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**Mineralogy of the Martian Surface:  
Crustal Composition to Surface Processes  
Final Report for NASA Award  
NAGW-3379**

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## **Introduction**

This final report for the grant NAGW-3379 covers the period 1/3/93-2/28/96. The main results have been published in the refereed literature, and thus this report serves mainly to summarize the main findings and indicate where the detailed papers may be found.

Reflectance spectroscopy has been an important tool for determining the mineralogic makeup of the near surface materials on Mars. Analysis of the spectral properties of the surface have demonstrated that these attributes are heterogeneous from the coarse spatial but high spectral resolution spectra obtained with telescopes (e.g. Adams and McCord, 1969; Singer et al., 1979; McCord et al., 1982; Bell et al., 1990; Clark et al., 1990), to the 22 km pixels from ISM in orbit (Bibring et al., 1989; Erard et al., 1991), to the high spatial but coarse spectral resolution Viking data (e.g. Arvidson et al., 1989; McEwen et al., 1989). Low albedo materials show strong evidence for the presence of igneous rock forming minerals while bright materials are generally interpreted as representing heavily altered crustal material. How these materials are physically and genetically related has important implications for understanding martian surface properties and processes, weathering histories and paths, and crustal composition. The goal of this research is to characterize the physical and chemical properties of low albedo materials on Mars and the relationship to intermediate and high albedo materials. Fundamental science questions to be pursued include (1) are the observed distributions of soil, rock, and dust a function of physical processes or weathering and (2) can different stages of chemical and physical alteration fresh rock be identified. These objectives will be addressed through detailed analyses and modelling of the ISM data from the Phobos-II mission with corroborating evidence of surface composition and properties provided by data from the Viking mission.

## **Spectral Calibration and Atmosphere**

A primary concern expressed by the LPGRP panel in the review of the previous full proposal centered on calibration of the ISM data and removal of a model atmosphere. This was a primary focus of early work on this project. In collaboration with colleagues in France and the U.S., we have made significant progress in this area (summarized below) and are confident that the major tasks regarding calibration have been successfully completed. The ISM data are currently being

converted into a PDS-compatible format by collaborator S. Erard (IAS, Paris) and the work completed under the previous award have been critical to the development of this final product.

### Spectral Calibration

Based on an exhaustive analysis ISM calibrations, we conservatively determine the absolute accuracy of the ISM reflectance is 15% (most recently discussed in papers by Erard et al, 1994 ; Mustard et al 1993; and Mustard and Bell, 1994 and is within 10% of the most recent estimate of absolute radiance given by Roush et al (1992). Uncertainties in the solar flux, effects of viewing geometry, and atmospheric variability, which are common to ALL such measurements of Mars, contribute to the error of the estimate. The relative accuracy is much high ( 1%) which permits detailed mapping and analyses of variations in surface spectral properties.

An important outgrowth of this work is presented in a paper by Mustard and Bell (1994). We exploited regions of common spatial coverage in ISM and telescopic data sets to derive new composite reflectance spectra for Mars. These update the previous composite spectra presented by McCord et al (1982) and incorporate the important new observations for ferric crystallinity (Bell et al 1990) and ferrous absorptions (Mustard et al., 1993). These spectra are a new benchmark for mission design and planning. Furthermore, the larger planetary community has voiced its support for the reflectance calibrations by the incorporation of ISM data and/or results directly into their analyses (e.g. Morris et al., 1993; Geissler et al., 1993; Reyes and Christensen, 1994; McSween, 1994).

### Atmospheric Considerations

Contributions to the ISM data by the atmosphere consist of two main components: absorptions by gas molecules in specific, narrow wavelength regions, and non-selective scattering by suspended particles and aerosols. Both contributions have been analyzed in detail to understand the effects on surface reflectance, most recently by Erard et al. (1994). Absorptions due to H<sub>2</sub>O, CO, and CO<sub>2</sub> are removed using an exponential function of wavelength-dependent absorptivity and atmospheric path length (elevation and viewing geometry). This procedure is considered the best approach given the spectral resolution of the ISM data and provides an excellent correction for the atmospheric absorptions to 2.6  $\mu$ m.

Scattering by aerosols and dust in the atmosphere is a function of atmospheric opacity and the ISM data were acquired during the period when atmospheric opacity is generally at its lowest (Zurek and Martin, 1993). The magnitude and spectral characteristics of the atmospheric scattering were derived for the ISM data using two methods. The first used several spectra that were obtained of the limb permitting direct measurement of atmospheric scattering. The second method made use of regions which were measured during different observing runs. The results of this analysis are that the aerosol particles have an average radius of 1.2 +/- 0.2  $\mu$ m. The spectrum of the aerosol contribution is dominated by a negative continuum slope which decreases exponentially toward a minimum near 2.6  $\mu$ m.

The total relative contribution to the surface signal is estimated to be 5-15%. Since this scattering is additive, analysis of differences in spectral slope between terrains due to surface spectral properties through derivatives (e.g. Fischer and Pieters, 1993, Mustard et al, 1993) is valid. This scattered component affects the position, shape and strength of mineral absorption features in two ways. First, absorption band strength is reduced which may explain why important crystalline ferric absorptions are observed at some times (e.g. Bell et al 1990; Singer et al 1990) but not others (e.g. McCord et al, 1982; Bell et al., 1994). The second effect is to cause an apparent shift to longer wavelengths of absorption band minima. This shift is small ( 10-30 nm) and does not significantly change previous analyses of surface composition from ISM data (e.g. Murchie et al, 1993; Mustard et al, 1993), but must be factored into future analysis of surface composition from absorption band position and shape.

### **Data Analysis and Interpretation**

The high spatial resolution, spectral coverage, and high signal to noise of the ISM data permitted the determination of a mineralogic basis for the spectral properties of two distinct morphogeologic regions on Mars (Eos Chasma, Nili Patera, Mustard and Sunshine, 1995). Through the use of the MGM, we showed that these areas are dominated by two-pyroxene basalts, analogous to the basaltic SNC meteorites. The differences in spectral properties between Eos Chasma and Nili Patera are best modelled as a change in relative modal abundance of low and high calcium pyroxene, with Nili Patera enriched in high-calcium pyroxene relative to Eos Chasma. However, there is a great deal of diversity within other spectra of weakly altered crust and we have recently analyzed many of these regions, the results of which were reported at the recent LPSC meeting in March, 1996 (Mustard and Sunshine, 1996).

### *Mineralogic Determinations with the MGM*

We have been working with a suite of ISM spectra that satisfy a set of criteria for spectral properties of weakly altered crustal (low to moderate albedo, flat to slightly negative spectral slope, absence of strong contamination by ferric components). On the basis of simple analysis of the position of the minima of the 1 and 2  $\mu\text{m}$  pyroxene absorption features, they fall into three primary classes: 1) Plateau Plains (longest wavelength band minima, Syrtis Major, Ophir Planum), 2) Valles Marineris (intermediate wavelength band minima), and 3) Western Arabia/southeastern Oxia Palus (shortest wavelength band minima). For the first two of these major groups, the mafic mineralogy and degree of homogeneity of each group has been determined using the Modified Gaussian Model (MGM, see Sunshine et al., 1990 for a description of the MGM). These results can then be used to determine if the different terrains represent distinct and unique compositions and thus related to the environment of formation, or are part of a continuum of compositions related in some other way.

The MGM was specifically developed for electronic transition absorptions and has been used successfully to deconvolve overlapping absorptions in mafic mineral mixtures, solid solution series, and natural lithologic samples (Sunshine et al., 1990; Mustard, 1992; Sunshine and Pieters, 1993). A very important strength of the MGM is that it is apparently not affected by particle size variations (Sunshine and Pieters, 1993). The ISM spectra were modelled using linear inverse theory as a series of superimposed, overlapping absorptions that are additive in log reflectance. The modelling employs the stochastic inversion methods of Tarantola and Valette (1982) where explicit, a priori information is included as constraints on the solutions. These constraints include general limits on the wavelengths of band minima, absorption widths, and/or mathematical coupling of absorption strengths.

It is necessary to perform these calculations one spectrum at a time, and thus progress is slow. Of the 50+ spectra examined thus far, 21 spectra (11 from the floor of Valles Marineris, 7 from the surface of Syrtis Major, and 4 from the surface of Ophir Planum) satisfy the criteria for weakly altered properties, and also provide acceptable solutions from the MGM. The parameters defining the absorption bands (center, strength, width) provide the essential information for analyzing the mineralogies. For pyroxene mixtures, the ratio of the strength of the low calcium pyroxene (LCP) to the high calcium pyroxene (HCP) bands has been shown to be a quantitative measure of the relative abundance of these minerals.

### *Context for Composition and Synthesis of Results*

It is clear that the three areas (Syrtis Major, Ophir Planum, and Valles Marineris) have distinct differences in the ratio of LCP to HCP. The volcanics in Syrtis Major are enriched in HCP relative to the materials on the floor of Valles Marineris, while the plateau plains of Ophir Planum are intermediate between these. The relationship between LCP:HCP ratio and relative abundance of these pyroxenes presented by Sunshine and Pieters (1993) was used to calculate the change in relative pyroxene abundance of these areas. It is evident from this, and previous analyses (Mustard and Sunshine, 1995) that two-pyroxene basalts with a high proportion of HCP are common on Mars. In addition, the low albedo and strong bands imply that pyroxenes make up a large fraction of the modal mineralogic abundances.

These compositions are comparable to the basaltic SNC meteorites that are thought to have crystallized from melts with major element composition analogous to terrestrial basaltic komatiites (Longhi, J. and V. Pan, 1991). The variability in the relative modal abundances of pyroxenes is likely associated with bulk CaO content of the melts. We hypothesize that the volcanics on the floor of Valles Marineris came from mantle sources depleted in calcium relative to the plains volcanics represented by Syrtis Major and Ophir Planum, though the differences could also be the result of fractionation processes. If true, these compositions may reflect the evolution of the composition of the martian mantle from enriched in calcium (source materials for early plains volcanism) to slightly depleted in calcium (source regions for later volcanism on floor of Valles Marineris).

The usefulness of these analyses comes from integrating the results with previous data bases and current understanding. The most important consequence of this result concerns the mantle. In the recent synthesis of the fundamental results from study of the SNC meteorites, McSween (1994) notes that all the SNC meteorites have calculated mantle melt compositions significantly different than melts from typical terrestrial-type volcanics. The unifying feature of the SNC melt compositions are that they are depleted in aluminum which explains the mineralogies dominated by both LCP and HCP. Every basaltic SNC shares this property, and thus the mantle source regions were depleted in aluminum at least as long ago as the Nakla meteorite which has an age of 1.3 Ga. The various terrains from which the ISM analyses have been performed have stratigraphic ages of Early to Late Hesperian. Adopting a conservative cratering curve provides an absolute age of between 2 and 3 Ga. Thus these results from the remote sensing show that the mantle of Mars was depleted in aluminum by at least 2-3 Ga ago. In the next year, these results will be synthesized with previous work and submitted for publication to provide a pre-Mars Global Surveyor view of the pristine composition of martian volcanics.

### *Analysis of Alteration in Transitional Soils*

Several outstanding science questions for Mars concern the chemical and physical pathways of alteration and weathering. From the ISM analyses, the regional characteristics and diversity of weakly altered and heavily altered materials have been identified and mapped (Mustard, 1995; Murchie et al., 1993). Areas on the surface that contain spectral properties intermediate between these endmembers compositions have also been mapped. Spectra from these areas have been analyzed to determine if the difference between insitu alteration and simple mixing between the compositional endmembers can be resolved. In most cases, spectra of intermediate materials are simply mixtures, either linear or nonlinear, between the weakly altered and heavily altered endmembers. The principal exceptions are dark red soils (discussed below) and mixing as thin coatings. Although neither mixture model accounts for the increase in spectral slope caused by thin coatings of ferric material, initial modelling of two postulated alteration sequences, one from Syrtis Major and one from Eos Chasma, with the MGM is very promising as a technique to explicitly model the substrate beneath a thin coating (Mustard and Sunshine, 1995; ).

### *Dark Red Soils*

Thermal inertia, radar, and Viking color data have been cited as supporting evidence that dark red regions are simple mixtures of bright red and dark gray material, indurated to a variable extent by duricrust (Arvidson et al., 1989; Christensen and Moore, 1992). However, comparative analysis of dark red units with dark gray and bright red regions using ISM data indicates that dark red units cannot be adequately modeled as mixtures of dark gray and bright red materials (Mustard, 1994; 1995). Mixtures have a 2.1  $\mu\text{m}$  pyroxene absorption band, not observed in spectra of dark red units, and cannot fit the absorption near 1.0  $\mu\text{m}$ . The flat spectral slope, distinct shape and position of the 1.0  $\mu\text{m}$  band, and lack of any pyroxene-related absorptions near 2.1  $\mu\text{m}$  observed in ISM spectra of dark red regions are consistent with several ferric oxyhydroxides such as ferrihydrite, jarosite, and goethite.

An assemblage of ferric oxyhydroxides, sulphates, and clay silicates is a reasonable model for martian duricrust. Viking lander measurements of soil and duricrust composition are readily

accommodated by these mineral components (e.g. Clark et al., 1982; Banin et al., 1992). Mechanisms for duricrust formation are not well understood (discussed in greater detail below), but may involve groundwater derived from weathering of iron-rich basalts (Burns and Fisher, 1993) or hydrothermal processes, or surface-atmosphere exchange of volatiles on the year to millennial time scales (Jakosky, 1986; Melon and Jakosky, 1995). Regardless, ferric oxyhydroxides within this assemblage are thermodynamically unstable relative to hematite under present surface conditions (Gooding, 1978). They may exist metastably, however if the kinetics of dehydration reactions are sufficiently slow, as would be expected in a cemented soil. This new perspective for soils on Mars, is still in the early stages of development. If it is correct, however, it has very important implications for physical and chemical pathways for alteration and weathering, surface-atmosphere and surface-subsurface interactions, and exchange of volatiles between reservoirs.

### **Effects of Hyperfine Particles on Vis-Mid IR Spectra**

Most of the systematic work on the spectroscopy of rocks and minerals have been conducted on samples with well sorted grain sizes or grain size distributions, generally with grain sizes  $>45 \mu\text{m}$  in size (e.g. Clark et al., 1991; Salisbury et al., 1992). In addition, there have been several systematic studies of the effects of particle size on spectra, where the finest fraction analyzed is generally a bulk separate  $<45 \mu\text{m}$ , or perhaps  $<25 \mu\text{m}$  (e.g. Crown and Pieters, 1987; Salisbury and Wald, 1992; Moersch and Christensen, 1995). There have few systematic studies of the effects of particle sizes  $<25 \mu\text{m}$ , largely because of the difficulty in extracting narrow separations of fine particles. However, this is a critical particle size region for remote sensing of Mars, the Moon, and other bodies in the solar system, since comminution and weathering process produce an enormous amount of material in this size range. For example, on Mars estimates for the size of the dust generally lie around  $1 \mu\text{m}$ . Particles in this size range also happen to be approximately the same size as the wavelength of the visible to mid-infrared radiation used extensively in the remote sensing of planetary surfaces. While models of reflectance and emittance for particulate surfaces where the particles are much larger than the wavelength of light are well established (e.g. Hapke, 1993; Hapke, 1996), such modelling becomes more complicated when particle size and wavelength are approximately the same size (e.g. Moersch and Christensen, 1995; Wald and Salisbury, 1995). It is therefore a critical area of understanding for which systematic studies and well controlled data are necessary.

We have recently completed and investigation of the effects of extremely fine particles ( $<25 \mu\text{m}$ ) on reflectance and emittance spectra from the visible to mid-infrared (Mustard and Hays, 1996). Narrow  $5 \mu\text{m}$  size fractions from  $0\text{-}25 \mu\text{m}$  were obtained of the minerals olivine and quartz. Reflectance spectra of the separates were measured with RELAB ( $0.3\text{-}25 \mu\text{m}$ ), and the olivine separates in J. Salisbury's directional hemispherical instrument ( $6\text{-}15 \mu\text{m}$ ), and emittance spectra with P. Christensen's emittance spectrometer ( $7\text{-}15 \mu\text{m}$ ). Spectra from all three systems exhibit important, fundamental effects, primarily due to particle size, which have not been previously reported. We find that when the wavelength of light approaches the dominant particle size of a given separate, the reflectance undergoes a steep decline. We also observe that the wavelength of maximum reflectance for the transparency feature is shifted systematically to shorter wavelengths with decreasing particle size. Finally, systematic changes in the relative strength and shape of absorptions in the restrahlen bands were observed.

The basic thrust of the research in the last year has been to develop a theoretical understanding for these observations and write the results up for publication. This paper has recently been re-submitted to *Icarus* and should be accepted for publication shortly. The basic observations can be understood through application of Mie theory for particles sizes wavelength of light. An equation for the critical diameter for the change to a Mie-type scattering was developed and shown to be relevant to many of the observations. These results were then taken farther and a Mie-Hapke hybrid scattering model for olivine and quartz particulate surfaces was developed, largely similar to that developed by Moersch and Christensen (1995).

These results have led to some new insights into reflectance spectroscopy, and will help to understand data from future missions. More importantly, the observations have implications for qualitative and quantitative analysis of remote sensing data. In particular, the correlation between transparency and Christiansen features for compositional determinations (Walter and Salisbury , 1989) needs to be re-evaluated, while the large reduction in scattering efficiency for small particles, and thus spectral contrast, may complicate some simple methods of analysis that rely on correlations between remotely identified spectral features and those observed in spectral libraries. Another consequence is that quantitative spectroscopic models need to accommodate a range of particle sizes, similar to that expected in natural soils. As an outgrowth of this study, we will continue to make observations of hyperfine particles. Observations to date have focused on silicate minerals for which optical constants were available. Our future studies are to include materials and samples more relevant to the surface of Mars. In particular, we are interested in hyperfine smectite clays and ferric oxides and oxyhydroxides. These will be prepared from laboratory samples, and also separated from natural samples we have collected from Hawaii of weathered basalt and basaltic glass. We will also be continuing the modelling efforts, with increased emphasis on developing more predictive capabilities that will lead to a better understanding of hyperfine particles on reflectance spectra and a capacity to model these effects.

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