whether or not there is a correlation between periods of calm or high wind and changes in the amount (or color) of particles adhering to the RTC magnet. Such a correlation would confirm the atmosphere as a source of at least some of the particles.

The particles on the RTC magnet on sol 0 must have been raised into the atmosphere by the retrorocket exhaust when the spacecraft landed. The increase in the amount adhering as seen on sol 15 (in particular) and sol 31, however, can be correlated with sample acquisition and delivery on sols 8, 14, 22, and 31. Because the material sampled is now known to contain a significant fraction of highly magnetic particles (as discussed below), dust raised by the surface sampler is considered to be the principal source of the particles on the RTC magnet.

The particles on this magnet are below

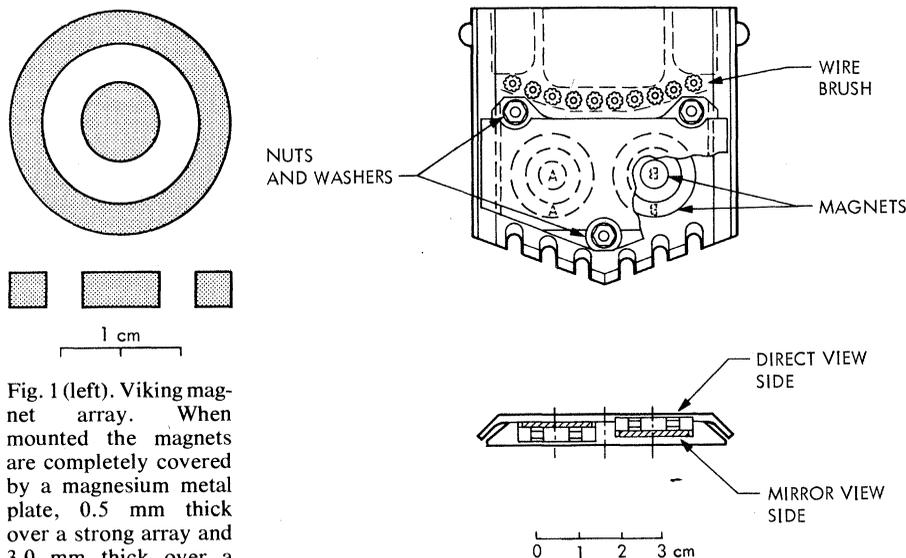


Fig. 1 (left). Viking magnet array. When mounted the magnets are completely covered by a magnesium metal plate, 0.5 mm thick over a strong array and 3.0 mm thick over a weak array.

Fig. 2 (right). Surface sampler backhoe showing the two magnet arrays. Although normally standing perpendicular to the sampler axis, the backhoe is spring-hinged so that it can fold back when the sampler advances into the surface.