Carbonaceous Chondrite Outgassing Experiments: Implications for Methane Replenishment on Titan.

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Introduction: Titan is the only known moon in the solar system with a substantial atmosphere of N_2 (95-98%) and CH_4 (2-5%). However, the current methane abundance in Titan's atmosphere is still a mystery even after the Cassini-Huygens mission [1]. Titan's present amount of atmospheric CH_4 was predicted to be destroyed photochemically on very short timescales (~10-100 Myrs) compared to the age of the solar system [2]. Given the short lifetime of methane, a replenishment mechanism must exist to explain the current abundance of methane on Titan. The isotope measurements of the Huygens Gas Chromatograph Mass Spectrometer (GCMS) suggested that Titan's current atmosphere is likely not primordial and is originated from the interior of Titan [3][4]. Recent theoretical modeling of Titan's atmosphere and interior [5][6] also suggests that Titan's atmosphere could have originated at least in part by outgassing of primordial organics in its interior. If this theory holds, volatiles like methane could be outgassing from Titan's interior to replenish its atmosphere.

Insoluble organic matter (IOM) found in carbonaceous chondrites may serve as an analog for the organic material in Titan's interior [6, 7]. By heating primitive meteorite samples and measuring the abundances of their released volatiles, specifically methane, we may be able to connect what we see in the lab to species in Titan's atmosphere today.

Meteorite Sample: In this study, we use three CM carbonaceous chondrites for our measurements: Murchison, Aguas Zarcas, and Jbilet Winselwan. CM chondrites are considered one of the most pristine meteorite samples available, which means they are similar in composition to the solar photosphere and therefore representative of the building blocks of the interior of planetary bodies in the solar system. Murchison and Aguas Zarcas are "fall" meteorites, and Jbilet Winselwan is a desert "find" meteorite. The fall meteorites are usually more pristine as they endured less terrestrial weathering on the surface.

Methods: We prepared two different sample sizes for all three of our meteorites, one being our small grain sample, < 20 µm, and the other being our normal grain sample, 20-106 µm. We measured ~3 mg of powdered meteorite samples for each heating experiment. Our heating set-up consists of a furnace connected to a residual gas analyzer (RGA) and a turbomolecular pump (base pressure of 10^{-5} torr at room temperature). The samples were heated from room temperature to 1200° C in a "step-heating" scheme (see Figure 1). The samples were first baked out at around 200°C for 8-10 hr for adsorbed water removal. Then we employ a fast heat (12-min) and steady hold (1-hr) for each 100°C step so that we can investigate volatile outgassing at each temperature step.

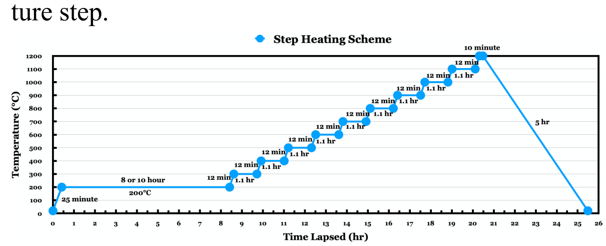

Figure 1: Adopted heating scheme (time vs. temperature).

Although we conduct each heating experiment under a vacuum, slight contamination may still be possible. Therefore, before we heat each meteorite sample, we would first perform a background measurement with no sample to properly calibrate the background signal. During both the background and the continuous (with-sample) experiment, we continuously monitored the partial pressures of ten outgassed volatile species using the RGA. We choose the following ten mass peaks to capture the major outgassed species and methane: 2 amu, 14 amu, 15 amu, 16 amu, 17 amu, 18 amu, 28 amu, 34 amu, 40 amu, and 44 amu. In Table 1, we listed all the species and the ion fragmentation patterns we used to retrieve the partial pressures of the species.

Table 1: Ion fragmentation pattern to retrieve the partial pressure of each species.

Species Name	Partial Pressure	Ion Fragmentation Pattern
Hydrogen (H_2)	P_{H_2}	$P_{2amu} - 0.02 \times P_{18amu}$
methane (CH_4)	P_{CH_4}	$P_{15amu}/0.8879$ (method 1) $P_{16amu} - 0.009 \times P_{18amu} - 0.0961 \times P_{44amu}$ (method 2)
Water (H_2O)	P_{H_2O}	P_{18amu}
Nitrogen (N_2)	P_{N_2}	$(P_{14amu} - 0.2042 \times P_{CH_4})/0.1379$
Carbon monoxide (CO)	P_{CO}	$P_{28amu} - P_{N_2} - 0.0981 \times P_{44amu}$
Hydrogen sulfide (H_2S)	P_{H_2S}	P_{34amu}
Argon (Ar)	P_{Ar}	P_{40amu}
Carbon dioxide (CO_2)	P_{CO_2}	P_{44amu}

We performed ion fragmentation on each species (i) for both the background and the continuous data, before we conduct background subtraction at each time step:

$$p_i = p_{i,\ continuous} - \frac{p_{Ar,\ continuous}}{p_{Ar,\ background}} p_{i,\ background}$$

Since each experiment may have slightly different vacuum conditions, instead of directly subtracting the background data from the continuous data, we multiply a ratio ($p_{Ar,\ continuous}/p_{Ar,\ background}$) to the background data using the reference Argon 40 amu peak. For each set of the experiment (background plus continuous), the Ar ratio varies between 0.5-2.0. The mole fraction of each species at each time step can be expressed as:

$$\chi_i = p_i / \sum_i p_i,$$

The outgassed mass fraction of each species can be then calculated as:

$$w_i = \frac{(\sum_T \chi_i) \times M_i}{\sum_i (M_i \times \sum_T \chi_i)},$$

where M_i is the molecular mass of each species.

Results and Discussion: Figure 2 (top) shows the reduced mole fraction for all the species for the normal grain sample of Murchison. The main outgassed species are H_2O, CO, CO_2, N_2, and H_2. There are also minor outgassing CH_4 and H_2S. Figure 2 (bottom) shows the reduced mole fraction for all the species for the small grain sample of Murchison. Similar to the normal grain sample, H_2O, CO, CO_2, N_2, and H_2 remain the dominant volatile species, and CH_4 and H_2S are minor volatile species. However, methane seems to outgas at different temperatures for the normal and small grain samples. For the normal grain sample, methane outgasses mainly at lower temperatures (< 600 K). While for the small grain sample, methane outgas at both lower temperatures (< 600 K) and higher temperatures (900-1200 K). In addition, the Murchison small grain sample also outgases a lot more methane than the Murchison normal grain sample (5 times more in mass).

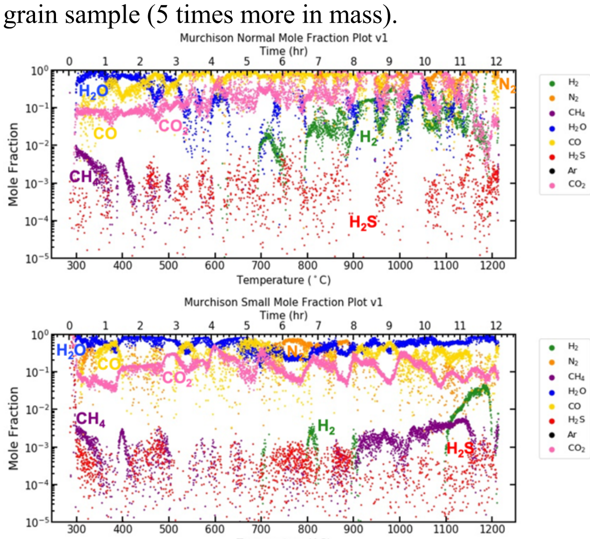

Figure 2: Mole fractions of volatile species outgassed at different temperatures for the Murchison normal grain sample (top) and small grain sample (bottom).

The Aguas Zarcas samples (both normal and small grains) have similar outgassing patterns as the Murchison sample, with more methane outgassed for the small grain sample.

For the Jbilet Winselwan sample (both normal and small grains), the outgassing patterns for the main volatile species are similar to the Murchison and the Aguas Zarcas samples. However, the Jbilet Winselwan samples (both normal and small grains) barely outgas any methane. This could be because this particular sample suffered thermal metamorphism and showed a significant volatiles deletion (e.g., [8]).

Using the chondrite outgassing data as represented above, we can calculate how long can the outgassed methane lasts in Titan's atmosphere. Here we assume the mass percentage of primitive organics in Titan's interior varies from 7-33% [6], and the CH4 outgassing efficiency is 6% following [5]. Table 1 shows the calculated methane extended age assuming a constant photochemical destruction rate in [2]. It looks like organic outgassing in Titan's interior, even if only a few percent of the volatiles made it to the atmosphere, could replenish methane that lasts at least a few hundreds of Myrs.

Table 2: Summary of CH_4 outgassing results.

Meteorite types	Outgassed CH_4 mass (10^{20} kg)	CH_4 age extended (Gyr)
Murchison (20-106 μm)	0.3-1.2	0.2-0.7
Murchison (<20 μm)	1.3-6.2	0.8-3.7
Aguas Zarcas (20-106 μm)	0.2-0.8	0.1-0.5
Aguas Zarcas (<20 μm)	0.4-1.7	0.2-1.0
Jbilet Winselwan (20-106 μm)	<0.01	<0.001
Jbilet Winselwan (<20 μm)	<0.01	<0.001

Conclusion and future work: The source of methane in Titan's atmosphere has been a long-lasting mystery. This work gives us more concrete evidence that outgassing of primitive organics (if there are indeed any in Titan's interior) could help replenish methane in Titan's atmosphere. Note that large amounts of CO are also outgassed in accompany with CH_4, and the triple-bonded CO is a much more stable species photochemically compared to CH_4. However, CO is a minor constitute compared to CH_4 in Titan's current atmosphere, and we are still looking for ways to possibly explain this degeneracy.

References:

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