Phase Behaviors of Pluto's Volatiles. S. M. Raposa[*,1,2], W. M. Grundy[1,2], S. P. Tan[3], G. E. Lindberg[1], J. Hanley[1,2], J. K. Steckloff[3,4], S. C. Tegler[1], A. E. Engle[1,2], and C. L. Thieberger[1,2], *Correspondence: smr676@nau.edu, [1]Northern Arizona University, [2]Lowell Observatory, [3]Planetary Science Institute, [4]University of Texas at Austin

Introduction: Nitrogen (N_2), methane (CH_4), and carbon monoxide (CO) are the most abundant highly volatile substances on Pluto. Sputnik Planitia, for example, is a giant glacial reservoir of N_2, CH_4, and CO. These materials shape Pluto's geology over time, carving out the landscape and creating surface features such as glaciers, valleys, and more. Since these materials play such a pivotal role in surface evolution, it is important to understand how these species interact with each other under various surface conditions.

One way we can better understand how composition affects these surface processes on Pluto is through phase diagrams, which indicate where phase changes happen, and what phases will be most stable under a given set of temperature, pressure, and composition conditions. However, there are gaps in planetary materials and ice databases for mixtures of N_2, CH_4, and CO at the cryogenic temperatures relevant to Pluto. As a result, models of Pluto's glaciers and icy terrains often assume pure N_2, pure CH_4 or rely on the dated N_2+CH_4 binary phase diagram [1]. In the case of Sputnik Planitia (which is often assumed to be pure N_2-ice), there are also small amounts of CH_4 and CO, which affect what phases are present at different surface conditions, as well as the general behaviors and physical properties of ice and liquid mixtures at and beneath the glacial surface.

This project aims to fill these gaps by first mapping the three binary phase diagrams within the ternary system (N_2+CH_4, CO+CH_4, and N_2+CO). Two experimental methods are used for phase diagram mapping and are discussed later. The three binary phase diagrams will be applicable to studies of Pluto and other places in the outer solar system where this ternary system is present, such as Triton, Eris and Makemake. The end goal for this project will be to combine the laboratory data and thermodynamic model to create an equation of state (EOS) that describes the interactions of the ternary system, which will be useful for Pluto glacier and geophysical models.

Methodology: The laboratory experiments conducted in this work take place in the Astrophysical Materials Laboratory at Northern Arizona University. Figure 1 shows an example of the sample cell (with CO+CH_4 inside), which is where materials condense and can be viewed during an experiment.

Experimental Method 1 (Solid-Liquid-Vapor Curve Mapping): The first laboratory method is the mapping of the three-phase solid-liquid-vapor (SLV) curve.

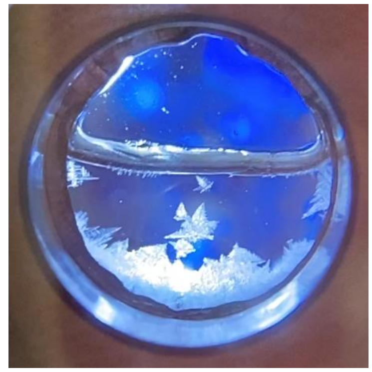

Figure 1: *Image of the sample cell where material goes and can be observed during an experiment.*

Using the N_2+CH_4 binary system as an example (see Figure 2), the first step is to start with a mixture in vapor-liquid equilibrium near the warmer triple point of pure CH_4. Next, we make injections of N_2 to change the composition (right arrows). After each injection, we cool the new mixture to find the freezing point (down arrows). At each freezing point, we note the temperature and pressure, and behavior of ice (e.g., sinks/floats in its liquid) and plot them on the diagram as a three-phase solid-liquid-vapor point (red X). Finally, we continue the injection and cooling steps until the mixture approaches the triple point of pure N_2.

Experimental Method 2 (Closed-System Cooling): The second method involves cooling a single mixture, slowly stepping down in temperature, and searching for where phase transitions occur using Raman spectroscopy. We can learn about the sample on a molecular level through the resulting Raman spectrum, which displays shifts in energy state. This resulting spectrum contains peaks for each species present in the mixture, where these Raman shifts (cm^{-1}) are outputted as x-values, and intensity as y-values. This spectrum provides information about what a sample is compositionally and if/how it has changed, making it useful to study phase transitions. We can track where these phase transitions occur by plotting the centroid of the Raman peaks for each species at each temperature step. When a phase boundary is crossed, this will be displayed through a change in the locations of the centroids. The determined phase boundary locations for each composition can later be added to a phase diagram of temperature vs. mole fraction.

Thermodynamic Model (CRYOCHEM): The laboratory methods are being compared and their results are modeled using a thermodynamic EOS,

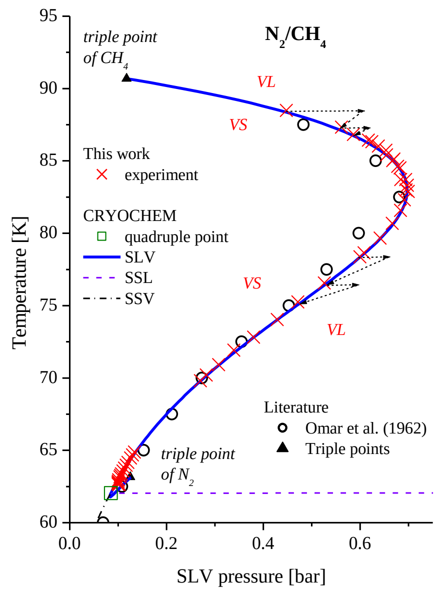

Figure 2: *Binary N_2+CH_4 SLV P-T phase diagram, compared to the literature [5]. Curves are calculated using CRYOCHEM 2.0. Figure from Raposa et al. 2022.*

CRYOCHEM, which is based on the Thermodynamic Perturbation Theory (TPT) by coupling the Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) for the fluid part with the Lennard-Jones Weeks-Chandler-Andersen approach for the solid part. The measured three-phase data were used for deriving the solid-phase binary parameter of a thermodynamic model, CRYOCHEM 2.0, which has been applied for phase equilibria on Pluto [3] [4]. All solid curves on the phase diagrams in this work were calculated using CRYOCHEM 2.0. With the solid-phase binary-interaction parameter derived from the experimental data, CRYOCHEM can be used for constructing the liquidus/solidus diagrams. Additionally, CRYOCHEM can calculate the densities of the equilibrium phases, so that it can also confirm density inversion if it occurs during the injection-cooling steps in the SLV experiments.

Results:

SLV Results: The first method has been completed for all three binary systems, and results are published [2]. For the N_2+CH_4 binary system, we found the results to be consistent with the literature [5], as displayed in Figure 2. Two density inversion points (ice transitioned from sinking to floating, then back to sinking in its liquid) were observed. The lower density inversion point is not at the minimum temperature of the liquidus curve, suggesting this is not a eutectic system (as previously thought), since a eutectic binary system has a single temperature where two solids are formed from a vanishing liquid phase upon cooling. Likely, this system has an azeotrope, or a peritectic point followed by an azeotrope. An azeotropic system contains a single composition that does not change through freezing or melting, and a peritectic binary system has a single temperature where a liquid phase and a solid phase form a new solid phase upon cooling. Thus, this has implications for the shapes/locations of the phase boundary lines of this binary system. Additional experimental studies are needed to determine whether there are one or two types of solid present at this point to make this distinction. The results for the CO+CH_4 binary system were very similar to the N_2+CH_4 system. Two density inversion points occurred, and this system likely also has an azeotrope with/without a peritectic. The N_2+CO system has no density inversion points, as the ice always sinks in its liquid.

Future Work: The next step of this project is the completion of method 2 for the three binary systems. Experiments are nearly complete for the N_2+CO binary system. This phase diagram will be published next year (2023). Then, the N_2+CH_4 and CO+CH_4 phase diagrams will be mapped. After completion of the binary phase diagrams, we will create the ternary N_2:CH_4:CO EOS, by applying CRYOCHEM with the solid-phase binary parameters derived or fine-tuned by the experimental data from both methods above. Finally, the EOS will be used in a current Pluto glacier model to see how it affects processes at places like Sputnik Planitia.

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