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Nitrogen isotope ratio and its evolution on Titan

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Abstract

$^{14}N/^{15}N$ ratios in the Sun, Jupiter, comets, and the inner planets indicate that Earth, Venus, and Mars got their nitrogen as N_2 gas and NH_3 ice in proportion 3 : 1. An alternative explanation is that planetesimals were another reservoir of N with $^{14}N/^{15}N = 270$.
$^{14}N/^{15}N = 168$ in N_2 and 60 in HCN on Titan, and the great difference is explained by strong enrichment in ^{15}N by a factor of 8 in predissociation of N_2 at 80-100 nm (Liang et al. 2007) and no fractionation in other 12 processes that form N. The calculated $^{14}N/^{15}N = 57$ in nitriles, in perfect agreement with the observations.
Modeling of nitrogen isotope fractionation by formation of nitriles and sputtering through the history of Titan with the much greater solar EUV and wind in the earlier epochs supports ammonia similar to that in comets as a source of nitrogen on Titan.

1. $^{14}N/^{15}N$ in the Solar System

It was thought 20 years ago that $^{14}N/^{15}N \approx 270$ everywhere in the Solar System, and the smaller value of 170 in the martian atmosphere is caused by preferential escape of the light isotope. The greater ratio in Jupiter measured by the Galileo probe and in the Sun, as well as the recent observations in comets (Rousselot et al. 2014), change the problem (Table 1).

Table 1. $^{14}N/^{15}N$ in the Solar System

Solar wind, Jupiter	$^{14}N/^{15}N$ = 440
Earth, Venus, Mars (mantle), chondrites	270
Mars (atmosphere)	170
Comets (NH_3)	130

It is believed that the protosolar nebula had nitrogen as N_2 with $^{14}N/^{15}N = 440$ and ammonia ice with $^{14}N/^{15}N = 130$. Accretion of the Sun and Jupiter began before the accretion of the inner planets and captured most of N_2. Therefore the inner planets got N as a mixture of N_2 and NH_3 in proportion 3 : 1. An alternative explanation is that planetesimals were another reservoir of nitrogen with $^{14}N/^{15}N = 270$.

2. $^{14}N/^{15}N$ on Titan

Table 2. Observed $^{14}N/^{15}N$ in Titan's atmosphere

Species	Ratio	Instrument
N_2	167.6 ± 0.6	Huygens/GCMS
HCN	60-70	IRAM
	94 ± 13	SMA
	72 ± 9	SMA
	56 ± 8	Cassini/CIRS
	≈ 60	mean

Why are $^{14}N/^{15}N$ so different in N_2 and HCN on Titan? Isotopic shift in predissociation of N_2 at 80-100 nm puts the lines of $^{14}N^{15}N$ in windows between the N_2 lines. Therefore ^{15}N is enriched in predissociation by a factor of 8 (Liang et al. 2007). HCN is produced by
$N + CH_3 \rightarrow H_2CN + H$
$H_2CN + H \rightarrow HCN + H$.
N, $N(^2D)$, N^+, and N_2^+ are formed in dissociation, ionization, and dissociative ionization by the EUV photons, photoelectrons, magnetospheric electrons and protons, and cosmic rays (Table 3).

Table 3. Column production rates of N, N^*, and N^+

#	Reaction	Column Rate ($cm^{-2}\ s^{-1}$)
1	$N_2 + h\nu$ (80-100 nm) $\rightarrow N + N^*$	9.01+7
2	$N_2 + h\nu$ (λ<51 nm) $\rightarrow N^+ + N^* + e$	5.49+7
3	N_2 + e (phot) $\rightarrow N + N^* + e$	1.10+8
4	N_2 + cosmic rays $\rightarrow N + N^*$	3.43+7
5	$N^+ + N^* + e$	1.03+7
6	N_2 + e (magn) $\rightarrow N + N^* + e$	2.03+6
7	$N^+ + N^* + e + e$	4.11+5
8	N_2 + protons $\rightarrow N + N^+$	1.23+7
9	$N^+ + N^* + e$	2.48+6
10	$N_2^+ + e \rightarrow N + N^*$	1.18+6
11	$N_2H^+ + e \rightarrow N + NH$	2.04+6
12	$N_2^+ + C_2H_4 \rightarrow HCN^+ + HCN + H_2$	5.59+5
13	$HCNH^+ + HCN + H$	5.59+5
14	Total	3.21+8

All these processes have been calculated in the photochemical model by Krasnopolsky (2009, 2014). N_2^+ mostly returns N_2 in

$N_2^+ + CH_4 \rightarrow N_2 + CH_3^+ + H$.

The model involves three reactions of N_2^+ that form either N or HCN. Predissociation with fractionation factor of 8 is responsible for 28% of total production of N, and the remaining 72% is expected without significant fractionation. Therefore

$$\frac{HC^{14}N}{HC^{15}N} = \frac{1}{\frac{0.28*8}{168} + \frac{0.72}{168}} = 57 \ ,$$

in excellent agreement with the observations.

3. Evolution of nitrogen on Titan

Table 4. Irreversible loss of N from Titan atmosphere

Process	Species	Loss of N
Condensation	HCN	107 g cm^{-2} Byr^{-1}
	HC_3N	46
	CH_3CN	6.0
	C_2N_2	1.9
Polymerization	C_XH_YN	231
Total		392

The C≡N triple bonds are strong and cannot be broken in Titan's atmosphere, and nitriles are irreversibly lost (Table 4). The N-H bonds are much weaker and comparable to the C-H bonds, and eleven species with N-H bonds return their nitrogen in the model. Total photochemical loss of N is 392 g cm^{-2} Byr^{-1} with fractionation factor of 168/60 = 2.8 (Table 2). Loss of nitrogen by sputtering, nonthermal and ion escape is ≈60 g cm^{-2} Byr^{-1} (Haye et al. 2007) with fractionation factor of 0.73 (Mandt et al. 2014).

The current abundance of N_2 in Titan's atmosphere is 1.1×10^4 g cm^{-2}, and its lifetime is 25 Byr. However, the young Sun was much brighter in the EUV and had stronger wind (by factors of 6 and 20, respectively, at 1 Byr, Fig. 1). We assume that the EUV is responsible for the deposition of nitriles and the solar wind for the escape. Reactions of the atmosphere to the variable EUV and solar wind are generally unknown, and we adopt two options with the linear and square root atmospheric responses. Mandt et al. (2014) argued that hydrodynamic escape occurred in the first Byr without isotope fractionation. Then numerical solutions of the balance equations result in initial $^{14}N/^{15}N$ = 108 and 125 for the linear and square root responses, respectively. Thus we conclude that the initial nitrogen isotope ratio on Titan was close to that of ammonia in comets. Ammonia on Titan is photochemically and thermally (in the interior) decomposes into N_2.

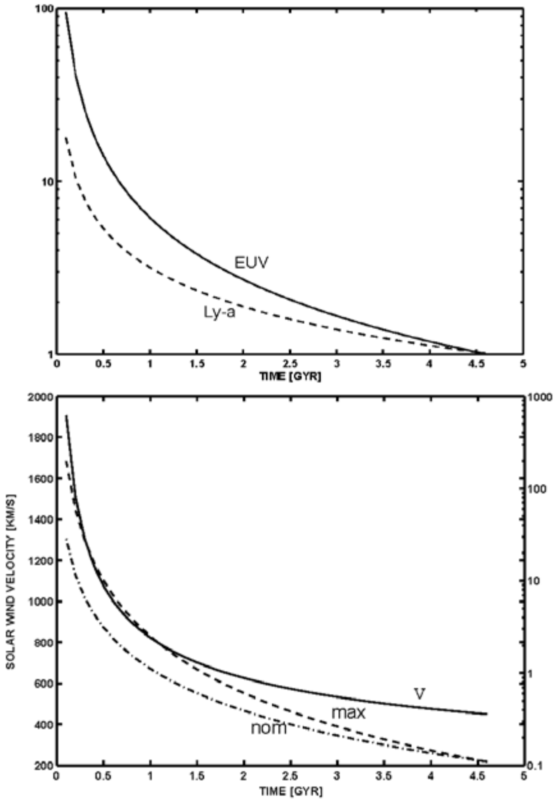

Fig. 1. Evolution of the solar EUV and wind (Penz et al. 2005).

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