Replacement and late formation of atmospheric N_2 on undifferentiated Titan by impacts

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Saturn's moon, Titan, has remarkable surface features—a massive N_2 atmosphere and hydrological cycle of CH_4—that are often compared with that of Earth[1]. However, the origin and evolution of Titan's atmosphere remains largely unknown. The proposed formation mechanisms for Titan's N_2 require a prolonged, warm proto-atmosphere during accretion[2-4]. These mechanisms accordingly would not have worked efficiently if Titan stayed cold, as indicated by the incompletely differentiated interior observed by Cassini[5]. Because formation of a massive secondary atmosphere on a planetary body would associate with a major differentiation of its sold body during accretion[6–8], the presence of such an atmosphere on undifferentiated cold Titan poses a serious dilemma on our view of how planetary bodies develop atmospheres. Here we propose a new mechanism for the post-accretion formation of Titan's N_2 to resolve this problem: conversion and replenishment of N_2 from NH_3 contained in Titan by impacts during the late heavy bombardment (LHB)[9]. Our results show that Titan, regardless of its thermal history, would acquire sufficient N_2 to account for the current atmosphere during the LHB and that most of the pre-LHB atmosphere would have replaced by impact-induced N_2. This is the first scenario capable of generating a N_2-rich and nearly primordial Ar-free atmosphere on undifferentiated cold Titan. We also suggest that Titan's N_2 was delivered from a different source in the solar nebula compared with Earth and that the origins of N_2

on Titan and Triton are fundamentally different with that of N_2 on Pluto.

Why Titan possesses a massive N_2 atmosphere is a longstanding question. One of the most important constraints on the origin of Titan's atmosphere is perhaps the low abundance of primordial Ar[10] ($^{36}Ar/N_2 \approx 2.8 \times 10^{-7}$) observed by Cassini–Huygens, suggesting that Titan's N_2 is of secondary origin, as with N_2 on Earth. If Titan's N_2 had been originated directly from the solar nebula, significant amounts of ^{36}Ar would have been present in the satellitesimals that formed Titan[8] ($^{36}Ar/N_2 \approx 10^{-1}$ to 10^{-2}). Therefore, the above observation suggests that N_2 was delivered to Titan in a less-volatile form, probably NH_3[8,11,12].

Previous studies have proposed three mechanisms for the conversion of NH_3 to N_2: photolysis[2], atmospheric shock heating[3], and endogenic[4]. However, there is at least one critical problem with these mechanisms: they all require a 'warm Titan' during its early history. For photolysis and shock heating, Titan would have required a prolonged, thick and warm NH_3 proto-atmosphere generated by substantial melting and vapourization of surface materials during accretion[7,8], which would have resulted in the rock–ice differentiation required for the production of endogenic N_2[4]. However, recent gravitational data from Cassini[5] reveal that Titan's interior is incompletely differentiated, suggesting that substantial melting and vapourization would have been unlikely[7,13]. Consequently, the proto-atmosphere would have been tenuous and short-lived[7,13], meaning in turn that photolysis and shock heating are unlikely to have been effective in converting NH_3 into N_2.

We investigate the importance of post-accretion exogenic events in converting NH_3 to N_2, especially cometary impacts during the LHB, which occurred at ~3.9 billion years ago[9]. Given both a high impact velocity ($v_{imp} \approx 11$ km/s[14]) and a large total impactor mass (~3×10^{20} kg[13], compared to ~5×10^{19} kg after the LHB[14]), the LHB would have been one of the most energetic events affecting Titan, as well as the other large icy satellites. Although the direct delivery of N_2 from comets has been proposed[15], a key factor in explaining the low $^{36}Ar/N_2$ ratio in Titan's atmosphere is the decomposition of NH_3 contained in Titan as a consequence of impacts. However, a lack of experimental studies of impact-induced N_2 formation has prevented investigating quantitatively the effect of the LHB on the origin of Titan's N_2.

In the present study, we conducted impact experiments to determine the efficiency of N_2 production from ammonium hydrate (NH_3–H_2O) ice. Because of both the difficulties in direct measurements of impact-induced gas species due to chemical contamination (such as, gun debris and combustion gases) by powder and light-gas guns and in the preparation of ice targets, impact chemistry of planetary ices has been poorly investigated. We develop a new experimental system: a chemically clean technique to accelerate projectiles with a high-energy laser pulse (laser gun) combined with isotopic-labelling and target-preparation techniques for $^{15}NH_3$–H_2O ice (see Methods). This experimental system allows us to quantify impact-induced N_2

production via measurements of $^{15}N_2$ with mass spectrometry.

Figure 1 shows the results of experiments on the efficiency of impact-induced N_2 production from NH_3–H_2O ice as a function of peak shock pressure. The efficiency exhibits a linear increase as a function of pressure. Based on a linear fit to the experimental data, we obtained peak shock pressures for incipient and complete N_2 degassing at ~8 and ~23 GPa, respectively. This figure also indicates that N_2 production efficiency does not depend on the NH_3 concentration in the target very much, suggesting that the experimental data are applicable to planetary impacts of icy materials with various NH_3 concentrations. The present result suggests that impact-induced N_2 conversion proceeds efficiently in cometary impacts on Titan, but is inefficient in satellitesimal impacts during accretion (Fig. 1).

Based on the present experimental results, we calculated the N_2 supplied by a cometary impact on Titan, based on numerical impact simulations using a three-dimensional smoothed-particle-hydrodynamics (SPH) method (Supplementary Information). The mass for partial and complete N_2 degassing in the target reaches ~8 times the impactor mass. More than 90% of supplied N_2 is derived from the dissociation of NH_3 in Titan, when the concentrations of NH_3, n_{NH3}, in both the impactor and target are the same. To investigate the evolution of Titan's N_2 inventory during the LHB, we conducted a one-box model calculation considering the impact-induced supply and loss of N_2 (Supplementary Information). We consider that the supplied N_2 is distributed in the atmosphere and surface based on the saturation vapour pressure of N_2 at a given surface temperature[15]. We take into account the loss of atmospheric N_2 by subsequent impacts, using the atmospheric–erosion model given by three-dimensional multi-material hydrocode calculations[16], and the impact-induced ballistic escape of surface N_2 ice, based on the present SPH results (Supplementary Information).

We consider two extreme primordial Titans as initial conditions: an airless cold Titan and a relatively warm Titan, as proposed previously, with substantial N_2 and CH_4 on its surface[17]. Even if Titan starts with an airless, cold environment (surface temperature $T_{surf} \approx 60$ K), its N_2 inventory reaches a pressure of one to several bars in the LHB aftermath, depending on n_{NH3} on Titan and impactor radius r_p (Fig. 2a). Accumulation of the current N_2 inventory on a cold Titan requires only 1–2% of n_{NH3} on Titan (Figs 2a and 3), which is consistent with both the proposed n_{NH3} level in the satellitesimals that formed the Saturnian system (~0.5–4.5%)[11,12] and constraints from Enceladus' plume (~1–4%; see the caption to Fig. 3)[18].

If Titan possessed substantial N_2 and CH_4 before the LHB, impacts would have replaced most of the preexisting atmosphere during the LHB. A relatively high T_{surf} (~70–85 K)[17], resulting from greenhouse effects, would have increased the mass of the atmosphere, leading in turn to efficient atmospheric erosion. The present results suggest that efficient atmospheric erosion would have resulted in the loss of most of the pre-existing N_2 during the

LHB, and impact-induced N_2 would have become dominant in the aftermath of the LHB (Fig. 2b). To accumulate the current N_2 inventory on a warm Titan, n_{NH3} on Titan would have been ~2–4% (Fig. 3), which is also within the range of the proposed n_{NH3} in satellitesimals, although close to the upper limit. Such a n_{NH3} might have been achieved in the NH_3-rich ocean beneath Titan's surface[5,8]. Alternatively, CH_4 may have been lost as a result of impacts, which would have led to a decline in T_{surf} and accumulation of N_2. Based on these results, we conclude that Titan acquired significant N_2 during the LHB.

The proposed scenario of the replacement of the atmosphere may provide a clue to an issue related to the abundance of ^{36}Ar in Titan's atmosphere. Although the low $^{36}Ar/N_2$ ratio is consistent with a non-primordial origin of N_2, the nebular–clathration models do not clearly explain the present abundance of ^{36}Ar (no ^{36}Ar[12] or some higher ^{36}Ar abundance[11]). Based on our scenario, even if primordial ^{36}Ar had been in the preexisting atmosphere, most of it would have been lost during the LHB. Consequently, the ^{36}Ar abundance would have approached to a value balanced by the input and output by impacts during the LHB. The present results suggest that a few percent of Titan's N_2 originated from cometary NH_3. To achieve the measured $^{36}Ar/N_2 \approx 2.8 \times 10^{-7}$ by cometary ^{36}Ar, the $^{36}Ar/H_2O$ ratio in comets would have to be $\sim 10^{-8}$ for an NH_3/H_2O value in comets of ~1%[19]. This $^{36}Ar/H_2O$ ratio is consistent with predictions of a nebular–clathration model for some comets[20], which explains the observed depletion of N_2 with respect to CO.

Moreover, our experimental results are useful for investigations of impact-induced alterations on other icy satellites and dwarf planets. Owing to the strong gravity of gas giants, comets collide onto icy satellites with high velocities ($v_{imp} \approx 6$–60 km/s)[14]. Figure 1 suggests that impacts at $v_{imp} > 6$ km/s efficiently dissociate NH_3 on the surface, which may explain the absence of any clear evidence for surface NH_3 on Saturnian mid-sized icy satellites[21], in contrast to NH_3 detected in Enceladus' plume from its interior[18]. Impact-induced N_2 conversion also would occur efficiently on Triton. Our calculation suggests that Triton's N_2 inventory reached ~10^{18} kg in the LHB aftermath (Supplementary Information), consistent with the proposed surface N_2 mass (~10^{16}–10^{19} kg)[22]. In contrast to icy satellites, impact-induced chemical alteration of NH_3 is highly inefficient on dwarf planets because of low impact velocities[14] (Fig. 1), suggesting that Pluto's N_2 is not impact-induced secondary material. This view is consistent with NH_3 detected on Charon[23]. Our results suggest that the origin of N_2 on Triton is different to that of Pluto's, even though both of these icy bodies have similar, N_2-dominated atmospheres.

Although our interpretations can explain the observations consistently, one important question remains unsolved: the high $^{15}N/^{14}N$ ratio in Titan's N_2 (~5.5×10^{-3})[10] relative to that of Earth (~3.7×10^{-3}). If the above scenario is correct, the high $^{15}N/^{14}N$ ratio is primordial, regardless of whether hydrodynamic escape induced fractionation in Titan's early history[24] or not[25]. We consider that the possible large-scale heterogeneity in the nitrogen isotope in the Solar System[26] might be interpreted in the similar framework as proposed for explaining that in the oxygen isotope[27,28]. Low temperature ion-molecule reactions[29] and N_2 self-shielding[30] would have formed ^{15}N-enriched NH_3 ices in the molecular cloud and solar nebula. In the outer solar nebula, the NH_3 ices in dust grains were not isotopically exchanged with ^{15}N-depleted protosolar N_2 gas[26] at least until the Saturn-forming region. In contrast, Earth's N_2 may have largely come from another light N source, such as N components associated with graphite and metal in chondrites ($^{15}N/^{14}N \approx (3.4 \pm 0.7) \times 10^{-3}$)[26], which may have exchanged with the protosolar gas and vapourized NH_3 in the inner solar nebula[26]. We predict that $^{15}N/^{14}N$ values in NH_3 in comets and Enceladus' plume would be as high as that of Titan's N_2. Measurements of these values by large telescopes and future planetary missions would advance our understanding of the origin and distribution of volatiles in the Solar System.

Methods

The laser gun uses a high-energy laser pulse (a Nd:YAG (oscillator) and Glass (amplifier) laser with energy of ~10–40 J and laser spot diameter of ~800 μm) for acceleration of a projectile. A laser pulse was irradiated on a gold (Au), platinum (Pt), or cupper (Cu) foil (thickness of 2.5 and 10.0 μm for Au, 5.0 μm for Pt, and 3.0 μm for Cu) set in a vacuum chamber (Supplementary

Fig. 1). The laser pulse vaporized the front surface (~1 μm) of metallic foil and generated a plasma vapor plume. The rear side of metallic foil was then accelerated by the reaction of the expanding plasma vapor and collided on an NH_3–H_2O ice target. We used an isotopic-labelling technique for NH_3–H_2O (i.e., $^{15}NH_3$–H_2O) ice to distinguish impact-induced gas species from laser-induced contaminated gas species. An $^{15}NH_3$–H_2O ice target was produced by cooling 100 μl of liquid $^{15}NH_3$ solution in H_2O at ~80 K. A fresh surface of $^{15}NH_3$–H_2O ice appeared in the vacuum chamber immediately before impact (Supplementary Fig. 2). The gas species formed by impacts were analysed with a quadrupole mass spectrometer (QMS) connected with the vacuum chamber. We obtained the amount of N_2 production by measuring the QMS signal for $^{15}N_2$ after impact (Supplementary Fig. 3). Impact velocities and peak shock pressures achieved by the impacts were calculated by an empirical equation and the one-dimensional impedance-match solution with the planar-impact approximation based on the Hugoniot equations, respectively. Full methods and any associated references are available in Supplementary Information.

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Author Contributions Y.S. designed the ice target system in the experiments, performed the experiments, modeled Titan's N_2 inventory, and wrote the manuscript. H.G. performed the SPH simulations. T.K. designed the laser gun system. All authors vigorously debated and contributed intellectually to the interpretation of the results.

Additional Information The authors declare no competing financial interests. Supplementary Information accompanies this paper on www.nature.com/naturegeoscience. Reprints and permissions information is available online at http://npg.nature.com/reprintsandpremissions. Correspondence and requests for materials should be addressed to Y.S.

Figure legends

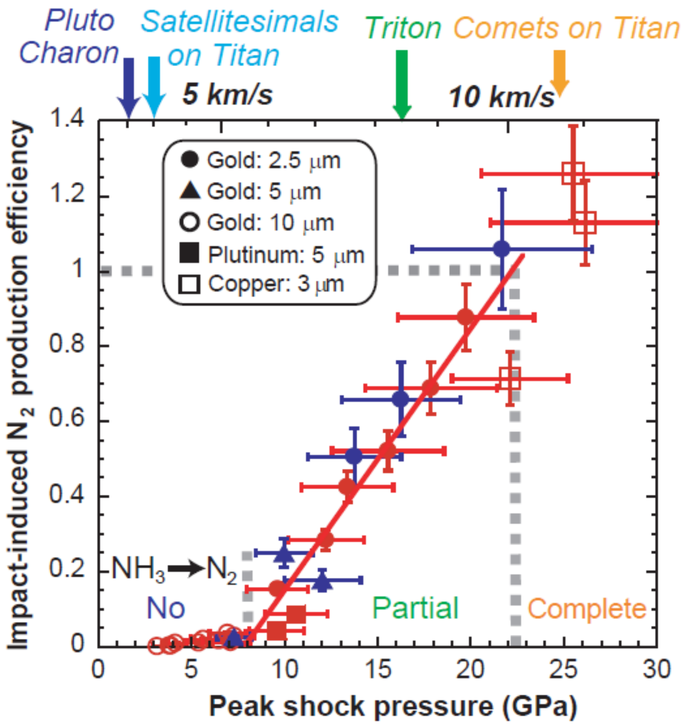
Figure 1. Efficiency of impact-induced N_2 production from NH_3–H_2O ice for different NH_3 contents (red: 50%; blue: 10%) (Symbols; see Methods). The vertical axis represents the amount of N_2 produced by impacts normalized by that contained in the isobaric core of the target as NH_3. The top axis represents the impact velocity of the H_2O–ice collision, which generates the peak shock pressure shown on the bottom axis (Supplementary Information). Arrows represent the average impact velocities onto icy planetary bodies[14].

Figure 2. Evolution of Titan's N_2 inventory during the LHB. Vertical dashed lines and horizontal yellow lines show the proposed LHB mass and current N_2 inventory, respectively. The concentration of NH_3, n_{NH3}, in comets is assumed to be 1%[19]. **a,** Cold Titan for different n_{NH3} values on Titan and impactor radius, r_p (20 and 30 km)[13]. **b,** Titan possessing N_2 (1.4 bar) before the LHB[17] for the surface temperature, T_{surf} = 75 K and 85 K, at n_{NH3} abundances of 3.0% and 4.3%, respectively (r_p = 20 km).

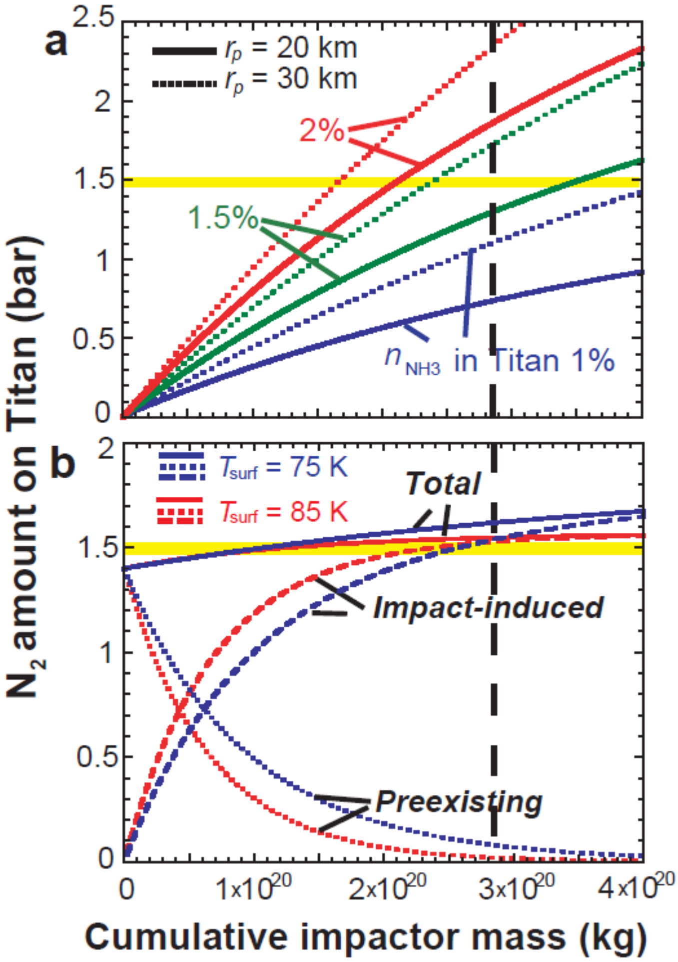
Figure 3. The concentration of NH_3, n_{NH3}, on Titan required for accumulating 1.5 bar of N_2 for various surface temperatures at impactor radius of 20 km (blue line) and 30 km

(red line). Black and grey arrows represent the possible ranges of n_{NH3} in satellitesimals that formed Saturnian satellites, as proposed by nebular models[11,12] and constrained from observations of Enceladus' plume[18], respectively. n_{NH3} in Enceladus' plume is ~1%[18], which provides a lower limit to n_{NH3} in the satellitesimals. In the case that the plume contains ~1% of N_2[18], which formed from NH_3, an upper limit of the initial n_{NH3} in the satellitesimals becomes ~4%.

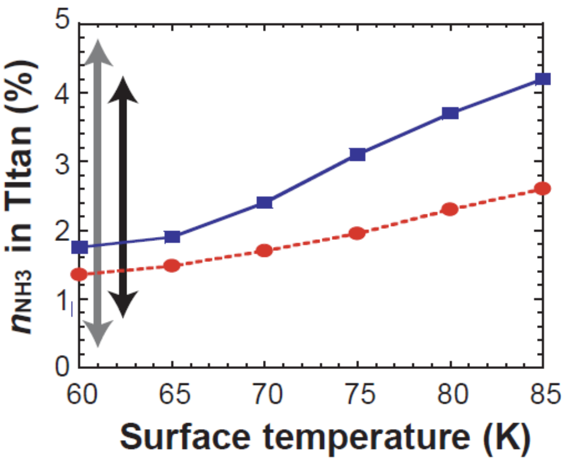
Figures



(Figure 1)


a
b
r_p = 20 km
r_p = 30 km
2%
1.5%
n_{NH3} in Titan 1%
T_{surf} = 75 K
T_{surf} = 85 K
Total
Impact-induced
Preexisting
N_2 amount on Titan (bar)
Cumulative impactor mass (kg)
0
1x10^{20}
2x10^{20}
3x10^{20}
4x10^{20}

(Figure 2)


n_{NH3} in Titan (%)
Surface temperature (K)
60
65
70
75
80
85

(Figure 3)