ANALYSIS OF UNIQUE MARTIAN SULFATE OUTCROPS BASED ON SAMPLES FROM THE PAINTED DESERT SULFATE HILL ANALOG SITE AND LAB MIXTURES. S. L. Perrin[1], J. L. Bishop[1], and A. M. Sessa[2], [1]SETI Institute, (Mountain View, CA; jbishop@seti.org), [2]Georgia Institute of Technology (Atlanta, GA).

Introduction: At Sulfate Hill, in the Painted Desert, coexisting jarosite and gypsum has been identified, yielding a "doublet-type" signature in visible/near-infrared (VNIR) spectra with bands near 2.22 and 2.26 µm [1]. Here, we evaluate the Painted Desert as an analogue for determining the presence of coexisting jarosite and gypsum on Mars. We utilize the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) and VNIR spectroscopy of specific analog sites. On Mars, "doublet-type" spectroscopic signatures have been observed in localities including Ius and Melas Chasma in Valles Marineris [2,3], Noctis Labyrinthus [4], and Mawrth Valles [5]; these spectral features could be attributed to coexisting jarosite and gypsum, but may also result from other mineral mixtures.

Previous investigations of the Painted Desert as an analog for Mawrth Vallis are due to expansive clay-rich horizons resembling the stratigraphy seen at Mawrth Vallis [6]. Recent discovery of gypsum and jarosite outcrops at Sulfate Hill further establishes the Painted Desert as an intriguing analog for the Mawrth Vallis region [1]. Noctis Labyrinthus, located west of Valles Marineris at the edge of the Tharsis Dome, contains a variety of hydrated minerals potentially indicating past active aqueous processes, including hydrothermal, and/or acidic, alteration of volcanic materials [4]. In Melas Chasma observations, "doublet-type" draping units were attributed to airfall deposits, potentially of volcanic ash [3]. This "doublet-type" material has also been observed at Ius Chasma in wallrock landslides, unconformably overlying layered Fe/Mg smectite clays, and overlying sulfates [2]. "Doublet-type" materials at these Valles Marineris sites may be less analogous to the Painted Desert site.

Painted Desert: Spanning from the Southeast rim of the Grand Canyon to the Petrified Forest National Park, Arizona's Painted Desert is characterized by badland morphology containing a diverse stratigraphy of phyllosilicates, many of which formed from lacustrine and fluvial alteration of ash deposites, resulting in bentonite and anoxically buried organic materials [6]. This diverse mineralogy has been observed both in the field and remotely, showing a high variability on a scale of 10s of km [6].

Samples were collected and analyzed from Sulfate Hill in the Petrified Forest National Park [1]. Gypsum ($CaSO_4 \cdot 2H_2O$) is present as a component of the surface crust material, in large tabular crystals, and in thin sheets of crystals 3-4 cm below the surface. One site also contains orange jarosite-rich soil with tan soil nearby. The soil samples were gently crushed and dry sieved to <125 µm and 125-1000 µm for this study. The white gypsum flakes of thin crystals were measured without grinding or sieving. VNIR spectra were measured in the lab using an ASD FieldSpecPro from 0.35-2.5 µm [1]. Particulate 45-125 µm fractions were measured by XRD showing that the gypsum flakes are nearly pure; the orange soil contains a roughly 2:1 natrojarosite:gypsum ratio (+quartz, montmorillonite); and the tan soil contains quartz, gypsum and montmorillonite.

The orange soil spectrum is characteristic of jarosite ($KFe_3(SO_4)_2(OH)_6$) / natrojarosite ($NaFe_3(SO_4)_2(OH)_6$) with bands at 0.44, 1.47, 1.85, 2.22, and 2.26 µm [7]; additional bands near 1.41 and 1.91 µm were attributed to montmorillonite. The spectrum of the white flakes contains multiple features consistent with gypsum including a strong triplet at 1.45, 1.49, and 1.52 µm, a band at 1.76 µm and a doublet at 2.22 and 2.26 µm [8].

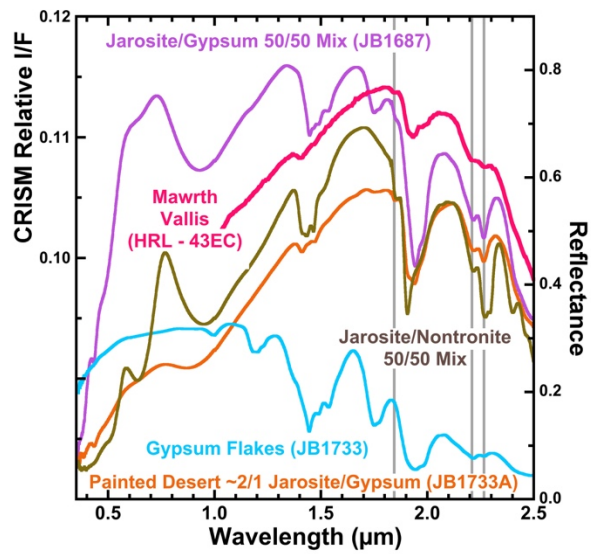

Fig. 1. Mawrth Vallis "doublet-type" spectrum from CRISM image HRL000043EC compared with VNIR lab spectra of Painted Desert samples and lab mixtures. Grey lines mark features at 1.85, 2.22, and 2.26 µm.

Mineral Mixtures: VNIR spectra of gypsum/jarosite [1], jarosite/nontronite [9] and gypsum/opal [10] mixtures were also used in this study. The gypsum/jarosite mixture spectrum contains 4 overlapping bands near 1.5 µm due to a combination of the gypsum H_2O stretching overtone triplet and the jarosite OH stretching overtone at 1.47 µm. The gypsum band at 1.75 µm is weaker in the mixture spectrum, but retains its shape, while the jarosite band at 1.85 µm is only present as a shoulder in the 50/50 wt.% mixture spectrum. OH combination

bands are present at 2.22 and 2.26 µm in spectra of both gypsum and jarosite, but these bands have different relative intensities in spectra of each mineral. The spectrum of gypsum has a stronger band at 2.22 µm and a weaker band at 2.26 µm, while jarosite has a stronger band at 2.26 µm with a shoulder at 2.22 µm. The mixture spectrum exhibits a doublet here with a clearly distinguishable band at 2.22 and a stronger band at 2.26 µm. In this study, we examine the 2.22 and 2.26 µm doublet as evidence for co-occurring jarosite and gypsum, while considering the presence of the 1.85 µm band to bolster the case for the presence of jarosite. Our previous work showed that the 1.85 µm band is present as a defined shoulder in spectra of mixtures of 2/1 jarosite/gypsum but is greatly subdued in mixtures of 1/1 jarosite/gypsum [1]. A similar result was observed for jarosite/nontronite mixtures [9]. Thus, the defined presence of this 1.85 µm band indicates that jarosite is likely a dominant component of the material measured.

Results – Mawrth Vallis: Spectra were collected previously from multiple small sites in CRISM image HRL000043EC where "doublet-type" signatures were detected [5]. Four of these potential jarosite-bearing 2x2 pixel sites were averaged together to create the "Mawrth Vallis" spectrum shown in Fig. 1 containing bands at 1.85, 2.22, and 2.26 µm. Spectra of Painted Desert samples containing jarosite and gypsum are shown for comparison, as well as lab mixtures of jarosite/gypsum [1] and jarosite/nontronite [9]. The ~2/1 jarosite/gypsum Painted Desert spectrum provides the features most consistent with this Mawrth Vallis spectrum. Similarly to the Painted Desert site, in the CRISM spectrum, the 2.26 µm band depth is only slighted greater than that of the 2.22 µm band. Spectra of both the 1/1 jarosite/gypsum and jarosite/nontronite samples exhibit much stronger 2.26 µm bands. Jarosite has been identified elsewhere in the Mawrth Vallis region based on the 2.26 µm band [11,12,13]. Ca-sulfate basanite has also been identified [14]. Additionally, gypsum/opal mixtures could be consistent with some doublet features observed at Mawrth Vallis [10]; doublet-type features could also result from jarosite/copiapite mixtures [15]. We suggest the "doublet-type" signature evaluated from Mawrth Vallis (Fig. 1) likely results from a jarosite-rich material that could contain gypsum or a poorly crystalline hydrated material. A more detailed study of "doublet-type" units at Mawrth Vallis is underway to characterize these materials [16].

Results – Noctis Labyrinthus: A "doublet-type" spectrum from Noctis Labyrinthus [4] was compared to spectra of Painted Desert samples [1] and lab mixtures of jarosite/gypsum [1] and gypsum/opal [10] in Fig. 2. The Noctis spectrum shows a stronger band at 2.22 than 2.26 µm, which is more consistent with spectra of the gypsum-rich Painted Desert sample and the gypsum/opal mixture. The 1.75 µm band characteristic of gypsum is clearly present, while the 1.85 µm is not.

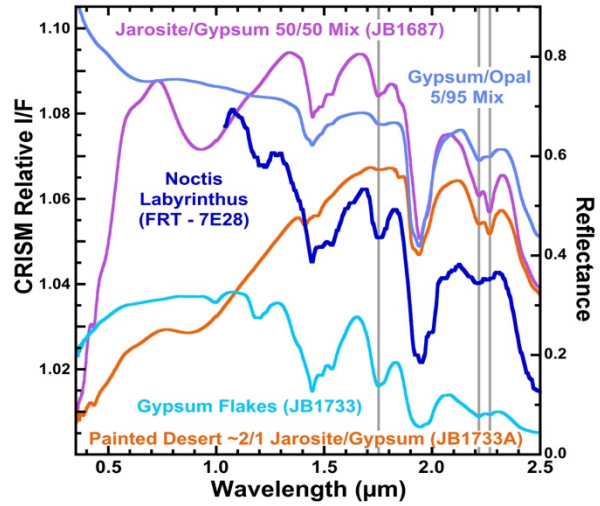

Fig. 2. *Noctis Labyrinthus "doublet-type" spectrum from CRISM image FRT00007E28 compared with VNIR lab spectra of Painted Desert samples & lab mixtures. Grey lines mark 1.75, 2.22, and 2.26 µm features.*

Implications for Mars: This study provides insights for identification of jarosite- and gypsum-bearing samples on Mars using VNIR spectra of natural mixtures from the Painted Desert's Sulfate Hill and lab mixtures. We show that VNIR spectra of jarosite-bearing samples is identifiable through the presence of bands at 1.85, 2.22, and 2.26 µm, with a stronger 2.26 band than 2.22 µm band. "Doublet-type" spectra with a stronger band at 2.22 than 2.26 µm could be due to gypsum-bearing mixtures. Further studies of jarosite/gypsum and jarosite/hydrated silica mixtures from the Painted Desert, other evaporative sites and lab mixtures would help further constrain orbital "doublet-type" signatures.

Acknowledgements: Samples were collected with permit #PEFO-2017-SCI-0009. Support from the CRISM instrument team, MDAP grant #NNX15AM47, and NAI grant #NNX15BB01 is much appreciated.

References: [1] Perrin S. et al. (2018) *LPSC,* #1801. [2] Ro-ach L. et al. (2010) *Icarus, 206,* 253. [3] Weitz C. et al. (2015) *Icarus, 251,* 291. [4] Weitz C. et al. (2011) *Geol., 39,* 899. [5] Bishop J. et al. (2016) *LPSC,* #1332. [6] McKeown N. et al. (2009) *LPSC,* #2509. [7] Bishop J. & Murad E. (2005) *Am. Miner.*, 90, 1100. [8] Bishop J. et al. (2014) *Am.Miner.*, 99, 2105. [9] Usabal G. & Bishop J. (2018) *AGU Fall Mtg*, #P31H-3806. [10] Miura J. & Bishop J. (2018) *AGU Fall Mtg*, #P31H-3811. [11] Farrand W. et al. (2009) *Icarus, 204,* 478. [12] Michalski J. et al. (2013) *Icarus, 226,* 816. [13] Farrand et al. (2014) *Icarus, 241*, 346-357. [14] Wray et al. (2010) *Icarus, 209,* 416. [15] Cull-Hearth S. et al. (2016) *Icarus, 271,* 387. [16] Danielsen J. et al. (2019) *LPSC*, #3017.