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SPECTRAL EVIDENCE FOR CARBONATES ON MARS: HYDROUS CARBONATES

W. M. Calvin, and T. V. V. King, U. S. Geological Survey, Denver

The presence of carbonates on Mars has long been argued based on the abundance of CO_2 in the atmosphere and geomorphological evidence of fluvial features. Numerous spectral searches have repeatedly failed to find evidence of carbonates (most recently by Blaney and McCord [1] and references therein). Recently Pollack *et al.* [2] report evidence of carbonate spectral features near 6.7 μm and on the shorter wavelength side of the atmospheric absorption at 7.3 μm, but assign no specific mineralogy to the features.

An extensive re-analysis of the Mariner 6 and 7 spectrometer data in the wavelength region from 2 to 6 μm (Calvin and King [3]) identified several new absorption features not noted in terrestrial observations, particularly a potential hydroxyl feature at 2.76 μm. Unfortunately this band occurs in the middle of strong atmospheric CO_2 features, but is also indicated in non-atmosphere removed spectra.

Laboratory reflectance measurements from 2.5 to 25 μm of several types of hydrous carbonates presented by Miyamoto and Kato [4] indicated that these minerals are likely candidates for the features identified by Calvin and King [3], as well as by Pollack *et al.* [2].

We have measured the spectral reflectance of 3 samples provided by M. Miyamoto (University of Tokyo) in the spectral region from 0.2 to 25 μm and find that these samples have additional spectral characteristics that make them plausible candidates for the martian surface. We have measured two samples of hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot XH_2O$) and one of artinite ($Mg_2(OH)_2CO_3 \cdot 3H_2O$). An additional sample of artinite provided by Gene Foord (U. S. Geological Survey) was also measured.

These samples are unique in that they do not exhibit the strong absorption features typically associated with carbonates [1,4,5,6]. That is, typical carbonate bands from 2.2-2.5 μm, from 3.2-3.6 μm, and from 3.8-4.1 μm, which are usually extremely strong, are only weakly present, if at all, and are shifted in wavelength. It is not necessarily that these samples are Mg-bearing, but the fact that they contain H_2O and OH in the crystal structure that gives them their unique spectral characteristics. (Although the presence of Mg may help to bind water to the structure during formation [7].) The presence of water gives these minerals broad adsorbed water bands near 3 μm, and washes out the typical CO_3 absorption features.

Both the hydromagnesite and the artinite have absorption features near 6.7 μm. In addition the hydromagnesites have a feature that occurs from 7.1-7.2 μm, depending on the sample. The location of these features is consistent with features reported by Pollack *et al.* [2], and attributed to CO_3.

All the samples have broad adsorbed water bands, consistent with the Mariner 6 and 7 data, although this is not a unique indicator of mineralogy. In addition, the artinite sample has a hydroxyl feature at 2.76 μm that correlates extremely well with that seen in atmosphere-removed spectra of Calvin and King [3]. As stated previously, this band can not be definitively identified due to possible difficulties in removing the model atmosphere. However, when the laboratory reflectance spectra are convolved to the Mariner instrument resolution and multiplied by the atmospheric transmission, the resulting spectra are extremely similar to the Mariner spectra. The hydroxyl feature in the artinite only broadens the atmospheric band near 2.78 μm, no separate feature can be discerned.

Spectral measurements from 2.25–2.45 μm, indicated that there are additional mineralogical features in this spectral region [8]. Much of this wavelength region is confused by the signature of atmospheric CO, and the exact contribution of the atmosphere to the observed spectra does not appear to be well determined [9, 10].

However, between 2.26 and 2.30 μm all the atmospheric models indicate that there is no atmospheric interference. Here, there is absorption feature centered on 2.28 μm [8]. This band has been associated with the mineral scapolite [8]. Our new spectral measurements indicate that this band is also well correlated with a feature in the spectrum of artinite and with a feature in hydromagnesite. The artinite has only the feature at 2.28 μm while the hydromagnesite has several features in this region. The strongest features in the hydromagnesite occur between 2.32 and 2.36 μm, depending on the sample. This latter region is obscured in the spectra of Mars due to atmospheric CO.

The only other stong features in the hydrous carbonates we have measured occur at 1.4 and 1.9 μm. Features in this region are unlikely to be observed from terrestrial observations because of atmospheric interference by water, and the Mariner spectra do not extend to short enough wavelengths. It is unknown if the PHOBOS/ISM experiment has the spectral resolution to characterize absorptions in these regions. In addition water in the martian atmosphere will also tend to obscur these bands.

The hydrous carbonates exhibit a spectral downturn in the visible, beginning about 0.5 μm, again consistent with observed Mars spectra, but not a unique indicator of mineralogy. This downturn would likely be obscurred due to the presence of abundant Fe-oxides on the surface which also have strong spectral downturns in the visible.

Hydrous Mg-carbonates form terrestrially as weathering products in aqueous environments often at low temperature [11]. Artinite and hydromagnesite occur along with coalingite ($Mg_{10}Fe_2CO_3(OH)_{24}\cdot 2H_2O$) in the surface weathering zone of a California serpentinite [12]. In addition, hydromagnesite and nesquehonite ($Mg(HCO_3)(OH)$ $\cdot 2H_2O$ have been identified as weathering products on Antarctic meteorites [13]. The exact formation mechanism on the meteorites is not yet well known [14], but one suggestion is that olivine weathers to nesquehonite and Fe-oxides such as goethite [12]. The stability of these minerals in the current martian environment is unknown. The current surface temperatures of Mars are compatible with the low-temperature, most hydrated phases, but the low atmospheric water abundance may lead to dehydration. Obviously more work is required to determine the stability of such minerals in the martian environment.

In summary, although many of the spectral features are not unique mineralogical indicators, much of the current spectral data is consistent with (possibly abundant) hydrous carbonates on the surface of Mars. The absorption features in the samples we have measured are quite weak compared to those of anhydrous carbonates. The weak features imply that significantly more hydrous carbonates can be incorporated onto the surface before becoming spectrally evident; however exact limits have yet to be determined. The stability of these minerals in the martian environment is not known, but their formation and occurence in low-temperature terrestrial environments makes them appealing candidates for weathering products on Mars.

[1]Blaney and McCord, 1989. *J. Geophys. Res.*, **94**, 10159–10166. [2]Pollack, *et al.*, 1990. *J. Geophys., Res.*, **95**, 14595–14627. [3]Calvin and King, 1990. *LPSC XXI*, 153–154, [Abstract]. [4]Miyamoto and Kato, 1990. *LPSC XXI*, 801–802, [Abstract]. [5]Hunt and Salisbury, 1971. *Mod. Geo.*, **2**, 23–30. [6]Gaffey, 1987. *J. Geophys. Res.*, **92**, 1429–1440. [7]Mackenzie *et al.*.,1983. In: *Carbonates: Mineralogy and Chemistry, Rev. Miner.*, **11**, 97–144. [8]Clark, *et al.*,1990. *J. Geophys. Res.*, **95**, 14463–14480. [9]Encrenaz and Lellouch, 1990. *J. Geophys. Res.*, **95**, 14589–14593. [10]Rosenqvist, *et al.*, 1990. *Bull. Amer. Astron. Soc.*, **22**, 1076 [Abstract]. [11]Ming, 1981. M.S. Thesis. Colorado State University. [12]Mumpton, *et al.*, 1965. *Amer. Min.*, **50**, 1893–1913. [13]Jull, *et al.*, 1988. *Science*, **242**, 417–419. [14]Gooding, J. 1991. Personal communication.