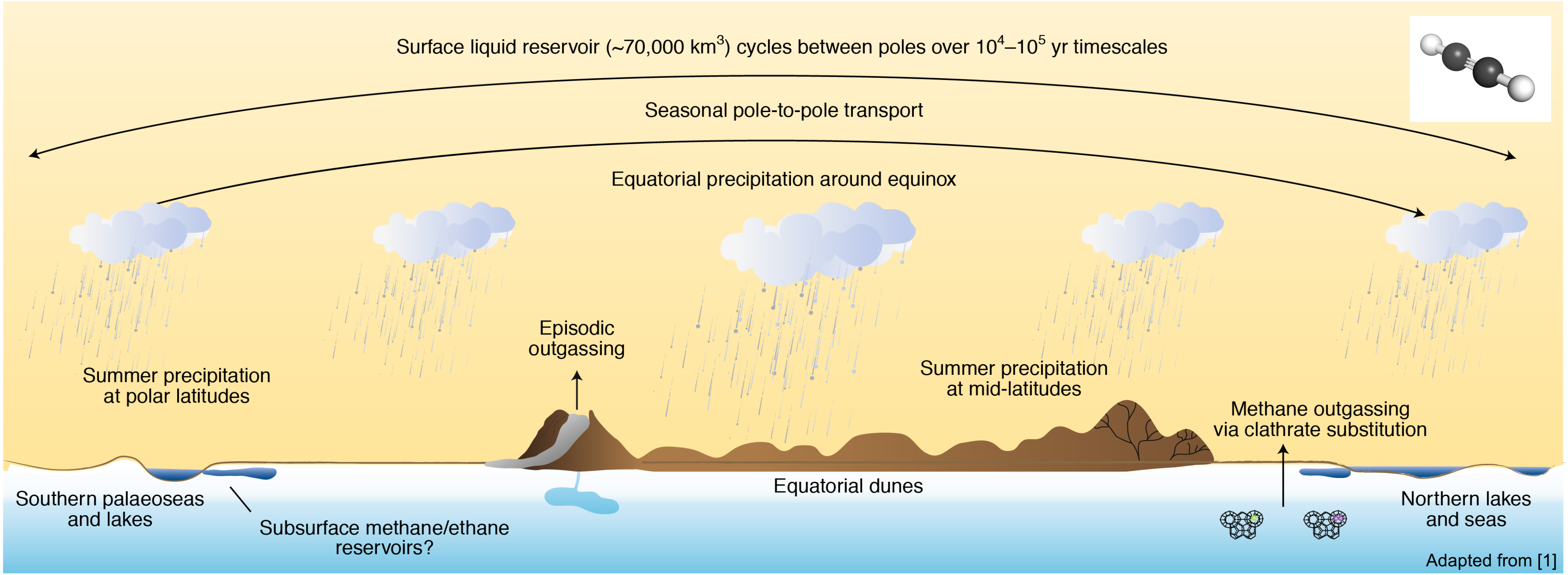

Virtual Research Presentation Conference

Using isotope mass spectrometry to study Titan's hydrocarbon cycle

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Program: Topic

Assigned Presentation # RPC-085

Jet Propulsion Laboratory
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Tutorial Introduction

Abstract

Titan's hydrocarbon cycle is, in many ways, similar to the terrestrial hydrologic cycle, albeit it is primarily methane (CH_4)—not water—that condenses out of a nitrogen-based atmosphere and flows across Titan's surface (**cover slide image**).

On Earth, the separation of isotopologues (molecules that differ only in their isotopic compositions, e.g., H_2O versus HDO) via processes like evaporation and condensation influence the range in hydrogen and oxygen isotopic compositions imparted to water vapor, liquid water, and ice & snow (**Figure 1, bottom**). On Titan, those same physical processes will affect the carbon and hydrogen isotopic compositions of CH_4 vapors and condensates (and, due to their relative abundances as primary photochemical products, likely ethane [C_2H_6] and acetylene [C_2H_2] as well).

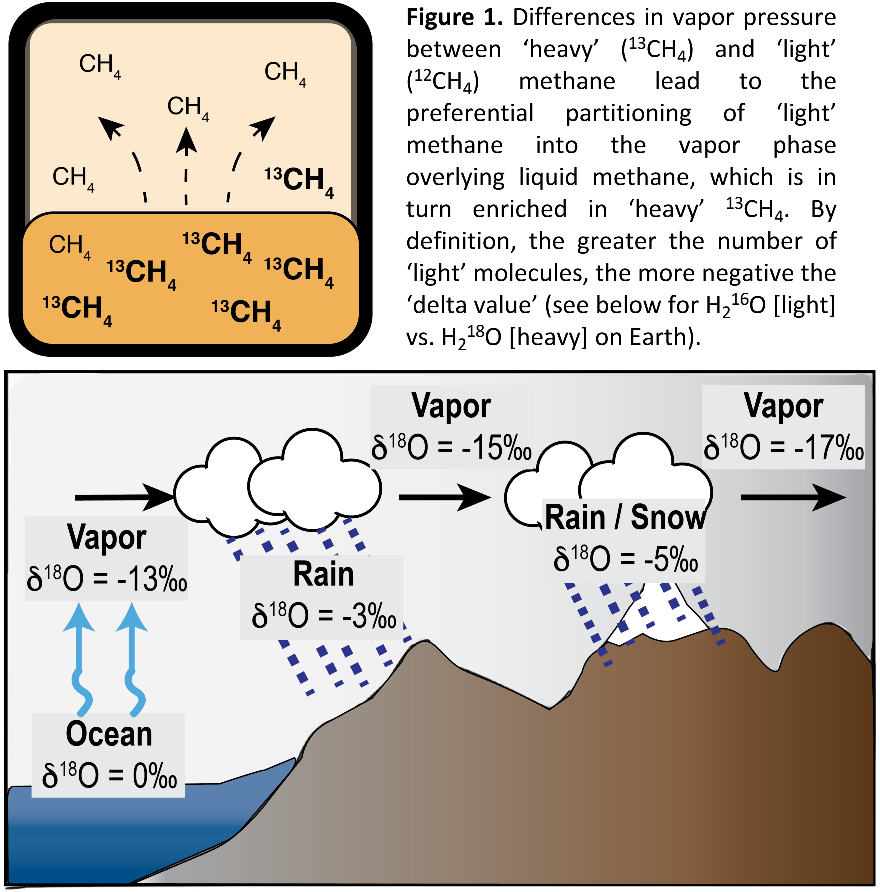


Figure 1. Differences in vapor pressure between 'heavy' ($^{13}CH_4$) and 'light' ($^{12}CH_4$) methane lead to the preferential partitioning of 'light' methane into the vapor phase overlying liquid methane, which is in turn enriched in 'heavy' $^{13}CH_4$. By definition, the greater the number of 'light' molecules, the more negative the 'delta value' (see below for $H_2{}^{16}O$ [light] vs. $H_2{}^{18}O$ [heavy] on Earth).

Problem Description

DRAGONFLY

Why this problem? Why now?

By establishing the isotopic 'fingerprint' of evaporation and condensation (or sublimation and deposition, as in the case of C_2H_2) for CH_4 and C_2H_6, we will enable future mission investigators to distinguish the isotopic signatures of surface volatile cycling and sequestration from those of photochemical and diffusive effects, thereby facilitating a more complete understanding of the processes, sources, and sinks at play in Titan's hydrocarbon cycle.

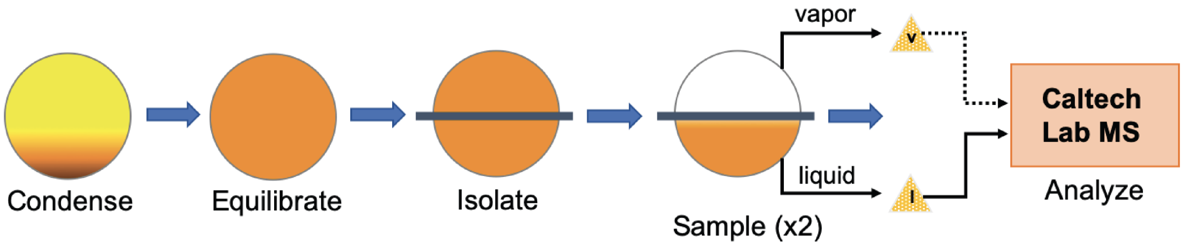
Comparison to State-of-the-Art: The isotopic data we are collecting in this study do not currently exist for Titan-relevant molecules at the appropriate temperatures. Furthermore, we are using mass spectrometers and associated laboratory instrumentation that are state-of-the-art.

Relevance to NASA and JPL: The key innovation of this work is in enabling new in situ science, namely analyses made by a mass spectrometer as part of an instrument suite sent to Titan's surface.

This project began prior to the *Dragonfly* selection and thus was positioned to evaluate the ability of JPL's QIT-MS to accurately and precisely resolve the major CH_4 isotopologues ($^{12}CH_4$, $^{13}CH_4$, $^{12}CH_3D$) from one another.

The data produced by this study will present hypotheses—some of which will be testable by *Dragonfly* in the equatorial dunes—and predictions to be assessed by future missions to Titan's northern lake district.

Methodology: Experimental



The experimental protocol used in these experiments is based on a methodology developed by Co-I Eiler for comparable, Mars-relevant CO_2 experiments, modified further by PI Hofmann and Co-I Eiler for later molecular systems, including those studied here.

A cartoon schematic laying out the progression of a vapor-pressure isotope effect (VPIE) equilibration experiment is presented above and explained in further detail in the audio-over. Briefly, gases are condensed onto a cryohead and allowed to equilibrate with overlying vapor. Following equilibration, the vapor and condensed phases are isolated, sampled separately, and prepared for analysis (see next slide).

Experiments are performed in a custom-designed glass vacuum line (**Figure 2**) using commercially available, high-purity gases.

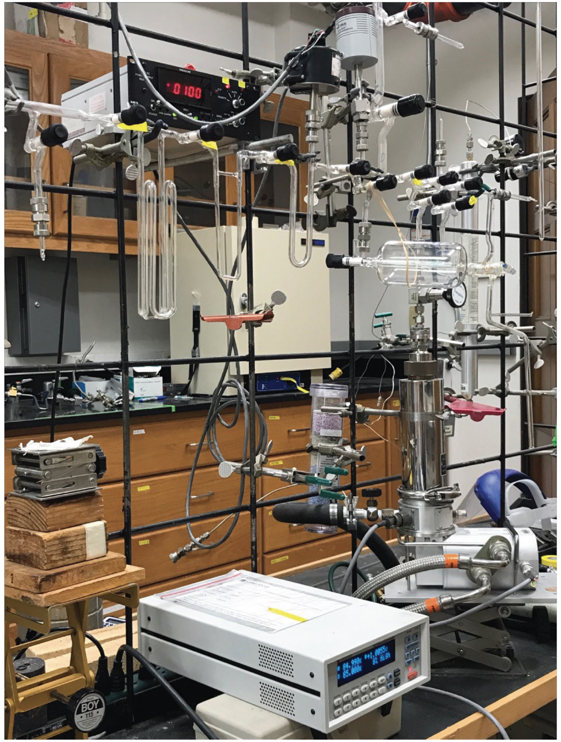


Figure 2. Portion of the vacuum line at Caltech used for performing the VPIE equilibration experiments described here.

Methodology: Analytical

Using an external liquid nitrogen bath, samples are frozen down into custom-prepared 'break-seals' (**Figure 3**), which are then welded shut to preserve the sample for analysis later.

The hydrogen isotopic composition of our starting materials and experimental products was determined using gas-chromatography isotope-ratio mass spectrometry (GC-IRMS). We used the ThermoFinnegan Delta+XP with a dedicated Trace GC system housed in the Laboratories for Stable Isotope Geochemistry at Caltech (**Figure 4**).

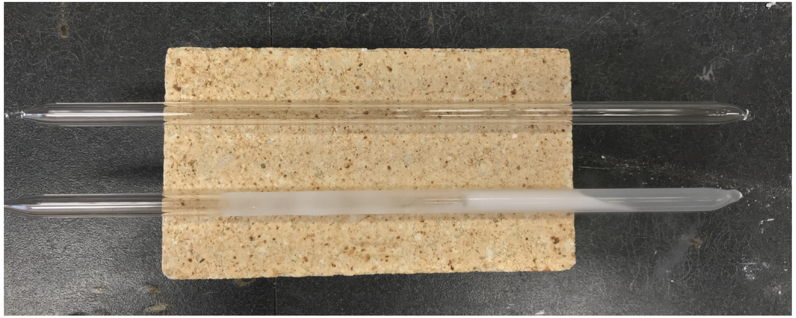


Figure 3. Two glass "break-seals" used for trapping experimental products (and starting materials) until they can be analyzed. Both break-seals contain C_2H_2. The top one is at room temperature; the bottom one was just removed from liquid nitrogen and the C_2H_2 ice (white solid) is still visible.

Figure 4. The mass spectrometer with dedicated gas chromatograph at Caltech used to analyze experimental products and starting materials in this study .

Results: Overview

Accomplishments:

- **Milestone 1**: Vapor-pressure isotope effect (VPIE) experiments on ethane (C_2H_6) were initiated during Q1 and Q2 of FY20. These experiments were to be completed by the end of Q3; however, upon the closure of Caltech laboratories due to COVID-19, this task was not completed. The remaining VPIE experiments on C_2H_2 were completed prior to laboratory closures.
- **Milestone 2**: Although the majority of the C_2H_2 experiments were analyzed, some C_2H_2 and the C_2H_6 experimental products remain in the queue for isotopic analysis next fiscal year.
- Preliminary drafts of two manuscripts (one for C_2H_2 and one for C_2H_6) were written; however, these manuscripts cannot be completed until all of the remaining experiments are analyzed.

Significance:

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 (and eventually in C_2H_6) and the $^{13}C/^{12}C$ ratios of the same (C_2H_6 only).

Ultimately, the results of experiments will constrain isotopic variations generated at and near the Titan surface by the current condensation/evaporation cycle of C_2H_6, thereby provide an equilibrium fractionation signature that can be evaluated against in situ measurements of C_2H_6 isotopologues by a future mission to Titan (e.g., *Dragonfly*).

Results

As previously noted, the products (and starting materials) from several C_2H_2 experiments remain to be analyzed; however, there is no expectation that the results will change the trend observed in the dataset presented in **Figure 5**.

Next Steps:

Due to laboratory shutdowns in response to the pandemic, the remaining 25% of R&TD funds were withheld, to be released in FY21. At that time, the final C_2H_2 experiments will be analyzed, as will the existing suite of C_2H_6 experimental products. The final array of C_2H_6 VPIE experiments will also be performed and the products analyzed.

The results of this work will be submitted in two manuscripts for peer-review and used in support of an SSW proposal resubmission.

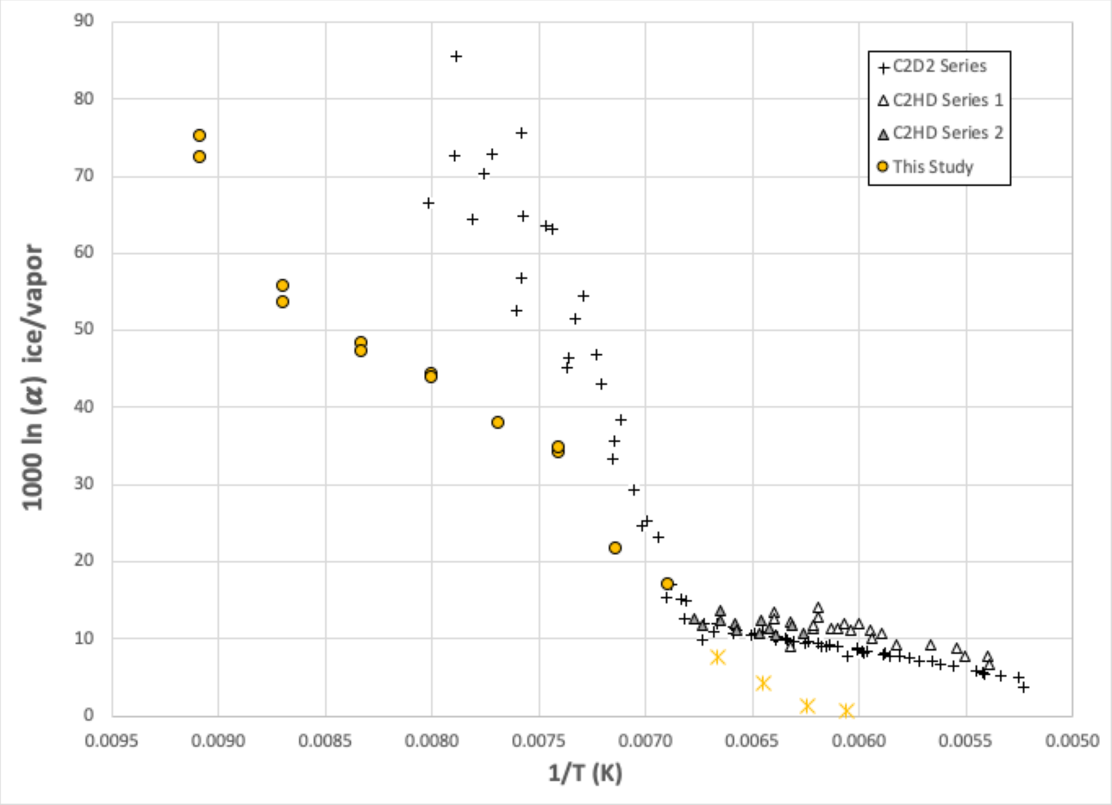


Figure 5. A comparison between the acetylene VPIE data collected in this study (yellow) and existing data from the literature (triangles and crosses from [2]). Audio-over provides full explanation.

Publications and References

Publications

[A] 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*.

References

[1] A.G. Hayes, R.D. Lorenz, J.I. Lunine, "A post-Cassini view of Titan's methane-based hydrologic cycle," *Nature Geoscience*, 11, 306–313 (2018).

[2] J.T. Phillips, W.A. Van Hook, "Vapor pressure isotope effects of the deuterated acetylenes", *Journal of Chemical Physics*, 52, 495–502 (1970).