Reflectance Spectroscopy of Palagonite and Iron-Rich Montmorillonite Clay Mixtures: Implications for the Surface Composition of Mars

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Mixtures of a Hawaiian palagonite and an iron-rich, montmorillonite clay (15.8 ± 0.4 wt% Fe as Fe_2O_3) were evaluated as Mars surface spectral analogs from their diffuse reflectance spectra. The presence of the 2.2-μm absorption band in the reflectance spectrum of clays and its absence in the Mars spectrum have been interpreted as indicating that highly crystalline aluminous hydroxylated clays cannot be a major mineral component of the soil on Mars. The palagonite sample used in this study does not show this absorption feature in its spectrum. In mixtures of palagonite and iron-rich montmorillonite, the 2.2-μm Al-OH clay lattice band is not seen below 15 wt% montmorillonite. This suggests the possibility that iron-rich montmorillonite clay may be present in the soil of Mars at up to 15 wt% in combination with palagonite, and remain undetected in remotely sensed spectra of Mars. © 1992 Academic Press, Inc.

INTRODUCTION

An acceptable mineralogical model for the surface of Mars must consider and conform to the constraints of existing observational and experimental data for Mars. These data include spectroscopic observations from both spacecraft and Earth-based telescopes and the analytical and chemical experiments performed by the Viking Lander spacecraft of 1976. The Viking Lander provided experimental information on the soil elemental composition using X-ray fluorescence spectroscopy (Toulmin *et al.* 1977, Clark *et al.* 1977, 1983), the magnetic properties of the surface material from the Viking Lander Magnetics Experiment (Hargraves *et al.* 1977), and surface soil chemical activity using GC–MS (Biemann *et al.* 1977) and the three life detection experiments: labeled release (LR) (Levin and Straat 1977, Banin and Rishpon 1979), gas exchange (GEX) (Oyama *et al.* 1976, Klein *et al.* 1976, Oyama and Berdahl 1977), and pyrolytic release (PR) (Horowitz *et al.* 1977). A mineralogical model of the Martian regolith which conforms well to one experimental data set, but which does not conform to other data sets or has

not been tested by other experimental methods does not provide a thoroughly convincing argument in favor of the model. The spectroscopic work described here is the first part of an integrated approach to elucidate the surface composition of Mars using data from spectroscopy, chemical composition, and surface chemical reactivity.

Because of the power of remote sensing reflectance spectroscopy in determining mineralogy, it has been used as the major method of identifying possible rock and mineral analogs of the Martian surface. A summary of proposed Martian surface compositions from reflectance spectroscopy before 1979 was presented by Singer *et al.* (1979, 1985). Since that time, iron-rich montmorillonite clay (Banin and Rishpon 1979, Banin *et al.* 1988a,b), nanocrystalline or nanophase hematite (Morris *et al.* 1989), and palagonite (Evans and Adams 1979, Allen *et al.* 1981, Singer 1982) have been suggested as Mars soil materials. Unlike hematite and montmorillonite clay, the petrological description of palagonite is rather loose. On Earth, palagonite is formed by the alteration of mafic volcanic glass (ash). In the case of the Hawaiian soils, palagonite is the result of secondary weathering of mafic volcanic glass in semiarid environments; these palagonites contain from 11 to over 16 wt% Fe as Fe_2O_3 (Singer 1982, Morris *et al.* 1990, Golden *et al.* 1991). Palagonite in petrological terms is best described, perhaps, as an amorphous, hydrated, ferric iron, silica gel. Montmorillonite is a member of the smectite clay group and its structure is characterized by an octahedral sheet in coordination with two tetrahedral sheets in which oxygen atoms are shared. The crystallinity of montmorillonite is well defined in contrast to palagonite, which is amorphous or poorly crystalline at best. Nanophase hematite is crystalline, but due to its very small crystal size, each particle has only short-range crystalline structure. Like palagonite, montmorillonite is the result of alteration weathering of volcanic ash usually in prehistoric lakes or estuaries; its origin is also attributed to the weathering of basic igneous rocks under conditions of poor drainage.

Based upon consideration of spectra with wide wavelength coverage (0.3–50 μm) and VIS–NIR similarities between the spectra of palagonite and Mars (Bell *et al.* 1990), Roush *et al.* (1992) concluded that palagonite is a likely surface mineral on Mars. In spite of the spectral agreement of palagonite and the Mars reflectance spectrum in the 2.2-μm region, palagonite shows poor correspondence with results of simulations of the Viking LR experiment (Banin and Margulies 1983, Banin *et al.* 1988b). In contrast, iron-rich montmorillonite clays show almost the same behavior in simulation experiments as did the Martian soils in the Viking LR experiment (Banin and Rishpon 1979, Banin and Margulies 1983, Banin *et al.* 1988a).

Terrestrial, lunar, and meteoritic samples all indicate that surfaces are composed of a variety of minerals, and thus, it is unlikely that any one mineral will be found to compose the surface of Mars. Palagonite appears to be a better spectral analog than iron-rich montmorillonite clay, but iron-rich clays give better matches to the LR results than does palagonite. The spectral study reported here was undertaken to evaluate the spectral properties of mechanical mixtures of palagonite and Mars analog iron-rich montmorillonite clay (16–18 wt% Fe as Fe_2O_3) as a possible Mars surface mineralogical model. Mixtures of minerals as Mars surface analog materials have been studied before (Singer 1982, Singer *et al.* 1985), but the mixtures were restricted to crystalline clays and iron oxides. There have been no previous reports regarding the spectral properties of mixtures of iron-rich montmorillonite clay with palagonite as Mars surface analog materials.

EXPERIMENTAL

Materials

SWy-1 montmorillonite (Clay Mineral Society Repository, Univ. of Missouri) a powdered, smectite clay, from Crook County, Wyoming (described by van Olphen and Fripiat 1979) was used without further treatment as the starting material for the preparation of a Mars soil analog. Using the "Quantitative Ion Exchange Method" of Banin (Banin 1973, Banin *et al.* 1988a), the crude clay was converted to a form containing 15.8 ± 0.4 wt% Fe as Fe_2O_3 as determined by wavelength dispersive X-ray fluorescence (XRF). This is equivalent to approximately 600% of the iron necessary to fill all of the cation-exchange sites available in the clay. The fraction of iron beyond 100% of the exchange capacity is thought to be adsorbed onto the surface of the clay as oxyhydroxy iron colloids at the nanocrystalline level (Ben-Shlomo and Banin 1989, Banin *et al.* 1991). The palagonite is a sample of basaltic glass collected at several locations on the upper slopes of Mauna Kea on the island of Hawaii. This palagonite contained 11.1 ± 0.5 wt% Fe as Fe_2O_3. X-ray diffraction

TABLE I
Average Elemental Composition of Mars Surface Fines, Palagonite, and Iron-Rich Montmorillonite Clay from XRF

Elemental oxide	% by weight		
	Mars[1]	Montmorillonite[2]	Palagonite[2]
SiO_2	43	53.0	38.8
Al_2O_3	7	16.8	19.0
Fe_2O_3	17.6	15.8	11.1
MgO	6	2.1	4.60
CaO	6	0.38	5.36
TiO_2	0.65	0.11	3.30
Cl	0.7	—	—
SO_3	7	—	—
MnO	—	<0.02	0.25
K_2O	—	0.31	0.58
Na_2O	—	0.30	2.60
P_2O_5	—	<0.02	0.85
LOI[3]	—	12.90	11.60

[1] Banin, Clark, and Wanke (1992).
[2] U.S. Geological Survey, Menlo Park.
[3] Loss on ignition.

scans of this sample detected plagioclase and pyroxene, in addition to amorphous glass, although no clay minerals are apparent (Bruckenthal 1987). It is virtually identical to sample Vo102A of Singer (1982) and HA34 of Evans and Adams (1979). The palagonite was sieved, without grinding, to <38 μm (Bruckenthal 1987). XRF elemental analyses of palagonite, the clay samples, and the Mars surface from Viking are shown in Table I. XRF analyses were carried out using an ARL Model XRD-8600B wavelength dispersive spectrometer and the Wahlberg-Taggart method (Taggart *et al.* 1987).

Mixtures of palagonite and iron montmorillonite were prepared on a weight percentage basis. The pure materials and the mixtures were ground mechanically and mixed for 1 min in a Wig-L-Bug. An estimate of the particle size of the palagonite and iron montmorillonite was done using a light microscope. In both samples, the vast majority of aggregate particles was estimated to be in the 1–5 μm size range, with a minority portion of each sample having some submicrometer particles as well as some particles in the 25–50 μm range. Since particle size distribution was similar in both samples, this parameter was not expected to be a variable of concern in the recorded spectra of the mixtures. Samples of approximately 1.2 g were pressed (1.2 kg cm⁻²) into stainless steel planchette sample holders 25.4 mm in diameter and 2.5 mm deep, resulting in a compact, but softly packed pellet. Using a standardized pressing technique obviated the need to account for particle packing as a variable in the reflectance spectra of this study (which was designed to investigate the effects of mixture composition and surface substitution). Mars may

not be expected to be compacted to the same level. The samples were stored in a desiccator before mixing, after mixing, and until their spectra were recorded. All had the same amount of exposure to ambient air. No further efforts were attempted in these experiments to control the relative humidity, and thus, the amount of adsorbed water.

Reflectance Spectroscopy

Hemispherical reflectance spectra from 0.3 to 2.5 μm were recorded on a Perkin-Elmer Lambda 9 spectrophotometer using a Labsphere DRTA-9A diffuse reflectance and transmittance accessory (North Sutton, NH). A constant spectral resolution (± 10%) was used in the UV/VIS. In the NIR, an automatic slit program was used to maintain a constant energy level during spectral scanning (120 nm/min). Halon was used as reference material in both beams of the spectrophotometer for instrument background correction and as the standard reflectance material in the reference beam during sample recording. The spectra were digitized and smoothed using the Savitzky/Golay smoothing function, which determines the best fit of a quadratic polynomial through successive data windows (25-point data window used).

RESULTS AND DISCUSSION

Figure 1 shows a composite reflectance spectrum of typical high albedo regions of Mars taken from telescopic observations from Earth (Singer et al. 1979). The ordinate is relative reflectance scaled to a value of 1.0 at 1.02 μm. Absolute reflectivity values for Mars at several different wavelengths can be found in Table II. From the UV to 0.75 μm, the spectrum is almost featureless except for an increase in reflectance and subtle slope changes at 0.5 and 0.6 μm. A shallow absorption band is seen with its central position at 0.87 μm. These features have all been attributed to Fe^{3+} (Singer 1982, Sherman et al. 1982), either as $O^{2-}-Fe^{3+}$ charge transfer absorptions or Fe^{3+} crystal field transitions. Weak, narrow bands at 1.45 and 1.62 μm and a stronger composite band in the 1.9 to 2.1 μm region seen in the Martian spectrum are attributed to CO_2 in the Martian atmosphere. A broad, shallow band observed in the region between 1.4 and 1.7 μm, which is superimposed on the sharper CO_2 band has been interpreted as being due to water ice in or on the surface of Mars (McCord et al. 1982). Beyond 2.1 μm, the Martian spectrum is relatively flat with some hint of fine structure around 2.3–2.4 μm. Recently obtained higher spectral resolution data from the 1988 opposition in the 2.0–2.5 μm region have resolved the absorption envelope of the 2.36-μm band into five distinct and relatively sharp bands. These have been interpreted by Clark et al. (1990) as being due to the mineral scapolite, but an alternative interpretation
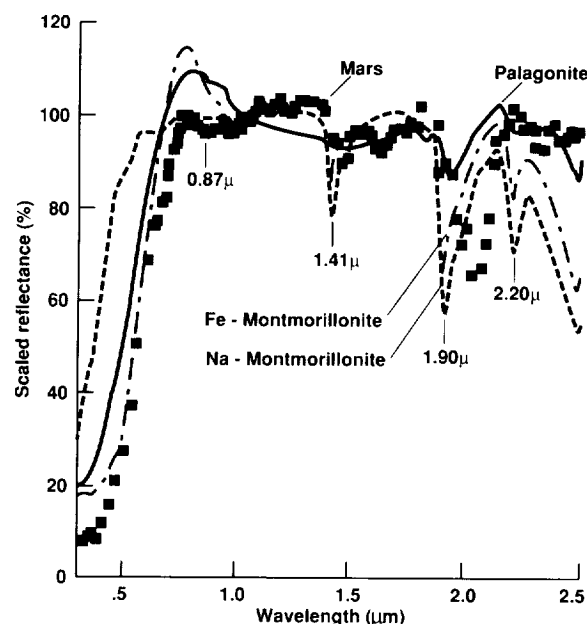

FIG. 1.   Diffuse reflectance spectra of palagonite, Na- and Fe-montmorillonites (15.8 ± 0.4 wt% Fe as Fe_2O_3), and a representative composite reflectance spectrum for Martian bright regions (McCord et al. 1977, 1982). All spectra are scaled to unity at 1.02 μm as was done for the Mars reference spectrum.

suggests that atmospheric CO as well as a solid phase contribute significantly to this 2.36-μm band envelope (Roush et al. 1992, Clark et al. 1990).

A comparison of the scaled reflectance spectra of palagonite and Na-montmorillonite, the natural cation form of Wyoming bentonite, to the Martian spectrum (Singer et al. 1979) appears in Fig. 1 (see Table II for absolute reflectivity values at several different wavelengths). Montmorillonite with its natural terrestrial cation was chosen for this comparison to facilitate showing which spectral features can be assigned to the clay structure itself and which can be attributed to exchanged and adsorbed iron. To facilitate comparison to the telescopic data which was scaled to a reflectance of 1.0 at 1.02 μm, the spectra of the two minerals were scaled similarly. In the region from 0.30 to 0.70 μm, the spectra are without marked features; all show a dropoff into the ultraviolet. The clay spectrum has a unique slope change occurring around 0.35 μm attributable to $O^{2-}-Fe^{3+}$ and other charge transfer bands or crystal field absorptions of iron (Karickhoff and Bailey 1973, Chen et al. 1979, Banin et al. 1985). At about 0.5 μm, a slope change is noticeable in all three spectra. A band at 0.62 μm in the clay spectrum is not observed in the other spectra shown, but has been recently observed by Bell et al. (1990) in the latest Mars opposition data. It has been attributed to an electronic transition in Fe^{3+}. The Mars spectrum exhibits a distinct band at 0.87 μm

TABLE II

Absolute Reflectivity Values of Palagonite, Iron Rich
Montmorillonite, and Mixtures of These at Several Wavelengths

Sample	Absolute reflectivity			
	.70 μm	1.02 μm	1.70 μm	2.14 μm
Mars[1]	0.39	0.40	0.39	0.38
Palagonite	0.31	0.30	0.29	0.30
Na-montmorillonite	0.75	0.75	0.76	0.70
Fe-montmorillonite	0.30	0.28	0.28	0.28
90% palag. + 10% Fe-m	0.31	0.28	0.27	0.29
80% palag. + 20% Fe-m	0.31	0.29	0.27	0.29
70% palag. + 30% Fe-m	0.32	0.31	0.29	0.30
50% palag. + 50% Fe-m	0.32	0.31	0.29	0.30

[1] Singer (1982).

which is much weaker in the spectrum of palagonite and very weak in the clay spectrum. This band has been assigned to Fe^{3+} by Huguenin et al. (1977) and others (Singer et al. 1979, Singer 1982). The better resolved spectra of Bell et al. (1990) possibly show two band centers in this region.

From 1.3 to 2.5 μm (Fig. 1), there are some marked differences between the analog mineral spectra and the Mars spectrum. Two relatively intense absorption bands at 1.4 and 1.9 μm are observed in both palagonite and Na-montmorillonite; in palagonite, these bands are both broader and weaker than in the clay, especially at 1.4 μm. The band at 1.4 μm has been suggested as being due to both adsorbed water and structural hydroxyls (OH stretch overtones); the band at 1.9 μm has been attributed solely to adsorbed water (H–O–H bend overtones) (Hunt and Salisbury 1970, Hunt 1977). The magnitude of these bands will be dependent to some extent upon the relative humidity of the ambient air under which the spectral measurements are taken (see under Experimental). As can be seen from the Martian spectrum, CO_2 in the Martian atmosphere causes some interference with the 1.4- and 1.9-μm bands. An intense band at 2.2 μm in the spectrum of Na-montmorillonite and a small, but noticeable, inflection in the spectrum of palagonite at the same wavelength (since palagonite by definition is a mixture of minerals, "contamination" of the palagonite with clay or other minerals is likely) are attributable to clay lattice hydroxyls from combinations of the O–H stretch and cation (Al) O–H bend or lattice modes (Hunt 1977, Hunt and Salisbury 1970). In dioctahedral clays like montmorillonite, the cation is generally Al^{3+}. This 2.2-μm band is diagnostic of mineralogy and is interpreted as being indicative of aluminous hydroxylated minerals such as montmorillonite or kaolinite. As previously suggested (McCord et al. 1982, Singer 1985, Roush et al. 1992), the absence of the 2.2-μm

band in the spectrum of Mars indicates that well crystallized, aluminous hydroxylated materials such as dioctahedral montmorillonite cannot be present on the surface of Mars as a major mineral. It does not exclude montmorillonite or other aluminous hydroxylated clays from being present as a minor and, perhaps significant, mineral on the surface.

Another point of comparison in Fig. 1 occurs in the spectral region from 2.2 to 2.5 μm. The clay spectrum shows a dropoff in reflectivity which is less obvious in the palagonite spectrum and not observed in the Mars spectrum. Since the dropoff has been attributed to the 3-μm fundamentals of water, this has been interpreted to indicate that the Mars soil is more desiccated than either the montmorillonite or the palagonite analogs (Bruckenthal 1987, Roush et al. 1992), and that there is less water in palagonite than in Na (as well as Fe) montmorillonite. Consideration of the LOI results (Table I), however, indicates that the amount of water in palagonite and Fe- and Na-montmorillonites (previous work showed LOI for Na-montmorillonite to be 13.3%; Banin et al. 1988a) should be at about the same level if we assume that the major volatile component of LOI is water. This indicates that the strength of the feature longward of 2.2 μm may not be directly related to the amount of water present, and should be interpreted circumspectly.

Also shown in Fig. 1 is the scaled reflectance spectrum of a Mars analog, iron-rich (15.8 ± 0.4 wt% Fe as Fe_2O_3) montmorillonite (see Table II for absolute reflectance values at several different wavelengths). The spectral analysis is similar to that of Fig. 1. In the 0.30 to 0.70 μm region, Fe-montmorillonite shows qualitatively a closer correspondence to the steep increase in slope of reflectance associated with the Mars spectrum than does palagonite. This agrees with the high spectral resolution data recently presented by Bell et al. (1989, 1990) where the investigators concluded that the bands and slope of the Mars spectrum in this wavelength region are indicative of crystalline iron oxide minerals which are suggested to be present in the Martian surface soil. As mentioned earlier, Banin (Ben-Shlomo and Banin 1989, Banin et al. 1991) has proposed that iron-rich clays with iron above the cation-exchange capacity contain the excess iron as adsorbed nanocrystalline iron oxide. This would explain the closer correspondence of the Fe-clay spectrum to that of Mars in the 0.30–0.70 μm spectral region as compared to the spectrum of Na-clay. The prominent 2.2-μm band is still obvious in the spectrum of this iron-enriched montmorillonite clay which is inconsistent with the Mars spectrum. The similar shape and depth of the 2.2-μm band in the iron-rich clay compared to the Na-clay implies that the clay lattice structure is unaffected by the iron substitution process. This result has been corroborated recently by Banin using transmission electron microscopy (Banin et
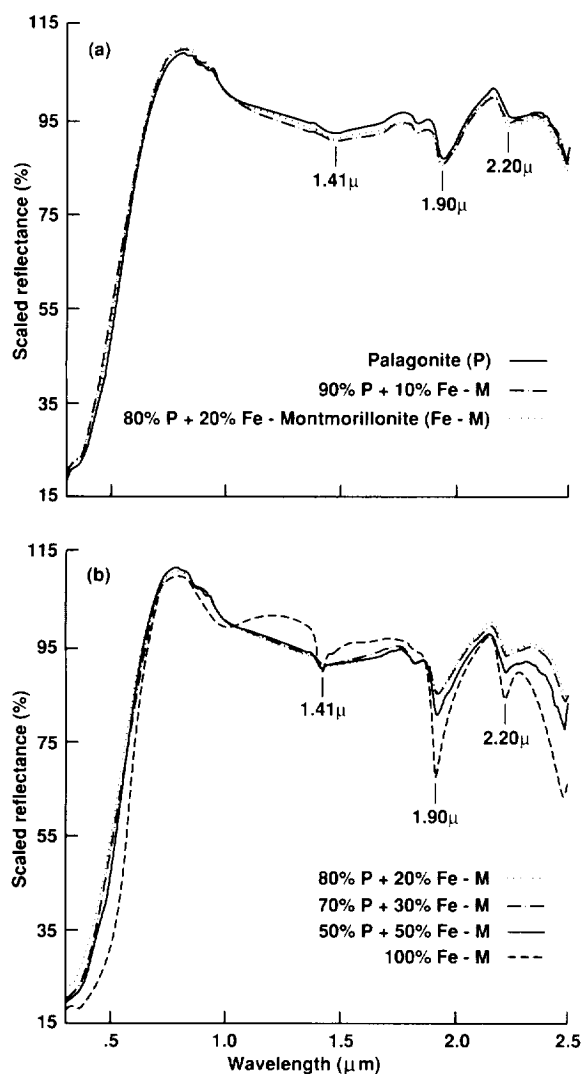
FIG. 2. A comparison of the diffuse reflectance spectra of different wt% mixtures of palagonite and Fe-montmorillonite (15.8 ± 0.4 wt% Fe as Fe_2O_3). All spectra are scaled to unity at 1.02 μm.

al. 1991) and x-ray diffraction (Ben-Shlomo and Banin 1989) analyses.

In an attempt to see if the match between analog mineral spectra and the Mars spectrum could be improved, various mixtures of palagonite with the Mars analog, iron-rich, montmorillonite were prepared. The scaled spectra of these mixtures are shown in Fig. 2 (see Table II for absolute reflectivity values at several different wavelengths). In the 0.30 to 0.70 μm region, the closeness of correspondence of the steep increase in slope of reflectance in the Mars spectrum is better with the pure Fe-clay than with any of the mixtures of palagonite and Fe-clay (Fig. 1). In the diagnostic 2.2-μm region, the band due to clay lattice structure becomes noticeable in mixtures at the 10–20 wt% Fe-montmorillonite level. In order to

evaluate this observation more quantitatively, a rigorous band depth analysis was carried out at 2.20 μm (Clark and Roush 1984). For each palagonite/montmorillonite mixture, a sloped continuum was defined by drawing a straight line tangent to the short wavelength side of the reflectance maximum at 2.13 μm to the straight lined slope of the reflectance curve between 2.25 and 2.35 μm. The long wavelength defining point of the continuum was moved as needed to provide the best tangent to the curve. The 2.20-μm band depth, $D_{2.20}$, was defined according to Clark and Roush (1984) as

$$D_{2.20} = 1 - \left(\frac{\text{reflectance minimum}}{\text{reflectance continuum}} \right).$$

Band depth as a function of wt% Fe-montmorillonite is plotted in Fig. 3 for the palagonite/montmorillonite mixtures. The curve is the result of fitting a second degree polynomial regression line (R^2 = 0.998) through the experimental points. This curve would be a horizontal line with a value equal to that of the pure palagonite sample if the addition of montmorillonite had no effect on the 2.20-μm band depth. The fitted curve indicates that band depth is insensitive to the presence of up to 15 wt% Fe-montmorillonite. Above this concentration, there is an increase in band depth with increasing weight percentage Fe-montmorillonite (decreasing palagonite) which is attributable to the 2.20-μm absorption feature characteristic of smectite clays. If one accepts the premise that palagonite is a "good" spectral analog of the Mars surface material, up to 15 wt% of Fe-montmorillonite can be present
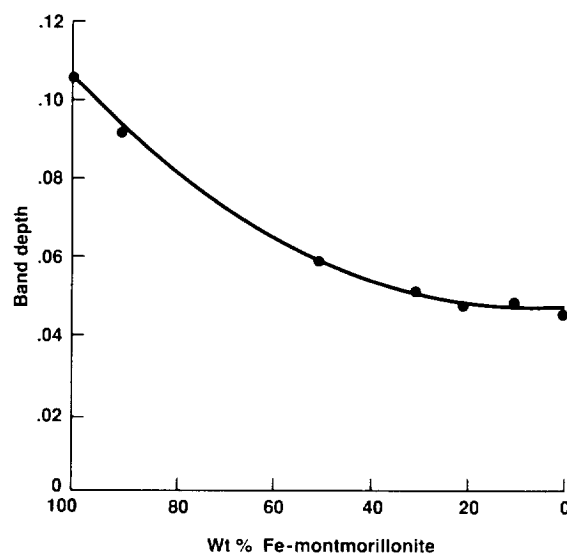

FIG. 3. Plot of band depth at 2.20 μm versus wt% Fe-montmorillonite. Band depth is defined as 1 - [(reflectance minimum)/(reflectance continuum)].

on the surface of Mars and remain undetected as shown by band depth analysis. In spite of the fact that the most recent telescopic observations of Mars do not show evidence of a 2.2-μm band (Clark *et al.* 1990), the absence of the 2.2-μm band cannot be used to eliminate iron-enriched montmorillonite as a component of the Mars soil. It remains a distinct possibility that an iron-rich, montmorillonite clay, a proposed Mars analog material, can be present on the surface of Mars as a component (up to 15 wt%) of the Mars soil in combination with palagonite and remain undetected in remotely sensed spectra of Mars.

CONCLUSIONS

The qualitative and quantitative spectral analysis presented here reveals that up to 15 wt% of an iron-rich montmorillonite can be present on the surface of Mars in combination with palagonite and perhaps other minerals, and the reflectance spectrum of Mars may not reveal this. The results are specific for the two minerals used in this study, and are suggestive that there may be greater amounts of clay in the surface material of Mars than recently thought. Thus the elimination of some minerals as potential Martian surface components solely on the basis of spectral data may be misleading.

ACKNOWLEDGMENTS

REFERENCES

ALLEN, C. C., J. L. GOODING, M. JERCINOVIC, AND K. KEIL 1981. Altered basaltic glass: A terrestrial analog to the soil of Mars. *Icarus* **45**, 347–369.

BANIN, A. 1973. Quantitative Ion Exchange Process for Clays. U.S. Patent No. 3,725,528.

BANIN, A., AND J. RISHPON 1979. Experimental simulation of the Viking labeled released (LR) results with iron-adsorbed smectite clay minerals. *Life Sci. Space Res. XVII*, 59–64.

BANIN, A., AND L. MARGULIES 1983. Simulation of Viking biology experiments suggests smectites not palagonite as Martian soil analogs. *Nature* **305**, 523–526.

BANIN, A., L. MARGULIES, AND Y. CHEN 1985. Iron-montmorillonites: A spectral analog of martian soil. *J. Geophys. Res. Suppl.* **90**(C), 771–774.

BANIN, A., G. C. CARLE, S. CHANG, L. M. COYNE, J. B. ORENBERG, AND T. W. SCATTERGOOD 1988a. Laboratory investigations of Mars: Chemical and spectroscopic characteristics of a suite of clays as Mars soil analogs. *Origins Life Evol. Biosph.* **18**, 239–265.

BANIN, A., L. MARGULIES, T. BEN-SHLOMO, G. CARLE, L. M. COYNE, J. B. ORENBERG, AND T. W. SCATTERGOOD 1988b. Constraining Mars soil mineralogical composition: Palagonite vs. iron enriched smectite clays. *Lunar Planet. Sci. Conf. XIX* 27–28.

BANIN, A., B. C. CLARK, AND H. WANKE 1992. Mars surface chemistry and mineralogy. Chapter submitted to *Mars Book* (H. H. Kiefer, B. M. Jakosky and C. Synder, Eds.), Space Science Series, U. of Arizona Press.

BANIN, A., D. F. BLAKE, AND T. BEN-SHLOMO 1991. Detection of nanophase lepidocrocite (γ-FeOOH) in iron-smectite Mars soil analog materials (MarSAM). *Lunar Planet. Sci. Conf. XXII*, 49–50.

BELL, J. F. III, T. B. McCORD, AND P. G. LUCEY 1989. High spectral resolution 0.3–1.0 μm spectroscopy and imaging of Mars during the 1988 opposition: Characterization of Fe mineralogies. In *4th International Conference on Mars, Tucson, AZ,"* pp. 66–67.

BELL, J. F., III, T. M. McCORD, AND P. D. OWENSBY 1990. Observational evidence of crystalline iron oxides on Mars. *J. Geophys. Res.* **95**, 14,447–14,461.

BEN-SHLOMO, T., AND A. BANIN 1989. Iron-enriched smectite clays as Mars soil analogs: Chemical and mineralogical characterization. *Lunar Planet. Sci. Conf. XX*, poster presentation.

BIEMANN, K., J. ORO, P. TOULMIN, III, L. E. ORGEL, A. O. NIER, D. M. ANDERSON, P. G. SIMMONDS, D. FLORY, A. V. DIAZ, D. R. RUSHNECK, J. E. BILLER, AND A. L. LAFLEUR 1977. The search for organic substances and inorganic volatile compounds in the surface of Mars. *J. Geophys. Res.* **82**, 4641–4648.

BRUCKENTHAL, E. A. 1987. *The Dehydration of Phyllosilicates and Palagonites: Reflectance Spectroscopy and Differential Scanning Calorimetry.* Master's thesis in Geology and Geophysics, University of Hawaii.

CHEN, Y., D. SHAKED, AND A. BANIN 1979. The role of structural iron(III) in the UV absorption by smectites. *Clay Miner.* **14**, 93–102.

CLARK, B. C., A. K. BAIRD, H. J. ROSE, JR., P. TOULMIN, III, R. P. CHRISTIAN, W. C. KELLIHER, A. J. CASTRO, C. D. ROWE, K. KIEL, AND G. HUSS 1977. The Viking X-ray fluorescence experiment: Analytical methods and early results. *J. Geophys. Res.* **82**, 4577–4594.

CLARK, R. N. 1983. Spectral properties of mixtures of montmorillonite and dark carbon grains: Implications for remote sensing minerals containing chemically and physically adsorbed water. *J. Geophys. Res.* **88**(B12), 10,635–10,644.

CLARK, R. N., AND T. L. ROUSH 1984. Reflectance spectroscopy: Quantitative analysis techniques for remote sensing applications. *J. Geophys. Res.* **89**, 6329–6340.

CLARK, R. N., G. A. SWAYZE, R. B. SINGER, AND J. POLLACK 1990. High resolution reflectance spectra of Mars in 2.3 μ region: Evidence for the mineral scapolite. *J. Geophys. Res.* **95**(B9), 14,463–14,480.

EVANS, D. L., AND J. B. ADAMS 1979. Comparison of Viking Lander multispectral images and laboratory reflectance spectra of terrestrial samples. *Proc. Lunar Planet. Sci. Conf. 10th*, 1829–1834.

GOLDEN, D. C., R. V. MORRIS, D. W. MING, R. K. VEMPATI, AND H. V. LAUER 1991. Mineralogy of palagonitic soils from Hawaii. *Lunar Planet. Sci. Conf. XXII*, 449–450.

HARGRAVES, R. B., D. W. COLLINSON, R. E., ARVIDSON, AND C. R. SPITZER 1977. The Viking magnetic properties experiment: Primary mission results. *J. Geophys. Res.* **82**, 4547–4558.

HOROWITZ, N. H., G. L. HOBBY, AND J. S. HUBBARD 1977. Viking on Mars: the carbon assimilation experiments. *J. Geophys. Res.* **82**, 4659–4662.

HUGUENIN, R. L., J. B. ADAMS, AND T. B. McCORD 1977. Surface mineralogy from reflectance spectra. *Lunar Sci. VIII*, 478.

HUNT, G. R., AND J. W. SALISBURY 1970. Visible and near infrared spectra of rocks. I. Silicate minerals. *Mod. Geol.* **1**, 283–300.

HUNT, G. R. 1977. Spectral signatures of particulate minerals in the visible and near-infrared. *Geophysics*, **42**, 510–513.

KARICKHOFF, S. W., AND G. W. BAILEY 1973. Optical absorption spectra of clay minerals. *Clays Clay Miner.* **21**, 59–70.

KLEIN, H. P., G. V. HOROWITZ, V. I. LEVIN, V. I. OYAMA, J. LEDERBERG, A. RICH, J. S. HUBBARD, G. L. HOBBY, P. A. STRAAT, B. J. BERDAHL, G. C. CARLE, F. S. BROWN, AND R. D. JOHNSON 1976. The Viking biological investigation: Preliminary results. *Science* **194**, 99–105.

LEVIN, G. V., AND P. A. STRAAT 1977. Recent results from the Viking labeled release experiments on Mars. *J. Geophys. Res.* **82**, 4663–4667.

McCORD, T. B., R. L. HUGUENIN, D. MINK, AND C. PIETERS 1977. Spectral reflectance of Martian areas during the 1973 opposition: Photoelectric filter photometry (0.33–1.10 μm). *Icarus* **31**, 25–39.

McCORD, T. B., R. N. CLARK, AND R. B. SINGER 1982. Mars: Near-infrared reflectance spectra of surface regions and compositional implications. *J. Geophys. Res.* **87**, 3021–3032.

MORRIS, R. V., D. G. AGRESTI, H. C. LAUER, JR., J. A. NEWCOMB, T. D. SHELFER, AND A. V. MURALI 1989. Evidence for pigmentary hematite on Mars based on optical, magnetic, and Mossbauer studies of supermagnetic (nanacrystalline) hematite. *J. Geophys. Res.* **94**, 2760–2778.

MORRIS, R. V., J. GOODING, H. V. LAUER, AND R. B. SINGER 1990. Iron mineralogy of Hawaiian palagonitic soil with Mars-like spectral and magnetic properties. *Lunar Planet. Sci. Conf. XXI*, 811–812.

OYAMA, V. I., B. J. BERDAHL, G. C. CARLE, M. E. LEHWALT, AND H. S. GINOZA 1976. The search for life on Mars: Viking 1976 gas changes as indicators of biological activity. *Origins Life* **7**, 313–333.

OYAMA, V. I. AND B. J. BERDAHL 1977. The Viking gas exchange experiment results from Chryse and Utopia surface samples. *J. Geophys. Res.* **82**, 4669–4676.

ROUSH, T. L., D. L. BLANEY, AND R. B. SINGER 1992. The Surface Composition of Mars. Chapter submitted for inclusion in *Remote Geochemical Analysis* (K. Pieters and P. Englert, Eds.). ACS/LPI, in press.

SHERMAN, D. M., R. G. BURNS, AND V. M. BURNS 1982. Spectral characteristics of the iron oxides with application to the Martian bright region mineralogy. *J. Geophys. Res.* **87**, 10,169–10,180.

SINGER, R. B., T. B. McCORD, R. N. CLARK, J. B. ADAMS, AND R. L. HUGUENIN 1979. Mars surface composition form reflectance spectroscopy: A summary. *J. Geophys. Res.* **84**, 8415–8426.

SINGER, R. B. 1982. Spectral evidence for the mineralogy of high albedo soils and dust on Mars. *J. Geophys. Res.* **87**, 10,159–10,168.

SINGER, R. B., P. D. OWENSBY, AND R. N. CLARK 1985. Observed upper limits for clay minerals on Mars. *Lunar Planet. Sci. Conf. XVI*, 787.

TAGGART, J. E., JR., J. R. LINDSAY, B. A. SCOTT, D. V. VIVIT, A. J. BARTEL, AND K. C. STEWART 1987. Analysis of geological materials by wavelength dispersive X-ray fluorescence spectrometry. In *Methods for Geochemical Analysis* (P. O. Becker, Ed.), U.S. Geological Survey Bulletin 1770, E1–E19.

TOULMIN, P. III, A. K. BAIRD, B. C. CLARK, K. KEIL, H. J. ROSE, JR., R. P. CHRISTIAN, AND P. H. EVANS 1977. Geochemical and mineralogical interpretation of the Viking inorganic chemical results. *J. Geophys. Res.* **82**, 4625–4634.

VAN OLPHEN, H., AND J. J. FRIPIAT (Eds.) (1979). *Data Handbook for Clays and Other Nonmetallic Materials*, p. 346. Pergammon Press, Oxford.