

VISIBLE-NEAR INFRARED SPECTRA OF HYDROUS CARBONATES AND IMPLICATIONS FOR THEIR DETECTION ON MARS. P. L. Harner^{1,2} and M. S. Gilmore², ¹Planetary Science Department, University of Arizona, Tucson, AZ 85715, ²Dept. of Earth and Environmental Sciences, Wesleyan University, Middletown, CT 06459 (plharn@email.arizona.edu)

Introduction: Thus far, the search for carbonates on Mars using CRISM data has focused primarily on the anhydrous carbonates common on Earth, where absorption features at 2.3, 2.5, 3.4 and 3.9 μm form the basis of standard CRISM search procedures [1, 2]. Calvin et al. [3] was the first to suggest hydrous carbonates might explain spectral features seen in Mariner 6/7 data and noted that some hydrous carbonates lack the spectral features typical of anhydrous carbonates. Here we present VNIR spectra of a suite of hydrous carbonates, many of which are rare on Earth, but which may be relevant to past or present Martian conditions. We show that several species are difficult to distinguish from other hydrated minerals, and thus may be overlooked. If so, the extent of carbonates on Mars may be underestimated.

Methods: Fourteen hydrous carbonates are presented here. Ten natural mineral specimens were purchased and the remaining four were synthesized: nesquehonite ($\text{Mg}(\text{CO}_3)\cdot 3(\text{H}_2\text{O})$) and lansfordite ($\text{Mg}(\text{CO}_3)\cdot 5(\text{H}_2\text{O})$) were synthesized using a method adapted from [4], ikaite ($\text{Ca}(\text{CO}_3)\cdot 6(\text{H}_2\text{O})$) was synthesized using the technique described by [5], and monohydrocalcite ($\text{Ca}(\text{CO}_3)\cdot (\text{H}_2\text{O})$) was made using an adaptation of the method described by [6]. Composition was confirmed with X-ray diffraction (XRD) when possible. VNIR spectra (350-2500nm) were collected at Wesleyan University using an ASD FR spectrometer; low-temperature minerals were kept on dry ice until immediately prior to measurement. IR spectra (800-5000nm) were collected at the NASA Reflectance Experiment Laboratory (RELAB) at Brown University.

Spectra of hydrous carbonates: The spectra of carbonates are dominated by fundamental internal and lattice vibrations of the carbonate (CO_3)²⁻ anion in the mid and far infrared, with overtone and combination modes in the VNIR [7]. Anhydrous carbonates typically have 5 bands in the NIR centered at ~ 1.86 , 1.98, 2.13, 2.33, 2.53, 3.4, and 3.95 μm assigned to CO_3 [8]. The hydrous carbonates, like other hydrous minerals, typically exhibit bands at 1.0, 1.2, ~ 1.4 , ~ 1.9 , and 2.8 μm attributable to OH and H_2O [e.g., 9]. These bands may mask weaker carbonate bands. The addition of water or hydroxyl is thought to distort the lattice, which may lead to changes in presence, shape and position of the absorption features of CO_3 [e.g., 10].

The low temperature, low water activity [11], hydrous Mg carbonates, nesquehonite and lansfordite, are

distinguished by doublets at ~ 1.2 and 1.4 μm , a feature at ~ 1.7 , a significant absorption at ~ 1.9 μm , and in nesquehonite, a small feature at 3.82 μm .

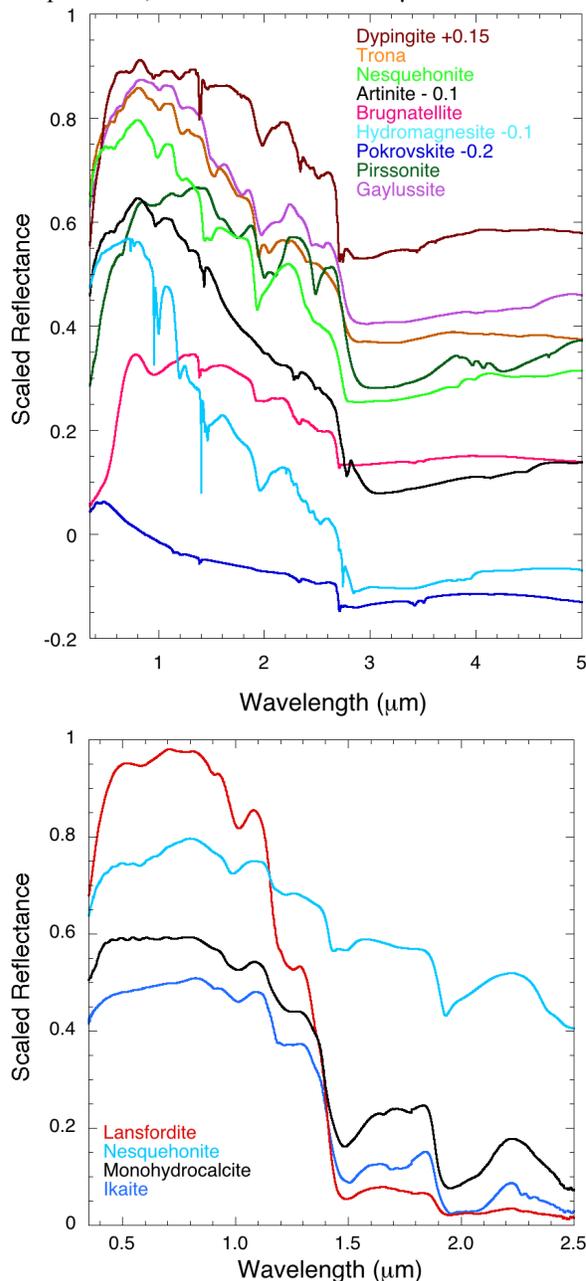


Fig 1. VNIR spectra of some hydrous carbonates.

The Mg-OH carbonates display similar features at 1.4 and ~ 1.9 μm as well as absorptions at 2.33 and 2.53 μm , with a few specimens exhibiting CO_3 -related absorptions between 3-4 μm but the width and strength

of these absorptions is smaller than for magnesite (MgCO_3). Hydrated Mg-Fe carbonates also include absorptions $\sim 0.5 \mu\text{m}$ due to Fe^{3+} and $\sim 0.9 \mu\text{m}$ due to Fe^{2+} replacement.

The hydrated Ca carbonates, ikaite and monohydrocalcite, are both found only in low temperature, Ca-rich environments on Earth [12]. These are distinguishable by ~ 1.0 , ~ 1.2 , ~ 1.5 , and $1.94 \mu\text{m}$ absorptions as well as small unique features between 1.5 and $1.8 \mu\text{m}$. Gaylussite ($\text{CaNa}_2(\text{CO}_3)_2 \cdot 5(\text{H}_2\text{O})$) exhibits a doublet at 1.49 and $1.56 \mu\text{m}$ and both gaylussite and pirssonite ($\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 2(\text{H}_2\text{O})$) have distinctive absorptions between 1.7 and 1.8 and at $2.1 \mu\text{m}$, as well as CO_3 -related features near 2.5 and faint absorptions near $4.0 \mu\text{m}$. The Na hydrated carbonates, natron ($\text{Na}_2(\text{CO}_3) \cdot 10(\text{H}_2\text{O})$) and trona ($\text{Na}_3(\text{HCO}_3)(\text{CO}_3) \cdot 2(\text{H}_2\text{O})$) have distinguishing features at ~ 1.5 , 1.7 and $2.0 \mu\text{m}$.

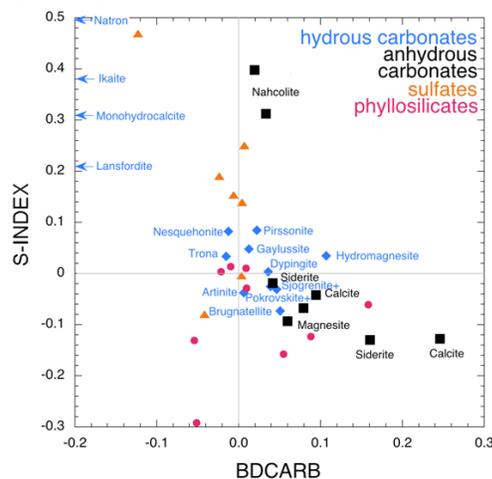


Fig. 2. Spectral summary parameters [2] for hydrated carbonates, anhydrous carbonates, phyllosilicates and sulfates.

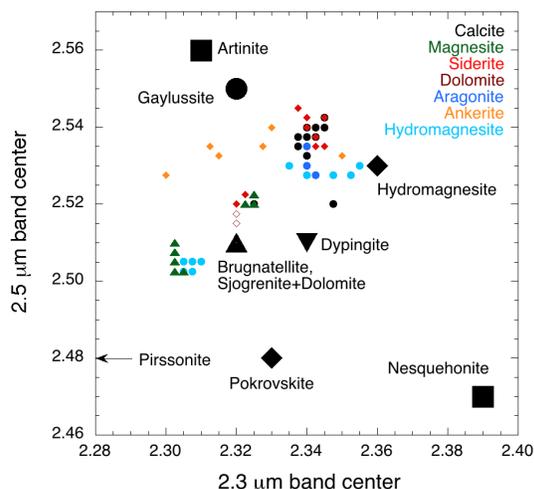


Fig 3. Band centers at 2.3 and $2.5 \mu\text{m}$ for anhydrous and hydrated carbonates.

Spectral Summary Products: Several CRISM spectral summary products [2] were calculated to better understand detection limits for these minerals (Fig. 2). The BDCARB parameter, a measure of the 2.3 and $2.5 \mu\text{m}$ absorptions depth, D2300, BD2500, BD3400 and the BD3900 parameter can be used to identify anhydrous carbonates [1,2]. The SINDEXT measures curvature related to the $2.4 \mu\text{m}$ feature typical of sulfates [13]. $\text{Mg}(\text{OH})$ carbonates display values more typical of anhydrous carbonates, whereas hydrated Ca, Mg, Na and Ca-Na carbonates often exhibit moderate to high SINDEXT values, and show absent or weaker carbonate band indicators. Combined use of spectral summary parameters and CO_3 band positions can be used to help discern some samples, but the major spectral features of these minerals are typical of a number of hydrated minerals [9], and they may therefore be difficult to recognize.

CO_3 Band Position: In the $\text{Mg}(\text{OH})$ hydrated carbonates nesquehonite, pokrovskite, dypingite, brugnattelite and hydromagnesite, the position of the $2.3 \mu\text{m}$ band center is shifted to longer wavelengths than the anhydrous carbonates; for artinite the $2.3 \mu\text{m}$ band center is at shorter wavelengths (Fig. 3). The $2.5 \mu\text{m}$ band center position of nesquehonite, pokrovskite and artinite and the Na-Ca carbonate pirssonite and gaylussite is quite separable from the anhydrous carbonates. Thus the position of the 2.3 and $2.5 \mu\text{m}$ band centers is distinctive and may be diagnostic for these minerals.

Conclusion: The $\text{Mg}(\text{OH})$ hydrated minerals may be recognized by elevated BDCARB, D2500 and BD1900 CRISM parameter values. The position of the band center of nesquehonite, pokrovskite, dypingite and artinite are distinctly different than the anhydrous carbonates. This is true of the position of the $2.5 \mu\text{m}$ band of the Na-Ca hydrated carbonates gaylussite and pirssonite. The shape of the water bands of the Ca and Mg hydrates, and the alkali carbonates natron and trona may be diagnostic, but difficult to separate from instruments and atmospheric noise in CRISM data.

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