CHARACTERIZATION OF CARBONATE COMPOSITIONS AND MINERAL ASSEMBLAGES IN NILI FOSSAE TO CONSTRAIN GEOCHEMICAL CONDITIONS. S. M. Wiseman[1], B. L. Ehlmann[2], and J. F. Mustard[1], [1]Geological Sciences, Brown University, Providence RI, [2]California Institute of Technology, Pasadena CA.

Introduction: The detection of carbonate-bearing deposits within coherent stratigraphic units on the surface of Mars [e.g., 1-7] (rather than Martian dust [8]) is significant because carbonate phases are important mineralogic indicators of neutral to alkaline aqueous geochemical condition(s) [e.g., 9]. The specific carbonate phases and accompanying mineral assemblages provide more refined environmental information (e.g., fluid cation chemistry, pCO_2, temperature) and alteration setting(s) (e.g., subaerial, hydrothermal grade, etc).

Diagnostic carbonate-related absorption features that are detectable with orbiting CRISM and OMEGA visible/near infrared (VNIR) spectrometers occur near 2300, 2500, 3400, and 3900nm and shift depending on the major cation in the carbonate [10, 11]. Characterization of carbonate composition using CRISM spectra has primarily focused on examination of carbonate-related vibrational features near 2300 and 2500nm because the exact wavelength center positions allow determination of the dominant cation (Fig. 1) [10, 11].

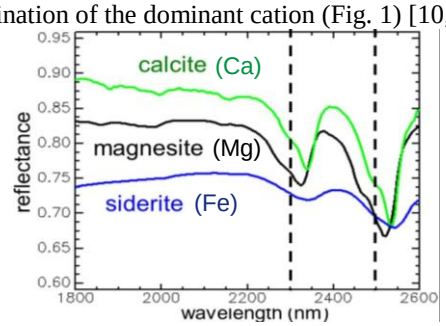

Figure 1. Carbonate library spectra.

Carbonate-bearing deposits have been reported on Mars using CRISM spectra in mapable units (Fig. 2) in the vicinity of Nili Fossae near the Isidis Basin [1, 6], and southwest towards Hellas Basin [3, 4] as well as within McLaughlin crater near Marwth Vallis [7]. Magnesite-bearing deposits identified in Nili Fossae are posited to have formed in the shallow subsurface at low grade hydrothermal conditions or subaerially under surface ambient conditions [1]. Deposits detected in Leighton crater and in Huygens basin have slightly different band positions and are inferred to be Fe- and/or Ca-bearing (e.g., siderite and/or calcite) rather than Mg-bearing [3, 4] and could have formed in the subsurface or at the surface and subsequently buried. Mg/Fe/Ca carbonates are broadly consistent with the $Mg_{0.62}Fe_{0.25}Ca_{0.11}Rh_{0.02}CO_3$ phase inferred from Mossbauer and APXS measurements made at the Columbia Hills, Gusev crater [2] and Ca-carbonate reported at the Phoenix landing site [12].

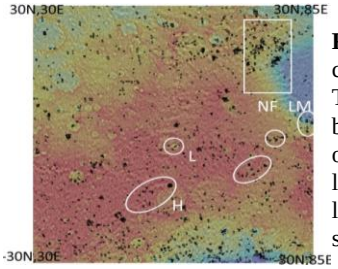

Figure 2. MOLA color coded topography on THEMIS day IR. Carbonate-bearing sites are outlined. Note, McLaughlin crater carbonate site located at 23N, -22E is not shown.

Although CRISM spectra identified as carbonate-bearing exhibit bands near 2300 and 2500nm, spectra are not entirely similar to any one terrestrial carbonate spectrum (Fig. 1) because other alteration phases are mixed with the carbonate. Therefore, detailed determination of specific carbonate mineral chemistry on Mars using CRISM spectra is complicated [13, 14] because the carbonate minerals are always mixed with other alteration phases (e.g., phyllosilicates) that have absorption features that overlap with and obscure diagnostic carbonate bands. For example, Nili Fossae carbonate spectra are a mixture of magnesite, nontronite (smectite), and olivine [1]. The difficulty in characterizing carbonate chemistry on Mars by examination of CRISM spectra of mixed pixels limits inferences that can be drawn about carbonate formation environment. In addition, it is challenging to intercompare spectra from different images and locations on Mars using the empirical volcano scan atmospheric correction because of the presence of atmospheric residuals and artifacts.

The goals of this work are to 1) Use quantitative Hapke mineral unmixing [15] to model carbonate spectra and determine specific carbonate compositions and 2) Map the distribution of mineral assemblages associated with carbonates and use their extents to better constrain environment of formation. CRISM spectra used in this study are atmospherically corrected with Discrete Ordinate Radiative Transfer (DISORT)-derived corrections [16-18] to overcome the challenges posed by using the volcano scan atmospheric correction and/or ratioed spectra.

Atmospheric Correction: CRISM spectra are atmospherically corrected using DISORT modeling [16-18]. DISORT is a public domain general purpose Fortran program for discrete-ordinate-method radiative transfer in scattering and emitting layered media. The atmosphere is treated as a plane-parallel medium in which individual layers are homogenous but interlayer properties can be varied. The numerical implementation is discussed in [16] and 'front-end' routines optimized for study of the Martian atmosphere in [17].

DISORT is used to calculate I/F for atmospheric conditions relevant to each CRISM image for a series of surface albedos. These forward models are used to generate lookup tables that are then used to convert CRISM I/F to surface albedo [e.g., 19].

Hapke Modeling: VNIR spectra of intimate mixtures are nonlinear with respect to end member compositions [20-22]. Volumetric proportions of minerals in mixtures do not correlate with spectral contribution. The Hapke model is an approximate analytic solution to the radiative transfer equation describing scattering of light from particulate surfaces and can be used to compute the reflectance of a surface at any geometry as a function of wavelength [15]. The Hapke model is linear in terms of single scattering albedo (SSA) (light scattered relative to light scattered + absorbed) and the SSA of a mixture is the sum of the SSAs of each component, weighted by areal abundance [15].

Initial Results: A Nili Fossae carbonate-bearing spectrum is shown in black in Fig 3. It was modeled as a combination of scene derived spectral classes (see Fig. 4) and laboratory carbonate spectra. This simple example shows that the Nili Fossae carbonate spectrum is relatively well modeled as a combination of spectra in the scene (smectite, olivine, bright, and dark material) and magnesite (Fig., 3, green; see Fig. 1 magnesite spectrum) and is poorly modeled by calcite (Fig. 3, red; see Fig. 1 calcite spectrum). Also, smectite is a necessary component (Fig. 3, blue) and the presence of smectite shifts the center wavelength of the ~2300nm band in the mixed smectite-carbonate spectrum.

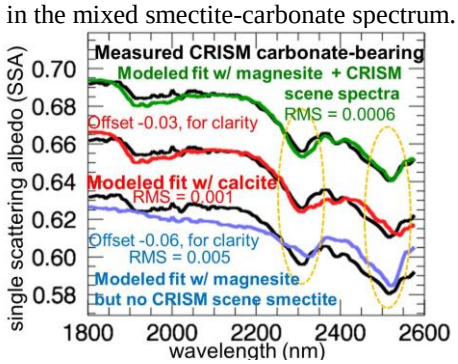

Figure 3. Hapke nonlinear mixing model results.

Figure 4 shows the distribution of smectite, kaolinite, and carbonate in Nili Fossae CRISM image FRT 3FB9. Note that mineral distributions reveal more information than simple parameter maps, as arrows indicate (Fig 4).

Discussion: Robust determination of carbonate minerals on Mars using CRISM spectra is complicated because previously identified carbonate-bearing deposits have spectral contribution from other alteration phases (e.g., phyllosilicates) that have absorption features that overlap with diagnostic carbonate bands near 2300 and/or 2500nm. Nonlinear Hapke modeling of DISORT-corrected carbonate-bearing spectra will allow us to test the hypotheses that Mg-carbonates and Fe/Ca- carbonates are the best spectral matches to previously identified deposits. Identifying specific carbonate chemistry and characterizing compositional variation is crucial for interpreting geochemical conditions. Multiple alteration phases (e.g., chlorite, prehnite, saponite, nontronite, serpentine, etc.) have been identified in association with carbonate exposures [1,3,4,6,7]. However, the extents of these phases have not been mapped because parameter images that identify key spectral features are often non unique (for example, the 2300nm parameter highlights nontronite, saponite, chlorite, serpentine, etc.). Characterizing and mapping the distribution of these mineral assemblages is important for understanding Martian paleo environments and putting carbonate formation into context.

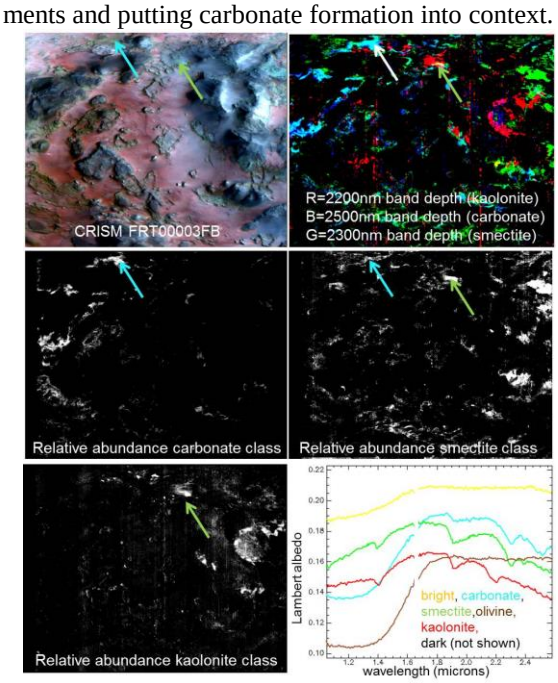

Figure 4. (upper) False color composite and parameter map. (lower) Mineral maps and type spectra.

References: [1] Ehlmann el al. (2008), *JGR*, [2] Morris et al. (2010), *Sci.*, [3] Michalski and Niles (2010), *Nat. Geo.*, [4] Wray et al. (2011), *LPSC*, [5] Carter and Poulet (2012), I*carus*, [6] Bishop et al. (2013), *JGR*, [7] Michalsk et al. (2013), *Nat. Geo.*, [8] Bandfield et al. (2003), *JGR*, [9] Catling (1999), *JGR*, [10] Hunt and Salisbury (1971), *Mod. Geo.*, [11] Gaffey (1986), *JGR*, [12] Boynton et al. (2009), *Sci.*, [13] Bishop et al. (2013), *LPSC*, [14] Wiseman et al. (2013), *LPSC*, [15] Hapke (1993), *Theory of Reflectance and Emittance Spectroscopy*, [16] Stamnes et al. (1988), *Appl. Opt.*, [17] Wolff et al. (2009), *JGR*, [18] Thomas and Stamnes (2002), *Radiative transfer in the atmosphere and ocean*, [19] Arvidson et al. (2006), *JGR*, [20] Nash and Conel (1974), *JGR*, [21] Singer (1981), *JGR*, [22] Johnson (1983), *JGR*.