No. 64 THE COMPOSITION OF THE SURFACE LAYER OF MARS*

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ABSTRACT

A comparison of the infrared spectra of the bright areas of Mars with that of terrestrial rock samples has resulted in some conclusions regarding the mineralogy and detrital cover of Mars. The bright deserts appear to consist of rock outcrops (e.g., in the basic crater structures as found by Mariner IV), and probably rock fragments of all sizes, coated for the most part with a hard surface stain of limonite. Limonite dust gives the polarization results of Dollfus (1955). Observations of the Martian dark areas and of terrestrial volcanic samples eliminate the hypotheses that the dark areas consist of either windswept basaltic lava fields or annual deposits of wind-blown volcanic ash. Color photographs of two areas in the southern Arizona (Sonoran) desert are appended with a brief discussion of the occurrence of limonite stains there.

1. Introduction

R ecently various authors have made infrared spectroscopic comparisons between Mars and terrestrial rocks, using observations of the full disk of Mars or only the bright desert areas. They conclude that some form of limonite ($Fe_2O_3 \cdot nH_2O$) occurs in the bright areas (Sharonov 1961; Draper *et al.* 1964; Binder and Cruikshank 1964 [hereafter referred to as Paper I]; Moroz 1964; Van Tassel and Salisbury 1964; and Sagan *et al.* 1965). Dollfus (1961) identified powdered limonite as the constituent of the deserts on the basis of polarization measurements of Mars and laboratory samples. This paper reports on a continuation of a study of the mineralogic surface composition of Mars from infrared reflection spectra of both the bright desert areas and the dark regions.

The spectral region studied $(0.90-2.20 \,\mu)$ is particularly important because it lies between the

region where the contribution of the Martian atmosphere is significant (ultraviolet to about $0.70 \,\mu$) and the region where the planet's thermal emission becomes important (longward of $3 \,\mu$).

2. Observations of Mars

The observations were made with the Kitt Peak National Observatory 36-in. reflector on March 29 and 30, 1965. The infrared spectrometer described by Kuiper *et al.* (1962) was used with a 0.25-mm PbS detector at dry ice temperature and with a 30° Littrow quartz prism. The spectrum (~0.70 to 2.60μ) was scanned in six minutes and the intensity profile traced on a Brown strip chart recorder.

Small portions of the disk of Mars were selected and observed in order to isolate certain desert regions and dark maria. A suitable signal-to-noise ratio was obtained with a diaphragm, in the usual position of the entrance slit, having a diameter about one-fourth that of the planet at the Cassegrain focus. The scale of the 36-in. telescope is 16.60 seconds of arc per millimeter, and the diameter of Mars at closest approach in 1965 was 14 seconds of arc. The diameter of the circular diaphragm used was 0.20 mm.

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This circular diaphragm was one of a series having diameters ranging from 0.08 to 0.60 mm. These were arranged in a linear array on a brass plate that had been ground and polished flat to about one-quarter wave and aluminized. These tiny diaphragms were painstakingly made by hand under a stereomicroscope by Dr. Alvar P. Wilska, whose generous assistance is gratefully acknowledged.

Figure 1 shows the aspect of the planet at the time of the observations with the area of the diaphragm superimposed. Because of image wandering due to imperfect seeing, the actual area observed was somewhat larger than indicated.

Each area was observed when it was on or near the central meridian. Six to eleven individual scans were obtained for each area and the weighted averages were used in the reductions. The guiding, which was done with great care, was facilitated by the high optical quality of the diaphragm plate and the high optical and mechanical qualities of the Kitt Peak telescope.

Each scan produced a spectrum similar to Figure 1 in Paper I. Resolution $(\lambda/\Delta\lambda)$ was about 60 at 1.50 μ , and the spectra show the telluric CO₂ bands at 2.01 and 2.06 μ .

3. Laboratory Observations

Frequent cloudy weather made it impractical to observe rock samples with solar illumination during the summer months. Rock samples were measured in the laboratory using two photographic flood lamps of 3400° K brightness temperature. Since this technique yielded spectra without the usual telluric water vapor and carbon dioxide absorptions, a template was prepared to locate the wavelengths at which amplitude measurements could be made (see next section). On a clear day calibration observations of a standard object were made with both solar illumination and the lamps so that the effects of telluric absorptions in the Mars data could be accounted for and the color characteristics of the lamp could be compared with those of the sun. The same spectrometer, diaphragm, prism, and detector were used for the laboratory work and the Mars observations. In Paper I our comparisons were made using a block of MgO for a reflecting surface, and we suggested that MgO may not be truly "white" in the infrared; such is indeed the case. The time-color variations of MgO smoke deposits have been investigated by Edwards et al. (1961). Since MgO chemisorbs CO₂ and H₂O from the atmosphere, new compounds form that have reflection curves different from fresh MgO. However, the conclusions and relative colors reported in Paper I still stand. We are grateful to Drs. A. L. Draper and J. A. Adamcik for a discussion of this problem.

4. Reduction of Data

Each of the Mars spectra obtained was divided into five regions by the telluric H₂O absorptions at 0.82μ , 1.13μ , 1.39μ , and 1.87μ , and the heights of the five maxima at 0.90μ , 1.05μ , 1.25μ , 1.55μ , and 2.10μ were measured. In the case of the laboratory spectra, the amplitudes of the points found by use of the template were measured. The standard quantity to which each of the measured points was compared is defined by

$$S = \frac{I_{1.05} + I_{1.25} + I_{1.55} + I_{2.10}}{4}.$$

The point at 0.90μ is omitted here because small variations in the water vapor content of the atmosphere make its amplitude variable. The ratios of each of the five measured points to S were taken and, for a given position on Mars, were averaged and plotted on graphs (Figs. 2, 3, and 4).

Although the observations show consistent relative color differences between the maria and the deserts (see Fig. 2), and although the laboratory observations of selected rock samples show definite characteristic colors for the rock families (Figs. 3 and 4), it has not been possible to cross-calibrate these two sets of data satisfactorily. At Kitt Peak, α Bootis was observed as a reference star. Attempts to use existing infrared magnitudes for the sun and α Bootis as a means of finding the color of the Martian deserts and maria with respect to the sun led to inconclusive results. Since the data that we obtained for Mars and α Bootis are accurate only to about 2 percent, and since similar errors exist in the infrared magnitudes of α Bootis and the sun and in the laboratory data, the cumulative errors in the absolute colors obtained were so large that the results were meaningless. It was decided to compare the data obtained at Kitt Peak and the corrected laboratory data directly. This is justified because the spectral response of the spectrometer is constant when used with the same detector, entrance diaphragm, and prism. Furthermore, the relative heights of the $1.05-\mu$, $1.25-\mu$, 1.55- μ , and 2.10- μ maxima are only slightly affected by changes in the amount of terrestrial water vapor, though the maximum at 0.90 μ is more affected (see next section). We have concluded that the age of the aluminum coatings of the telescope mirrors and



Fig. 1 Drawings of Mars by Mr. Binder showing the aspect of the planet corresponding to the times when the infrared observations were made. The circles indicate the area of the diaphragm used in the spectrometer. In A ($\lambda = 185^{\circ}$) the circle includes part of Zephyria. In B ($\lambda = 220^{\circ}$) the lower circle covers part of Elysium and the upper circle, parts of Mare Cimmerium and Mare Tyrrhenum, as well as some desert material. In C ($\lambda = 250^{\circ}$) the circle covers Syrtis Major.

heliostat mirrors has little effect. However, in view of the assumptions made, the results obtained here are still regarded as preliminary. Our earlier work (Paper I) was subject to the same assumptions but was done with a different telescope and with a different set of instrumental parameters. The consistency of the two sets of conclusions gives confidence in the results.

5. Discussion of the Observations

Figure 2 gives the observations of maria and deserts compared to the weighted average of the desert measurements (horizontal line). The vertical bars give the magnitude of the errors for each point. The errors are roughly inversely proportional to the measured amplitude; thus, at 2.10μ , where the amplitude is lowest, the errors are largest. As shown in Figure 2, the deviations of maria from the average desert line are significant but small, usually less than 6 percent. The 0.90- μ point is affected by changes in telluric water vapor so that an external error exists in addition to the normal error of observation. This external error of unknown but probably small magnitude is indicated by dashes in the average desert line.

The deserts included in the average desert line of Figure 3 are Elysium (28° N, 210° W) and Zephyria (0° N, 185° W). Elysium was very prominent and was one of the few areas virtually free from contamination by dark material. Zephyria was somewhat contaminated, but still clearly a desert area. The

average desert line in Figures 2, 3, and 4 was made from Zephyria and Elysium observations weighted slightly in favor of the latter because of its lack of contamination.

The average mare curve is shown relative to the average desert line in Figure 4. The maria observed were Syrtis Major (0° N, 290° W) and Mare Cimmerium-Mare Tyrrhenum (20° S, 220° W). Visually, Syrtis Major was the more uniformly dark, and the observations of this area were probably contaminated with desert material only because of image wandering due to seeing conditions. The region in Mare Cimmerium-Mare Tyrrhenum was not solidly dark, and there was abundant contamination by desert-type material. In fact, the curves in Figure 2 for the Mare Cimmerium-Mare Tyrrhenum region and for Syrtis Major show that the former contaminated region was more nearly desert-like than was Syrtis Major. The measurements of these two areas were weighted slightly in favor of Syrtis Major in compiling the average mare curve.

The rock samples used in this investigation were selected on the basis of the results of Paper I, in which all fresh rock surfaces were rejected when compared to the Martian deserts. In the earlier study, only igneous rocks with a weather-produced surface stain of limonite were found to compare with the deserts. The limonite curve in Figure 3 is an average of three individual samples collected from the southern Arizona desert. The deviations in the spectra of the







Fig. 3 Average laboratory observations of limonite-stained rocks compared to the Martian deserts. Vertical bars indicate the approximate errors at the wavelengths indicated. The dashes in the Average Desert line between 0.90μ and 1.05μ indicate the added uncertainty at 0.90μ caused by variations in terrestrial water vapor content.

individual samples were small. Each rock has a heavy surface stain of yellow-orange limonite, which extends approximately 2 mm into firm rock and much further into friable rock, as determined from cut samples.

Laboratory observations of black basalt and volcanic ash are shown in Figure 4. The black-basalt curve is the average of three samples; one of these is glassy pahoehoe from Hawaii, another is a slab of aa from the Bonito Flow at Sunset Crater, Arizona, and the third is pahoehoe from the Pinacate volcanic field in northern Sonora, Mexico. The deviations in the color curves were greater among these samples than in the limonite-stained rocks, but the profiles of the color curves were always the same. All of the measurements were made on surfaces that had been exposed (no clean fractured surfaces) but not noticeably chemically weathered. The volcanic ash was collected from the Sunset Crater area and had also been exposed but not noticeably chemically weathered. The particle sizes of the ash varied from about 1 to 10 mm, and most pieces were about 4-6 mm in size. The similarity in the color profiles of the basalts of Sunset Crater and the volcanic ash is consistent with the probable similar composition of these materials. The similar profiles further verify the observation that the samples had not been weathered significantly (in the same environment, pulverized ash would have weathered much faster than the solid lava on the flow).

6. Composition of the Bright Areas

The results of this work corroborate our findings (Paper I) that the infrared colors of the Martian deserts closely match those of igneous rocks with a weather-produced stain or coating of limonite. Since Paper I was written, we have continued field observations and have noted that in areas of alluvial fill where the limonite stain is highly developed on fragments of igneous rocks, the soil and sedimentary rocks and fragments are also heavily stained. This limonite in the soil and on the nonigneous rocks is derived from the igneous rocks.

Limonite is a general term that includes the minerals goethite and lepidocrocite, and iron oxide of undetermined crystallization and hydration. In papers dealing with the composition of the Martian surface there has been some confusion in the use of the term limonite. The weather-produced limonite stain referred to in this paper is an amorphous mixture of iron oxides that matches the visual color of a mixture of 70 percent goethite and 30 percent hematite. This comparison was made with synthetic samples of goethite and hematite in the above ratio prepared by Drs. Draper and Adamcik. The ratio is consistent with the spectral observations in Figure 2 of Paper I. This form of limonite is produced on igneous rocks by the oxidation and hydration of iron in iron-bearing minerals such as biotite, augite, olivine, and hornblende. A more familiar form of limonite is a yellow, earthy limonite consisting largely

Fig. 4 Laboratory observations of volcanic black basalt (average of three samples) and volcanic ash compared to the average Martian maria and the deserts. The additional errors at 0.90μ in the Mars observations are indicated by the open circle in the Average Mare line and the dashed portion of the Average Desert line. The laboratory observations do not have these additional errors.



of powdery hydrated goethite; it does not match the spectrum of Mars (Paper I). Although the development of limonite from the above iron-bearing minerals is not completely understood, one reaction sequence in which limonite can form from weathering of an iron-bearing mineral has been described by Keller (1957): Simultaneous oxidation and reduction of iron sulfide (e.g., marcasite) proceeds according to the following simplified equation

$$2\text{FeS}_2 + 2\text{H}_2\text{O} + 7\text{O}_2 \rightarrow 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4. \quad (1)$$

FeSO₄ will most likely oxidize and hydrate further in a weathering solution:

$$FeSO_4 + 2HOH \rightarrow Fe(OH)_2 + H_2SO_4.$$
 (2)

The $Fe(OH)_2$ is unstable and quickly oxidizes to form $Fe(OH)_3$, which then loses water to form limonite:

 $4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3, \quad (3)$

$$2Fe(OH)_3 \rightarrow Fe_2O_3 \cdot H_2O + 2H_2O \qquad (4)$$

or $Fe_2O_3 \cdot nH_2O + nH_2O$. (5)

The H_2SO_4 produced in Equation (2) may come in contact with more FeS₂ and produce H_2S according to

$$\operatorname{FeS}_2 + \operatorname{H}_2\operatorname{SO}_4 \to \operatorname{FeSO}_4 + \operatorname{H}_2\operatorname{S} + \operatorname{S}.$$
 (6)

The sulfur may be released as fine-grained free S if it is not oxidized in the reaction. Some H_2S may dissolve in H_2O and some may oxidize incompletely, forming free S. However, H_2SO_4 can react with clays and iron-bearing minerals to produce alunite [KAl₃ (OH)₆(SO₄)₂] and jarosite [KFe₃(OH)₆(SO₄)₂].

As weathering proceeds on crystalline rocks, making their surfaces more friable, the limonite forms in cracks and crevices. In a desert environment, where rocks decompose largely by exfoliation, this results in the fragments as well as the newly exposed surface being coated with the limonite stain.

We have noted that limonite surface stains can form in a very short time in a favorable environment. A light stain has begun to form on moderately coarsegrained granite in a fresh road cut on Kitt Peak (U.S. Geological Survey Baboquivari Peak Quadrangle), where the average annual precipitation is 15–20 in. (Sellers 1960), after only three years of exposure. In the Santa Catalina Mountains north of Tucson, Arizona, where precipitation is about the same as at Kitt Peak, road cuts about 35 years old show extensive stains on the granite-gneiss rocks.

Atmospheric pressure (found by Kaplan *et al.* 1964; Owen and Kuiper 1964) and water vapor con-

tent (found by Kaplan *et al.* 1964; Dollfus 1963) on Mars indicate that limonite is probably not now forming there (Fish 1966). Therefore, the presence of limonite on Mars suggests that in the earlier history of the planet, the atmosphere may have been more conducive to chemical alteration of the surface materials. The chemically formed limonite has been preserved because of a lack of intense mechanical weathering on Mars since the development of this mineral stain and deposit.

The occurrence of limonite stain on rock outcrops, fragments, and all sizes of detrital material on earth holds important implications in constructing a general model for the desert areas of Mars. The large-scale structures evident in the television photographs from Mariner IV (Leighton et al. 1965) indicate that detritus probably does not cover the entire surface and that solid rock outcrops may occur. As noted above, the weathering and exfoliation fragments and new outcrop surfaces were probably already coated with limonite stain when they were formed. Even the smallest fragments of clay or silt size can consist of limonite dust or of tiny silica or clay minerals coated with limonite. It is probably this smallest size range of particles that gives the polarization curve observed by Dollfus (1955, 1961). Dr. T. Gehrels (private communication, 1965) has pointed out that the Dollfus polarization results could be realized even if only 5 to 10 percent of the surface of Mars is covered by the powdery, earthy limonite and the remainder of the surface consists of much larger fragments, for the latter would not contribute significantly to the polarization. The presence of extremely fine material on Mars is further corroborated by the results of Koval' and Morozhenko (1962) who found from optical-depth estimates that the average particle radius in the 1956 dust clouds was about 1.4 microns. Thus, we suggest that the desert areas are composed of rock outcrops, detritus with particles ranging in size from large rock fragments to sand-size grains, and some limonite dust; the outcrops and detrital fragments are, in general, covered with a hard surface stain of limonite as is found in terrestrial desert regions.

7. Additional Considerations

From their observations of Mars in the 8–14 micron atmospheric window, Sinton and Strong (1960) concluded that less than 20 percent of the surface of the planet is composed of silicates. In the samples that we have measured and those noted in the field, the limonite stain efficiently covers all min-

erals in the rocks, even free quartz, to a thickness easily sufficient (approximately one wavelength [F. J. Low, private communication, 1965]) to mask the spectral properties of the minerals beneath. Normally, the stain on the surface approached 0.2 mm in thickness but, as noted before, it can permeate the rocks to a greater depth.

Regarding the very small disintegration products, Salisbury and Van Tassel (1965) have noted Correns' (1937) observation that tiny angular silica and other grains having sizes up to about 10 microns and blown about in the earth's atmosphere are often coated with limonite. In view of this and our aforementioned observation that even free silica (quartz) in weathered rocks can retain at least a thin coating of limonite, the occurrence of stained sand-size and much smaller particles can be understood. The limonite stain has a hardness of 6 and is not easily worn off by attrition, as was suggested by Rea (1965).

Loomis (1963, p. 6) has raised the possibility that the Martian bright areas may be covered by a desert-varnish type of encrustation. While the exact mineralogic composition of desert varnish is unknown, analyses by Engle and Sharp (1958) show that Fe₂O₃, Al₂O₃, and MnO are the most abundant oxides having coloring properties. A discussion of desert varnish relative to the Martian surface is pertinent because the varnish is composed in part of an iron oxide, forms a hard surface stain, and occurs in desert environments. Although the limonite stain discussed in this paper is probably related to desert varnish, the latter is much darker and its visual color is greatly different from that of Mars. The exposures of desert varnish studied by Engle and Sharp occur in regions of rather less rainfall (1.5-4 in. annually) than do exposures of the limonite stains we have observed.

From studies of the chemical depletion with depth from the varnished surfaces of rocks, Engle and Sharp concluded that the desert varnish is an accretion and not a secretion product. Both accretion and secretion of limonite stains occur in terrestrial deserts since the stain may originate from within or be transferred to a rock, as is the case with our samples.

8. The Dark Areas

The color of the Martian dark areas is not well known, even in the visual part of the spectrum where observations are relatively easy. Accurate color values are essential to any attempt, such as this

study, to identify the materials comprising the dark areas. For the reasons mentioned above, however, it has been possible to determine only the relative color of the dark and bright areas. It may, in fact, be impossible to find the true color of the materials making up the dark areas on Mars from terrestrial observations because of the patchy nature of these regions. Focas (1961), for example, has noted that the Martian maria are made up of patches of dark material superimposed on the lighter background. This is evident in his high-resolution planisphere of Mars made in 1958 (Focas 1961, Fig. 11; also reproduced in Dollfus 1961, Plate 19). The most significant exception is the northern portion of Syrtis Major, which on Focas' map is the most solidly dark region on the planet. This was visually confirmed during our observations.

The rocks observed in this investigation in connection with the Martian dark areas were selected specifically to test the hypothesis that the Martian maria are composed of relatively fresh basaltic lava and/or basaltic volcanic cinders. In a series of papers, McLaughlin (1954 and many others) expressed the view that the dark areas on Mars are deposits of volcanic ash expelled by a large number of active volcanoes and emplaced by prevailing winds on the planet. McLaughlin's hypothesis has been criticized, mostly on theoretical grounds, by several authors (e.g., Kuiper 1955). The observations reported above provide physical evidence against the volcanic ash and basalt hypotheses.

Comparisons of the colors of various black basalts and ash given in Figures 3 and 4 indicate that the maria are not composed of fresh lava or ash fields. Our infrared observations indicate that color differences between the deserts and the maria are small and that contamination of the maria by desert material probably occurs even in Syrtis Major, which is one of the most uniformly dark areas on Mars. In view of this and Focas' picture of the patchwork nature of the maria, the maria appear to consist of a "normal desert surface" partially covered by dark material, or vice versa. The seasonal variations in tone of the maria, particularly areas like Pandorae Fretum which can become completely desert-like in tone, indicate that the former case is more likely.

The irregular shape of the color curves of the maria as compared with the more regular color curves of the limonite-stained rocks and the basaltic materials seems to preclude the possibility that any combination of desert material and basalt or ash could reproduce the mare curve. We have already noted that an increase in the amount of stain causes uniform changes in the color curves.

While there is some uncertainty in the absolute calibration and comparison of laboratory data with the telescopic observations as described above, it appears that the maria of Mars do not consist of fresh or nearly fresh exposures of black basalt or volcanic basaltic ash. This result adds credence to the statement of Sagan *et al.* (1965) that the study of the dark areas on Mars is most properly undertaken in a biological context.

9. Conclusions

The observations reported in this paper suggest a general model for the Martian bright areas. The bright regions may be composed of rock outcrops, detritus with particles ranging in size from large rock fragments to sand-size grains, and some limonite dust. The outcrops and detrital fragments are, for the most part, covered with a hard surface stain of the type of limonite that is formed and preserved in a desert environment. This surface stain yields the colorimetric results reported here, and the limonite dust would account for the polarimetric results of Dollfus (1955, 1961). The limonite stain is a naturally occurring substance that readily forms in a suitable environment during normal chemical weathering of igneous rocks.

The maria do not appear to consist of basaltic lava flows or deposits of volcanic ash.

Note added in proof. Younkin (1965, 1966) has called attention to a dip between 0.76 and 1.15 μ in the reflection spectrum made by Draper *et al.* (1964) of their mixture of 70 percent goethite and 30 percent hematite. A similar strong minimum is shown by Sagan *et al.* (1965, Fig. 18). Because the spectra of Mars do not show this intensity depression, Younkin (1966) has objected to limonite as a major constituent of the surface layer. Although this objection is valid for synthetic mixtures of limonite, pulverized brown limonite, yellow earthy limonite, etc., we have made spectrophotometric measurements of the weather-produced limonite stain on igneous rocks and find that the intensity depression between 0.76 and 1.15 μ does not occur.

Analyses of many varieties of limonite by Sagan et al. (1965) show that this depression in the spectrum is often reduced or removed completely upon heating the samples. This result suggests that the

spectral feature may result from interstitial water, or water of hydration, which is not significant in our samples formed in the desert.

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APPENDIX

Plates 1-4 are included here to give a general impression of the occurrence of limonite stain in terrestrial deserts. Plates 1 and 2 were taken in the Sonoran Desert in the vicinity of the Glove Mine, south of Tucson, Arizona (coordinates 31° 40' N, 110° 58' W, U.S. Geological Survey Mount Wrightson Quadrangle). Plates 3 and 4 were taken near Tucson, at the end of North Campbell Avenue (coordinates 32° 20' 16" N, 110° 55' 30" W, U.S. Geological Survey Tucson North Quadrangle). Included in each photograph is a chart of Kodak Color Control Patches and a Kodak Gray Scale so that accurate comparison of colors may be made with the final printed copy of each plate.

The rocks from near the Glove Mine consist of mostly limestone fragments and granitoid igneous rocks. The alluvium is derived from the Santa Rita Mountains and contains considerable soil. The location near Tucson has mostly granite-gneiss rocks derived from the Santa Catalina Mountains, and the soil is less well developed than at the Glove Mine location.

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Plate 1 Desert rocks and soil heavily stained with limonite and hematite. The rock fragments consist of both igneous and sedimentary rocks. The ratio of goethite to hematite in this location is approximately 2:1.



Plate 2 Ditch cut through alluvial material heavily stained with limonite and hematite, which indicates that the stain is highly developed at depth in the alluvial fill.



Plate 3 Limonite stain on granite-gneiss at the base of the Santa Catalina Mountains, north of Tucson, Arizona. The stain in this location is richer in goethite than the stain shown in Plates 1 and 2.



Plate 4 Limonite stain on granite-gneiss at the base of the Santa Catalina Mountains, north of Tucson, Arizona. Close-up view showing stain development on soil and rock fragments.