

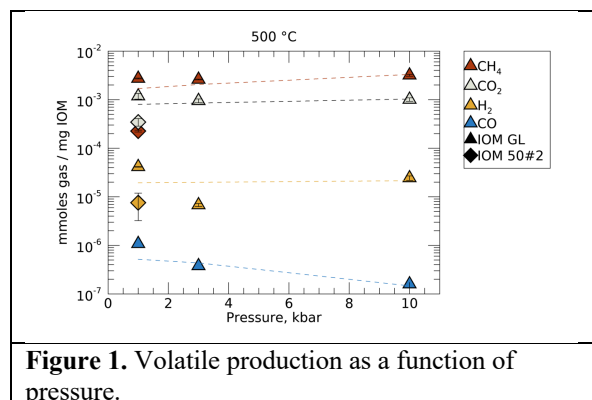
**EXPERIMENTAL VOLATILE PRODUCTION FROM COMPLEX ORGANICS AT TITAN INTERIOR CONDITIONS.** K. E. Miller<sup>1\*</sup>, D. I. Foustoukos<sup>2</sup>, G. D. Cody<sup>2</sup>, and C. M. O'D. Alexander<sup>2</sup>, <sup>1</sup>Southwest Research Institute, San Antonio, TX, <sup>2</sup>Carnegie Institution for Science, Washington, DC. \*kmiller@swri.edu.

**Introduction:** The origin of Titan's atmosphere, including atmospheric methane, is currently constrained by noble gas and isotopic measurements from the Cassini and Voyager missions [1, 2]. Low abundances of noble gases, including subsolar <sup>36</sup>Ar/N and non-detection of Xe and Kr, rule out accretion of N<sub>2</sub> as a primary molecule, and instead point to processing of other N-bearing molecules [3]. The <sup>15</sup>N/<sup>14</sup>N ratio of N<sub>2</sub> is consistent with NH<sub>3</sub> in comets as a major source [4]. Detection of <sup>40</sup>Ar in Titan's atmosphere, a radioactive decay product from <sup>40</sup>K, suggests outgassing from the interior [5]. While transformation of NH<sub>3</sub> into secondary N<sub>2</sub> may occur via photolysis or impact processes [3], processing in the interior is an alternative [6]. Organic material similar to insoluble organic matter (IOM) found in chondrites or complex organics found in cometary nuclei may provide an additional source reservoir for volatile N [7]. Such processes may also produce CH<sub>4</sub>, which would primarily be sequestered in clathrates, but may also contribute atmospheric methane during outgassing events [8]. Previous analysis suggests that CH<sub>4</sub> is isotopically compatible with either primary accretion [9, see also 10] or interior organics [7] as the source.

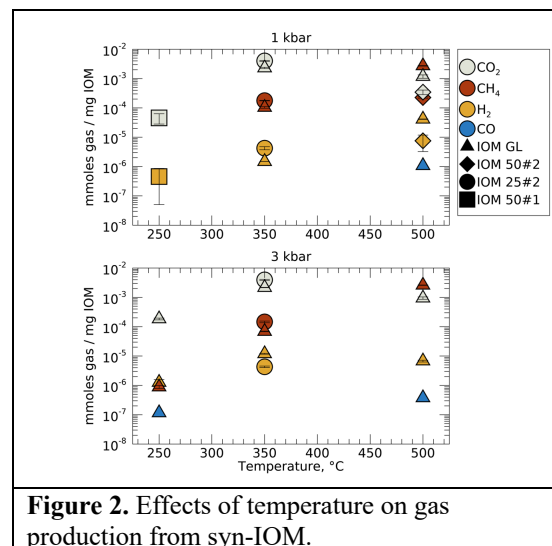
Here, we report the results of experimental work and subsequent thermodynamic analysis to test the endogenic origin hypothesis for Titan's atmosphere. Experiments bracket the pressure for Titan's rocky interior, which starts at about 8 kbar [11].

**Methods:** Synthetic IOM-like material ("syn-IOM") was produced from dextrose and ammonium chloride via previously established methods [12-14]. N/C atomic ratios for syn-IOM were 0.06 ("GL"), 0.05 ("50#2"), 0.07 ("25#2"), and 0.06 ("50#1"). Experimental charges with approximately 20 mg of syn-IOM and an equal mass of water were sealed in gold capsules and then heated in cold seal (1-3 kbar) or piston cylinder (10 kbar) apparatuses for 48 hours. Experimental temperatures ranged from 250 °C to 500 °C. The capsules were quenched to atmospheric conditions, placed in Ar-filled vials with 1 mL of 0.1N HCl, and the contents were extracted. Volatile production was measured via gas chromatography (GC), and ammonium ions (NH<sub>4</sub><sup>+</sup>) were measured via spectrophotometry. Other N volatiles were not measured, but are covered briefly in the Discussion. The bulk elemental and isotopic composition of solid residues were characterized using mass spectrometry.

**Results:** Volatiles measured by GC analysis include CO<sub>2</sub>, CH<sub>4</sub>, CO, and H<sub>2</sub>. Error bars shown here correspond to standard deviation of multiple GC measurements for a single experimental charge. Volatile production rates change slightly as a function of pressure (Figure 1). For a single syn-IOM starting composition and temperature, the ratio of final gas concentrations at 10 kbar to 1 kbar is 0.58±0.04 (H<sub>2</sub>), 0.15±0.25 (CO), 1.17±0.04 (CH<sub>4</sub>), and 0.85±0.09 (CO<sub>2</sub>). Production of non-hydrocarbon gases is somewhat inhibited by increased pressure under the experimental conditions. However, generation of CH<sub>4</sub> increases slightly with increasing pressure.



The effects of temperature at 1 kbar and 3 kbar on gas production are shown in Figure 2. In general, higher temperatures lead to increased gas production, with a

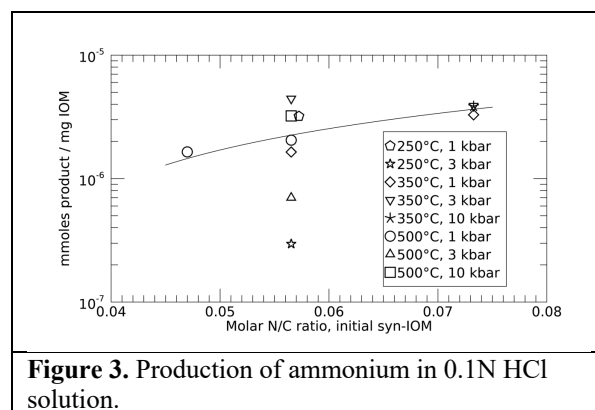


shallower slope from 350 °C to 500 °C that may be related to the presence of supercritical water above 374.5 °C and 0.221 kbar [15, 16]. While changes in pressure lead to measurable differences in gas production, the dependence on temperature is stronger.

Production of ammonium is most strongly predicted by the initial N/C atomic ratio of the syn-IOM (Figure 3), with the best fit shown calculated as

$$P = 8.34 \times 10^{-5} \times R - 2.46 \times 10^{-6}$$

where P is the mmoles of ammonium normalized to the initial mass of syn-IOM in mg, and R is the initial N/C atomic ratio in the syn-IOM starting material. The variation observed at N/C~0.057 may be related to pH during syn-IOM synthesis [17].



**Discussion:** Terrestrial kerogen has been cited as an analog material for chondritic IOM [18]. Previous studies on the effects of pressure on degradation of kerogen and kerogen-bearing rocks have reported conflicting results [19] and with a few exceptions [20, 21] have mostly been performed at lower pressures. Mi et al. [19] report different trends versus pressure for production of hydrocarbon and non-hydrocarbon gases and cite high-temperature cracking of oil and C<sub>2</sub> to C<sub>5</sub> hydrocarbons to form CH<sub>4</sub>. Our results may therefore represent increasing extraction of oil as pressure increases, but less production of primary gases directly from the syn-IOM. Recently, the role of supercritical water has been cited as a possible explanation for increased degradation of complex organics at higher pressures, with increases in degradation associated with the critical point [15]. Properties of supercritical water vary continuously throughout the supercritical region [16], and production of primary gas may decrease as distance from the critical pressure increases. Results from [15] confirm a different pressure relationship for hydrocarbon and non-hydrocarbon gases. While their results show non-hydrocarbon gases dominating at higher pressures, their experiments were performed at

much lower pressures (< 1 kbar) and demonstrate some differences depending on the starting composition.

For an interior that includes 25 wt.% IOM [22], gas production rates that are consistent with these experimental results (including all pressures and temperatures tested), and an outgassing efficiency of 0.7%, production of the full present-day mass of Titan's atmospheric CH<sub>4</sub> would require degassing of only the top 1 km of the core or less. Experimentally produced ammonium is not sufficient to generate 50% of the mass of Titan's present-day atmosphere, even with full degassing of the core. However, compositional changes reported [23] for IOM subjected to dry pyrolysis up to 450°C with an N/C ratio of 0.03 are consistent with volatilization of at least 50× as much N as was measured here as NH<sub>4</sub><sup>+</sup>. Hydrous pyrolysis tends to increase volatilization of complex organics, and it is likely that ammonium, which is not reported by [23], is a minor component of all volatilized N.

Future experiments include pyrolysis of IOM extracted from Murchison at similar pressure and temperature conditions for comparison; as well as measurement of a broader range of N-bearing products to verify our hypothesis that NH<sub>4</sub><sup>+</sup> is a minor component.

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