OPTICAL CONSTANTS AND REFLECTANCE SPECTRA OF MARS CARBONATE ANALOGS II. K. M. Pitman¹, C. S. Jamieson², E. Z. Noe Dobrea³, J. B. Dalton III⁴, W. J. Abbey⁵. ¹Planetary Science Institute, 1700 E. Fort Lowell Road, Suite 106, Tucson, AZ 85719 USA <pitman@psi.edu>, ²Space Science Institute, 4750 Walnut Street, Suite 205, Boulder, CO 80301 USA <pitman@spacescience.org>, ³SETI Institute, 189 Bernardo Ave., Suite 100, Mountain View, CA 94043 USA, ⁴Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109 USA.

Introduction: Morphological evidence suggests that several of the carbonates identified thus far on Mars may have been exhumed from some depth (e.g., [1-2]), and others may have been exposed to hydrothermal conditions [3]. Constraining the mineralogy of carbonates on Mars would prove important to our understanding of their genesis and the environmental conditions to which they have been exposed. Increasing the number of optical constants datasets and available laboratory comparison spectra for a range of Ca-, Na-, Mg-, and Fe-carbonates is necessary to better identify the specific chemical compositions and quantify the abundances of the known carbonates on Mars.

What is needed are diffuse reflectance spectra of (a) variations on carbonate polymorphs and hydration states, (b) carbonates which have only been measured in one particle size range or in poorly bounded grain sizes, (c) other carbonates that would be stable on Mars but have yet to be explored. 2014 marked a resurgence of interest in and production of carbonate reflectance spectra for the Mars community (e.g., [4-6]). Most of these studies focused on aspect (a) but are not suitable for deriving optical constants for various reasons (e.g., the spectra were obtained for only one grain size; diameter was not recorded or too roughly estimated at the time of measurement). Continuing from [7], our work addresses aspects (a-c) by characterizing Mars-relevant carbonate polymorphs and hydration states to fill in the gaps in chemistry and also to measuring these in enough grain sizes to permit improved optical constants derivation.

Methodology: For this study, we focused on the following: nahcolite [NaHCO₃], vaterite [hexagonal CaCO₃], nesquehonite [Mg(HCO₃)₂(OH)·2(H₂O)], and brugnatellite [Mg₃Fe³⁺(CO₃)(OH)₃·4H₂O]. Transmission spectra of nesquehonite and nahcolite, and IR modes of calcite, vaterite, and aragonite were considered by [8]. Nahcolite is also relevant to Type 1 brines formed from basaltic weathering fluid evaporation [9]. Nesquehonite, a Mg-carbonate that forms on other carbonates, serpentines, or volcanic breccias, was mentioned in [10], who noted that a comparison between this compound and Mars data would potentially be of interest but that sufficient laboratory spectral data do not exist. Brugnatellite was cited in [11] as a Fe-bearing carbonate worth studying for Mars.

We purchased a suite of samples from Minerals Unlimited and Excalibur Mineral Corp., in sample sizes of 10-100 grams per mineral. 10 grams is the minimum for a sample that would perfectly separate into our desired ASTM sieve fractions. Having up to 100 grams of material guards against losses of the natural carbonates during sieving and allows us to better isolate the purest mineral grains. We synthesize any carbonates that we cannot find in pure form from vendors. For example, we synthesized the high purity nahcolite for Fig. 1 from Sigma-Aldrich reagent. Samples chemistries were confirmed via XRD analysis. Three 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 (e.g., Fig. 2), 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 [12]. 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(λ) using the method of [13]. In Fig. 1-2, we plot k and the real indices of refraction n(λ) derived via subtractive Kramers-Kronig relations [14].

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 are only very roughly estimated. 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.

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**Fig. 1:** Optical constants (real and imaginary indices of refraction $k(\lambda)$ and $n(\lambda)$) for nahcolite. Solid blue line indicates the average $n$, $k$ based on several sieve fractions.

**Fig. 2:** Laboratory diffuse reflectance spectra at $i=30^\circ$, $e=0^\circ$ and optical constants for vaterite with calcite. MRO CRISM wavelength range shown; full data range extends to $\lambda \sim 25 \mu m$. 