National Aeronautics and Space Administration

Using isotope mass spectrometry to study Titan's hydrocarbon cycle

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Program: FY21 R&TD Topics   Strategic Focus Area: Planetary Atmospheres and Geology

Goal & Objectives

The overarching goal of the proposed work was to better understand the processes governing Titan's hydrocarbon cycle at the interface between the surface and the near-surface atmosphere, particularly as they apply to regions near and over Titan's lakes and seas.

Our primary objective was to constrain the expected variability in the carbon and hydrogen isotopic compositions of acetylene (C_2H_2) and ethane (C_2H_6) vapor and condensates during processes of sublimation/deposition (C_2H_2) or evaporation/condensation (C_2H_6) at Titan-relevant temperatures.

Our secondary objective was to demonstrate the ability of an in-development-for-flight instrument, JPL's QIT-MS, to accurately resolve compound-specific carbon and hydrogen isotopic signatures in our high-purity starting materials.

Background

In-situ isotopic measurements of Titan's organics can reveal much about the geologic, chemical, and potentially astrobiological processes that occur on Titan; however, the isotopic fractionations that occur under Titan's cryogenic conditions are unknown. ***Titan's hydrocarbon cycle is poorly understood; in-situ isotopic measurements of the major species could reveal how the atmosphere and surface interact—a major step forward in Titan science***. Our work is a unique approach to devising a metric by which equilibrium thermodynamic processes can be disentangled from both kinetic processes and photochemistry via in situ measurements made of the surface and near-surface atmosphere some day on Titan.

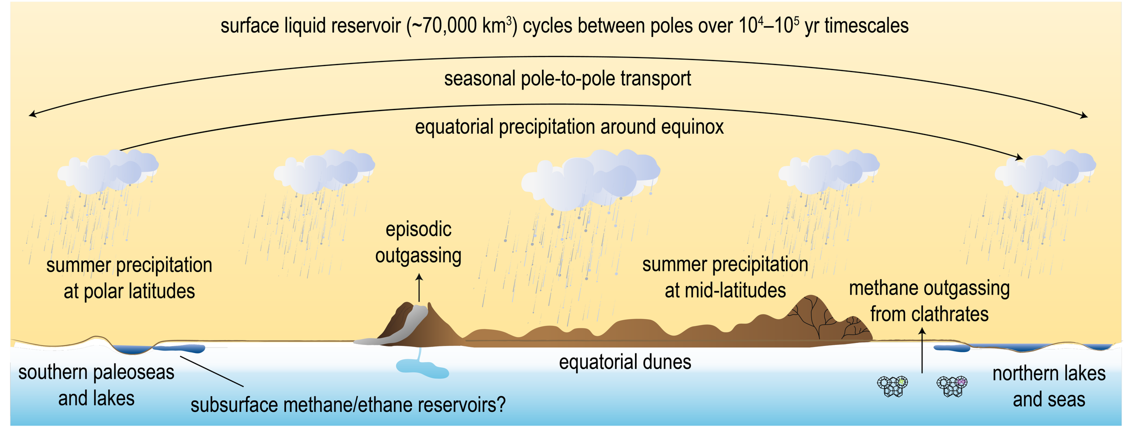

Figure 1. Titan's hydrocarbon cycle operates on multiple timescales and lengths scales, transporting CH_4 (and other minor hydrocarbons like C_2H_6 and C_2H_2) to and from various sources and sinks, some of which are shown here. Sublimation / deposition and evaporation / condensation cycles will modify the hydrocarbons' isotopic compositions in quantifiable ways, thereby offering a means by which the transport and storage of these species can be traced over time and space. *Figure adapted from Hayes et al. (2018) Nature Geoscience 11: 306–313.*

Significance / Benefits to JPL and NASA

The results of this study establish the first quantifiable, temperature-dependent relationships between the D/H ratios of coexisting, equilibrated condensed- and vapor-phase hydrocarbons in single-component systems of C_2H_2—the most abundant solid on the surface of Titan. The difference between the isotopic composition of the vapor-phase species and the condensed-phase species plotted against the corresponding temperature defines the vapor pressure isotope effect (VPIE) for a given phase transition (e.g., sublimation-deposition) and thus constitutes the isotopic "fingerprint" of that process under Titan-like conditions. These experiments constrain isotopic variations generated at and near the Titan surface by the current sublimation/deposition cycle of C_2H_2, thereby providing an equilibrium fractionation signature that can be evaluated against in situ measurements of C_2H_2 isotopologues by a future mission to Titan (e.g., Dragonfly). Preliminary work on ethane (C_2H_6) indicates the need for methodology modifications, which will be undertaken as part of the newly funded Solar System Workings proposal to PI Hofmann.

The fractionation factors calculated from these results can also be fed into future Titan global climate models (GCMs) in order to trace the isotopic composition of major hydrocarbons as a function of both equilibrium (this study and new SSW) and non-equilibrium (e.g., diffusion, gravitational escape) processes in addition to photochemically-driven fractionation, thereby providing a more comprehensive picture of the sources, sinks, and transport of these species across, onto, and perhaps into Titan.

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Publications

Amy E Hofmann, John M Eiler, "Hydrogen isotope fractionation in acetylene ice/vapor systems under Titan-like conditions", *In preparation for submission to Geochimica et Cosmochimica Acta.*

Approach & Results

Our technical approach combined experimental and analytical work, all of which was performed at the Laboratories for Stable Isotope Geochemistry in the Geological & Planetary Sciences Division at Caltech.

METHODOLOGY

The experimental methodology can be simplified as shown in the flow chart below.

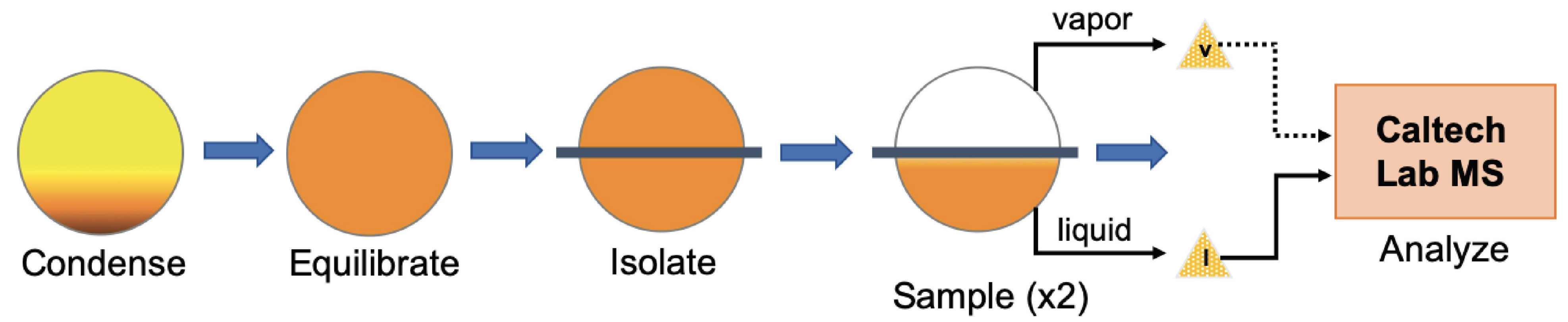

Figure 2. Schematic of a vapor pressure isotope effect (VPIE) experiment: vapor is condensed at cryogenic temperatures and the remaining overlying vapor (at its saturated vapor pressure) is allowed to isotopically equilibrate with the condensate. The two phases are isolated, sampled, and their isotopic compositions measured via mass spectrometry.

MILESTONES

1. Complete the remaining necessary acetylene and ethane VPIE equilibration experiments (roll-over from FY20) over temperature ranges relevant to Titan and experimentally accessible based on the vapor pressures of each species.

2. Quantify the compound-specific carbon and hydrogen isotopic compositions of our experimental products using the Thermo Finnegan Delta+XP isotope ratio mass spectrometer.

3. Quantify the compound-specific isotopic signatures of our starting material and some experimental products using the QIT-MS at JPL.

RESULTS

Progress against specific milestones is as follows:

Milestone 1: Acetylene VPIE experiments were completed. Ethane VPIE experiments gave anomalous isotopic results (i.e., no consistent trend was observed with respect to any of the variables). Discussion of these results with Co-I Eiler led to a possible methodological solution, which unfortunately could not be implemented because the JPL portion of the funding for this project was exhausted at that point.

Milestone 2: The acetylene experiments were never planned for carbon isotope measurements; all hydrogen isotope measurements were completed. Hydrogen isotope measurements of the ethane reactants and products indicated something anomalous occurring during the experiments themselves (see above).

Milestone 3: High-purity methane and ethane of known isotopic composition (i.e., the internal standard gases used by Co-I Eiler's research group) were delivered to the Mass Spectrometry Group at JPL. Due to other obligations (e.g., DALI instrument development), the group has not yet analyzed the hydrocarbon samples provided.

PI Hofmann has completed a draft (updated to include the final acetylene experimental results) manuscript and is currently iterating with Co-I Eiler on the text prior to submission. The manuscript will be further revised prior to submission early in FY22.

NOTE: PI Hofmann was awarded a Solar System Workings (SSW) grant to continue the work begun as part of this Topical R&TD. The scope of the funded SSW proposal continues the single-component ethane experiments begun during the Topical and extends the investigation to include comparable experiments in methane-ethane systems and then methane-ethane-nitrogen system designed to simulate the compositions of actual Titan lakes.

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Clearance Number:
RPC/JPL Task Number: R19104