NITROGEN ON EARLY TITAN. A.A. Berezhnoy, Sternberg Astronomical Institute, Moscow State University, Universitetskij pr., 13, Moscow, Russia, Email: ber@sai.msu.ru

Introduction: The origin of volatiles on Titan can be understood based on isotopic abundances of N, C, and H in Titan's atmosphere. The initial mass of volatiles on early Titan is a very important parameter for constructing the early history of the system of Saturnian satellites. In this work we try to understand the early history of Titan's main N-containing compounds, N_2 and NH_3.

Model of calculation of isotopic composition of nitrogen on Titan: The nitrogen in Titan's atmosphere is assumed to be escaping from the exobase level. Below the exobase and above the homopause diffusive separation of species with different molar masses occurs and leads to enrichment of lighter species at the exobase level. Dissociative mass fractionation occurs due to differences between the rate constants of removal processes such as electron impact, solar wind bombardment, and photodissociation and between the velocity distributions of photolysis products for species containing different isotopes. The initial mass of Titan's atmosphere M_0 is calculated from the current atmospheric mass M_{pr} and $^{14}N/^{15}N$ ratio assuming that this ratio was changed from its original value mainly by two processes: 1) dissociative fractionation y_d and escape, which depends on the probabilities of removal processes for different isotopes (y_{d1} factor), escape velocity, and velocity distribution of N-containing species (y_{d2} factor) produced by photolysis, electron impact, and solar wind bombardment; and 2) diffusive fractionation y_f, which depends on the heights of the homopause and exobase and the temperature of the upper atmosphere.

Based on the available $^{14}N/^{15}N$ ratio in HCN on Titan, about 60 (Hidayt and Marten [1]), the initial mass of Titan's atmosphere is estimated in wide range between 10-1000 M_{pr} [2]. In this work the exobase radius R_{ex} as measured from the center of Titan is taken as 4175 km [3]. The homopause level R_{hp} has been constrained from Voyager UV methane spectra to lie at 3560 to 3700 km [3]. Here it is assumed that homopause and exobase levels on early Titan were the same as they are today.

Measurements made by the Huygens probe show that $^{14}N/^{15}N$ value in N_2 on Titan is 183 ± 5 [4]. This N_2 ratio is representative of nitrogen in the entire atmosphere because N_2 is the main N-containing compound. It is also 1.5 times lower than terrestrial value, which is assumed to be the same as the primordial value for early Titan. Using enrichment factor F = 1.5 instead of 4 [2] Niemann et al. [4] estimated the initial atmospheric mass as 2 - 10 M_{pr}. Here we re-examine this estimate by study of N_2 and NH_3 photolysis on Titan.

Fractionation of nitrogen isotopes during photolysis of N-containing molecules: In [2] it was assumed that N_2 was the main N-containing compound in the early Titan's atmosphere just as it is today. However, calculated values of N loss rate from Titan [5] are low and Titan's N_2 is therefore thought to have been stable over billions years. Loss of several current atmospheric masses required for explanation of current $^{14}N/^{15}N$ ratio can occur during short strong flashes of intensity of the solar wind at the early period of history of the Solar system [6]. Dissociative fractionation on early Titan is difficult to estimate because the energy distributions of solar photons, solar wind particles, and electrons are unknown at that time.

The calculated mole fractions of CN and HCN at the exobase level of Titan are about 10^{-3} [7]. The photolysis rates calculated here for CN, HCN, and N_2 show that most of the N loss from Titan today comes from N_2. However, based on P-T conditions of stability of N-containing clathrates, on early Titan NH_3 is considered as the main N-containing compound. An early NH_3-rich atmosphere can be quickly converted into N_2-rich atmosphere because present-day NH_3 photolysis rate is very high [8].

The dissociative fractionation y_d of N_2 was allowed to vary from 0 to 0.6 in paper [2]. Let us estimate this value more precisely. The present-day fractionation of N isotopes depends mainly on the ratio of the relative removal rates of $^{14}N^{15}N$ and $^{14}N_2$. The main reaction controlling N loss from current Titan is electron-impact dissociation of N_2 but, unfortunately, the cross section of this reaction is known only for $^{14}N_2$ [9], and not for $^{14}N^{15}N$. The photolysis rate of $^{15}NH_3$ is 12 % higher than that of $^{14}NH_3$ [10]. One can expect a higher photolysis rate and a lower lifetime against electron-impact dissociation for $^{14}N^{15}N$ than for $^{14}N_2$. Electron-impact dissociation can even lead to negative values of the factor y_{d1}. Based on the discussion above, the factor y_{d1} is estimated in the range of -0.2 – 0.2. Higher values are unlikely because there are no known processes that produce nitrogen with typical velocities that approach the escape velocity. Lower values are also unlikely because we do not expect a significant difference (more than 20 %) in rates of photolysis, electron-impact dissociation and dissociative recombination of ^{14}N and ^{15}N-containing species.

Additional dissociation fractionation characterised by the factor y_{d2} occurs when the typical velocity of N-containing photolysis products is close to the escape velocity from Titan. The velocity distribution of N and NH_2 produced via N_2 and NH_3 photolysis is estimated from the present-day solar photon flux [8] and the wavelength-dependent photolysis rates of N-containing species [11]. We assume that the kinetic energy of molecules before photolysis is negligible in comparison to the kinetic energy of the products of this reaction. The kinetic energy of the photolysis products is estimated from the laws of conservation of energy and angular momentum with the added but experimentally based assumption [12] that 25 % of all excess energy (the difference between the energy of photon and the threshold energy for photodissociation) is converted to kinetic energy. The velocity distribution of photolysis products is non-Maxwellian; most probable velocities of NH_2 produced via NH_3 photolysis are 600 - 800 m/s. The factor y_{d2} is significantly lower than the values of the present-day diffusion fractionation y_f, about 0.25 – 0.4 [2]. Specifically, y_{d2} is close to zero for N_2 and NH_3 photolysis, also for different reasons. The typical velocity of N atoms formed by N_2 photolysis is about 4 km/s, a value is significantly higher than the escape velocity from the current exobase level, 2.07 km/s, while photolysis-generated NH_2 radicals remain on Titan. The NH_3 photolysis does not change significantly the isotopic composition of Titan's atmosphere because nitrogen is remaining in the atmosphere after NH_3 photolysis and NH_3 is minor reservoir of hydrogen on Titan.

In paper [2]'s treatment of early Titan it was assumed that the temperature, homopause and exobase levels of Titan's atmosphere remained constant though time. Changing of these parameters gives additional uncertainty to estimates of the initial atmospheric mass. For example, at R_{ex} = 4175 km, R_{hp} = 3700 km, y_d = 0, and F = 1.5 the initial mass M_0 is equal to 7, 14, 26 M_{pr} at temperatures of upper atmosphere equal to 150, 200, and 250 K, respectively. However, if we assume that the exobase and homopause altitudes increase linearly with increasing temperature of the upper atmosphere, then M_0 is independent of the temperature of the upper atmosphere.

Further, the presence of NH_3 may have influenced of R_{ex} and R_{hp}. Specifically, the scale height, which depends inversely on average molar mass, would have been 1.7 larger in an NH_3-rich atmosphere than in a N_2-rich one. A 1.5–2 × increase of the exobase altitude leads to a decrease of the escape velocity from Titan to 1750 – 1900 m/s, but it does not increase significantly the rate of N loss from Titan and y_{d2} value. The fractionation of nitrogen isotopes is controlled by diffusive separation of isotopes between homopause and exobase on the present-day Titan. Discussed above estimates of the y_{d1}, y_{d2},and y_f factors corresponds to the value of the initial mass of the Titan's atmosphere of about 3-20 M_{pr}.

Fractionation of hydrogen isotopes during photolysis of NH_3: The observed D/H value on Titan cannot be explained only by isotopic fractionation during CH_4 photolysis. The D/H ratio on early Titan is estimated to be 3.6 – 4.3× and 2.7 – 3.6× the protosolar values for the cases of presence of CH_4 reservoir on Titan during 0.6 and 4.5 Gyr, respectively [13]. The loss of NH_3 from early Titan may have increased the D/H ratio by an additional factor of 1.1. For these calculations we take the ratio of NH_2D and NH_3 photolysis rates equal to be 0.71 [14] and the N/C ratio in the protosaturnian nebula equal to the solar value, 0.275 [15]. Such small enrichment factor, about 1.1, disagrees with assumption of low D/H value in protosaturnian nebula equal to that in protosolar nebula. Thus, primordial D/H value on Titan is higher than corresponding protosolar value [13]. Primordial $^{14}N/^{15}N$ ratio on Titan is also suggested to be lower than corresponding protosolar value [16].

Comet-like objects as sources of Titan's volatiles can lead to additional ^{15}N enrichment of Titan's atmosphere because the average $^{14}N/^{15}N$ ratio in cometary CN, about 140, is 1.9 times less than the terrestrial value [17]. If the primordial $^{14}N/^{15}N$ ratio on Titan was lower than the corresponding protosolar ratio then our estimation of the initial mass of Titan's atmosphere can be considered as an upper limit.

Conclusions: The mechanisms of losing nitrogen from early Titan's atmosphere are still unknown. An early NH_3-dominated atmosphere can be quickly converted into the present-day N_2-rich atmosphere without significant changes in the isotopic composition of N and H. The value of the dissociative fractionation factor y_d is estimated for present-day photolysis, it can vary in wide range of -0.2 to +0.2. This range leads to significant uncertainty in estimates of the upper limit of the initial atmospheric mass of Titan, about 3-20 M_{pr}. Additional fractionation of N isotopes in the protosaturnian nebula may be important.

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