Total Reflection Spectrophotometry and Thermogravimetric Analysis of Simulated Martian Surface Materials

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The ultraviolet, visible, and near infrared reflection spectra of the Martian bright areas have been compared with the corresponding laboratory reflectivities, measured with an integrating sphere, of a variety of minerals containing ferric oxides and silicates, as solids and in pulverized form. Except in the ultraviolet, where the effects of the Martian blue haze are prominent, pulverized limonite, a ferric oxide polyhydrate, matches the shape and amplitude of the Martian Russell-Bond albedo within experimental and observational error. Further observational tests of this identification are outlined. If water-rich limonite is a primary constituent of the Martian bright areas, conditions in the earlier history of Mars were probably much more equable than contemporary conditions, and the origin and evolution of life on primitive Mars becomes easier to understand.

1. INTRODUCTION

The bright areas of the planet Mars, often described as deserts, have remarkable photometric, colorimetric, and polarimetric properties. Their visible reflectivities are low, their colors are ruddy, and their polarization phase curves show a striking negative branch for phase angles $\Phi < 23^{\circ}$. All three observables point to ferric oxides as a primary constituent of the bright areas.

The geochemically most abundant minerals with strong blue-absorbing chromatophores are the iron oxides (e.g., hematite, Fe_2O_3); the ruddy color of Mars has long been used as an argument for iron oxides on that planet (see, e.g., Wildt, 1934). The visual reflectivities and color indices of a wide range of common terrestrial minerals have been compared by Sharonov (1961)

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with the corresponding parameters of the Martian bright areas. Sharonov stresses that the astronomical observations refer to Martian areas several hundreds of kilometers across; accordingly, he averages the laboratory measurements of a large number of samples of a given mineral type before comparing with Mars. But since the present physical conditions and earlier history of the planets Earth and Mars are dissimilar, there is no guarantee that a terrestrial averaging has Martian relevance. While many categories of minerals were found to match the Martian reflectivities, only one matched the bright areas of Mars in color. Of the 12 broad categories of terrestrial minerals surveyed, Sharonov found concordance with the Martian bright areas only for the yellow ochre variety of the mineral limonite. We emphasize that apparently only solid mineral samples were used in Sharanov's studies.

Limonite is the hydrated form of goethite, Fe O(OH), also described by the empirical formula $Fe_2O_3 \cdot H_2O$. A common hydration state of limonite is $2Fe_2O_3 \cdot 3H_2O_3$, but the number of water of crystallization bonds varies from sample to sample; in the present paper we will describe limonite as $Fe_2O_3 \cdot n H_2O$, where n is a number, not necessarily an integer, greater than unity. In addition to the water of hydration there is, characteristically, adsorbed water in any sample of limonite. On the Earth, limonite rarely appears as a pure mineral. It is most often mixed with goethite, hematite, and bauxite. In mixture with hematite and bauxite, it is called laterite; lateritic soils comprise a significant fraction of the Earth's surface area (Sivarajasingham et al., 1962).

A third, and most convincing, piece of evidence for ferric oxides in the Martian bright areas is provided by polarimetry (Dollfus, 1957; 1961). The polarizationphase angle curve of the Martian deserts has a negative branch for $0^{\circ} \leq \Phi \leq 23^{\circ}$; positive polarizations prevail between 23° and 43° , the maximum phase angle for Earth-based observations of Mars. The maxima, minima, and zeros of the curve point strongly to polarization due to scattering by strongly absorbing particles of small dimensions-characteristic diameters are 100μ and smaller. Of the many hundreds of samples investigated by Dollfus (1957) in the laboratory, only finely pulverized limonite matched the polarization curve of the Martian bright areas.

One additional argument in favor of limonite on Mars has been provided by Adamcik (1963), who notes that the equilibrium partial pressure of water vapor above limonite at typical Martian daytime temperatures is just that anticipated earlier, on theoretical grounds (Sagan, 1961), and subsequently verified spectroscopically (Spinrad, Münch, and Kaplan, 1963).

In recent years, a series of infrared observations of Mars has been performed from the ground (Sinton, 1959; Moroz, 1964) and from balloon altitudes (Danielson *et al.*, 1964). Together with older measurements of the ultraviolet reflectivity of Mars, these observations permit a further, critical test of the hypothesis that ferric oxides are the predominant constituent of the Martian bright areas.

In the following discussion, we shall be concerned only with explaining the properties of the bright areas. The dark areas show other features altogether; while they have a reddish cast (Kuiper, 1957), they are not so red as the bright areas (Sharonov, 1961); their visible albedo is substantially smaller, and their polarization curve corresponds to some still unidentified material, more strongly absorbing than pulverized limonite (Dollfus, 1957). Both the reflectivity and the polarization are dependent on the local Martian seasons. A study of the dark areas is most properly undertaken in a biological context (Sagan, 1965a), and we will not pursue it further here.

II. EXPERIMENTAL PROCEDURE

To explain the infrared and ultraviolet photometric results for the Martian bright areas, we undertook a program of diffuse reflection spectrophotometry of selected terrestrial minerals. Eight mineralogically distinct samples of limonite, hematite, and goethite, as listed in Table I, were obtained from Ward's Natural Science Establishment, Rochester, New York.

Mineral fragments were pulverized with an impact mortar and passed through a 40-mesh screen. The powder from a given sample was then homogenized and a fraction removed for a rough determination of particle size distribution. The fraction was suspended in low vapor pressure immersion oil, placed between a glass slide and cover slip, and examined with a Unitron Model MMA monocular metallurgical microscope, fitted with a Bausch and Lomb $10 \times$ objective filar micrometer calibrated in millimeters. In transmitted light, the particle size varied considerably from point to point on the objective slide, due, e.g., to clumping and nonuniform crushing. In an effort to obtain a representative mean particle size, 20 randomly selected particles were measured for each pulverized sample. The particles were selected by moving the

	SAMPLES
BLE I	C OXIDE
TAI	OF FERRI
	Properties

	GA fractional mass loss		0.0% H ₂ O		0.3%		9.8% H ₂ O		8.8% CO ¹		9.0% CO ²		$6.6\% H_{2}O$		0.5%		8.4% CO ₃	
	TGA temperature range T (°C)		30-350° 1		30~1000° <		30-400°		500-850° 1		500-850° 1		200-450°		30-1000° <		$30-400^{\circ}$	
article diameter	Mean (microns)	127	131	10	21	130	180	79	140	74	130	71	290	28	63	140	220	
	Minimum (microns)	3.4	4.2	2.4	2.4	17.0	17.0	2.5	1.7	17.0	100.0	17.0	17.0	1.8	5.1	4.2	6.6	
-	Maximum (microns)	580	370	26	140	580	580	360	680	310	400	290	1500	100	330	390	650	
	State	Powder	TGA residue	Powder	TGA residue	Powder	TGA residue	Powder	TGA residue	Powder	TGA residue	Powder	TGA residue	Powder	TGA residue	Powder	TGA residue	
	Source	Tuscaloosa, Ala.		Ironton, Minn.		Biwabik, Minn.		Rochester, N.Y.		Chilton, N.Y.		Cartersville,	Ga.	Ishpeming,	Mich.	Pelican Pt.,	Utah	
	Sample	Limonite		Hematite		Geothite		Fossiliferous	hematite	Oolitic	hematite	Yellow ochre	limonite	Specular	hematite	Limonite	pseudomorphs	after numite
	No.	1		6		က		4		5		9		7		ø		

MARTIAN SURFACE MATERIALS

45

microscope stage at random intervals and measuring that particle which happened to fall on a preselected location on the cross hair of the filar micrometer. Maximum, minimum, and mean particle diameters, obtained through this procedure, are listed in Table I. The sizes fall within the range of those deduced on polarimetric grounds for Mars.

For each pulverized mineral of Table I, a sample was taken through thermogravimetric analysis (TGA). A Harrop TGA apparatus was employed, coupled to a Seko recording semimicro analytical balance, having a sensitivity of 5×10^{-5} gm. Samples were suspended in air beneath the balance, in a furnace wound with (platinum-20% rhodium) wire. The furnace temperature was increased at a rate of 20 C°/min and the fractional mass loss measured as a function of temperature between 30° and 1000°C. Bound water is characteristically lost at 350-450°C; carbon dioxide evolution from carbonates characteristically at 750-850°C. The TGA residues were then examined microscopically by the same technique used for size determination of the pulverized samples. The results on TGA residue sizes are also displayed in Table I; we note that the TGA residue particle sizes tend to be somewhat larger than their precursor powders, probably due to high-temperature sintering.

The original solid samples were, in many cases, mineralogically complex. Limonite, Variety 1, for example, had faces speckled with small yellow grains; but other faces were smooth and very dark. Thus, observations performed on a solid sample of a given variety of mineral were much more variable from sample to sample (i.e., face to face) than were observations performed on various samples of the same mineral when pulverized.

Bright colors characterized the pulverized samples. Limonites ranged in color from dull gray-brown, through bright mustard, to orange ochre, the color of limonite pseudomorph after pyrite, Variety 8, which seemed, of all the samples, to bear the closest resemblance to the Martian bright areas. Goethite samples were of yellow

ochre hue, while the hematites ranged from claret to brownish purple. Samples which had been heated to high temperatures during TGA took on colors characteristic of the unheated hematite samples, but usually darker. This circumstance may be attributed to the loss of water of crystallization from the limonite and goethite samples during heating (and possibly to a change in oxidation state); with the water removed, they have been converted to hematite. The colors of the pulverized samples were always more vivid than the colors of the unpulverized minerals, either in direct comparison, or when streaked on paper. No solid sample of yellow ochre limonite, Variety 6, was available.

Ultraviolet, visible, and infrared spectra were obtained for monochromatic light specularly reflected, diffusely reflected at a fixed angle, or reflected into all 4π sterradians from the sample, using a specially constructed integrating sphere on a modified Beckman DK-2 ratio-recording spectrophotometer. Sunlight reflected from the Martian surface is generally observed at a range of diffuse reflection angles. The reflectivity into 4π sterradians is of interest if we wish to compare laboratory spectra with Russell-Bond albedos. For Mars, the spherically integrated albedo in the visible is approximately equal to a typical diffuse reflectivity observed at the same wavelengths; the infrared phase integral is so however, that the wavelengthlarge, integrated diffuse reflectivity is about 25% less than the bolometric Russell-Bond albedo (de Vaucouleurs, 1964). To minimize any serious dependence of our results on the detailed scattering phase functions, it is the spherically integrated reflectivity which we have principally measured in the laboratory. Above 6000 Å, these measurements should, therefore, be compared only with the corresponding Russell-Bond albedo of Mars. [Note that the astronomical and laboratory measurements are still not quite strictly comparable; the integrating sphere sums all angles of reflection, but not all angles of incidence. However, the effect of this difference will be minor; the polarization of sunlight reflected from Mars (and

from the Moon) is essentially independent of surface inclination (Dollfus, 1957).]

The spectrometer has a useful wavelength range between 2000 Å and 2.7 μ . The wavelengths are calibrated to an accuracy of approximately 40 Å in the ultraviolet, 15 Å in the visible, and 0.012 μ in the near infrared. Periodic verification of the wavelength calibration was made with fixed bandpass filters. The apparatus, including the integrating sphere, was continuously purged with dry nitrogen to minimize residual atmospheric absorption in the light path and to protect the optical components.

The optical path of the DK-2 spectrophotometer is illustrated in Fig. 1. An image of oxide plate with a 5-degree optical wedge inserted to measure total reflectance (specular and diffuse reflected components). The sample path contains the sample to be measured, and, as in the case of the reference sample, a 5-degree wedge to measure total reflectance. Alternation of the light beam provides ratio recording of the sample reflectance and the reference magnesium oxide plate. The detector, either a lead sulfide cell or photomultiplier (K), measures the integrated reflected light within the magnesium-oxide-coated integrating sphere (L). Ancillary to the integrating sphere is a first reflection shield at the detector opening. The first reflection shield, a tube



Fig. 1. Schematic diagram of modified Beckman DK-2 spectrophotometer, with integrating sphere. See text for details.

the light source, either a tungsten or hydrogen lamp (A), is focussed on a condensing mirror (B) and then on a 45-degree mirror (C). The light then passes through the entrance slits at (D) into a Littrow monochromator. Light falling on the collimating mirror (E) is rendered parallel and reflected toward the prism (F). The back surface of the prism is aluminized so that light refracted at the first surface is reflected back through the prism, and undergoes further dispersion. The collimating mirror (E) then focuses the spectrum in the plane of the slits. Light of the wavelength for which the prism is driven is transmitted out of the monochromator through the exit slit to the oscillating mirror (G). The oscillating mirror passes the light beam alternately to mirrors (H), first along the reference path (HI), then along the sample path (HJ). The reference path contains a freshly prepared magnesium

approximately 2 cm in length, prevents erroneous results when highly specular components are present.

Absolute spectral reflectance data, as presented in this study, were obtained by correcting the measured sample reflectivities for the reflectivity of the magnesium oxide comparison plate. The absolute reflectivity of freshly prepared magnesium oxide surfaces has been measured by Edwards *et al.* (1961). The magnesium oxide surfaces for the reference sample and integrating sphere are prepared by burning magnesium wire and depositing thicknesses of at least 6 mm on the surfaces.

Solid mineral samples were placed directly in the sample port; however, for powdered samples, a quartz holder was used. In these cases, approximately 3 mm thickness of powdered magnesium oxide and sample were used in the reference and sample beams, respectively, thereby com-



FIG. 2. Total reflectance of solid, powdered, and TGA residue forms of limonite, Variety 1, Tuscaloosa, Alabama.



FIG. 3. Total reflectance of solid, powdered, and TGA residue forms of hematite, Variety 2, Ironton, Minnesota.

pensating, in this ratio-recording instrument, for the effect of the quartz holders common to both beams.

III. DISCUSSION OF RESULTS

The infrared spectra of solid, pulverized, and powdered TGA residue samples of the minerals of Table I are displayed in Figs. 2-9. The corresponding TGA plots are given in Figs. 10-17. For the yellow ochre limonite, Variety 6, no solid samples were available. For all spectra, we note that the total reflectivities of pulverized samples and of powdered TGA residues exceeded at all wavelengths the corresponding reflectivities of the solids. This result is to be ex-



Fig. 4. Total reflectance of solid, powdered, and TGA residue forms of goethite, Variety 3, Biwabik, Minnesota.



Fig. 5. Total reflectance of solid, powdered, and TGA residue forms of fossiliferous hematite, Variety 4, Rochester, New York.

pected; for a given mass of absorber, the more interfaces encountered by a randomwalking photon, the greater the likelihood of back-scattering. The particles of Table I, like the particles in the Martian bright areas (Dollfus, 1957), have radii a $>> \lambda/2\pi$, where λ is the wavelength of observation. Accordingly, the particle phase functions must have a somewhat pronounced forward-scattering lobe. Thus, a backscattered photon has a significant probability of escape from the particle array.

Many of the spectra exhibited a reflectivity decline longward of 2.5 or 2.6 μ . Since



FIG. 6. Total reflectance of solid, powdered, and TGA residue forms of oolitic hematite, Variety 5, Chilton, New York.



FIG. 7. Total reflectance of powdered and TGA residue forms of yellow ochre limonite, Variety 6, Cartersville, Georgia.

Figs. 2-9 terminate at 2.6 μ , these declines are not in all cases evident in the figures; they can be attributed to absorption by water, either present as water of crystallization, or adsorbed in the sample. Thermogravimetric analysis of limonite and goethite (Figs. 10, 12, 15, and 17) clearly shows the presence of both forms of water in the samples. For example, in Fig. 10, the slow mass decline at $30^{\circ}C \leq T \leq 250^{\circ}C$ is a consequence of the loss of adsorbed water. The abrupt mass decline at $T \simeq 300^{\circ}C$ is characteristic of the loss of water of hydration. At higher temperatures, smaller quan-



FIG. 8. Total reflectance of solid, powdered, and TGA residue forms of specular hematite, Variety 7, Ishpeming, Michigan.



FIG. 9. Total reflectance of solid, powdered, and TGA residue forms of limonite pseudomorphs after pyrite, Variety 8, Pelican Point, Utah.

tities of both adsorbed water and water of crystallization are lost, and the mass of the sample asymptotically approaches a constant value. In Figs. 13 and 14, the abrupt decline in mass at $T \simeq 800^{\circ}$ C is due to the loss of CO₂; oolitic and fossiliferous hematite are both rich in carbonates. No dis-

tinctive carbonate absorption features appear in the spectra of these hematites (Figs. 5 and 6); they are expected at longer infrared wavelengths. The identification of the 3μ feature of limonite and goethite with water absorption is borne out by the general absence of such features in the spectra



FIG. 10. Thermogravimetric analysis of pulverized limonite, Variety 1, Tuscaloosa, Alabama, performed in air, heating rate 20 C°/min .



FIG. 11. Thermogravimetric analysis of pulverized hematite, Variety 2, Ironton. Minnesota, performed in air, heating rate $20 \text{ C}^{\circ}/\text{min}$.

of dehydrated TGA residues of the same samples. Water vapor has a well-known absorption band at 2.7 μ . A better appreciation of the depth of the 3μ limonite absorption feature may be gained from the figures of the accompanying paper by Hovis (1965).

A typical range of the monochromatic total reflectivity (integrated over all solid angles) of pulverized limonite and goethite is displayed by the shaded area of Fig. 18. The lower boundary of this area corresponds to the reflectivity of pulverized limonite, Variety 1. It exhibits the characteristic 0.85μ absorption feature of all samples—both powders and TGA residues -in Figs. 2-9, a feature which must be ascribed to absorption in the Fe_2O_3 moiety of these minerals. The upper boundary of the shaded area has been smoothed to remove the 0.85 μ and other features, for reasons of clarity. Beyond 2.7 μ , the curve is due to Hovis (1965). Spectra of solid samples of limonite, goethite, or hematite tend to fall below the shaded area. A combination of solid and powdered samples will have lower albedos than the powdered samples alone. Individual solids will have a wide range of albedos, depending on their surface granularities. For these reasons, even if an unequivocal demonstration were forthcoming that limonite is the principal



Fig. 12. Thermogravimetric analysis of pulverized goethite, Variety 3, Biwabik, Minnesota, performed in air, heating rate 20 C°/min.



FIG. 13. Thermogravimetric analysis of pulverized fossiliferous hematite, Variety 4, Rochester, New York, performed in air, heating rate $20 \text{ C}^{\circ}/\text{min}$.

constituent of the Martian bright areas, it would be difficult to determine the grain size of the dust from albedo observations alone.

Laboratory infrared spectra of limonite



Fig. 14. Thermogravimetric analysis of pulverized oolitic hematite, Variety 5, Chilton, New York, performed in air, heating rate 20 C°/min.

obtained by Moroz (1964) do not fall within the shaded area of Fig. 18, even when corrected for the probable infrared phase function of Mars, probably because Moroz' samples were not pulverized. His



Fig. 15. Thermogravimetric analysis of pulverized yellow ochre limonite, Variety 6, Cartersville, Georgia, performed in air, heating rate 20 C°/min .



FIG. 16. Thermogravimetric analysis of pulverized specular hematite, Variety 7, Ishpeming, Michigan, performed in air, heating rate 20 C°/min.

spectra agree well with those of solid samples in Figs. 2-9. A single spectrum between 0.7 μ and 2.3 μ of a mixture of pulverized goethite and hematite (at a fixed phase angle) by Draper, Adamcik, and Gibson (1964) agrees well with our data for pulverized samples.

The mineral reflection spectra are compared in Fig. 18 with the observed monochromatic spherical albedos of Mars within the best current knowledge. In the ultraviolet, visible, and near infrared, the Russell-Bond albedos, $A_{\lambda} = p_{\lambda}q_{\lambda}$, are taken from de Vaucouleurs' (1964) compilation; here p_{λ} is the geometric albedo ($\Phi = 0^{\circ}$), and q_{λ} is the phase integral. For $0.8 \leq \lambda \leq$ 3.0μ , the dashed curve shows an approxi-

mate continuation from an estimate by Woolf (1965), based in part on Stratoscope II infrared spectra, and compatible with earlier observations by Kuiper (1952; see also Harris, 1961). We have converted Woolf's estimate of p_{λ} to A_{λ} by setting the infrared phase integral at $\lambda > 1 \mu$, $q_{ir} \simeq$ 1.4 (de Vaucouleurs, 1964). The curve for wavelengths $\lambda > 3 \mu$ is from a rough estimate by Sinton (1965; see also Sinton, 1959), similarly corrected by $q_{ir} = 1.4$. We should note that most of the observations leading to the solid and dashed line of Fig. 18 were performed on the entire planetary disk. In the present paper, we are concerned exclusively with the Martian bright areas; unfortunately, the available



FIG. 17. Thermogravimetric analysis of pulverized limonite pseudomorphs after pyrite, Variety 8, Pelican Point, Utah, performed in air, heating rate 20 C°/min.



FIG. 18. Comparison of measured and estimated Russell-Bond monochromatic albedos of Mars with laboratory total reflectances of pulverized ferric oxides. See text for details.

data apply to some unspecified linear combination of bright and dark area albedos. If we assume that the dark areas have lower reflectivities in the infrared as well as in the visible (cf. Sinton, 1959), it follows that the infrared reflectivities of an unalloyed Martian bright area will lie somewhat above the heavy curve of Fig. 18.

Also plotted in Fig. 18 are four reflectivities measured by Moroz (1964), and corrected to spherical albedos using $q_{ir} = 1.4$. These points are in clear disagreement with

the dashed line. We believe that calibration errors have crept into Moroz' discussion; his values of p_{λ} in the 1-2 μ region do not join smoothly with the observations at slightly shorter wavelengths (cf. de Vaucouleurs, 1964), corresponding to the thick solid line of Fig. 18. To derive p_{λ} in the 3-4 μ region, Moroz assumes p_{λ} independent of λ , as his laboratory spectra of solid limonite samples suggest. This assumption is equivalent to the statement that a typical mean temperature of the observed disk of Mars is $\overline{T} = 290^{\circ}$ K, a serious overestimate. With more reasonable temperatures, Sinton (1959: 1965) derives a reflectivity increasing sharply from 3 to 4 μ ; and Hovis (1965) finds the same behavior for a sample of pulverized limonite.

We see from Fig. 18 that between 5500 Å and 2.2 μ the albedos of pulverized ferric oxides in the 10–100 μ size range and the albedo of Mars are in good general agreement. For $\lambda > 2.2 \mu$, the shapes of the Martian and limonite albedos are closely similar, but there is only marginal agreement on the magnitude of the albedo. But we are here comparing a single laboratory measurement (Hovis, 1965) with one approximate estimate of the Martian albedo; more laboratory and observatory measurements are clearly needed.

At $\lambda < 5500$ Å, the albedos of ferric oxides systematically fall above the albedos of Mars. This is an indication of the existence of the Martian blue haze. Let us assume that limonite is the principal constituent of the bright areas. The obscuration of Martian surface detail in the blueviolet is then not attributable to a decline in contrast between bright and dark areasa purely surface effect—but must, instead, be due to extinction by some component of the Martian blue haze (cf. Kellogg and Sagan, 1961; Sagan and Kellogg, 1963; Sagan, Hanst, and Young, 1965). A marginal rocket observation by Boggess and Dunkelman (1959) suggested a geometrical albedo at 2700 Å, $p_{\lambda} \simeq 0.24$. The phase integral of Mars at 3200 Å is q_{λ} $\simeq 0.96$ (de Vaucouleurs, 1964), and is unlikely to be much smaller at 2700 Å. A spherical albedo $A_{\lambda} \simeq 0.23$ at 2700 Å is

inconsistent with our ultraviolet reflection spectra of pulverized limonite and goethite (Figs. 2 and 4). Solid samples have even lower reflectivities. No reasonable source of Ravleigh or fluorescent scattering has been suggested which provides a high albedo. Despite a recent confirmation of the Jovian ultraviolet albedo obtained on the same rocket flight (Stecher, 1964), the original experimenters give very low weight to the high Martian ultraviolet albedo (Boggess, 1965), and we conclude that no discrepancy between the ultraviolet albedo of Mars and the limonite identification is apparent at the present time. Further ground-based and rocket-borne observations of the Martian ultraviolet albedo-particularly during moments of blue clearing-would be of great value.

The steep slope of the Martian albedo in the visible and near infrared (the thick solid line of Fig. 18) is a significant composition index. It is characteristic of ferric oxides and of very few other materials. In Figs. 19 and 20 are displayed the total reflectances of solid samples of the common silicates olivine [(Mg, Fe)₂SiO₄] and serpentine $[3MgO \cdot 2SiO_2 \cdot 2H_2O]$. Pulverized samples have the same form, but with amplified reflectivities. The two curves of Fig. 20 correspond to two different faces of the same serpentine sample, and illustrate the difficulties in spectrum reproducibility of heterogeneous or conglomerate samples. We see that silicates do not exhibit the steep albedo slope of Mars-in accord, of course, with the common observation that silicates are not commonly colored red.

In Fig. 21, a serpentine sample sufficiently small to be partially transparent was prepared; total reflectance and transmittance could then be measured, so the total absorptance could be computed. We see that the absorption coefficient tends to be low in the near infrared, and higher at longer and at shorter wavelengths, corresponding, respectively, to vibrational and electronic transitions. Indeed, the absence of absorption features in the red and near infrared is a general property of most minerals, and leads us to predict a near infrared reflectivity maximum for most



FIG. 19. Total reflectance of olivine.



FIG. 20. Total reflectance of two faces of the same sample of a serpentine conglomerate.

minerals, as is indeed observed. It is the steepness of the slope, rather than the wavelength of the albedo maximum, which is diagnostically useful.

A silicate which does display a steep albedo slope is felsitic rhyolite, generally a conglomerate of free silica and alkali feldspar of volcanic origin. Kuiper (1952) first drew attention to the similarity in infrared reflectivity of felsitic rhyolite and Mars. The measured spherical albedo of a solid sample is exhibited in Fig. 22. The increased reflectivity of pulverized samples will place this material within the shaded area of Fig. 18, confirming Kuiper's (1952) conclusions. Yet the similarities between the albedo of felsitic rhyolite and, for example, yellow ochre limonite, Variety 6 (Fig. 7),



FIG. 21. Measured total reflectance and transmittance and deduced absorptance of a serpentine sample.



FIG. 22. Total reflectance of felsitic rhyolite. The steep slope towards the infrared is due to ferric oxide impurities.

e.g., the 0.85–0.90 μ feature, and the decline at $\lambda > 2.6 \mu$, are not accidental. Ferric oxides are often present as a dusty inclusion in the feldspar component of felsitic rhyolite, and are responsible for the red color of the mineral (see, e.g., Chapman, 1960). It is difficult to avoid the conclusion that ferric oxides are prominent on Mars.

But even if ferric oxides are prominent, need they be a major constituent of the Martian surface? Arguing from terrestrial analogy, Van Tassel and Salisbury (1964) have argued that silicates must be the predominant constituent, with ferric oxides present as an impurity. The spectra of felsitic rhyolite are not inconsistent with this conclusion. However, the polarimetric evidence (Dollfus, 1957; 1961) argues persuasively for the predominance of ferric oxides. While large quantities of silicates transparent at 2000 Å $\leq \lambda \leq 2.7 \,\mu$ make little contribution to the total reflectivity of Mars, the same is not true for polarization, which occurs, through Fresnel's laws. at silicate as well as at limonite interfaces. The polarization phase curve of silicates does not resemble that of Mars (Dollfus, 1957; 1961). In particular, large amounts of rhyolite can be excluded on polarimetric grounds (Dollfus, 1964). While a Martian surface of limonite-coated siliceous rocks cannot be excluded, it does not provide a very striking economy of hypothesis. Explanations have been proposed for the source of a surface layer of ferric oxides on Mars (Sagan, 1965a). We are forced to conclude that the Martian bright areas, at least down to the depth observed at infrared frequencies, are largely ferric oxide.

Future astronomical and laboratory spectrophotometry could put this identification on a firmer basis. Almost all ferric oxide samples show a reflection minimum in the $0.85-0.90 \mu$ region; there is no published photometric investigation of the Martian bright areas in the same wavelength interval. Some of the pulverized samples showed a pronounced reflection minimum near 1.9μ ; Mars has yet to be investigated photometrically at 1.9μ . Moroz (1964) found a relative minimum in the light reflected from the integrated disk of Mars

near 1.4μ . Such a feature does exist in limonite pseudomorph after pyrite (Fig. 9), but Moroz' observations need confirmation.

IV. Conclusions

Within the range of observational uncertainty, laboratory diffuse reflection spectrophotometry does tend to support the identification of powdered ferric oxides as a principal constituent of the Martian bright areas. Pulverized limonite pseudomorph after pyrite shows the 1.4μ Martian feature tentatively identified by Moroz, and also has a hue and brightness: closely resembling that of the visual image of Mars at the telescope. Mixed with other varieties of goethite, limonite, and hematite, a close fit to the well-observed Martian albedo can be generated.

It is highly unlikely that the Martian bright areas are covered by a pure mineral. If limonite is present, we expect goethite and hematite in varying proportions. On Earth, limonite appears commonly mixed with hematite and bauxite in lateritic soils. Lateritic soils on Earth are produced in high-humidity tropical environments and generally require free oxygen for their oxidation (Sivarajasingham et al., 1962); the high oxidation state and water content of limonite point to similar conditions for its formation. The present environment of Mars is characterized by low temperatures. low water contents, and low oxygen partial pressures. We may provisionally conclude that the presence of limonite on Mars points to an earlier epoch in which the environmental conditions more nearly resembled the present environment of Earth. This conclusion is in accord with the views of Wildt (1934), who proposed that most of the oxygen complement of an earlier Martian atmosphere is now combined in the Martian crust. The source of the extensive quantities of reduced iron required remains to be discussed; the iron may be of meteoritic origin and related to the proximity of Mars to the asteroid belt (Sagan, 1965a). The possibility of warmer and more humid times in early Martian history increases the probability of the origin of life on primitive Mars (cf. Kellogg and Sagan, 1961, p. 33; Sagan, 1965b).

The possible presence of limonite on Mars is also of relevance for problems of contemporary Martian biology. For every Fe_2O_3 moiety in limonite, there is more than one molecule of water. The Martian surface may be composed of as much as 5-10% water by mass (cf. Table I), water bound by weak crystallization bonds. Is it not possible that Martian organisms are capable of tapping this vast supply of water? Perhaps Mars seems no more arid to the indigenous organisms than do, to the organisms common in our experience, the terrestrial oceans. The possible role of limonite in hypothetical Martian ecologies is discussed elsewhere (Sagan, 1965a).

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