DIFFUSE REFLECTANCE SPECTRA OF PIGMENTARY-SIZED IRON OXIDES, IRON OXYHYDROXIDES, AND THEIR MIXTURES: IMPLICATIONS FOR THE REFLECTANCE SPECTRA OF MARS. Richard V. Morris, Geochemistry Branch, NASA Johnson Space Center, Houston, TX, and Stanley C. Neely, University of Oklahoma, Norman, OK.

INTRODUCTION

The remote sensing of Mars by reflectance spectroscopy provides a means of obtaining compositional information about its surface. In order to properly and completely abstract this information from the reflectance spectra, it is necessary to understand through theoretical and laboratory studies the reflectance properties of particulate (mat) surfaces. Important variables to be considered include particle shape and size and composition, especially when the particulate system is a mixture of particles having different compositions. Useful conceptual and theoretical discussions of the nature of radiation reflected from particulate surfaces are given by several authors (e.g., 1,2,3). Diffuse reflectance spectra are available in the literature for a wide variety of minerals and rocks, although documentation of such information as mean particle diameter, particle shape, chemical composition, and petrography, which may affect the reflectance spectra, is generally incomplete (e.g., 4,5,6). A few studies have investigated the relationship of the reflectance spectra of mixtures to the spectra of the individual pure components (e.g., 6,7,8,9). These studies almost exclusively involve mixtures whose components have mean particle diameters large compared to the wavelength of visible and near-infrared radiation.

The above and related laboratory studies have provided considerable qualitative and quantitative insight for the interpretation of the reflectance spectra of Mars and also of particulate surfaces in general. However, additional laboratory and theoretical studies are required to refine present understanding and explore alternate interpretations of the reflectance spectra of Mars. The present study focuses on the spectral properties in the near-UV, visible, and near-IR of pigmentary-sized iron oxides, iron oxyhydroxides, and their mixtures. Pigmentary-sized particles are in the micron to submicron diameter range and thus are useful for evaluation of the reflectance properties of particulate regimes where the particle diameters are comparable to or less than the wavelength of visible and near-IR radiation. The results are also applicable to assemblages which contain micron to submicron grains of iron oxides and/or iron oxyhydroxides.

SAMPLE DESCRIPTION AND EXPERIMENTAL PROCEDURES

The iron oxides and oxyhydroxides were obtained in particulate form as commercially available reagents; all were synthetically prepared. The particle shape and mean particle size, determined from TEM photomicrographs, are given in Table 1. The iron compounds were combined into intimate mixtures (blends) by means of ultrasonic agitation in ultra-pure freon; after blending, the freon was evaporated at ∼ 30°C.

The diffuse reflectance spectra were recorded on a Cary 14 spectrophotometer having a 25 cm integrating sphere. With a N2 gas purge, the useable range is ∼ 0.35 μm to ∼ 2.20 μm. Halon was used as the reference material.

RESULTS AND DISCUSSION

Pure Oxides and Oxyhydroxides

The diffuse reflectance spectra of the pure oxides and oxyhydroxides are shown in Figure 1. The spectrum of hematite (α-Fe2O3; HMS3) is similar to those published by other workers (e.g., 5,6). The spectrum is characterized by a band at ∼ 0.86 μm, and inflection near 0.62 μm, and strong absorption
shortward of ~0.55 μm. The spectra of the goethites (α-FeOOH; GTS2, GTS3) are somewhat different from those published in the geologic literature (e.g., 5, 6) but are similar to those published by the paint industry (e.g., 10). Bands are centered near ~0.65 μm and ~0.92 μm, the former of which is not usually distinct in spectra published in the geologic literature. Strong absorption occurs shortward of ~0.43 μm. The presence or absence of the 0.65 μm band may reflect relative chemical purities (10, 11). The goethites studied by (5) and (6) are naturally occurring and may contain significant impurities; major element analyses of GTS2 and GTS3 (not shown) showed they are nearly chemically pure. The spectrum of lepidocrocite (γ-FeOOH; LPS2) is similar to that of goethite except the two bands occur at slightly longer wavelengths (~0.68 and ~0.97 μm). This spectrum shows that Fe(III) bands can occur in the region around 1.0 μm where bands are usually interpreted to indicate the presence of Fe(III).

The spectrum of magnetite (Fe₃O₄; MTS4) is similar to those published by others for magnetite samples having a small mean particle size (e.g., 5). The reflectance of magnetite MTS4 is 2-4%. The spectrum of maghemite (γ-Fe₂O₃; MHS3) is characterized by a weak band centered at ~0.93 μm, a shoulder near 0.63 μm, and strong absorption shortward of ~0.45 μm. Maghemite has been suggested by (12) to be present on the Martian surface as a minor (1-7%) component in or on most of the surface particles. Comparison of the spectrum for MHS3 to those for the bright areas of Mars (13) shows no strong spectral indication for maghemite, assuming the spectrum of MHS3 is representative of maghemites in general. However, this test for the presence of maghemite is probably not very sensitive because MHS3 has no distinctive strong bands longward of ~0.80 μm and the UV-blue absorption edge is not unique to maghemite.

Blends

In Figure 2 are the diffuse reflectance spectra of the blends of hematite (HMS3), maghemite (MHS3), and goethite (GTS2 and GTS3) with 10 wt.% magnetite (MTS4). Such blends might approximate, in an optical sense, a rock, a rock coating, or a soil which is a mixture of a Fe(III)-bearing phase and an opaque phase such as magnetite. All four spectra have the same general form. There is a moderate to steep positive slope from the UV-blue to the reflectance maximum at ~0.58, ~0.77, ~0.75, and ~0.76 μm for the GTS2, GTS3, HMS3, and MHS3 blends, respectively. The GTS2 blend is olive-green in color; the GTS3 blend is yellow-brown; the HMS3 blend is red-brown; and the MHS3 blend is dark brown.

The hematite blend spectrum has many features also characteristic of the Martian dark region spectrum as represented by the spectrum of a dark region in Iapygia with the effects of atmospheric CO₂ and 20% surface coverage by bright material numerically removed (14). Both have strong UV-blue absorption, a reflectance maximum at ~0.75 μm, an apparent band minimum at ~0.89 μm, and a negative slope in the near-IR. They are different in that for the blend the UV-blue absorption edge occurs at a longer wavelength and the slope in the near-IR is steeper. In addition, a band at ~0.99 μm is also present in the Mars, but not the blend, spectrum. An explanation for this situation is that the Martian spectrum is a composite of two optically non-interacting components. One of these is similar to the HMS3 blend and the other would contribute the 0.99 μm band.

The reflectance maximum at ~0.58 μm for the GTS2 blend renders it a poor spectral analogue for the Martian dark region spectrum. The GTS3 blend is better, but the 0.65 μm band is not apparent in the Mars spectrum. However, it is possible that some combination of blends like HMS3 and GTS3 might closely approximate the Mars spectrum (except for the 0.99 μm band). The MHS3 blend is a relatively poor spectral analogue, primarily because it does not have the ~0.89 μm band and the UV-blue absorption is too far into the visible.
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addition, the prominent shoulder near \( \sim 0.62 \) \( \mu m \) in the MHS3 blend is not readily apparent in the Mars spectrum.

Spectra have been published (15) of mixtures of limonite and a much coarser-grained magnetite, and these spectra have a slope in the near-IR. It was suggested (15) that the finer-grained limonite can be thought of as forming a coating on the larger magnetite grains and that the spectra reflect this physical situation. Coating of one component by the other does not seem physically realistic for our blends because the mean particle diameters are not too dissimilar (cf., Table 1). Thus, we suggest there are other alternatives to a coating phenomenon for the negative slope in the near-IR of the Martian dark region spectra.

Table 1. Selected properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>GTS2</th>
<th>GTS3</th>
<th>LPS2</th>
<th>HNS3</th>
<th>MHS3</th>
<th>MTS4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal Comp.</td>
<td></td>
<td>( \alpha )-FeOOH</td>
<td>( \alpha )-FeOOH</td>
<td>( \gamma )-FeOOH</td>
<td>( \alpha )-Fe(_2)O(_3)</td>
<td>( \gamma )-Fe(_2)O(_3)</td>
<td>Fe(_3)O(_4)</td>
</tr>
<tr>
<td>Shape</td>
<td></td>
<td>acicular</td>
<td>acicular</td>
<td>nodular</td>
<td>acicular</td>
<td>cubical</td>
<td></td>
</tr>
<tr>
<td>( M_z )</td>
<td>( \mu m )</td>
<td>0.05x0.4</td>
<td>0.1x0.7</td>
<td>0.03x0.9</td>
<td>0.2</td>
<td>0.05x0.3</td>
<td>0.5</td>
</tr>
<tr>
<td>( M_z + \sigma )</td>
<td>( \mu m )</td>
<td>0.07x0.5</td>
<td>0.15x1.0</td>
<td>0.04x1.2</td>
<td>0.3</td>
<td>0.06x0.4</td>
<td>0.7</td>
</tr>
<tr>
<td>( M_z - \sigma )</td>
<td>( \mu m )</td>
<td>0.03x0.3</td>
<td>0.05x0.4</td>
<td>0.02x0.5</td>
<td>0.1</td>
<td>0.03x0.2</td>
<td>0.4</td>
</tr>
</tbody>
</table>

\( M_z = \) mean grain size; \( \sigma = \) standard deviation

Fig. 1 (left). Reflectance versus wavelength for pure iron oxides and oxyhydroxides.

Fig. 2 (above). Reflectance versus wavelength for blends. Spectra are offset for clarity.