Titan aerosol analogs from aromatic precursors: Comparisons to Cassini CIRS observations in the thermal infrared

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Background

Since Cassini's arrival at Titan, ppm levels of benzene (C_6H_6) and possibly polycyclic aromatic hydrocarbons (PAHs) have been detected in the atmosphere.[1] Aromatic molecules, photolytically active in the ultraviolet, may be important in the formation of the organic aerosol comprising the Titan haze layer even when present at low mixing ratios. Yet there have not been laboratory simulations exploring the impact of these molecules as precursors to Titan's organic aerosol.

Observations of Titan by the Cassini Composite Infrared Spectrometer (CIRS) in the far-infrared (far-IR) between 560 and 20 cm^{-1} (~18 to 500 μm) have been used to infer the vertical variations of Titan's aerosol from the surface to an altitude of 300 km.[2] Titan's aerosol has several observed emission features which cannot be reproduced using currently available optical constants from laboratory-generated Titan aerosol analogs [2,3,4], in particular a broad far-IR feature centered approximately at 140 cm^{-1} (71 μm).

Analog Studies

There is a need to revisit the infrared spectrum of laboratory-produced aerosol, particularly in the far-IR. We speculate these features may be a blended composite of low-energy vibrations of two-dimensional lattice structures of large molecules, such as PAHs or nitrogenated aromatics. Such structures do not necessarily dominate the composition of analog materials generated from CH_4 and N_2 irradiation.

We are performing studies forming aerosol analogs via UV irradiation of several aromatic precursors – with and without nitrogen heteroatoms – to understand how the unique chemical architecture of the products influence observable aerosol characteristics. The optical and chemical properties of the aromatic analog will be compared to those formed from CH_4/N_2 mixtures [5,6], with a focus on the as-yet unidentified far- and mid-IR absorbance features. These studies show that the aerosol formed from aromatic precursors have distinct chemical composition as compared to previously studied analogs, which has implications for the optical properties of Titan's aerosol.

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[3] Khare, B.N., et al. (1984) *Icarus* **60** 127 – 137.
[4] Imanaka, H., et al. (2012) *Icarus* **218** 247 - 261.
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Calcite farming in Florida caves: Calibrating modern calcite δ^{18}O and δ^{13}C to ventilation and *in situ* air temperature

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Stable isotope records (δ^{18}O and δ^{13}C) in cave speleothems are typically interpreted as climate changes in rainfall amount and source, cave air temperature, atmospheric CO_2, and overlying vegetation. But these records are difficult to interpret without *in situ* calibrations between cave microclimate (e.g., ventilation) and contemporaneous calcite isotopic composition. In this study at Hollow Ridge Cave (HRC) in Marianna, Florida (USA), cave dripwater and modern calcite (farmed *in situ*) were collected in conjunction with continuous cave air pCO_2, temperature, barometric pressure, relative humidity, radon-222 activity, airflow velocity and direction, rainfall amount, and drip rate data [1, 2]. We analyzed rain and dripwater isotopes, dripwater [Ca^{2+}], pH, δ^{13}C and TCO_2, cave air pCO_2 and δ^{13}C, and farmed calcite δ^{18}O and δ^{13}C to examine the relationships among rainwater isotopic composition, cave air ventilation, cave air temperature, seasonal calcite growth rate and timing, and calcite isotopic composition. Farmed calcite δ^{13}C decreases linearly with distance from the front entrance to the interior of the cave during all seasons, with a maximum ventilation-induced entrance-to-interior gradient of Δδ^{13}C = -7‰. Farmed calcite δ^{18}O exhibits a +0.82 ± 0.24‰ offset from values predicted by both theoretical calcite-water calculations and by laboratory-grown calcite (Figure). Unlike calcite δ^{13}C, oxygen isotopes show no ventilation or evaporation effects and are a function only of temperature. Combining our data with other speleothem studies, we find a new empirical relationship for cave-specific water–calcite oxygen isotope fractionation across a range of temperatures and cave environments: **1000 ln α = 16.1(10^3 T^{-1}) - 24.6** (light blue dashed line in the Figure).

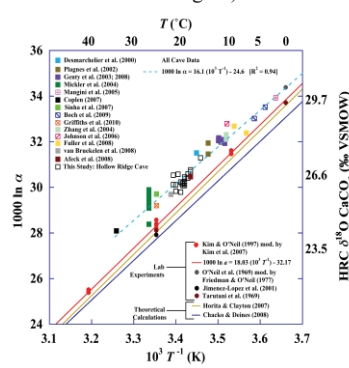**Figure:** 1000 ln α vs. 10^3 T^{-1} for HRC calcite (black open squares) plotted with other modern cave studies (solid & crossed squares), laboratory inorganic precipitation values (circles), and theoretical calc-ulations (solid lines). The red line is the best-fit line from [3] as modified by [4]: 1000 ln α = 18.03 (10^3 T^{-1}) - 32.17.

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