SEQUESTRATION OF ETHANE IN THE CRYOVOLCANIC SUBSURFACE OF TITAN

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Abstract. Saturn's largest satellite, Titan, has a thick atmosphere dominated by nitrogen and methane. The dense orange-brown smog hiding the satellite's surface is produced by photochemical reactions of methane, nitrogen and their dissociation products with solar ultraviolet, which lead primarily to the formation of ethane and heavier hydrocarbons. In the years prior to the exploration of Titan's surface by the *Cassini-Huygens* spacecraft, the production and condensation of ethane was expected to have formed a satellite-wide ocean one kilometer in depth, assuming that it was generated over the Solar system's lifetime. However, *Cassini-Huygens* observations failed to find any evidence of such an ocean. Here we describe the main cause of the ethane deficiency on Titan: cryovolcanic lavas regularly cover its surface, leading to the percolation of the liquid hydrocarbons through this porous material and its accumulation in subsurface layers built up during successive methane outgassing events. The liquid stored in the pores may, combined with the ice layers, form a stable ethane-rich clathrate reservoir, potentially isolated from the surface.

1 Introduction

Any discussion on the reservoirs of ethane condensate at the surface of Titan should take into account the recently revised condensation rate of 5.9×10^{-14} g cm^{-2} s^{-1} for this molecule, consistent with Cassini CIRS observations (Atreya et al. 2006). This lower ethane condensation rate implies a reduction of the depth of the initially expected satellite-wide ocean to a value of ∼155 m, if methane was continuously released over Titan's life. This value is even smaller if we consider Titan's recent thermal evolution models supporting the idea that the methane outgassing has occurred episodically (Tobie et al. 2006). If the actual atmospheric methane is outgassing at the current rate since only ∼0.6 gigayears (Gyr) (Tobie et al. 2006), the depth of the hypothetical global ethane ocean reaches no more than ∼20 m. Indirect evidence has been obtained for the presence of lakes at high latitudes in the northern hemisphere during several Cassini Radar flybys of Titan (Stofan et al. 2007; Lorenz et al. 2008). But with a likely current inventory of 3×10^4–3×10^5 km^3 of liquid (Lorenz et al. 2008), these lakes are not expected to store more than about 20% of the produced ethane. This value can even be lower if we consider alternative photochemical models which lead to the condensation of twice as much ethane and predict the presence of substantial amounts of liquid propane (Vuitton & Yelle 2005).

The apparent deficiency in liquid ethane on Titan has been interpreted as supporting the theory that ethane mostly condenses onto smog particles forming different types of thick deposits, including dunes and dark areas (Hunten 2006). However, the haze production rate is only 8 to 50% of the ethane value (Atreya et al. 2006). With all the liquid and solid condensates taken into account, the liquid-to-solid volume ratio ranges between 2.5 and 23. No granular material, even extremely microporous, can adsorb more than 30% of its volume in its pores at saturation. Any liquid above this value will wet the saturated haze, up to the point where the plastic and then the liquid limits of the material are reached. With liquid-to-solid volume ratios larger than 2.5, these limits are largely exceeded and the rheological properties of such wet material are incompatible with the stability of the observed dunes. In the most favorable case, the dunes and the wetter dark flat area could probably retain up to 20% of the total liquid inventory, but the remaining 80% should escape the haze deposits and migrate to other reservoirs.

An alternative interpretation is that a liquid ocean would fill the empty space of the upper crust consisting in a 10,000 m regolith layer generated by impacts during Titan's early history (Kossacki & Lorenz 1996). After

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4.5 Gyr of Titan's evolution, the porosity of this layer would decrease to 1–4%, allowing the incorporation of a liquid ocean with an equivalent depth of ~100–400 m (Kossacki & Lorenz 1996). However, these calculations do not consider the porosity closing off and the depth below which it becomes isolated from the surface. On Earth, the porosity close-off in pure water ice is ~10% for Greenland's ice cap, but for the finer grain size of the regolith this value is probably even higher. The resulting amount of trapped liquid is then lower than predicted. Moreover, the *Cassini* Radar and optical images show that the satellite surface is geologically young (Elachi et al. 2005). Therefore, it is unlikely that large extents of the early regolith remain currently in contact with the atmosphere since the deposition of photochemical debris, pluvial erosion or deposition, tectonic processes or cryovolcanism may have contributed to their burial.

None of the aforementioned ethane trapping scenarios is fully supported by the *Cassini-Huygens* observations of Titan (Atreya et al. 2006; Elachi et al. 2005; Stofan et al. 2007). However, the detection of cryovolcanic features (Elachi et al. 2005; Lopes et al. 2007), together with the theoretical estimates of strong resurfacing rates (about 50 m of "cryolava" deposited per 10^6 yr; Elachi et al. 2005), lead us to propose a geological process that solves the ethane deficiency issue in a manner which is in agreement with our current knowledge of Titan: the incorporation of liquid hydrocarbons in the porous cryovolcanic subsurface. However, note that, at present, no extensive cryovolcanic deposits have yet been clearly identified on the surface of Titan but the presence of some distinct cryovolcanic features makes our scenario worth developing.

2   Cryovolcanism on Titan

We investigate the conditions of such incorporation by considering two different mechanisms of cryovolcanism and methane delivery:

Ascent of liquid from the subsurface ocean.   The methane coming from the saturated deep ocean (Tobie et al. 2006; Fortes et al. 2007), is transported close to the surface of Titan in ammonia-water pockets which erupt through the ice shell and lead to cryovolcanism (Mitri et al. 2006). The release of dissolved methane creates gas-rich eruptions and very porous cryovolcanic materials since, even with only 1% of dissolved methane, the gas volume expelled largely exceeds that of the cryovolcanic ice.

Destabilization of clathrates in the ice shell of Titan.   In this case, clathrates of methane stored in the close subsurface are destabilized by ascents of hot thermal plumes and melt (Tobie et al. 2006). The cryolava expelled to the surface of Titan releases the large amount of methane initially trapped in clathrates. A very porous ice is produced from this clathrate decomposition (Schmitt 1986).

In both cases, a highly porous icy material is generated, probably similar to basaltic lava flows. Since the cooling of the cryolava is expected to take less than one year to decrease down to Titan's surface temperature (Lorenz 1996), it should be fast enough to allow the preservation of most of the porosity created by the methane release.

3   Trapping of liquid hydrocarbons in the subsurface layers

The liquid composition formed on Titan's surface can be inferred if it is considered in thermodynamic equilibrium with the atmosphere and that the organic materials mixed with the fluid have only minor effects on this equilibrium. With a methane mole fraction of $\sim 4.9 \times 10^{-2}$ measured near the surface by *Huygens* (Niemann et al. 2005), the predicted mole fractions of methane, ethane and nitrogen are ~0.35, ~0.60 and ~0.05 in the liquid, respectively (Dubouloz et al. 1989). We adopt these fractions as the nominal composition of the liquid currently present at and below the surface of Titan.

We now consider two different Titan evolution scenarios and estimate the equivalent depth of a global liquid layer condensed on its surface: over a 0.6 Gyr period of cryovolcanism (Tobie et al. 2006), and over the lifetime of the Solar system (4.55 Gyr). In the first case, the thickness of the liquid layer is ~30 m, including 21, 8 and 1 m of ethane, methane and nitrogen, respectively. In the second case, the thickness increases to 225 m, with 155, 62 and 8 m of ethane, methane and nitrogen, respectively. If the upper layers of Titan's subsurface are mostly constituted by an homogeneous deposit of cryolavas with a mean porosity of 25%, icy crust thicknesses of only ~120 and 900 m are required to bury these oceans for the two scenarios. Even if the porosity is 10%, ice crust thicknesses of only 300 and 2250 m deep, respectively, are required.
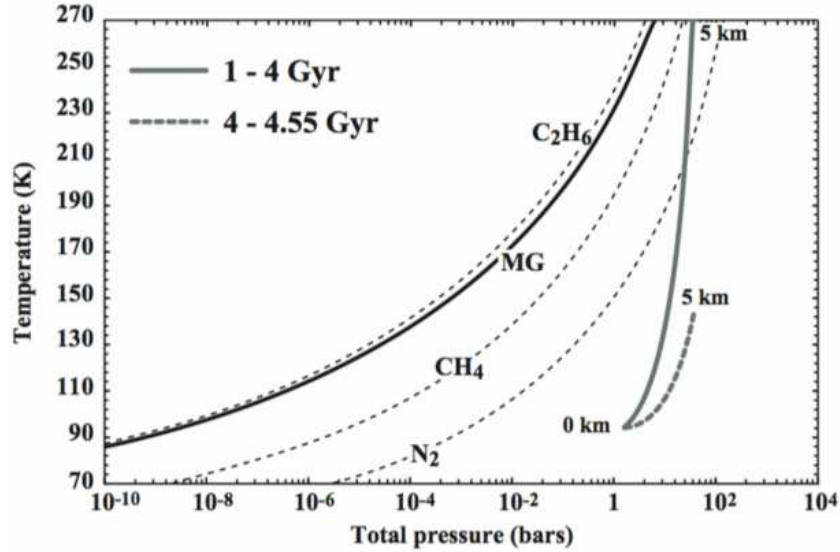
Fig. 1. From left to right: equilibrium pressures of C_2H_6, multiple guest (MG in the figure), CH_4 and N_2 clathrates as a function of temperature (black curves). The hydrostatic pressure within a column of CH_4-C_2H_6-N_2 liquid is also represented as a function of local temperature in the porous subsurface of Titan at two different periods of its thermal history. The first temperature profile (grey curve) corresponds to the 1–4 Gyr period of Titan's evolution. During this period, the upper water ice crust is conductive and its thickness does not exceed ∼5 km. A linear temperature profile can then be constructed between an assumed temperature of ∼94 K at the surface and ∼270 K at the inner ice-ocean interface. The second temperature profile (dotted grey curve), which is valid at epochs later than 4 Gyr, postulates the existence of a ∼50 km thick icy crust. In the outer conductive layer of the icy crust, about 15 km deep, the temperature varies linearly between ∼94 K and ∼250 K. In our calculation, we only consider the first 5 km of the icy crust since it can largely contain all the liquid hydrocarbons generated over Titan's life (see text).

Presuming that the liquid at a given depth is in thermal equilibrium with the ice surrounding the pores, we consider two different temperature profiles derived from Titan's interior models and covering its overall thermal history (Tobie et al. 2006). Assuming that the ice porosity remains open within the first 5 km of the icy shell, the two hydrostatic pressure-vs-temperature curves in a column of liquid are calculated and compared to the stability curves of clathrates in Fig. 1. The equilibrium pressure curve of the multiple guest clathrate (hereafter MG clathrate) is determined for the nominal liquid composition. The equilibrium pressure curves of methane, ethane and nitrogen single guest clathrates are determined by fitting the available laboratory data and their equations are of the form $\log P_{eq} = A/T + B$, where P_{eq} and T are the partial equilibrium pressure (bars) and the temperature (K) of the considered species, respectively. Table 1 shows the values of constants A and B from our fits to laboratory measurements. Equilibrium pressure curves for MG clathrate formed from the liquid mixture, can be expressed as (Hand et al. 2006):

$$P_{eq,MG} = \left[\sum_i \frac{y_i}{P_{eq,i}} \right]^{-1} \tag{3.1}$$

where y_i is the mole fraction of the component i in the fluid phase. Figure 1 displays the dissociation pressures of methane, ethane, nitrogen and MG clathrates as a function of temperature. At a given temperature, these clathrates are stable at pressures equal or higher than their equilibrium pressures. They are also more stable than the liquid with corresponding composition provided sufficient water ice is available. In both cases, the column of liquid is located within the thermodynamic stability domains of ethane, methane and MG clathrates. The methane-ethane-nitrogen liquid filling the pores of Titan's icy crust thus likely forms, at all depths, a MG clathrate with the available water ice.

4   Discussion

Although the hydrostatic stability of the liquid column is achieved at any depth for both types of temperature profiles when the column is filled up to the surface (hydrostatic pressure always larger than the equilibrium vapour pressure of the liquid), this is not the case for a shallow column of liquid accumulated at great depths, and thus at higher temperatures. For example, if the porosity close-off currently occurs at 3 km depth the vapour pressure at the bottom of the liquid column (123 K) is larger than 2 bars and requires at least 300 m of liquid to stabilize. For porosities of 10–25%, a minimum equivalent ocean depth of 30–75 m is necessary, larger than the total amount of liquid produced in the scenario of recent methane outgassing. In such cases the liquid may ascend the column under the vapor pressure and erupt. However the much colder upper crust layers will probably recondense the boosting gas before it reaches the surface. Clathrate formation provides a more efficient way to stabilize the stored methane-ethane-nitrogen mixture at great depth. Its formation also greatly reduces the equilibrium gas pressure and thus stabilizes the remaining liquid phase. With our current knowledge of clathrate formation, the amount of liquid trapped in the form of MG clathrate remains difficult to estimate. Indeed, the extent of clathrate formation from the liquid phase can be limited by the very slow (and poorly known) kinetics at these low temperatures and the availability of water ice to clathration around the pores. Finally, the formation process of clathrates strongly reduces the porosity of the crust. With a volume expansion of the clathrate structure of ∼20% compared to that of water ice, its formation in an ice layer with an initial porosity of 25% reduces this quantity to 10%, namely the close-off value observed in terrestrial ice caps. So clathrate formation may well induce its self isolation by closing the pore network that allowed the liquid hydrocarbons to percolate the ice down to these dept hs.

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