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 N2 (98%) and CH4 (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 \(^{36}\text{Ar}/\text{N}_2\) (\(\approx 2.8 \times 10^{-7}\)) ratio is extremely low in Titan. Since Ar and N2 have similar trapping temperatures, an atmosphere formed from primordial nitrogen should also contain substantial amounts of \(^{36}\text{Ar}\). An observed low \(^{36}\text{Ar}/\text{N}_2\) ratio rules out a primordial N2 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:

14N\(^{15}\text{N}\) 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 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 \(^{15}\text{N}\) \((^{14}\text{N}/^{15}\text{N} \approx 160-240)\) compared to that of the Earth (= 272). HCN is even more enriched in \(^{15}\text{N}\) where the ratio is \(\approx 60-110\). In geochemical referencing the enrichment in N\(_2\), e.g., \(\delta^{15}\text{N}_{\text{air}} \approx 150 - 700 \text{‰}\) and HCN is \(>1500 \text{‰}\). On the same scale the N-isotopic composition of the solar wind and Jupiter’s atmospheres (measured in NH\(_3\)) is \(-400 \text{‰}\). The comets (in NH\(_3\) and HCN) and insoluble organic matters (IOM) in meteorites are also enriched in \(^{15}\text{N}\) up to a few thousand \(\text{‰}\) [7, 8].

12C/13C in CH\(_4\) and HCN: The value of \(^{12}\text{C}/^{13}\text{C}\) 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 \(^{12}\text{C}/^{13}\text{C} \approx 90\) 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 \(^{12}\text{C}/^{13}\text{C}\) to be 91.4 \(\pm\) 1.5 for CH\(_4\) in Titan’s atmosphere [5]. The same ratio in HCH is enriched in \(^{13}\text{C}\), e.g., 82.3 \(\pm\) 2.8.

D/H in Molecular Hydrogen: The D/H ratio in H\(_2\) obtained by the GCMS in Cassini–Huygens probe is \(1.35 \times 10^{-4}\). 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 \(1.32 \times 10^{-4}\) derived from CH\(_2\)/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 \(\approx 2.1 \times 10^{-4}\). The Titan’s D/H ratio is lower than the D/H ratios in cometary water, which varies from \(2.9 \times 10^{-4}\) to \(4.1 \times 10^{-4}\) (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 \(2.9 \times 10^{-4}\). The low D/H ratio in Titan’s atmosphere is unclear [5]. However, the recent ALMA measurement from HCN measured the ratio as \(2.3 \times 10^{-4}\), about 2 times greater than that measured in CH\(_4\) [10]. The isotopic results are summarized in Figure 1 in \(\delta\)-notation (%-fractionation with respect to ambient air for N\(_2\), V-
of NH₃ (pre-cleaned) was irradiated for 1 to 6 hours in different sets of experiments. Following reaction, the product N₂ and H₂ was separated cryogenically from the residual NH₃. Separation of N₂ and H₂ was performed using two sample tubes, containing molecular sieve and Palladium foil, respectively. Pd foil absorbs H₂ at room temperature and desorbs at around 350 °C. The isotopic composition of N₂ and H₂ was measured in the mass-spectrometer and shown in Figure 2.

**Previous Experiments and Results:** We have performed extensive low temperature (80 K) photodissociation of N₂ [Ref] (in presence of H₂) 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 NH₃ is > 2500 ‰ over the N₂ 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 NH₃ and not as N₂ [5] from Saturnian sub-nebula. We have shown that N₂ photodissociation in the solar nebula could produce ¹⁵N-enriched NH₃ [6]. Therefore, about 25-30 % of the accreted NH₃ could came from the 1st generation photolytically produced NH₃ in the solar nebula enriched in ¹⁵N. Later, NH₃ converted to N₂ in a bulk fashion (within Titan). The new results of NH₃ photodissociation show that the product N₂ is slightly fractionated [Figure 2] compared to NH₃. We infer that the measured ¹⁵N enriched N₂ in present day Titan [Figure 1] is the N₂ 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 N₂ photodissociation of the present day atmospheric N₂. Per our experimental results the N-atoms produced from N₂ photodissociation is enriched by >2500 ‰ relative to starting N₂. Therefore, the further ¹⁵N enriched HCN is consistent with 2nd generation N₂ photolysis in the modern Titan’s atmosphere. This proposed scenario is consistent with measured δD values in HCN and H₂ in Titan’s atmosphere [Figure 1]. The present experiments show that the hydrogen produced by NH₃ photodissociation is enriched by about 300 ‰. Photolytically produced hydrogen might be the source of H₂ as well as H-atom in HCN molecule in Titan’s atmosphere. If that is the case, then the δD enrichments in HCN and H₂ as measured is totally consistent with in situ photochemical processes at effect.

As mentioned, CH₄ in Titan’s atmosphere is enigmatic. From the isotopic fingerprint it does not seem to be formed in the atmosphere since the δD value is lower compared to that of HCN or H₂. CH₄ 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](image-url)