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Nitrogen isotopes in early Titan's atmosphere

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Abstract

Molecular nitrogen could be produced on early Titan from NH₃·H₂O without significant changes in the isotopic composition of nitrogen and hydrogen. During NH, NH₂, and NH₃ photolysis almost all nitrogen remains in the atmosphere of Titan and ¹⁴N/¹⁵N ratio remains constant. Effects of fractionation of isotopes of nitrogen and hydrogen during collisions between comets and Titan are also negligible. Thus, early Titan was enriched by ¹⁵N isotope.

1. Introduction

The most important mechanisms of changes of the isotopic composition of Titan's atmosphere include diffusive fractionation [8], sputtering [7], and chemical and escape fractionation [9]. Main mechanisms of nitrogen isotope fractionation are not so sufficient to be able to increase ¹⁵N/¹⁴N value on early Titan from the protosolar value on about 50 % to the present-day value, 1/183 [9]. It means that Titan was formed from icy planetesimals with incorporation of significant fraction of ices formed in dense cloud cores and enriched by ¹⁵N isotope [11]. However, influence of photochemical and impact processes on isotopic composition of Titan's atmosphere was not considered in details so far.

2. Isotopic fractionation during NH, NH₂, and NH₃ photolysis

Early Titan accumulated nitrogen in the form of $NH_3 \cdot H_2O$. Present N_2 -rich atmosphere of Titan could be created during photochemical reactions in the upper atmosphere, $NH_3 \cdot H_2O$ decomposition in interiors of Titan, and collisions between comets and Titan.

Atmosphere of early Titan could contain both N_2 and NH_3 . Let us estimate the period of time required for transformation of early NH_3 -rich Titan's atmosphere to present N_2 -rich one. During first $T(NH_3, g) =$

 3×10^5 years after formation of Titan the temperature on its surface was higher than 250 K [4], it is suitable for existence of NH3 in the atmosphere. Masses of the current atmosphere M_{pr} and exosphere M_{ex} of Titan are equal to 3×10^{22} and 5×10^{10} g, respectively. The rate of NH3 photochemical destruction on early Titan need to be more than M_{pr} / T(NH3, g) = 10^{17} g/year. However, the intensity of UV-radiation of young Sun was just about 100 times higher than that of the present-day Sun [10]. This value of the intensity of UV-radiation corresponds to NH3 destruction rate on early Titan of about 100 M_{ex} τ_{ph} (NH3) $^{\sim}$ 3×10 14 g/year, where τ_{ph} (NH3) = 2×10 $^{-6}$ s $^{-1}$ is the NH3 photolysis rate on present-day Titan [3]. Thus, photochemical destruction of early Titan's NH3-atmosphere seems to be unfavorable.

Velocities of photolysis-generated species can be estimated based on laws of energy and momentum conservations and knowing the flux of solar radiation [3] and photolysis cross sections available at http://amop.space.swri.edu. Then the most probable velocities of NH, NH₂ and N produced during NH₂, NH₃, and N₂ photolysis are 1.2, 0.6-0.8, and 5.5 km/s, respectively, while the escape velocity is 2.07 km/s for Titan. Thus, NH₃ photolysis did not change the isotopic composition of nitrogen on Titan because photolysis-generated NH and NH₂ species remain in the atmosphere.

During NH photolysis additional fractionation of nitrogen isotopes can occur if all four conditions are valid simultaneously: 1) NH photolysis rate is higher that 10⁻⁵ s⁻¹; 2) ¹⁴NH and ¹⁵NH photolysis rates are quite different; 3) typical velocities of photolysisgenerated nitrogen atoms are higher than the Titan's escape velocity; 4) during NH photolysis significant amounts of nitrogen were lost. Simultaneous validity of all these conditions seems to be unrealistic.

The observed D/H ratio on present Titan cannot be explained by isotopic fractionation of hydrogen during CH_4 photolysis. The D/H ratio on early Titan is estimated as $2.7 - 4.3 \times$ protosolar value [2]. Using the photolysis model [8], the ratio of photolysis rates

of NH_2D u NH_3 equal to 0.71 [1], and N/C ratio assumed to be that of the solar value, 0.275, we found that early Titan was enriched by deuterium during NH_3 photolysis by about 10 % or less. Thus, NH_3 photolysis did not change significantly the isotopic composition of hydrogen.

3. Isotopic fractionation during impact processes

Collisions of comets with Titan can lead to additional enrichment of the atmosphere by heavy isotopes 15 N and D because the average C^{14} N/ C^{15} N, about 140, in comets less in 1.9 times than that of Earth [12] and the D/H ratio in comet Halley, $(31.6 \pm 3.4) \times 10^{-5}$ [6], higher in 12 times than that for Sun.

Additional isotopic fractionation can occur during impact processes because impact-produced H₂, N₂, and CH₄ are able to escape from Titan's atmosphere while H₂O and NH₃ are delivered to the surface. Based on comparison between hydrodynamic and chemical time scales quenching of the chemical composition of impact-produced fireballs occur at about 800 - 1000 K and 10 - 1000 bars, respectively. For these temperatures and pressures H₂O and N₂ are main compounds, H2, CH4, and NH3 are minor compounds. Using the constant of isotopic exchange between CH₄ and H₂O [5] the D/H ratio in CH₄ less on about 10 % than that in H₂O at the quenching temperature of 1000 K. The difference between ¹⁴N/¹⁵N ratios in N₂ and NH₃ is even smaller because isotopic effects are usually proportional to ratios of masses of isotopes.

High-temperature component of fireballs can escape the atmosphere. If Maxwell distribution is valid and main N-bearing compound in fireballs is atomic nitrogen than the atmosphere of Titan will be enriched by ¹⁵N isotope on 6, 7, and 7.6 % at 3000, 4000, and 5000 K, respectively. Thus, during impact processes we expect just weak enrichment of Titan by heavy isotope ¹⁵N.

4. Summary and Conclusions

Effects of enrichment of Titan by ¹⁵N and D during NH₃ photolysis and comet impacts are negligible. These results can be considered as additional evidence of enrichment of early Titan by ¹⁵N and D isotopes in comparison with the Sun.

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