NITROGEN AND WATER ICE MIXTURES: SPECTRAL ANALYSIS OF HOMOGENEOUS AND HETEROGENEOUS CONDENSATION WITH POSSIBLE CLATHRATION. J. R. Sandtorf-McDonald[1] ,V. F. Chevrier1, C. J. Ahrens2 1 Arkansas Center for Space and Planetary Science, University of Arkansas, Fayetteville, AR, 72701, jrm071@uark.edu, 2 NASA GSFC, Greenbelt, MD 20771

Introduction: Clathrate hydrates are repeating crystal structures composed of water ice with trapped guest gas molecules, most commonly small molecules like methane, nitrogen, carbon dioxide, and carbon monoxide. [1] Clathrate materials have been observed on Earth under low temperature, high pressure conditions, but it is difficult to distinguish between water ice and clathrates using remote sensing methods.[1]. While clathrates appear similar to water ice, they do exhibit some differences in thermal and mechanical properties [2]. Clathrate hydrates are capable of obscuring large volumes of gas in a small amount of ice, up to 160 m^3 of guest gas per cubic meter. [3]

During Solar System formation, the timing and rate of clathrate synthesis would have determined how much guest gas was incorporated into various bodies. Examining clathrate formation processes allows for better remote detection and modeling throughout the Solar System. This work attempts to demonstrate that clathrate formation may be possible under lower pressure conditions than previously assumed.

Experimental Approach: The University of Arkansas W. M. Keck Laboratory houses the Outer Solar System Simulation Chamber (OSSC), capable of reaching low temperature and low pressure conditions (<120K and <25µbar) comparable to the conditions found in the presolar nebula.

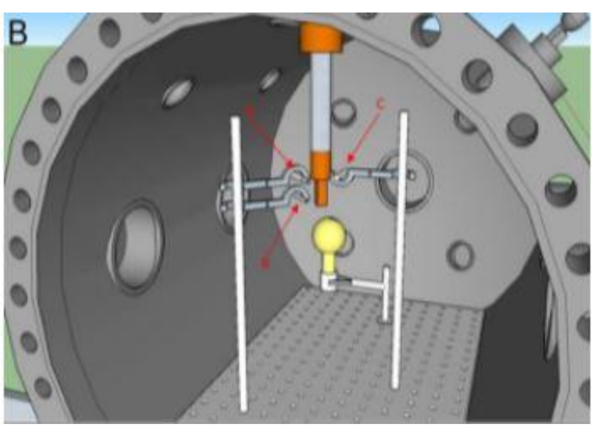

Figure 1: Outer Solar System Simulation Chamber (OSSC) schematic drawing. Cold finger at center. Image from McMahon et al (2016) [4]

The OSSC pressure vessel is made of stainless steel, with 22 ports for introducing instrumentation and sample materials into the chamber interior. Temperature control comes from a Janis Special CSS DE-204SL Cryogenic Cryocooler Closed Cycle Refrigeration System. An Acatel Pascal vacuum roughing pump evacuates the chamber to relevant pressure.

Inside the chamber, a target surface is attached thermally to the cold finger, which is cooled by the cryochilling system. A flexible stainless steel tube delivers the experimental gas mixture onto this surface. Pressure and temperature are monitored to maintain desired range as gas enters the chamber. A light bulb can briefly illuminate the chamber interior for imaging with a GoPro optical USB camera.

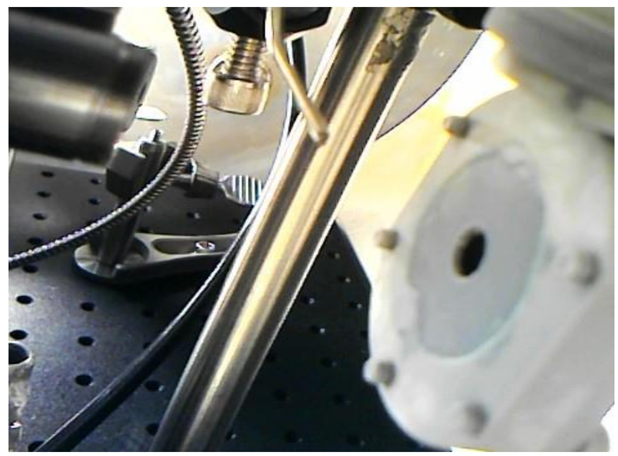

Figure 2: Condensation target surface and cold finger at right, gas inlet tube center, FTIR probe at left. This ice was produced using the direct condensation method (DCM).

Experimental ice mixtures are characterized spectroscopically using a Thermo Nicolet 6700 Spectrometer with liquid nitrogen-cooled InSb detector. This device is capable of 4 cm-1 resolution. The chamber is connected to the spectrometer via a ZrF4-doped fiber optic probe. Each spectrum results from averaging 450 individual measurements

Experimental Protocol: For each data collection, atmospheric gas was evacuated from the chamber interior by the roughing pump. The cooling system was then engaged to bring the cold finger and the thermally-attached target surface to the desired temperature Each experimental run began at the lowest temperature and progressed to higher temperatures.

This work explores the spectral differences produced by two condensation pathways, a one-step method and a two-step method. In the one-step direct condensation method (DCM), water vapor and nitrogen are mixed together using the mixing apparatus in Figure 3. This mixture is directed onto the surface of the cold finger by the gas inlet tube. The vapor mixture condensed and froze onto the target surface and was analyzed spectroscopically. This process was performed at 20 K and 50 K.

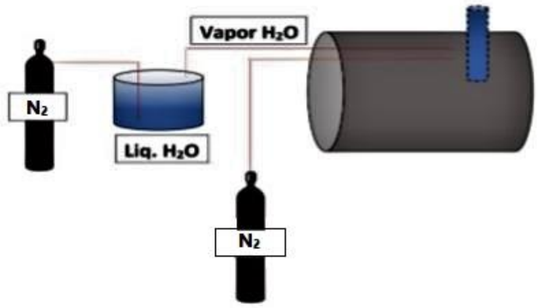

Figure 3: Gas mixing apparatus for introducing water vapor and/or nitrogen gas into the OSSC.

In the two-step heterogeneous condensation method (HCM), water vapor is first introduced onto the target surface, then nitrogen gas is flowed over the water ice. Then the resulting ice is analyzed spectrally. This process was performed at 25 K and 50 K.

Results: There are noticeable differences between the DCM and HCM protocols. In Figure 4 we see the results from the DCM. There are distinct bands visible at 1.39 µm, 1.88 µm, and 2.21 µm in the 20 K spectrum, but none of these bands are apparent in the 50 K spectrum. There may be some increased reflectance at the 1.38 µm area in the 50 K spectrum, instead of the drop shown at 20 K.

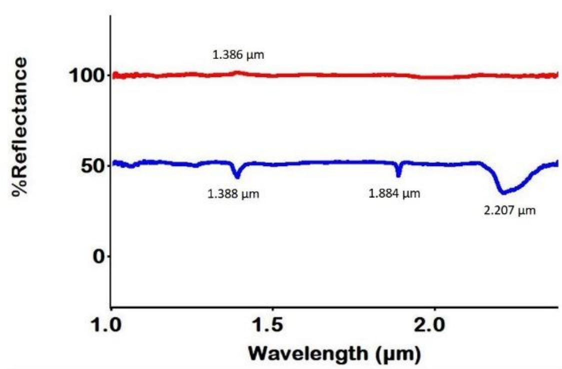

Figure 4: Direct Condensation Method (DCM) 20 K (Blue) and 50 K (Red)

The HCM protocol spectra are much more consistent with each other. The bands are in the same locations at 1.39 µm, 1.88 µm, and 2.21 µm, but the band at 1.89 µm has much less strength at 50 K than at 20 K.

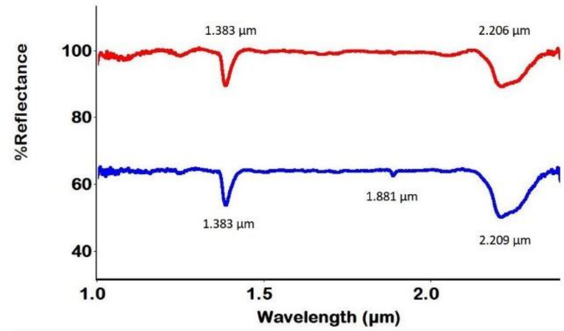

Figure 5: Heterogenous Condensation Method (HCM) 25 K (Blue) and 50 K (Red)

The two experimental pathways exhibit some marked differences from each other spectrally. The HCM produces much deeper and more noticeable bands for both temperatures studied. The 50 K spectrum shows spectral bands at 1.39 µm and 2.21 µm.

Both the DCM and the HCM show the disappearance or flattening of the spectral feature at 1.88 µm between the 20 K/25 K and the 50 K observation. This may be due to nitrogen's shift in crystal structure at 35.6 K. [5]

Conclusions: The Outer Solar System Simulation Chamber allows us to explore conditions like those during the formation of the Solar System. I have used the OSSC to study two different methods of condensing ice from water and nitrogen gas. There are intriguing differences in the spectra produced by the two condensation protocols, warranting further attention.

Nitrogen clathrates have been spectrally characterized in other wavelengths, but there are no studies of nitrogen clathrates in the near-infrared range. Therefore, it is difficult to determine the degree of clathrate synthesis achieved here. With the purchase of a Raman spectrometer, the author will have more conclusive information in future.

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References:

[1] Hester, K. C., & Brewer, K. G., *Annual Review of Marine Science*. 303-327. [2] Gabitto, J. F., & Tsouris, C. (2010). *Journal of Thermodynamics, 2010*, 1–12. [3] Kvenvolden, K. A. (1993). *U S Geological Survey*, (93), 173–187. [4] McMahon, Z. et al. (2016) LPSC XLVII, Abstract 1728. [5] Dartois, E., Bouzit, M., Duret, P., & Schmitt, B. (2014). *BIO Web of Conferences*, *2*, 03005.