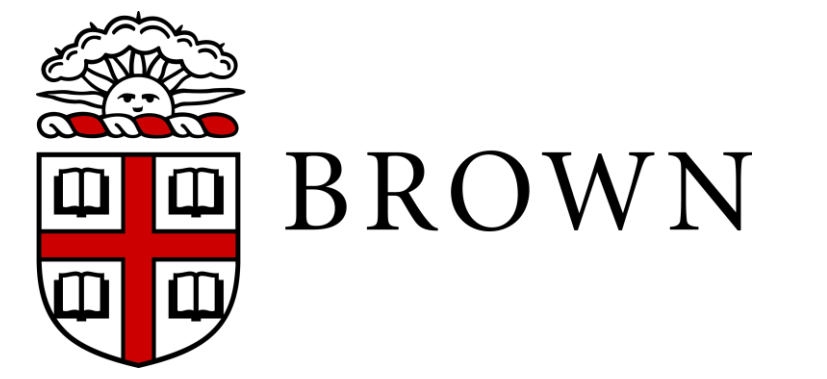


# Investigating the Antarctic meteorite analog of carbonate formation on Mars.

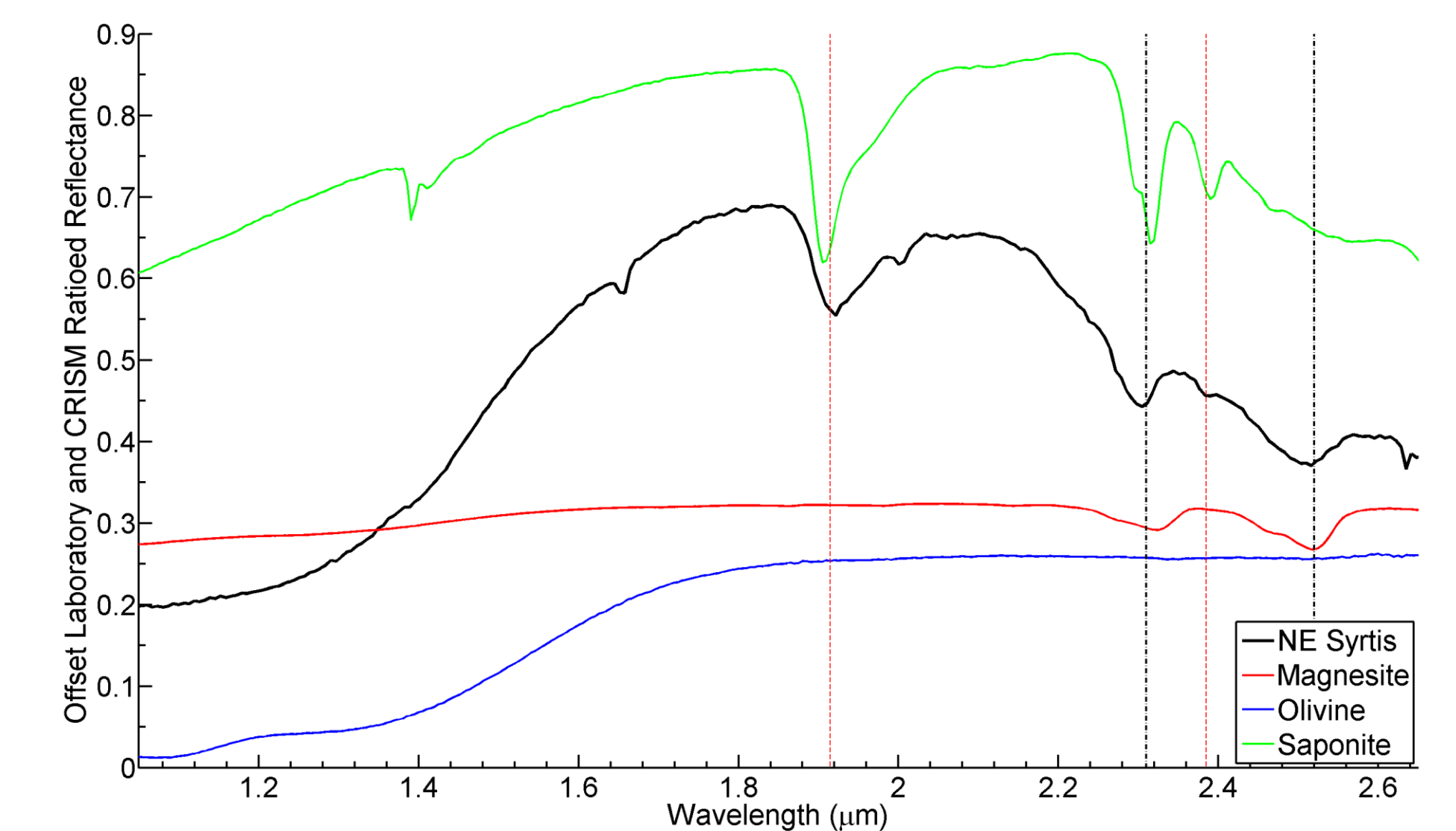


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**Introduction** Orbital spectroscopy, lander investigations, and meteoritical studies have confirmed the presence of carbonate minerals on Mars [1], with the most significant carbonate deposits observed in conjunction with the Nili Fossae olivine-rich unit [2,3]. Multiple formation mechanisms have been suggested for the carbonate [1,4,5]. They involve alteration of an ultramafic host rock at slightly elevated temperatures, contact hydrothermal alteration, or precipitation from transitory shallow lakes. An additional mechanism that has not received equal scrutiny is the weathering of olivine-rich rocks exposed at the surface at ambient temperatures in a manner akin to the weathering of olivine-rich meteorites in Antarctica [1]. Here we assess this hypothesis and compare its predictions with laboratory and remotely-sensed observations, and present an additional explanation of the martian carbonate spectral features supporting this running hypothesis.

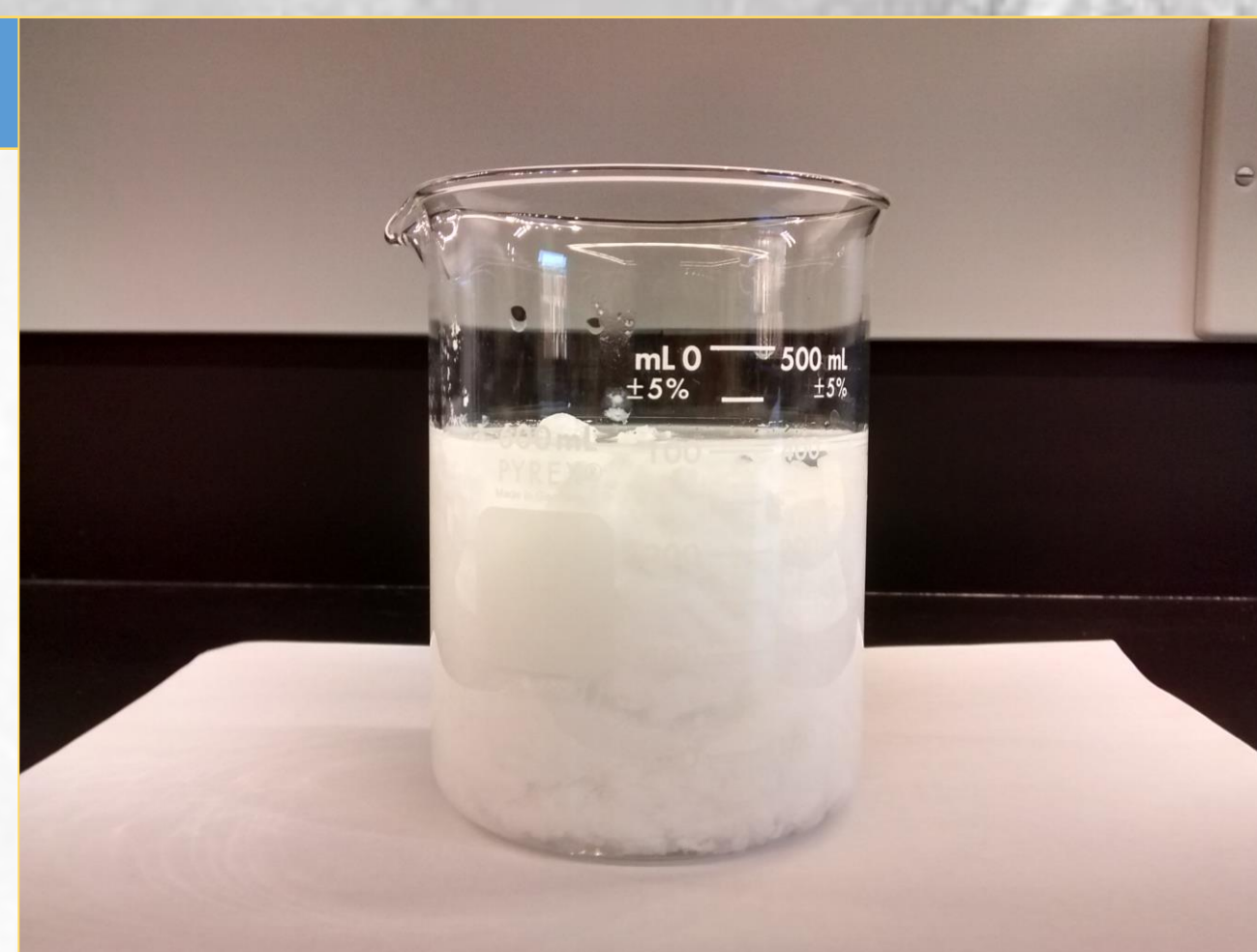
**Carbonates on Mars** Martian carbonates are largely observed in ancient, olivine-rich, Noachian rocks. It has been identified by paired absorptions at  $\sim 2.3$  and  $2.5 \mu\text{m}$  (Fig.1) as well as at  $\sim 3.45$  and  $3.9 \mu\text{m}$  indicative of an anhydrous carbonate mineralogy (though these 3–4  $\mu\text{m}$  absorptions are difficult to observe in CRISM data) [1]. Martian carbonates also bear an absorption at  $\sim 1.9 \mu\text{m}$  inferred to be a mixture of a phyllosilicate phase [6] or the presence of hydrous carbonates [7]. Carbonates observed on Antarctic meteorites (see below) are hydrous, and here we investigate the spectral properties of a hydrous carbonate and see if mixtures of its spectral features, and those of olivine and Fe/Mg smectite, can also explain the inferred carbonate spectra of Mars.

**Figure 1 (right):** CRISM spectrum from image FRT00024C1A consisting of a spectrum collected from the olivine-rich Fractured Unit of Bramble and Mustard [8] and ratioed to a spectrally-bland spectrum spanning the same along-track detector distance. This spectrum (black) is typical of the inferred olivine-carbonate-bearing materials of Mars. The broad absorption at  $\sim 1 \mu\text{m}$  matches that of olivine, the  $\sim 1.9$  and  $2.3 \mu\text{m}$  absorptions match Fe/Mg smectite, and paired  $\sim 2.3$  and  $2.5 \mu\text{m}$  absorptions match those of anhydrous carbonate minerals. Shown are laboratory spectra from the CRISM Spectral Library [9], including magnesite (KACB03A), olivine (C1PO58), and saponite (LASA53).

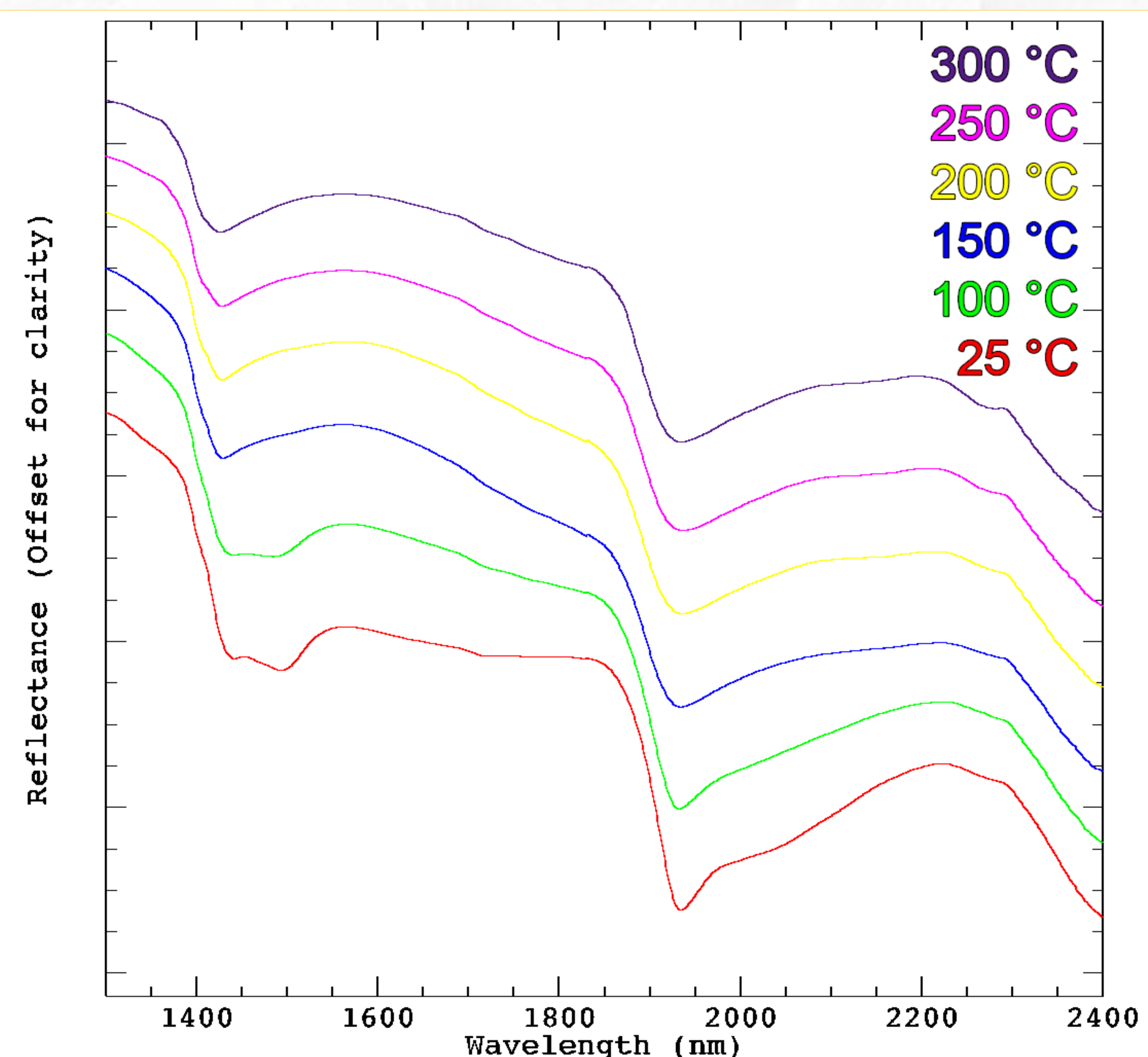
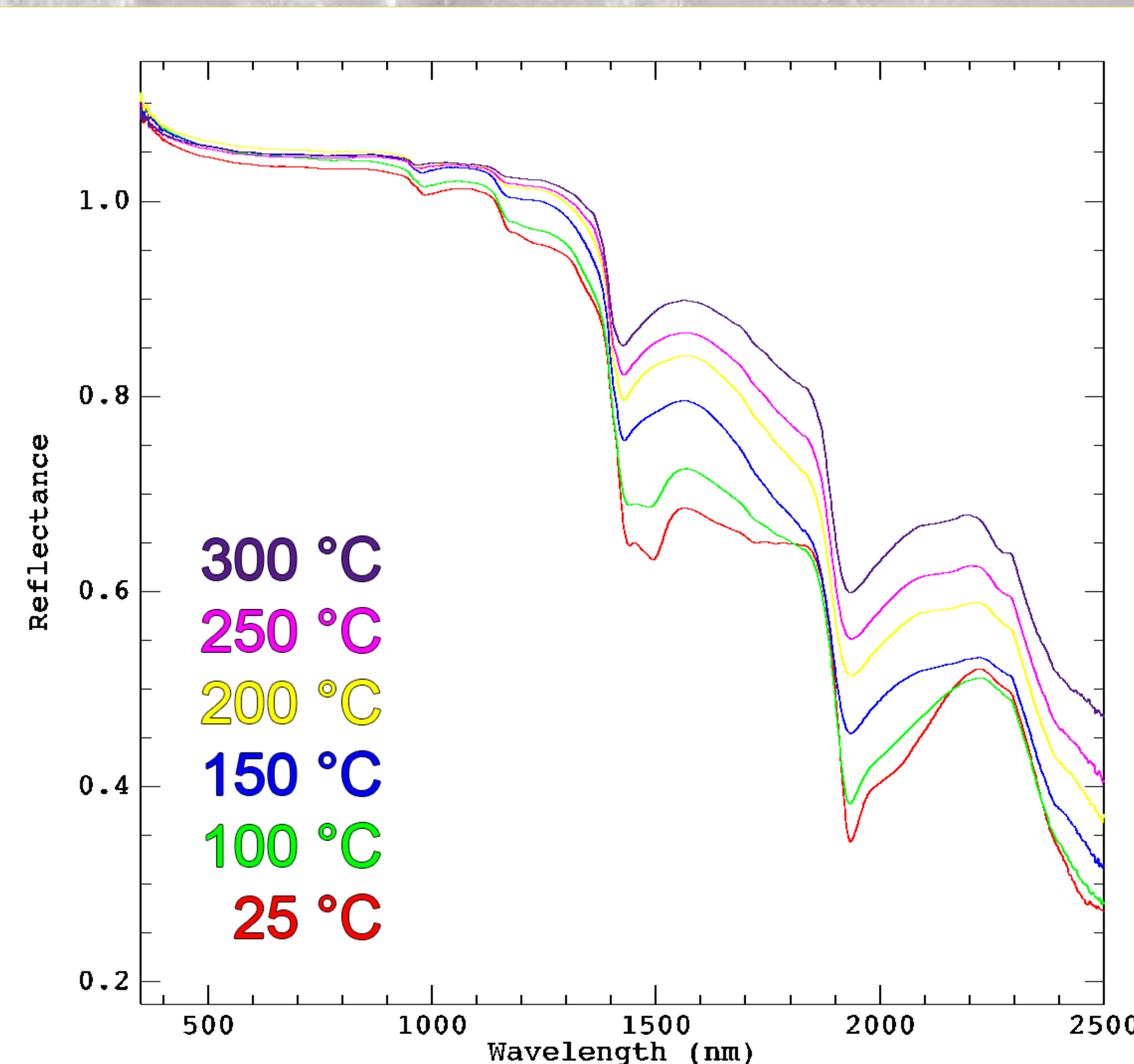


## Carbonates on Antarctic Meteorites

White efflorescences have been observed on a subset of meteorites collected in Antarctica. These white deposits were found to be hydrous carbonates and sulfates, and X-ray diffraction patterns matched the carbonates nesquehonite, hydromagnesite, and barringtonite [10–12]. The  $\text{CO}_3$  ions are of terrestrial origin, and the Mg originated from the weathering of the meteoritic olivine and not contamination [13]. Nesquehonite forms as a product of leaching at the borders of permeability of Mg-rich rocks, and the presence of this mineral in surface deposits and fractures [10] suggests it formed as a result of the interaction of the atmosphere, the local hydrosphere, and leached meteoritic cations.



**Figure 2:** Synthesized nesquehonite in a beaker. Crystals were allowed to grow for 5 days at ambient laboratory conditions.



## Laboratory Analysis of Nesquehonite

We synthesized Nesquehonite ( $\text{Mg}(\text{OH})(\text{HCO}_3) \cdot 2\text{H}_2\text{O}$  [14] or  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$  [15]) with the method of [13], and confirmed the mineralogy with a Bruker D2 PHASER X-ray diffractometer. Visible to near-infrared (VNIR) data were collected with an ASD Fieldspec spectrometer covering wavelengths  $0.35$ – $2.5 \mu\text{m}$ . Initially at ambient temperature under dry air, a temperature ramp was applied using a controlled environment chamber. Data were collected at 15 minute intervals as the sample was heated in  $25 \text{ }^\circ\text{C}$  increments from  $25$  to  $300 \text{ }^\circ\text{C}$  with 1 hour temperature dwell times (Figs. 3 and 4). Over this temperature range, we confirmed nesquehonite undergoes dehydration as the structure decomposes at  $\sim 75$ – $115 \text{ }^\circ\text{C}$  to transition to a crystalline phase and then an amorphous phase with a mass loss equivalent to  $\sim 2.5 \text{ H}_2\text{O}$  [15].

The  $2.5 \mu\text{m}$   $\text{CO}_3$  absorption observed here, when paired with a  $\sim 1 \mu\text{m}$  absorption of olivine, and a  $2.3 \mu\text{m}$  absorption of a Fe/Mg smectite mineral, together can match the olivine-carbonate spectra observed on Mars (Fig. 5). The  $\sim 1.9 \mu\text{m}$  absorption is observed in both hydrous carbonates and Fe/Mg smectites.

**Figure 3 (top right):** Laboratory VNIR spectra of nesquehonite dehydration. Data were collected every 15 minutes and with 1 hour dwell times at each temperature, and a subset is shown here of data collected after 45 minutes at the indicated temperature.

**Figure 4 (right):** Focus view on changing bands from  $1300$  to  $2400 \text{ nm}$  of the nesquehonite dehydration from Figure 2. Spectra are vertically offset.

## Conclusion – Low-Temperature Carbonate Formation on Mars

This mineral assemblage of low-temperature olivine weathering products has important implications for martian carbonates. The fundamental structural elements of nesquehonite are preserved throughout the dehydration process as the system returns to nesquehonite following rehydration [15], which we also confirmed. Once formed on Earth as well as Mars, nesquehonite could provide a sink for carbon even if the conditions depart from the normal stability field. Indeed,  $\text{CO}_2$  is not lost from the system until temperatures reach  $\sim 365 \text{ }^\circ\text{C}$  [15]. The stability fields of phases in the  $\text{MgO}-\text{CO}_2-\text{H}_2\text{O}$  system at extreme conditions are poorly understood, and understanding the stability of carbonates in this system at these conditions is of great interest to current Mars research. The possibility exists that the Nili Fossae carbonates have formed in a manner akin to the carbonates observed on Antarctic meteorites, and if true this may require only thin films of water at the surface of these rocks for the carbonate to form, as observed by the Phoenix Lander [16].

**Figure 5 (right):** VNIR spectra of a proposed low-temperature olivine weathering mineral assemblage matching martian olivine-carbonate spectral features. Shown are ASD spectrum of nesquehonite, and spectra from the CRISM Spectral Library [9], including saponite (LASA53), and olivine (C1PO58).

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**References:** [1] Ehlmann B.L. et al. (2008) *Science*, 322, 1828–1832. [2] Ehlmann B. L. & Mustard J. F. (2012) *GRL*, 39, L11202. [3] Bramble M. S. & Mustard J. F. (2015) *LPS XLVI*, Abstract #2090. [4] Brown A.J. et al. (2010) *EPSL*, 297, 174–182. [5] Viviano C.E. et al. (2013) *JGR-Planet.*, 118, 1858–1872. [6] Bishop J.L. et al. (2013) *JGR-Planet.*, 118, 635–650. [7] Calvin W.M. et al. (1994) *JGR-Planet.*, 99, 14659–14675. [8] Bramble M. S. & Mustard J. F. (2016) *LPS XLVII*, Abstract #2582. [9] CRISM Science Team, 2006. MRO CRISM Spectral Library. *PDS Geosci. Node*, St. Louis, MO. [10] Marvin U. B. (1980) *Antarct. J. US*, 15, 54–55. [11] Yabuki H. et al. (1976) *Sci. Pap. Inst. Phys. Chem. Res.*, 70, 22–29. [12] Jull A. J. T. et al. (1988) *Science*, 242, 417–419. [13] Velbel, M. A. et al. (1991) *Geochim. Cosmochim. Ac.*, 55, 67–76. [14] Frost R.L. & Palmer S.J. (2011). *Spectrochim. Acta A*, 78, 1255–1260. [15] Jauffret G. et al. (2015) *J. Therm. Anal. Calorim.*, 122, 601–609. [16] Boynton, W. V. et al. (2009) *Science*, 325, 61–64.

