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The hydrologic cycle on Saturn's moon, Titan

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Abstract. Titan is Saturn's Mercury–sized moon with the densest atmosphere-save that of Venus–of any solid body in the solar system. The presence of large amounts of liquid and solid hydrocarbons, discovered by the Cassini-Huygens mission, implies a cycling between vapor, liquid and possibly solid states akin to the hydrological cycle on the Earth. A number of interesting sites for chemistry may be identified on Titan, despite the cold temperatures, including zone of recent impacts, areas of enhanced geothermal activity, the polar lakes and seas, and basins where acetylene may have collected and is polymerizing over time, releasing stored chemical energy as heat.

Key words. Planets and satellites: general– Planets and satellites: Titan – Space vehicles: instrumentation

1. Introduction

Saturn's largest moon–the second largest moon in the solar system–is Titan. With an atmosphere of nitrogen four times denser at the surface than sea level air density on Earth, Titan is a unique body in the solar system (Coustenis and Taylor 2008). And yet, paradoxically, it may represent the most common type of body in the cosmos with a stable surface "volatile cycle" (Lunine 2009). In Titan's case, the secondary gas in the atmosphere, methane (CH_4), condenses at altitudes above 8 km in the equatorial region, and several kilometers lower at the poles. Condensed methane is a liquid at the equatorial surface temperature of 94 K, and is only completely frozen above 14 km altitude thanks to the freezing point depression afforded by atmospheric nitrogen (Lorenz & Lunine 2002). It occurs in lakes and seas in the polar regions (Stofan et al. 2007), mixed with ethane (Brown et al. 2008) and a number of other organic species (Cordier et al. 2010). Imaging evidence for fluvial erosion on a variety of scales suggests that sediments composed of a mixture of organics and water ice are being transported poleward (Lunine & Lorenz 2009), while a significant portion of the solid organics may be trapped in the equatorial region as dune particles (Neish et al. 2010). The successful NASA/ESA/ASI Cassini-Huygens mission continues to track the shifting patterns of meteorology as equinox gives way to northern spring and then summer over the next several years. Here rather than try to provide a comprehensive description of Titan's hydrologic cycle, I focus on the interesting highlights and

Send offprint requests to: J. I. Lunine implications for surface organic chemistry afforded by this subtly active volatile system.

2. Methane cycle

The methane cycle on Titan (figure 1) involves passage of methane through all three physical forms as does water on the Earth, but with a number of important differences. First, Titan lacks a global ocean, so that the bulk of the surface liquids are concentrated at high latitudes. Second, methane is not as tightly bound in the lower atmosphere (troposphere) as is water on Earth, because of the steeper temperature gradient in the lower atmosphere of our home world. While the mixing ratio of methane drops by only a factor of three from the surface to the top of the troposphere (tropopause) on Titan, water drops by three *orders of magnitude* from the surface to the tropopause on Earth. Thus methane is in rapid escape to the stratosphere where ultraviolet light breaks up the molecule and results in irreversible loss of hydrogen – hence, of methane. The same happens to water in Earth's stratosphere but at a vastly slower rate.

All the methane in Titan's atmosphere will be lost in a time span of 100 million years or less, suggesting that either we are fortunate to be seeing the last stage of a long history of methane decline, or that methane is resupplied over geologic time. One of the goals of the Cassini – Huygens extended mission is to seek evidence for ongoing outgassing that might hint at subsurface reservoirs of methane. Should no such reservoir exist, Titan as we observe it might provide an interesting analog for our home world in one to two billion years, when the luminosity of the Sun rises sufficiently to warm the troposphere to the point at which water escapes to our stratosphere (Caldeira & Kasting 1992) at a rate comparable to that of methane on Titan at present.

The destruction of methane by ultraviolet light from the Sun has another, profound consequence for the methane cycle on Titan, again making it quite distinct from that of the Earth. As hydrogen is lost from the stratosphere, methane that is broken apart cannot be put back together. Instead, the highly reactive fragments, such as CH, CH_2, and CH_3, recombine to produce higher hydrocarbons – those with higher C/H ratios than the 1/4 in methane – and nitriles (H,C,N bearing compounds). Among the most abundant products are ethane (C_2H_6), acetylene (C_2H_2), and hydrogen cyanide (HCN). Ethane together with propane (C_3H_8) are liquid at Titan's equatorial surface temperature; all other products of Titan's stratospheric photochemistry are solid. However, many of these dissolve to a significant extent in the liquid. The vapor pressures of methane, ethane and propane range over six orders of magnitude at a given lake temperature (figure 2), and yet thermodynamic data indicate that they are fully miscible (Cordier et al. 2010). Therefore, we have the unique situation that methane, and in its absence ethane, will migrate from summer to winter pole by evaporation and recondensation as the Sun moves over a Titan year (30 Earth years), while other organics will remain stable. Ethane mixed with methane in a lake or sea is immobile because the evaporation of methane dominates and uses essentially all the available solar flux. The phasing of Titan's seasonal tilt with respect to the perihelion of Saturn's orbit shifts on timescales of tens of thousands of years, akin to the terrestrial Croll-Milankovitch cycles (Aharonson et al.2009). On these timescales less volatile constituents–ethane and propane–can move from pole to pole, along with solid acetylene. HCN, on the other hand, cannot move significantly on either of these timescales. Over an annual cycle lakes and seas will alternate between compositions richer in methane and those richer in ethane and propane. This, in turn, has surprising consequences on the appearance of the lakes and seas, because the viscosity of an ethane-propane lake is seven times larger than that of a pure methane lake at the same temperature (Lorenz et al. 2010). There are also implications for solubility and cyclical deposition of minor constituents on seasonally shrinking and expanding lake shores (Moriconi et al. 2010).

Although the lakes and seas of Titan have generated keen interest by virtue of being the first liquid features to be definitively identified

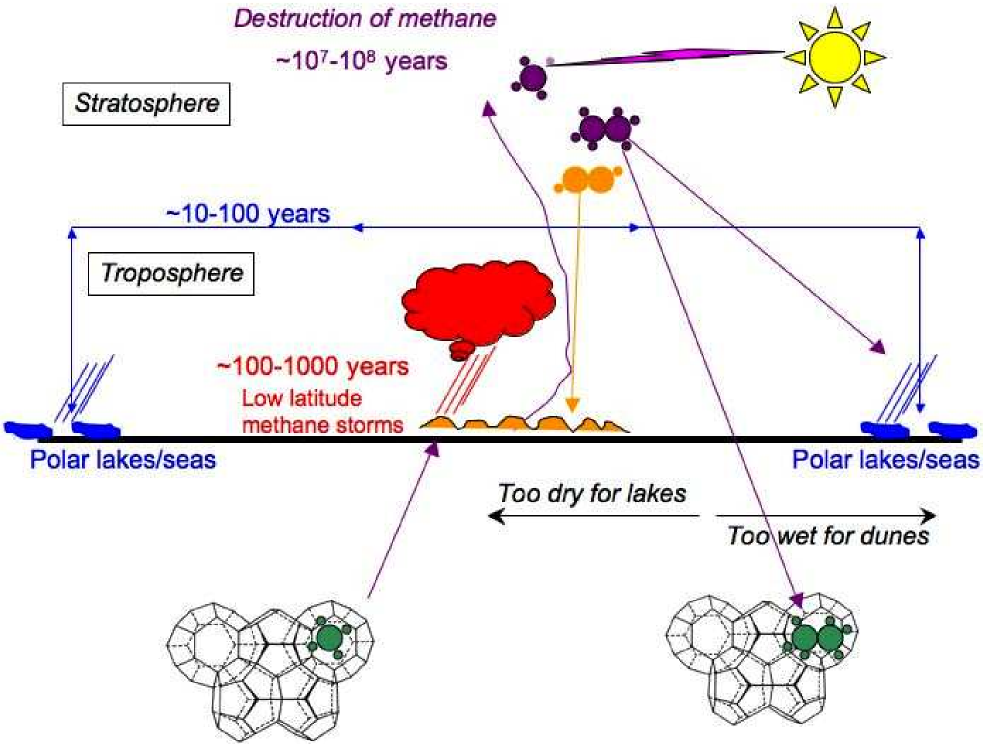

Fig. 1. Elements of Titans methane cycle known or strongly suspected to be present, along with timescales for destruction of methane (10^7 – 10^8 years), cyclical humidification of low latitudes (100 – 1000 years) and seasonal cycling of methane between the poles (10 – 100 years). Adapted from a figure originally in (Lunine & Atreya 2008).

on another world, the largest reservoir of organic material on Titan's surface is solid, and mostly confined to an equatorial belt of dunes which occupy roughly 20% of the entire globe. Measurement of the dielectric constant of the dunes at 2 cm wavelength (Lorenz et al. 2006) and near-infrared color mapping (Barnes et al. 2008) are both consistent with the dune particles being made largely of solid organics.

3. Chemistry

The production in the stratosphere and presence of acetylene on Titan's surface provides the potential for a source of heat usable for chemical reactions. Acetylene's unsaturation carbon bonds allow for the possibility of exothermic chemical reactions producing either benzene (C_6H_6) from three acetylene molecules or various types of polyacetylenes depending on the presence of impurities or application of pressure (Ceppatelli et al. 2000). The heat available from the "cyclization" reaction to form benzene is about 334 kJoule per mole of acetylene (McKay & Smith 2005), but an activation energy barrier of about 140 kjoule/mole must be overcome. Cosmic rays seem to be the most predictable energy source for overcoming the barrier, exciting the acetylene to the triplet state (Zhou et al. 2010), but putative cryovolcanism, thermal and shock effects over a wide area surrounding a hypervelocity impact, fluvial transport, or even tidally induced wave action on lake shores might be effective in inducing the conversion. Indeed, handling of solid acetylene in the laboratory is

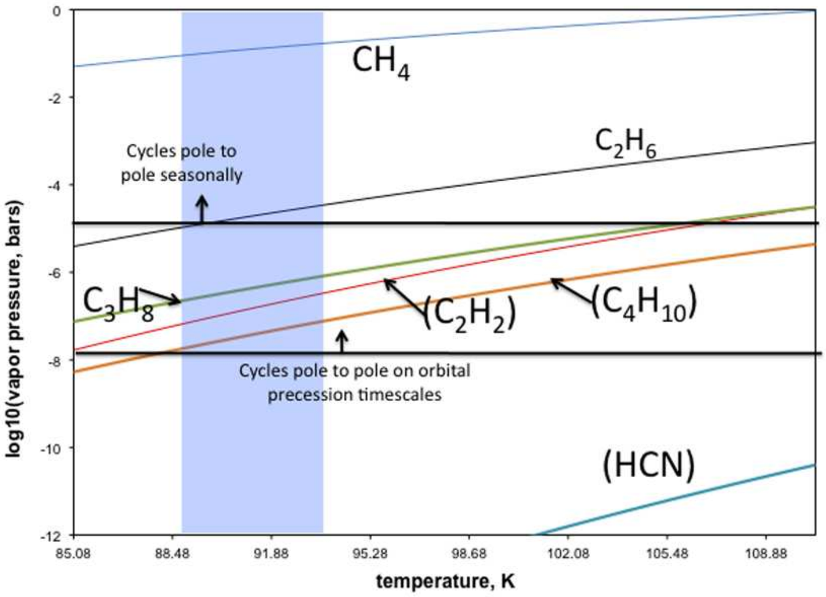

Fig. 2. Plot of saturation vapor pressure versus temperature for various hydrocarbons and for HCN. Molecules in parentheses are in the solid phase for the depicted temperature range. The blue shaded area represents a plausible range of surface temperatures on the lakes and seas observed in the polar regions. The two horizontal lines depict the lower bounds for species to undergo significant evaporation and hence hemispherical transport on seasonal (upper) and "Croll-Milankovitch" (lower) timescales. See text for a discussion of these timescales.

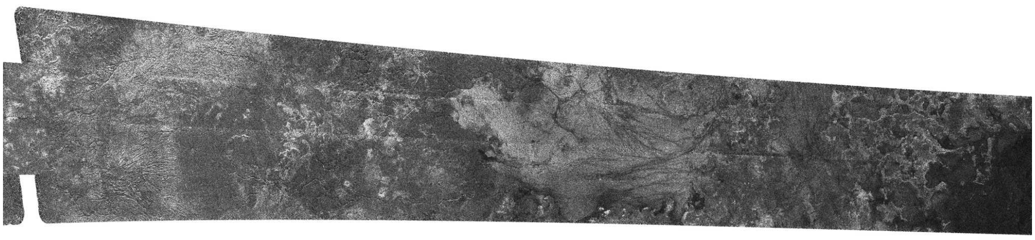

Fig. 3. This swath from the Cassini RADAR system covers about 700 kilometers of terrain, at high southern latitudes and moving poleward from let to right. The resolution of the image varies from near 1 km at the left end to about 350 meters on the right hand side. The center of the swath is at about 56^o south latitude. Various channels, which look like they were carved by running liquid (presumably methane), seem to trend roughly poleward. Cassini RADAR image originally shown in (Lunine et al. 2008)

hazardous because modest mechanical shock can induce conversion which in the presence of oxygen is an explosive reaction (Matteson 1984).

The chemical energy released as heat during the cyclization of acetylene to benzene would be sufficient, on Earth, to sustain a methanogenic metabolism on a per mole basis (McKay & Smith 2005). However, the liquid water required for all forms of terrestrial life is not thermodynamically stable on Titan's surface; its occurrence would be transient and limited to subsurface zones associated with impacts and melting of the "bedrock" water ice in a process called "cryovolcanism" by analogy with terrestrial silicate volcanism (O'Brien et al. 2005). More speculative but also more intriguing is the possibility that a form of life could exist in liquid methane and ethane, albeit one so primitive that it might be considered a precursor to life or transitional between living and nonliving chemistry (Benner, et al. 2004). If such a chemical system were to exist in Titan's lakes and seas, it might be sustained energetically by the ultraviolet light from the Sun stored in the unsaturated chemical bonds of acetylene produced high in Titan's stratosphere.

Of course, a methane-based life form would have no biochemical resemblance to life on Earth, down even to the fundamental units of biopolymers such as amino acids and nucleic acid bases. In being so exotic at a deep chemical level, its identification would be difficult for any but the most elaborate spacecraft laboratory. However, its exotic nature also confers an advantage: there is no possibility that such a form of life would be a contaminant from Earth. Theoretically calculated probabilities for delivery of impactors from the inner solar system to Europa and Titan are large enough that each of the latter two bodies has received material from Earth and Mars multiple times over the age of the solar system (Gladman et al. 2006). Survival of martian organisms, if they exist, is possible during launch of a rock by hypervelocity impact off Mars (Burchell et al. 2004), though the same may not necessarily be true for launch off the Earth (G. Consolmagno, pers. comm.).

In summary, one cannot rule out introduction of terrestrial or putative Martian organisms into the environments of Europa or Titan. Europa's strongly suspected subcrustal liquid water ocean would provide a viable environment for such organisms, whereas the surface methane-ethane lakes and seas of Titan would not. Therefore, any form of life or transitional organized chemistry found in the lakes and seas of Titan should have had an entirely separate origin from terrestrial life (Lunine 2009). Such life is a very remote possibility, but were it found to exist, it would bolster the notion that life can form wherever the general requirements of thermodynamic free energy, organic molecules and liquid phases are present. The lakes and seas of Titan are an important target for future exploration with chemical analysis laboratories to test for a possible second origin of life in our solar system.

Aside from the exotic biological possibilities, there is almost certainly an intriguing variety of chemistry taking place on the surface of Titan, modifying the abundances of species from the abundances established in the stratosphere and introducing oxygen into organic molecules from the underlying water ice bedrock or from occasional episodes of crustal melting of water. by impact or cryovolcanism. This material is mobile thanks to fluvial transport (figure 3), and based on the global topography of Titan the trend is poleward (Zebker et al. 2009). Therefore, much of the organic sedimentary material, along with water ice grains, may eventually end up in deposits at high latitudes or even in the lakes and seas near the poles. The Cassini near-infrared spectrometer sees deposits of benzene (Clark et al. 2010) but not, surprisingly, of acetylene, even though the latter is abundant in stratospheric products of methane chemistry (Lavvas, Coustenis & Vardavas 2008). The ability of the spectrometer to diagnose minor surface constituents through the dense, methane – rich, hazy Titan atmosphere is limited, and so this discrepancy between stratospheric production and surface abundance of simple hydrocarbons may be the strongest indication we will get from the Cassini-Huygens mission that additional surface chemistry is occurring.

Another mystery is why so little liquid is present on Titan's surface, given that methane photolysis should have produced a global layer of ethane hundreds of meters thick if it has been ongoing over the age of the solar system. The presence of substantial "solid seas" of dunes composed of organic materials suggests that indeed methane has been present in the atmosphere for geologically significant periods of time. The stability of ethane (and propane) against conversion to solid organics suggests that much of the ethane produced in the atmosphere is not present in the polar lakes and seas, but has been sequestered in the crust of Titan, or even below the crust. Whether the ethane simply drains into a porous water ice crust, is trapped as clathrate hydrate in water ice after cryovolcanic (Mousis & Schmitt 2008) or impact (Lunine Artemieva & Tobie) events, or has been lost in some other way (Hunten 2006) is likely to remain unresolved despite the ongoing stream of data from the Cassini – Huygens mission.

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