MEASURING METHANE CLATHRATE DISSOCIATION AT LOW TEMPERATURE & PRESSURE WITH RAMAN SPECTROSCOPY. James. R. Johnson¹, C. M. Phillips-Lander¹, and M. E. Elwood Madden¹, ¹School of Geology and Geophysics, University of Oklahoma, 100 E. Boyd St., Rm. 710 Norman, OK 73019 james.r.johnson-1@ou.edu

Introduction: Gas clathrates are comprised of a framework of ice molecules, which form large and small cages around a guest molecule. These guest molecules are typically methane (CH₄) in terrestrial systems, but may also contain other molecules such as CO₂, H₂S, etc. Gas clathrates may have played a role as a reservoir volatile phases during the accretion of gas giants, their moons, and comets from the pre-solar nebula [1,2]. Clathrates may (have) also store(d) and dissociation rates at planetary -relevant conditions will help us build more accurate models of volatile fluxes, as well as long-term carbon reservoirs. This study is focused on determining the dissociation rates of methane clathrate at Mars-analog (-60°C) temperature conditions.

Methods:
Clathrate Preparation: Water ice pellets were prepared using an aluminum weigh boat filled with liquid nitrogen. We created pellets by dripping ultrapure water from a squirt bottle into the LN₂; this resulted in pellets with diameters of 1-2mm. We placed the ice pellets into a pre-cooled (-18°C) Parr high-pressure reactor and pressurized the reactor to 3.5 MPa using research grade methane within a standard chest freezer. Temperature and pressure were monitored using thermocouples and a pressure transducer connected through LabView.

Approximately every 24 hours, we removed the reactor from the freezer and allowed it to slowly warm at room temperature until the internal temperature of the reactor reached about -2°C. We then returned the reactor to the freezer and allowed it to cool back to -18°C. This process was repeated every day for a week to drive clathrate formation. After seven days of temperature cycling, we depressurized the reactor, disassembled it, and removed the clathrate pellets. We placed the pellets into a sealed plastic vial and stored the clathrate in a LN₂ dewar to preserve the clathrate pellets at room pressure during storage.

Analysis: We collected Raman spectra from the clathrate pellets using a Linkam cooling stage precooled to -100°C, well below the expected dissociation temperate at 1 atm (-83°C). We placed a clathrate pellet onto the silicon wafer stage and inserted the stage immediately into the Linkam, then cooled the stage back to -100°C to prevent clathrate dissociation.

We then analyzed the clathrate pellet using a Renishaw InVia Reflex Raman mapping microscope with a 50x long working distance objective lens. Spectral analyses were gathered using a 532 nm, 100mW diode laser in streamline mode. We used a 2400 line/cm grating, resulting in a spectral range of 2644 cm⁻¹ to 3226 cm⁻¹. We scanned the sample five times at 20-second increments (100 seconds total accumulation time) using 50% laser power to ensure an adequate signal-to-noise ratio. We employed the automatic depth analysis protocol provided with the WiRE 4.1 software package to obtain spectra at predetermined intervals below the surface. Each scan was conducted at 5um intervals, providing data at the sample surface, as well as depths 5um, 10um, 15um, and 20um below the surface.

We then warmed the Linkam stage to -60°C for a five-minute period to allow partial dissociation of the clathrate at 1 atm. After five minutes, we returned the stage to -100°C. We then repeated the identical depth analysis in the same location to compare depth profiles before and after clathrate dissociation.

Once all data were collected, we subtracted the baseline to eliminate background noise. We then normalized all the spectral curves and fitted them using the WiRE 4.1 software package. Once data was normalized, we determined the peak heights for both clathrate cage bands and the main water ice band. We then compared the data to determine trends in the Raman peaks with depth before and after dissociation.

Results: The Raman analysis of the clathrate pellets yielded significant peaks at 2902, 2914, and 3106 cm⁻¹ (Figure 1a). The peak at 2902 cm⁻¹ represents the large cage containing methane in the clathrate structure [6]. The 2914 cm⁻¹ peak is generated by the smaller cage of water molecules, which also contains methane [6]. The peak at 3106 cm⁻¹ is formed by water ice [7].

Prior to heating, the clathrate peaks are most intense at the surface and decrease with depth (Figure 1b,c), suggesting that the ice pellets have not been fully transformed to clathrate and the gas had insufficient time to fully diffuse into the sample over the week-long synthesis period.

Following 5 minutes of clathrate dissociation at -60°C, the relative intensity of both the 2902 (large cage) and 2914 (small cage) peaks decrease with
respect to the water ice peak, suggesting loss of methane from the sample during the warmer period (Figure 1b,c). However, the also 2902/2914 peak height ratio decreases significantly after heating (Figure 1d). In addition, the clathrate peak intensities no longer vary with depth.

**Discussion:** The decrease in intensity observed for both the 2902 and 2914 peaks indicates clathrate in the outer 20 μm largely dissociated within a fairly short time period. However, results also show more substantial methane loss from the large cavity (2902 cm\(^{-1}\)) within the clathrate compared to the small cavity (2914 cm\(^{-1}\)). This supports previous results suggesting small cavity clathrate is more stable at low T and P [8,9]. Therefore, if Raman analyses of permafrost on Mars contain primarily large cavity (2902 cm\(^{-1}\)) peaks, it is likely the sample experienced little to no dissociation in its history. However, if the spectra indicate primarily small cage (2914 cm\(^{-1}\)) peaks, then the clathrate has undergone at least some dissociation during its history. Indeed, ice formed from dissociation of clathrate at low temperatures may preserve small cage structures even after the clathrate has fully dissociated [10].

**Implications for Mars:** If methane clathrate is present on Mars, it may be detected using the Raman spectrometer on the ExoMars 2018 mission or SHERLOC installed on the Mars 2020 rover [11,12]. Based on these observations, Raman analyses of water ice, which formed via dissociation of methane clathrate, may also produce a residual Raman signature, indicating a past history of clathrate even following dissociation.

**Future Work:** Further experimentation will be conducted over a range of temperatures to determine if the same patterns of dissociation between large and small cavity clathrates continue with increased temperature. In addition, further analysis will be conducted using deeper depth profiles, which will provide further data for determining diffusion coefficients for methane through clathrate and ice.

**References:**