

Titan's methane cycle

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Abstract

Methane is key to sustaining Titan's thick nitrogen atmosphere. However, methane is destroyed and converted to heavier hydrocarbons irreversibly on a relatively short timescale of approximately 10–100 million years. Without the warming provided by CH₄-generated hydrocarbon hazes in the stratosphere and the pressure induced opacity in the infrared, particularly by CH₄-N₂ and H₂-N₂ collisions in the troposphere, the atmosphere could be gradually reduced to as low as tens of millibar pressure. An understanding of the source-sink cycle of methane is thus crucial to the evolutionary history of Titan and its atmosphere. In this paper we propose that a complex photochemical-meteorological-hydrogeochemical cycle of methane operates on Titan. We further suggest that although photochemistry leads to the loss of methane from the atmosphere, conversion to a global ocean of ethane is unlikely. The behavior of methane in the troposphere and the surface, as measured by the Cassini-Huygens gas chromatograph mass spectrometer, together with evidence of cryovolcanism reported by the Cassini visual and infrared mapping spectrometer, represents a "methalogical" cycle on Titan, somewhat akin to the hydrological cycle on Earth. In the absence of net loss to the interior, it would represent a closed cycle. However, a source is still needed to replenish the methane lost to photolysis. A hydrogeochemical source deep in the interior of Titan holds promise. It is well known that in serpentinization, hydration of ultramafic silicates in terrestrial oceans produces H_{2(aq)}, whose reaction with carbon grains or carbon dioxide in the crustal pores produces methane gas. Appropriate geological, thermal, and pressure conditions could have existed in and below Titan's purported water-ammonia ocean for "low-temperature" serpentinization to occur in Titan's accretionary heating phase. On the other hand, impacts could trigger the process at high temperatures. In either instance, storage of methane as a stable clathrate-hydrate in Titan's interior for later release to the atmosphere is quite plausible. There is also some likelihood that the production of methane on Titan by serpentinization is a gradual and continuous on-going process.

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1. Introduction

Strobel (1974) was the first to show that photolysis destroys methane (CH₄) on Titan. Indeed, the Voyager observations of Titan in 1980 revealed the existence of a number of simple and C₂-, C₃-, and C-N-H hydrocarbons (Hanel et al., 1981; Coustenis et al., 1989; Coustenis et al., 1991), presumably the result of methane-nitrogen photo-

chemistry in Titan's stratosphere. Several comprehensive photochemical models were developed following the Voyager results, most notably by Yung et al. (1984), Lara et al. (1996), Lebonnois et al. (2001), and Wilson and Atreya (2004). These authors found the photochemical lifetime of CH₄ to be in the 10–100 million year range, which is small compared to Titan's age. Once methane is destroyed, Titan's stratosphere and troposphere may become too cold for nitrogen to remain in the gas phase. In the extreme case, under conditions of fainter young sun and high surface albedo, condensation of large quantities

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of nitrogen gas to liquid would follow, leaving behind a fraction of the current amount as N_2 vapor in the atmosphere. Lorenz et al. (1997) calculate that the atmospheric pressure of N_2 could be reduced to as low as tens of millibar in this case. The loss of nitrogen from the atmosphere would be less severe for the current solar luminosity. Even if Titan's atmosphere does not undergo periodic collapse, a mechanism for replenishment of methane lost to photolysis needs to be found in order to maintain a stable atmosphere. In this paper, using the data from Cassini–Huygens, we discuss a “methalogical” cycle on Titan, complete with evaporation from the surface, condensation, rain-out, and release of methane from the interior. Like the terrestrial hydrological cycle, this is expected to be a closed cycle. However current data are inadequate for evaluating whether all of the methane that does seep from the surface into the interior is recirculated back out again. If it is not, condensation would also represent loss of methane from Titan's atmosphere, exacerbating the need for replenishment. We also outline briefly how water-rock reactions in Titan's interior could help generate methane in Titan's interior.

2. Methane loss

Photochemistry and condensation are effective mechanisms for removing methane from Titan's atmosphere. Non thermal escape from the atmosphere could also occur (Yelle et al., 2005), but it would represent a relatively small loss. This is indicated by the $^{13}C/^{12}C$ ratio measured by the Huygens Gas Chromatograph Mass Spectrometer (GCMS) which is quite close to the terrestrial (inorganic) value, unlike the $^{15}N/^{14}N$ ratio (Niemann et al., 2005). First, we review the photochemical loss briefly, as it has been discussed extensively in recent literature. This is then followed by a discussion of the removal from the troposphere due to condensation.

2.1. Loss from stratosphere: photochemistry

Destruction of methane is dominated by photochemistry that occurs at approximately 700 km and above, with a small contribution by the charged particles. Photolysis of methane below 140 nm leads to the production of short-lived, fast-reacting radicals, CH_3 , CH_2 , and CH . The self-reaction of methyl radicals (CH_3) forms ethane (C_2H_6). Reactions of other radical species with atmospheric molecules, including nitrogen and hydrogen, followed by photolysis and subsequent reactions of stable heavier hydrocarbons result in the formation of more and more complex C_xH_y and nitrile (C–N–H) species. Treating the atmosphere and ionosphere as a coupled system, the latest photochemical model by Wilson and Atreya (2004) predicts the height profiles of three dozen stable hydrocarbons. An important result of this work and others (e.g. Cabane et al., 1992; Lebonnois et al., 2002; Wilson and Atreya, 2003) is the condensation of hydrocarbons to

hazes. Polymers of polyacetylenes/polyyenes and nitriles form hazes in the upper atmosphere (>500 km), whereas polycyclic aromatic hydrocarbon (PAH) polymers condense to form hazes in the middle and lower stratosphere (<200 km). We illustrate this with a simplified schematic in Fig. 1. Despite this conversion process, some hydrocarbons survive condensation, until they approach the tropopause cold trap where a vast majority of them condense out. This is illustrated in Fig. 2. Condensation of methane will be treated separately in the next section.

Here we discuss briefly the fate of ethane, since it has a strong bearing on the fate of methane itself. As carbon atoms are primarily found to be in the form of methane in Titan's atmosphere, one of the ultimate destinations of these atoms is expected to be synthesis into the stable molecule, ethane, through methane destruction and subsequent methyl radical recombination, followed by condensation of the ethane product. Consideration of this process led to the suggestion by Lunine et al. (1983) of an ethane ocean covering significant areas, perhaps even 100% of Titan's surface. Later photochemical models supported this idea as illustrated by Yung et al. (1984) who calculated a C_2H_6 downward flux at the tropopause of $5.8 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$ to be removed by condensation. With the inclusion of additional carbon sinks, especially chemical pathways leading to the end product, Titan haze, Wilson and Atreya (2004) determined a smaller C_2H_6 net production rate of $1.6 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$ to be balanced by ethane condensation. Barth and Toon (2003) used a microphysical model to predict possible ethane ice clouds between 8 and 50 km.

Despite these predictions, the Cassini–Huygens observations so far do not show evidence of “wide-spread” reservoirs of C_2H_6 condensate on the surface or indicate significant condensation in the troposphere of Titan. Ethane is a very volatile constituent, compared to other higher-order hydrocarbons, and its high saturation vapor pressure undermines its condensation in Titan's atmosphere except in a region of about 15 km, just above the tropopause, as shown in Fig. 2 and detailed in Fig. 3b. Neglecting condensation, the distribution of C_2H_6 in Titan's lower atmosphere is governed exclusively by downward diffusive transport of ethane produced at higher altitudes. Assuming nominal eddy diffusion profile (Fig. 3a) and a boundary condition of net zero flux at the surface, the photochemical model yields an ethane condensation flux of $1.6 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$ and C_2H_6 stratospheric abundances that are consistent with the Cassini orbiter infrared spectrometer (CIRS) observations (Fig. 3b). As CIRS abundances are derived assuming a uniform mixing ratio down to the condensation region, matching the converted column density requires less mixing in the stratosphere, as given by eddy profile K2 (Fig. 3a). Assuming a smaller eddy diffusion profile yields the required larger C_2H_6 densities in the stratosphere and a column density of $1.4 \times 10^{20} \text{ cm}^{-2}$ above 60 km or a column mixing ratio of 1.9×10^{-5} . This reduction in eddy

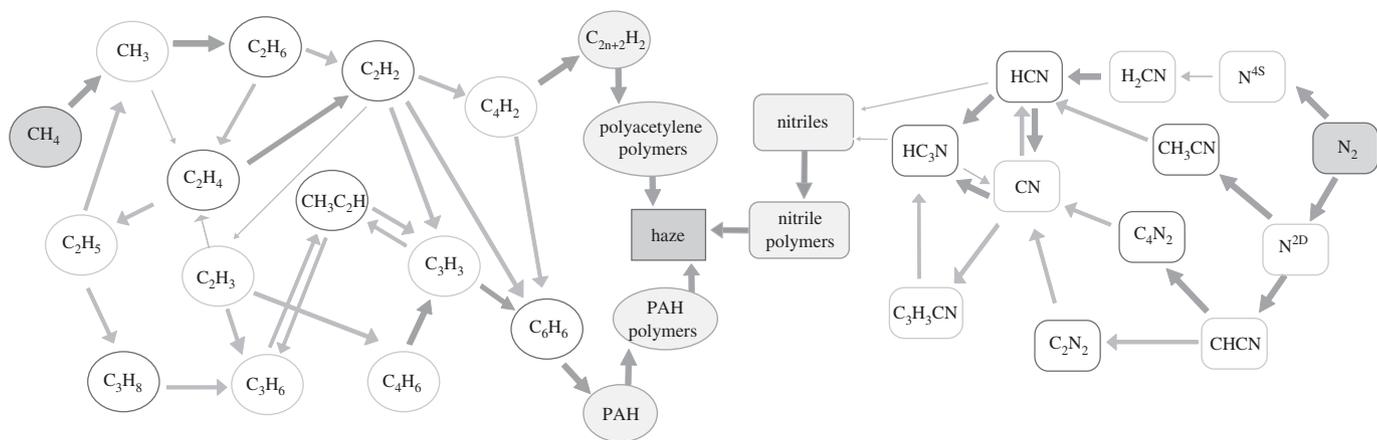


Fig. 1. A simplified photochemical scheme for the formation of hazes in Titan's atmosphere is shown. The photolysis of methane leads to the formation of polycyclic aromatic hydrocarbon (PAH) and polyacetylene polymers, whereas the presence of nitrogen allows for the formation of the nitriles and nitrile polymers, all leading to the production of haze and the resulting loss of methane from the atmosphere. The species in bold have been detected in Titan's atmosphere to date. For full photochemical scheme, see Wilson and Atreya (2004).

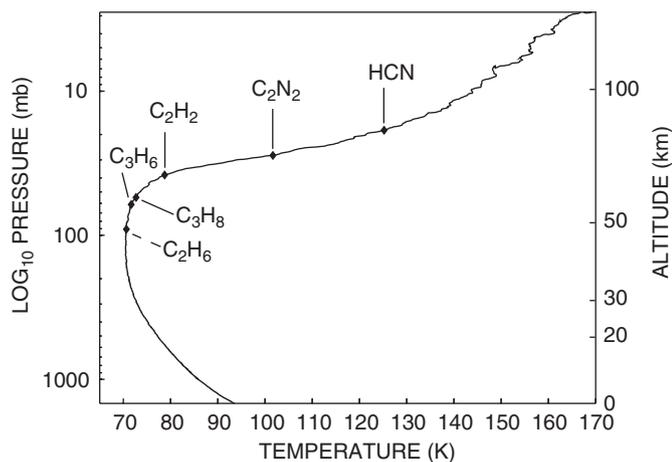


Fig. 2. Condensation of hydrocarbons and nitriles in the atmosphere of Titan is shown as a function of altitude. The mole fractions for the atmospheric species are taken from Wilson and Atreya (2004), and are based on observations and model predictions. HCN, C_2N_2 , C_2H_2 , C_3H_8 , and C_3H_6 will condense above the tropopause. There is also a possibility of ethane condensation (as indicated by the dashed line), but see text and Fig. 3 for a full discussion of ethane condensation. Methane condensation is shown Fig. 5.

mixing in the lower atmosphere results in a smaller C_2H_6 condensation flux of $1.2 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$. Such a condensation rate, corresponding to $5.9 \times 10^{-14} \text{ g cm}^{-2} \text{ s}^{-1}$, primarily in the form of ice condensate, compares with a haze production rate of $0.5\text{--}3 \times 10^{-14} \text{ g cm}^{-2} \text{ s}^{-1}$ (McKay et al., 2001; Wilson and Atreya, 2003) deposited on the ground, assuming a steady-state haze abundance. Thus, on the surface, ethane condensate is expected to compete with the haze material. However, the amount of condensed ethane is expected to vary, due to temperature changes at the surface and the troposphere, as measured by Voyager. Flasar et al. (1981) found the surface temperature change of $\sim 2.5 \text{ K}$ equator-to-pole and the tropopause change of

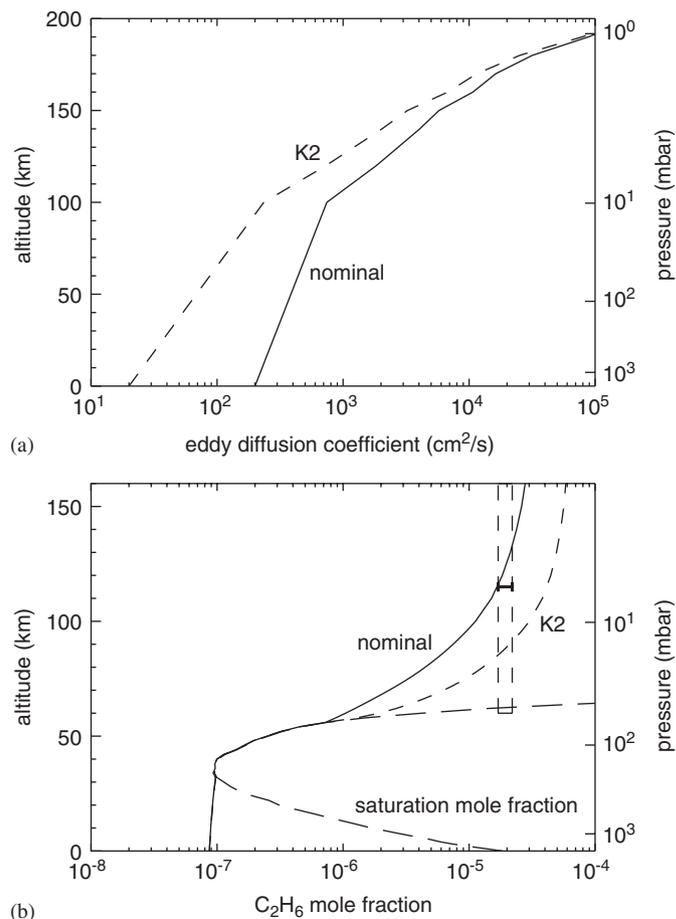


Fig. 3. (a) Nominal and reduced (K_2) eddy diffusion coefficients below 200 km, used in the photochemical model of Wilson and Atreya (2004). (b) C_2H_6 mole fraction profile in the lower atmosphere for nominal (solid line) and reduced (short-dashed line) eddy diffusion profiles, compared with the saturation mole fraction profile (Ziegler, 1959). The horizontal bar represents the CIRS C_2H_6 stratospheric observations at an altitude typical for the peak in C_2H_6 contribution function, while the dashed box represents the CIRS observation assuming a uniform mole fraction extending to the condensation region (Flasar et al., 2005).

roughly 3 K. Also, as these temperature changes might cause the evaporation of the surface condensate, the resulting gaseous ethane might be incorporated into compound clathrate–hydrates possibly present on Titan’s surface (Osegovic and Max, 2005).

From the above discussion we conclude that the end product of photochemistry is a conversion of methane to ethane and hazes in comparable amounts, with ethane condensate far smaller than previously predicted. Methane is thus destroyed in Titan’s stratosphere.

2.2. Loss from troposphere: “methological cycle”

The mole fraction of methane was measured in situ from 140 km to the surface by the Huygens GCMS. The measurements continued for another 70 min after landing on the surface. The CH_4 mole fraction down to the surface is shown in Fig. 4 (Niemann et al., 2005). There are several points to be made about this distribution that are relevant to the existence of a methological cycle on Titan. The methane mole fraction has a constant value of $(1.41 \pm 0.07) \times 10^{-2}$ in the stratosphere, in agreement with the CIRS result of $(1.6 \pm 0.5) \times 10^{-2}$ (Flasar et al., 2005). Since methane photolysis occurs at approximately 700 km and higher (Wilson and Atreya, 2004), finding a uniform mixing ratio in the lower stratosphere and upper troposphere was not surprising. However, direct in situ measurements of mole fraction were not previously available to confirm it. Below 32 km and down to approximately 8 km, a gradual increase in the CH_4 mole fraction was measured by the GCMS. In particular, as the probe descended through approximately the 16 km level, a sudden and substantial increase in the gradient of methane signal was recorded, as shown in the inset of Fig. 4. From 8 km down to a level close to the surface the methane mole fraction remained constant at $4.92 \pm 0.25 \times 10^{-2}$. Upon impact the GCMS inlet was heated to temperatures well above the ambient temperature, to facilitate evaporation of surface material into the mass spectrometer. During the

time it took to heat the inlet (~ 2 min), the methane mole fraction rose by approximately 40%, and then remained unchanged for the rest of the time the GCMS collected data on the surface (Niemann et al., 2005).

The behavior of the methane mixing ratio (a) at 16 km, (b) at the surface, indicating evaporation of liquid, and (c) that below 8 km to just above the surface, together with the possibility of rain, is representative of a methological cycle on Titan, provided that any methane transported from the surface to the interior circulates back out to the surface, as also happens with water in the hydrological cycle on Earth. We illustrate the CH_4 condensation process in Fig. 5, by showing the saturation mole fraction of methane vapor over (i) pure liquid methane, and (ii) N_2 dissolved in CH_4 over liquid, together with the GCMS measured mole fractions as a function of altitude. Both of the cases and their implications are discussed below.

2.2.1. Case (i): CH_4 vapor over pure CH_4 liquid

Fig. 5 shows the methane saturation curves for: (i) “central” value of the temperatures (T_{HASI}) measured by the Huygens Atmospheric Structure Instrument (HASI, Fulchignoni et al., 2005); (ii) $T_{\text{HASI}} + 1^\circ$, where the temperatures are systematically increased by 1° everywhere; (iii) $T_{\text{HASI}} - 1^\circ$, where the temperatures are systematically decreased by 1° ; and (iv) $T_{\text{HASI}} - 1.3^\circ$, where the temperatures are systematically decreased by 1.3° , at all altitudes. We have chosen this range to accommodate the published range of uncertainty ($\pm 0.25^\circ$) in the HASI temperatures as well as uncertainty in the GCMS data. The $T_{\text{HASI}} - 1.3^\circ$ case was chosen to match the saturation mole fraction at 8 km to the GCMS data at that level, to reach 100% relative humidity.

Comparison of the saturation profiles with the GCMS data shows that methane is greatly subsaturated below 8 km, so that its relative humidity just above the surface is 45%. The two points at the surface indicate an increase in CH_4 due to evaporation from the surface. Even more importantly, the mixing ratio is uniform from just above

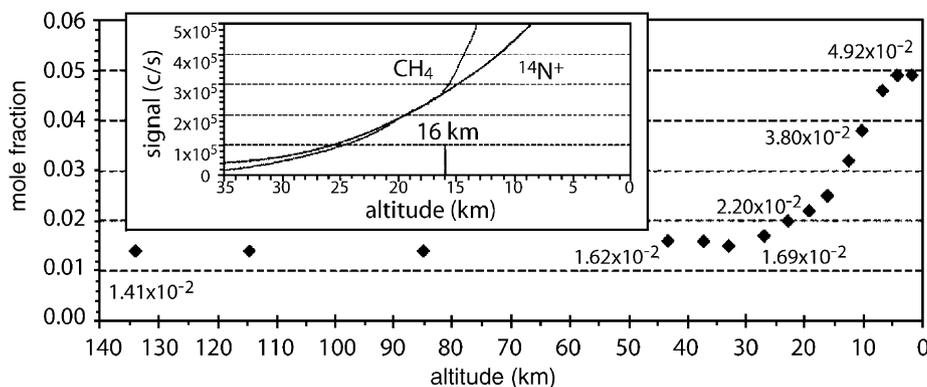


Fig. 4. The mole fraction of methane (CH_4) to nitrogen (N_2) measured by the Huygens GCMS in the Titan atmosphere is plotted versus altitude (Niemann et al., 2005). The CH_4 mole fraction is 1.41×10^{-2} in the stratosphere. It began increasing below 32 km. At about 8 km, it reached a plateau of approximately 4.9×10^{-2} . The inset shows an increase of methane at $m/z = 16$, when compared to nitrogen (in this case $^{14}\text{N}^+$) at $m/z = 14$, near 16 km. This is likely due to CH_4 condensate particles evaporating in the inlet system of the mass spectrometer as the probe passed through the methane haze.

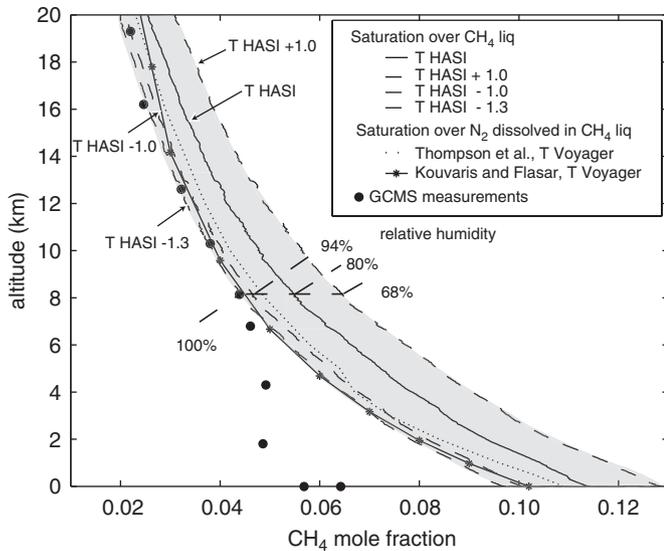


Fig. 5. The GCMS measurements of the CH_4 mole fraction are shown against the saturation mole fraction curves for the CH_4 vapor over pure CH_4 liquid (solid line) and for the N_2 dissolved in the CH_4 liquid (Kouvaris and Flasar, 1991; Thompson et al., 1992). The dashed curves demonstrate the effect of 1 K temperature variation on the saturation vapor profile. The GCMS mole fraction is subsaturated below 8 km, and follows the saturation vapor curve for HASI temperatures lowered by 1.3 K above 8 km. Both of the saturation curves for N_2 dissolved in CH_4 liquid were calculated for the Voyager temperatures, which are slightly (~ 0.2 – 1.0°) colder than those measured by HASI in the region of interest, implying a shift to the right in the saturation profiles.

the surface to approximately 8 km, but with increasing relative humidity with altitude. This can be seen from the ever closing gap between the CH_4 data and the saturation curves with height. At 8 km, the relative humidity reaches 100%, if we assume $T_{\text{HASI}} - 1.3^\circ$, 94% with $T_{\text{HASI}} - 1.0^\circ$, 80% with T_{HASI} , and 68% with $T_{\text{HASI}} + 1^\circ$. It is important to note the GCMS measured mole fractions track the saturation vapor profile for the $T_{\text{HASI}} - 1.3^\circ$ above 8 km. Assuming that Titan's methane distribution is governed by "equilibrium" thermodynamics of methane vapor over "pure liquid methane", the $T_{\text{HASI}} - 1.3^\circ$ case would represent the classic textbook example, where a subsaturated parcel of methane undergoes expansion and cooling as it rises, but maintains a constant mixing ratio, it reaches 100% relative humidity at the lifting condensation level (LCL), here 8 km, condenses, and is then limited to the saturated value above 8 km. If the temperatures in the troposphere were truly like the "central" HASI values, at 8 km the condensation could still occur even at the relative humidity of 80%, either by a small adiabatic expansion, or if the appropriate cloud condensation nuclei were present.

2.2.2. Case (ii): N_2 dissolved in CH_4 liquid

Another consideration is that the assumption of saturation of CH_4 vapor over "pure liquid methane" may not be entirely correct. It is known that nitrogen is partially soluble in liquid methane, forming a solution whose saturation vapor pressure lies approximately halfway

between that computed from Raoult's law for a gas (CH_4) in equilibrium with an ideal liquid solution of nitrogen and methane, and that for a gas in equilibrium with pure liquid methane (Kouvaris and Flasar, 1991; Thompson et al., 1992). Fig. 5 shows the saturation curves computed for the Voyager temperature profiles adapted from the aforementioned sources. The saturation profiles are valid to approximately 14 km (700 mb) above which droplets should freeze in thermal equilibrium. At 8 km, the GCMS mole fraction is subsaturated by only 4.7% for the Kouvaris and Flasar model, and by 11% percent for the Thompson et al. model. It is important to note that only a small degree of fine tuning within the $\pm 0.25^\circ$ uncertainty of the HASI temperatures yields 100% relative humidity at 8 km. Conversely, the Voyager temperatures were on average 0.2 – 1° colder at the altitudes of interest, which would shift the Thomson et al. and Kouvaris and Flasar's saturation curves to the right, decreasing the overlap between them and the GCMS data. Such fine tuning is not warranted, because: (i) condensation could occur even if methane is somewhat subsaturated; and (ii) existence of a perfect mixture between nitrogen gas and liquid methane in Titan's troposphere is doubtful, for the lower atmosphere and the surface will have other condensables, which when mixed with the solution, could alter its vapor–liquid equilibrium further. Finally, it is interesting to note that within the range of uncertainties, there is little difference in the values of relative humidity obtained from Case (i) $T_{\text{HASI}} - 1^\circ$ and (ii) $T_{\text{HASI}} - 1.3^\circ$, and Case (ii).

The most direct evidence of condensation is the behavior of the methane signal as the probe descended through the 16 km level (inset, Fig. 4). The increase in the gradient of signal at this altitude has been interpreted as being due to evaporation of condensed methane aerosol upon entering the heated inlet of the mass spectrometer (Niemann et al., 2005). It appears that the methane condensation at 8 km resulted in a tenuous cloud or haze that extended to at least the 16 km level. The above behavior of methane—uniform mixing ratio from just above the surface to 8 km, lifting condensation level, i.e. 100% relative humidity, at 8 km, nearly saturated air parcel above 8 km, and an increase in the GCMS CH_4 signal at 16 km—is the strongest evidence there is of any cloud or haze in the 8–20 km region in the Huygens landing site of 10°S . A lack of widespread cloud activity at these latitudes is consistent with it being a dry season in this region. Titan's southern summer solstice was in October 2002, with each season on Titan lasting roughly 7.4 years. Clouds extending from approximately 20–46 km are now being detected at mid-southern latitudes of 37 – 44°S , with the Cassini visual and infrared mapping spectrometer (VIMS, Griffith et al., 2005) and from the Keck telescope (Roe et al., 2005) as the southern summer moves northward.

As the CH_4 clouds persist, the rain-out of methane is expected to follow, depending on the nature of the cloud condensation nuclei (CCN) present (Toon et al., 1988;

Lorenz, 1993). The yearly average amount of rain is expected to be relatively insignificant due to small convective activity, a result of Titan's distance from the Sun and abundance of the stratospheric haze (Lorenz, 2000; Ingersoll et al., 2005). Once the liquid methane is on the surface, little evaporation is expected as Titan's surface temperature of 93.8 K is close to the triple point of (pure) methane, 90.67 K. Combined with the possibility of liquid methane being present in the surface, as indicated by the GCMS observation of an increase in the CH₄ mole fraction due to evaporation from the surface shortly after impact (Niemann et al., 2005), the above behavior of methane represents a full cycle—a methanological cycle, of evaporation of liquid from the surface, condensation at LCL, followed by precipitation from the troposphere. So far, no evidence of large bodies of liquid methane on Titan has been found. The “pool” in the Huygens landing site is interpreted to be a small amount of liquid methane mixed in with other surface material, most likely the hydrocarbon hazes that fell from the atmosphere. However, such geologic features as fluvial and dendritic outflow channels, cryovolcanoes, etc., detected in the images made from the Synthetic Aperture Radar (Elachi et al., 2005) and the Visual and Infrared Mapping Spectrometer (Sotin et al., 2005) on the Cassini orbiter and the Descent Imager (DISR) on the Huygens probe (Tomasko et al., 2004) appear to be indicative of communication between the surface and the subsurface. In that case, methane rain from the atmosphere may not just form a puddle or pool on the surface, but the liquid could drain or seep into the interior, where it might be stored in icy regolith (Stevenson, 1992; Kossacki and Lorenz, 1996), thus resulting in a temporary loss of methane until it is re-released to the atmosphere.

In the best possible scenario, the above meteorological process, combined with the eventual release of methane from the interior, would represent a closed cycle. However, mixing of methane from the troposphere to the upper atmosphere would still cause a relatively rapid destruction of this species in the stratosphere. In the following section we discuss some possible sources for replenishing methane.

3. Methane source, and outgassing

In Fig. 6 we illustrate the fate of methane, including the photochemical loss processes. The resulting hydrocarbons are transported from their region of production in the stratosphere to the lower atmosphere where they condense to form hazes. The hazes deposit on to the surface, from where they could be washed into river basins or the interior by methane rain. Unlike the giant planets, the relatively cold, hydrogen-poor interior of Titan does not permit recycling of the hydrocarbon products of the methane chemistry back into methane. Either methane arrived at Titan in the form of methane clathrate from the subnebula at the time of formation (Mousis et al., 2002), or it was produced on Titan—a possibility we have introduced previously (Niemann et al., 2005; Owen et al., 2005; Atreya

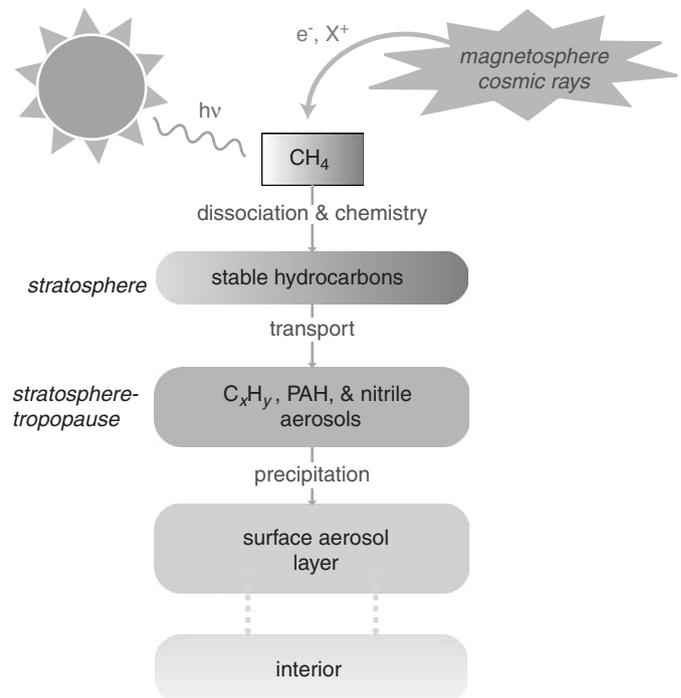


Fig. 6. A schematic illustrating an irreversible sink of methane in Titan's atmosphere is shown. Photolysis, effects of Saturn's magnetosphere and impacts of cosmic rays irreversibly convert methane to stable hydrocarbons and then hazes in the stratosphere. Once CH₄ is lost to haze, it cannot be reconverted back to methane. The hazes precipitate onto the surface, and are washed into the interior, leading to the loss of CH₄.

et al., 2005a, b; Atreya, 2004). The very low “upper limit” of the heavy noble gases, especially xenon, as measured by the Huygens GCMS make the former source less appealing (Niemann et al., 2005), but further work is needed. If methane was produced on Titan, either biology or geology could be at work.

McKay and Smith (2005) and Schulze-Makuch and Grinspoon (2005) have proposed microbial production of methane on Titan. In their scenario, microbes utilize acetylene and hydrogen from Titan's atmosphere and produce methane as the product of their metabolism:



As evidence of such biological activity, Schulze-Makuch and Grinspoon (2005) cite the isotopically “light” carbon, i.e. with ¹²C/¹³C = 95.6 measured by the Cassini INMS (Waite et al., 2005). Indeed, on Earth such isotopic fractionation relative to the inorganic standard V-PDB value (¹²C/¹³C = 89.44) is due to biology. However, the ¹²C/¹³C value used by the above authors as evidence of a biological source of methane on Titan is for the “upper atmosphere”. In the lower well-mixed atmosphere, the ¹²C/¹³C = 82.3 as determined by Huygens GCMS (Niemann et al., 2005), and in fact, a similar value (81) has been reported by the INMS team after extrapolating the upper atmospheric measurement to the lower atmosphere (Waite et al., 2005). Thus, Titan's methane is isotopically “heavy”, which is not an indicator of

methanogens as a source of methane on Titan in the conventional sense. One could argue that Titan's inorganic standard value may be different than the terrestrial value, for example the starting value may be enriched in heavier isotope, in which case the Cassini–Huygens data could still be explained by the presence of life on Titan. This would be an extraordinary coincidence, and as Carl Sagan used to say, “extraordinary claims require extraordinary evidence”, but the Cassini–Huygens data do not provide such an evidence. A simpler explanation for Titan's $^{12}\text{C}/^{13}\text{C}$ ratio being less than the inorganic standard value of 89.4 may lie in the possible non thermal escape of methane from Titan's atmosphere (Yelle et al., 2005) but further studies are needed to evaluate this process.

An attractive alternative is that methane is produced in Titan's interior by a hydrogeochemical process—serpentinization. Such a process has been studied for Earth, and has been applied to Mars to explain the presence of methane on that planet (Atreya et al., 2004; Formisano et al., 2004; Atreya, 2005; Atreya et al., 2006; Oze and Sharma, 2005). The possibility of hydrogeochemical production of methane on Titan has also been introduced previously (e.g., Niemann et al., 2005; Owen et al., 2005; Atreya et al., 2005a, b; Atreya, 2004). Here we discuss the relevance of appropriate geochemical reactions in the context of available models of the thermal structure and composition of Titan's interior.

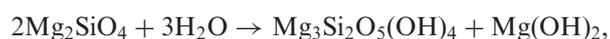
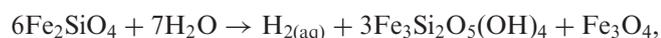
3.1. Hydrogeochemical (serpentinization) source

In the following paragraphs we outline a possible mechanism for the production of methane by water-rock reactions in the interior of Titan. Our objective in doing so is (i) to provide the context for such reactions, by relating them to Titan's interior structure models developed by other scientists, and (ii) to point out the need for laboratory studies of geochemical processes at “low” temperatures, including the appropriate Fischer–Tropsch reactions, in order to evaluate the validity of such a process for producing the required quantities of methane on Titan.

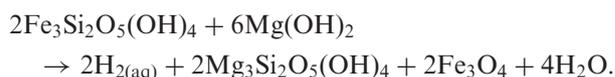
In the terrestrial oceans, hydrothermal fluids and seawater react with rocks to bring about chemical changes. One important process involves ultramafic silicate (Mg, Fe-rich) minerals, such as olivine $[(\text{Mg}, \text{Fe})_2\text{SiO}_4]$ and pyroxene $[(\text{Mg}, \text{Fe})\text{SiO}_3]$, whose hydration first results in the formation of, in particular, molecular hydrogen $[\text{H}_{2(\text{aq})}]$, together with serpentine $[(\text{Mg}, \text{Fe})_3\text{Si}_2\text{O}_5(\text{OH})_4]$, Mg-brucite $[\text{Mg}(\text{OH})_2]$ and magnetite $[\text{Fe}_3\text{O}_4]$, i.e.,

olivine/pyroxene + water \rightarrow hydrogen + serpentine + brucite + magnetite.

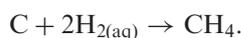
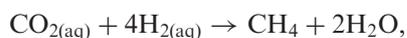
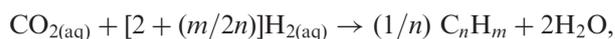
Key geochemical reactions are:



followed by



Some thermodynamic and kinetic data of these reactions are discussed in Oze and Sharma (2005) and Sleep et al. (2004), however applicability of the data to Titan's interior conditions is not at all apparent. The $\text{H}_{2(\text{aq})}$ produced in the above serpentinization process is key to the formation of methane by hydrogeochemical process. $\text{H}_{2(\text{aq})}$ reacts with carbon grains or CO_2 in the crustal pores to produce methane and possibly higher order hydrocarbons in decreasing abundances, i.e.



Should sulfur exist in an oxidized state in the interior of Titan, there is some likelihood that it could react with $\text{H}_{2(\text{aq})}$ preferentially to produce H_2S at the expense of CH_4 . As in the context of Mars (Oze and Sharma, 2005), without a better knowledge about the mineralogy and hydrology related to S, and the amount and redox state of S in the interior of Titan, the relevance of sulfur in relation to methanogenesis on Titan is difficult to access. Although the above sulfur possibility cannot be ruled out, it is interesting to note that no evidence of H_2S or other sulfur compounds has been found in the surface material or the atmosphere of Titan by the Huygens GCMS. If H_2S were being produced in the interior, it would be expected to be released to the surface along with methane, argon, etc.

In laboratory experiments, simulating the Black Smoker vents ($T \sim 390^\circ\text{C}$, $p \sim 400$ bar), Foustouskos et al. (2004) found that methane is indeed produced in the above reactions, catalyzed by Fe–Cr oxide. In addition to being rich in Mg and Fe, oceanic rocks—ultramafic silicates—are also rich in Cr, and metal catalysis is important to such Fischer–Tropsch type reactions.

Although Black Smokers, first discovered twenty-five years ago in the mid-Atlantic Ridge by the submersible Alwyn, are commonplace in spreading centers, their occurrence in the interior of Titan is unlikely. This is because the needed high temperatures may be reached only in the core of Titan where water is not expected to be present (e.g. Grasset et al., 2000). On the other hand, water–rock reactions could also proceed at much milder temperatures. Kelley et al. (2005) have found a relatively large production of methane in “Lost City”, 15–20 km from spreading centers where Black Smokers are seen. The typical temperatures in the Lost City region are only 40–90 °C. The process of methane formation follows a path similar to the one outlined above for the Black Smokers, except that it represents serpentinization at relatively “low” temperatures. The source of carbon on Titan could be

carbon grains, CO₂, as well as any CO trapped in the interior at the time of formation.

In principle, the water–rock reactions at low temperatures could occur in the water–ammonia ocean purported to be present in Titan’s interior. However, models of the interior indicate that temperatures of 40–90 °C could be reached only in the core of Titan, whereas the temperatures in the water–ammonia ocean reach a maximum value of only 0 °C (Grasset and Pargamin, 2005). In the absence of appropriate laboratory data for such low temperatures but a liquid medium, it is not apparent whether the above low temperature serpentinization is taking place today to produce methane in Titan’s interior. The kinetics of Fischer–Tropsch type reactions in the water–rock medium (by which methane is ultimately produced) are complex, as they depend on a number of factors, including pressure, temperature, and catalysts, about which little relevant data are currently available. It is also important to note that temperatures and structure of the interior depend on assumptions about the concentration of ammonia dissolved in water, nature of the core, etc., none of which can be constrained with certainty. Moreover, the transition between the various layers in the interior may be more gradual than that given by Grasset and Pargamin (2005).

As is apparent from the above considerations, appropriate laboratory data are presently missing to evaluate fully the extent to which methane may be generated under current conditions in the interior of Titan. On the other hand, early in the history of Titan’s accretionary heating phase, the interior could have been much warmer, with the water–ammonia ocean extending all the way down to the core (Engel et al., 1994). In that case, methane production by the “low-temperature” serpentinization mechanism appears more promising. For example, a chemical equilibrium computer model of basaltic alteration at low temperatures yields as much as 0.2 bar of CH₄ on Mars (Wallendahl and Triemann, 1999). Scaling it to Titan’s surface area, and assuming Titan to be made up of half water–half rock (as indicated by its density) with the rocky component same as Mars, yields a value of approximately 0.06 bar, which is comparable to the amount of methane in the atmosphere of Titan today. However, over the geologic time, the total amount of methane generated on Mars, and Titan, is expected to be substantially greater. This can be seen by examining the assumptions made in the above basaltic alteration calculation (Wallendahl and Triemann, 1999). The Mars CH₄ calculations were based on a low water:rock ratio (1:10), and the “carbon” abundance was limited to the amount of CO₂ diffusing from the current atmosphere into the regolith. The CO₂ pressure on primordial Mars is expected to have been over 300 times greater than today. Even more relevant to Titan, the carbon abundance in the rocks of Mars is far greater than that resulting from the CO₂ diffusing from the 6 mb atmosphere, which was the basis of the above 0.2 bar CH₄ calculation. A larger carbon abundance would directly lead to greater methane production. In addition to carbon, the

other major factor affecting the CH₄ production is the amount of H₂ generated in the water–rock reactions. The 1:1 water:rock ratio on Titan—especially if the ocean extended to the core in the past—compared to the very low water:rock ratio in the above calculation for the Martian methane, would result in greatly enhanced H₂, hence CH₄, on Titan. In summary, the enhanced amounts of both carbon and hydrogen are expected to result in substantially greater CH₄ on Titan over the geologic time than that scaled from the calculation valid for current Mars. This would help mitigate the effect of photochemical loss of methane from Titan’s atmosphere over time. Although the Martian analogy discussed here may not be an exact guide for Titan, the above estimates nevertheless show that the hydrogeochemical reactions are quite capable of producing large quantities of methane to replenish the loss of the species due to stratospheric chemistry.

Once produced, methane could be stored as a stable clathrate–hydrate (CH₄•5.75 H₂O). Methane clathrates have been found in terrestrial oceans, and models show that methane can be stored in the form of clathrates in the interior of Mars (Max and Clifford, 2000) and Titan (e.g. Lunine and Stevenson, 1987; Grasset and Pargamin, 2005). Neutron and synchrotron X-ray diffraction studies on thermodynamic properties of CH₄ at high pressures show that stable methane hydrates can exist to at least the 10 kilobar pressure level, forming a 100-km thick clathrate layer near the core of Titan (Loveday et al., 2001). This thickness is derived from laboratory experiments, but it does not necessarily represent the thickness of the layer actually present in the interior of Titan, nor does it necessarily represent the thickness required for replenishing the methane in the atmosphere.

3.2. Methane outgassing

Methane stored as clathrate in Titan’s interior needs to be released to the atmosphere in order to replenish the methane lost to photolysis, thus maintaining a stable CH₄ mole fraction. Indirect evidence of outgassing from the interior is found in certain Cassini VIMS (Sotin et al., 2005) and the Cassini Synthetic Aperture Radar images, including a large circular structure named Ganesa Macula (Elachi et al., 2005; Lopes et al., 2005). These images have been interpreted as being representative of cryovolcanoes. As discussed previously (Niemann et al., 2005) a direct evidence of outgassing comes from the detection of radiogenic argon (⁴⁰Ar) in Titan’s atmosphere by the Huygens GCMS (Niemann et al., 2005) and the Cassini Orbiter Ion and Neutral Mass Spectrometer (Waite et al., 2005). ⁴⁰Ar is a radioactive decay product of ⁴⁰K. Potassium was presumably sequestered in the rocks that differentiated to the core of Titan at the time of formation. The half-life of ⁴⁰K is 1.3 billion years, which implies its conversion into ⁴⁰Ar in Titan’s interior must have been completed billions of years ago. However, the volume mole fraction of ⁴⁰Ar is $(4.32 \pm 0.1) \times 10^{-5}$, as measured by the

GCMS (Niemann et al., 2005). This is roughly one-half of the value ($^{40}\text{Ar}/\text{N}_2 = 10^{-4}$, Owen, 1982) that would be expected if Titan's rocky component was similar to the Earth's and outgassed as efficiently. The interior structure of Titan together with the above outgassing scenario is illustrated in Fig. 7.

Even though the exact calculation of the actual release rate of methane (or ^{40}Ar) from the interior must await a thorough understanding of Titan's interior structure, a rough estimate can be made by considering the rate of "volcanic" material upwelled. Baines et al. (2006) estimate a value of approximately $0.02 \text{ km}^3 \text{ yr}^{-1}$ of the material upwelled and exposed at the surface, if spread uniformly over Titan. However, the material will be most concentrated over cryovolcanic features similar to those imaged by VIMS (Sotin et al., 2005). Scaling the rate of volcanism for the Earth and Venus, which are, respectively, ~ 3 and $\sim 1 \text{ km}^3 \text{ yr}^{-1}$ (Fegley and Prinn, 1989; Basilevsky and Head, 2002), to Titan's surface area, Baines et al. (2006) yields values of approximately 0.6 and $0.2 \text{ km}^3 \text{ yr}^{-1}$, respectively for Titan. If the upwelling rate given by Baines et al. is correct, it implies that cryovolcanism results in a smaller rate of upwelled material on Titan than that based on the Earth- or Venus-like volcanism. Nevertheless, on average, it seems sufficient to replenish the methane lost to photochemistry. This could be checked by comparing the average resurfacing rate due to cryovolcanism to the rate at which methane is destroyed by photochemistry.

The global mean resurfacing rate based on the above estimate of $0.02 \text{ km}^3 \text{ yr}^{-1}$ of cryovolcanic material, is

approximately 24 cm per million years (Baines et al., 2006). Assuming that CH_4 is brought to the surface by cryovolcanic process, approximately 4 cm of the above global mean resurfacing will be in the form of CH_4 liquid, considering the $5.75:1$ ratio for $\text{H}_2\text{O}:\text{CH}_4$ clathrate. This is roughly of the same order as the methane lost to chemistry. The global mean photochemical destruction rate of CH_4 is approximately $4.8 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$ (Wilson and Atreya, 2004), or $1.3 \times 10^{-16} \text{ kg cm}^{-2} \text{ s}^{-1}$. Using a value of 447 kg m^{-3} for the density of liquid methane corresponding to Titan's surface temperature and pressure, the above destruction rate implies that a layer equivalent to approximately 8 cm million yr^{-1} of liquid methane is being destroyed by photochemistry on global average basis. This is comparable to that replenished by the cryovolcanic process, considering the uncertainty in the rates of both photochemical destruction and cryovolcanic upwelling. Naturally, if the outgassing is occurring also at times other than cryovolcanism, even greater amounts of CH_4 could be upwelled.

4. Summary

We show in this paper that even though the photochemical destruction of methane in the stratosphere of Titan produces ethane, contrary to previous assertions the C_2H_6 condensation flux is found to be much smaller. Furthermore, the ethane condensate competes with the haze material at the surface. This is consistent with the lack of a global ocean of ethane on Titan. Latitudinal variations in the surface and tropospheric temperatures are expected to result in seasonal changes in the ethane condensate also. In the troposphere, there is evidence of methane condensation, which can be explained by classical thermodynamics, either with pure liquid methane or N_2 dissolved in the methane liquid. Methane lost primarily to photochemistry, and to a lesser extent escape and possibly to the interior, is expected to be replenished by the water-rock-reactions, especially those involving serpentinization at low temperatures. This, as well as the possibility of such a process occurring at higher temperatures at times of impacts, requires further study. Little is presently known about such reactions. Laboratory measurements of the geochemical reactions between the Titanic rock and water-ammonia brine, as well as the catalytic Fischer-Tropsch reactions, especially under the low temperature and high pressure conditions of Titan's interior, are critical. The CH_4 clathration properties, and the non-equilibrium thermodynamic properties relevant to the temperature, pressure, and the aerosol and gas composition in Titan's troposphere and the lower stratosphere are also essential in order to make further breakthroughs in our understanding of the complex photochemical-meteorological-hydrogeochemical cycle of methane on Titan.

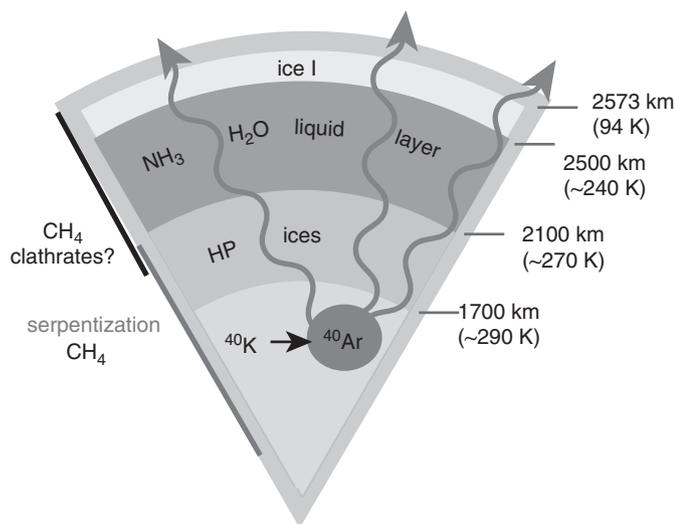


Fig. 7. Schematic view of the interior of Titan and the outgassing of ^{40}Ar are shown for the 5% NH_3 –95% H_2O liquid layer concentration. The p – T structure is taken from a model by Grasset and Pargamin (2005). The pressures range from 0.01 MPa (surface, 2575 km) to roughly 800 MPa at the ice-silicate interface ($\sim 1700 \text{ km}$). The methane clathrates might be trapped between the high pressure (HP) ices and the ice I region. The region of serpentinization shown could apply to the past when the water-ammonia ocean could have extended to the core. Detection of ^{40}Ar in the atmosphere by the GCMS provides the most compelling evidence of outgassing from the interior.

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