A model for formation of dust, soil, and rock coatings on Mars: Physical and chemical processes on the Martian surface

Janice L. Bishop,1 Scott L. Murchie,2 Carlé M. Pieters,3 and Aaron P. Zent4

Received 31 August 2001; revised 14 February 2002; accepted 18 April 2002; published 6 November 2002.

A model is presented here to explain the generation of surface material on Mars using chemical, magnetic, and spectroscopic data from Mars and geologic analogs from terrestrial sites. One basic premise is that the dust/soil units are not derived exclusively from local rocks, but are rather a product of global, and possibly remote, weathering processes. Another assumption in this model is that there are both physical and chemical interactions of the atmosphere with dust particles and that these two processes create distinctly different products. Physical processes distribute dust particles on rocks and drift units, forming physically aggregated layers; these are reversible processes. Chemical reactions of the dust/soil particles create alteration rinds on rock surfaces and cohesive, crusted surface units between rocks, both of which are relatively permanent materials. According to this model the dominant components of the dust/soil particles are derived from alteration of volcanic ash and tephra and contain primarily nanophase and poorly crystalline ferric oxide/oxyhydroxide phases as well as silicates. These phases are the alteration products that formed in a low-moisture environment. These dust/soil particles also contain a smaller amount of material that was exposed to more water and contains crystalline ferric oxides/oxyhydroxides, sulfates, and clay silicates. These components could have formed through hydrothermal alteration at steam vents or fumeroles, thermal fluids, or through evaporite deposits. Wet/dry cycling experiments are presented here on Mars soil analogue mixtures containing poorly crystalline and crystalline components dominated by nanophase to ~2 μm diameter particles. Cemented products of these soil mixtures are formed in these experiments, and variation in the surface texture was observed for samples containing smectites, nonhydrated silicates, or sulfates. Reflectance spectra were measured of the initial particulate mixtures, the cemented products, and ground versions of the cemented material. The spectral contrast in the visible/near-infrared and midinfrared regions is significantly reduced for the cemented material compared to the initial soil and somewhat reduced for the ground, cemented soil compared to the initial soil. The results of this study suggest that transient fluvial activity on Mars will have a profound effect on the texture and spectral properties of the dust/soil particles on the surface. The model developed in this study provides an explanation for the generation of cemented or crusted soil units and rock coatings on Mars and may explain albedo variations on the surface observed near large rocks or crater rims.

INDEX TERMS:


1. Introduction and Background

[2] This paper describes analysis of the spectral, chemical and magnetic data from Mars Pathfinder soil, together with analog materials and the products of laboratory alteration experiments, in order to describe possible mechanisms for the formation of drift, cemented soil and rock coatings on Mars. Soil analog mixtures have been prepared, characterized and tested through wet/dry cycling experiments for
changes in binding and spectroscopic properties that are related to what could be expected for cemented soil units on Mars. Hydrothermal and solfataric alteration of volcanic tephra frequently produces reactive sulfate species that may attack the surfaces of dust particles and rocks to form cemented soil units and rock coatings. This idea is pursued here. Recent magnetic, chemical, spectral and imaging data from Mars Pathfinder suggest that surface alteration and/or weathering has taken place on Mars and that there may be coatings on the rocks resulting from these processes [Madsen et al., 1999; McSween et al., 1999; Bell et al., 2000]. Combining these results from Pathfinder with results from laboratory studies [e.g., Bishop et al., 1995, 1998a; Bishop and Murad, 1996; Banin et al., 1997; Morris et al., 1997, 1998, 2000, 2001] provides the clearest picture of the mineralogy and potential alteration processes on Mars.

1.1. Composition of Martian Surface Rocks and Soils

Characterization of the composition of Mars has been approached through telescopic observations as well as instruments on landers and orbiters. The spectral properties of bright and dark regoliths on Mars have been summarized by Söderblom [1992] and Roush et al. [1993] and of alteration minerals on Mars by Bell [1996]. More recent spectroscopic analyses of Mars have shown that global rock compositions are basaltic to andesitic [Bandfield et al., 2000; Christensen et al., 2000b], that coated rocks are present at the boundaries of bright regions in Arabia and Tharsis [Murchie et al., 2000a], and that a large region of specular gray hematite is present in Sinus Meridiani [Christensen et al., 2000a, 2001a]. Thermal inertia data measured by Viking indicate that regional dust deposits are found on Mars at Arabia, Tharsis and Elysium [Christensen, 1986]. More recent thermal inertia data from the Thermal Emission Spectrometer (TES) on Mars Global Surveyor (MGS) have enabled mapping of global dusty regions [Mellon et al., 2000] and a newly reported boundary for much of the dusty regions that may consist of well-indurated duricrust [Christensen et al., 2001b]. These indurated regions identified by Christensen et al. [2001b] as having intermediate inertia and albedo are consistent with the areas found by Murchie et al. [2000a] to have intermediate near-infrared brightness and band depths, plus a negative slope, which are attributed to coated rocks.

The Viking landers in Chryse Planitia and Utopia Planitia provided evidence of fine-grained drifts and blocky material superposed on a rocky substrate, impact crater rims, slow erosion rates of rocks and surface material, soil redistribution, surface condensate formation, and freeze-thaw processes in some regions on the surface [Binder et al., 1977; Mutch et al., 1977; Jones et al., 1979; Arvidson et al., 1989]. Thin layers of dust were observed to accumulate at both sites during the first two Martian years [Arvidson et al., 1989]. The MPF site is located at Ares Vallis in a rocky transition region between typical bright and dark regions [Golombek et al., 1997]. The chemical and mineralogical compositions of the rocks near the Mars Pathfinder (MPF) lander indicate that they are andesite-basaltic and that many rocks are covered with alteration rims [McSween et al., 1999]. Analysis of the Pathfinder soil units has shown that they are chemically and mineralogically distinct from the rocks, and that they may contain goethite, maghemite or other iron oxyhydroxides [Bell et al., 2000], but do not show the expected evidence for crystalline hematite based on previous telescopic measurements of Mars [Bell et al., 1990]. Chemical mixing models have shown that simple soil-rock mixing scenarios are inadequate to explain the chemical composition of the Martian rocks and soils [McLennan, 2000; McSween and Keil, 2000] and that the global dust on Mars resulted from weathering of basaltic rather than felsic rocks [McLennan, 2000; McSween and Keil, 2000; Morris et al., 2000].

The magnetic tests on the Viking and MPF landers indicated the presence of a magnetic component intimately mixed with nonmagnetic components, such as silicates, in the dust/soil particles [Hargraves et al., 1977; Pollack et al., 1977; Hviid et al., 1997; Madsen et al., 1999]. Saturation magnetization, $J_s$, has been estimated from the magnetic experiments on the MPF lander and depends on the assumed particle density, Madsen et al. [1999] estimate $J_s$ at 4 ± 2 Am$^2$/kg, while Morris et al. [2001] estimate $J_s$ at 2.5 ± 1.5 Am$^2$/kg. A few wt.% Fe$_2$O$_3$ as maghemite [Hargraves et al., 1977; Hviid et al., 1997; Madsen et al., 1999] and magnetite/titanomagnetite [Pollack et al., 1977; Morris et al., 2000] have both been proposed as the magnetic minerals present in the Martian dust/soil based on these data, leaving the bulk of the iron in the Martian dust/soil in ferrous silicates or nonmagnetic (probably nanophase) ferric oxides/oxyhydroxides.

1.2. IMP Spectra

The Imager for Mars Pathfinder (IMP) has produced numerous spectra of specific rock and soil units near the lander [Smith et al., 1997]. These spectra have been recalibrated and compared with both chemistry and viewing geometry in a recent study [Bridge et al., 2001]. Spectral analyses of laboratory soil analog materials and several soil units measured by the IMP showed that there are specific differences in the soils observed by Pathfinder that are attributed to differences in mineralogy and composition of the soils [e.g., Bishop et al., 1998d; Bell et al., 2000; Morris et al., 2000]. Specifically, many of the soils are characterized by a smooth upward slope from 0.5 to 0.7 μm and a broad maximum near 0.75–0.80 μm. Some soil units have a stronger shoulder feature near 0.6 μm and some exhibit a weak, broad band near 0.9 μm. Variations in the chemical abundances of these soils indicate a good correlation of wt.% SO$_3$ with the red/blue reflectance ratios [Bridge et al., 2001]. This suggests that the ferric minerals responsible for the reflectance maximum near 0.75 μm are correlated with sulfates in the soils. Ratios of numerous spectral parameters have been performed in order to characterize the subtle variations in the IMP spectra and are summarized by Bell et al. [2000].

The spectral features observed in the extended visible region are due to electronic transitions and charge transfer bands [Morris et al., 1985; Sherman and Waite, 1985; Burns, 1993]. Spectral analysis using second derivatives is useful for identifying minerals in mixtures from their specific crystal field splitting parameters and electronic transitions [Scheinost et al., 1998]. A study involving spectral analysis with second derivatives of Martian soil spectra and analog soil spectra enabled determination of the $^6A_1 \rightarrow ^4T_{2g}$ and $^6A_1 \rightarrow ^4T_{2g}$ electronic transitions and crystal field splitting...
parameters [Bishop et al., 1998d]. This enabled separation of groups of iron oxyhydroxide-silicate aggregates according to both chemical conditions during formation and sulfate content. This study showed that the spectral character of many of the Martian soils measured by IMP includes a reflectance maximum near 0.8 μm that is consistent with nanophase ferric oxides/oxyhydroxides. It also demonstrated variability in the shape of the 0.6 μm shoulder feature that would be consistent with variable abundance of a sulfate (e.g., schwertmannite, jarosite) or goethite. A related study of Martian rocks measured by IMP attributed this ~0.6 μm shoulder to the presence of goethite or sulfate minerals in the rock coatings [Barnouin-Jha et al., 2000].

If magnetite is also a soil component it could be responsible for weakening the ~0.9 μm absorption characteristic of ferric oxides. Preliminary analyses (unpublished spectral mixing experiments) indicate that adding the ~6% maghemite estimated for the Martian soils near the MPF lander [Hvid et al., 1997; Madsen et al., 1999] would not greatly alter the spectral character of these samples. Natural soils containing magnetite are darker than otherwise similar samples, exhibit a weaker 0.9 μm band and a broad, shallow absorption centered near 1.5 μm [Scheinost et al., 1998; Morris et al., 2000]. Morris et al. [2000] further observed that the finest size fractions of altered tephra become darker with increasing magnetic susceptibility due to the presence of magnetic Fe,Ti-oxides.

1.3. Terrestrial Alteration of Volcanic Tephra/Ash

Recent studies of the fine-grained fractions of volcanic material indicate that there are multiple alteration processes taking place: palagonitic, pedogenic or solfataric alteration of volcanic tephra, ash or lava [e.g., Morris et al., 1993, 1996, 2000; Bishop et al., 1998a, 2002; Schiffman et al., 2000, 2002]. Long-term palagonitic weathering of volcanic tephra in a dry environment have been contrasted with the more rapid and/or intense solfataric alteration in the vicinity of steam vents and cinder cones [Bishop et al., 1998a]. Solfataric (or sulfatetic) alteration indicates that sulfuric fumes from cinder cones, fumeroles and volcanic exhalations of H₂S or hydrothermal waters containing H₂SO₄ or sulfate ions, are actively participating in the alteration process. Palagonitic weathering involves hydration and vitrification of basaltic glass to form fine-grained and poorly crystalline ferric oxides/oxyhydroxides and silicate phases under low-temperature and low-moisture conditions, with the formation of smectite and serpentine clay minerals under higher temperature and higher moisture conditions [e.g., Bates and Jackson, 1984; Bishop et al., 2002; Morris et al., 2001; Schiffman et al., 2002]. The solfatarically altered tephra often contain significant amounts of crystalline iron oxides/oxyhydroxides and jarosite/alunite, while the palagonitic tephra tend to contain poorly crystalline and/or nanophase minerals. Recent studies included chemical, mineralogical and spectroscopic analyses of jarositic tephra from Mauna Kea [Morris et al., 1996], from a cinder cone in the Haleakula crater basin [Bishop et al., 1998a], and from the Kilauea region [Morris et al., 2000]. Analysis of Martian bright region spectra and spectra of sulfate minerals formed in terrestrial steam vents or fumeroles found that a number of these alteration products are consistent with the visible/near-infrared (NIR) spectra of Mars [Calvin et al., 1999]. Potential factors contributing to ferric oxide/oxyhydroxide formation along with jarosite and other sulfates in such soils include the temperature and composition of the volcanic gases, duration of hydrothermal exposure, and oxidation following hydrothermal alteration.

Palagonitic alteration of glassy basalts and andesites has been characterized using a variety of geochemical and mineralogical techniques [e.g., Colman, 1982; Staudigel and Hart, 1983; Nesbitt and Young, 1984; Fisher and Schminke, 1984]. These studies have shown that volcanic glass and olivine are generally the least stable components of basaltic deposits, while Fe,Ti-oxides are the most resistant to alteration. According to these and other studies, the typical low-temperature alteration products of mafic volcanic rocks are a mixture of short-range ordered aluminosilicates (e.g., allophane and imogolite), amorphous iron oxides/oxyhydroxides, and poorly crystalline and crystalline clay minerals (including smectite and kaolinite). Palagonitization and formation of weathering rinds on basalts and andesites are also accompanied by large reductions in Ca, Mg, Na and K, depletion in Si, oxidation of the Fe, and incorporation of water [e.g., Fisher and Schminke, 1984].

1.4. Possible Alteration Scenarios on Mars

Our model is based upon mixing and distribution of dust/soil components and chemical reaction of selected species in the dust/soil particles. The aeolian processes invoked for our model are similar to patterns of dust deposition and removal described by McSween et al. [1999] in order to explain variable rock coatings. Our model is distinct from others presented recently including "acid-fog" weathering, where atmospheric aerosol particles are the active force behind chemical alteration of rocks [Settle, 1979; Banin et al., 1997] and hydrothermal fluids (neutral chloride and acid-sulfate) associated with impact events or volcanism as a source of the mobile elements in the soil [Newsom et al., 1999]. Our model involves chemical reactions of minerals and alteration phases in the dust/soil. Other alteration scenarios that have been described as potentially contributing to soil formation on Mars include chemical alteration of Martian meteorite-like rocks [Dreibus et al., 1998; Brückner et al., 1999; Wänke, 1999], partial palagonitization of volcanic ash [Morris et al., 2001] and physical alteration of rocks [Bridges et al., 1999; Ruff and Christensen, 1999]. Impacts have also been suggested as mechanisms of producing glassy alteration products containing ferric oxides on Mars [Morris et al., 1995; Schultz and Mustard, 1998; Minitti and Rutherford, 2000; Yen, 2001].

These potential alteration scenarios are built upon observations of Mars and evidence for water, condensates, dust and duricrust on the surface. Early studies of Mars suggested the possibility of water and/or ice on the surface [Salisbury, 1966; Anderson et al., 1967; Wade and de Wys, 1968; Masursky, 1973; Baker and Milton, 1974]. Analysis of the channels in Viking images led Masursky et al. [1977] and Carr [1979] to suggest the possibility of fluvial activity. Seasonal reservoirs of water and ice have been described in terms of interactions with the regolith, ice caps and atmosphere [Jakosky, 1983a, 1983b; Hart and Jakosky, 1986; Kahn, 1990; Svitk and Murray, 1990]. Squyres et al.
water and/or redox reactions of Fe

chemical processes (e.g., chemical reactions of the sulfates 

rocks, (2) physical processes (e.g., wind, dust devils) "soil" covering the tops of rocks and the surface in between 
surface of Mars, and are compositionally similar to the 
suspended in the atmosphere on Mars are redeposited on the 
include interactions between ice and the dust particles [Gooding, 1986; Saunders et al., 1986]. Sulfate aerosol calculations indicate that they may have formed globally on Mars from surface volcanism and that these sulfate aerosols would be suspended with ice condensates and dust particles in the atmosphere for long periods [Settle, 1979]. Dust has long been observed to be active on the surface of Mars [e.g., Martin et al., 1979; Pollack et al., 1979; Colburn et al., 1989] and analysis of Viking images produced evidence of optically dense dust clouds and much smaller features that may include dust devils [Briggs et al., 1977, 1979]. A large number of dust devils were later identified on Mars by evaluating selected Viking orbiter images for transient small, elongated clouds with nearly vertical orientation [Thomas and Gierasch, 1985]. Cemented soil or duricrust units were first observed on the surface of Mars near the Viking landers [Binder et al., 1977; Mutch et al., 1977]. Analysis of radar and thermal inertia measurements on Mars were best explained by a global distribution of duricrust in a study by Jakosky and Christensen [1986]. They cite the presence of water and migration of salts as contributing to the duricrust formation.

2. Model Outline

A model was developed that describes potential mechanisms of rock coating and duricrust formation on Mars [Bishop et al., 1999]. We acknowledge that the data available at this time are insufficient for unique determination of any given surface model and we are proposing this as one of many possibilities for consideration. This model states that (1) the ~2 µm sized “dust” particles that are suspended in the atmosphere on Mars are redeposited on the surface of Mars, and are compositionally similar to the “soil” covering the tops of rocks and the surface in between rocks, (2) physical processes (e.g., wind, dust devils) primarily govern distribution, aggregation and disaggregation of the dust, soil and dust layers on rocks, and (3) chemical processes (e.g., chemical reactions of the sulfates with the ferric oxide and silicate surfaces in the presence of water and/or redox reactions of Fe²⁺/Fe³⁺) are primarily responsible for the formation of rock coatings and duricrust and that once formed, these chemical layers cannot be simply disaggregated by the wind. This model has been refined and expanded into the present form and has the advantage that it incorporates both chemical and physical processes observed on Mars in previous studies and, further, that it builds on alteration processes observed in the field and laboratory.

In this model for surface alteration on Mars volcanic steam vents and hydrothermal activity associated with volcanism are primarily responsible for the production of crystalline, Fe and S-bearing minerals such as hematite, maghemite/magnetite, and jarosite/alunite. Evaporite deposits may be another source of sulfates and salt minerals. These minerals form in high concentrations (~ half of the composition of the altered ash/soil) in specific locations – abundant, yet not ubiquitous. In contrast, palagonitic alteration of volcanic ash is more common and prevalent, and results in nanophase Fe oxide phases, poorly crystalline clays and/or protoclyays (e.g., allophane and imogolite), poorly crystalline grains of feldspar and pyroxene, and tiny glass particles. Aeolian mixing of these two alteration materials produces a nonhomogenous but regionally similar, fine-grained material. This explains the subtle differences in dust/soil composition measured at the Viking and Pathfinder lander sites [Clark et al., 1982; Bell et al., 2000; Bridges et al., 2001; Foley et al., 2001].

2.1. Physical Interactions

Mars sustains periodic large-scale dust storms that can vary in size and intensity up to complete global coverage. A persistent background optical depth of 0.3–1.0 was measured at the Viking Lander sites for visible wavelengths [Pollack et al., 1979]. Changes in atmospheric pressure, temperature and wind direction measured by Schofield et al. [1997] were consistent with dust devils passing the Pathfinder lander. These events were described as small-scale convective vortices lasting for a few minutes or less at the lander position and accompanied by a pressure drop of ~0.03 mbar in the seconds preceding a local temperature maximum, followed by a return of the atmospheric pressure. Wind tails have been observed at the Viking and MPF landing sites and suggest that aeolian processes have been active [Arvidson et al., 1989; Greeley et al., 1993, 1999]. Localized dust devils have been identified on Mars in images taken by Viking [Thomson and Gierasch, 1985], Pathfinder [Metzger et al., 1999] and MOC [Edgett and Malin, 2000]. A mean dust particle size at the MPF lander site of ~1.6 µm in radius was determined from pressure changes and calculations of dust loading [Smith and Lemmon, 1999; Tomasko et al., 1999], which was also observed at the Viking sites [Pollack et al., 1995]. Evidence for aeolian distribution of dust particles on Mars has been observed in nearly every measurement/experiment suggesting that it is a pervasive surface process [Greeley et al., 1999]. Metzger et al. [1999] estimated that a dust devil located on the southern flank of the South Twin Peak had a vortex 14 m wide by 230 m high and a ground speed of 0.5 m/s. This indicates that dust transport is a dynamic process, even at the small spatial scales of the MPF landing site and the small temporal scales of the three month MPF mission.

According to our model dust particles settle on the rocks to form physical dust coatings (a thin layer sprinkled on the surface) and cover the surfaces in between rocks to form drift deposits on Mars. The physical coatings and drift units in this model are compositionally similar to the atmospheric dust particles; the primary difference is that the drift deposits and rock coatings contain larger aggregates of dust particles, held together by electrostatic or physical forces. We suggest that these local dust devils
could be disaggregating and suspending soil particles and redistributing them as 1–3 μm sized dust particles. We further suggest that there is a reversible interaction between these dust particles suspended in the atmosphere and the soil particles covering the surface. As long as the particles are kept in motion and are prevented from forming chemical bonds, they can be readily disaggregated and/or redistributed. A diagram of this process is shown in Figure 1, where particles can be transformed from atmospheric dust to drift and from atmospheric dust to physical rock coatings and back to dust again with the next dust devil or dust storm.

[18] Spectral and chemical evidence from Mars Pathfinder revealed that many of the surface soil units are compositionally similar, and that spectral differences for many units are thought to be due to grain size and compaction [Bell et al., 2000]. The “brown” soil unit is among those that are compositionally distinct from the primary soil type near the MPF lander. The spectral properties of dust particles suspended in the atmosphere near MPF appear different from spectral properties of the drift deposits, especially in the blue wavelengths [Thomas et al., 1999; Bell et al., 2000]. However, the spectral properties of suspended particles are not well characterized because they are difficult to measure and would include scattering through greater distances than for dust deposited on a surface, so this is not necessarily inconsistent with our model.

[19] McSween et al. [1999] suggest based on laboratory studies that coatings of drift material on rocks near the MPF site may be responsible for some of the rock spectral variability [Fischer and Pieters, 1993; Johnson, 1999; Morris et al., 2000]. Rock coatings were suggested in earlier studies as well to explain the Viking lander multispectral observations [Adams et al., 1986; Guinness et al., 1987]. Fischer and Pieters [1993] showed that an optically thin coating of fine-grained ferric particles on a dark neutral substrate (e.g., basalt) induces an increase in the visible/NIR region reflectance and the red/blue ratio, and produces ferric absorption bands. Johnson and Grundy [2001] found that the NIR spectral properties of thin dust layers on a basalt substrate are difficult to model because of the wavelength dependence of the single-scattering phase function, thus supporting the need for additional laboratory studies. Thin coatings of fine-grained, altered volcanic ash were also observed to influence the mid-IR reflectance and emission spectra of basaltic rocks [Crisp and Bartholomew, 1992; Johnson, 1999]. Crisp and Bartholomew [1992] found that a layer 25 μm deep of fine-grained ash on basalt suppressed the silicate bands near 10 and 19 μm by about 50%. Based on these studies a layer as thin as a few microns is sufficient to induce measurable changes in the visible/NIR and mid-IR spectral properties of basalts. Analyses of the effect of thin dust coatings on the rock chemistry showed that the rock “Wedge” would have a silica content of 56% and a S content of 0.1% after removing a thin layer of A5 composition dust [Crisp, 1998].

2.2. Chemical Interactions

[20] In contrast to physical aggregates of particles, chemical interactions of dust particles in the soil or on rock coatings form more permanent, cemented products. These are shown as irreversible pathways in Figure 1 and this process requires the formation of chemical bonds. These bonds can be broken again, but this would require a more active process than simply a dust devil. Sand abrasion that forms ventifacts on rock surfaces [Bridges et al., 1999], for example, would be sufficient to remove rock varnishes. Shown in Figure 2 are examples of the kinds of bonds that may be formed when the physical dust layer is transformed into a chemically bound cemented soil or rock varnish. Sulfates or ferric oxides/oxyhydroxides are likely to be the binding agents in these chemically bound materials.

[21] Sulfate species are particularly reactive because of their polar nature, as are Fe³⁺ bearing phases because they readily accept electrons. For these reasons dust/soil particles containing ferric oxides/oxyhydroxides and jarosite/alunite would be particularly reactive even on the dry surface of Mars. If these dust particles are allowed to remain undis- turbed on the surfaces of rocks sufficiently long to enable chemical reactions between the ferric, sulfate and salt species and the primary rock minerals, then alteration rinds are expected to form that may be resistant to dust devils or wind storms. Although interactions of the dust particles in this manner may explain observations of cemented soil units
and rock coatings near the Viking and Pathfinder landers, this process, if it indeed occurs, would be expected to be more widespread on the surface of Mars. Only minimal water is required for these chemical reactions (given long timescales), and this could be provided via atmospheric water ice particles. Evidence for these exists through diurnal variations in the atmosphere observed using data from the Viking orbiters [Farmer et al., 1977], telescopic observations [Sprague et al., 1996], ISM on the Russian orbiter [Titov et al., 1995] and MPF lander [Smith and Lemmon, 1999]. Hart and Jakosky [1986] estimated an ice condensate thickness of 10 μm near the Viking lander 2 site and estimated stability of this condensate for much of the colder season through cycling of daily sublimation and nightly recondensation. Models of atmospheric water vapor, ice haze and water in the soil layer on Mars suggest that dust particles may be nucleating water frost condensation and, further, that ice hazes appear to play a major role in the seasonal water cycle on Mars [Kahn, 1990]. Laboratory experiments and theoretical analysis of dust-ice nucleation indicate that molecular structure, chemical bonding and the nature of active sites are important factors [Gooding, 1986]. This study suggested that a number of clay minerals would be good nucleators of water ice on Mars and that glass and palagonitic material would be poor ice nucleators. Saunders et al. [1986] performed laboratory experiments on montmorillonite-ice condensates and sublimes, and found that sublimated montmorillonite—ice particles became stronger, more flexible and more elastic. Calculations on the montmorillonite-water system under current Martian conditions [Anderson et al., 1967] indicate that a monolayer of adsorbed liquid water would be present on montmorillonite grains, followed by ice at higher hydration levels.

[25] Chemical reactions would have progressed much faster on Mars in the presence of liquid water than under current conditions. Although there is no direct evidence of past liquid water on Mars, hypotheses for liquid water abound. As described earlier, Carr [1979, 1981] and others have suggested that abundant flowing water best explains the many runoff and outflow channels depicted in Viking images of Mars. Analyses by Baker et al. [1991], Clifford [1993], and Parker et al. [1993] support the presence of aqueous processes and perhaps sedimentary deposits and an ancient ocean on Mars. Recently observed erosional features on Mars have been explained by groundwater seepage and surface runoff [Malin and Edgett, 2000b] and sedimentary deposits [Malin and Edgett, 2000a]. Nonaqueous explanations have also been submitted for these Martian surface features [e.g., Hoffman, 2000; Musselwhite et al., 2001], and a number of scenarios involving aqueous and subaqueous processes on Mars are possible; thus, consideration of potential chemical alteration mechanisms is warranted.

3. Laboratory Alteration Studies

[24] Samples for this study were prepared by combining powders of sulfate-bearing volcanic soils and magnesium sulfate with either iron oxyhydroxide-montmorillonite aggregates or fine-grained altered volcanic ash. All endmembers were dry sieved to <45 μm prior to mixing. Mixing was performed by combining the specified amount of each component, shaking the particles, and dry sieving the mixture to <125 μm particle size. The sulfate-bearing soils are examples of products forming from solfataric alteration and the magnesium sulfate is an example of what could form through an evaporite deposit on Mars. The first mixture (Mix-1) contains 70 wt.% of sample jb11 (synthetic iron oxyhydroxide-montmorillonite aggregate soil, from Bishop et al. [1995]), 10 wt.% of sample jb250 (sulfate-bearing volcanic soil, collected on the rim of a cinder cone, Haleakala crater basin [from Bishop et al., 1998a]), 10 wt.% of sample jb182 (sulfate-bearing volcanic soil, collected near an active steam vent, Santorini, from Bishop et al. [1998a]), and 10 wt.% of hydrated magnesium sulfate (MgSO₄•7H₂O from Fisher Scientific). The second mixture (Mix-2) contains 70 wt.% of sample jb248 (fine-grained altered volcanic ash, Haleakala crater basin, from Bishop et al. [1998a]), and 10 wt.% each of the other three samples as described for Mix-1. The ferric oxyhydroxide-montmorillonite aggregate soil was produced in the laboratory by
exchanging the Ca/Na interlayer cations with Fe using a standard cation exchange procedure; these hydrated Fe complexes react further to form oxyhydroxides [Bishop et al., 1995]. This is a chemical mixture of nanophasic to micron-sized particles bound together. The volcanic soil samples included in these mixtures contain a variety of poorly crystalline, altered phases including nanophasic ferric oxyhydroxide particles, fine-grained sulfates, and silicates. These soil samples include both chemical and physical mixing of nanophasic to micron-sized particles. Shown in Figure 3 is an example of how these chemically and physically mixed particles may appear.

[Bishop et al., 2001] and found to be on the order of what was observed for the dust at the MPF site, and slightly higher for Mix-2 than for Mix-1 (R. V. Morris, personal communication, 1999).

3.2. Reflectance Spectroscopy

[26] Visible-infrared reflectance spectra were measured as described in previous experiments [Pieters, 1983; Bishop et al., 1995]. Bidirectional visible/NIR spectra were measured relative to Halon under ambient conditions at the Reflectance Experiment Laboratory (RELAB) at Brown University. Biconical reflectance spectra were measured relative to a rough gold surface using a Nicolet 740 Fourier transform infrared interferometer (FTIR) in a H2O- and CO2-purged environment. Composite, absolute reflectance spectra were prepared by scaling the FTIR data (~1 nm spectral resolution NIR and ~2 cm⁻¹ spectral resolution mid-IR) to the bidirectional data (5 nm spectral resolution) near 1.2 μm.

3.3. Hydration/Dehydration Cycling Experiments

[27] Wet/dry cycling experiments were performed on four samples: the two new mixtures described here plus each of the dominant end-members for these mixtures. The samples were exposed to repeated cycles of dehydration and rehydration in the laboratory. The samples were hydrated by adding about 500 μl of distilled, deionized water to the sample surface; rehydration was performed by adding 100–300 μl H2O. Dehydration was performed by drying the samples in air, in a desiccator and by heating at low temperature in an oven. These experiments were performed by pouring the freshly dry sieved (fluffy) mixtures into sample dishes 10 mm in diameter, where the samples remained for the duration of the experiment. The specific hydration history for the samples in this study included several steps: dehydration in a desiccator, hydration with H2O, drying in air, dehydation in a desiccator, rehydration with H2O, dehydration in a desiccator, tapping of the dishes in order to break the surface tension of the crust, rehydration with H2O, heating in an oven for 1 hour at 50°C. The degree of moisture used in these experiments is more representative of past climatic regimes on Mars, when liquid water is thought to have been present [e.g., Carr, 1981], than the current one. Chemical reaction of sulfates and oxides in the soil/dust particles is expected to occur more slowly for drier conditions. The timescale for crust formation would vary depending on available water and would require much more data

Table 1. Chemical Composition of Mars Soil and Laboratory Samples

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>40.6</td>
<td>43.7</td>
<td>28.0</td>
<td>54.3</td>
<td>31.9</td>
<td>33.2</td>
<td>23.2</td>
<td>0.0</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.9</td>
<td>0.4</td>
<td>3.8</td>
<td>0.1</td>
<td>5.0</td>
<td>1.3</td>
<td>2.1</td>
<td>0.0</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>9.6</td>
<td>13.9</td>
<td>19.3</td>
<td>16.2</td>
<td>23.9</td>
<td>15.0</td>
<td>10.4</td>
<td>0.0</td>
</tr>
<tr>
<td>Fe₂O₃*</td>
<td>22.3</td>
<td>13.6</td>
<td>18.7</td>
<td>12.0</td>
<td>19.3</td>
<td>9.0</td>
<td>43.2</td>
<td>0.0</td>
</tr>
<tr>
<td>MgO</td>
<td>8.3</td>
<td>3.1</td>
<td>3.1</td>
<td>1.9</td>
<td>1.9</td>
<td>0.1</td>
<td>1.1</td>
<td>16.4</td>
</tr>
<tr>
<td>CaO</td>
<td>5.8</td>
<td>0.5</td>
<td>4.0</td>
<td>0.1</td>
<td>5.2</td>
<td>0.4</td>
<td>3.4</td>
<td>0.0</td>
</tr>
<tr>
<td>Na₂O</td>
<td>3.5</td>
<td>1.3</td>
<td>0.8</td>
<td>1.6</td>
<td>0.8</td>
<td>1.0</td>
<td>1.1</td>
<td>0.0</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.9</td>
<td>0.5</td>
<td>0.6</td>
<td>0.3</td>
<td>0.4</td>
<td>1.6</td>
<td>1.1</td>
<td>0.0</td>
</tr>
<tr>
<td>SO₃</td>
<td>6.1</td>
<td>4.9</td>
<td>5.0</td>
<td>0.0</td>
<td>0.2</td>
<td>10.8</td>
<td>5.8</td>
<td>32.5</td>
</tr>
<tr>
<td>LOI</td>
<td>n.d.</td>
<td>17.9</td>
<td>14.8</td>
<td>14.2</td>
<td>9.9</td>
<td>20.9</td>
<td>7.5</td>
<td>51.2</td>
</tr>
<tr>
<td>Sum</td>
<td>98.0</td>
<td>99.8</td>
<td>98.1</td>
<td>100.7</td>
<td>98.5</td>
<td>93.5</td>
<td>98.9</td>
<td>100.1</td>
</tr>
</tbody>
</table>

*Note: Data are in wt.%, Fe is shown as Fe₂O₃* and includes FeO and Fe₂O₃, n.d. is not determined, LOI is lost on ignition at 850°C, mixture chemistries are calculated from their components, Mars Pathfinder (MPF) soil average is determined from data reported by Foley et al. [2001], iron oxyhydroxide-montmorillonite aggregate (Fe-mont) sample chemistry is from Bishop et al. [1998a].

aPercentages in parentheses refer to the weights of the constituent silicate phases.

bMix-1(364): 70wt% (11) + 10wt% (182) + 10wt% (250) + 10wt% (366).

cMix-2 (365): 70wt% (248) + 10wt% (182) + 10wt% (250) + 10wt% (366).
longer using actual Martian diurnal water variation levels and would thus be impractical for laboratory experiments.

4. Results: Composition and Spectroscopic Properties of Mixtures

Shown in Figures 4 and 5 are visible/NIR and mid-IR reflectance spectra of the two new mixtures and end-member components used in this study. The spectrum of the hydrated magnesium sulfate (MgSO$_4$$\cdot$7H$_2$O) is brightest in the visible/NIR region and the altered volcanic soils are the darkest. Soil Mix-1 (364) is darker than its dominant iron oxyhydroxide-montmorillonite aggregate soil and Mix-2 contains 70 wt.% of palagonitically altered ash from Haleakala.

The mid-IR spectra are shown in Figure 5 in terms of wave number, in cm$^{-1}$, in order to best show the spectral features and facilitate comparison with TES and miniTES spectra. The hydrated magnesium sulfate spectrum has the strongest contrast in this region and the altered volcanic soils exhibit the least spectral contrast. All of the spectra have a water band near 1630–1650 cm$^{-1}$ (~6.1 μm). The magnesium sulfate powder spectrum contains a strong band near 950 cm$^{-1}$ (~10.5 μm) as shown in Figure 5 which is shifted to 1150 cm$^{-1}$ (~8.7 μm) for cemented magnesium sulfate [Cooper and Mustard, 2002]. Silicate bands are observed near 1075–1150 cm$^{-1}$ (~9 μm) and 470–540 cm$^{-1}$ (~20 μm) for Mix-1, the iron oxyhydroxide-montmorillonite (11) and the Santorini soil (182).

Figure 4. Reflectance spectra from 0.3 to 5 μm of the new mixtures and their end-members. Each mixture contains 10 wt.% each of hydrated magnesium sulfate (MgSO$_4$$\cdot$7H$_2$O), and sulfate-bearing volcanic soils from both Santorini and Haleakala. Mix-1 contains 70 wt.% of an iron oxyhydroxide-montmorillonite aggregate soil and Mix-2 contains 70 wt.% of palagonitically altered ash from Haleakala.

Figure 5. Reflectance spectra from 400 to 2000 cm$^{-1}$ (5 to 25 μm) of the new mixtures and their end-members. The mixtures are as described in Figure 4 and in the text.
Comparison of the chemistry, mineralogy and spectral properties of the two soil mixtures prepared for this study shows that although they each are a mixture of related components, there are major differences. Mix-1 contains a large amount of smectite, while Mix-2 contains a very small amount of smectite. Mix-1 has a higher Si abundance and lower Al and Fe abundances compared to Mix-2, and Mix-1 also has a greater LOI value which is consistent with smectites in this sample retaining more water than in Mix-2. Mix-1 has brighter reflectance in the visible/near-IR region and stronger ferric and sheet silicate absorption bands, while Mix-2 has a more broad and rounded water band near 2.9–3.1 μm. In the mid-IR region Mix-1 exhibits more spectral contrast than Mix-2.

5. Results: Influence of Wet/Dry Cycling on Sample Texture and Spectroscopic Properties

Hydration/dehydration experiments were performed in order to test the effect of compositional differences on the formation of cemented crusts and to examine the effects of the resulting textures on the spectral properties of these cemented crusts. Images of the samples taken during this experiment are shown in Figure 10. The pair of smectite-bearing samples (soil Mix-1 and the iron oxyhydroxide-montmorillonite aggregate sample, “Fe-mont”) exhibited swelling and cracking through the hydration/dehydration process as expected for smectites. Little difference was observed due to the addition of a sulfate component for this sample pair. For the palagonitic soil samples the presence of sulfates produced changes in the sample behavior as a function of hydration and dehydration. The palagonitic soil sample (Hal. Soil) showed a small amount of cracking and bubble formation, while the palagonitic soil plus sulfates mixture exhibited additional cracking and bubbling, as well as separation of some of the sulfate material from the sample mixture. The dehydration/rehydration cycling of sulfate-bearing soils appears to induce migration of the sulfate components to the surface. A lighter-colored rim is observed in Figure 10 for Mix-2, image 3, and small white flakes crystallized on the surface.

![Figure 6. Reflectance spectra from 0.3 to 5 μm of two dust/soil analog mixtures (A) particulate samples of fine-grained aggregates passed through a <125 μm sieve, (B) cemented samples hardened into crusts by adding H₂O and drying, and (C) ground crusted samples that were passed through a <125 μm sieve.](image)

![Figure 7. Reflectance spectra from 400 to 2000 cm⁻¹ (5 to 25 μm) of two dust/soil analog mixtures (A) particulate samples of fine-grained aggregates passed through a <125 μm sieve, (B) cemented samples hardened into crusts by adding H₂O and drying, and (C) ground crusted samples that were passed through a <125 μm sieve.](image)
for Mix-2, image 4. These white sulfate flakes became more apparent after the final dehydration cycle, but are not shown in Figure 10. This was not observed for the other samples in this experiment. That sulfates precipitate out of mixtures with silicate upon dehydration was observed in another study [Cooper and Mustard, 2002] where the samples were heated for 20 min at 150 °C in order to retain the sulfate within the cemented crusts. Comparison of the cemented crusts formed from these two different materials showed that a harder, thicker crust (throughout the ~4 mm sample depth) formed for the smectite-dominated material, while a thinner (upper ~1 mm of the sample) and more friable crust resulted for the palagonitic soil (low smectite) based material.

[32] Reflectance spectra are shown of the soil Mix-1 and Mix-2 samples in Figures 6 and 7 for the visible/NIR and mid-IR regions. In each case spectra were measured (A) of the particulate samples of the fine-grained aggregates that passed through a <125 μm sieve prior to the dehydration experiments, (B) of the cemented samples hardened into crusts following the hydration/dehydration experiments, and (C) of the ground cemented samples that were passed through a <125 μm sieve. The smectite-based sample, Mix-1, exhibited much larger differences in NIR brightness as a function of sample texture than the palagonitic soil-based sample, Mix-2. For both samples the spectrum of the initial powder is the brightest, the reground sample is darker and the cracked sample is the darkest. The NIR and mid-IR absorption bands are significantly enhanced in the spectrum of the ground Mix-1 sample compared to the other textures. The influence of sample texture and the presence of sulfates in soils observed here compare well with the recent work by Cooper and Mustard [2002] that explores these parameters in detail. Anhydrous magnesium sulfate was used in that study and strong sulfate bands were observed in the palagonitic soil crusts containing as little as 12.5 wt.% MgSO_4. Weaker sulfate bands are observed in our study because the total sulfate abundance is less than this. The spectrum of the cemented Mix-1 sample includes significantly enhanced Si-O smectite bands near 1075–1150 cm⁻¹ (~9 μm) and 470–540 cm⁻¹ (~20 μm) compared with these bands in the initial and final powders (Figure 7). This suggests that if smectite clays are present in the dust/soil on Mars, miniTES would be most likely to identify them in cemented soil units. The silica bands near 800 cm⁻¹ (~12 μm) are weak in the particulate Mix-1 spectra, and disappear in the cemented spectrum. The water band near 1630–1650 cm⁻¹ (~6.1 μm) in the particulate Mix-1 and Mix-2 spectra become weaker in the cemented spectra and nearly disappears for the Mix-1 cemented spectrum (Figure 7). This decrease in intensity of the ~6 μm water band in the mid-IR region is in contrast with the great increase and broadening of the ~3 μm water band in the NIR region for the cemented Mix-1 and Mix-2 spectra (Figure 6).

[33] TES data of Mars include atmospheric and surface components. Three distinct surface types have been identified to date and are attributed to basalt, andesite and a gray hematite [Bandfield et al., 2000; Christensen et al., 2000a, 2000b]. The Martian basaltic and andesitic components have bands near 900–1100 and 300–500 cm⁻¹ that compare well with bands observed in laboratory spectra of basaltic and andesitic rocks [Hamilton and Christensen, 2000; Hamilton et al., 2001]. The silicate bands observed in spectra of Mix-1 and Mix-2 in this study fall in the same region as the silicate bands in the Martian basaltic and andesitic components and would be difficult to identify in the 3–5 km TES spot size on Mars if present as crusts scattered on the surface between rocks. Cooper and Mustard [2002] found that the sulfate band near 1150 cm⁻¹ varies with both sulfate concentration and cementation in their laboratory experiments. They determined that cemented soil units would need to comprise at least 10% of the area of a pixel in order to be identified in TES data. Recent investigations by Cooper and Mustard [2001] with TES data indicate that sulfate cemented crusts may be present on Mars in several medium albedo regions including Lunae Planum, Isidis, parts of Arabia and others. They argue against evaporation of large-scale bodies of water as the formation mechanism for the sulfate crusts because these units are not found in topographic lows. Their study suggests that the sulfate crusts are widely distributed on the planet, which is consistent with the results of Jakosky and Christensen [1986] and our model presented here.

6. Results: Comparison With IMP Spectra of Martian Soils and Rocks

[34] The bidirectional reflectance data were convolved to Pathfinder Multispectral data using the filter positions and band passes of Smith et al. [1997]. These resampled laboratory spectra of the initial particulate Mix-1 and Mix-2 samples and the ground, cemented crusts of Mix-1 and Mix-2 are shown in Figure 8. The ground cemented crust spectra for both the smectite-based Mix-1 and the palagonitic soil based Mix-2 are darker than their respective particulate spectra measured prior to hydration/dehydration exposure. This suggests that sample texture and the degree of binding of the individual aggregates in the dust/soil particles contribute to the spectral brightness in this region. Particle size and soil texture contribute well-known effects on the spectral properties of soils [e.g., Pieters, 1983]. What is new in this study is a change in spectral properties resulting from repeated hydration/dehydration of soils. The bright, dark and disturbed Mars soil spectra are each an average of multiple IMP point spectra from bright, dark and disturbed soil deposits reported by Yingst et al. [1999]. The spectral character and composition of soils near the MPF lander have been described in detail by Bell et al. [2000] and Morris et al. [2000]. The Fe and S ratio of Mix-2 fall very close to the correlation line for Pathfinder soils reported by Morris et al. [2000, Figure 39] and that of Mix-1 falls somewhat below this line.

[35] Resampled laboratory spectra are also shown in Figure 8 for the two solfataric volcanic soils used as endmembers in the mixtures. The sulfate-bearing Haleakala soil (250) spectrum contains a strong band minimum near 0.86 μm due to hematite and is less consistent with the MPF soil spectra. The character of the sulfate-bearing Santorini soil (182) spectrum includes the stronger curvature (0.6–0.67–0.75 μm) of the disturbed soils shown in Figure 9. Bridges et al. [2001] analyzed the spectral properties of rocks and soils measured by the IMP and compared spectral ratios with Si, Fe, Cl and S abundance of MPF soils and found multiple trends that are best explained by homogeneity in
the soil units. Comparison of trends in many elements with S for soils at the MPF and Viking sites \[McSween and Keil, 2000; Morris et al., 2000\] shows variations in the soil chemistry at the MPF site and between the MPF and Viking sites. Chemical analyses of MPF \[Bell et al., 2000; Foley et al., 2001\] and Viking \[Clark et al., 1982\] soils in other studies also suggest compositional differences between the two sites.

\[36\] Resampled laboratory spectra of the Mix-1 and Mix-2 cemented crusts and ground crusts are shown in Figure 9 along with IMP spectra of rocks near the MPF lander (from Barnouin-Jha et al. [2000] and resampled laboratory spectra of a Martian meteorite (from Bishop et al. [1998b, 1998c]). The gray rocks, i.e., “Shark”, exhibit fairly typical spectral properties in this region for the MPF site, and a few anomalous rocks such as “Black” have also been identified [Murchie et al., 2000b; Bell et al., 2002]. Additional red or pink rocks and others, such as “Maroon” and “Orange”, exhibit unique spectral character and probably contain coatings. “Orange” has an \(\sim 0.6\) \(\mu\)m shoulder and reflectance maximum near \(0.75\) \(\mu\)m that have been attributed to the presence of ferric oxide or sulfate coatings and “Maroon” is brighter and thought to contain an additional ferric component [Barnouin-Jha et al., 2000]. The spectra of Martian meteorite ALH 84001 contain a strong band near \(0.93\) \(\mu\)m due to low-Ca pyroxene [Bishop et al., 1998b, 1998c]. This band is much weaker in spectra of the MPF rocks and may be shifted toward longer wavelengths, which would be more consistent with a high-Ca pyroxene [McSween et al., 1999].

\[37\] The spectrum of a ground portion of Martian meteorite ALH 84001 is brighter than the ALH 84001 chip spectra and has a strong band near \(0.93\) \(\mu\)m and relatively high reflectance near \(0.45\) \(\mu\)m. The spectral character of this particulate ALH 84001 sample near \(0.45\) and \(0.93\) \(\mu\)m are very unlike the Martian soil spectra shown in Figure 8. Typical MPF rocks such as “Shark” may exhibit different
spectral properties from Martian meteorites because they are mineralogically dissimilar or the rocks on Mars may be altered. Pyroxene and other minerals in these rocks may be weathered or the rocks may all contain coatings. Rocks like “Black” are more similar spectrally to Shergottites such as ALH 84001, although the spectrum of “Black” shown in Figure 9 is darker and has a weaker band near 0.9–1.0 μm compared to the ALH 84001 chip spectra. Differences between the typical gray rocks (e.g., “Shark”) and the coated rocks (e.g., red, pink, “Maroon”, or “Orange”), suggest that rock coatings are responsible for brighter reflectance in this region and/or stronger features near 0.6, 0.75–0.8, and 0.9–1.0 μm in the spectra [Barnouin-Jha et al., 2000; Murchie et al., 2000b].

[38] Spectra of the Mix-1 and Mix-2 cemented crusts (“B” in Figure 9) are darker in this region than spectra of the respective ground crusts (“C” in Figure 9). A cemented rock coating formed from something similar to Mix-1, comprising 10–15 wt.% Fe₂O₃ as nanophase Fe³⁺ oxyhydroxide in a silicate-sulfate matrix, could be responsible for the spectral features observed for the rock “Orange”. Experiments involving abrasion of rock coatings by Kraft and Greeley [2000] found that varnishes composed of amorphous silica are resistant to abrasion and if present at the MPF site would be protecting the rocks. They further noted that dust aggregate particles would be ineffective abrasive agents on the surface of Mars. The results of Kraft and Greeley [2000] support the formation of rock varnishes on Mars in accordance with our model of dust aggregates containing ferric oxides and sulfates in a poorly crystalline silicate matrix.

[39] These chemically hardened coatings covering portions of the MPF rock surfaces are expected to be tens to hundreds of microns thick as observed for desert varnish on Earth. Because the spectral properties of altered rocks are distinct from those of cemented soil and appear to contain components due to the rock and the coating [McSween et al., 1999; Morris et al., 2000; Bridges et al., 2001] it is assumed that these rock coatings are not optically thick. McSween et al. [1999] showed that the rock “Scooby Doo” rock coating created from dust similar to Mix-2, comprising 15–20 wt.% Fe₂O₃ as both Fe²⁺ in poorly crystalline silicates or glass and nanophase Fe³⁺ oxyhydroxides in a silicate-sulfate matrix, could be responsible for the spectral features observed for the rock “Maroon”. Experiments involving abrasion of rock coatings by Kraft and Greeley [2000] found that varnishes composed of amorphous silica are resistant to abrasion and if present at the MPF site would be protecting the rocks. They further noted that dust aggregate particles would be ineffective abrasive agents on the surface of Mars. The results of Kraft and Greeley [2000] support the formation of rock varnishes on Mars in accordance with our model of dust aggregates containing ferric oxides and sulfates in a poorly crystalline silicate matrix.

Figure 10. Images of samples in wet/dry cycling experiments. Mix-1 is shown at the top, followed by the iron oxyhydroxide-montmorillonite aggregate sample (Fe-mont) that makes up a substantial portion of Mix-1. Mix-2 is shown next followed by the palagonitically altered Haleakala ash sample (Hal. soil) that makes up a substantial portion of Mix-2. The samples were (1) dried in a desiccator, (2) hydrated with H₂O, (3) dehydrated in the desiccator, and (4) dehydrated in the desiccator following a second hydration cycle.

Figure 11. Drift and cemented soil deposits from (a) a rocky plain in western Iceland in the Laugarvatn mountain range (the red bar is ~1 m), and (b) a cemented deposit of altered volcanic ash in the SW region of the island of Hawaii (the red bar is ~1 m). Fine-grained dust, rocky outcrops and crusted soil were observed in both regions. The surface in Figure 11b was scraped with a plastic trowel to reveal dark, fine-grained material below, shown in Figure 11c. The image of the broken crust is expanded (the red bar is ~10 cm) and includes the region within the white box in Figure 11b.
could be coated by as little as 50 μm of dust and chemical analyses of “Scooby Doo” indicate that it is intermediate between rock and soil. Fischer and Pieters [1993] found that viewing geometry, as well as composition and thickness of dust coatings, influences the spectral properties of fine-grained particles on a rock surface. Spectra measured of a 225 μm thick layer of ferric oxide particles on basalt at incidence and emergence angles of 30° and 0°, respectively, produced a negative slope in the NIR region, while the spectra measured under specular configurations exhibited a much smaller positive slope [Fischer and Pieters, 1993]. The illumination geometry of the rocks at the MPF site, coupled with unknown thicknesses of dust layers or rock coatings, increases the challenge of spectral analysis of these rocks. In general a decrease in reflectance has been observed with increasing phase angle for these rocks [Johnson et al., 1999; Bridges et al., 2001].

7. Results: Physical Evidence in Volcanic Environments

Volcanic ash is observed on Hawaii and Iceland at great distances from the active volcanic centers and is frequently observed as drift and cemented soil deposits. Shown in Figure 11 are examples of the terrain observed in these volcanic regions. Figure 11a is an image taken of a rocky plain in western Iceland in the Laugarvatn mountain range. Fine-grained dust covered most surfaces in this region and multiple, rocky outcrops and crusted soil deposits were also observed. Figure 11b is an image of an orange-colored, cemented deposit of altered volcanic ash in the southwestern region of the island of Hawaii. The ash in this region ranged from orange to light brown to black and at this location the orange crusted material was fixed and the black ash was loosely covering the surface and transported occasionally in the wind. A portion of this crusted material was tapped with a plastic trowel. The crust broke with a small force and revealed slightly darker, loose orange-brown ash underneath as shown in Figure 11c.

Drift deposits on Mars near the MPF lander were described by McSween et al. [1999] and analyses of the drift bedding by Metzger [2000] indicated deposition from multiple wind regimes. Three images of Mars near the MPF lander are shown in Figure 12. A super-resolution image containing Barnacle Bill in the lower right corner is shown in Figure 12a. This image was provided by T. Parker and is similar to that used by Metzger [2000]. The super-resolution images are prepared by deconvolving individual image frames and co-registering the group of images which enabled improved resolution [Parker, 1998]. Directional drift deposits are clearly visible in this image. The material contained in these drift deposits is the fine-grained dust/soil particles transported by aeolian processes. Some of this drift material is blown up onto the upper portions of rocks and may be trapped in crevices or ventifacts where it is less free to be transported away by aeolian forces.

The cemented crusts shown in Figures 11a–11c are terrestrial examples of what may be happening to the undisturbed ash deposits on Mars. Hardened crusts formed in laboratory experiments using fine-grained silicate-sulfate components shown in Figure 10 and reported by Cooper and Mustard [2002] may also explain the “duricrust” and “hardpan” soil units observed by the Viking and Pathfinder cameras [Binder et al., 1977; Greeley et al., 1992; Smith et al., 1997]. Shown in Figures 12b and 12c are images of hardened or cemented soil units near the MPF landing site. Shown in Figure 12b is the rock “Scooby Doo” which appears to be covered by cemented material and has spectral and chemical properties intermediate between the rocks and soil [McSween et al., 1999]. Shown in Figure 12c are disturbed soil in the rover tracks and the rock “Poptart”, which is also thought to be covered by cemented material. Sulfate transport through the ash particles during diurnal moisture cycling on Mars may be responsible for formation of the cemented soil units. Sulfate efflorescence to the sample surface can be seen in Figure 10 for soil Mix-2 after slowly dehydrating the sample in air and then in a desiccator. The lighter-colored ring along the outer surface of this sample is due to a higher concentration of sulfates. This was not observed for faster dehydration at 150 °C [Cooper and Mustard, 2002]. These observations suggest that a small amount of sulfate in dust/soil particles would
become more concentrated at the sample surface through mild/slow moisture cycling. Therefore, the diurnal moisture cycling on Mars may force these sulfate components to sample surfaces where they would be more readily able to react with other particles. Recent results by Zent et al. [2001] evaluating the H₂O adsorption kinetics on smectites found that the equilibration timescale for water vapor in smectites is too slow under Martian early morning conditions. Their results suggest that the moisture is being adsorbed by another soil component. Possibly sulfates or nanophase ferric oxyhydroxides can adsorb H₂O faster than smectites and could account for adsorption of the early morning moisture.

8. Model Summary

[43] Observations from the Viking and MPF landers have shown that many of the rock surfaces have coatings/alteration rinds and that the particles suspended in the atmosphere have many properties similar to those of the cemented soil and drift. This model was designed to explain the chemical, magnetic and spectroscopic properties of the surface material on Mars and is based on a combination of palagonitically and solfataric alteration processes associated with volcanism and may include sulfates and other salts from evaporite deposits. This model involves both physical interactions, such as aeolian winds that distribute particles and electrostatic charges that bind the fine-grained, dry particles, and chemical interactions including reaction of the sulfate and/or ferric phases and salts with water provided either by the diurnal moisture variations over long time periods or by melting ice flows or other more speculative forms of water.

[44] The idea presented here is that 1–3 μm diameter dust/soil particles on Mars contain fine-grained silicate particles, formed through palagonitization or other alteration processes, that are mixed via aeolian processes with reactive sulfate or ferric oxyhydroxide phases, produced on Mars via solfataric or evaporitic processes. The products formed through these processes are not required to be located near palagonitically altered volcanic material. The dust storms on Mars are continually transporting mobile fines across the surface and would, according to this model, actively mix nanophase to micron-sized particles across vast regions of the surface of Mars. Over time these dust particles become somewhat homogenized, although it is assumed that there would be regional differences. This dust is then transported and converted into the drift and cemented soil units observed on the surface, as well as rock coatings and varnishes on horizontal rock surfaces. The corrosive agents in the dust particles react over time forming the cemented soils/crusts and rock varnishes. These processes would also modify the chemistry and mineralogy of the surface crusts and rock alteration rinds as some elements are leached out of the silicate matrices and less resistant minerals are altered.

[45] Cemented crusts in this study were formed using a mixture of silicates, sulfates and nanophase ferric oxyhydroxides that is dominated by smectites and another that is dominated by palagonitically altered volcanic soil. The smectite-based Mix-1 exhibited significantly greater changes in both its binding properties throughout the hydration/dehydration cycling experiments and in its spectral properties following grinding of the hardened crust than did the palagonitic soil-based Mix-2. The hydration/dehydration experiments showed that a smectite component is not required for cementation of potential Mars analog soils into cratered material. The less reactive palagonitic soil Mix-2 allowed transport of water and sulfate to the surface forming a thin crust at the upper ~1 mm of the sample, while the more reactive smectite soil Mix-1 formed a cemented crust throughout the ~4 mm sample depth. The high smectite crust was also much harder than the low-smectite crust. Future experiments on cemented soils are required in order to better characterize the influence of specific silicate and sulfate minerals on crust formation mechanisms.

[46] Acknowledgments. Support for JLB from NASA’s Mars Data Analysis Program is much appreciated. Reflectance spectra were measured at RELAB, a multiuser, NASA-supported facility (NAG5-3871). Thanks are due to R. V. Morris for thoughtful discussions of the ideas presented here, to T. Hiroi for assistance with the bi-directional spectra, to L. Günter with the Hawaii images and to T. Parker for donating the MPF super-resolution image. This manuscript has benefited from the helpful comments of W. Calvin and an anonymous reviewer.

References


J. L. Bishop, SETI Institute/NASA Ames Research Center, MS-239-4, Moffett Field, CA 94035, USA. (jbishop@mail.arc.nasa.gov)

S. L. Murchie, Applied Physics Laboratory, Johns Hopkins University, Laurel, MD 20723, USA.

C. M. Pieters, Department of Geological Sciences, Brown University, Box 1846, Providence, RI 02912, USA.

A. P. Zent, NASA Ames Research Center, MS-245-3, Moffett Field, CA 94035, USA.