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THE CHEMISTRY AND MINERALOGY OF THE MARTIAN SOIL

HARRY ROSE jr.
Products International, 14413 Ash Court, Rockville, MD 20853

It is a great pleasure and honor for me to be here today. To walk the same ground as Galileo at the renowned University of Padova with its long and rich history has given me a most exhilirating feeling. Professor CARAPEZZA's introductory remarks were most kind, and I like he, have only one regret this day, that my two colleagues. FRANK CUTTITTA and IRVING BREGER, could not be here to share my elation. When I accepted an invitation to come here, I had no idea that I would be the first recipient of the Plinio medal. I can only say that I am deeply honored to accept this award with great humility and satisfaction and convey to the Società Geologica Italiana and the Società Italiana di Mineralogia e Petrologia my sincere appreciation for inviting me to attend your meeting.

The chemistry and mineralogy of the Martian soil

In the tradition of Gaius Plinius Secundus, who had an insatiable thirst for scientific knowledge, man continually searches the skies exploring the planets in an attempt to understand the origin and evolution of our solar system and of life itself, and to gain knowledge about the dynamic processes that shape our terrestrial environment. Mars, of all our sister planets, seemed the most likely candidate to have, or to have had in the past, the proper ingredients to support life. While the search for life was the principal objective of the Viking program, a number of other scientific investigations were also included as shown in table 1.

TABLE 1
Viking science objectives

ORBITER
SELECT LANDING SITES
MONITOR SITES AFTER LANDING
DYNAMIC CHARACTERISTICS OF SURFACE AND ATMOSPHERE
GRAVITATIONAL FIELD, ATMOSPHERE, LANDER LOCATION
ENTRY
ATMOSPHERE STRUCTURE AND COMPOSITION
LANDER
IMAGING OF LANDING SITES
SEARCH FOR EVIDENCE OF LIFE
ORGANIC ANALYSIS OF SURFACE
INORGANIC ANALYSIS OF SURFACE
ATMOSPHERIC COMPOSITION ANALYSIS
METEORLOGICAL CHARACTERISTICS
SEISMOLOGICAL CHARACTERISTICS
PHYSICAL PROPERTIES OF SURFACE
MAGNETIC PROPERTIES OF SURFACE

The one of immediate concern to this paper is that of inorganic chemical analysis of the Martian surface. As the last experiment to be added to the Viking program, serious constraints of size and weight were imposed on the instrumentation. The characteristics of the x-ray spectrometer developed to analyze the surface material are shown in table 2. The largest saving in weight and size for the unit was effected by replacing an x-ray generator with radioisotope sources and electronic circuitry capable of stepping through 128 energy channels to replace a multi-channel analyzer. Even with stringent restrictions which limited both resolution and sensitivity, the Viking x-ray spectrometer can detect all elements above sodium ($Z = 11$) in atomic number. Sensitivity is exceptionally good for the geochemically important elements Rb, Sr, Sr and Y (about 50 ppm). The full instrument is shown in figure 1. Due to the possibility of strong winds (as high as 200 km/hr) a thin aluminum windspoiler was attached to the sample funnel to deflect the sample down the delivery tube to the analysis chamber. Figure 2 is a cross section through the analysis chamber showing the placement of detectors and sources. For a more descriptive detail of the construction and operation, the reader is referred to CLARK et al., 1977 (1).

TABLE 2

Characteristics of Viking x-ray unit

WEIGHT, Kg	2.1
SIZE, cm	15 x 7.6 x 24
VOLUME, cm^3	2750
POWER, WATTS	3.5
CONSTRUCTION, metal	Aluminum
X-RAY SOURCES	^{55}Fe, ^{109}Ca
STRENGTH AT LANDING, mCi	240, 55
DETECTORS	SEALED PROP. COUNTERS

SPECIFICATIONS: ALL COMPONENTS TO WITHSTAND STERILIZATION, VIBRATION, THERMAL AND PRESSURE TESTS REQUIRED FOR LIFTOFF, FLIGHT TO AND LANDING ON MARS.

Analytical spectra showing two of the Martian samples along with two U.S.G.S. standards, RGM-1 rhyolite and BCR-1 basalt are shown in figure 3 (Fe-55 source) and figure 4 (Cd-source). The spectra clearly delineate the high concentrations of S and Fe in the Martian surface materials. A summary of the analyses of the various types of samples at both the Chryse and Utopia landing sites is given in table 3. Although separated by about 6,500 km, the chemistry of the samples show little variation between sites, except for sulfur and chlorine. Also noted in the data is a deficit in the summation, the difference between 100 % and the sum of the constituents reported. This deficit must be attributed to (1) analytical error, (2) the presence of elements lighter than Mg ($Z = 12$) and (3) the sum of small amounts of heavier elements present in concentrations below detection.

Every precaution to reduce systematic errors has been taken by both frequent calibration of the instrument and normalization of all results to the back-scattered primary radiation. Random errors should, further, not produce consistently underestimated data. For these reasons analytical

TABLE 3

Analysis summary of Martian surface fines

SAMPLE	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O	TiO_2	SO_3	Cl
Chryse Planitia									
FINES	43	7.5	17.6	6	6.0	0	0.65	7.0	0.7
CRUST	42	6.9	17.4	7	5.0	0	0.60	9.5	0.9
DEEP FINES	44	7.3	17.3	6	6.0	0.04	0.61	6.7	0.8
BULK	45	7.5	18.9	5	6.0	0	0.71	7.2	0.8
Utopia									
FINES	42	7.3	18.9	6	5.8	0.03	0.60	8.4	0.3
UNDER ROCK	43	7.3	17.6	6	5.8	0.02	0.63	8.1	0.6
BULK	43	7.5	16.3	5	5.3	0	0.44	8.3	0.6
DEEP FINES	42	7.3	17.5	6	5.5	0	0.48	7.9	0.3
AV. CHRYSE	44	7.3	17.8	6	5.9	0.01	0.64	7.2	0.8
AV. UTOPIA	43	7.4	17.6	6	5.7	0.01	0.52	8.2	0.45

error is not considered to be the major cause of the deficit. As for the heavier elements not being detected, the x-ray spectrometer is particularly sensitive to major rock forming elements. The only possible exceptions are Mn and Ni, each of which has a detection limit of about 2 % being obscured by the large presence of iron.

It seems, therefore, that the principal constituents of the deficit are most likely elements of low atomic number. The most likely choices are H_2O, CO_2, Na (as Na_2O) and oxides of nitrogen. Other possibilities such as Li_2O, B_2O_3, NH_3 andF can be discounted based on known geochemical principles or the fact that some of these candidates should have been detected by the Gas chromatograph-mass spectrometer (GCMS) were they present.

Both CO_2 and H_2O were detected by the GCMS experiment which can heat the sample only up to 500° C. Up to several percent of H_2O has been detected by the GCMS and therefore may account for a significant fraction of the mass deficit in the analyses. While CO_2 has been detected by GCMS, the possibility of stable carbonates such as calcite would not give up CO_2 at 500° C. It is possible then that CO_2 evolved from these carbonates could amount to 4 to 5 %.

TABLE 4

Chemical composition of computer modeled mixtures composition, wt. percent

OXIDE	MIXTURE 1	MIXTURE 2	MIXTURE 3	MARS
SiO_2	55.1	46.0	43.6	44
Al_2O_3	8.3	8.0	7.2	7.0
Fe_2O_3	19.5	19.0	18.4	17.8
MgO	10.1	9.6	7.0	6
CaO	2.4	2.0	5.6	5.8
K_2O	0	0	0	0.01
TiO_2	0	0	0.9	0.6
SO_3	0	9.4	7.3	7.7

MINERAL		PERCENT OF MIXTURE	
Nontronite	51	52	47
Montmorillonite	19	21	22
Saponite	30	13	13
Kieserite	0	16	10
Calcite	0	0	7
Rutile	0	0	1

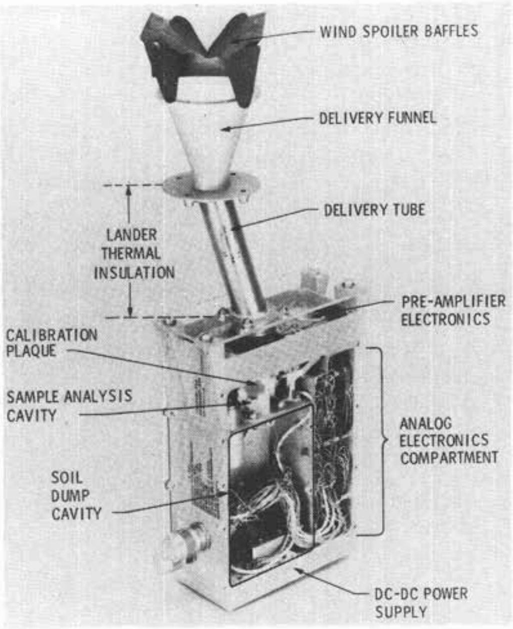

Fig. 1.

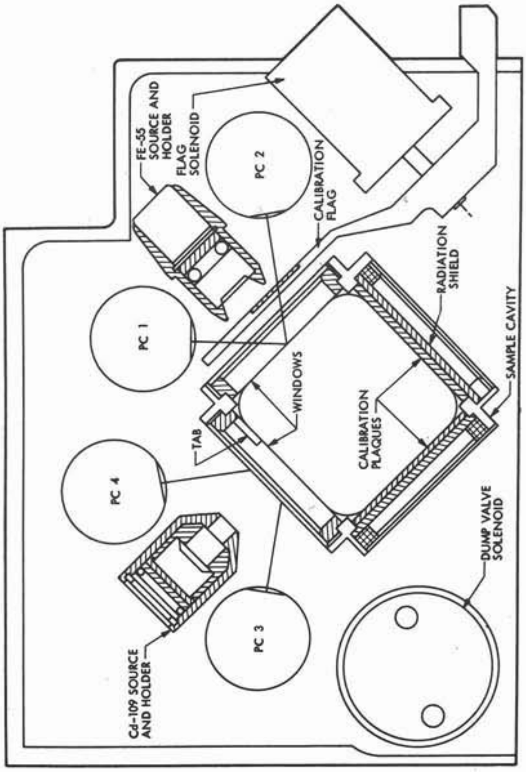

Fig. 2.

The role of Na_2O is more difficult to assess. Based on geochemical coherence, the very low content of other alkali metals (K, Rb) seems to be consistent with a low value for sodium as well. Also, the most stable nitrate compounds are those of the alkalies, and for this reason nitrogen oxide is not believed to be a part of the summation deficit.

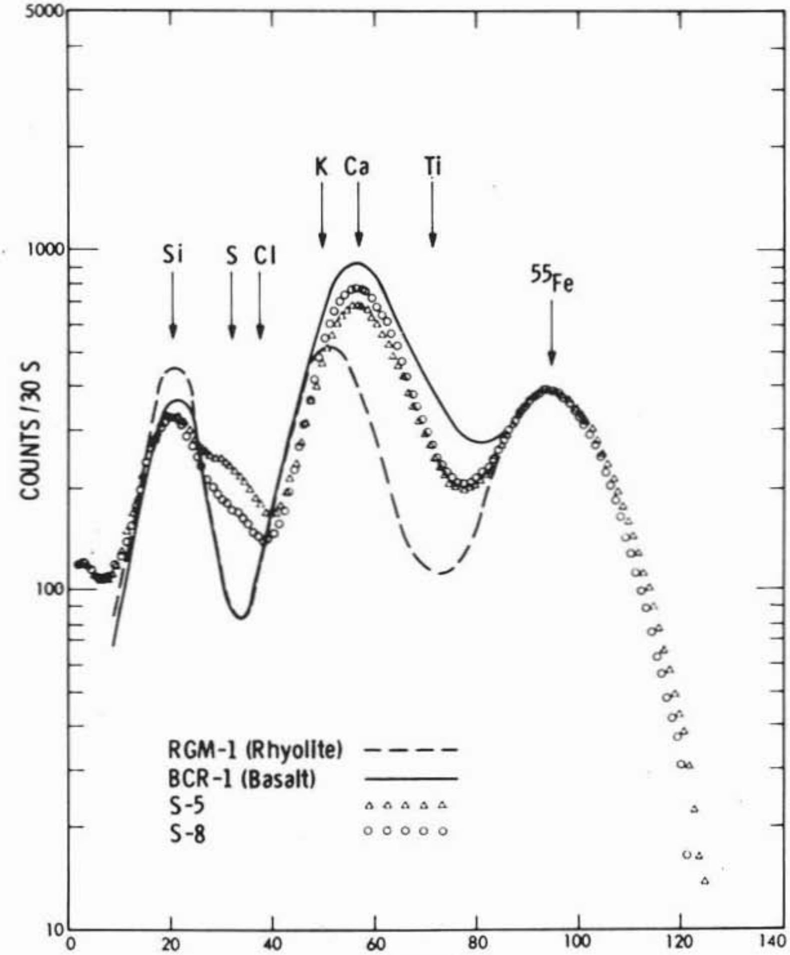

Fig. 3.

Sulfur is presumed to be in the highest oxidation state based on evidence that both Chryse and Utopia have highly oxidyzing surface environments. The pervasive red color at these sites is generally regarded as resulting from the abundance of ferric oxides or hydroxides derived by oxidation of ferrous minerals in the primary rocks. The results of the Viking biology experiments indicate that elemental oxygen is released upon moistening the soil and that the soil is capable of rapidly oxidizing the carbon of organic nutrients with which it comes in contact. The magnetic properties experiment indicate the presence of a few percent of a nighly magnetic mineral whose color is more suggestive of maghemite (γ-Fe_2O_3) than strongly magnetic minerals such as magnetite (Fe_2O_3), pyrrhotite or native iron. In such a highly oxidizing environment the sulfur is more likely to be present as sulfates. As the results show in table 3, SO_3 is much higher in the duricrust and as the sulfate is most probably the cementing medium for the silicate particles.

Given the analytical data and the above discussion of summation deficits and the role and oxidation of sulfur how can we take a step further in trying to determine the mineralogy of the Martian surface material.

The overall composition of the samples is suggestive of mafic rocks, or more likely, their weathering or alteration products. As a consequence of an assumed high oxidation state of the iron, the low alkali and alkaline-earth elements, the relatively low SiO_2 content of the material, and the low value for Al_2O_3 there is ample support to indicate the presence of Al-poor, Fe-rich smectite clays. On this basis a series of computer-modeled mixtures were compared to the approximate average value of the Martian fines (table 4). The mixtures contain the clay minerals montmorillonite, sapronite and nontronite, as well as kiserite, calcite and rutile. The mineral assemblages are, significantly, characteristic of mafic igneous rocks or their weathering or alteration products.

It must be realized that further changes in the mineralogy may occur even after the bulk chemistry has become a closed system and therefore the mineral assemblage as it presently exists may differ from that presented in table 4. If Fe-rich smectite such as nontronite was the major constituent when the chemical composition of the Martian fines was set, it may be quite different today representing the products of destruction of an earlier mineral assemblage.

Interlayer H_2O can be removed from terrestrial nontronite at room temperature and low humidity and it is possible that only « hydroxyl water » may be retained under Martian conditions. The intense ultraviolet radiation and low vapor pressures on

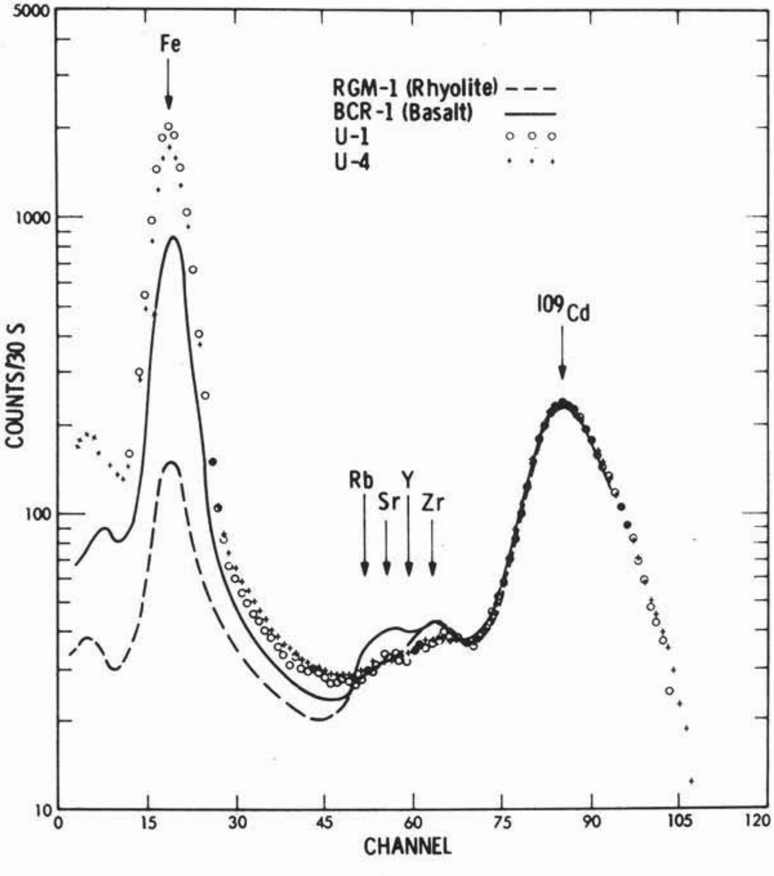

Fig. 4.

Mars may even result in dehydroxylation and crystal-structural rearrangements which may lead to the presence of free iron oxides. Maghemite (γ-Fe_2O_3) is the first product of structural breakdown in the thermal dehydroxylation of nontronite (2) under oxidizing conditions. The material adhering to the Viking magnets on the sampler head is most likely maghemite (3). It can also be proposed that other dissociation products such as free SiO_2 and calcite may also be present.

The question then arises as to a plausible explanation for the formation of Fe-rich clays. Because of lack of evidence for long-lived and widespread Martian seas, little support can be given to a common terrestrial mechanism for their formation by devitrification of volcanic glasses in a deep-sea environment. It is more reasonable to concentrate on possible mechanisms related to the weathering or alteration of mafic rocks and hydrothermal alteration associated with volcanic activity as a possibility.

Fig. 5.

One mechanism that seems consistent with present facts about the Martian environment is the formation of palagonite tuffs by subglacial volcanic activity. Such activity is well documented in Iceland (4) where basaltic eruptions under large glaciers have produced both catastrophic floods and huge masses of smectite-rich altered volcanic glass (palagonite). The analogy to the Martian conditions is striking. There are large areas (see figure 5) of chaotic terrain at the heads of major canyons that have been interpreted as result of subsidence resulting from melting permafrost reacting to local magmatic activity. The large number of subsidence areas indicate that if violent interaction between Fe-rich basaltic magma and subterranean ice occurred it would represent a vast source for the production of palagonite. Devitrification and smectite formation occurs to some extent on cooling of the volcanic glass, but most probably forms later through weathering.

It is unfortunate that neither time or weight restraints permitted development of a more sophisticated analytical instrument for the Viking adventure. The task of interpreting the mineralogical make-up of the Martian surface material from the chemical data would have been made infinitely easier if x-ray diffraction results were available. A combination x-ray fluorescence and diffraction spectrometer would have produced positive interpretations instead of the speculative ones submitted in this presentation.

In summary, the following comments are the most important inferences that can be made regarding the Martian surface material.

1. The material is predominantly fine-grained silicate particles either admixed with or coated by iron oxide particles.
2. The chemistry of the samples is indicative of mafic source rocks rather than more highly differentiated salic materials.
3. The surface fines are identical at the two Viking landing sites and is presumed due to homogenization by aeolian processes which occur on a planetary scale.
4. The most plausible model for the mineralogical contribution of the surface material is a mixture containing primarily iron-rich smectites (or their degradation products) with ferric oxides including maghemite, minor amounts of carbonates such as calcite, and sulfate minerals cementing the fines into a continuous or fragmented duricrust.
5. The duricrust may have formed by a process of leaching, surfaceward migration and evaporative precipitation.
6. Much of the material may have been derived from palagonite-like products through interaction of mafic magmas with subterranean ice.

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