

Simulation of Phase Behavior on Titan Using Synthetic Fluid Inclusions Combined with Raman Spectroscopy. H. R. Edwards¹ (ehunter5@vt.edu), M. Sublett¹, and R. J. Bodnar¹. ¹ Department of Geosciences, Virginia Tech, 926 W. Campus Drive, Blacksburg, VA, 24061.

Introduction: The icy moons of Jupiter (Io, Europa, Ganymede, and Callisto) and Saturn (Mimas, Enceladus, Tethys, Dione, Rhea, Hyperion, Iapetus, Phoebe, and Titan) contain abundant H₂O, CO₂, H₂S, CH₄, and NH₃, and have a range of near-surface temperatures between 70K and 223K [1]. In this study, we simulate phase behavior on Titan based on Raman spectroscopic analyses of synthetic fluid inclusions (SFI). Future studies will investigate phase equilibria relevant to the other icy moons of Jupiter and Saturn.

Titan's surface is primarily composed of H₂O, CO, CO₂, and CH₄, with surface temperatures of 70K to 200K [1]. Although we know the general conditions and compositions of the icy moons, experimental studies of the phase behavior of volatiles on these icy moons are lacking. Lunine and Stevenson reported the thermodynamic stability of CH₄, N₂, and CH₄-N₂ clathrates in the presence of ammonia (NH₃) [2], but little information is available to constrain the phase behavior and conditions of the icy moons.

The volatile components can exist in many forms, including vapor and liquid as well as various solid phases that include several different clathrate compounds if H₂O is present. Clathrates (also known as hydrates, clathrate hydrates, gas hydrates, or clathrate-gas hydrates) have been extensively studied because of their importance to the oil and gas industry [3, 4]. Clathrates are also found in terrestrial permafrost, polar ice caps, and seafloor sediments [5], and are also predicted on Mars [6], Titan [7, 8] and Enceladus [8]. Additionally, clathrates may be present on the other icy moons of Jupiter and Saturn [9].

Clathrates form cage-like structures that fit into one of three main groups (I, II, and H) [10], and are composed of gas(es) and H₂O [11]. Volatiles such as CH₄, CO₂, NH₃, etc. have different sizes and occupy different sites [10]. Larger molecules commonly occupy structure I sites, whereas smaller molecules occupy structure II sites [10]. The H structure requires both small and large molecules to occupy its cages [10], unlike structures I and II.

This study investigates the phase behavior of volatiles in SFI, with phases identified by Raman spectroscopy. We focus here on phase behavior in the CH₄-CO₂-H₂O system, and include a discussion of future studies of more complex systems.

Methods and Materials: SFI with compositions similar to those reported for Titan were created using the technique described by Sterner and Bodnar [12]. A

Raman spectrometer was used to identify phases. A TMS 92 Linkam stage was used to control the temperature and identify the phases present. The Linkam stage is capable of reaching the lower limit of temperatures measured on the surface of Titan (70K to 200K) to observe possible phase changes throughout most of Titan's surface temperature range.

A SFI in the system CH₄-CO₂-H₂O was analyzed at room temperature (24°C or 297K), 0°C (273K), and -50°C (223K). Raman spectra were collected, and relative abundances of volatiles in each phase were calculated.

Results and Discussion: The phases present in the system CH₄-CO₂-H₂O at room temperature (24°C or 297K) are a H₂O-rich liquid phase and a CH₄-CO₂ liquid phase (Figure 1). At 0°C (273K), a CH₄-CO₂ vapor phase is present in addition to the two other phases that are present in the inclusion at room temperature. The new vapor phase contains a higher molar fraction of CH₄ than the CH₄-CO₂ liquid phase because CO₂ is more soluble than CH₄ in the liquid phase at this temperature [13]. This behavior continues with cooling to -50°C (223K), and the vapor phase increases in size (Figure 1).

The Raman spectra of the inclusions at 0°C and -50°C are shown in Figure 2. CH₄ has a peak located at 2917 cm⁻¹, and CO₂ has peaks at 1285 cm⁻¹ and 1388 cm⁻¹ [14]. Although H₂O is not shown in Figure 2, it should be noted that H₂O has a broad peak between 2,800 cm⁻¹ and 3,800 cm⁻¹ [14, 15]. Figure 2 shows a decrease in the intensity of CH₄ in the liquid phase at -50°C compared to the 0°C spectrum. This indicates that CH₄ is less soluble in this phase at lower temperatures. Additionally, the CO₂ peaks show lower intensity in the vapor phase at -50°C which agrees with it being more soluble in the liquid phase.

Clathrates are present at -50°C, although a clathrate phase is not easily recognizable, the inclusion shown in Figure 1. There were no clathrates observed at 0°C, although clathrates are stable at this temperature. There are stoichiometric restrictions for the formation of clathrates under ideal conditions. CH₄-clathrate is more stable at higher temperatures than CO₂-clathrate [16], which means under equilibrium conditions where only one component (in this case, CH₄ or CO₂) is being consumed at a time in the formation of clathrate, CH₄ will be consumed first. The molar CH₄:H₂O ratio for CH₄-clathrate is 4:23. If the bulk fluid CH₄:H₂O molar ratio is greater than 4:23 (i.e., an excess of CH₄), then

CH_4 will remain after all of the H_2O has been consumed, inhibiting the future production of CO_2 -clathrate. However, if the $\text{CH}_4:\text{H}_2\text{O}$ ratio is lower, then there will be an excess of H_2O . The $\text{CO}_2:\text{H}_2\text{O}$ molar ratio of CO_2 -clathrate is 1:8, but if all of the H_2O is consumed during CH_4 -clathrate production, then CO_2 -clathrate cannot form. The $\text{CH}_4:\text{CO}_2:\text{H}_2\text{O}$ molar ratio in ternary clathrates is 4:2:39. If any one of the three components (CH_4 , CO_2 , or H_2O) remains after clathrate formation is complete, that component would be present as a fluid or solid phase, depending on the pressure and temperature conditions.

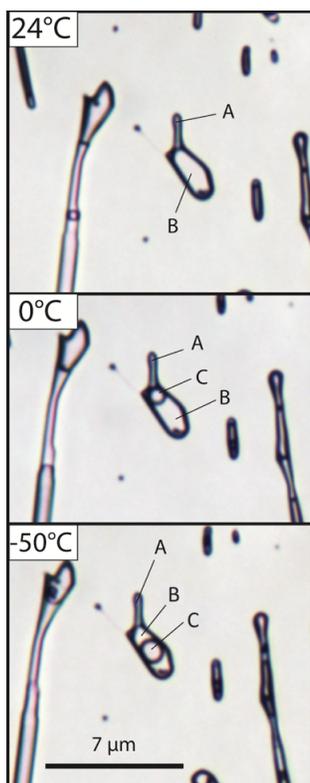


Figure 1. Images of fluid inclusions at 24°C (297K), 0°C (273K), and -50°C (223K). A is the H_2O -rich liquid phase, B the $\text{CH}_4\text{-CO}_2$ -rich liquid phase, and C is the $\text{CH}_4\text{-CO}_2$ -rich vapor phase. C has a higher molar fraction of CH_4 than B.

The investigation of phase relations contributes to our understanding of the phases that might be present on the surface of Titan. If the $\text{CH}_4:\text{CO}_2:\text{H}_2\text{O}$ molar ratio of the bulk Titan crust is equal to 4:2:39, only clathrates would be present. For molar ratios that differ from this value, other phases, including pure H_2O ice may exist on the surface of Titan. CH_4 , CO_2 , and H_2O are critical for the sustenance of life on Earth, and possibly on Titan or the other icy moons.

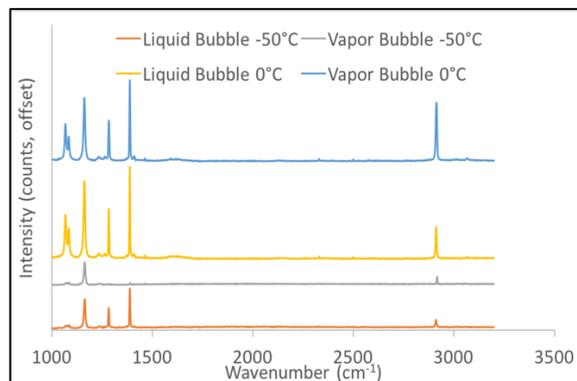


Figure 2. Raman spectra of liquid and vapor phases in the system $\text{CH}_4\text{-CO}_2\text{-H}_2\text{O}$ at 0°C (273K) and -50°C (223K).

Future Work: Additional components, such as N_2 , will be added to this system to create a more realistic analog to the surface composition of Titan. The phase behaviors of near-surface volatiles for other icy moons of Jupiter and Saturn will be investigated, including Enceladus. Enceladus has surface temperatures that range between 33K-223K and has a surface composition similar to that of Titan [1]. Salt hydrates have also been predicted to occur on the surface [1], which is an additional component that can be added to SFI to constrain the phase behaviors for this moon.

Acknowledgements: The authors thank Charles Farley for his assistance with the Raman spectrometer.

References: [1] Dalton, J. B. (2010) *Space Sci. Rev.*, 153, 219-247. [2] Lunine, J. I. and D. J. Stevenson (1985) *Astrophys. J. Supplement Series*, 58, 493-531. [3] Davis, J. A. et al. (1962) *AIChE Journal*, 8, 537-539. [4] Donnelly, H. G. and Katz, D. L. (1954) *Ind. Eng. Chem. Res.*, 46, 511-517. [5] Solar System Ices (1995) *Astrophysics and Space Science Library*: Kluwer Academic Publishers, 227. [6] Miller, S. L. and Smythe W. D. (1970) *Science*, 170, 531-533. [7] Osegovic, J. P. and Max, M. D. (2005) *JGR: planets*, 110, E08004. [8] Shin, K., et al. (2012) *PNAS*, 109, 14785-14790. [9] Grasset, O., et al. (2017) *Space Sci. Rev.*, 212, 835-875. [10] Sloan, E. D. and Koh, C. (2008) *CRC Press*, 721. [11] Waals, J.H.v.d.P., Platteeuw, J. C. (1958) *Adv. Chem. Phys.*, 2, 1-57. [12] Sterner, S. M. and Bodnar, R. J. (1984) *Geochim. Cosmochim. Acta*, 48, 2659-2668. [13] van den Kerkhof, A. M. (1988) Ph.D. Thesis. [14] Shimanouchi, T. (1972) *Tables of Molecular Vibrational Frequencies Consolidated*. U.S. Government. [15] Baumgartner, M. and Bakker, R. J. (2009) *Mineralogy and Petrology*. 95, 1-15. [16] Sun, R. and Duan, Z. (2005) *Elsevier*, 69, 4411-4424.