

REFLECTANCE SPECTROSCOPY OF HYDRATED CARBONATE MINERALS. D. M. Applin^{1*}, E. A. Cloutis¹, and M. R. M. Izawa¹
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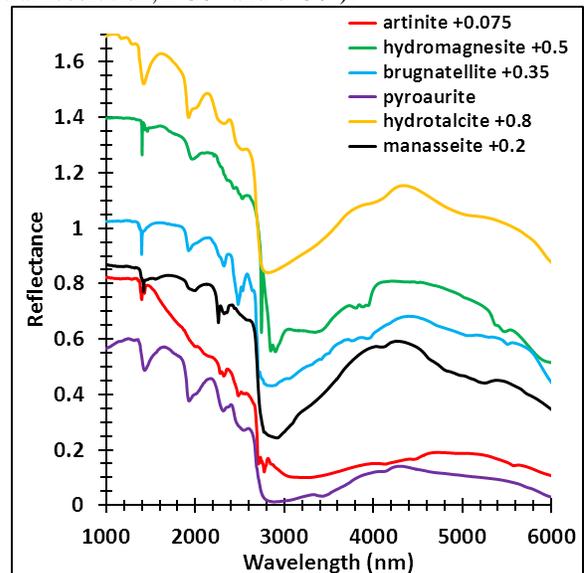
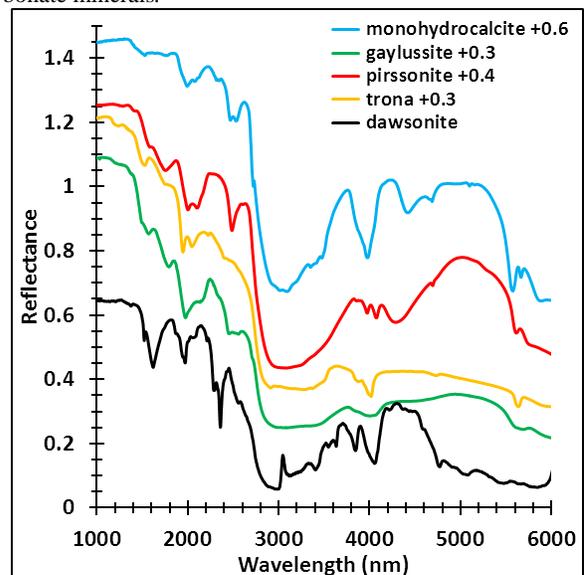
Introduction: Anhydrous carbonate minerals have been detected on Mars by Earth-based telescopes [1], orbiting spectrometers (TES: [2]; OMEGA: [3]; PFS: [4]; CRISM: [5,6]), in pyrolysis experiments (Phoenix: [7]; MSL: [8], and by multi-technique *in situ* analyses by the Spirit rover [9]). Most spectroscopically identified carbonates are calcian or magnesian. Abundances range from 1 to 5 wt.% over larger scales imaged by orbiting spectrometers, and $\ll 1$ wt.% to $\sim 35\%$ in concentrated deposits investigated by rovers/landers. Some Earth-based observations of Mars also show spectral features consistent with hydrous carbonates [10]. Hydrous carbonates constitute the majority ($\sim 65\%$) of known carbon-bearing mineral species [11] and are common precursors to anhydrous carbonates. Although their formation conditions and stability fields are commonly more restricted than anhydrous carbonates, hydrous carbonates occur in a wide variety of settings including weathering ultramafic assemblages [12], low-temperature hydrothermal systems [13], and saline/hypersaline evaporitic deposits [14]; all of which have been suggested to occur on Mars. Hydrous carbonates are often metastable/intermediate phases on Earth [17], but given the low temperatures and CO_2 -dominated atmospheric composition of Mars, the hydrous:anhydrous ratio could be much higher. Therefore they may be useful as thermodynamic indicators and can constrain geological history of carbonate-bearing martian rocks [11].

Table 1. Hydrous carbonates used in this study.

Mineral	Ideal formula
Artinite	$\text{Mg}_2(\text{CO}_3)(\text{OH})_2 \cdot 3\text{H}_2\text{O}$
Brugnatellite	$\text{Mg}_6\text{Fe}^{3+}(\text{CO}_3)(\text{OH})_{13} \cdot 4(\text{H}_2\text{O})$
Dypingite	$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5(\text{H}_2\text{O})$
Hydromagnesite	$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4(\text{H}_2\text{O})$
Hydrotalcite	$\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16} \cdot 4(\text{H}_2\text{O})$
Manasseite	$\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16} \cdot 4(\text{H}_2\text{O})$
Pyroaurite	$\text{Mg}_6\text{Fe}^{3+}_2(\text{CO}_3)(\text{OH})_{16} \cdot 4(\text{H}_2\text{O})$
Malachite	$\text{Cu}_2(\text{CO}_3)(\text{OH})_2$
Azurite	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$
Hydrocerussite	$\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$
Gaylussite	$\text{CaNa}_2(\text{CO}_3)_2 \cdot 5(\text{H}_2\text{O})$
Pirssonite	$\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 2(\text{H}_2\text{O})$
Trona	$\text{Na}_3(\text{HCO}_3)(\text{CO}_3) \cdot 2(\text{H}_2\text{O})$
Monohydrocalcite	$\text{Ca}(\text{CO}_3) \cdot (\text{H}_2\text{O})$
Dawsonite	$\text{NaAl}(\text{CO}_3)(\text{OH})_2$

Methods: A suite of naturally occurring hydrous carbonates (Table 1) have been characterized by reflectance spectroscopy ($< 45 \mu\text{m}$ fractions), atomic absorp-

tion/emission, ICP-MS, wet chemistry, and X-ray diffraction. Reflectance spectra were measured at the NASA-supported RELAB facility at Brown University. Spectra were measured from 300-26000 nm relative to halon (300-2600 nm; 5 nm spectral resolution; $i=30^\circ$, $e=0^\circ$) and brushed gold (2500-26000 nm; 4 cm^{-1} spectral resolution; $i=30^\circ$ and $e=30^\circ$).


Figure 1. Reflectance spectra of Mg-bearing hydrous carbonate minerals.

Figure 2. Reflectance spectra of Na- and Ca-bearing hydrous carbonate minerals.

Results and Discussion: Reflectance spectra are separated into two groups: Mg-bearing (Fig. 1) and Na- and Ca-bearing (Fig. 2). There are marked differences between these two groups, which is consistent with the discussion by [10]. The most obvious difference is the shape of the 3 μm hydration feature; which generally has a flat longwave tail in Mg-bearing phases, while the feature is broader in Na- and Ca- phases. This difference also exists in other hydrated C-bearing minerals, such as oxalates [17]. Some Na-bearing phases have absorption bands $\sim 1.75 \mu\text{m}$.

Continuum-removed spectra in the second overtone region used for carbonate detection are shown in Figs. 3 and 4. Only pyroaurite and hydrotalcite have 2.3 and 2.5 μm bands similar to those in anhydrous phases, and most of the hydrous carbonate absorption bands are at shorter wavelength than anhydrous phases. Na- and Ca-bearing phases typically only have a 2.5 μm feature (aside from dawsonite).

There is a general absence of 3.4 and 3.5 μm features in the hydrous carbonate spectra. This can be only partially due to low albedo from hydration, as they are apparent in some spectra (brugnatellite, monohydrocalcite), and similar features are apparent in hydrous oxalates. The 3.8 and 3.9 μm features are only resolvable in two Mg-bearing phases (hydromagnesite and brugnatellite), while features in this region for Na- and Ca-bearing phases are relatively strong.

Implications for Mars: The inclusion of H_2O and OH in the crystal structure makes these minerals spectrally distinct from anhydrous counterparts. Most hydrous carbonates show an absorption band at 2.48 μm . Discrimination between Mg- and Na- and Ca-bearing phases can be made by the inclusion of a $\sim 2.28 \mu\text{m}$ feature (Mg-bearing), and by absorption bands $\sim 1.75 \mu\text{m}$ (Na-bearing) and $\sim 4 \mu\text{m}$.

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References: [1] Blaney, D.L. & McCord, T.B. (1989) JGR, 94, 10159-10166. [2] Bandfield, J.L. (2003) Science 301, 1084-1087. [3] Michalski, J.R. and Niles, P.B. (2010) Nat. Geo. 3, 751-755. [4] Palomba, E. et al. (2009) Icarus 203, 48-65. [5] Ehlmann, B.L., et al. (2008) Science 322, 1828-1832. [6] Carter, J. & Poulet, F. (2012) Icarus 219, 250-253. [7] Boynton, W.V., et al. (2009) Science 325, 61-64. [8] Leshin, L.A., et al. (2013) Science 341, 1238937 [9] Morris, R.V., et al. (2010) Science 329, 421-424.

[10] Calvin, W.M. et al. (1994) JGR, 99, 14659-14675. [11] Hazen, R.T., et al. (2013) Rev. Min. & Geochem. 75, 7-46. [12] Hostetler, P.B., et al. (1966) Am. Min. 51, 75-98. [13] [14] Levy, D.B., et al. (1998) App. Geochem. 14, 53-65. [15] Jull, A.J.T., et al. (1988) Science 242, 417-419. [16] Miyamoto, M. (1989) EPSL 96, 229-234. [17] Kelleher, I.J. and Redfern, S.A.T. (2010) Mol. Sim. 28, 557-572. [17] Applin, D.M., et al. (2012) LPSC XLIV, Abstract #2839

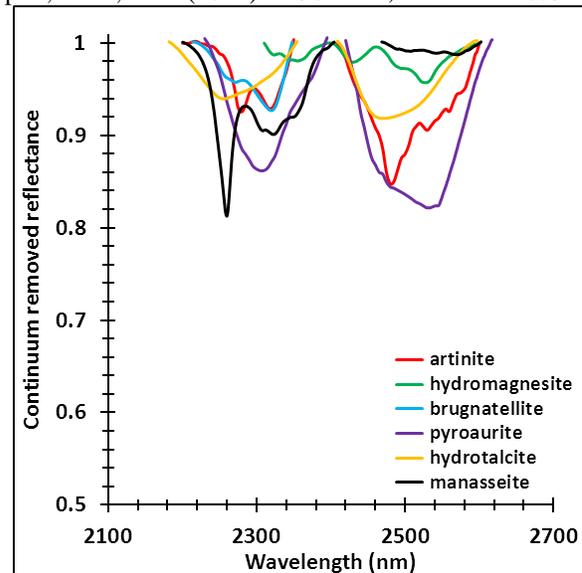


Figure 3. Continuum-removed reflectance of the second overtone region of Mg-bearing hydrous carbonate minerals.

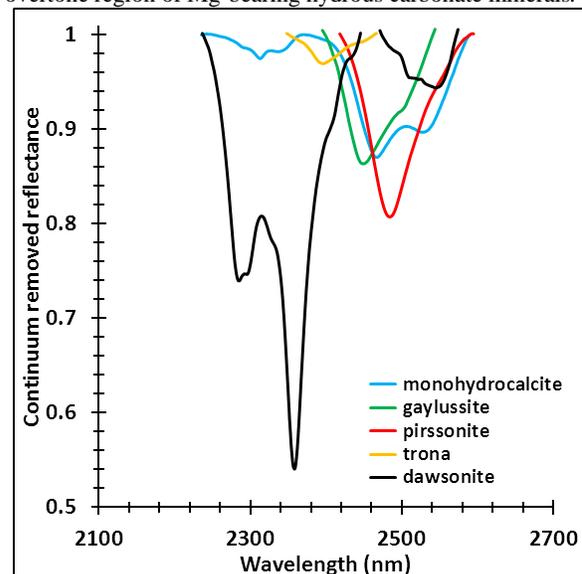


Figure 4. Continuum-removed reflectance of the second overtone region of Na- and Ca-bearing hydrous carbonate minerals.