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# The Origin and Evolution of Saturn's Earth-like Moon, Titan

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**Abstract.** How did Titan, not Ganymede or any other moon, get endowed with a massive atmosphere is the focus of this paper. The two main components of Titan's atmosphere are nitrogen and methane. Nitrogen is almost certainly secondary, as on Earth, whereas methane may be primordial or secondary, or their combination. Methane to Titan is like water to Earth, with the cycle of methane on Titan resembling the hydrological cycle on Earth. The long-term fate of nitrogen and methane on Titan is intertwined through the methane cycle. Though biology has little to do with Titan's methane, unlike Earth, life as we don't know it – "weird" life – cannot be entirely ruled out. Irrespective of any life, the chemistry between methane and nitrogen on Titan may be similar to that on prebiotic Earth, thus providing a serendipitous window into the beginnings of habitability of our own planet. Though monumental progress has been made in unraveling the unique nature of Titan in the solar system, numerous unsolved mysteries remain, so, it is highly desirable to continue the exploration of Titan in the future.

## 1. Introduction

Titan is in a class of its own, but more like the Earth. It is the only moon with a substantial atmosphere amongst 173 or so known planetary satellites of the solar system. The atmospheric pressure at Titan's surface exceeds Earth's by 50%, and is second only to Venus amongst rocky planets and satellites. The atmosphere of Titan is made up of nitrogen ($N_2$) for the most part (94% by volume), like Earth (78%). Much of the rest of Titan's atmosphere is methane( 6% $CH_4$). Earth too has its methane( 1800 ppbv), nearly 95% of which is a metabolic byproduct of life. An important question is: does life have anything to do with Titan's methane too? Like Earth, Titan has water, but it is frozen solid at its cold surface, where the temperature is 94 K (-179 C). On the other hand, methane is close to its triple point at that temperature, so that it can, and does, exist in liquid, solid and the vapor phases on Titan, like water on Earth. The cycle of methane, complete with evaporation from the surface reservoirs of liquid methane, condensation and clouds in the troposphere, followed by rain and snow is so much like the hydrological cycle on Earth. Titan's geological features of mountains, dunes, rivers, network of channels flowing into lake basins, and islands are all too familiar features on Earth. Like Earth, Titan is a coupled system of the interior, surface and the atmosphere, so that communication between them is essential for the maintenance of an atmosphere. Finally, the present composition of Titan's surface and the atmosphere may provide a window into prebiotic chemistry of the Earth, i.e. Titan is like primordial Earth in deep freeze. In view of the above, it is evident that in many ways Titan resembles the

Earth. This paper is a brief synopsis of our current understanding of how Titan acquired its volatiles, particularly nitrogen and methane, how they evolved, and what their fate might be. For a comprehensive treatment of the topic the reader is referred to Atreya et al. (2009), with updates contained in this paper.

## 2. Where did Titan's nitrogen come from?

The discovery of an atmosphere on Titan has a long history. Titan was discovered in 1655 by Chritiaan Huygens. A quarter of a millenium later, in 1908 José Comas Solá detected limb darkening, which he attributed to the existence of an atmosphere around Titan. Nearly half a century later, in 1944, Gerard Kuiper's detected methane. A number of modelers predicted an atmosphere dominated by either $N_2$, Ar or Ne, with $CH_4$ as a minor constituent. Atreya et al. (1978) developed the first photochemical model that showed how a copious nitrogen atmosphere could be generated on primordial Titan starting with ammonia ($NH_3$). It wasn't until Voyager 1 made the first flyby of Titan in 1980 that $N_2$ was actually detected. As the detection of $N_2$ was in the UV, it corresponded to high altitudes, so there was no way of knowing whether the bulk of the $\sim$1500 mb surface pressure measured by Voyager was due to $N_2$ or some other gas, though $N_2$ was heavily favored on the basis of (somewhat uncertain) mean molecular weight derived from the radio occultation data. A quarter of a century later, on 14 January 2005 the Huygens probe of the Cassini-Huygens Mission descended through the smog filled atmosphere of Titan over a course of two and a half hours before landing on the surface. The probe carried a gas chromatograph mass spectrometer (GCMS), which made the first in situ measurement of the composition of the atmosphere (Niemann et al. 2005). The GCMS found that $N_2$ indeed makes up the bulk of the atmosphere, comprising 94% by volume, with methane at 5.65%, while the rest is in the form of $H_2$ (0.1%, and a product of $CH_4$) and trace constituents resulting from the coupled $N_2$-$CH_4$ photochemistry.

Cassini-Huygens was one of the most successful missions ever flown. Launched in 1997, it arrived at Saturn in 2004 just after northern winter solstice, and, after 13 years of highly productive life, the mission ended with the plunge into the planet on 15 September 2017 just after the northern summer solstice on Saturn. Wing-Huen Ip was instrumental in getting the Cassini-Huygens Mission going. Much of what follows is based on the unprecedented set of data sent back by this mission.

### 2.1. Did Titan acquire its nitrogen directly?

Nitrogen could be either primordial or secondary. Figure 1 illustrates the possible scenarios. If primordial, it would have been captured directly as $N_2$ in Titan's building blocks, like the gas giant planets (where it was subsequently converted to its present reservoir, ammonia, by Fischer-Tropsch process). In that case, other primordial constituents, especially the noble gases such as argon, would also be delivered along with $N_2$. Moreover, they would be in the solar ratio to $N_2$, which is 0.1 for $^{36}Ar/N_2$. Thus, $^{36}Ar$ was a key measurement for Huygens. The GCMS measurements, found $^{36}Ar/N_2$ = $2\times10^{-7}$, or about a factor of a million less than the solar ratio. Thus, it is clear that Titan's $N_2$ is not primordial. That is also consistent with the fact that trapping of both $N_2$ and Ar requires temperatures less than 40 K, which is much colder than 70-80 K where Titan formed.

### 2.2. Did nitrogen form on Titan from ammonia, instead?

Theoretical considerations in the 1980's (e.g., Prinn & Fegley 1981) had previously favored $NH_3$, instead of $N_2$, as the main nitrogen-bearing species on primordial Titan (details in Atreya et al. 2009). Ammonia can be converted to nitrogen either through photochemistry, by impacts, or endogenically (Fig. 1).

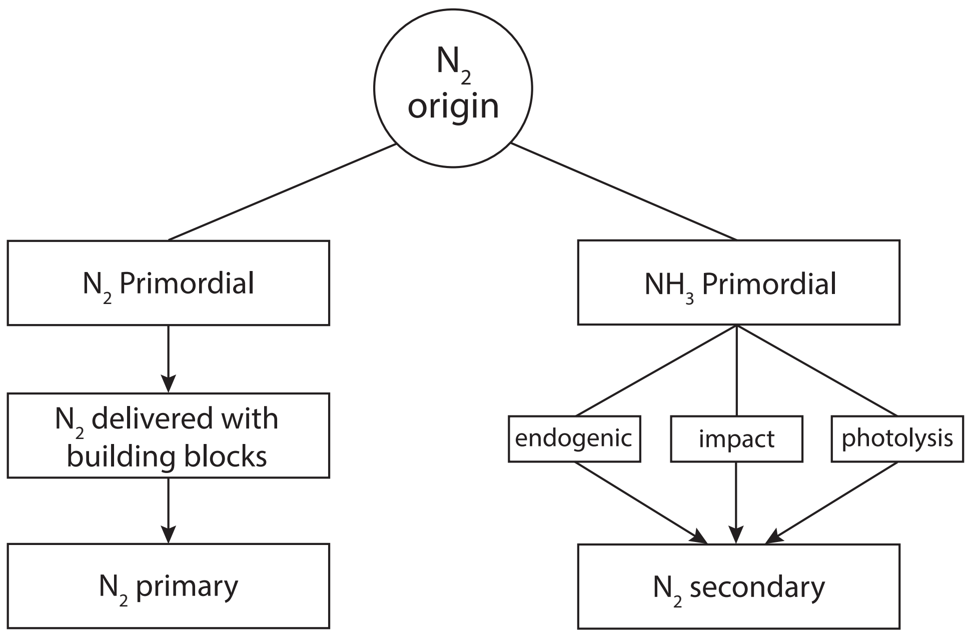


Figure 1. Potential origin of nitrogen ($N_2$) on Titan: primary or secondary?

#### 2.2.1. due to heat?

Early in its geologic history, Titan was warm due to the decay of short-lived radioactive elements. Surface temperatures may have reached 400 K, and the interior even hotter so as to thermally dissociate some of the $NH_3$ and convert it into $N_2$. A fraction of that $N_2$ would have been released to the atmosphere, while the rest could be trapped in the ice as clathrate. From time to time the trapped nitrogen would be expelled from the clathrates and replenish the nitrogen lost to space by escape. This scenario of endogenic production of $N_2$ was first proposed by Matson et al. (2007) and pursued further by Glein (2015). As discussed by Atreya et al. (2009), this mechanism is not borne out by the nitrogen isotope ratio measured in Titan's $N_2$. Thus, the endogenic production of $N_2$ on Titan is an interesting idea, but it does not seem to be responsible for the bulk of the nitrogen on Titan, unlike Earth, where it was the main mechanism for producing $N_2$ from nitrogen-bearing compounds, including organics.

#### 2.2.2. from comets?

While comets are deficient in nitrogen, ammonia is one of their principal components. So, in principle, cometary impacts could deliver nitrogen to Titan. Ammonia and other nitrogen bearing species such as HCN of the comets would be readily dissociated upon impact and could go on to form nitrogen. If that were the case, Titan should carry the imprint of cometary nitrogen isotope ratio. The difficulty is that there is no single nitrogen isotope ratio associated with the comets. Comets display a huge diversity, so that their $^{15}N/^{14}N$ ratio is all over the map, as shown in Figure 2. Moreover, it varies from one nitrogen reservoir to another (HCN, CN, $NH_2$), as expected from photochemical fractionation. A word of caution about $^{15}N/^{14}N$ in $NH_2$ is in order. Not only that it too has a huge range, it cannot be taken as a proxy for $NH_3$, the main N-reservoir in comets, for which no measurement presently exists. Thus, the $^{15}N/^{14}N$ ratio in Titan's atmosphere is between <0.5 to >2 times the known cometary values (Figure 2, shaded areas). Though the $^{15}N/^{14}N$ ratio in cometary $NH_3$ has not yet been measured, it is suspected from photochemical considerations that the discrepancy with Titan may become even larger, as discussed in Atreya et al. (2009). When adjusted for isotope fractionation due to escape, Titan's $^{15}N/^{14}N$ ratio is likely to be more in line with the value in the Earth's atmosphere, as is the case for similarly sized object, Mars, whose larger value in the atmosphere compared to that in Martian meteorites reflects loss of nitrogen by escape.

The D/H isotope ratio tells a similar story. When the D/H ratio was available in just 3 comets (Hale-Bopp, Hyakutake and Halley), it was consistent at $\sim 3\times10^{-4}$. A similar value of D/H=2.3(±0.5)$\times10^{-4}$ was also initially reported in Titan's atmosphere from Huygens GCMS (Niemann et al. 2005). That led some researcher to claim a cometary origin of volatiles on Titan. It was further bolstered by the measurement of D/H in the plume of Saturn's moon Enceladus, where a value of $2.9\times10^{-4}$ was found (Waite et al. 2009). The idea was that while the Titan's D/H measured by the GCMS was similar to the cometary value, it was from HD ($H_2$), not HDO ($H_2O$), but the value in the water vapor plume of Enceladus can be taken as a proxy for Titan's D/H in $H_2O$. And, that value is nearly identical to the value in above comets. New developments have made the cometary source considerably less attractive, however. First, Titan's D/H in HD has been revised downward to about half the early results, i.e. $1.35\times10^{-4}$ (Niemann et al. 2010) or close to terrestrial and consistent with the value in Titan's $CH_3D$; second, the value for Halley has been revised downward to $\sim 2.1\times10^{-4}$ because of laboratory data showing isotope fractionation in the sublimation of ice (Brown et al. 2012); and, third, most importantly, D/H ratio has now been measured in a dozen comets, and like $^{15}N/^{14}N$, it displays a huge spread, ranging from terrestrial (Hartley 2) to 4× terrestrial (2012F6/Lemmon). As shown in Figure 3, no single value can be assigned to the cometary D/H! Titan's D/H is for the most part in disagreement with the cometary values. Thus, current evidence argues against comets as being the sole source or even a major contributor to Titan's volatile inventory. The argument goes for both $N_2$ and $CH_4$.

Thus, neither the nitrogen nor hydrogen isotope ratios provide compelling evidence for cometary impacts as being responsible for the bulk of Titan's nitrogen (or methane – Sec. 3). There are other complicating factors to take into account as well. Cometary impacts would deliver hydrogen, not just from the dissociation of $NH_3$, but also from the breakdown of $H_2O$ and $CH_4$. Either all that hydrogen is still present on Titan, which it is not, or it was lost to space due to escape. The latter would require unrealistically large escape rates, 1000–10,000 times greater than the best models. In addition to hydrogen, the comets would introduce oxygen from $H_2O$ into Titan's atmosphere. The main oxygen-bearing species on Titan, CO, would then be substantially greater than measured. It's possible that some of the hydrogen would recombine with oxygen to produce water right back, but the total amount of hydrogen from all the cometary sources ($NH_3$ $CH_4$, $H_2O$) is just too large to get rid of or hide somewhere.

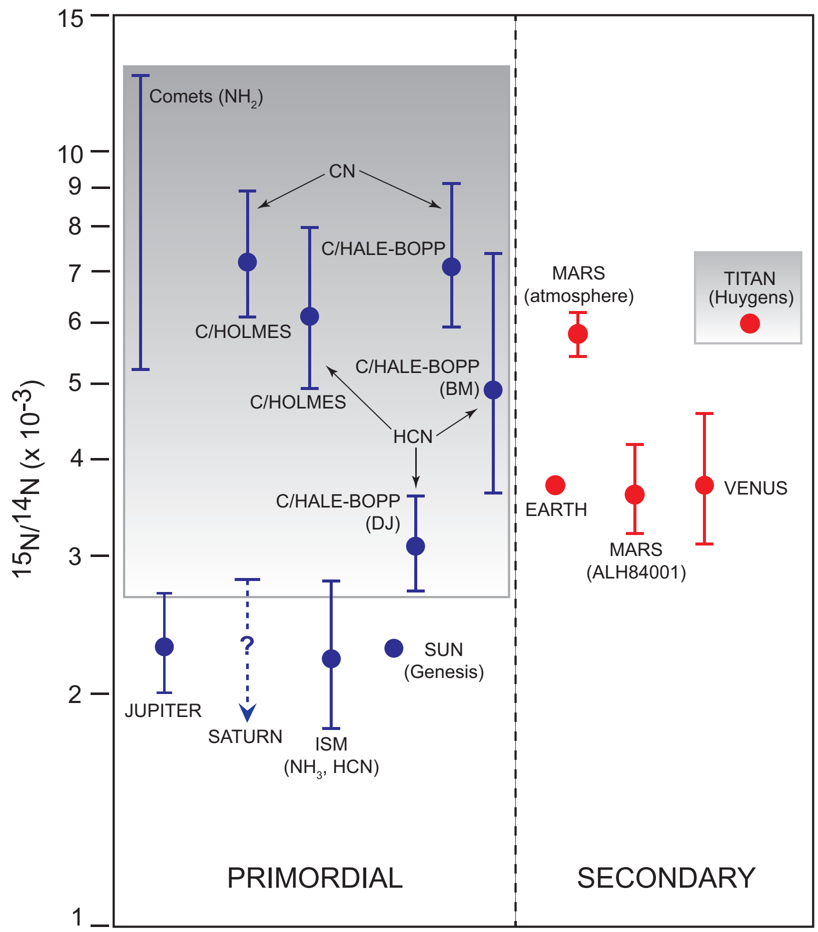


Figure 2. A comparison of the nitrogen isotope ratio in Titan's atmosphere with comets. For reference, values for the other solar system objects are also shown. Adapted from Fig. 7.2 of Atreya et al. (2009) with permission from Springer, and updated. Current values are listed in Atreya (2018). For HCN in C/Hale-Bopp, two values are reported: DJ, by David Jewitt (Jewitt et al. 1997) and BM, by Bockelee-Morvan.

Thus, comets may have contributed a fraction of the total initial inventory of $N_2$ on Titan, but all available evidence indicates bulk of Titan's nitrogen must have come from other means.

### 2.2.3. due to sunlight?

One obvious way of generating nitrogen on Titan is by the UV photolysis of ammonia, an idea proposed by a number of researchers in the 1970's, including John Lewis and Donald Hunten. There is no getting around it, especially considering that the solar UV flux was 1000-10,000 times greater in the past during the period of likely nitrogen formation on Titan. Atreya et al. (1978) showed that photochemistry is capable of producing more than 10 bars of $N_2$ on Titan. That was before any measurement of nitrogen on Titan existed, and the atmospheric pressures were speculated from negligible to as

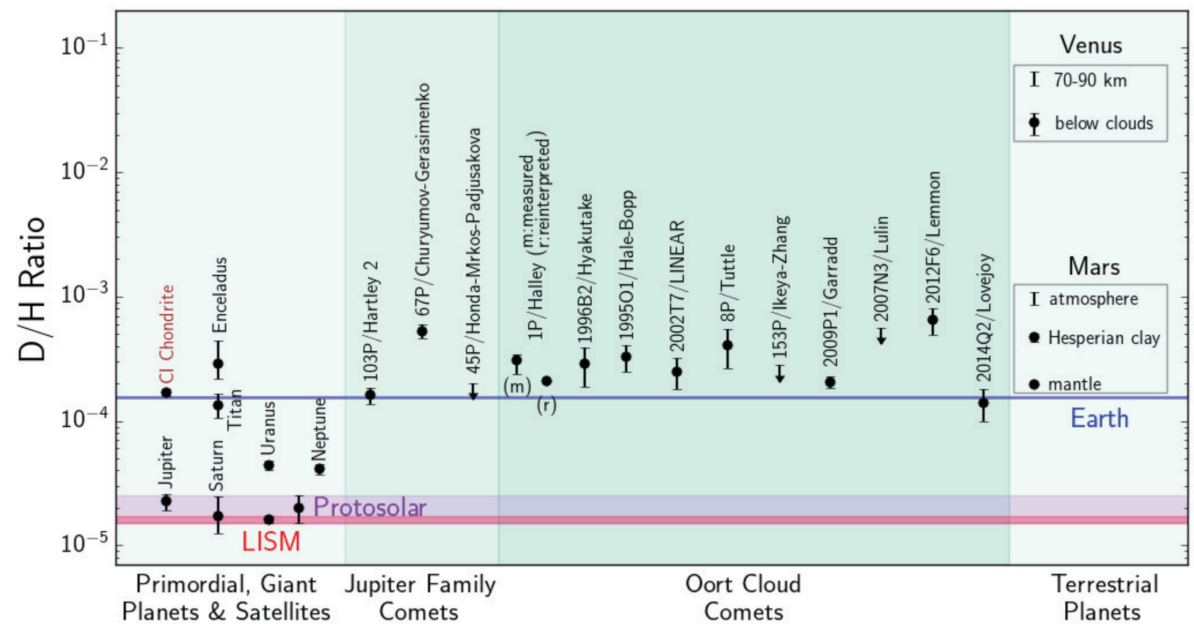


Figure 3. A comparison of the D/H isotope ratio in Titan's atmosphere and the comets. For reference, values for the other solar system objects are also shown. Earth's value is $1.558\times10^{-4}$ in SMOW (Standard Mean Ocean Water). D/H in Halley is shown as the actual measured value in water vapor (m) and its reassessment based on laboratory data, which show fractionation in the sublimation of ice to vapor (Brown et al. 2012). References for a number of values, especially the comets, plotted in this figure may be found in Hartogh et al. (2011) and Hartogh's update on pp12-13 in The European Far-Infrared Space Roadmap, ESA (2017): https://arxiv.org/ftp/arxiv/papers/1701/1701.00366.pdf.

much as 20 bars! During accretionary heating phase, ammonia would be prevented from freezing. Substantial quantities of $NH_3$ would exist in the vapor phase, which is essential for efficient photolysis. Figure 4 illustrates the conversion of $NH_3$ to $N_2$ on primordial Titan. The sweet spot is when Titan's temperature was between 150 K and 250 K. Below 150 K, ammonia would freeze out. Above 250 K, substantial water vapor would be present to interfere with the $NH_3$ chemistry, which would, for all practical purposes shut down the path to $N_2$. In the 150-250 K Goldilocks range, photolysis of ammonia would have generated 10 bars of nitrogen in ~25 million years (Atreya et al. 1978; Atreya et al. 2009). Models show that it took up to 100 million years for Titan to cool down from its initial 400 K warm surface in the past to the current temperature of 94 K. Thus there was plenty of time available for sufficient conversion of $NH_3$ to $N_2$ allowing for all uncertainties in the models. Today, the $N_2$ surface pressure on Titan is 1.5 bars, but larger production was necessary in the past to allow for loss of $N_2$ to space over time.

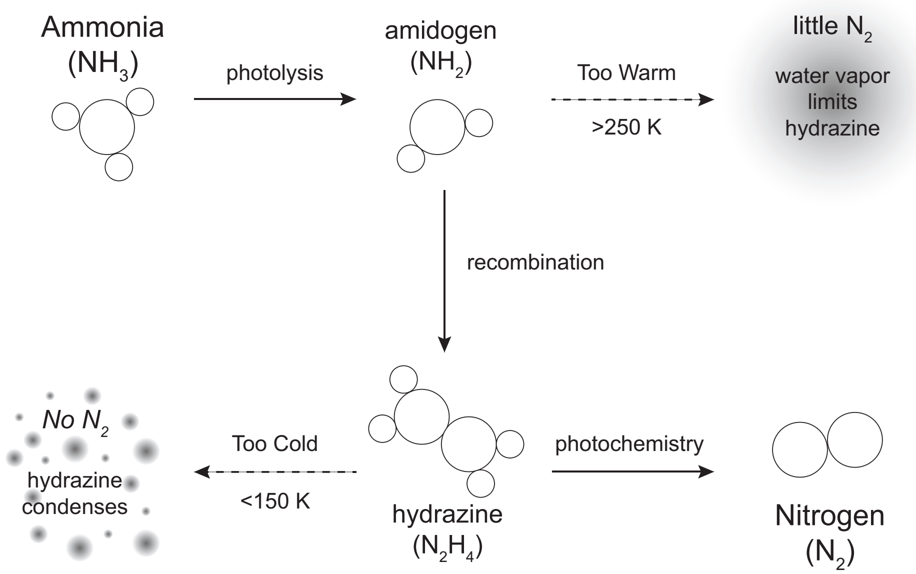


Figure 4. Chemical pathways for the conversion of ammonia ($NH_3$) to nitrogen ($N_2$) on primordial Titan. Adapted from Fig. 3 of Atreya (2010) with permission from Cambridge University Press, and updated.

## 3. Where did Titan's methane come from?

Like nitrogen, there are at least two possibilities for the existence of methane on Titan. It could have been delivered as methane in the building blocks of Titan, or it may have formed on Titan from "C" in the form of CO or $CO_2$, if the latter were the original C-bearing compounds instead of $CH_4$. There is yet another possibility: Titan's methane is biological in origin, as the bulk of Earth's methane. These possibilities are illustrated in Figure 5.

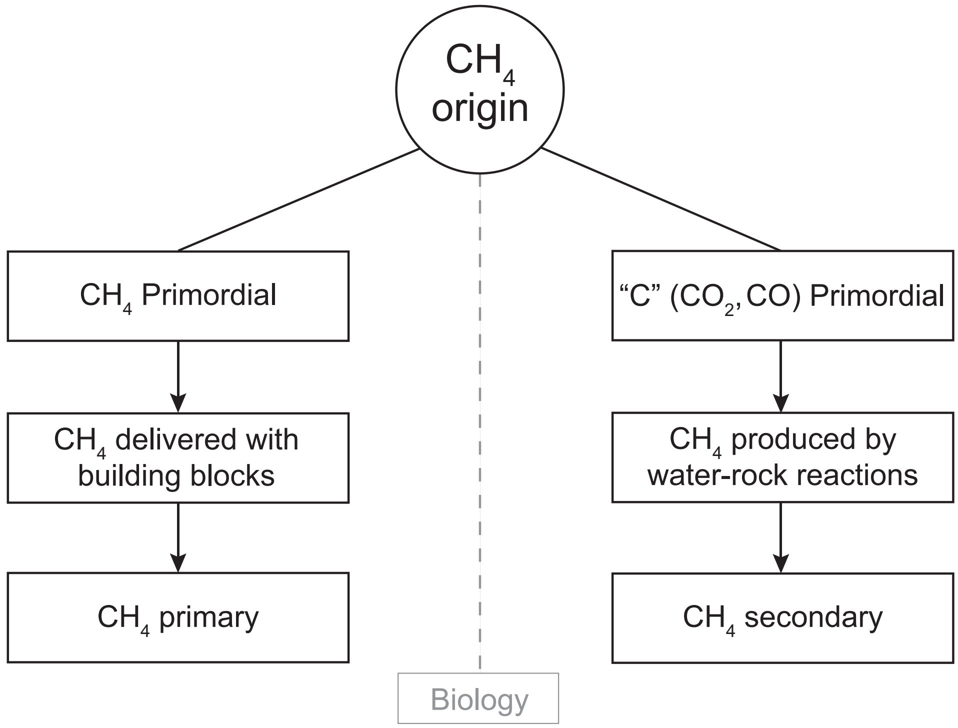


Figure 5. Potential origin of methane ($CH_4$) on Titan: primary, secondary, or biological?

### 3.1. Did methane arrive at Titan directly?

Some models in the 1980's indicated $CH_4$, not CO or $CO_2$, was the main C-bearing compound in Saturn's sub-nebula, the nursery of satellites. In that case, methane would be delivered directly as $CH_4$ by Titan's building blocks. Amongst other volatiles, Xe and Kr would also have been brought in along with $CH_4$, in solar proportions, as they get trapped in planetesimals at the same temperature range as $CH_4$. However, the Huygens GCMS did not detect Kr and Xe; their upper limits were $10^{-8}$, significantly below their expected mixing ratios of $5\times10^{-5}$ for Kr and $5\times10^{-6}$ for Xe! This implies that $CH_4$ was not directly delivered to Titan. A caveat is in order, however. Arguments have been made that Kr and Xe may still be present in the right proportion, but just not in the atmosphere – they may be trapped in clathrates beneath Titan's surface. Though that may be a possibility for Xe, it does not seem Kr would not be in the atmosphere. Furthermore, it seems odd that Xe and Kr are "permanently" trapped, as clathrates can be destabilized by any number of mechanical or thermal stresses, including impacts and cryovolcanism, which would release the volatiles into the atmosphere. Indeed, that is how methane is believed to be released from time to time (more on that later), and the presence of radiogenic argon in the atmosphere is evidence for communication with the interior. Considering that no data exist on the composition of Titan's clathrates, it would be wise to still consider the direct capture of methane as a possibility for some, if not all of Titan's methane.

### 3.2. Did methane form on Titan from water-rock reactions?

If the original C-bearing compounds were CO and $CO_2$, as certain satellites formation models showed, they could be converted to $CH_4$ by a process known as serpentinization. Serpentinization is actually a 2-step process. In the first step, $H_2$ is liberated from reaction between rock and water, the latter being in liquid phase in Titan's interior all the way down to the rocky core during the accretionary heating phase of primordial Titan. In the second step, the $H_2$ molecules react with CO or $CO_2$ to produce $CH_4$ by metal-catalyzed Fisher-Tropsch process. This is a well-studied phenomenon in the Earth's oceans, especially near spreading centers such as Lost City and Black Smokers. Once produced, methane would be stored in subsurface clathrate hydrates in Titan. From time to time, when the clathrates are destabilized methane would be released, forming pools, ponds and seas of methane on Titan's surface. It would exist in the vapor phase in the atmosphere, in equilibrium with the liquid at the surface. Atreya et al. (2006) showed that serpentinization is a viable mechanism for generating Titan's observed methane, and Glein (2015) reaffirmed the idea.

### 3.3. Bugs?

Microbes produce most of the methane on Earth, so it seems logical to consider that as a possibility for Titan also. McKay & Smith (2005) proposed that Titanian microbes would metabolize hydrogen and acetylene ($C_2H_2$) or ethane ($C_2H_6$) to produce methane. If that were indeed the case, the nutrients, $C_2H_2$ and $H_2$ would be severely depleted at the surface, particularly $H_2$. However, Huygens GCMS did not find any evidence of such depletion. The long-lived $H_2$, with a lifetime of a million years, was found to have a uniform mixing ratio (0.1%) from the upper atmosphere to the surface (Niemann et al. 2010). Another point to make is that the methanogenic argument is circular, i.e. in order to make methane, it would have had to be present already since the nutrients, $C_2H_2$, $C_2H_6$ and $H_2$, can come only from the $CH_4$ photochemistry. Despite above difficulties with the methanogenesis hypothesis, life as we don't know it is an interesting idea for Titan, even if on the fringe. Liquid hydrocarbons, in place of water, may serve as the medium for nutrient transport and biochemical reactions, and both solar and chemical energy exist on Titan, so future observations should make an effort to explore the possibility of "weird" life on Titan.

## 4. No methane, little nitrogen: Titan's methane cycle

Methane is critical to the maintenance of Titan's atmosphere. If methane disappeared, Titan's atmosphere would be a relic of its glorious past. This is due to the fact that methane serves as a strong greenhouse gas on Titan. The photochemical haze produced from the $CH_4$-$N_2$ photochemistry (Wilson & Atreya 2004) together with the collision induced opacity between various combinations of $CH_4$, $N_2$ and $H_2$ (product of $CH_4$) results in the greenhouse warming of both the stratosphere and the troposphere, which is essential for keeping nitrogen from condensing as liquid $N_2$. But, the fact is methane has a finite lifetime against photochemical destruction. In ~30 Myr, all of the 250 trillion tons of methane in Titan's atmosphere would be irreversibly converted to its products (Wilson & Atreya 2009). The greenhouse warming due to $CH_4$ would drop. Temperatures would drop precipitously. And, nitrogen would begin to condense, forming lakes and ponds of liquid $N_2$ on the surface. The atmospheric pressure would drop to a maximum of tens of millibars compared to 1500 mb currently. Thus, in order to sustain an atmosphere on Titan, the methane destroyed must be replenished at fairly regular intervals not to exceed a few tens of millions of years. Estimates based on cosmogonic considerations indicate Titan should have amassed sufficient methane to last several billion years (Atreya et al. 2009), likely stored in the subsurface. There does not appear to be an energy crisis on Titan!

Evaporation from Titan's hydrocarbon lakes and seas is the source of methane gas in the atmosphere. In the troposphere, methane condenses and rains or snows out. That cycle starts all over again, much like the hydrological cycle on Earth. However, some methane vapor punches through the cold trap, the tropopause, and gets into the stratosphere. The neutral chemistry below ~900 km and charged particle chemistry above then destroy methane irreversibly. Figure 6 is an illustration of these phenomena. The process continues until all the methane has evaporated from the lakes and seas. Titan's lakes and seas are big. The largest, Kraken Mare, has a surface area of 400,000 km$^2$. By way of comparison, Kraken Mare is five times larger than Lake Superior, the largest lake on Earth, and 50,000 times the area of Sun Moon Lake, Taiwan's largest lake. Even though the amount of liquid (methane, together with other dissolved hydrocarbons such as ethane and propane) in Titan's lakes and seas is huge, estimated to be 40–100 times the proven oil reserves on Earth, it still amounts to a relatively small fraction (~1%) of the 250 trillion tons in the atmosphere, which is being constantly eroded away by atmospheric photochemistry, as discussed above. Thus, in order to prevent Titan's atmosphere from collapsing, the lakes must be recharged with methane either episodically or at regular intervals, not to exceed a few tens of millions of years. Impacts, small thermal perturbations and cryovolcanism could all trigger the release of a portion of methane stored in the clathrates and recharge the lakes and seas, which would in turn replenish the gas destroyed in the atmosphere. It is also conceivable that Titan's atmospheric pressure fluctuates between its high value seen today and somewhat lower values when methane levels drop and before the lakes are recharged. Future observations should search for any evidence of such possible fluctuations in Titan's atmospheric mass.

## 5. What went wrong with Ganymede, gas-wise?

It is puzzling that while Titan has a massive atmosphere, Ganymede, the largest moon in the solar system, has practically none, especially considering that the two bodies are nearly equal in mass, comprising approximately half rock and half water/ice, have similar escape velocity (~2.7 km s$^{-1}$) and lie at approximately same distance (~10$^6$ km) from their planets. Since the fate of any atmosphere was set into motion billions of years ago, it is difficult to know what really happened on Ganymede. Nevertheless, one can make a reasonable guess about the processes that made Titan so different from Ganymede in so far as the atmosphere goes. Why any rocky body has an atmosphere depends on a number of factors, such as the acquisition, evolution, and maintenance of volatiles over time. It is conceivable that, unlike Titan, Ganymede never really acquired nitrogen in any form. As discussed in Sec. 2.1 direct capture of $N_2$ did not happen at Titan, and it would be even more difficult at Ganymede because of the even higher temperatures in the Jovian sub-nebula, as $N_2$ can only be trapped at $< 40$ K. In fact, the higher temperatures may prevent even $NH_3$ from getting trapped in Ganymede's building blocks, or at least greatly reduce its amount. Even if Ganymede did acquire some

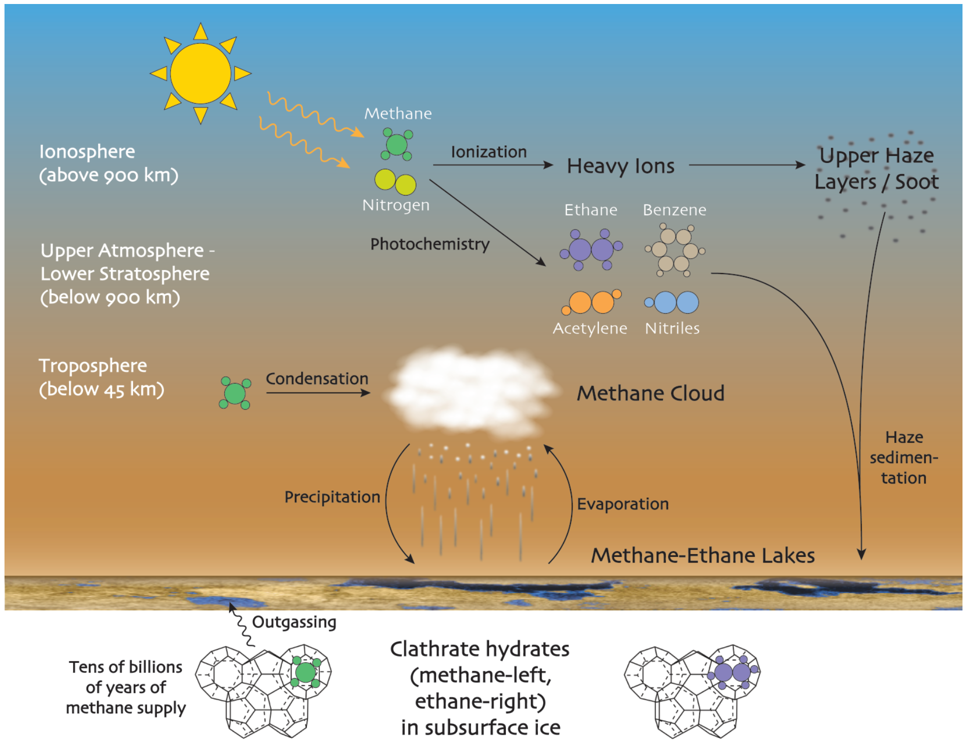


Figure 6. The cycle of methane on Titan. Figure 4 of Atreya (2010), reproduced here with permission from Cambridge University Press. Parts of the original figure were inspired by figures in the author's previous publications, including a figure on pp. 48–49 of Atreya (2007b), Figure 1 of Atreya (2007a) and Figure 3 of Lunine & Atreya (2008). Choukroun & Sotin (2012) and Christophe Sotin (personal comm. 2016) propose ethane substitution in the methane clathrates (not shown), which would displace a fraction of methane that would subsequently find its way into lakes and the atmosphere.

ammonia, it needs to be processed to a stable terminal molecule, nitrogen. That takes time. At Titan, it may have taken as much as 25 Myr to produce the atmosphere of nitrogen. During that "evolutionary" phase, first, ammonia cannot be eroded away, and second, it needs to be continually supplied to the atmosphere to keep the conversion to $N_2$ going until sufficient quantities have accumulated. The erosion of any nascent atmosphere at Ganymede is expected to be severe due to impacts and radiation, both of which are much more intense at Ganymede than Titan. In particular, the magnetospheric power at Jupiter is 1000–10,000 times greater than at Saturn. Even though Titan spends a good fraction of its time in Saturn's magnetosphere (depending on the solar wind), Ganymede is constantly bombarded by high-energy charged particles exceeding MeV's in energy. As a result, any atmosphere trying to get a foot-hold on Ganymede would be rapidly stripped away. The effect of radiation is clearly evident in the traces of $O_2$, $O_3$, H and $H_2O_2$ detected at the surface of Ganymede, but not Titan. They are best explained by radiolysis of surface ice by the energetic charged particles at Ganymede. Their lack at Titan implies that radiolysis of surface ice now or in the past was benign at Titan compared to Ganymede, as expected. In view of the above factors, either Ganymede never acquired the volatiles needed to form an atmosphere, or if any atmosphere did begin to form, it had little chance of hanging around for long. Other factors, including a deep internal ocean and a small intrinsic magnetic field that set Ganymede apart from Titan, may also have contributed to the lack of an atmosphere on Ganymede in some mysterious ways. However, my own preferred explanation is the one described above.

## 6. Summary

Titan's massive atmosphere of nitrogen is secondary, formed from a nitrogen-bearing molecule, most likely ammonia, which is the dominant form of nitrogen in the outer solar system. In principle, Titan's building blocks could have delivered methane directly; however, pending future work, available isotopic evidence and theoretical considerations tend to favor its formation on Titan. Methane is key to the maintenance of Titan's atmosphere. In the absence of methane, Titan's atmosphere would undergo a dramatic reduction. However, models indicate there is no energy crisis on Titan! Sufficient methane is believed to be stored in the subsurface clathrates, so as to keep the lakes and subsequently the atmosphere supplied with methane for billions of years, and thus make up for the erosion of this gas due to photolysis. Despite methane replenishment, diminution of the atmosphere is inevitable due to the escape of nitrogen to space over time, unless some nitrogen is also stored in clathrates, a reasonable assumption. Though methane is unlikely to be of biologic origin, likelihood of "weird" life in Titan's vast lakes and seas of hydrocarbons can not be entirely ruled out. There is yet another potential medium for life on Titan – its water ocean – some tens of kilometers beneath the surface. Minerals dissolved in the ocean when it was still in contact with the rocky core during Titan's accretionary heating period may serve as nutrients to any microbes, provided that they could adapt to the high concentration of ammonia in the ocean. Whether or not any form of life exists on Titan, chemistry in the atmosphere and possibly surface is likely to produce the molecules that would have existed on prebiotic Earth. Not only Titan resembles the Earth in many ways, it is an ideal laboratory to learn about our own planet before life emerged. Studying Titan as a coupled system of the interior, surface and the atmosphere, with special attention to the surface and the surface-atmosphere interactions, would serve any future missions to Titan well.

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### References

Atreya, S. 2007a, Science, 316, 843. `http://science.sciencemag.org/content/316/5826/843.full.pdf`

Atreya, S. K. 2007b, Scientific American, 296, 42

— 2010, in Galileo's Medicean Moons: Their Impact on 400 Years of Discovery, edited by C. Barbieri, S. Chakrabarti, M. Coradini, & M. Lazzarin, vol. 269 of IAU Symposium, 130

— 2018, The Origin and Evolution of Saturn, with Exoplanet Perspective (Cambridge: Cambridge University Press). URL `2016arXiv160604510A`

Atreya, S. K., Adams, E. Y., Niemann, H. B., Demick-Montelara, J. E., Owen, T. C., Fulchignoni, M., Ferri, F., & Wilson, E. H. 2006, Planetary and Space Science, 54, 1177

Atreya, S. K., Donahue, T. M., & Kuhn, W. R. 1978, Science, 201, 611

Atreya, S. K., Lorenz, R. D., & Waite, J. H. 2009, Volatile Origin and Cycles: Nitrogen and Methane (Dordrecht: Springer Netherlands), 177. URL https://doi.org/10.1007/978-1-4020-9215-2_7

Brown, R. H., Lauretta, D. S., Schmidt, B., & Moores, J. 2012, Planetary and Space Science, 60, 166

Choukroun, M., & Sotin, C. 2012, Geophysical Research Letters, 39, n/a. L04201, URL http://dx.doi.org/10.1029/2011GL050747

Glein, C. R. 2015, Icarus, 250, 570

Hartogh, P., Lis, D. C., Bockelée-Morvan, D., de Val-Borro, M., Biver, N., Küppers, M., Emprechtinger, M., Bergin, E. A., Crovisier, J., Rengel, M., Moreno, R., Szutowicz, S., & Blake, G. A. 2011, Nat, 478, 218

Jewitt, D., Matthews, H. E., Owen, T., & Meier, R. 1997, Science, 278, 90

Lunine, J. I., & Atreya, S. K. 2008, Nature Geoscience, 1, 159

Matson, D. J., Atreya, S. J., Castillo-Rogez, J. J., Johnson, T., Adams, E., & Lunine, J. 2007, AGU Fall Meeting Abstracts, P21D-04

McKay, C. P., & Smith, H. D. 2005, Icarus, 178, 274

Niemann, H. B., Atreya, S. K., Bauer, S. J., Carignan, G. R., Demick, J. E., Frost, R. L., Gautier, D., Haberman, J. A., Harpold, D. N., Hunten, D. M., Israel, G., Lunine, J. I., Kasprzak, W. T., Owen, T. C., Paulkovich, M., Raulin, F., Raaen, E., & Way, S. H. 2005, Nat, 438, 779

Niemann, H. B., Atreya, S. K., Demick, J. E., Gautier, D., Haberman, J. A., Harpold, D. N., Kasprzak, W. T., Lunine, J. I., Owen, T. C., & Raulin, F. 2010, Journal of Geophysical Research: Planets, 115, n/a. E12006, URL http://dx.doi.org/10.1029/2010JE003659

Prinn, R. G., & Fegley, B., Jr. 1981, ApJ, 249, 308

Waite, J. H., Jr., Lewis, W. S., Magee, B. A., Lunine, J. I., McKinnon, W. B., Glein, C. R., Mousis, O., Young, D. T., Brockwell, T., Westlake, J., Nguyen, M.-J., Teolis, B. D., Niemann, H. B., McNutt, R. L., Perry, M., & Ip, W.-H. 2009, Nat, 460, 487

Wilson, E. H., & Atreya, S. K. 2004, Journal of Geophysical Research: Planets, 109, n/a. E06002, URL http://dx.doi.org/10.1029/2003JE002181

Wilson, E. H., & Atreya, S. K. 2009, Journal of Physical Chemistry A, 113, 11221