ARE MARTIAN CARBONATES HIDING IN PLAIN SIGHT? VNIR SPECTRA OF HYDROUS CARBONATES.

P. L. Harner[1,2] and M. S. Gilmore[2], [1]Planetary Science Department, University of Arizona, Tucson, AZ 85715, [2]Dept. of Earth and Environmental Sciences, Wesleyan University, Middletown, CT 06459 (plharn@email.arizona.edu)

Introduction: Carbonates have long been predicted to form on an ancient Mars with a thicker carbon dioxide atmosphere and surface water [e.g., 1]. Carbonates have been identified at the 1-3% level in the global dust [2], and have been measured in surface outcrops [3-4] and in the SNC meteorites [5]. However regional carbonate deposits identified by orbital CRISM VNIR data are limited in extent and likely formed as alteration products of ultramafic rocks [6]. The lack of widespread carbonate deposits on Mars may be indicative of a colder, drier early Mars or some process in Mars' past that would have erased the carbonate record, such as acidic conditions [7].

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 [6, 18]. Calvin et al. [8] 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 (or Europa [9]). We show that several of these look very similar to hydrous sulfates, and thus may be overlooked. If so, the extent of carbonates on Mars may be underestimated.

Methods: Sixteen hydrous carbonates were examined for this study. Twelve natural mineral specimens were purchased and the remaining four were synthesized: nesquehonite ($Mg(CO_3)\bullet 3(H_2O)$) and lansfordite ($Mg(CO_3)\bullet 5(H_2O)$) were synthesized using method adapted from [10], ikaite ($Ca(CO_3)\bullet 6(H_2O)$) was synthesized using the technique described by [11], and monohydrocalcite ($Ca(CO_3)\bullet (H_2O)$) was made using an adaptation of the method described by [12]. Composition was confirmed with X-ray diffraction (XRD) when possible. VNIR spectra (350-2500nm) were collected at Wesleyan University using as ASD FR spectrometer, and IR spectra (800-4000nm) we collected at the NASA Reflectance Experiment Laboratory (RELAB) at Brown University.

Spectra of hydrated 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 [13]. Anhydrous carbonates typically have 5 bands in the NIR centered at ~1.86, 1.98, 2.13, 2.33, and 2.53 μm assigned to CO_3 [13]. The hydrous carbonates, like other hydrous minerals, typically exhibit bands at ~1.4 μm due to OH and ~1.9 due to H_2O [14] with overtones at 1.0 and 1.2 μm. 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 [15]. For many of the hydrous carbonates, the effect is to lose the 2.3 μm feature entirely.

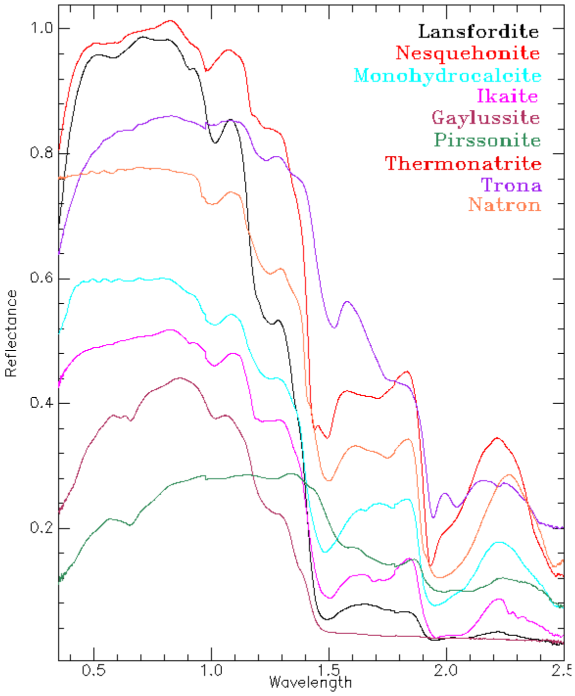

Fig 1. VNIR spectra of hydrous Mg, Ca, Na and Ca-Na carbonates.

The, low temperature, low water activity [16], hydrous Mg carbonates, nesquehonite and lansfordite, are distinguished by doublets at ~1.2 and 1.4 μm, a feature at ~1.7 and a significant absorption at ~1.9 μm. The Mg-OH carbonates display similar features at ~1.9 and 1.4 μm due to OH and H_2O. These minerals also display absorptions at 2.33, and 2.53 μm, but the width and strength of these absorptions is smaller than for magnesite ($MgCO_3$).

The hydrous Ca carbonates, both found on only in low temperature, Ca-rich environments on Earth [17]: ikaite and monohydrocalcite, are distinguishable by ~1.0, ~1.2, ~1.5, and 1.94 μm absorptions as well small unique features between 1.5 and 1.8 μm. Gaylussite ($CaNa_2(CO_3)_2 \bullet 5(H_2O)$) exhibits a doublet at 1.49 and 1.56 µm and both gaylussite and pirssonite ($Na_2Ca(CO_3)_2 \bullet 2(H_2O)$) have distinctive absorptions between 1.7 and 1.8 and at 2.1 µm. The Na hydrated carbonates, natron ($Na_2(CO_3) \bullet 10(H_2O)$), thermonatrite ($Na_2(CO_3) \bullet (H_2O)$), and trona ($Na_3(HCO_3)(CO_3) \bullet 2(H_2O)$) have distinguishing features at ~1.5, 1.7 and 2.0 µm.

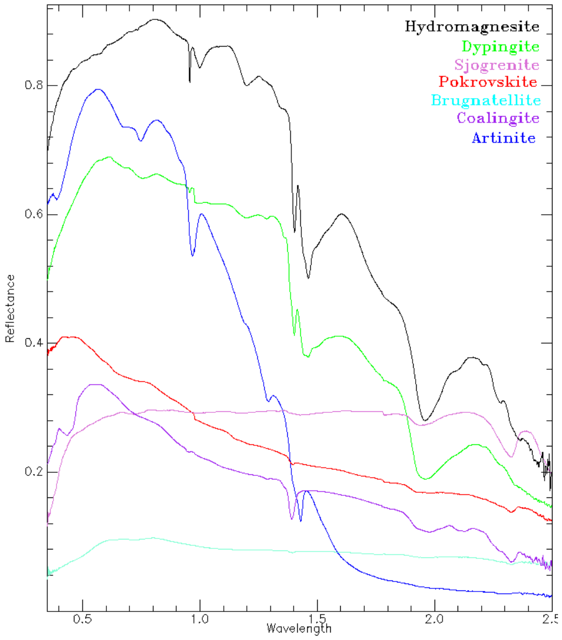

Fig 2. Spectra of hydrous Mg-OH and Mg-Fe carbonates.

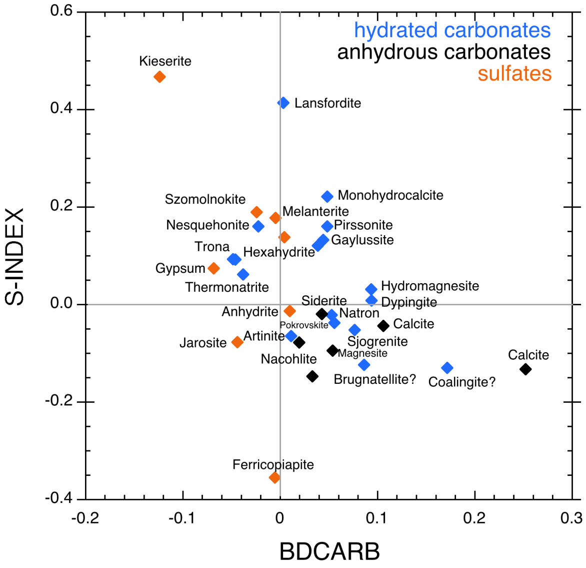

Fig. 3. Spectral summary parameters [18] for hydrous carbonates, anhydrous carbonates and sulfates.

Hydrous Mg-Fe carbonates include absorptions ~0.5 µm due to Fe^{3+} and ~0.9 µm due to Fe^{2+} replacement, features at 1.4 and 1.9 µm due to water and/or OH, and the 2.3 and 2.5 µm features typical of siderite ($FeCO_3$) and magnesite.

Spectral Summary Products: We calculated several CRISM spectral summary products for the hydrous carbonates to better understand detection limits for these minerals (Fig. 3). The BDCARB parameter, a measure of the depth of the 2.3 and 2.5 µm absorptions, and the CINDEX parameter, a measure of the 3.9 µm band [18], are commonly used to identify anhydrous carbonates. The SINDEX measures curvature related to the 2.4 µm feature typical of sulfates [19]. Mg hydroxide and hydrous Mg-Fe carbonates typically plot with anhydrous carbonates in bimodal--spectral summary plots, whereas hydrous Ca, Mg, Na and Ca-Na carbonates, particularly the low temperature hydrous carbonates, generally have SINDEX, CINDEX, and relevant band depth values typical of hydrous Mg-sulfates.

Conclusion: VNIR spectra of hydrous carbonates are dominated by the water and hydroxyl features typical of many hydrous minerals. Most hydrous Ca, Mg, Na and Ca-Na carbonates lack the 2.3 µm absorption typical of anhydrous carbonates. Several of these minerals have distinguishing features, e.g., nesquehonite has doublet 1.4 and 1.9 µm absorptions and lansfordite, and monohydrocalcite and ikaite all exhibit unique 1.5-1.8 µm absorptions. However, these features are typically small and may be lost due to noise and/or proximity to the 2.0 CO_2 µm band in CRISM data. The major spectral features of these minerals are typical of a number of hydrous sulfates and chlorides [15].

Acknowledgements. We appreciate funding from NASA CT Space Grant.

References: [1] Carr, M. H. (1986) *Icarus* 68.2, 187-216. [2] Pollack, J. B., et al. (1990) *JGR*, 95(B9), 14595. [3] Boynton, W. V., et al. (2009) *Science*, 325, 5936, 61-64. [4] Morris, R. V., et al. (2010) *Science* 329, 421. [5] McSween, H. Y. (1994) *Meteoritics*, 29.6, 757-779. [6] Ehlmann, B. L., et al. (2008) *Science*, 322, 1828. [7] Bibring, J. P., et al. (2006) *Science*, 312.5772, 400-404. [8] Calvin, W. M., et al. (1994) *JGR*, 99.E7, 14659-14675. [9] Dalton, J. B., et al. (2005) *Icarus*, 177, 472. [10] Coleyshaw, E. E., et al. (2002) *Spectrochim. Acta*, 59, 2231. [11] Johnston, J. (1916) *AJS*, 246, 473. [12] Nishiyama, R., et al. (2012) *GCA*, 100, 217. [13] Hunt, G. R., et al. (1971) *Modern Geol.*, 2, 23. [14] Gaffey, S. J., et al. (1993) in: *Remote geochemical analysis: Elemental and mineralogical composition*, 43-77. [15] Crowley, J. K. (1991) *JGR*, 96, 16231. [16] Langmuir, D. (1965) *J. Geol*. 730. [17] Dahl, K. and Buchardt, B. (2006) *J. Sed. Res.*, 76, 460. [18] Pelkey, S. M., et al. (2007) *JGR*, 112, E8. [19] Roach, L. H., et al. (2009) *JGR*, 114, E2.