INVESTIGATING THE ANTARCTIC METEORITE ANALOG OF CARBONATE FORMATION ON MARS.
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Introduction: Orbital spectroscopic data have confirmed the presence of carbonate minerals on the martian surface [1], and multiple formation mechanisms have been suggested [1–3]. The carbonate detections in Nili Fossae are observed in conjunction with a regional olivine-rich unit [4,5]. Most of the proposed formation mechanisms 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].

Over the past four decades, teams from the United States, Japan, and Europe have collected numerous meteorites from Antarctica, and white efflorescences were commonly reported on select samples. These white deposits were found to be carbonates and sulfates, and the carbonates were identified as having varying levels of hydration, with X-ray diffraction patterns matching nesquehonite, hydromagnesite, and barringtonite [6–8]. Isotopic analysis of LEW 85320 showed that the carbon was terrestrial in origin and the carbonate formed since 1950 despite the meteorite residing in Antarctica for ~32,500 years [8]. The carbonate ions are likely of terrestrial origin, and the Mg in the efflorescences likely originated from the weathering of the meteoritic olivine and not contamination by terrestrial salts [9]. Nesquehonite forms as a product of leaching at the borders of permeability of Mg-rich rocks [10], and the presence of this mineral in surface deposits and fractures [6] suggests its formation as a result of the interaction of the atmosphere, the local hydrosphere, and leached meteoritic cations. Most meteorites are ultramafic rocks with high abundances of pyroxene and olivine, therefore the terrestrial formation of carbonates on the surfaces of these rocks at cold and dry conditions remains an intriguing possible analog to the observation of olivine-carbonate-bearing outcrops on Mars. Our study of these carbonate minerals relevant to both Antarctic meteorites and Mars begins with nesquehonite.

Laboratory analyses: Nesquehonite ($Mg(OH)(HCO_3) \cdot 2H_2O$ [11] or $MgCO_3 \cdot 3H_2O$ [10,12]) was synthesized using the method of [13]. After the solution was left standing at ambient laboratory conditions for 5 days, the sample was filtered and allowed to dry in a furnace at 40 °C overnight prior to analysis to avoid
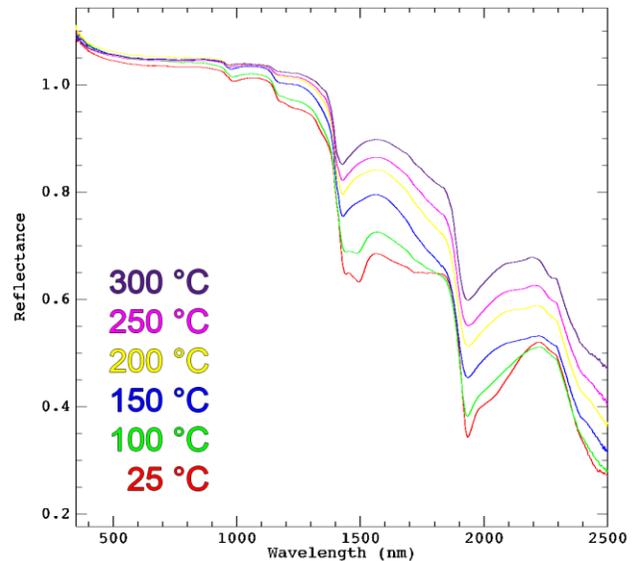

Figure 1: Laboratory VNIR spectra of nesquehonite dehydration.

thermal decomposition between 50–100 °C [12,14]. Mineral identification was confirmed using a Bruker D2 PHASER X-ray diffractometer. Nesquehonite was identified as the primary phase, but trace amounts of the reactants were observed in the diffraction pattern (K_2CO_3 and $MgCl_2 \cdot 6H_2O$).

Visible to near-infrared (VNIR) data were collected with an ASD Fieldspec spectrometer covering wavelengths 0.35–2.5 μm. The fiber optic measured reflectance at a vertical 0° (nadir) emission angle and an external light source illuminated the sample at an incidence angle of 30° from vertical. A pressed Halon tablet was used as a reference. Analysis began with data collection at ambient laboratory conditions and then under dry air. Using a controlled sample environment chamber and collecting spectra in tandem with a temperature ramp, we investigated the VNIR properties of nesquehonite as a function of increasing temperature. Data were collected at 15 minute intervals as the sample was heated in 25 °C increments from 25 to 300 °C with 1 hour temperature dwell times (Fig. 1). Over this temperature range, nesquehonite is expected to undergo dehydration as the structure decomposes at ~75–115 °C to transition to a crystalline phase and then an amorphous phase with a mass loss equivalent to ~2.5 H_2O [12,15,16].

Our analysis confirms the VNIR spectrum of nesquehonite presented by [17] at ambient laboratory conditions. At 100 °C, the spectrum starts to signifi-

cantly lose the 1.494 μm absorption and ~2 μm shoulder band, and these absorptions are gone by 125 °C (Figure 2). The concave spectral shape between ~1.6 and ~1.8 μm also disappears during this temperature range and at ~125 °C evolves to a H_2O dominated spectrum. As the temperature approaches 300 °C, an absorption at 2.277 μm becomes more distinct.

Discussion and Implications: Our analyses corroborate the literature with regards to the thermal decomposition of nesquehonite. Our most significant VNIR spectral change occurs at ~100 °C where two absorptions disappear (~1.5 and 2 μm). Over the remaining temperature range, no major alterations of the spectrum occur, but the absorptions continue to shallow and the long wavelength portion of the spectrum rises with heating and dehydration.

Once nesquehonite forms, the fundamental structural elements are preserved throughout the dehydration process as the system returns to nesquehonite following rehydration [12], which was also confirmed in our experiments. 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, CO_2 is not loss from the system until temperatures reach ~365 °C under flowing nitrogen [12]. The stability fields of phases in the MgO–CO_2–H_2O system at extreme conditions are poorly understood, and understanding stability 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. Perhaps the carbonates in Nili Fossae formed similarly to those observed *in situ* by the Phoenix Lander where thin films of water on the particle surfaces were inferred [18]. Future work aims to acquire meteorite samples bearing carbonate efflorescences from the NASA or Japanese National Institute of Polar Research Antarctic Meteorite Collections, and apply hyperspectral imaging and other geochemical analytical techniques to better understand the formation of carbonates on ultramafic surfaces in cold and dry environments.

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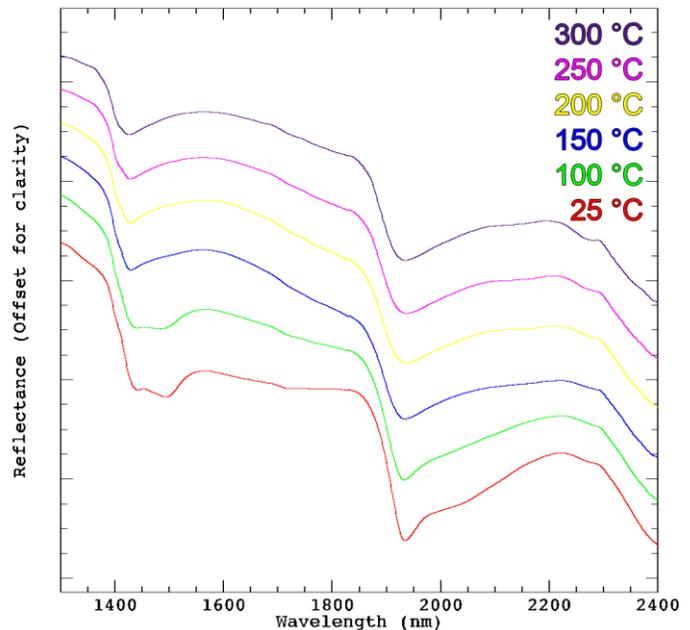
Figure 2: Focus view on changing bands from 1300 to 2400 nm of the nesquehonite dehydration from Figure 1.