

SPECTROSCOPIC IDENTIFICATION OF CARBONATES IN THE MARTIAN DUST. J. L. Bandfield, T. D. Glotch, and P. R. Christensen, Department of Geological Sciences, Arizona State University, Tempe AZ (joshband@asu.edu).

Introduction: Carbonates play a significant role in determining the history of the Martian atmosphere, geology, and hydrology. Their presence and properties can give useful information about the specific environment in which they formed in the past. The work presented here demonstrates that the spectral character of Mars is consistent with and unique to the presence of small amounts of carbonates within a fine particulate dust.

The systematics and accuracy of the TES data has allowed for the isolation of the thermal infrared emissivity spectra of the surface dust, providing a new measurement with unique mineralogical sensitivities [1]. Absorptions at $\sim 800\text{cm}^{-1}$ and $>1300\text{cm}^{-1}$ are due to fine particulate silicates that contain an unknown concentration of plagioclase or zeolites [1,2]. While the absorption present at $>1300\text{cm}^{-1}$ is consistent with volume scattering effects in fine-particulate silicates [1,3], the spectral shape and depth requires the presence of a material that is highly absorbing at these wavenumbers to raise the emissivity to the level seen on Mars.

Similar to the $4.5\mu\text{m}$ absorption [4-6], the spectral character near $7\mu\text{m}$ ($\sim 1500\text{cm}^{-1}$) in the Martian spectrum appears to be sensitive and unique to small quantities of carbonates intimately mixed with silicates in fine particulate materials. The extent and variability of this spectral character is investigated with the TES and laboratory data to both confirm the compositional implications of the Martian spectral features as well as attempt to put constraints on the abundance present.

Methods and Results: Twenty-one multiple emission angle sequences were selected from a variety of longitudes and latitudes between 30 S and 15 N and the surface emissivity was derived using an atmospheric correction method similar to [1]. The distribution of the selected observations is highly correlated with moderate to high albedo regions, which have a large dust contribution to the measured spectra.

All surface spectra have the same spectral character. The standard deviation in the spectral shape of the surfaces is <0.01 from 250cm^{-1} to 1610cm^{-1} and climbs from 0.01 to 0.02 for the $1620\text{-}1650\text{cm}^{-1}$ wavenumber range.

A series of laboratory samples were prepared to compare with the Mars dust spectrum. Labradorite was used as a base because of its rough similarity to the Martian spectrum and because of its known purity. $0\text{-}63\mu\text{m}$ size fraction mixtures were prepared by adding silicates, sulfates, oxides, and carbonates to the labra-

dorite (Figure 1). Only the carbonate-labradorite mixture displays significant changes to its spectrum, though the bound water in gypsum contributes to the 1620cm^{-1} peak. Similar mixtures using specific carbonate compositions were prepared. The spectra of these mixtures display systematic differences between the different compositions that correlate with the positions of their emission absorptions [7]. The magnesite-labradorite mixture closely matches the Martian dust spectrum in both magnitude and shape at wavenumbers $>1300\text{cm}^{-1}$.

Specific magnesite-labradorite particle size fraction samples were prepared to test the sensitivity of the short wavelength spectral features to particle size. The spectral response to minor amounts of magnesite was highest at $0\text{-}10\mu\text{m}$ size fractions. At these sizes, the spectral character of the Martian spectrum could be reproduced using $\sim 2\text{-}3\%$ magnesite.

Using water vapor removed [1] 1 ppd binned TES emissivity data [8], three indices were created to map the spectral character present at short wavelengths that is the focus of this study. The average emissivity of $1428\text{-}1608\text{cm}^{-1}$ was used to map the distribution of the depth of the broad absorption present in the retrieved surface spectra discussed above. A second index was produced that maps the depth of the narrow absorption centered at 1600cm^{-1} . The third parameter mapped is a curvature index produced by computing the second derivative centered near 1500cm^{-1} .

The high wavenumber emissivity and the curvature index are both highly correlated with each other and anti-correlated with albedo. The narrow absorption depth map is highly correlated with albedo and is anti-correlated with the other two indices. All three indices are either correlated or anti-correlated with each other and there is little, if any, independent variability of any of these features.

Discussion and Conclusions: The spectral character at wavenumbers $>\sim 1300\text{cm}^{-1}$ is extremely sensitive to small amounts of the highly absorbing carbonates mixed within the weakly absorbing silicates. As shown in Figures 1 and 2, a high absorption coefficient at these wavenumbers is necessary to match the increased emissivity and spectral shape of the Mars surface spectrum. No other common mineral class is highly absorptive in this spectral region and other oxides, silicates, and sulfates have little influence on the spectral character within this wavenumber region. The spectral signature at high wavenumbers is essential for carbonate detection while it is insensitive to the specific sili-

cate/sulfate/oxide mineralogy. In addition, the spectral signature at wavenumbers $<1300\text{cm}^{-1}$ is insensitive to the presence of carbonates in fine particulates.

Figure 2 displays several specific carbonate compositions mixed with the same labradorite substrate. The position of the spectral features migrates to higher wavenumbers with increasing Mg content. The Martian spectrum is consistent with a magnesite composition. Similar to their shorter wavelength features, hydrous carbonates have subdued spectral absorptions and it is not clear if they could be detected in low abundances at any wavelength [9].

The abundance of carbonate present is difficult to determine precisely as it is highly dependent on the particle size distribution of the measured surface. It is expected that most moderate to high albedo regions on Mars have a thin (less than a few millimeters) layer of particles with diameters $\sim 10\mu\text{m}$ [1,10,11], most likely due to airfall dust. The 0-10 μm particle size fraction spectra of the laboratory carbonate-silicate mixtures were the most sensitive to the addition of small amounts of carbonate and the Martian features could be reproduced with $\sim 2\text{-}3\%$ magnesite.

It is possible to form carbonates in a thin Martian atmosphere [12]. It is unclear how much water needs to be present for the weathering to occur. Mg carbonates are a thermodynamically stable weathering product under the relatively dry and thin present Martian atmosphere, whereas smectite clays and Ca carbonates would be present if weathering occurred under wetter conditions in a thicker CO_2 atmosphere [13].

This type of carbonate formation would serve as a buffer for Martian atmospheric CO_2 . It has been proposed that carbonates would form at a rapid rate when the Martian atmospheric conditions allow for the rela-

tive stability of liquid water. This formation mechanism would slow considerably when the atmosphere became thin enough that liquid and/or adsorbed water would be less stable at the surface [14]. Alternatively, the carbonate present in the Martian dust may also have been widely distributed in the source lithology from which the dust was created. Several Martian meteorites have small, disseminated concentrations of Mg, Ca, and Fe carbonate that formed by precipitation from groundwater in fractures [e.g. 15].

A concentrated source may also have been present and mechanically weathered and mixed with the other components of the dust. Extensive searches with TES and other spectroscopic measurements indicate that high concentrations of carbonates are not widely exposed on the Martian surface at the $\sim 10\text{ km}$ scale [16]. A putative source region may have been subsequently buried however, and not detected.

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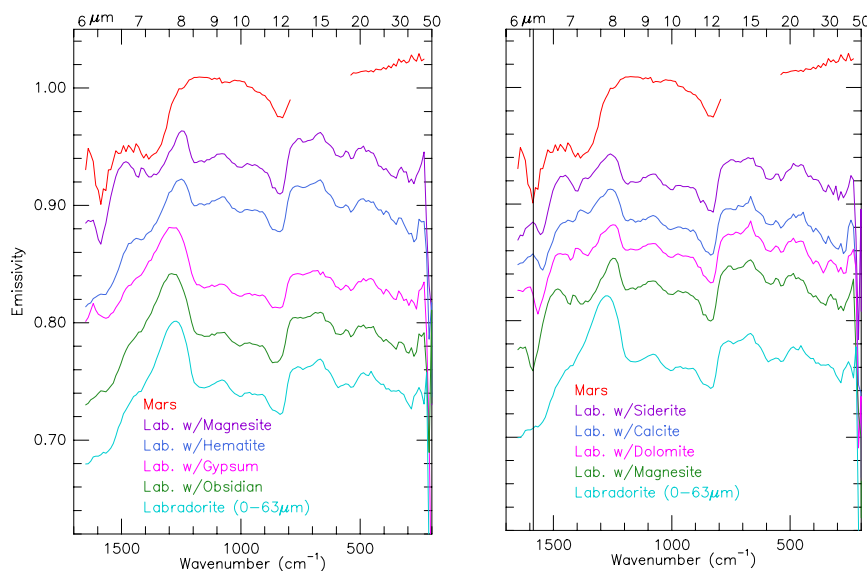


Figure 1 (left). The Martian surface dust spectrum compared with fine particulate labradorite and mixtures. The silicate features are only modified where they are weakly absorbing at wavenumbers $>\sim 1300\text{ cm}^{-1}$ and the added material is highly absorbing at the same frequencies.

Figure 2 (right). The Martian surface dust spectrum compared with several carbonate compositions. The position and shape of the spectrum at wavenumbers $>1300\text{ cm}^{-1}$ is sensitive to the specific carbonate composition.