Hydrous carbonates on Mars?: Evidence from Mariner 6/7 infrared spectrometer and ground-based telescopic spectra

Wendy M. Calvin
U. S. Geological Survey, Flagstaff, Arizona

Trude V. V. King and Roger N. Clark
U. S. Geological Survey, Denver, Colorado

Abstract. Absorption features at 2.28 and 5.4 \textmu m identified in Mariner 6/7 infrared spectrometer and terrestrial telescopic spectra are consistent with the spectra of hydrous magnesium carbonates such as hydromagnesite and arfinitite. Spectral characteristics of these hydrous carbonates are different from those of the anhydrous carbonates, as the former do not have the strong spectral features typically associated with anhydrous carbonates such as calcite and siderite. Theoretical mixing indicates that, depending on the type of hydrous carbonate, 10–20 wt % can be incorporated into the regolith without contradicting the spectral observations or the Viking x ray fluorescence chemical analysis. Hydrous carbonates form as weathering products of mafic minerals in the presence of H\textsubscript{2}O and CO\textsubscript{2}, even in the Antarctic. Their formation as evaporate minerals from either original magmas or hydrothermally altered rocks is consistent with the Martian environment, provided liquid water is or has been at least transiently present. On Earth, formation of hydrous Mg carbonates is associated with the production of amorphous iron oxides, which is consistent with both the environment and the inferred surface mineralogy of Mars. These minerals are about 60 wt % H\textsubscript{2}O, CO\textsubscript{2}, and OH; if they are abundant everywhere at the 10% level, then about 6% of the surface weight could be volatiles bound in this type of mineral. Although the stability of hydrous carbonates in a Martian environment is uncertain, there may be kinetic factors inhibiting the dehydration of these minerals, which may persist metastably in the current environment. Although the spectroscopic evidence for anhydrous carbonates is scant, the possible presence of hydrous carbonates provides an appealing mechanism for the existence of carbonates on Mars.

1. Introduction

In spite of varied and prolonged examinations of Mars, very little is known about the specific mineralogy of the surface. The Viking lander experiments provided information on elemental abundances but no information on volatile elements such as H (important for water-bearing minerals), C (associated with carbonates), and Na. In general, the Viking x ray fluorescence (XRF) results indicate that surface materials contain high levels of Fe and S, low levels of K, presumably low Na given the low K value, and low levels of Al, all of which indicate mafic source material [Arvidson et al., 1989]. There is a wide and growing body of supporting evidence that SNC meteorites have come from Mars [e.g., Gooding et al., 1990; Pepin and Carr, 1992, and references therein]. Analysis of the compositions of SNC meteorites indicates that Martian magmas are similar to terrestrial mafic and ultramafic basalts [Longhi et al., 1992, and references therein]. It is thus commonly assumed that the surface of Mars is composed of such ultramafic source material and the weathering products of these rocks. Salts and other evaporites are often proposed based on analogies with terrestrial desert environments and the detection of sulfur and chlorine by the XRF [e.g., Clark and van Hart, 1981, and references therein]. Salts are thought to be the cementing agents in blocky material because of increased levels of chlorine and sulfur with respect to fine material [Arvidson et al., 1989].

Spectroscopic observations have identified frozen forms of water and carbon dioxide in addition to pyroxene (for a recent review, see Soderblom [1992]). Evidence for bound water based on a characteristic 3 \textmu m absorption band exists in both terrestrial and spacecraft data [e.g., Honck et al., 1973; Pimentel et al., 1974; Erard et al., 1991]. Spectral characteristics in the visible and near infrared suggest that amorphous, rather than crystalline, iron oxides must be dominant [Singer, 1982]; however, recent spectroscopic work indicates that some crystalline iron-oxide phase, most likely hematite,
is also present [Morris et al., 1989; Bell et al., 1990]. Palagonite has been widely used as the best spectral analog of Martian soils. However, Banin and co-workers have shown that palagonites fail to replicate the Viking Labeled-Release experiment results [e.g., Banin, 1986, and references therein]. In addition, some palagonites have an absorption feature near 2.2 μm from Al-OH, which is not observed on Mars. This indicates that palagonites are reasonable spectral analogs for the visible and near-infrared and that they share general spectral characteristics of the 3-μm region, but that they may not be good soil analogs.

Recent terrestrial observations have identified several weak features in the spectrum of Mars. Atmospheric absorption bands from species such as CO₂ and CO add to the difficulty in the interpretation of many of these features. An absorption centered near 2.35 μm was originally described by Singer et al. [1984] and tentatively attributed to Mg-bearing clays. Encrenaz and Lellouch [1990] have shown that much of the envelope from 2.3 to 2.45 μm is correlated with absorption by atmospheric CO. However, Clark et al. [1990] examined the spectral region from 2.15 to 2.46 μm at higher spectral resolution, and they have demonstrated mineralogical as well as atmospheric absorptions in this region. In particular, features at 2.28 and 2.44 μm have limited or no atmospheric contribution. Clark et al. [1990] attributed absorption features near 2.3 μm to the presence of carbonate, bicarbonate, and bisulfate in the mineral scapolite. Recent observations in this spectral region by Bell and Crisp [1993] indicate that features of mineralogical origin occur at 2.25 μm and that the variations in the band at 2.33 μm include a mineralogic component. Blaney and McCord [1990] and Rouxh et al. [1993] presented spectra of weak features near 3.8 and 4.5 μm. The 3.8-μm feature is well correlated with an atmospheric feature that arises from different isotopes of O in CO₂ [Encrenaz and Lellouch, 1990]. The narrow 4.5-μm feature is on the slope of a strong absorption by atmospheric CO₂ and has been associated by Blaney and McCord [1990] with sulfates, although no specific mineralogy has been identified. Pollack et al. [1990] presented evidence of weak features in the infrared. In particular, they attributed bands near 6.7 μm and on the short wavelength side of the atmospheric CO₂ band at 7.3 μm to carbonate-, or bicarbonate-bearing minerals; they also attributed features at 8.7 and 9.8 μm to sulfates- or bisulfate-bearing minerals, but without a specific mineralogy.

Many hypotheses suggest the existence of carbonates on the surface of Mars. These include formation of carbonates during an early epoch when liquid water was sufficiently stable to form the channel systems seen in ancient cratered terrain and participation of carbonate rocks in recycling of CO₂, as recently summarized by Fmeanle et al. [1992]. Additionally, carbonates have been shown to be stable chemical weathering products in the current Martian environment [e.g., Gooding et al., 1992, and references therein]. Wide and varied searches for the strong spectral signatures of anhydrous carbonates in the visible and near-infrared, most recently by Blaney and McCord [1989, and summary therein], have been unsuccessful.

This study of the Mariner 6 and 7 infrared spectrometer (IRS) data set sought to expand on terrestrial observations by using a spacecraft instrument not subject to absorption by the terrestrial atmosphere. This data set is unique in its spectral coverage and wavelength resolution at the shorter wavelengths. Later spaceborne experiments from the United States, such as Mariner 9 IRS, obtained spectral coverage only at longer wavelengths. Although the French Imaging Spectrometer for Mars (ISM) experiment aboard the Soviet PHOBOS spacecraft obtained information in this spectral region, the data are at dramatically reduced spectral resolution [e.g., Erard et al., 1991]. Work by Mustard et al. [1993] and Marchie et al. [1993] has described variation in broader spectral features such as the 0.9-μm pyroxene band and the 3.0-μm adsorbed water band. Our study yielded several identifications (some tentative) of absorption features at spectral regions unavailable to terrestrial observations. These are discussed at length in the next section. One of these new spectral features, coupled with absorptions identified by Clark et al. [1990a], led to the consideration of different types of carbonate minerals, namely, hydrous magnesium carbonates, for the surface of Mars. The compatibility of these minerals with spectral and environmental characteristics of Mars is discussed in the third section.

2. Absorption Features

2.1. Mariner 6/7 Infrared Spectrometers

The Mariner 6 and 7 spacecraft each were equipped with two infrared spectrometers. The work here is confined to examination of the data obtained by the second spectrometer on each spacecraft, which is the wavelength region from about 2 to 6 μm. During the summer of 1969, the IRS recorded approximately 240 spectra of the Martian surface, predominantly over the southern hemisphere. The observations were obtained in that hemisphere's spring, at Lₚ = 200°, when the polar cap edge was near -60°. T. Z. Martin has written a comprehensive description of the data set and spatial coverage (Mariner 6/7 infrared spectrometer: Data set restoration, submitted to Journal of Geophysical Research, 1993, hereinafter referred to as submitted manuscript, 1993).

Each spacecraft carried the same instrument design, but there are slight differences in the signal-to-noise ratio and filter transmissions. The instrument design is described in detail by Herr et al. [1972]. It is a circular variable filter instrument with a PbSe detector. The average spectral resolution of the filters is approximately 1.6% full width at half maximum (FWHM) (see appendix). The filter wheels were made by bonding together two halves with a slight gap in filter coverage at the seam. This allows unfiltered light into the detector every half revolution of the filter wheel and provides a fiducial spike for wavelength calibration. There are then two wavelength segments, correlated to the two
halves of the filter wheel, which cover the spectral regions from 1.9 to 3.7 \( \mu m \) and 3.0 to 6.0 \( \mu m \).

The original instrument team published only two articles pertaining to the surface composition based on the spectrometer data. Their authors are Herr and Pimentel [1969], who discussed absorptions over the south polar cap, and Pimentel et al. [1974], who discussed the presence of water of hydration. Apparently, there were no other published examinations of the data set until restoration was undertaken for the Pilot Planetary Data System. The lack of interest is likely because the data were calibrated in neither wavelength nor intensity and were available only on microfiche. Martin [1985] restored a digital data set, converted the geometry information from the coordinate system used at the time of the flyby to the current latitude and longitude system, and provided a wavelength calibration based on atmospheric CO\(_2\) bands in the 1.9- to 3.7-\( \mu m \) region and fiducial spikes for other regions. This restoration spurred a few subsequent examinations such as those of Roush et al. [1986] and McKay and Nedell [1988], both of which were searches for the signature of anhydrous carbonates with negative results; Calvin [1990], an examination of the south polar cap; and the current analysis.

When we began our examination, the fully calibrated IRS data set was not yet available, so we were obliged to perform detailed wavelength and radiometric calibrations. This work paralleled that done by T. Z. Martin (submitted manuscript, 1993) for the full data set restoration and is described in the appendix. The major difference between our initial calibration and that of T. Z. Martin is that we were unable to perform a radiometric calibration for the 2- to 4-\( \mu m \) segment. This does not affect our conclusions regarding the presence of spectral absorption features.

In the following analysis we compare the observations with theoretical models of the Martian atmosphere. These models are not intended to be precise fits to the observing geometry and atmospheric path lengths. Rather, the models are provided to alert the reader to the wavelengths where atmospheric absorptions are currently predicted and how their strength can be expected to vary with path length. The absorption features that we correlate with spectral features of hydrous Mg carbonates lie adjacent to, but outside, regions of atmospheric interference.

An average of five spectra obtained by Mariner 7 over the Oxia Palus region, latitude (lat) 2°S to 19°S, longitude (long) 4° to 11°, is shown in Figure 1. The modeled Martian atmosphere provided by Crisp [1990], convolved to the resolution of the Mariner instrument, is also shown (see the appendix for details on the convolution). Aside from the strong atmospheric absorptions caused by CO\(_2\) near 2.0 and 2.7-2.8 \( \mu m \), the most obvious feature in this spectrum is the absorption beyond approximately 2.9 \( \mu m \), attributed to water in surface minerals. The broad feature near 3.4 \( \mu m \) arises from absorptions in the circular variable filter (CVF) rather than from either the surface or atmosphere of Mars [Herr et al., 1972; Pimentel et al., 1974].

**Figure 1.** An average of five spectra from the region of Oxia Palus (M7:92,93,94,94,98) compared with a scaled model Martian atmosphere.

The absorption that is evident are an absorption from 2.3 to 2.4 \( \mu m \) and two weaker absorptions, one centered near 2.5 \( \mu m \) and one expressed as a slope change from 2.55 to 2.65 \( \mu m \). The absorption between 2.3 and 2.4 \( \mu m \) appears to correlate with the envelope identified by Clark et al. [1990a], but it occurs at slightly longer wavelengths in the Mariner data. The wavelength calibration is fixed only at isolated points. For this spectral region, the tie points are at 2.05 and 2.7 \( \mu m \), and, in spite of the wavelength correction, the region between approximately 2.1 and 2.6 \( \mu m \) appears shifted slightly to longer wavelengths. Because of this uncertainty in wavelength, it is difficult to distinguish atmospheric from mineralogic absorption features in the 2.3- to 2.4-\( \mu m \) region.

We examined several averages of raw spectra to look for features not attributable to the atmosphere. Figure 2 shows an expanded scale of the spectral region 2.65 to 2.98 \( \mu m \) for two averages of Mariner 7 spectra. The first average of six is over Meridiani Sinus (lat 0° to 10°S, long 357° to 3°). The second average of seven was taken over the eastern side of Argyre (lat 45°S to 50°S, long 78°W to 95°W).

**Figure 2.** Plots of average of six spectra over Meridiani Sinus (M7:99,100,103,104, 105,106); average of seven spectra over Argyre (M7:111,112,113,116,117,118, 121); two model atmospheres at 2% resolution (solid line) and 1.6% resolution (dotted line). Error bars reflect standard deviation of the mean.
long 30° to 36°). These spectra are compared to the model Martian atmosphere convolved to resolutions of 1.6% and 2.0%. Different resolutions were tried because of the uncertainty associated with the determination of the instrument resolution (see the appendix). Independent of the resolution, it appears that the Mariner spectra have slight inflections not attributable to the anticipated smooth variation of the atmosphere spectrum. Inflections near 2.77, 2.79, 2.82, 2.84, 2.88, and 2.89 μm can be noted, and they do not correlate from one region to another. Such variations are probably not induced by the wavelength correction because this region has good tie points; minima and maxima in the atmosphere spectrum can be used in the wavelength-registration routine. We note that these features are weak, and there is sufficient uncertainty that they need to be confirmed before being considered definitive. They are suggestive of OH−, but without detailed spectral modeling which is beyond our intended scope (and possibly beyond the data quality of Mariner 6/7), the assignment of these features to mineralogy rather than to details of the atmospheric absorption cannot be made. If confirmed, the features at 2.77, 2.84, and 2.89 μm correspond well with features seen in hydrous magnesium carbonates (section 3), but many other hydrated minerals have OH− absorptions in this spectral region.

In some Mariner spectra of the longer wavelength segment, a weak feature near 5.4 μm was noted. Figure 3 shows two Mariner 6 spectra, an individual spectrum from Meridiani Sinus (lat 4°S, long 0°), and an average of four from Margaritifer Sinus (lat 13°S to 18°S, long 23° to 38°). These spectra are compared with a calculated blackbody spectrum that has been multiplied by the model atmospheric transmission. The blackbody was calculated according to temperatures determined by Pimentel et al. [1974], approximately 289 K. The feature near 5.4 μm appears on the edge of the atmospheric CO2 absorption. To get a better indication of the depth and shape of this feature, we removed a polynomial fit continuum from the M6 spectra in Figure 3. Figure 4 shows the Mariner 6 average and the best fit polynomial. Figure 5 shows the two Mariner 6 spectra from Figure 3 and an average of five spectra from Mariner 7, all with continua removed, compared with two model atmospheres of varied path length. Additional absorption on the right side of the atmospheric absorption band is evident, but it is most obvious in spectrum M6:195. The individual M6 spectrum and the M6 average suggest that the 5.4-μm absorption is related to the atmospheric path, i.e., as the 5.2-μm CO2 absorption increases, so does the 5.4-μm. However, the M7 average shows that this is not the case. The M7 average and M6:195 have equivalent absorption at 5.2 μm but are very different at 5.4 μm, suggesting a surface or atmospheric-dust origin for the 5.4-μm feature. There is no evidence in any of the instrument calibration spectra from the appendix, from T. Z. Martin (submitted manuscript, 1993), or from Herr et al. [1972] that this is an instrument-dependent feature.

We have not attempted a systematic search of the entire data set given the time- and user-intensive nature of the calibration; however, to date, the strong 5.4-μm absorption has been observed only in this single Mariner 6 spectrum. Mariner 7 also observed this region, but the temperatures were slightly higher and the instrument saturated, flattening the peak of the intensity distribution and eliminating even the atmospheric feature at 5.2 μm. This saturation effectively frustrates the attempt at a further confirmation of a strong feature at this location. It is significant that this geographic region is close, both spatially and temporally, to a region associated with anomalies in radar reflectivity [Zent et al., 1990]. The radar data were aquired in 1971, one Martian year after the Mariner flyby, at lat 14° 17°S, long 0°–3°. Although Zent et al. felt that the transient brine model is “far from compelling,” they also noted that “the Sinus Meridians site constitutes the best case for periodic brine formation on Mars.” As postulated later, the 5.4-μm spectral band appears to be associated with hydromagnesite known to form terrestrially as a brine precipitate (section 3), supporting the possi-

![Figure 3](image3.png)  
**Figure 3.** Spectra for the long wavelength segment. Solid line, M6:195; long dash-dot line, average of four (M6:202,203,207,208). Dotted line, approximate blackbody curve for region multiplied by model atmosphere transmission.

![Figure 4](image4.png)  
**Figure 4.** M6:average spectrum from Figure 3 (solid line) shown with best fit polynomial continuum (dotted line).
3. Hydrous Magnesium Carbonates

To verify that these minerals have no other obvious spectral features that should be observed but are not, it was necessary to examine the wavelength region below 2.5 μm, where most of the terrestrial spectral observations of Mars have been performed. M. Miyamoto kindly provided two samples of hydromagnesite, Mg₅(CO₃)₄(OH)₂·4H₂O, and one of arfite, Mg₂CO₃(OH)₂·3H₂O, so that spectral measurements in the visible and near infrared could be obtained. In addition, two more samples of arfite were available, one from California, obtained from Gene Forand, U. S. Geological Survey, and one fromSsten Island, New York, obtained through Ward's Natural Science Company. A sample of dypingite, Mg₅(CO₃)₄(OH)₂·5H₂O, was provided by TedTrousl at NASA Ames.

In the remainder of this section, we address issues pertaining to the compatibility of these minerals with Mariner 6/7 IRS and terrestrial telescopicspectral observations and the potential for such minerals to occur and persist in the Martian environment. Analyses of the reflectance spectra indicate that hydrous carbonates can contribute to weak absorption features observed on Mars, and that they have no strong absorption features that should exclude them from consideration as potential Martian minerals. Theoretical calculation of the reflectance of mixtures indicates that the required abundance levels are consistent with both observed reflectance spectra and the Viking XRF elemental analysis. Formation scenarios are consistent with the current and past Martian environments and with the inferred Martian source rock.

3.1 General Spectral Characteristics

Miyamoto and Kato [1990] presented spectra of several hydrous carbonates from 2.5 to 25 μm. They noted that, in contrast to anhydrous carbonates, these minerals show no spectral contrast near 3.5 and 4 μm. Carbonates typically have quite strong absorption features in this region as well as between 2 and 2.5 μm (e.g., see Figure 7 and Gaffey [1987]). The suppression of these features in the spectra of hydrous carbonates is due to the presence of water in the crystal structure. We found that the hydrous Mg carbonates are spectrally distinct from the hydrous Na and Ca carbonates examined by Crowley [1991]. The latter two have the typical strong 1.4- and 1.9-μm water absorptions, but they also have several strong spectral features from 1.5 to 2.5 μm not seen in the hydrous Mg carbonates.

Representative reflectance spectra of hydromagnesite, arfite, and dypingite are shown in Figure 8.
Figure 7. Spectra of typical anhydrous carbonates. Magnesite sample includes some hydromagnesite, as indicated by broad $\text{H}_2\text{O}$ absorptions at 1.4 and 1.9 $\mu$m and lowered reflectance level beyond 3 $\mu$m. Magnesite offset 0.3, dolomite offset 0.75, calcite offset 1.1. All samples from Hunt and Salisbury collection, U.S. Geological Survey Spectroscopy Laboratory, Denver.

Beyond approximately 4 $\mu$m the Mariner spectral observations are measuring surface emission. Fundamental vibrational absorptions appear as absorption features in emission spectra [e.g., Christensen et al., 1992; Wenrich and Christensen, 1993]. Given Kirchoff's law, we then expect these vibrational features to appear as peaks in reflectance. However, due to the small grain size of the samples and the biconical nature of the measurement, these vibrational modes appear as absorption features in our reflectance spectra [e.g., Salisbury et al., 1987, 1991; Hapke, 1993].

The most obvious features in all the spectra are related to water and/or hydroxyl. All the minerals show broad adsorbed water bands beginning near 3 $\mu$m. The arctinite has a fairly broad hydroxyl feature at 2.77 $\mu$m, and the hydromagnesite has several sharp hydroxyl features at 2.71, 2.74, 2.84, and 2.89 $\mu$m. The hydromagnesite and dypingite have broad bands near 1.4 and 1.9 $\mu$m associated with water and also sharp hydroxyl features on the short-wavelength side of the 1.4- $\mu$m band. The arctinite has only the sharp hydroxyl feature near 1.4 $\mu$m. All the spectra have a "red edge" in the visible, i.e., a rise from shorter to longer wavelengths that is common to many minerals.

In addition to these features, weaker absorptions occur between 2 and 2.6 $\mu$m in the arctinite and hydromagnesite that can be attributed to either Mg-OH modes or the presence of CO$_2$. Apparently, the abundant water in the dypingite reduces spectral contrast and effectively suppresses bands in this wavelength region for this sample. Arctinite has an additional broad doublet from 4 to approximately 4.5 $\mu$m and a narrow feature near 5.6 $\mu$m. The doublet appears similar to carbonate features seen in anhydrous carbonates but is shifted to longer wavelengths. The hydromagnesite has a small doublet near 5.4 $\mu$m and a triplet structure between 3.8 and 4.0 $\mu$m. Comparison of this triplet structure and other spectral features with other carbonate and carbonate-bearing minerals suggests the presence of bicarbonate in the hydromagnesite sample. Work by Swayne and Clark [1990] indicates that the cen-
tral feature in a triplet near 3.8–4.0 μm in scapolite minerals is associated with bicarbonate. Bicarbonate in scapolite also causes absorption features near 2.33, 2.35, and 2.85 μm. Hydromagnesite also exhibits features in these spectral regions, strengthening the evidence for bicarbonate in the hydromagnesite. The presence of bicarbonate suggests that perhaps the formulation for hydromagnesite may be more like that for nesquehonite (Mg(HCO₃)OH·2H₂O), with an explicit bicarbonate (HCO₃). Alternatively, the hydromagnesite samples may contain some amount of nesquehonite. Slow alteration of hydromagnesite to nesquehonite has been noted in some instances [Ming, 1981, and references therein, and personal communication, 1991].

3.2. Spectral Comparison, Theoretical Mixes, and Abundance Limits

Of the spectral features identified in hydrous Mg carbonates, only a few would lead to a diagnostic mineral identification, particularly when considered in the context of the Martian environment. The red edge is common to many minerals, and, when hydrous carbonates are coupled with the inferred amorphous iron oxides present on the surface, it is unlikely that they could be identified from this spectral region. Many of the water features will be difficult to observe terrestrially, given the presence of telluric water. Features at wavelengths shorter than 2.1 μm would not be observed from Mariner 6/7 IRS, as the instrument did not cover this wavelength region. Carbon dioxide and water in the atmosphere of Mars will tend to obscure bands at 1.4 and 1.9 μm. In addition, absorption features arising from water and hydroxyl are also common to many different minerals, and they would not be diagnostic of hydrous carbonates specifically. Carbon dioxide in the atmosphere of Mars will obscure features from 2.7 to 2.8 μm and from 4.2 to 4.5 μm.

Therefore, we might expect to see absorption features due to hydrous Mg carbonates in the following spectral regions: 2 to 2.5, possibly near 2.7, 3.8 to 4.0, and 5.4 or 5.6 μm. In addition, we are interested in limits on abundance and a general confirmation that no inconsistent spectral features are produced. To these ends, we have calculated spectra of hydrous carbonates mixed with spectrally neutral material such as hematite and palagonite. We are not attempting a precise spectrophotometric model of the surface because the specific mineralogy is not yet well defined and there are too many possible mineral combinations for the surface of Mars. Although beyond approximately 4 μm the Mariner spectra record surface emission, theories for calculating emission have only recently been developed [Hapke, 1993] and have not yet been tested against laboratory measurements of emission. As our reflectance measurements show the required features as absorptions, equivalent to what we expect to see in emission, we perform our calculations using a reflectance model for the full wavelength range. We note, however, given variation in contrast between emission and reflectance [Hapke, 1993], that the abundances derived may not be accurate for the 5.4-μm absorption band.

Optical constants for hydromagnesite and aragonite were derived from the reflectance spectra according to a theory developed by Hapke [1986]. Knowing the grain size and an approximation of the index of refraction, one can invert the reflectance spectrum of a pure sample to obtain the absorption coefficient for a particular mineral. The index and absorption coefficient can then be used to calculate the reflectance of mineral mixtures at a wide variety of grain sizes and abundances. For a more comprehensive description of the technique, the reader is referred to Calvac [1990].

Both the aragonite and hydromagnesite samples had been ground and sieved to a grain size less than 100 μm; to derive the optical constants, an average value of 50 μm (confirmed by optical microscopy) was used. The index of refraction was approximated by using an average value for carbonates from the visible, by assuming a slight decrease toward longer wavelengths, and by incorporating an inflection near 8 μm to duplicate the strong absorption in this spectral region due to water. The derived absorption coefficients range from values around 50 cm⁻¹ in the 2-μm region to a maximum near 1500 cm⁻¹ in the 3-μm region. Similar techniques were applied to a 0- to 74-μm grain size fraction of hematite (HS45 from the Hunt and Salisbury collection in Denver) and to a <0.1-μm grain size fraction of VOLS02 palagonite. These optical constants were then convolved to informed instrument wavelengths and spectral resolutions to facilitate comparison with actual observations.

Because the hydrous carbonates are weathering products, they are presumed to reside in the fine component of the surface material. From the Viking Gas Exchange Experiment (GEX), particles within clods of soil were found to range in size from 0.1 to 10 μm [Arvidson et al., 1989]. The average grain size of globally distributed dust at the end of a dust storm was close to 3 μm [Toon et al., 1977]. However, thermal inertia measurements indicate an effective grain size of fine material of 2 to 40 μm; cementation of fines by salts tends to increase the effective grain size [Christensen, 1986; Jakosky and Christensen, 1986]. Analyses of polarization measurements by Dollfus and Deschamps [1986] indicate grain sizes in the range of 20 to 45 μm. To be consistent with these values, we have used grain sizes in the 10- to 30-μm range in the model calculations.

We begin with the Mariner observations. Due to the uncertainty in the wavelength calibration (see the appendix) and the weak mineralogic signatures, it is difficult to distinguish atmospheric from mineralogic absorption features in the 2- to 2.5-μm region. However, we might expect to see the sharp hydroxyl absorption features from 2.7 to 2.9 μm in aragonite and hydromagnesite. Hydromagnesite has two doublets, one at 2.70–2.75 μm and the other at 2.80–2.95 μm. Aragonite has a broader singlet centered on 2.77 μm. All of these features lie directly in the strong atmospheric absorption by CO₂ (e.g., see Figure 1). Depending on the abundance, these features may alter the appearance of the atmospheric features, or they may appear only as weak inflections on top of the atmospheric signature. The largest effect would be expected from hydromagnesite
because the shorter doublet lies at the same wavelength as the maximum of the atmospheric doublet. If hydromagnesite is highly abundant, the distinctive atmospheric doublet might be expected to appear as a broad single band.

To examine the effects of the OH features on the atmospheric signature, several mixtures were calculated. Figure 9 shows two mixtures of arfinitie, hydromagnesite, hematite, and palagonite. Because both the hydrous carbonates and the palagonite have strong, broad, water features beyond 3 μm, these models suggest that large quantities of hydrated minerals may be required to match the observed 3-μm water band of Mars. However, we were unable to calibrate this wavelength region radiometrically, and so we can say very little about the actual water abundance. Figure 9 also demonstrates that at the Mariner instrument resolution, the sharp hydroxyls from 2.7 to 2.9 μm and the weak features between 2 and 2.5 μm are not spectrally obvious (the feature near 2.3 μm arises from the model atmosphere). The resulting model times atmosphere looks similar to the Mariner observations.

For the longer-wavelength segment of Mariner, the doublet in arfinitie at 4.2-4.4 μm lies exactly on top of the strong atmospheric CO₂ absorption (e.g., Figure 3). Given the strength of the atmospheric feature, not even inflections would be expected. Arfinitie also has a feature at 5.6 μm, but this is near the limit of good signal-to-noise levels for the Mariner spectrometer. If arfinitie is highly abundant, a feature here might be anticipated. For hydromagnesite, the triplet structure from 3.8 to 4.0 μm would not be observed given the poor signal-to-noise and low spectral resolution. However, the 5.4-μm doublet of hydromagnesite correlates well in position and width with the feature identified in section 2.

Figure 10 shows a mixture of 10% arfinitie and 30% each of hydromagnesite, hematite, and palagonite compared with the same model multiplied by the Crisp [1990] model atmosphere. This figure demonstrates that the broad arfinitie doublet at 4.2-4.4 μm is lost in the atmospheric signature, and at the 10% level the 5.6-μm feature is not spectrally obvious. Additionally, at the 30% level the 3.8-μm structure of hydromagnesite may be visible because it slightly distorts the atmospheric absorptions, but it is not likely to be observed at the signal-to-noise level of the Mariner instrument. Although the 5.4-μm absorption from hydromagnesite is fairly obvious in the pure mixture, the atmospheric band at 5.2 μm will affect the continuum level in such a way as to effectively suppress the band depth. After consideration of the atmospheric effects, with 30% hydromagnesite the 5.4-μm band appears only 1%-2% deep, consistent with the strongest band in M6:195 shown in Figure 5. To better demonstrate the match in the spectral region near 5.4 μm, we have removed a straight-line continuum from the model in Figure 10 and compared it with the M6:195 observation from Figure 5 in Figure 11. Here the band correlation at 5.4 μm is quite strong. Differences in the continuum level at 5.3 μm are probably due to reflectance versus emission.
modeling, to the thermal slope in the Mariner data, and to how the continua were fit to the individual spectra. In other ways the hydromagnesite band at 5.4 $\mu$m is a close match to the feature observed in the Mariner spectrum.

Recent terrestrial observations have identified mineralogical features due to carbonates in two wavelength regions, 2 to 2.5 $\mu$m and near 7 $\mu$m. The Clark et al. [1990a] data from 2.2 to 2.5 $\mu$m were shown in the previous section. Figure 12 shows the absorption features for arzinite and hydromagnesite when a continuum slope is removed from the spectra. Both these features fall nicely into the broad envelope identified as mineralogic as well as atmospheric in origin [Clark et al., 1990a; Bell and Crisp, 1993]. In regions relatively free of atmospheric absorption there are strong features, in particular at 2.28 and 2.40-2.44 $\mu$m. Clark et al. [1990a] attributed the mineralogic absorption to carbonate and bicarbonate in the mineral seacopolyte. We find that the hydrous carbonates can also contribute to this spectral region and can match certain aspects of the spectral structure.

Mixtures of either arzinite or hydromagnesite with hematite in this wavelength region are shown in Figure 13. The calculated spectra have been multiplied by the model atmosphere spectrum from Figure 6 to better approximate the actual observations. As shown in Figure 13, small amounts of arzinite can provide a reasonable match to the observed spectrum at 2.28 $\mu$m. Abundances of 10% or slightly more provide an excellent fit to this band. Larger quantities of hydromagnesite are required to approach the observed band depths. Hydromagnesite does not match the 2.28-$\mu$m band as well as arzinite does; however, abundances of approximately 30% begin to reproduce the band shape near 2.44 $\mu$m.

A combination of the two minerals could contribute to both features. Figure 13 indicates that there must be additional absorption in the region from 2.35 to 2.43 $\mu$m that hydrous carbonates cannot explain. Strong absorption in this spectral region was attributed to the presence of bisulfate in seacopolyte by Swagze and Clark [1990]. Other sulfate minerals, in particular hydrous sulfate salts suggested by Clark [1978], may also contribute to this spectral region. Some spectra presented by Crowley [1991], in particular the hydrous sulfates leonite, picromerite, and bloedite, also exhibit strong absorption near 2.4 $\mu$m. However, these particular minerals also exhibit strong, broad absorptions from 1.4 to 1.8 $\mu$m and from 1.8 to 2.2 $\mu$m, which limit their compatibility with spectra of Mars.

Pollack et al. [1990] made observations at longer wavelengths than those that are the focus of this paper. They identified absorption features at 6.7 $\mu$m and on the short-wavelength side of the atmospheric band at 7.3 $\mu$m as caused by CO$_3^{2-}$ or HCO$_3^-$. The variability of the hydrous carbonate samples in this spectral region is shown in Figure 14. Although no single mineral matches all of the data of Pollack et al., all of the samples show absorptions in this region. Both dypgite and hydromagnesite have a feature at 6.7 $\mu$m; in addition, hydromagnesite has a feature at 7.1 $\mu$m. As demonstrated in Figure 14, hydrous carbonates exhibit abundant spectral variability in this region. Perhaps some other type of hydrous carbonate not yet examined may match both features in the data of Pollack et al. Alternatively, combinations of types of hydrous carbonates or a hydrous carbonate in conjunction with other minerals may provide a more precise spectral match.

Finally, there is a long history of terrestrial observations in the wavelength region from the visible to 2.5 $\mu$m. To confirm that hydrous Mg carbonates introduce no spectral features that should be noted but
are not, a mixture was calculated at the wavelengths and resolution of the laboratory Beckman spectrometer. Figure 15 contrasts mixtures of artinite and palagonite and of hydromagnesite and palagonite with the spectrum of pure palagonite in the visible and near-infrared. In the mixtures the dominant features near 1.4 and 1.9 μm arise from the palagonite. At the 30% level, hydromagnesite introduces weak features at 2.2–2.4 μm (previously discussed) and a sharp hydroxyl feature at 1.4 μm. This would not likely be observed from Earth given the interference by telluric water. At the 10% level, artinite only introduces the weak feature at 2.28 μm that has already been shown to be a reasonable match to telescopic observations. Therefore we can conclude that the hydrous carbonates introduce no features inconsistent with observations of Mars in this spectral region.

Hydrous carbonates cannot account for all spectral features of Mars, but this would not be expected of a surface that is likely a mixture of many minerals. To summarize the spectral data, we find that artinite has a feature at 2.38 μm that matches a particular mineralogic absorption feature identified in spectra of Mars. Hydromagnesite has features at 2.28, 2.33, and 2.44 μm that can contribute to observed spectral features. In addition, hydromagnesite has an absorption feature at 5.4 μm that provides an excellent match to a feature observed in Mariner 6 and 7 NIRS spectra. As little as 10 wt% artinite provides a reasonable spectral match, whereas quantities of hydromagnesite required for the strong 5.4-μm feature are slightly higher, near 30 wt%.

At these mixing levels and at wavelengths from the visible to approximately 6 μm, no features from hydrous carbonates are inconsistent with observed spectra of Mars.

Given the compatibility of the hydrous carbonate spectra with many of the weak absorption features identified in the spectra of Mars, we next consider the formation and stability of such minerals in a Mars-like environment.

3.3. Formation and Compatibility With the Martian Environment

On Earth, hydromagnesite has been found as a precipitate in an ephemeral lake environment where both the HCO$_3^-$ concentration and the Mg/Ca ratio are high [Alderian and von der Borch, 1960; von der Borch, 1966]. Typically, hydrous carbonates are associated with the alteration of serpentines or olivine [e.g., Burgh, 1946; Raade, 1970; Ming, 1981, and references therein]. In a study of the weathering zone of a California serpentinite, Mumpion et al. [1965] found that iron-rich brucite (Mg$_{10}$Fe$_2$(OH)$_{24}$) formed during the serpentinization of an olivine rich parent magma. In the surface weathering zone, that is, in the presence of atmospheric O$_2$, H$_2$O, and CO$_2$, this brucite rapidly oxidizes and is transformed into pyroaurite (Mg$_6$Fe$_2$CO$_3$ (OH)$_{15}$·4H$_2$O) and coalingite (Mg$_{10}$Fe$_2$CO$_3$(OH)$_{24}$·2H$_2$O), both iron bearing hydrous Mg carbonates. In the presence of CO$_2$-rich groundwater, the brucite dissolves, leaving an amorphous iron-oxide residue; the magnesium ions remain in solution to precipitate later as hydromagnesite [Mumpion and Thompson, 1966]. Similar reactions were described by Hosteller et al. [1966]. Reesite (Ni$_6$Fe$_2$CO$_3$(OH)$_{16}$·4H$_2$O) has been reported as a weathering product in the Wolf Creek iron meteorite [White et al., 1967].

In addition, nesquehonite and hydromagnesite are reported to form as evaporative weathering products on the surface of Antarctic meteorites [Jull et al., 1988; Velbel et al., 1991]. These workers proposed that ferromagnesian silicates (mostly olivine) in the meteorites react with terrestrial water and CO$_2$ to form nesquehonite and iron oxides like goethite or lepidocrocite that contribute to the visible rust on these weathered meteorites.

Extrapolation to formation in a Martian environment then requires (1) brackish or ultramafic source material, (2) a source of CO$_2$ and H$_2$O, and (3) the potential to form or persist in the present surface environment. An additional constraint on the quantity of hydrous Mg
carbonates is the abundance of magnesium in the Martian soil as determined by the Viking XRS experiment. The value for Mg was not measured at the second lander site; the nominal value as an oxide is given as 6 wt. %, but the uncertainty is large (-3 to +5) [Clark et al., 1982; Arvidson et al., 1988]. In arctinite and hydromagnesite, MgO is approximately 40 wt. % of the total mineral. Therefore, if the surface contains 20 wt. % of a hydrous carbonate, it would be 8 wt. % MgO. This implies that all the magnesium would be bound in the hydrous carbonate, which seems unlikely. We believe that an upper limit of 10 wt. % hydrous carbonates is more appropriate for the global abundance level. Ten weight % arctinite is still sufficient to cause spectral features similar to those seen in the spectra of Mars. In addition, if iron substitutes for some of the magnesium, abundances could be slightly higher and still be consistent with the XRS data. Also, to date, only one region has been identified with the very strong 3.4-μm feature characteristic of higher levels of hydromagnesite. As discussed in section 2, this region appears to be unique.

Martian upper mantle material is inferred to be rich in olivine, and magnas derived from such source material can be expected to contain some amount of olivine [Longhi et al., 1992]. Additionally, Longhi and Pan [1989] inferred the SNC parent magnas to be similar to komatites (terrestrial mafic rocks rich in olivine). Hydrothermal alteration of olivines commonly produces serpentine minerals, among others, and alteration of komatites yields serpentine minerals, brucite, and magnetite [e.g., Beatty and Taylor, 1982]. These minerals can subsequently alter to hydrous Mg carbonates. The Martian surface also contains amorphous iron oxides, which could be produced as by-products of Mg carbonate formation as well as other processes. CO₂ is plentiful as the primary constituent of the current Martian atmosphere.

The major missing factor in the formation of hydrous carbonates is the presence of liquid water to catalyze the chemical reactions. Water in the liquid phase is currently not stable in the Martian environment, although it is present in both the gaseous and solid phases. Mars is considered to be dry due to the low absolute value of water in the atmosphere; however, the atmosphere near the surface may reach saturation at night [Jakosky, 1985], and water frost condenses on the surface in winter [Jones et al., 1979, Arvidson et al., 1989]. In chemical weathering in the Antarctic, water can be present as thin films in subfreezing temperatures and may be sufficient to drive weathering processes [Gooding, 1986]; similar conditions can be envisioned for Mars. In addition, many arguments can be made for transient liquid phenomena in either the past or the present Martian environment. If the early, wet Mars model is correct [e.g., Pollack et al., 1987], liquid water may have been abundant in Mars' past. In its current environment, water may be stable in subsurface brines, which may be sufficient to produce hydrous salts.

The terrestrial weathering environment most similar to what is inferred for Mars is that of the Dry Valleys of Antarctica [Gibson et al., 1983]. Chemical weathering has been shown to operate there, and the presence of Mg salts is attributed to weathering of ferromagnesian minerals rather than seafalls [Clayard and Campbell, 1977; Keys and Williams, 1981]. In such cold environments, evaporites typically form hydrous mineral species [Sonnefjeld, 1984, p. 5]. In addition, Mg has an affinity for H₂O that leads characteristically to the formation of hydrous rather than anhydrous Mg carbonates [Lippmann, 1973 p. 71; Mackenzie et al., 1983]. This characteristic, coupled with the formation specifically of hydrous Mg carbonates on Antarctic meteorites, suggests that their formation is not prohibited under current Martian conditions. However, Fegley and Treiman [1992] cautioned that it is not clear what, if any, chemical weathering reactions should occur on Mars. Clark and van Hart [1981] noted that Mg carbonates are stable in the presence of other salts expected on Mars, although they suggested that such salts would be destroyed by the presence of atmospheric sulfur. Sidorenko and Zolotov [1986] studied reactions between minerals and gaseous SO₂ and concluded that such reactions should be negligible at current Martian temperatures. Banin et al. [1992, and references therein] noted that, in simulations of the Viking GEX experiment, the inclusion of calcite vastly reduces soil reactivity. However, these workers also noted that higher levels of magnesite and siderite cannot be tolerated and that the presence of nanophase hematites in Mars' soil could significantly increase soil reactivity. Whether hydrous carbonates behave in the same way as anhydrous carbonates in such reactivity experiments is also not known.

The presence of mafic source material, H₂O, CO₂, and amorphous iron oxides on Mars is consistent with the formation of hydrous magnesium carbonates. The main objection to stability in the current Martian environment is the possibility of dehydration. Fegley and Treiman [1992] concluded that several types of hydrous Mg carbonates are not stable against dehydration under current Martian atmospheric partial pressures of water. They suggested that if such minerals do exist, they are relics of weathering products whose dehydration is prohibited by kinetic factors. Also, Ming [1981, and personal communication, 1991] noted the tendency of synthetic hydrous Mg carbonates to dehydrate at room temperatures. In contrast to those observed by Ming, our samples were not specially stored to prevent dehydration, and they do not exhibit signs of alteration to less hydrated forms. Additionally, several samples were left at room temperatures in an evacuated environment for periods on the order of several weeks with no loss of water noticeable in the reflectance spectra. Differential thermal analyses of dypingite and hydromagnesite by Raade [1970] indicate that temperatures of 125° and 265°C are required before samples release their water of crystallization. The maximal temperatures on the Martian surface range from 20° to 30°C, and so they are not expected to drive dehydration. Finally, the Martian atmosphere holds about as much water as it can under current conditions, so much so that
water is often condensed as frost [Jakosky, 1985]. Periodic atmospheric saturation would inhibit the loss of water chemically bound in hydrated surface minerals, and much of the current atmosphere-surface exchange of water could be through physically adsorbed, rather than chemically bound water. In any event, it is clear from the Mariner reflectance spectra in the 3-μm region that even in the warmest areas of the planet some amount of water remains in the surface.

The chemical stability of hydrous Mg carbonates in the Martian environment remains uncertain. However, a wide range of both historic and modern conditions controlling the concentration of water in the surface makes the possibility of formation and stability plausible.

4. Summary and Conclusions

The first part of this paper focused on analysis of Mariner 6 and 7 IRS data. This data set remains unique in terms of spectral coverage and wavelength resolution for the wavelengths examined, i.e., approximately 2 to 6 μm. We performed extensive calibrations in wavelength and intensity to make the data as useful as possible. Because we were unable to radiometrically calibrate the 2- to 4-μm segment, we could not constrain the depth of the water band near 3 μm. Knowledge of the water abundance is critical to address questions regarding current and past volatile inventories. The recent release of a completely calibrated Mariner data set (T. Z. Martin, submitted manuscript, 1993) may allow this problem to be addressed as well as facilitate a systematic search of all Mariner 6/7 spectra for specific spectral features.

Absorption features were tentatively identified in spectral regions unavailable to terrestrial observations. Weak inflections from 2.7 to 2.9 μm are observed but need to be confirmed. There is strong evidence of a feature at 5.4 μm inferred to be due to surface or atmospheric dust absorption. This feature is consistent with the spectra of hydrous magnesium carbonates, as are features near 2.3 μm identified from terrestrial observations of Clark et al. [1990a], although the latter are not unique indicators. The spectral characteristics of these hydrous carbonates are quite different from those of the anhydrous carbonates and the hydrous Na and Ca carbonates. Theoretical mixing indicates that, depending on the type of hydrous carbonate, 10 wt % to 20 wt % can be incorporated into the regolith and it will still be consistent with the spectral observations and the Viking XRFS chemical analysis.

Hydrous carbonates form as weathering products of mafic minerals in the presence of H₂O and CO₂, even at subfreezing temperatures. Their formation as evaporite minerals from either original magmas or hydrothermally altered rocks is consistent with the Martian environment, provided liquid water is or has been present at least transiently. Although the stability of hydrous carbonates in a Martian environment is uncertain, there may be kinetic factors that inhibit their dehydration, and they may persist metastably in the current environment. These minerals are about 80% by weight H₂O, CO₂, and OH. If they are abundant everywhere at the 10% level, then about 6% of the surface weight could be volatiles bound in this type of mineral. They also provide an appealing mechanism for the formation of carbonates on Mars, whereas spectral evidence for anhydrous carbonates has been scant.

Several arguments support the presence of hydrated mineral salts as weathering products on Mars. Recent abstracts by Zolotov [1989], DeBraal et al. [1992], and Plumlee et al. [1992] predict the stability of some types of hydrous carbonates and hydrous sulfates. Crowley [1991] presented spectra of a variety of evaporite salts; however, many of these have strong absorptions not seen in the reflectance spectrum of Mars, although a few, such as thenardite and eugsterite, may be compatible. More of these types of evaporites need to be characterized in the laboratory before the uniqueness of the spectra of the hydrous Mg carbonates studied here can be assessed. In particular, sulfate and chloride minerals are expected on Mars due to the identification of both sulfur and chlorine from the Viking XRFS. Spectral data of low-temperature hydrous Mg carbonates such as lansfordite should be obtained, as these may be more applicable to the Martian environment. Iron-bearing hydrous carbonates such as coalingite, sjögrenite, brugnatellite, and pyroaurite should also be characterized, as these may be more appropriate as candidates for Martian soils. Examination of hydrous carbonate spectra at longer wavelengths and comparison with existing longer wavelength data sets of Mars are pertinent to the Thermal Emission Spectrometer instrument.

The recent crop of spectroscopic observations and analyses, both terrestrial and from spacecraft, indicates a plethora of weak mineralogical features in the visible and near-infrared. These weak features strongly point to the need for a calibrated, high spectral resolution, visible and near-infrared imaging spectrometer to observe Mars. Such an instrument is being developed by the French to be flown on the next Russian Mars orbiter. The resulting data will benefit both atmospheric and mineralogical scientists interested in Mars.

Appendix: Calibration of the Mariner 6/7 IRS Data Set

T. Z. Martin (submitted manuscript, 1993) has completely restored the data set. Our work began before his restoration was complete. We performed the calibration steps described here using the data release provided by Martin [1985].

In spite of the partial wavelength correction in the short-wavelength segment, additional corrections were required. The use of the fiduciary spikes for wavelength calibration was found to yield inaccurate wavelengths, apparently because of variation in the rotation rate of the filter wheel. This variation causes errors when a linear interpolation in wavelength between fiduciary spikes is used. Corrections using atmospheric hands
at one side of a wavelength segment also will not accurately predict wavelengths on the other side of the wavelength segment. The instrument team planned to use observations of polystyrene film for wavelength calibration; every twelfth spectrum acquired superimposed the polystyrene on the observations of Mars. However, these polystyrene and Mars spectra were not released with the 1985 digital data set.

In addition to the wavelength calibration, corrections for the instrument response function are also required. This correction accounts for the varying transmission through the filter wheel, as well as spectral variations in detector sensitivity. Detailed descriptions of the intensity corrections and the wavelength calibration used for this examination of the IRS data set are provided in the following sections.

Space Background and Instrument Response

For accurate intensities, a dark calibration must be performed, which corrects for instrument performance in the absence of sources, i.e., the scattered light. For the short-wavelength segment, from 2 to 3.7 \( \mu m \), the space background observations do not deviate significantly from the zero level. Given a dark level of virtually zero, we decided not to subtract the actual dark measurement, as this operation would add significant noise to the original spectra. For the wavelength segment from 3 to 6 \( \mu m \), a significant nonzero dark level, due to the thermal contrast between the instrument and space, was seen. Some space observations contain radiation scattered from the planet. These spectra can be differentiated because they exhibit lower peak intensities and have a slight absorption feature that is well correlated to the strong CO\(_2\) absorption at 4.2–4.4 \( \mu m \). We chose 11 spectra from M7 observations and six spectra from M6 as being free from any apparent scattered radiation. These spectra were averaged. Because the average was still relatively noisy, it was smoothed by performing a fast Fourier transform (FFT), smoothing the high-frequency component of the transform by hand, and then doing the inverse FFT. Figure A1 shows the original and the smoothed space background spectra for M7. The fiducial spikes from every half-revolution of the filter wheel can also be seen in the figure.

Because the wavelength calibration is performed using atmospheric absorption features, and the dark calibration spectrum does not exhibit these absorptions, the dark spectrum can be matched to the spectra of Mars only by using the fiducial spikes. Because the dark spectrum varies smoothly, we can assume that matching the dark and signal spectra in this way will introduce only small errors in intensity levels for any given wavelength.

In addition to the dark calibration, correction for the instrument response function must also be performed. This process corrects for wavelength-dependent instrument factors such as the transmission of the circular variable filters (CVF) and the sensitivity of the PbSe detector. Several preflight blackbody observations were included in the digital data set received from Martin [1986]. The highest temperature of these blackbodies was 296 K. Given the low flux of such sources at short wavelengths, these calibration spectra are reasonable only for wavelengths longer than approximately 4 \( \mu m \), which precludes correction for the instrument response for the short-wavelength segment. However, Pimentel et al. [1974] showed a spectrum for the short-wavelength segment of the Sun reflected off “an unknown part of the spacecraft” that was measured by Mariner 6. This spectrum is reasonably flat between 2.1 and 2.8 \( \mu m \), with a slight downturn at either end, suggesting that the relative intensities of the raw data may be close to the actual values but may increase slightly at either end of the wavelength segment. T. Z. Martin (submitted manuscript, 1993) noted that radiometric calibration of this segment remains problematic even if preflight observations of a Nemst glower source are used.

For the instrument response function of the long-wavelength segment, 3 to 6 \( \mu m \), the blackbody observations were used. No note was made of which instrument recorded the spectra, so the same blackbody observation was used for both M6 and M7. We used the observation of the 296 K blackbody minus the appropriate dark spectrum, ratioed to the Planck distribution at the same temperature. Again this function was fairly noisy, so the FFT smoothing was performed as for the space background spectrum. The wavelength region less than 4 \( \mu m \) was excessively noisy, requiring that the instrument response function be extrapolated in a smooth curve. Figure A2 shows the original and smoothed instrument response functions for the long-wavelength segment of M7. As with the space background, the instrument response can be matched to the Mars spectra only by using the fiducial spikes. Again we assume that because the response function is smoothly varying, only small errors in intensity are introduced at a given wavelength.

Due to the smoothing, instrument features at 3.4 and 5.8 \( \mu m \) are not removed and can be seen in our calibrated spectra. Other than the effects of smoothing, all
our dark and instrument response curves closely match those derived by T. Z. Martin (submitted manuscript, 1993), and the release of the full calibration will not affect our conclusions regarding spectral features.

Wavelength Calibration

For this analysis the wavelengths were calibrated by using absorptions in the Martian atmosphere. A high-resolution model of the atmospheric transmission of Mars was obtained [Crisp, 1990] and convolved to the resolution of the Mariner instrument. Herr et al. [1972] published values for the instrument resolution; however, in their paper the y axis was mislabeled in the figure associated with resolution. Not only are the y axis increments uneven (i.e., 0.6, 0.7, 0.8, 1.0), but they disagree with the statement of resolution range in the text, causing some confusion as to the actual resolution. After several convolutions of the model atmosphere spectrum to varied resolutions, it appears that the best fit to the Mariner data is obtained by using the values from the y axis of the figure, but after it is relabeled at consistent increments (i.e., 0.6, 0.7, 0.8, 0.9). Figure 4 of Herr et al. [1972] shows the value of the half bandwidth at half maximum (HWHM) in percent; to get the actual resolution, i.e., the full bandwidth (FWHMI), these values are doubled. This procedure results in filter resolutions (FWHMI) of 1.0% to 1.8% with an average near 1.6%. Only isolated points about 0.5 μm apart are plotted; between points we approximated the resolution by a straight line. This line-segment approximation was used to convolve the high-resolution [Crisp, 1990] atmosphere to the Mariner wavelengths and resolution. The convolution was performed by using Gaussian band passes at specified center wavelengths with widths according to the filter resolution given above. This lower-resolution model atmosphere was then used to adjust the wavelengths of the Mariner spectra.

To expedite the wavelength calibration, a program was written that overlays plots of the reference atmosphere and the observed Mariner spectra. The user picks features in the reference spectrum to be used for wavelength standards. The wavelength of the feature as determined from the reference atmosphere spectrum is then assigned to the channel number of the corresponding feature in the spectrum of Mars. For isolated points in the data, a given channel will have a specified wavelength value, and a linear interpolation of wavelengths between fixed points is performed to generate a new wavelength file for the entire spectrum.

In practice, the three CO₂ bands near 2.0 μm, the CO₂ doublet at 2.7 μm, an instrument feature at 3.4 μm [Pimentel et al., 1974], and the fiducial spikes were used to adjust the wavelengths of the short-wavelength segment. For the long-wavelength segment, the fiducial spikes, the instrument feature at 3.4 μm, and CO₂ features at 4.2-4.4, 4.6, 4.8, and 5.2 μm were used to make the adjustment.

This wavelength calibration had to be made for each spectrum individually, and it resulted in a different wavelength set associated with each spectrum. To facilitate working with the data, e.g., averaging many spectra, the wavelength-adjusted spectra were interpolated to a single consistent wavelength set. By this method, absorption features may be expected to have shifts of 0 to 0.05 μm, depending on where they are with respect to the calibration points. Interpolation to a common wavelength set introduces no significant wavelength error.

Unless otherwise noted, all Mariner data presented here have been redetermined in wavelength, and the 3 to 6-μm segment has been corrected for space background and instrument response.

Signal to Noise

We estimate the signal to noise (S/N) in any given spectrum by examining the peak-to-peak (ptp) jitter. This value appears to be fairly constant: for the short wavelength segment, 1/4/1/2 unit and for the long-wavelength segment, 1/2/1 unit, where the units are those of the raw instrument signal level. At 3 μm in the long-wavelength segment, the raw signal can be as low as 5, so the S/N is 5 to 10. In regions of high raw signal, the S/N can be as good as 100 to 150. Performance of M6 was typically worse given the presence of a periodic noise component. For the long-wavelength segment, where the raw levels are divided by the instrument response, the ptp values and the signal level scale are reduced accordingly, but the S/N is unchanged (e.g., for M6:195 in Figure 3 in the 3-μm region, the ptp values are about 0.03 unit and the signal level is 0.3 for a S/N of 10). We have significantly improved S/N in many spectra presented here by performing regional averages (e.g., by contrasting the small fluctuations in the individual M6 spectrum with the average in Figure 3).

Acknowledgments. We wish to thank M. Miyamoto, Gene Foord, and Ted Roush for providing hydrous carbonate samples. Thanks also go to Terry Martin for helpful comments on the Mariner data set and to Gregg Swasey for discussions regarding band assignments and origins. The original version of the manuscript benefited from helpful comments by reviewers Jim Bell and Diana Blauny. This work was supported by NASA Interagency agreements W15805 and W17077 to the U.S. Geological Survey.
References


W. M. Calvin, U.S. Geological Survey, Branch of Astrogeology, 2255 N. Gemini Dr., Flagstaff, AZ 86001. (wcalvin@bulk.wr.usgs.gov)

T. V. V. King and R. N. Clark, U.S. Geological Survey, Branch of Geophysics, MS964, Box 25046, Denver Federal Center, Denver, CO 80225. (tking@speclab.cr.usgs.gov, rclark@speclab.cr.usgs.gov)

(Received February 9, 1993; revised April 13, 1994; accepted April 21, 1994.)