REFLECTANCE SPECTRA AND OPTICAL CONSTANTS OF MARS CALCIUM, MAGNESIUM, AND IRON CARBONATE ANALOGS K. M. Pitman[1], C. S. Jamieson[2], E. Z. Noe Dobrea[1], J. B. Dalton III[3], W. J. Abbey[3]. [1]Planetary Science Institute, 1700 E. Fort Lowell Road, Suite 106, Tucson, AZ 85719 USA <pitman@psi.edu>, [2]SETI Institute, 189 Bernardo Ave., Suite 100, Mountain View, CA 94043 USA, [3]Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109 USA.

Introduction: Carbonates are among the hydrous mineral classes identified on the martian surface [1-4] that suggest a rich and complex aqueous history. Carbonates, including the major species calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), and magnesite ($MgCO_3$), have been found in martian meteorites [5-9], detected with ground-based telescopes and Mariner 6/7 IRS spectra [10-11], and have been posited to exist in the martian dust at small concentrations (2-5 weight %) on the basis of matches between Mars Global Surveyor TES and laboratory thermal infrared emissivity spectra [12]. The exciting MRO CRISM detection of carbonates in outcrops at Nili Fossae [1] Leighton Crater [3], and Huygens Crater [4] and MER Spirit's detection of 16-34 weight % carbonate in at the Comanche outcrops in Columbia Hills [2] further suggested that Ca-, Mg- or Mg-Fe carbonate species are present on Mars. Most of these identifications on Mars have been made via comparison to laboratory carbonate analog spectra but the abundances have yet to be constrained.

Whereas significant progress is being made in the determination of optical constants for phyllosilicates and sulfates, the optical constants for polymorphs of certain carbonates relevant to Mars have not yet been determined. Carbonate VNIR reflectance spectra and a few optical constants datasets (e.g., [14]) are available for the major forms, e.g., calcite, dolomite, and magnesite, based on prior work and relevance for the martian atmosphere [11-12, 15-17]. There exist some VNIR spectra of other Mars carbonate species within the MRO CRISM, RELAB, USGS, ASTER, and University of Winnipeg/HOSERLab spectral databases but very few of these spectra are suitable for deriving optical constants because the diameter was too roughly estimated at the time of measurement. Here we remedy these issues by providing diffuse reflectance spectra and optical constants at visible to near-infrared wavelengths (VNIR, λ=0.35 - 5 μm) for more particles size ranges of different polymorphs and hydration states of Ca-, Mg-, and Fe-carbonates.

Methodology: We purchased a suite of Mars-relevant carbonates: ankerite [$Ca(Fe,Mg,Mn)(CO_3)_2$], hydromagnesite [$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$], artinite [$Mg_2(CO_3)(OH)_2 \cdot 3H_2O$], and aragonite [$CaCO_3$]. Aragonite and ankerite were selected for their relevance to the Phoenix landing site [13]. Artinite has been suggested for Mars by [15] and [11]. Hydromagnesite is a more controversial choice, having been posited for Mars [11] but also rejected in favor of magnesite [12]. Given the carbonate formation sequence (siderite -> calcite -> hydromagnesite; [18]), we consider it here. All of the samples purchased are nearly 100% mineralogically pure based on XRD analysis. Five to eight grain size fractions and three viewing geometries (incidence and emission angles i=0º, e=10º; i=0º, e=15º; i=30º, e=0º) were measured for each carbonate at the Planetary Ice Characterization Laboratory at JPL (Fig. 1), with diameters confirmed via optical microscopy. The rationale for acquiring spectra on multiple grain size fractions is to provide a robust estimate for the imaginary index of refraction k [19]. Multiple viewing geometries permit cross-checks on the optical constants values using different (Hapke vs. Shkuratov) derivation methods. We then used the spectra to derive imaginary index of refraction $k(\lambda)$ using the method of [20], in which k is derived from directional-hemispherical reflectance as a function of real index of refraction at the sodium "D" line, porosity and optical path length in the sample, and transmission and reflectance coefficients. In Fig. 2, we plot k and the real indices of refraction $n(\lambda)$ derived via subtractive Kramers-Kronig relations [21].

Significance: Optical constants are important for generating synthetic spectra of intimately mixed minerals to compare to spacecraft data and quantify the amount and distribution of carbonates on Mars. However, optical constants currently have not been published for the rarer forms of carbonates or, in the case of hydromagnesite, are only very roughly estimated. Having spectral data is also important because the spacecraft spectra of martian carbonates do not always match existing library spectra, and it is likely that we are observing hydrated phases for which spectral data is not yet available. Because the hydration state and mineralogy imply particular environmental and chemical conditions as well as the duration of those conditions, Mars abundances modeled using our carbonate analog data could be used to constrain these conditions at different Mars epochs and used to infer transport and alteration mechanisms at work on Mars during their formation.

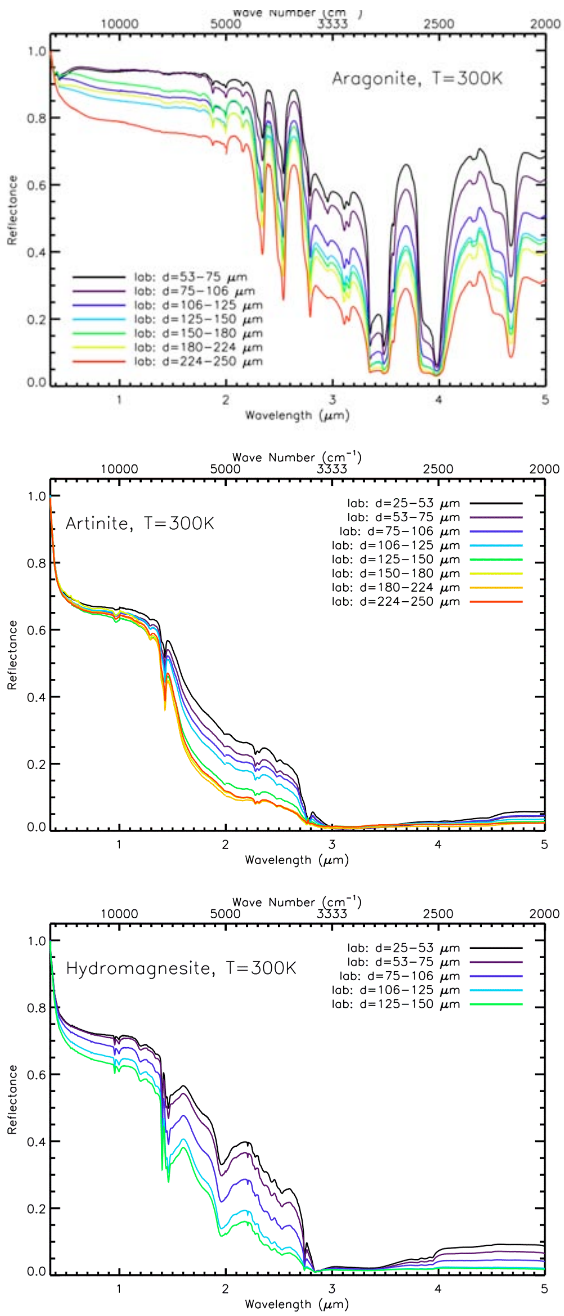

Fig. 1: Laboratory diffuse reflectance spectra at i=30º, e=0º for (a) aragonite, identified at the Phoenix landing site; (b): artinite, suggested for Mars by [14, 18] and (c): hydromagnesite, suggested for Mars by [14]. Mars mission spectrometer wavelength range shown here; full laboratory range extends to λ ~ 25 μm.

Acknowledgments: This work was supported by NASA's Mars Fundamental Research Program (NNX13AG78G; PI Pitman) and partly performed at the Jet Propulsion Laboratory, California Institute of Technology, under contract to the National Aeronautics and Space Administration.

References: [1] Ehlmann B. L. et al. (2008) *Science*, *322*, 1828-1832. [2] Morris R. V. et al. (2010) *Science*, *329*, doi:10.1126/science.1189667. [3] Michalski J. R. and Niles P. B. (2010) *Nature Geoscience*, *3*, 751-755. [4] Wray J. J. et al. (2011) *LPS XLII*, 2635. [5] Gooding J. L. et al. (1988) *Geochim. Cosmochim. Acta*, *52*, 909-915. [6] Clayton R. N. and Mayeda T. K. (1988) *Geochim. Cosmochim. Acta*, *52*, 925-927. [7] Treiman A. H. et al. (1993) *Meteoritics*, *28*, 86-97. [8] McKay D. S. et al. (1996) *Science*, *273*, 924-930. [9] Lane M. D. and Christensen P. R. (1997) *JGR*, *102*, 25,581-25,592. [10] Blaney D. L. and McCord T. B. (1989) *JGR*, *94*, 10,159-10,166. [11] Calvin W. M. et al. (1994) *JGR*, *99*, 14,659-14,675. [12] Bandfield J. L. et al. (2003) *Science*, *301*, doi: 10.1126/science.1088054. [13] Boynton W. V. et al. (2009) *Science*, *325*, doi: 10.1126/science.1172768. [14] Roush T. L. and Orenberg J. B. (1993) *LPS XXIV*, 1215. [15] Pollack J. B. et al. (1990) *JGR*, *95*, 14,595-14,627. [16] Erard S. et al. (2000) *LPS XXXI*, Abstract #1325. [17] Lellouch E. et al. (2000) *Planet. Space Sci.*, *48*, 1393-1405. [18] Catling D. C. et al. (1999) *JGR*, *104*, 16,453-16,469. [19] Lucey P. G. (1998) *JGR*, *103*, 1703–1713. [20] Shkuratov Y. et al. (1999) *Icarus*, *137*, 235-246. [21] Warren S. G. (1984) *Appl. Opt.*, *23*,1206–1225.

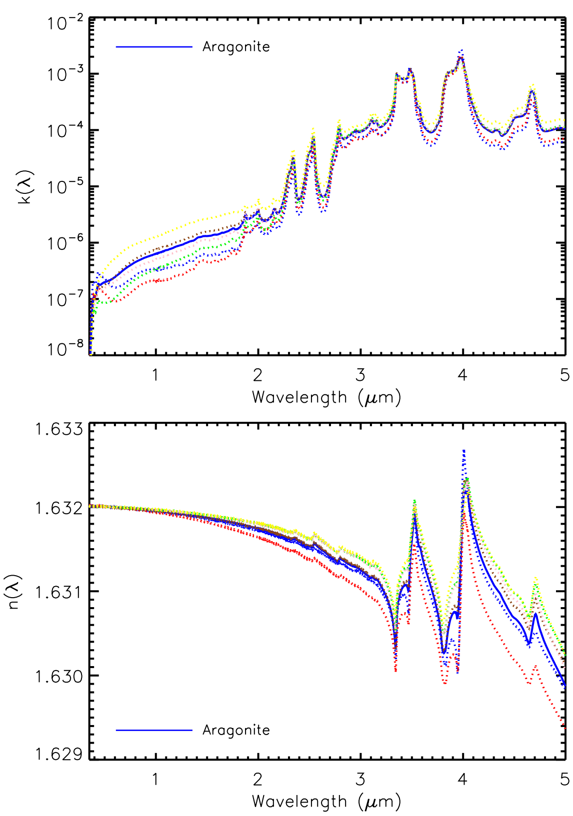

Fig. 2: Optical constants (imaginary and real indices of refraction k(λ) and n(λ)) for aragonite.