

REVIEW

Evolution of Titan and implications for its hydrocarbon cycle

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Measurements of the carbon and nitrogen isotopic ratios as well as the detection of ⁴⁰Ar and ³⁶Ar by the gas chromatograph mass spectrometer (GCMS) instrument on board the Huygens probe have provided key constraints on the origin and evolution of Titan's atmosphere, and indirectly on the evolution of its interior. Those data combined with models of Titan's interior can be used to determine the story of volatile outgassing since Titan's formation. In the absence of an internal source, methane, which is irreversibly photodissociated in Titan's stratosphere, should be removed entirely from the atmosphere in a time-span of a few tens of millions of years. The episodic destabilization of methane clathrate reservoir stored within Titan's crust and subsequent methane outgassing could explain the present atmospheric abundance of methane, as well as the presence of argon in the atmosphere. The idea that methane is released from the interior through eruptive processes is also supported by the observations of several cryovolcanic-like features on Titan's surface by the mapping spectrometer (VIMS) and the radar on board Cassini. Thermal instabilities within the icy crust, possibly favoured by the presence of ammonia, may explain the observed features and provide the conditions for eruption of methane and other volatiles. Episodic resurfacing events associated with thermal and compositional instabilities in the icy crust can have major consequences on the hydrocarbon budget on Titan's surface and atmosphere.

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1. Introduction

Photochemistry in the stratosphere of Saturn's moon Titan would remove the present-day atmospheric inventory of methane in a time-span of a few tens of millions of years. Before the Cassini–Huygens mission arrived at Saturn, widespread liquid methane or mixed hydrocarbon seas hundreds of metres thick were proposed as reservoirs from which methane might be re-supplied in a continuous fashion over geological time (Lunine *et al.* 1983). The first remote sensing observations performed by the Cassini spacecraft (Elachi *et al.* 2005; Porco *et al.* 2005; Sotin *et al.* 2005) and the Huygens probe (Tomasko *et al.* 2005) ruled out the presence of extensive bodies of liquid hydrocarbons at present. Even though lakes potentially filled with hydrocarbon liquids have recently been identified on Titan's North and South Poles (Stofan *et al.* 2007), they do not contain enough methane to sustain the atmosphere over geological time (Lorenz *et al.* 2008). This means that methane must be derived from another source over Titan's history. The absence of extensive liquid bodies of hydrocarbon also raises another question: where is the hydrocarbon detritus resulting from the photolysis of methane and from the subsequent complex chemistry? Indeed, assuming a constant supply of methane, photochemical processes acting since Titan's formation should result in the accumulation of a 0.5–1 km thick organic layer, mostly liquid, on the surface.

Thermal evolution models (Tobie *et al.* 2006) as well as remote sensing observations (Sotin *et al.* 2005; Lopes *et al.* 2007; Le Corre *et al.* 2007) suggest release of volatiles from a subsurface reservoir through cryovolcanic processes, as a potential source of atmospheric methane. Methane could have been incorporated in the interior during accretion, reflecting its presence in the primordial bricks that formed Titan (Hersant *et al.* 2008), or it might have come from the conversion of CO₂ through serpentinization in the silicate-rich core in a way similar to the process involved in the Earth's hydrothermal systems (Atreya *et al.* 2006). Whatever its origin, laboratory experiments (Dyadin *et al.* 1997; Hirai *et al.* 2001; Loveday *et al.* 2001; Choukroun *et al.* 2008) show that methane under the temperature–pressure conditions of Titan's cold, undifferentiated proto-core would rapidly combine with water molecules to form clathrate hydrates of methane. Clathrate hydrates are water ice compounds in which a distinctive open lattice structure of the ice forms cages stabilized by the inclusion of molecules of other chemical species, such as methane. On the Earth, for instance, large amounts of methane are trapped in the form of clathrate hydrates within sediments on the seafloor (e.g. Sloan 1998). As clathrates that are composed mainly of methane are highly stable in Titan's interior, their dissociation (and subsequent outgassing) can occur only when the internal temperature reached sufficiently high values during Titan's history. Observational constraints, in particular the composition of Titan's atmosphere determined by the GCMS on board Huygens (Niemann *et al.* 2005), combined with experimental constraints (Choukroun *et al.* 2008) and theoretical considerations (Tobie *et al.* 2006), can be used to determine the timing of methane outgassing and its consequences for the hydrocarbon budget on Titan.

In the present paper, we review the different processes that controlled methane outgassing during Titan's evolution and its implications for the surface and atmosphere hydrocarbon cycle. In §2, the different observational constraints in favour of internal outgassing are presented. Methane outgassing would occur only when the conditions required to dissociate methane clathrate are reached within the icy mantle of Titan's interior. In §3, we describe the possible models of Titan's interior, and the stability and distribution of methane clathrate hydrate within the interior, and in §4 we describe a selection of long-term evolution simulations using the model of *Tobie et al. (2006)*, in order to quantify the efficiency and the possible timing of methane outgassing from the interior. Finally, we discuss in §5 the implications of episodic outgassing events for the evolution of Titan's atmosphere and the hydrocarbon inventories on Titan's surface.

2. Observational constraints on the evolution of Titan and its atmosphere

Remote sensing from the Cassini spacecraft (*Elachi et al. 2005*; *Porco et al. 2005*; *Sotin et al. 2005*; *Lorenz et al. 2006*; *Barnes et al. 2007a,b*; *Stofan et al. 2007*) and *in situ* measurements by the Huygens probe (*Niemann et al. 2005*; *Tomasko et al. 2005*) revealed that Titan is a complex world, which appears to be influenced by tectonic, cryovolcanic, fluvial and aeolian processes, in many ways similar to the Earth. Only a few impact craters have been identified so far, suggesting that an active resurfacing is operating (*Lorenz et al. 2007*).

Even though several possible cryovolcanic flows and domes, suggesting release of volatiles from Titan's interior, have been identified (*Sotin et al. 2005*; *Barnes et al. 2006*; *Le Corre et al. 2007*; *Lopes et al. 2007*), the nature of cryomagmatic materials still remains poorly constrained. Spectral information in the infrared domain suggests the presence of water ice, different hydrocarbons and possibly carbon dioxide ice on the surface (*Tomasko et al. 2005*; *Rodriguez et al. 2006*; *McCord et al. 2008*). The analysis of spectral data is currently in progress to possibly correlate the geological setting of the observed cryovolcanic regions with surface composition variations. This analysis includes the correction of the atmospheric contribution to the observed spectra and the acquisition of laboratory spectra of surface-material candidates (hydrocarbon ices, tholins, water ice, clathrates, hydrates, etc.). In addition, the correlations between infrared I/F and radar reflectivity variations are carried out in order to understand better the chemical and physical nature of Titan's exotic surface (*Barnes et al. 2007a,b*; *Soderblom et al. 2007*; *Le Mouélic et al. 2008*).

Direct atmospheric measurements by the GCMS on board the Huygens probe indicated that Titan's atmosphere contains up to 5 per cent of methane near its surface (*Niemann et al. 2005*). In the observed conditions, methane can condense, preferentially at high latitudes (*Rannou et al. 2006*), and precipitations of liquid methane can play an active role in the surface processes in a way similar to water on the Earth, as indicated by the numerous observed river networks and lake features. Numerous cloud features have also been detected from ground-based observations (e.g. *Griffith et al. 2000*) and Cassini observations (*Griffith et al. 2005, 2006*; *Porco et al. 2005*). Even though some

of the observed features have been speculated to be indicative of cryovolcanic activities (Roe *et al.* 2005), most of the observed features can be understood in the framework of the general circulation model of Titan's atmosphere (Rannou *et al.* 2006; Rodriguez *et al.* 2007) and do not require any particular activity on Titan's surface.

The most convincing evidence for internal outgassing over Titan's history is provided by the GCMS that detected a significant amount of ^{40}Ar in Titan's atmosphere (Niemann *et al.* 2005). Radiogenic ^{40}Ar is the decay daughter of ^{40}K , which is contained in the rocky part of Titan's interior. Its detection in the atmosphere indicates that significant outgassing from the interior has occurred over Titan's history. Moreover, carbon and nitrogen isotopic ratios measured by the GCMS indicate that nitrogen and methane, the two major compounds in Titan's atmosphere, have followed two distinct evolutionary paths. The carbon isotopic ratio $^{13}\text{C}/^{12}\text{C}$ in hydrocarbon molecules, which is relatively close to the terrestrial value (Niemann *et al.* 2005), reflects a bulk carbon inventory that did not participate in the massive escape phase that followed the formation of an ancient post-accretional atmosphere. By contrast, the isotopic ratio $^{15}\text{N}/^{14}\text{N}$ shows strong enrichment relative to the terrestrial value and hence suggests a large escape. This constraint together with the low abundance in ^{36}Ar , which implies that the nitrogen was captured as NH_3 and converted just after accretion (Niemann *et al.* 2005), indicate that nitrogen has been present in Titan's atmosphere since its formation, whereas today's methane has been injected much later. The exact timing of volatile outgassing is difficult to constrain from only these measurements, but they clearly indicate that internal outgassing has occurred at some period during Titan's history.

3. Stability and distribution of methane clathrate hydrate within the interior

At the end of accretion, only the inner undifferentiated portion of Titan's interior was able to hold volatiles. Most of the region outward of this proto-core was probably warm liquid-water ($T \geq 300$ K), in which gas molecules have very low solubility, and so potentially very large amounts of gas compounds, notably methane, ended up in the primitive atmosphere. By contrast, ammonia has a high solubility in water, so that most of the available ammonia remains in the liquid phase and only a relatively small fraction is extracted from the liquid phase and is then converted into nitrogen. Most of the methane initially present in the building blocks ended up in the primitive atmosphere and has been lost shortly after accretion owing to the combined effect of strong atmospheric escape and enhanced solar UV photolysis.

After that early epoch, most of the remaining mass of methane is stored in the undifferentiated proto-core. For an undifferentiated proto-core representing 15–25 per cent of Titan's total mass ($R_{\text{proto-core}} \approx 1400\text{--}1600$ km) and assuming a mass fraction of methane relative to water in Titan's building blocks equal to 1 per cent and a silicate mass fraction of 50 per cent, the total available mass of methane in Titan's interior would range from 1 to 1.7×10^{20} kg, i.e. 360–610 times the present-day mass of atmospheric methane (estimated to be 2.8×10^{17} kg after Niemann *et al.* 2005). Methane in the cold proto-core is stable in the

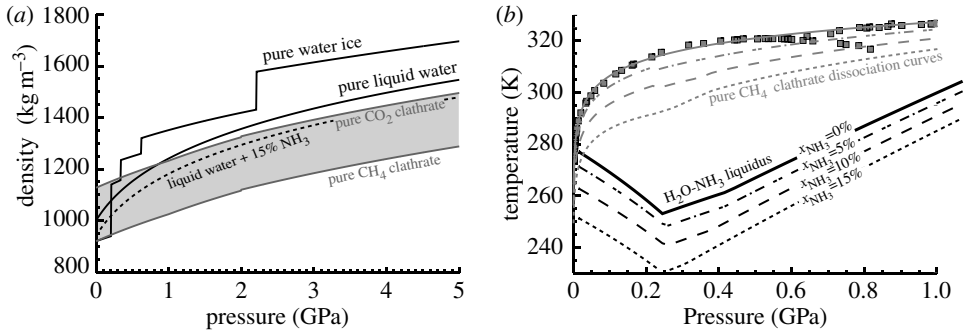


Figure 1. (a) Density as a function of pressure for different materials potentially present within Titan's interior, (b) stability curve of methane clathrate hydrate compared with the melting curve of ice for different ammonia mass fractions x_{NH_3} in the liquid phase. Squares represent experimental data given by Dyadin *et al.* (1997). Curves with similar line styles correspond to the same ammonia fraction.

form of clathrate hydrate (e.g. Loveday *et al.* 2001), but would be released after the proto-core overturn (approx. 0.5 Gyr after accretion according to Lunine & Stevenson 1987).

The internal differentiation that leads to the formation of a discrete rocky core is driven by the density contrast between the different materials composing the interior (silicate, ice, liquid water, hydrate, etc.). The lighter materials rise towards the surface, whereas the denser materials (silicate) converge towards the centre. Densities as a function of pressure for different candidate materials are displayed in figure 1a. The density of clathrate hydrate mainly depends on the type of gas molecules trapped in their cages. Clathrates of pure methane have a density of 920 kg m^{-3} at ambient pressure, whereas clathrates of carbon dioxide have a density of 1130 kg m^{-3} . Whatever the pressure values, pure methane clathrate is the least dense material, being equal in density to water ice at low pressure ($P < 0.2 \text{ GPa}$). Even for 15 per cent ammonia–water liquid, methane clathrate is still 2 per cent less dense. Therefore, only clathrates that are mostly composed of methane would have a density lower than ammonia–water solutions, and would be able to rise through the thick primordial ammonia–water layer during differentiation.

The ascent of methane-rich clathrates and their accumulation at the top of the ammonia–water layer also depend on their stability with respect to the ammonia–water solution. For simplicity, the effect of minor gas compounds on the stability is neglected. The stability curve of pure methane clathrate in water solutions can be parametrized from available experimental data over a wide range of pressures (Sloan 1998) by performing a polynomial fit,

$$T_d^0 = 264.395 + 21.105 \times \log P - 0.0424805 \times (\log P)^2, \quad (3.1)$$

with T_d^0 the dissociation temperature in the binary water–methane system in Kelvins and P the pressure in MPa.

The inhibiting effect of ammonia on methane clathrate has long been suspected, but its net effect on the stability of methane clathrate has only recently been experimentally investigated (Choukroun *et al.* 2008). Preliminary

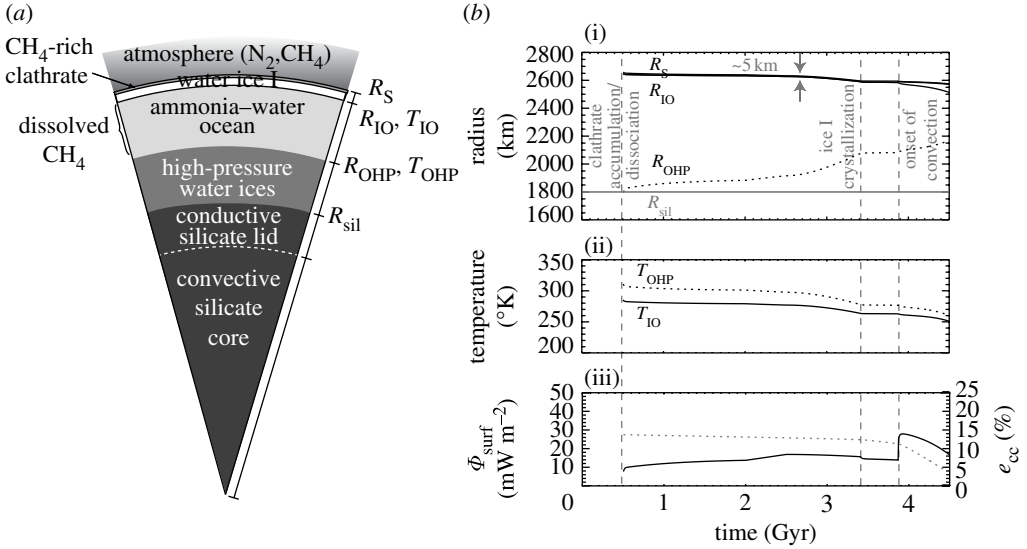


Figure 2. (a) Internal structure after differentiation, (b) surface radius R_s (solid line), and upper (solid line) and lower (dotted line) ocean interface radius, R_{IO} and R_{OHP} (i), corresponding interface temperature, T_{IO} and T_{OHP} (ii) and surface heat flux Φ_{surf} (solid line) and eccentricity e_{cc} (dotted line) (iii), as a function of time.

results indicate that a 7.5 per cent NH_3 concentration could decrease the dissociation curve by up to 20 K. In the absence of additional experimental constraints, the effect of ammonia on the methane clathrate stability can be estimated from the binary ammonia–water system that is well-known (e.g. Grasset & Pargamin 2005; Choukroun & Grasset 2007), by using the parametrization proposed for clathrate stability in salt–water solutions (Dickens & Quinby-Hunt 1997)

$$T_d^{x_{\text{NH}_3}} = \left\{ \frac{1}{T_d^0} - \frac{n\Delta H_m}{\Delta H_d} \left[\frac{1}{T_m^0} - \frac{1}{T_m^{x_{\text{NH}_3}}} \right] \right\}^{-1}, \quad (3.2)$$

where T_m^0 and $T_m^{x_{\text{NH}_3}}$ are the melting temperature of ice for the pure water system and ammonia–water system, respectively, computed using the method described by Grasset & Pargamin (2005), ΔH_d is the enthalpy of dissociation for methane clathrate to liquid water and methane gas, n is the hydration number ($\Delta H_d/nR$ is estimated to 1090 K) and ΔH_m is the enthalpy of melting for pure water to ice (6008 J mol⁻¹ at 273.2 K, Sloan 1998).

As illustrated in figure 1b, ammonia reduces the stability of methane clathrate to almost the same extent that it decreases the crystallization point of ammonia–water solutions. Therefore, any methane clathrate released during the proto-core differentiation would rise to the top of the outer liquid layer without being dissociated, leading to the formation of a methane-rich clathrate layer. Once the differentiation is achieved, the internal structure consists of a rocky core, overlain by a high-pressure layer, a liquid ammonia-enriched water layer and a clathrate-enriched icy layer (figure 2a).

4. Long-term evolution models of Titan's interior

Subsequent to core overturn, methane outgassing would have occurred only when the conditions required to dissociate methane-rich clathrate were reached within the icy mantle of Titan's interior. Owing to the low thermal conductivity and high viscosity of methane clathrate as compared with water ice, incorporating methane clathrate in Titan's crust is expected to strongly influence the cooling rate of Titan's interior. The subsequent thermal evolution of Titan's interior can be constrained by applying the coupled orbital–thermal model described and used in Tobie *et al.* (2005, 2006). This model includes heat transfer through the outer layer, clathrate dissociation and crystallization of the liquid layer, thermal evolution of the silicate core, and tidal dissipation and its effect on orbital eccentricity decay (see Tobie *et al.* (2005) and the electronic supplementary materials associated with Tobie *et al.* (2006) for further details). Titan shows an orbit with an eccentricity of 3 per cent that cannot be explained by orbital resonance. Titan's current free eccentricity is probably the fossil of a higher primordial eccentricity possibly ranging between 10 and 20 per cent (Tobie *et al.* 2005).

Figure 2*b* illustrates one typical simulation. For this simulation, the initial eccentricity is set equal to 13.5 per cent, the mass fraction of NH₃ relative to H₂O is set equal to 5 per cent and the silicate mass fraction is assumed to be 55 per cent. This simulation shows that after differentiation the internal ammonia–water layer cools down very slowly owing to the insulating effect of the overlying clathrate-rich layer. This results in a slow crystallization of the water layer from the bottom, leading to a slow thickening of the high-pressure layer. As the outer layer remains relatively thin during the 3.5 first billion years, tidal dissipation remains small and the eccentricity only slowly decays. After 3.5 Gyr, the ocean starts to crystallize from the top (figure 2*b*), thus forming an ice I layer below the clathrate-rich crust. And when the ice I layer reaches a critical thickness of 15 km at approximately 3.9 Gyr, thermal convective instabilities initiate in the ice layer. As thermal convection is more efficient than thermal diffusion to transport internal heat, crystallization of the ocean water accelerates and the convective ice shell rapidly thickens.

In addition, as the total energy dissipated by tidal friction is proportional to the thickness of the convective ice I layer (Tobie *et al.* 2005), tidal dissipation increases as the ice shell thickens and the orbital eccentricity rapidly decays to its present-day value. As a consequence, the surface heat flow strongly increases when thermal convection starts owing to the combined effect of enhanced tidal dissipation and ocean crystallization, which releases accretional and differentiation energy that have been stored in the form of latent heat in the internal water ocean since the satellite formation and differentiation. The presence of CH₄-rich clathrates in the crust thus delays the crystallization of the primordial ocean, and reduces the dissipation rate during the first 3 Gyr. Those effects allow the maintenance of a large eccentricity over approximately 4 Gyr and the triggering of thermal activities in the outer layer very late in Titan's history, which can destabilize the subsurface clathrate reservoir several billion years after accretion.

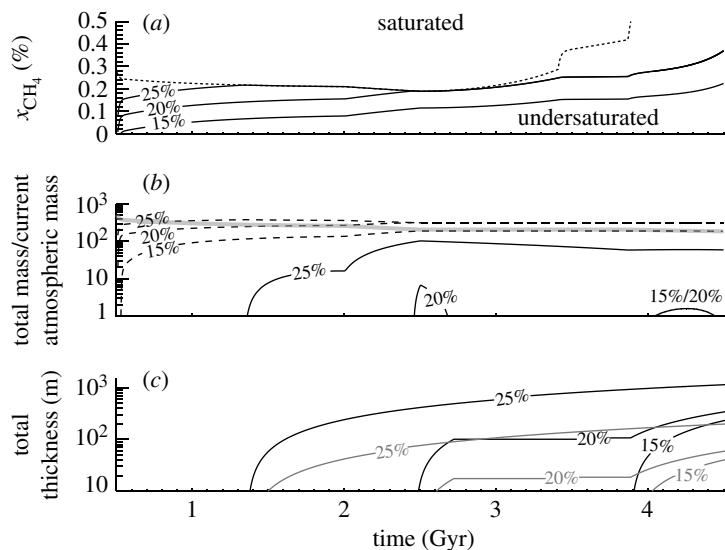


Figure 3. (a) Evolution of methane content in the internal ocean for three different initial mass fractions of the proto-core (15, 20 and 25%) corresponding to the simulation presented on figure 2. The dotted curve indicates the maximum content of methane that can be dissolved in the ocean as a function of time. (b) Mass of methane, normalized to the current atmospheric mass, contained in the ocean (dashed line) in the crust (grey line) and in the atmosphere and on the surface (solid line) as a function of time for different mass fractions of the proto-core. (c) Total thickness of ethane (black, $\rho_{\text{C}_2\text{H}_6} \approx 550 \text{ kg m}^{-3}$) and acetylene (grey, $\rho_{\text{C}_2\text{H}_2} \approx 745 \text{ kg m}^{-3}$) produced by CH_4 -based photochemistry, accumulated at the surface as a function of time, for different mass fractions of the proto-core and assuming the conversion rate of Toubanc *et al.* (1995).

5. Implications for the hydrocarbon cycle

(a) Evolution of atmospheric methane

Differentiation and subsequent evolution of Titan's interior as described above naturally leads to the accumulation of CH_4 -rich clathrates in Titan's crust and to their subsequent dissociation during three main epochs: (i) during and just after differentiation between 0.5 and 1 Gyr, (ii) at the onset of convection in the silicate core between 2 and 2.5 Gyr and (iii) when thermal instabilities in the crystallizing outer ice layer occurs between 4 and 4.5 Gyr. However, the two first episodes have to be distinguished from the last one. Before 2.5 Gyr, the dissociation of methane clathrate occurs at the crust–ocean interface, whereas after 3.9 Gyr the dissociation is induced by upwellings of warm ice at the base of the remaining crustal reservoir (Tobie *et al.* 2006).

Figure 3a shows the methane content in the internal water ocean as a function of time, for different mass fractions of the undifferentiated proto-core relative to the total mass of Titan (15, 20 and 25%). The accumulation of free gas at the crust–ocean interface and its subsequent outgassing to the surface are possible only once the methane content in the liquid phase exceeds its saturation solubility. The solubility of methane as a function of pressure and temperature at

the crust–ocean interface can be evaluated from the Henry's Law constant $H_0(T)$ given by Sloan (1998) and the fugacity coefficient of the gaseous methane f_{CH_4} determined from Duan *et al.* (1992)

$$x_{\text{CH}_4,\text{sat}} = \frac{f_{\text{CH}_4}}{H_0(T)\exp[\bar{V}^\infty(P - P_0)/RT]}, \quad (5.1)$$

where \bar{V}^∞ is the partial molar volume of methane in water at infinite dilution ($\bar{V}^\infty = 34.5 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$; Handa 1990), and $P_0 = 1$ bar. For simplicity, we neglect the effect of ammonia on the solubility of methane in the aqueous solution.

According to the model of Tobie *et al.* (2006), during the early stage, most of the methane is stored as clathrate hydrate in the crust (figure 3*b*), and the decomposition of clathrate progressively enriches the water ocean in methane. For a 25 per cent mass fraction of the proto-core, the ocean gets saturated in gaseous methane at 1.5 Gyr and all the exceeding gas methane reaches the surface and rapidly replenishes the atmosphere with methane. Even if one uses an upper limit for methane loss rate taken from Toubanc *et al.* (1995) ($\partial M_{\text{loss}}/\partial t \approx 288 \text{ kg s}^{-1}$), the very high outgassing rate leads to methane accumulation on the surface. At 2.5 Gyr, the total mass of methane on the surface is 100 times larger than the present-day atmospheric mass. And at 4.55 Gyr, a huge mass of methane (60×observed mass) should still be present on Titan's surface, which is obviously inconsistent with the present-day inventory of methane (Lorenz *et al.* 2008). By contrast, for a proto-core mass fraction of 15 per cent, the water ocean never gets saturated, and methane outgassing occurs only during the last epoch between 4 and 4.5 Gyr. Following Tobie *et al.* (2006), the outgassing rate during the last episode is assumed to be proportional to the surface heat flow and leads to the decomposition of 10 per cent of the available crustal-clathrate reservoir. For a proto-core mass fraction of 20 per cent, in addition to the late outgassing period, a short outgassing event occurs at approximately 2.5 Gyr, and the atmospheric methane totally vanishes after 200 Myr.

In this model, when the last outgassing episode starts, the clathrate-rich crust still contains approximately 200 times the current mass of atmospheric methane, which seems *a priori* largely sufficient to replenish the atmosphere in methane. However, the outgassing rate strongly depends on the vigour of thermal convection in the underlying ice shell and in the ability of thermal plumes to penetrate the overlying clathrate-rich crust. Efficient dissociation may occur only if upwelling icy plumes with temperatures of 200–250 K penetrate the upper crust to relatively shallow depths (1–2 km below the surface). Recently, Choukroun *et al.* (2008) showed that the presence of ammonia hydrate in the crust could facilitate the dissociation of methane clathrate and the formation and rise of low viscosity cryomagmas enriched in methane. Even if ammonia hydrates can help, thermal convective instabilities in the ice shell are still required to trigger the decomposition process. If a 5 km diameter plume triggers a cryovolcanic event that dissociates all the overlaying clathrate-rich crust, the maximum amount of methane outgassed is 10^{12} kg, which is less than 1/100 000 of the total atmospheric CH_4 mass. As such a small amount would be photochemically destroyed within 100–1000 years, similar cryovolcanic events should occur at least every thousand years to sustain a few percent of methane in the atmosphere. If such processes are really operating on Titan, future mapping of the surface should reveal more and more cryovolcanic features.

(b) Inventories of hydrocarbon on Titan's surface

The present-day inventories of hydrocarbon on the surface are strongly dependent on the initial amount of methane stored within the interior. If the interior initially contained a relatively large methane fraction [$\geq 0.25\%$ ($25\% \times 1\%$)], massive outgassing should have occurred in the past and a very thick layer (more than 1000 m) of a mixture of liquid methane and ethane should still be present on Titan's surface. This is obviously inconsistent with the Cassini–Huygens observations. Therefore, this scenario can be ruled out.

By contrast, for low initial methane content ($\leq 0.15\%$), outgassing of methane has occurred only very recently, and no methane is present in the atmosphere during the major part of Titan's history. Nevertheless, the presence of a significant amount of ^{40}Ar in the atmosphere indicates that mobilization of argon contained in the water ocean through methane-bubble formation has occurred (Tobie *et al.* 2006), thus suggesting that ancient outgassing, at least during a relatively short period of time, existed. The ocean was able to reach the saturation point only if the interior contained at least a total mass of methane equivalent to 200 times the current atmospheric mass. Any methane in excess then outgassed to the surface, transporting part of the argon dissolved in the ocean. However, future modelling efforts are required to quantify the efficiency of such argon extraction processes.

Even in a scenario with low methane content, episodic moderate outgassing of methane and subsequent photolysis lead to the accumulation of liquid ethane onto the surface, possibly reaching a thickness of up to 200 m (figure 3c). This is still large compared with the present-day inventory of liquid hydrocarbons (Lorenz *et al.* 2008). This implies that liquid ethane has been removed from the surface. Ethane could be hidden in the crust as a liquid if the crust porosity is sufficiently large (Kossacki & Lorenz 1996), and/or in the form of clathrate hydrates (Osegovic & Max 2005; Mousis & Schmitt 2008).

Indeed, clathrate hydrate formation is known to be stable relative to water ice on the surface and in the upper crust. Therefore, any liquid water or water ice that is exposed at the surface, after a cryovolcanic event or an impact cratering (Artemieva & Lunine 2005), should progressively transform into a clathrate structure whose composition depends on the composition of the atmosphere and of liquid hydrocarbons. Nitrogen and methane will enter the clathrate structure to some extent, but ethane is the molecule that preferentially enters it (Osegovic & Max 2005). Interestingly, clathrates of a mixture of nitrogen, ethane and methane are much denser than pure methane clathrate or water ice ($\rho \approx 1000\text{--}1200 \text{ kg m}^{-3}$ depending on the ethane and nitrogen fraction), so that the accumulation of ethane/nitrogen-rich clathrates at the surface is gravitationally unstable. The destabilization of such a heavy crustal material and its recycling into the interior can be envisaged. During the process, part of the atmospheric nitrogen and the atmospheric methane may be recycled into the interior. In return, the sinking of such a heavy crust would also help the rise of warm upwelling from deeper levels and hence favour the destabilization of the ancient crustal methane-rich clathrate reservoir. Numerical simulations are currently carried out to determine the conditions required to initiate crustal overturning and to quantify its effect on the hydrocarbon budget.

The other major product of CH_4 -based photochemistry is acetylene (C_2H_2). By contrast to ethane, Titan's surface is cold enough for acetylene to freeze. Figure 3c shows that a thickness of up to 60 m of solid acetylene can accumulate on the

surface, for a proto-core mass fraction of 20 per cent. Solid acetylene may be one of the major constituents of the superficial crust. If so, it must be affected by aeolian and fluvial erosion processes, and must be one of the main sedimentary materials on Titan. It could be dissolved in some places, precipitated and accumulated in other places and could therefore play a key role in the morphology of lakes on Titan (Bourgeois *et al.* 2008). However, solid acetylene has not been detected on Titan's surface so far. Dedicated remote sensing observations or *in situ* analysis in the future are required to identify solid acetylene on the surface and to determine its potential role on the surface morphology.

6. Conclusion

Data gathered by the Cassini–Huygens mission provide circumstantial evidence that releases of methane from the interior have occurred along Titan's history. Methane outgassing is also supported by thermal evolution models which indicate that the destabilization of methane stored as clathrate hydrates within the crust is a natural consequence of the interior evolution. However, those models show that outgassing is not a continuous process, and suggest that Titan has probably experienced long periods of time without methane in the atmosphere, possibly resulting in a partial condensation of the N₂ atmosphere (Lorenz *et al.* 1997).

According to thermal evolution models (Tobie *et al.* 2006), outgassing processes should be able to counterbalance the photochemically induced loss rate and should be triggered by warm ice intrusions into a near-surface reservoir of methane-rich clathrate. The initiation of the thermal instabilities is related to the late crystallization of the subsurface ammonia–water ocean, which is a consequence of the tidal evolution of Titan (Tobie *et al.* 2005, 2006). More ancient outgassing episodes related to the exsolution of the internal ocean must have also occurred to explain the abundance of radiogenically derived argon detected in the atmosphere. This implies that the interior contains more than 0.15 per cent of methane relative to water. On the other hand, the initial methane content must be lower than 0.25 per cent to explain the absence of extensive liquid bodies on the surface. These estimates provide upper and lower limits for the methane content in the interior of Titan.

Other primordial C-bearing compounds may also be present in Titan's interior to some extent. Carbon monoxide has been detected in the atmosphere and is suspected to originate from the interior (Baines *et al.* 2006). Carbon dioxide has been detected on the surface and seems to be correlated with cryovolcanic provinces, suggesting an internal origin (McCord *et al.* 2008). The incorporation of CO₂ during Titan's accretion is also suggested from formation models (e.g. Hersant *et al.* 2008). The conversion of CO and CO₂ through serpentinization processes has also been proposed as a potential source of methane in the interior (Atreya *et al.* 2006). However, the production of several masses of atmospheric methane would require the serpentinization of a significant part of olivine minerals contained in the rocky core (Oze & Sharma 2005). Even though olivine serpentinization is a possible process, it is still uncertain whether it is efficient enough to renew the atmospheric methane over geological time scales. Further laboratory measurements and modelling are required to better assess the role of serpentinization on the methane inventory on Titan.

Photodissociation of atmospheric methane at high altitudes irretrievably leads to the accumulation of photochemical by-products on Titan's surface. Part of the photochemically derived materials, in particular ethane, may have been incorporated into the crust in the form of clathrate hydrates and would have been later recycled into the satellite's interior owing to crustal overturning. However, solid organic materials should still be present on the surface. Even though the interior is mostly composed of water ice and various hydrates, the near-surface is probably dominated by organic materials. Interaction of liquid methane and other liquid hydrocarbons with such solid organic deposits probably shaped the landscape of Titan. Water ice and hydrated materials should dominate only in cryovolcanically active provinces.

Ammonia has long been suspected to be present inside Titan, and direct sampling of Titan's atmosphere by the GCMS on board Huygens provides circumstantial evidence that ammonia is the primordial source of atmospheric nitrogen, confirming its presence in the interior. However, there is still no unambiguous detection of ammonia ice or hydrate on the surface, even if its presence is suspected in cryovolcanic flow-like features. Besides, the initial ammonia fraction required to explain the formation of the massive nitrogen-dominated atmosphere is still unconstrained. Sulphur compounds may also contribute to the complex history of Titan. Fortes *et al.* (2007) recently proposed a chemical evolution model of Titan in which primordial NH_3 reacts with sulphate-rich brines and leads to the formation of ammonium sulphate. Such a compound is expected to affect the thermal equilibrium of the liquid layer. Both ammonia and ammonium sulphate are expected to favour the formation of cryomagma and their rise to the surface. Titan's interior is probably composed of a complex mixture of primordial compounds and recycled compounds, and future experimental and theoretical works are required to understand how each species interacts and affects the chemical evolution of Titan.

Future Cassini observations will be helpful to understand the processes at work on Titan's surface. Identification of cryovolcanic provinces from radar and near-infrared imaging and correlation with surface composition from near-infrared spectroscopy will give constraints on the outgassing mechanism and on its likelihood. Further acquisition of reference spectra in the laboratory will also help to characterize the surface composition, and in particular the composition of organic materials, which is essential to better constrain the global carbon cycle. Beyond this, a future exploration mission dedicated to Titan is required to understand the real nature of Titan's exotic surface and the link with the evolution of its interior and its atmosphere. Important goals for such a mission might be to assess the location of the volatile reservoirs inside Titan, to determine the mechanism of volatile release and to quantify the inventories of hydrocarbon deposits on the surface.

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