HEATED KAOLINITE/HALLOYSITE IN THE BARRIER RANGE COBBLE, JEZERO CRATER, MARS?

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Introduction: NASA's Mars 2020 Perseverance rover mission is exploring Jezero crater and collecting a cache of rock and soil samples for planned return to Earth in the future [1]. During its traverse, it is interrogating rocks and regolith as it traverses the crater floor.

On Sol 554, the rover encountered the buried light-toned cobble Barrier Range located in the Cannery Passage area, that appeared when soils were removed by the rover's wheel track. This cobble was analyzed by the rover's SuperCam instrument, including passive VIS (0.40-0.85 µm) and IR (1.3-2.6 µm) reflectance spectra and laser-induced breakdown spectroscopy (LIBS).

The three LIBS points that hit this cobble (#3, 4, 5) exhibited high abundances of SiO_2 (47.3-50.2 wt. %) and Al_2O_3 (37.6- 42.7 wt.%.)

VIS and IR reflectance spectra of these points show broadly similar features: red-sloped spectra with reflectance peaking at ~850 nm, no or weak Fe^{3+} signatures in the ~380-850 nm range, blue-sloped spectra in the 1300-1800 nm region, a flattening of the slope around 2200 nm, a local maximum around 2300 nm, a subsequent steepening beyond 2300 nm, and an absorption feature around 2500 nm (Figs. 1 and 2).

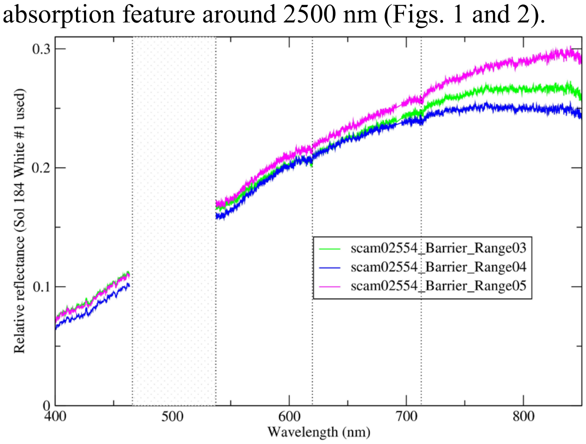


Figure 1. SuperCam VIS spectra of Barrier Range cobble – locations 3, 4, and 5 (<465 nm data smoothed). Dotted lines are joins between detectors or absent data.

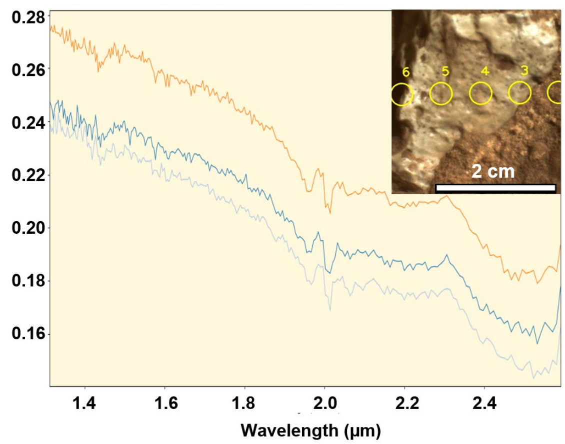


Figure 2. SuperCam IR spectra of Barrier Range cobble –locations 3, 4, and 5. Inset shows RMI image of the three points on the target.

Interpretation: Using the LIBS data as a starting point for interpretation, a few plausible mineralogies suggest themselves as possible candidates; here we focus on kaolinite and halloysite.

1. Halloysite/kaolinite ($Al_2Si_2O_5(OH)_4$): These minerals have identical compositions, but vary in terms of crystallinity and structure. Their spectra are characterized by an OH-related absorption feature near 1400 nm, and Al-OH bands in the 2150-2200 nm region (Figs. 3 and 4) [2]. Upon exposure to Mars surface conditions of atmospheric pressure and composition (CO_2-rich), there is very little change in their spectra, suggesting that they are stable under Mars surface conditions (Figs. 3 and 4) [3].

2. Heated halloysite/kaolinite. Heating of kaolinite and halloysite to ~400-700°C leads to dehydroxylation [4, 5]. At temperatures above ~900°C, formation of pseudo-mullite occurs, which can have two stoichiometric forms ($3Al_2O_3 2SiO_2$ or $2Al_2O_3 SiO_2$). We heated samples of kaolinite and halloysite to 700°C

in air for one hour to determine how their reflectance spectra may change upon dehydroxylation (Figs. 5, 6).

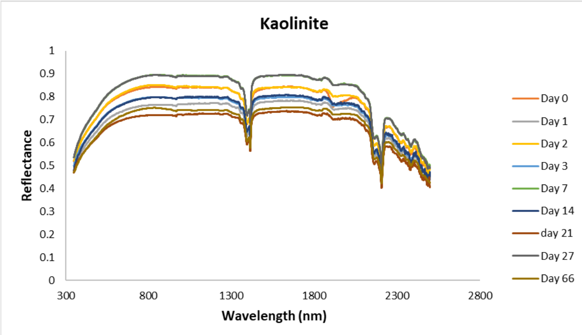


Figure 3. Reflectance spectra of kaolinite acquired during 66 days of exposure to 5 Torr CO2.

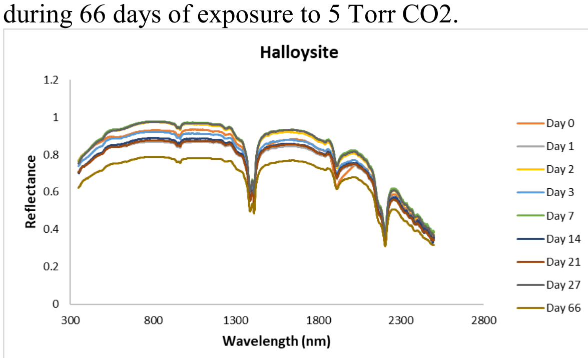
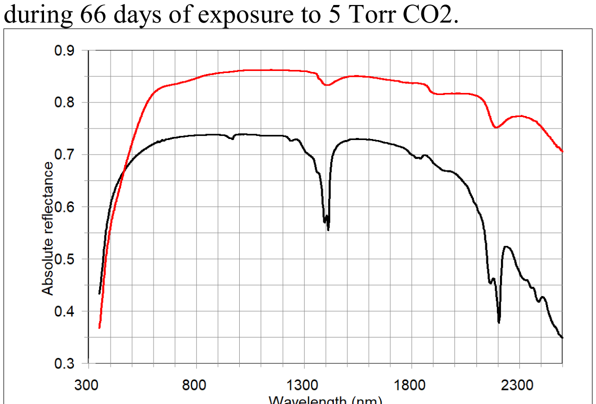


Figure 4. Reflectance spectra of halloysite acquired during 66 days of exposure to 5 Torr CO2.

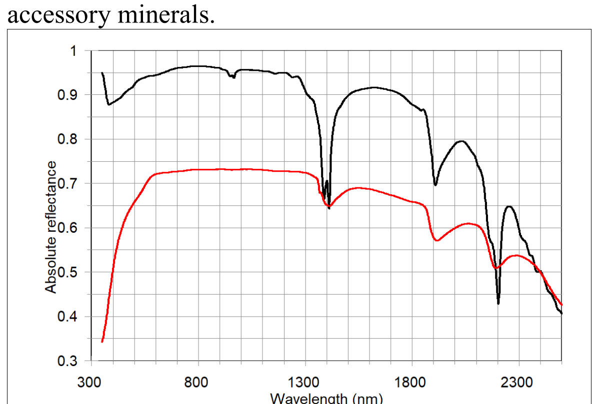


Kaolinite (KAO103): <45 µm. Black: unheated; red: 700°C in air.

Figure 5. Reflectance spectra of unheated kaolinite (black) and after heating to 700°C in air for 1 hour (red).

After heating, both spectra show subdued 1400 and 2200 nm absorption bands. Both become shallower and less distinct, appearing as a more-featureless absorption feature around 2200 nm, a local maximum near 2300 nm, and a steepening of spectral slope beyond ~2300 nm, similar to the Barrier Range spectra.

Discussion: dehydroxylated kaolinite and halloysite show some IR spectral features consistent with Barrier Range, specifically, a subdued and more featureless 1400 nm region absorption feature, generally declining reflectance beyond ~1300 nm, a broad/weak absorption feature near 2200 nm, and a local reflectance maximum at ~2300 nm. The samples are also compositionally consistent with the LIBS data: Si- and Al-rich. XRD analysis of the heated samples reveals that both are largely amorphous – heating temperatures were low enough to promote dehydroxylation but not recrystallization. This suggests that if these phyllosilicates are present, they were heated to a few hundred degrees C at some point in the past. We note that VIS spectra of the heated samples exhibit sharp fall-offs <600 nm that are not observed in the Barrier Range spectra. These types of spectral differences between lab minerals and Barrier Range may be due to the presence of accessory phases, which are suggested by the LIBS data. Bright minerals such as kaolinite and halloysite would be susceptible to changes in properties such as albedo and spectral slopes in the presence of darker accessory minerals.



Halloysite (HAL001): <45 µm. Black: unheated; red: 700°C in air.

Figure 6. Reflectance spectra of unheated halloysite (black) and after heating to 700°C in air for 1 hour (red).

Future work: we are exploring additional Al-Si-rich minerals, such as the metamorphic minerals andalusite, kyanite, sillimanite, staurolite, and spinels, as well as halloysite and kaolinite heated to higher temperatures and under Mars-like atmospheric conditions to better constrain candidate minerals for Barrier Range.

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References: [1] Farley K.A. et al. (2020) *Space Sci. Rev., 216,* 142. [2] Clarke R.N. et al. (1980) *JGR, 95,* 12653-12680. [3] Cloutis, E.A. et al. (2008) *Icarus, 195*, 14-168. [4] Johnson, S.L. et al. (1990) *Clays Clay Min., 38*, 477-484. [5] Yeskis, D. et al. (1985) *Amer. Mineral., 70*, 159-164.