Reports

Lunar and Martian Surfaces: Petrologic Significance of Absorption Bands in the Near-Infrared

Abstract. *A reflection minimum at 1 micron, reported for Moon and for Mars, indicates olivine or iron- and calcium-bearing clinopyroxene, or both—major constituents of many basaltic rocks. If the 1-micron absorption features are real, both chondritic and acidic rocks are ruled out as primary constituents of the surfaces of the bodies. The reflectance spectrum of Mars matches closely that of an oxidized basalt.*

Broad absorption bands occur between 0.5 and 2.6 μ in the reflectance spectra of many rock-forming minerals. Bands at such wavelengths are now reasonably well understood in terms of crystal-field theory. Measurements of the diffuse reflectance spectra of various analyzed minerals, rocks, and meteorites (this report) indicate that individual bands and combinations of bands can be used to identify mineral species or to narrow the possible choices. Characteristic reflectance spectra are usually yielded by solid rocks, coarse particulate materials, or fine powders.

Absorption bands, recorded in the visible and near-infrared spectra of Moon and Mars (*1, 2*), now appear to correlate well with a narrow choice of minerals. If the bands in the lunar and Martian spectra are real, they provide a perhaps unique means of remote analysis of some of the abundant mineral phases on the surfaces of the bodies.

Previous studies of light reflected from Moon and Mars have provided some suggestions regarding gross rock type (not mineralogy) and particle size on the basis of photometric and polarimetric properties and the slopes of spectral curves (*3, 4*). Several investigators have searched for the so-called limonite band at 0.87 μ in the Martian spectra; it has not been found, and now it appears that a band at or near this wavelength is not unique to limonite.

Diffuse reflectance spectra of mineral and rock powders were measured with a Beckman DK-2A ratio-recording spectroreflectometer. Specimens were mounted tangentially to a MgO-lined integrating sphere, and measurements were made relative to a standard surface of smoked MgO. A PbS cell, mounted atop the integrating sphere, was used for the spectral region under discussion: 0.5 to 2.6 μ.

Minerals and rocks were identified and analyzed by standard optical, x-ray diffraction, and chemical methods; they were crushed and sized, and the fractions passing a 400-mesh screen (< 37 μ) were used for the reflectance measurements. The particle-size fraction that gives the most pronounced structure in the reflectance curve depends on the absorption coefficient of the material, but for silicates it is typically coarser than 37 μ. If there is structure in the curve of a powder finer than 37 μ, almost always it will be even more pronounced in coarser mixtures. The effects of changes in particle size, particle packing, and particle shape on reflectance spectra of rocks have been discussed (*5*).

Absorption bands in the region between 0.5 and 2.6 μ can be conveniently classified in two types: broad bands due to electronic transitions, and narrow bands arising from vibrational modes. Most of the vibrational bands are due to OH^- and H_2O, but additional bands occur in carbonates (*6*). The vibrational bands rarely are present in the diffuse reflectance spectra of mafic rocks and minerals, but bands at 1.4 and 1.9 μ appear typically in the spectra of quartz and feldspar (*5*); in this portion of the spectrum the hydroxyl bands are not reliable indicators of hydrous minerals.

The broad electronic bands seen for the common rock-forming minerals are almost entirely caused by a single element—iron—in various valence and coordination states. Although only the strong absorption features appear in the reflectance spectra of powders, assignments of most of these major bands are now well established (*7*).

Significant conclusions from the reflectance measurements on mineral and rock powders (Table 1 and Fig. 1) are as follows:

1) As predicted by crystal-field theory, only minerals containing transition metals (especially Fe) exhibit the broad absorption bands caused by electronic transitions. For example, quartz, the feldspars, pure forsterite, pure enstatite, and such do not show electronic bands. Quartz, the feldspars, and other light-colored minerals, however, typically have the hydroxyl and water bands at 1.4 and 1.9 μ.

2) Most of the common iron-bearing silicates have characteristic spectra. One can readily distinguish the olivine group, the orthopyroxenes, and the clinopyrox-

Table 1. Absorption bands in diffuse reflectance spectra of common iron-bearing minerals.

Mineral, formula	Centers of major absorption bands (μ)				
Silicates					
Forsterite, Mg_2SiO_4 (with minor Fe^{2+} for Mg)			1.02		
Fayalite, Fe_2SiO_4			1.05		
Enstatite, $MgSiO_3$ (with minor Fe^{2+} for Mg)		0.90		1.85	
Bronzite, $(Mg,Fe^{2+})SiO_3$		.90		1.80	
Hypersthene, $(Mg,Fe^{2+})SiO_3$		.90		1.79	
Diopside, $CaMgSi_2O_6$ (with minor Fe^{2+} for Mg)			1.03		2.3
Pigeonite, $(Mg,Fe^{2+},Ca)(Mg,Fe^{2+})Si_2O_6$			1.0		
Augite, $(Ca,Mg,Fe^{2+},Fe^{3+},Ti,Al)_2(Si,Al)_2O_6$	0.8				
Hedenbergite, $CaFe^{2+}Si_2O_6$	.7	.9			2.3
Hornblende, complex iron-bearing silicate	.6				2.3
Biotite, complex iron-bearing silicate	.7				2.3
Oxides					
Hematite, Fe_2O_3	.85			~1.7	
Goethite, FeO(OH)		.89			
Carbonates					
Dolomite, $CaMg(CO_3)_2$ (with minor Fe^{2+} for Mg)			1.0	1.72 1.83 1.95	2.28 2.48
Siderite, $FeCO_3$			~1.1	1.92	2.31 2.52

enes. The common amphiboles and Fe-bearing micas also have characteristic curves. The major bands in the mafic silicates are between 0.9 and 1.1 μ. These absorption features are caused by Fe^{2+}, and the positions of the bands reflect different coordinations according to the crystal structures.

3) The ferrous oxides (magnetite and ilmenite) are opaque even as small particles and do not show structure in a reflectance curve. However, the ferric oxides (hematite, goethite, limonite, and such) show an absorption feature at 0.85 to 0.89 μ that is produced by Fe^{3+}. The fact that various amorphous ferric compounds also exhibit this band suggests that it is not a reliable indicator of mineralogy. It is notable that goethite and limonite do not have OH$^-$ or water bands in their diffuse reflectance spectra.

4) Iron-bearing carbonates have a broad band near 1 μ, but they also show various other (vibrational) bands between 1.7 and 2.6 μ. These features are highly diagnostic and prevent confusion with the silicates or oxides.

5) Mixing of different minerals averages the spectra; if, for example, orthopyroxene and olivine occur together in a basalt, the reflectance curve of the rock or rock powder shows a single minimum near 0.95 μ—the two bands are not resolved at 0.90 and 1.02 μ. (The orthopyroxene content can be qualitatively estimated, however, from the strength of the 1.8-μ band.) Although a rock spectrum is some average of the spectra of the constituent minerals, there are rarely more than two principal iron-bearing silicate phases in a rock. The rock type can be inferred from petrologic arguments based on evidence of the mafic phases.

6) The absence of structure in a reflectance curve is ambiguous. A monotonous curve may reflect the absence of iron-bearing minerals, very small (< 10 μ) particles, or the presence of sufficient amounts of highly absorbing materials such as magnetite, metallic iron, and carbon.

A broad band has been reported at approximately 1 μ in reflectance curves of Moon. A flattening of the spectral curve was found near 1 μ for Mare Tranquillitatis, but a compositional interpretation could not be made (*8*); Tull's (*1*) recalculation of the curve indicated a distinct minimum at 1 μ, in agreement with the data of Moroz (*2*). The band lies between 0.95 and 1.0 μ, although the exact position is in doubt. An interpretation (*3*) that this band indicates a basic rock can now be refined in the light of the above discussion. We know that the 1-μ band requires the presence of Fe^{2+} and that ferrous iron typically resides in the mafic silicate minerals. The oxides and carbonates can be excluded on the basis of the evidence in Table 1. The band at 1 μ, therefore, indicates olivine or an iron- and calcium-bearing pyroxene, or both. A predominantly olivine rock (dunite) probably can be excluded because the normal albedo of powdered olivine is far higher than the lunar maximum (*5*). A deep band centered at 1.02 μ or higher also would be expected for a dunite.

The single broad band at 1 μ in the lunar spectrum does not correlate with those of most of the stony meteorites—which contain enstatite, bronzite, or hypersthene—which instead show the characteristic pair of bands at 0.9 and 1.8 μ (Fig. 1D). Thus it is highly unlikely that the surface of Moon is chondritic. If, however, the lunar minimum is nearer 0.95 than 1.0 μ, the presence is indicated of some orthopyroxene in addition to olivine or clinopyroxene, or both.

The evidence points to mineralogy consistent with a rock of basaltic composition (Fig. 1D). This conclusion is in good agreement with the alpha-scattering analyses performed by Surveyor V in Mare Tranquillitatis and

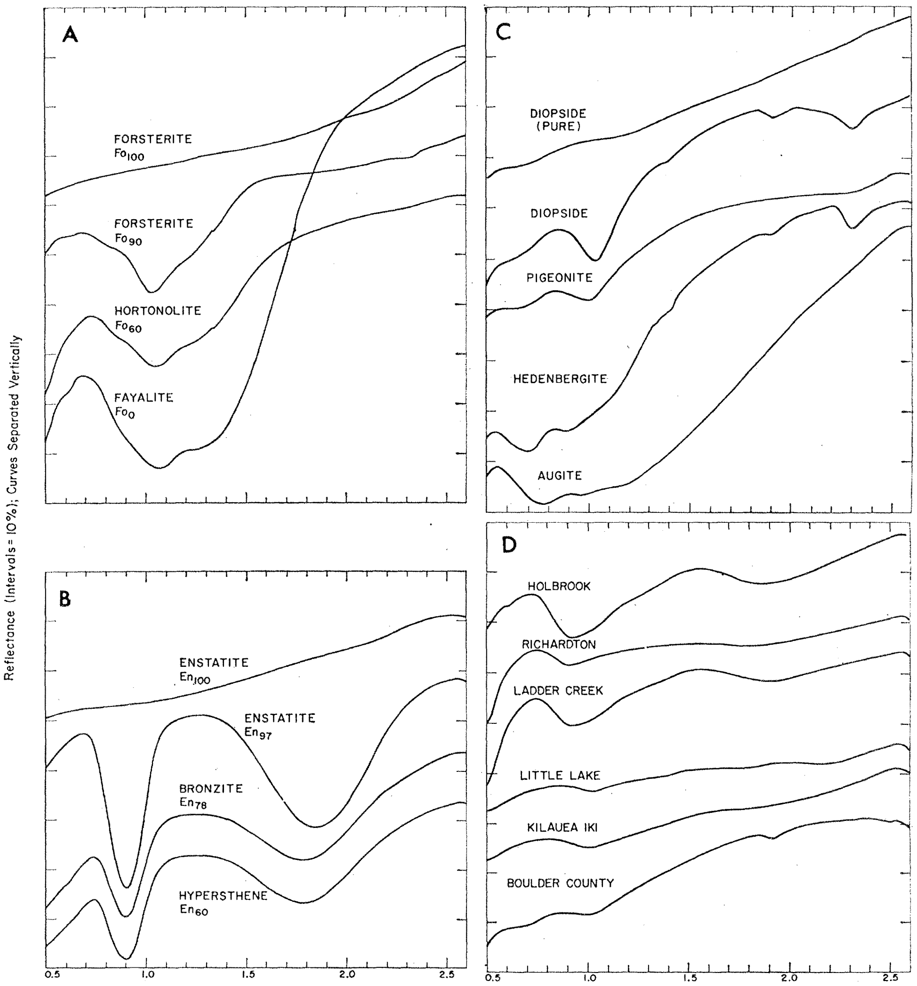

Fig. 1. (A–C) Reflectance spectra of the common iron-bearing rock-forming silicates; specimens were powders finer than 37 μ. The olivines (A) have a single minimum at 1.02 to 1.05 μ due to Fe^{2+} in sixfold coordination. The orthopyroxenes (B) have a minimum at 0.90 μ due to Fe^{2+} in sixfold coordination and one at 1.8 to 1.9 μ that is probably caused by Fe^{2+} in a highly distorted octahedral site (*7*). The clinopyroxenes (C) and hornblende and biotite (not shown) have multiple minima at the shorter wavelengths, except that diopside and pigeonite have bands at 1.03 and 1.0 μ, respectively. (D) Reflectance spectra of representative chondritic meteorites and basalts, showing how iron-bearing silicate minerals determine the positions of absorption bands in rocks. Orthopyroxene-rich chondrites (Holbrook, Richardton, Ladder Creek) each have a minimum at or near 0.90 μ and another at 1.9 μ. Basalts bearing olivine or clinopyroxene, or both (Little Lake, Kilauea Iki, Boulder County), each have a single minimum at or near 1.0 μ. Specimens were powders finer than 37 μ.

by Surveyor VI in Sinus Medii (*9*). (The alpha-scattering experiments, of course, determined elemental abundances, not mineralogy.)

Moroz (*2*) gave similar spectral curves for highlands and maria, implying similar rock types in both regions. The visible albedo contrasts are not necessarily in conflict with this conclusion (*3*). Analyses by Surveyor VII (still unreleased) may clarify this point.

An absorption band in the lunar spectrum allows estimation of the maximum amount of opaque material that could be present as coatings on the rock particles. Completely coated particles could transmit no light and so would not contribute bands to the reflectance spectrum. This argument bears on the problem of whether or not the lunar surface is darkened by exposure to the solar wind, either by addition of carbon or by sputtering and consequent deposition of metal coatings (*10*).

In the laboratory, progressive addition of carbon to a basalt powder leads to complete removal of any absorption bands; the amount of carbon necessary to erase the bands depends on the surface area to be coated and therefore on particle size. The 1.0-μ band from a basalt powder finer than 37 μ is removed entirely by addition of 5 percent by weight of carbon powder. This fact suggests an upper limit of about 3 percent for carbon in the optically thick layer at the lunar surface. Sputter-deposited iron or other metals may constitute 5 to 6 percent by weight if an anology can be drawn with the coating behavior of carbon. These upper limits are in agreement with the results of Surveyors V and VI (*9*).

The red color of Mars, alone, strongly suggests the presence of one or more ferric oxides. Recent discussion has concentrated on the possibility of limonite. I shall not consider further the various laboratory and telescopic measurements bearing on the limonite question (*1*). Existence of the so-called limonite band (in fact the Fe^{3+} band) at 0.87 μ on Mars is, however, still in doubt (*1, 11, 12*).

The importance of identification of iron oxide at the surface of Mars should not be overemphasized, however. Several workers (*13*) have discussed plausible models in which iron oxide only coats the surfaces of silicate rock particles on Mars. Gemini color photographs of Earth show clearly that vast desert areas range from reddish to light orange. Ubiquitous ferric oxides—strong pigments — account for these colors, and it is well known that terrestrial deserts are not made of hematite, goethite, or limonite but are rather largely silicates. If the setting is comparable on Mars, we should look for evidence of other minerals in addition to the ferric oxides.

The spectral curves of Mars given by Tull (*1*) and Moroz (*14*) are of considerable interest for they show a minimum at 1.0 μ; as I have mentioned, this fact is evidence of Fe^{2+}; therefore, if the band is real, it must arise from the surface rock, not from the ferric oxide. Sinton (*12*) shows the Mars curve rising from 2.0 to 2.5 μ, which finding probably rules out the carbonates as major contributors. So one is led to the conclusion that the 1.0-μ band is from the mafic silicates, olivine or iron- and calcium-bearing pyroxene, or both. Much of the surface of Mars, then, appears to be composed of rock containing these minerals as principal phases.

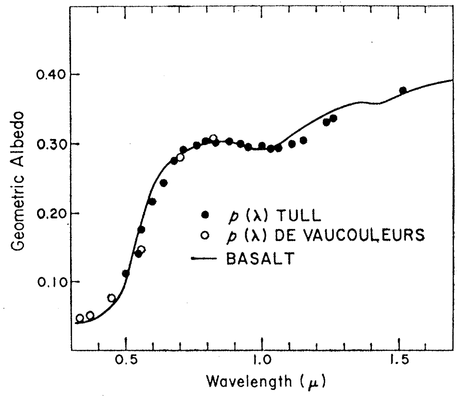

Fig. 2. Comparison of the geometric albedo of Mars (*1*) with the reflectance of an oxidized basalt. The basalt measurement was made on an integrating sphere. The specimen, a powder finer than 100 μ, consisted of 50 percent Little Lake basalt and 50 percent Boulder County basalt. Oxidation was by treatment in dilute HNO$_3$ which partially dissolves and oxidizes small grains of magnetite. Curves agree well with the data of Younkin (*11*) although he showed only the suggestion of minimum at 1.0 μ.

Continued addition of ferric oxide pigment to the Martian surface would eventually obscure the 1.0-μ band. In the laboratory, as basalt particles are mixed with more and more ferric oxide, the minimum at 1.0 μ is progressively removed, while the Fe^{3+} band at or near 0.87 μ is enhanced. This change is manifested in the reflectance curve by a progressive shift of the minimum from 1.0 to 0.87 μ, and also by emergence of the steep slope and characteristic shape of the curve of the ferric oxide in the visible portion of the spectrum. The amount of ferric oxide required to displace the 1.0-μ band depends on whether hematite or goethite is added, on the surface area (particle size) of the basalt powder, and on the effectiveness of the coating process.

Coating is most effective in the presence of liquid water. Less than 1 percent of ferric oxide (and hydroxides) precipitated on basalt particles imparts a rust color to the powder without affecting the 1.0-μ band (Fig. 2). Dry mixtures of goethite and basalt powders require about 25 percent by weight of goethite to obscure the 1.0-μ feature of the basalt. This is probably an upper limit for goethite (or limonite) on the Martian surface. A dry mixture of hematite and basalt powder is purplish gray, distinctly different in color from the Martian surface.

Further search for near-infrared absorption bands in planetary reflectance spectra may yield important results; of special interest will be differences in absorption features between the light and dark areas on Mars, and between highlands and maria on Moon. One should be able to estimate by this method the gross composition of the surface of Mercury.

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