MOLECULAR MINERALS ON TITAN: THE ACETYLENE SERIES. Morgan L. Cable[1] , Tuan H. Vu[1], Helen E. Maynard-Casely[2], Mathieu Choukroun[1] and Robert Hodyss[1], [1]NASA Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA (Morgan.L.Cable@jpl.nasa.gov), [2]Australian Nuclear Science and Technology Organisation, NSW, Australia (helen.maynard-casely@ansto.gov.au).

Introduction: Titan, the largest moon of Saturn, contains a plethora of organic molecules and is considered a prebiotic chemical laboratory on a planetary scale. Photochemistry in the atmosphere induced by solar radiation and energy from Saturn's magnetosphere causes a chemical cascade, as N_2 and CH_4 dissociate and generate organic molecules ranging from simple (ethane, acetylene, HCN) to complex (>10,000 Da). These molecules continue to react as they move through Titan's atmosphere, forming aerosol haze layers and eventually depositing on the surface [1].

Some of these molecules will be transported via fluvial (rivers, streams) or pluvial (rain) processes into the hydrocarbon lakes of Titan. Those with relatively high solubilities might precipitate via evaporation or other mechanisms, forming evaporite layers akin to those observed by the Cassini Visual and Infrared Mapping Spectrometer (VIMS) and Synthetic Aperture Radar (SAR) around some of the lakes in the north polar region of Titan [2].

We have demonstrated in previous work [3-5] that two common organic molecules on Titan, ethane and benzene, form a unique and stable co-crystalline structure at Titan surface temperatures. This molecular mineral represents an exciting new class of compounds for Titan's surface [6], and implies that lake edges and evaporite basins could serve as hydrocarbon reservoirs.

This finding has motivated our search for other co-crystals that may form under Titan surface conditions. We have shifted our focus to acetylene, as this molecule is the primary solid photochemical product generated in Titan's atmosphere [7] and should be abundant on the surface of this moon.

We have previously reported the formation of a co-crystal between acetylene and ammonia at Titan surface temperatures [8]. Here we expand on the analysis of this Titan mineral, and describe a detailed thermal stability study and the resilience of this co-crystal when exposed to fluvial and pluvial events [9]. We also describe preliminary evidence for two more co-crystals where acetylene is one of the constituents.

Experimental: *Acetylene-ammonia co-crystal.* Anhydrous ammonia and acetylene (purified to remove acetone stabilizer) were condensed sequentially or co-deposited from the gas phase into a liquid nitrogen-cooled cryostage (Linkam Scientific Instruments Ltd.) at 90 K. Raman spectra within the cryostage were obtained using a high-resolution confocal dispersive micro-Raman spectrometer (Horiba Jobin Yvon LabRam HR) equipped with a 50 mW Nd:YAG laser (frequency-doubled 532 nm) as the excitation source. Thermal stability studies were performed by warming in 5 K increments and obtaining Raman spectra following a 5-minute equilibration time. Pluvial events were simulated by condensing liquid methane, ethane or propane onto the acetylene/ammonia condensate at 90 K.

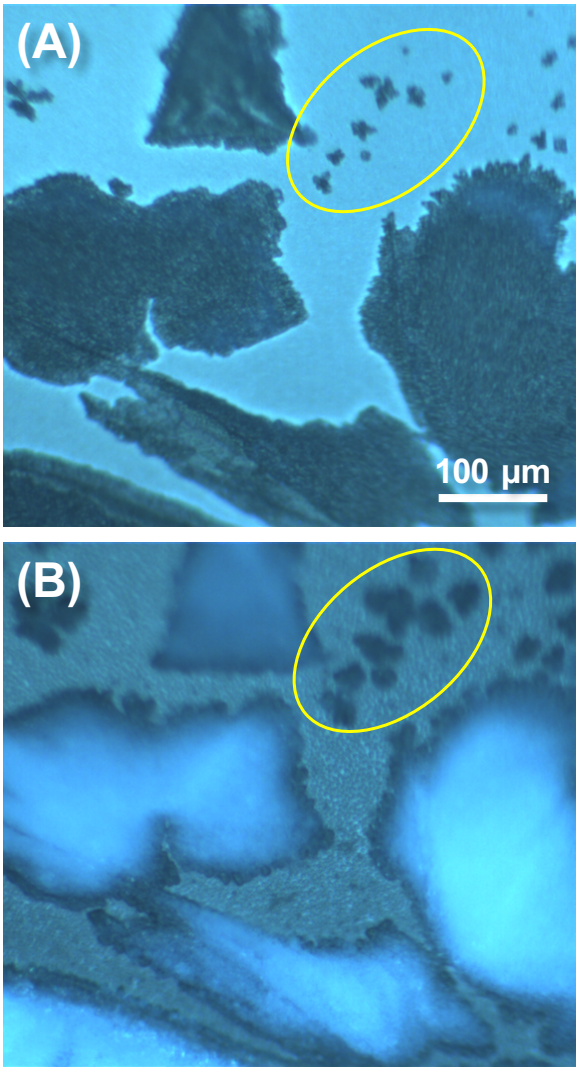

Figure 1. (A) The acetylene-ammonia co-crystals appear phase-dark at 90 K. (B) Upon heating to 110 K, the acetylene begins to equilibrate with the vapor phase and sublime, leaving the ammonia behind as smaller, phase-bright crystals. Note that some of the remaining acetylene-ammonia co-crystals have expanded in size (yellow circles).

Acetylene-benzene co-crystal. Approximately 1 cubic centimeter of solid acetylene was condensed at 94 K in a custom-built cryostat under N_2 atmosphere at 1 bar. About 5 mL of liquid ethane was condensed and mixed with the acetylene, forming an opaque suspension. A 200 µL aliquot of benzene was frozen on a glass substrate in the liquid nitrogen-cooled cryostage maintained at 90 K. A ~2 mL aliquot of the acetylene-ethane mixture was deposted on top of the solid benzene. The ethane was evaporated by heating to 110 K and purging with N_2.

Acetylene-HCN co-crystal. Hydrogen cyanide was generated by reacting 230 mg KCN with ~400 µL H_2SO_4 and purging the headspace into a gas sampling bag (0.7 L 2 mil Tedlar film, SKC, Inc.) with N_2. Acetylene was added in approximately 50/50 v/v to the gas bag; this mixture was condensed onto the liquid nitrogen-cooled cryostage maintained at 90 K.

Results: *Acetylene-ammonia co-crystal.* Red shifts (7.3–15.5 cm^{-1}) of the C≡C and C-H stretching modes, as well as large blue shifts (42–66 cm^{-1}) in the low frequency regions of lattice vibrations and C-H bending modes, both suggest the formation of a co-crystal [9]. This structure forms within minutes, and appears to be stabilized by a network of C-H···N interactions. A detailed thermal stability study indicates that this co-crystal remains intact up to 115 K, though longer equilibration times of thinner layers at 110 K leads to loss of most of the co-crystal (Fig. 1). Exposure to methane, ethane or propane at 90 K does not appear to significantly affect co-crystal stability [9].

Acetylene-benzene co-crystal. A preliminary experiment where acetylene was dissolved in liquid ethane at 94 K and mixed with solid benzene generated interesting features once the ethane evaporated [8]. These new features are stable up to 143 K, are not consistent with benzene, acetylene or ethane alone, and are distinct to the signature from the known acetylene-benzene co-crystals [10]. Further work is needed to determine if this is indeed a co-crystal, and if so, whether ethane is required for it to form.

Acetylene-HCN co-crystal. Red and blue shifts are observed on the order of 1–4 cm^{-1} for various features throughout the Raman spectrum (subset shown in Fig. 2). These are not as large as the shifts observed for other co-crystals (typically 2–16 cm^{-1} [3,9]), which may be due to weaker associations between the species. Subsequent experiments are underway to better characterize this possible co-crystal.

Conclusions: The acetylene-ammonia co-crystal has been confirmed to form at Titan surface temperatures and remain stable after exposure to hydrocarbon pluvial events. Preliminary evidence for two other acetylene co-crystals, one with benzene and another with HCN, suggest that a series of acetylene-based molecular minerals may exist on Titan. These structures may influence surface material characteristics such as particle size, dissolution rate, structural hardness, and resistance to erosion. Differences in physical or mechanical properties may also lead to chemical gradients on Titan, which life could potentially exploit [6]. The catalytic hydrogenation of acetylene has been proposed as a possible energy-yielding reaction for metabolism [11-13]. It is possible that acetylene-based co-crystals might be a mechanism for storing acetylene, in a manner similar to how carbon dioxide is stored in carbonate deposits on Earth, where it might be more readily accessible to a putative microbial community.

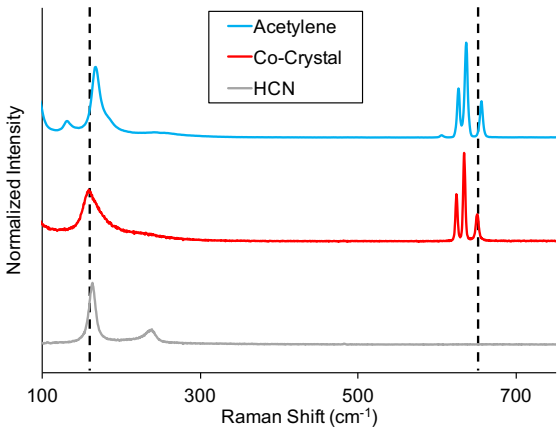

Figure 2. The acetylene-HCN co-crystal has unique features, including red shifts in the low frequency regions of lattice vibrations and C-H bending modes (dashed lines).

Acknowledgements: The authors gratefully acknowledge funding from the Solar System Workings Program. This work was conducted at the Jet Propulsion Laboratory, California Institute of Technology, under contract with NASA.

References: [1] Cable, M.L. et al. (2012) *Chem. Rev., 112,* 1882-1909. [2] Barnes, J.W. et al. (2009) *Icarus, 201,* 217-225. [3] Vu, T.H. et al. (2014) *J. Phys. Chem., 118,* 4087-4094. [4] Cable, M.L. et al. (2014) *GRL, 41,* 5396-5401. [5] Maynard-Casely, H.E. et al. (2016) *IUCrJ, 3,* 192-199. [6] Maynard-Casely, H.E. et al. (2018) *Am. Mineral.*, in press. [7] Lara, L.M. et al. (1996) *JGR*, 101 (E10), 23261-23283. [8] Cable, M.L. et al. (2017) 48th *LPSC*, abstract no. 1964. [9] Cable, M.L. et al. (2018) *Earth Space Chem.*, in review. [10] Boese R. et al. (2003) *Helv. Chim. Acta*, 86, 1085-1100. [11] Schulze-Makuch, D. et al. (2005) *Astrobiology*, 5(4), 560-567. [12] McKay, C.P. et al. (2005) *Icarus*, 178(1), 274-276. [13] Tokano, T. (2009) *Astrobiology*, 9(2), 147-164.