

NEAR INFRARED SPECTROSCOPY OF CLATHRASILS: IMPLICATIONS FOR DETECTIONS ON THE SURFACE OF MARS. A. Vakkada Ramachandran¹ and V.F. Chevrier¹, ¹Arkansas Center for Space and Planetary Sciences, University of Arkansas, Fayetteville, AR, 72701; av034@uark.edu.

Introduction: Recent analysis of the Martian surface by Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) has identified large deposits of hydrated silica [1,2]. Such environments are geochemically unusual (by terrestrial standards) but are also potential sources of methane reservoirs in the form of clathrasils. Clathrasils are compounds related to silica with crystalline structures similar to the cubic structure-I gas hydrate which can host simple organic molecules [3,4]. Clathrasils were first discovered in the form melanophlogite, a rare silica mineral [5] found in in Sicily, Italy and a few other locations. It is reported to have incorporated gas molecules such as methane (CH₄), carbon dioxide (CO₂), nitrogen (N₂) and hydrogen sulfide (H₂S) into its cages [6,7,8]. The fact the structure is made of silica molecules makes them more stable at higher temperatures and lower pressures compatible with the Martian surface. Therefore, these compounds could store significant amounts of methane and could be used by future human explorers. These structures, although highly interesting, remain anecdotal on Earth and have never been studied in Martian geochemical environments. Therefore, our goal is to determine if these phases could constitute potential reservoirs of methane on Mars, how they would have formed and where they would be accessible. The first step of this study is to gather diagnostic data that could help identify them via remote sensing. Here we present near infrared (NIR) reflection spectral results of two melanophlogite samples, which will be completed by MIR FTIR and Raman spectroscopy.

Methods: Natural samples of clathrasils with various surface textures would be the best analogs to study the spectral properties. We obtained melanophlogite samples from two different locations (i) Fortullino, Tuscany, Italy (ii) Mt. Hamilton, Santa Clara, California, USA (Figure 1). We measured reflectance spectra using Fourier transform infrared spectroscopy (FTIR) with an Thermo Nicolet 6700 FTIR equipped with a diffuse reflectance accessory at the University of Arkansas. This instrument was set to acquire data from 0.8-2.5 μm with a white light source, calcium fluoride beam splitter and TECInGas 2.6 μm detector. Each sample was crushed and powdered to be placed in a sample cup to be inserted into the spectrometer. The final spectrum was an average of 450 scans.

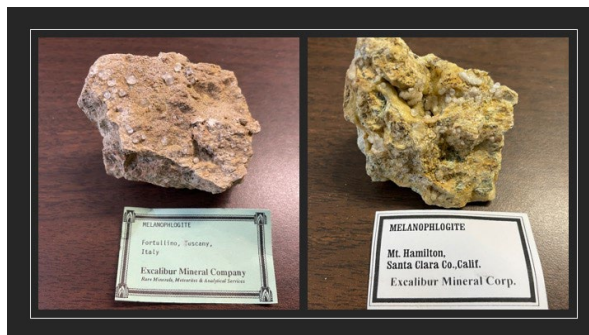


Figure 1: Melanophlogite samples used in this study. Left: geological origin from Tuscany, Italy; Right: geological origin from Mt. Hamilton, Santa Clara, California, USA.

Results and Discussions: For the investigation of the NIR spectra of melanophlogite, we present the results comparing the spectral data (Figure 2) from two locations. We observe both the samples follow the same pattern showing the signature of hydrated silica dominated by water related absorption bands. At 1.4 μm an overtone of O-H stretching in bonded silanols (Si-OH) is observed along with 1.9 μm O-H for free molecular water and 2.21 μm attributing to free Si-OH [2].

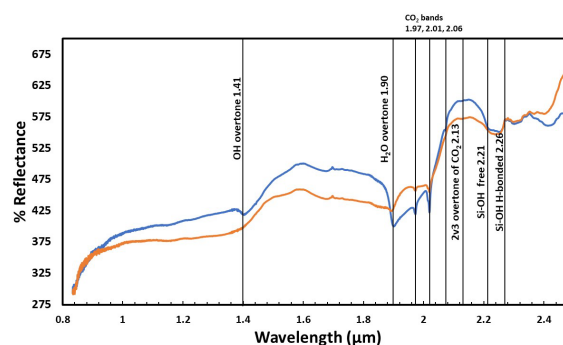


Figure 2: NIR reflectance spectra of the two different terrestrial sample of melanophlogite used in this study (blue: Tuscany, Italy; orange: California, USA). The absorption bands of hydrated silica at 1.4, 1.9 and 2.2 μm and the triplet for CO₂ at 1.97, 2.01 and 2.07 μm are observed.

We also observed small bands around 2 μm attributed to CO₂. This can be highlighted with the enhancement of the CO₂ (2v₃) overtone band near 2.13 μm which is

an indicator of solid CO₂. The smaller peaks at 1.96, 2.01 and 2.06 μm are usually from CO₂ in H₂O.

Significance of this work: Our results will provide a study which can be used to anticipate where methane resources should be expected by future robotic and human exploration. Clathrasils are a mineralogical curiosity on Earth but could be abundant on Mars because of the different geochemical conditions, particularly related to these recently identified silica deposits. We will use similar tools to the work done on clathrates (thermodynamic modeling) to understand the formation and stability of these compounds on Mars and where they would be likely to be found. Because they are theoretically much more stable, clathrasils could be easily accessible on the surface by future explorers and capable of retaining much more methane than water clathrates (the methane would remain trapped in the structure rather than degassing very rapidly in the low-pressure atmosphere). Therefore, understanding these compounds is very important for finding future methane sources as well as how to properly extract methane from these sources.

Conclusion: Clathrasils samples are studied using NIR spectroscopy. We observed the absorptions bands for CO₂ and hydrated silica. This result shows that CO₂ gas can be entrapped in the cage like structures. Because it is the most abundant gas in these hydrothermal environments. Furthermore, we need to search for other gas signatures assuming they are abundant enough in the clathrasils. Future studies will be done to have a database of clathrasils reflectance and Raman spectra to help with their identification on Mars, especially when combined with geochemical arguments on their stability and therefore possible environments. Future studies will also include recently discovered clathrasils such as Chibaite from Japan [4,8].

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References: [1] Pan, L. et al. (2021) *The Planetary Science Journal*, 2(2), p. 65. [2] Pineau, M. et al. (2020) *Icarus*, 347, p. 113706. [3] Kamb, B. (1965) *Science*, 148(3667), pp. 232–234. [4] Momma, K. et al. (2011) *Nature Communications*, 2(1). [5] von Lasaulx, A., 1876. *Neues Jahrbuch fuer Mineralogie.*, 250-257. [6] Gies, H., et al (1982) *Neues. Jahrb. Mineral. Monatsh.* 3, 119–124. [7] Yagi, Takehiko et al. (2007) *Physical Review B* 75 174115. [8] Momma, K. et al. (2020) *Mineralogical Magazine*, 84(6), pp. 941–948.