INVESTIGATING FORMATION AND EVOLUTION OF TITAN'S ATMOSPHERE THROUGH IT'S ISOTOPIC INVENTORY AND NEW PHOTOCHEMICAL STUDIES. S. Chakraborty*, Christopher Immekus and M. H. Thiemens, University of California, San Diego, Department of Chemistry and Biochemistry, 9500 Gilman Drive, La Jolla, CA 92093-0356 (subrata@ucsd.edu).

Introduction: Saturn's largest satellite, Titan, is the only moon in our Solar System with a dense atmosphere dominated by N_2 (98%) and CH_4 (2%). The surface pressure on Titan is 50% greater than that of Earth's. The origin of this atmospheric nitrogen has long been a subject of debate [1, 2]. The Cassini–Huygens mission added a complex part to this debate– is Titan's atmosphere primordial or secondary [3,4]? As observed by the Huygens probe, the $^{36}Ar/N_2$ ($\approx 2.8\times10^{-7}$) ratio is extremely low in Titan. Since Ar and N_2 have similar trapping temperatures, an atmosphere formed from primordial nitrogen should also contain substantial amounts of ^{36}Ar. An observed low $^{36}Ar/N_2$ ratio rules out a primordial N_2 component in Titan.

Fortunately, the isotopic compositions of Nitrogen, Carbon, Hydrogen and Oxygen in different constituents, i.e., N_2, HCN, CH_4, H_2, CO have been measured [Figure 1] by several means [5, 6] and based on these isotopic compositions, it is possible to address the formation and evolution of Titan's atmosphere. Here we report new isotopic results of NH_3 photodissociation and convoluting the present and past photodissociation results, a mechanism for Titan's atmosphere will be made.

Isotopic Inventory of Titan's Atmosphere: ***$^{14}N/^{15}N$ in Molecular Nitrogen and in HCN:*** In the evolutionary scenario of nitrogen-rich Titan's atmosphere, if NH_3 is primordial, the immediate question arises whether the source of that material is Saturnian-sub nebula or cometary. The isotopic compositions of the Titan's atmospheric constituents are relevant to addressing this. The isotopic composition of nitrogen is striking. N_2 is enriched in ^{15}N ($^{14}N/^{15}N \approx$ 160-240) compared to that of the Earth (= 272). HCN is even more enriched in ^{15}N where the ratio is ~ 60-110. In geochemical referencing the enrichment in N_2, e.g., $\delta^{15}N_{air} \approx$ 150 - 700 ‰ and HCN is >1500 ‰. On the same scale the N-isotopic composition of the solar wind and Jupiter's atmospheres (measured in NH_3) is –400 ‰. The comets (in NH_3 and HCN) and insoluble organic matters (IOM) in meteorites are also enriched in ^{15}N up to a few thousand ‰ [7, 8].

$^{12}C/^{13}C$ in CH_4 and HCN: The value of $^{12}C/^{13}C$ determined in the local interstellar medium is ~43. It is important to remember that the Sun has revolved around the center of the galaxy 15–20 times since the origin of the solar system. Thus the "local" Interstellar Medium today is not the one in which the solar system formed. There is, however, a remarkable uniformity of $^{12}C/^{13}C$ ~ 90 as measured in Titan's atmosphere, like that of the solar system [9]. The GCMS measurement from Cassini–Huygens probe found the carbon isotope ratio ($^{12}C/^{13}C$) to be 91.4 ± 1.5 for CH_4 in Titan's atmosphere [5]. The same ratio in HCH is enriched in ^{13}C, e.g., 82.3 ± 2.8.

D/H in Molecular Hydrogen: The D/H ratio in H_2 obtained by the GCMS in Cassini–Huygens probe is 1.35×10^{-4}. The D/H ratio is determined from the measurement of the ratio of HD to H_2 present in the atmosphere of Titan. The D/H ratio of 1.32×10^{-4} derived from CH_3D/CH_4 measured by the CIRS instrument in the stratosphere of Titan. The low enhancement of this Titan D/H ratio for hydrogen relative to the protosolar D/H ratio in hydrogen of ~2.1×10^{-5}. The Titan's D/H ratio is lower than the D/H ratios in cometary water, which varies from 2.9×10^{-4} to 4.1×10^{-4} (recently measured D/H ratio from Jupiter family comet 67P/Churyumov-Gerasimenko by the ROSINA mass spectrometer aboard the European Space Agency's Rosetta spacecraft, is found to be $(5.3 \pm 0.7) \times 10^{-4}$, and in the water plumes escaping from Enceladus, as measured by the INMS experiment, which is 2.9×10^{-4}. The low D/H ratio in Titan's atmosphere is unclear [5]. However, the recent ALMA measurement from HCN measured the ratio as 2.3×10^{-4}, about 2 times greater than that measured in CH_4 [10]. The isotopic results are summarized in Figure 1 in δ-notation (‰-fractionation with respect to ambient air for N_2, V-PDB for carbon and V-SMOW for D/H).

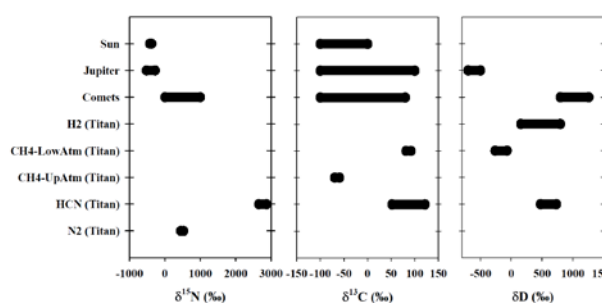

Fig 1. *Nitrogen, carbon and hydrogen isotopic compositions in different component in Titan's atmosphere. The range of measured values are shown (and not the error in measurement).*

New Experiments and Results: NH_3 photodissociation experiment was performed using different UV resonance lamps as photon source, i.e., H_2 lamp (121.6 nm), Kr lamp (116.5 and 123.6 nm), and Hg lamp (184.9 and 253.7 nm). Cell pressures of 50 to 250 torr

of NH_3 (pre-cleaned) was irradiated for 1 to 6 hours in different sets of experiments. Following reaction, the product N_2 and H_2 was separated cryogenically from the residual NH_3. Separation of H_2 and N_2 was performed using two sample tubes, containing molecular sieve and Palladium foil, respectively. Pd foil absorbs H_2 at room temperature and desorbs at around 350 °C. The isotopic composition of N_2 and H_2 was measured in the mass-spectrometer and shown in Figure 2.

Previous Experiments and Results: We have performed extensive low temperature (80 K) photodis-

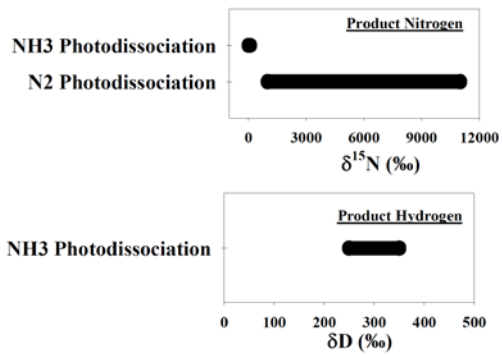

Fig 3. Summary of experimental results, Top: $\delta^{15}N$ in product N_2 from NH_3 photodissociation described in the present experiment. Also, the $\delta^{15}N$ in product NH_3 from N_2 photodissociation [8] are shown in range form. Bottom: δD measured in the product H_2 from NH_3 photodissociation. The wavelength dependent fractionation values are shown as the range.

sociation of N_2 [Ref] (in presence of H_2) at VUV wavelengths to measure the isotopic fractionation in the products. The N-isotopic fractionation is hugely wavelength dependent and show a wide range [Figure 2]. The wavelength integrated instantaneous fractionation in the product NH_3 is > 2500 ‰ over the N_2 dissociation regime (80-100 nm).

Proposition: These laboratory measurements along with the measurements by Cassini–Huygens spacecraft constrain the origin of volatiles in Titan's atmosphere. Titan accreted nitrogen as NH_3 and not as N_2 [5] from Saturnian sub-nebula. We have shown that N_2 photodissociation in the solar nebula could produce ^{15}N-enriched NH_3 [6]. Therefore, about 25-30 % of the accreted NH_3 could came from the 1st generation photolytically produced NH_3 in the solar nebula enriched in ^{15}N. Later, NH_3 converted to N_2 in a bulk fashion (within Titan). The new results of NH_3 photodissociation show that the product N_2 is slightly fractionated [Figure 2] compared to NH_3. We infer that the measured ^{15}N enriched N_2 in present day Titan [Figure 1] is the N_2 photodissociation signature in solar nebula. Interestingly, the HCN is enriched by ~1500 ‰. HCN is photochemically produced in Titan's modern atmosphere and the N-atoms may come from N_2 photodissociation of the present day atmospheric N_2. Per our experimental results the N-atoms produced from N_2 photodissociation is enriched by >2500 ‰ relative to starting N_2. Therefore, the further ^{15}N enriched HCN is consistent with 2nd generation N_2 photolysis in the modern Titan's atmosphere. This proposed scenario is consistent with measured δD values in HCN and H_2 in Titan's atmosphere [Figure 1]. The present experiments show that the hydrogen produced by NH_3 photodissociation is enriched by about 300 ‰. Photolytically produced hydrogen might be the source of H_2 as well as H-atom in HCN molecule in Titan's atmosphere. If that is the case, then the δD enrichments in HCN and H_2 as measured is totally consistent with in situ photochemical processes at effect.

As mentioned, CH_4 in Titan's atmosphere is enigmatic. From the isotopic finger prints it does not seem to be formed in the atmosphere since the δD value is lower compared to that of HCN or H_2. CH_4 might be primordial, but still needed a constant replenishing source. The nitrogen isotopic composition of other bodies, e.g., Pluto, Enceladus, Triton, would be of interest to understand the formation and evolutionary history of the solar system.

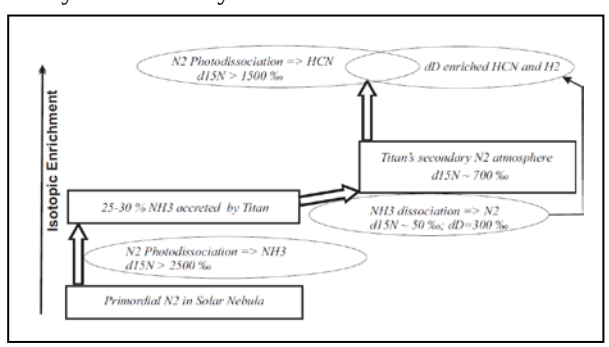

Fig 3. *Schematic showing the isotopic trail in Titan's atmosphere*

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