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## The global cycle of methane on Titan

OCEAN CIRCULATION TRENDS
Veiled by variability

HINDU KUSH EARTHQUAKES
A slab breaking off

MISSISSIPPI SUBSIDENCE
Peat compaction

# The methane cycle on Titan

Saturn's moon Titan is the second largest natural satellite in the solar system, and the only one that possesses a substantial atmosphere. With a surface temperature of 93.7 K at the equator, Titan's water is almost completely frozen out of the atmosphere; water ice comprises between 35% and 45% of the mass of Titan depending on the interior model. But methane seems to play many of the roles on Titan that water does on Earth: clouds have been observed, fluvial and dendritic features have been imaged suggesting episodic heavy rainfall, and there is compelling but circumstantial evidence for near-polar lakes or seas of methane and its atmospheric photochemical product, ethane. However, whereas Earth possesses a massive global ocean of water, Titan lacks a global methane ocean, and on Titan, low-latitude rainfall appears to be an occasional process limited by the small amount of available solar energy compared with that of Earth. Titan is therefore distinct from the Earth, but is also different from Venus in retaining an active cycle of precipitation and evaporation, and from Mars in the preponderance of active fluvial and pluvial processes in the present day.

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Following two flybys by the Voyager spacecraft in 1980 and 1981, Titan has been examined in detail since 2004 by the Cassini–Huygens mission, consisting of an orbiter around Saturn that ma kes multiple flybys of Titan, and a probe that descended to the moon's surface in 2005[1]. The dominant atmospheric constituents are nitrogen and methane, with the latter comprising 5% by number of gas molecules near the surface, and 1.5% at a temperature minimum some 50 km above the surface[2,3]. The temperature of the atmosphere, shown in Fig. 1, decreases from the surface value to 70 K at the temperature minimum (the 'tropopause')[4]. From about 8 km upwards from the surface, the binary mixture of nitrogen and methane is saturated[5,6]. Above this altitude, direct evidence for cloud (or methane haze) formation in the equatorial region was seen in the Huygens Gas Chromatograph Mass Spectrometer (GCMS) data — the counts in the methane channel suddenly increased as the probe descended through the 16 km level [2] — and in the Descent Imager–Spectral Radiometer (DISR) data beginning at around 20 km (ref. 7). However, mid-latitude clouds are sparse and transient[8–10]. More persistent, apparently convective, clouds formed around the south pole during southern hemisphere summer, and then dissipated as equinox approached[11]. Evidence for a stratospheric cloud of ethane has been seen in Cassini Visual and Infrared Mapping Spectrometer (VIMS) data at high northern latitudes[12,13].

The temperature gradient in Titan's lower atmosphere (the 'troposphere') is significantly shallower than in the equivalent part of the Earth's atmosphere. The maximum ('dry adiabatic') lapse rate is 1.3 K km$^{-1}$ compared with the Earth's 9.8 K km$^{-1}$, and convection is restricted to a thinner layer near the surface on Titan relative to the Earth. Because of the shallower temperature gradient in Titan's troposphere, cloud formation causes the methane concentration to drop from the surface to the tropopause by only a factor of three, some two orders of magnitude less than the drop in water concentration from Earth's surface to tropopause. Although the relative humidity of methane in the equatorial region — 45% — would be sufficient to trigger convective rainstorms on the Earth, it is insufficient in the case of Titan where available sunlight is more than 100 times smaller in the troposphere; values closer to 80% are required for moist convective methane rainstorms[14].

On Earth the very low mixing ratio of water (about 10 parts per million) at the interface between the troposphere and stratosphere — that is, the tropopause — and shielding by other gases such as molecular oxygen, strongly limits the rate of destruction of water by ultraviolet photolysis in the stratosphere. On Titan, where the methane mixing ratio at the tropopause is large, the limiting factor for ultraviolet photolysis is the availability of photons[15], and shielding by the photochemically produced haze is limited. Additional loss of methane occurs owing to the impact of charged particles in the ionosphere[16,17]. Hydrogen is removed from the methane, and escapes to space. The remaining fragments form higher-order hydrocarbons (ethane, acetylene, propane, polyynes, benzene, and so on), and nitriles (hydrogen cyanide, cyanoacetylene, cyanogen, and so on). The process is irreversible because of the escape of the hydrogen and because the more complex molecules polymerize and subsequently condense into aerosols, which fall to the surface[2,15,18]. As the total atmospheric inventory of methane has been removed in this way over a timescale of several tens of millions of years, there must be a source of replenishment[18,19]. Moreover, the Huygens GCMS

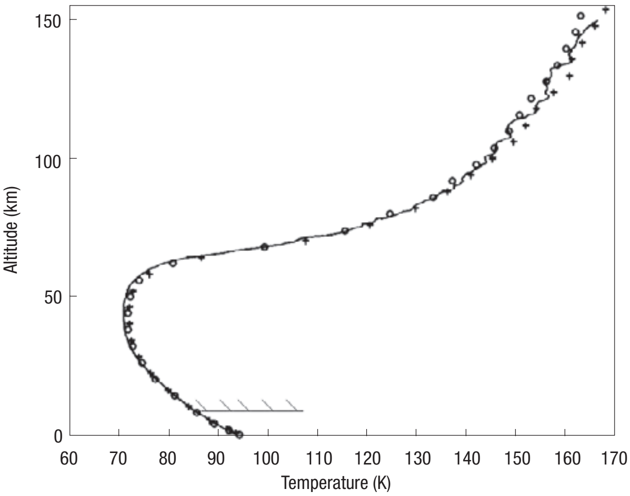


**Figure 1** Temperature versus altitude is shown for Titan's atmosphere. The solid line represents the temperatures measured by the HASI instrument on the Huygens probe[4], whereas the symbols are from the Voyager radio occultation data[53]. The horizontal line shows the base of the Huygens-inferred methane cloud[6].

data yield a nearly terrestrial $^{12}C/^{13}C$ ratio[2], thus giving a further affirmation to methane replenishment.

The primary products of the photochemistry are ethane and acetylene, consistent with the stratospheric inventory of the hydrocarbons observed by Voyager and Cassini[20]. At the surface temperature of 94 K, condensed ethane is, like methane, a liquid, and the two are fully miscible. Acetylene is a solid and is only weakly soluble in any methane–ethane liquid[21]. However, ethane is the most volatile of the products of the stratospheric destruction of methane and, at the tropopause minimum, is able to condense out to some extent, although perhaps only at higher latitudes[5]. Indeed, a cloud observed by Cassini in the north polar lower stratosphere has been interpreted to be the condensation of photochemically produced ethane[11]. If ethane is efficiently condensed in the stratosphere rather than being subject to further chemistry that converts it into other hydrocarbons, continuous methane photolysis over the age of the solar system will have created the equivalent of a global liquid layer hundreds of metres thick on Titan's surface. Cassini observations show no evidence for such a deep, global layer[22]. So, to fully understand Titan's methane cycle, the sources of methane that re-supply the atmosphere against photolysis, and the sinks of ethane in the absence of a deep surface liquid layer need to be determined.

Circumstantial evidence for liquids on the surface comes in the form of the so-called lakes and seas, which are features of varying shapes and sizes that have extremely low reflectivity in Cassini RADAR data[23] and are seen mostly in the high northern latitudes (with one in the south). Many of these features return no radar signal — that is, the received power from these regions is at the noise level of the instrument — which would suggest that they are smooth flat surfaces as the Orbiter radar transmits to the surface at an oblique angle[24]. (Wind speeds required to trigger significant wave roughening are much larger than those measured[7] near the surface, at least at equatorial latitudes). Other lakes have subtle features within their dark regions, including channels, and are more difficult to interpret. One possibility for these is that they are filled with liquid to a shallow depth — of the order of metres to tens of metres — the depth to which radio waves penetrate liquid hydrocarbons[25]. The thermal emission at radio wavelengths from the lakes is higher than that from the surroundings, which is consistent with them being formed of hydrocarbons if the background material is water ice[23]. This inference is supported by infrared mapping of the surface[26]. The confinement of the lakes to latitudes above 70°, along with an occurrence equator-ward of features of similar form but with brightness equal to the background surface[27], suggests that they are filled with material that condenses and rains out at lower temperatures than the equatorial value. Perhaps the most compelling evidence that the features are filled (or were filled recently) with liquid are the evocative landscapes adjacent to the largest of such features, including what appear to be flooded hills within them and dendritic valleys that extend into them (Fig. 2). As discussed below, somewhat similar features on a smaller scale, including dendritic drainages, were seen by the DISR instrument near the Huygens landing site[7] but no evidence of exposed bodies of liquid was found.

## SHORT-TERM METHANE CYCLES

Under Titan conditions the only suitable materials to form large bodies of liquid are methane and its photochemical product ethane (higher saturated hydrocarbons such are propane will also be present but in smaller quantities). Some global circulation models of Titan's atmosphere suggest that persistent seasonal clouds should form above 70° latitude[27], though whether they will be precipitating is unclear. Evidently, on the basis of morphology, the south polar clouds are convective[11] and could be precipitating. If the lakes and seas are filled with liquid hydrocarbons, they most likely contain ethane and methane because pure methane lakes have a sufficiently high vapour pressure to cool and freeze[28], which would potentially lead to rough surfaces and temperatures inconsistent with the elevated emissions relative to the surroundings at radio wavelengths. With significant quantities (>50%) of ethane present, the vapour pressure over the lakes, and the cooling effect, are suppressed sufficiently to maintain temperatures in the liquid field. Moreover, modelling[28] suggests that the polar coverage of the lakes is marginally sufficient to maintain global relative humidities at the high levels measured today (~45% for $CH_4$ at the equatorial landing site of Huygens[2]), provided the lakes are typically tens of metres deep. Lake depths are unknown, but the radar blackness of the largest ones[23] and RADAR stereo-derived topography of the landscapes surrounding the hills suggest that tens to hundreds of metres depth is possible[29].

Fluvial features are seen at radar spatial resolution of 300–500 m (ref. 30), and in the region of the Huygens probe landing site by its camera at several metres resolution[7]. All these features appear young, in the sense that there are no impact craters that overlay them, and the Huygens channels appear very fresh on the basis of steep topography derived from stereo imagery and lack of evident degradation in the high resolution camera images[31]. It is therefore plausible, but impossible to prove with the data available, that at least the Huygens channels have been carved over recent geological time. Estimates based on assuming the mechanical properties of water ice for the crust and methane liquid for the working fluid of the channels suggest that a very small fraction — 10 parts per million — of the total atmospheric content of methane is required in the form of heavy rainfall typical of a convective storm in order to carve the channels at the Huygens site (S. Hörst, personal communication).

The radar data indicate that about 1% of the surface imaged so far is covered with fluvial features[30], although only 20% of the surface has been imaged so far with the Cassini radar. If we take this number as typical, then in fact the known inventory of fluvial features could be carved easily with the amount of methane in the present day atmosphere, or equivalently in the lakes, if they are of sufficient average depth (tens to hundreds of metres).

Assuming the channels are relatively young, or indeed are being actively carved, how and when does the rainfall occur? Models of convective methane storms[14] indicate that a relative humidity of 80% — about twice that at the equator on Titan today — must be present. The source of the additional methane required might plausibly be the lakes. Evaporation of sufficient methane to 'wet down' the troposphere would take centuries, just on the basis of the latent heat of evaporation of the methane and the limited available solar flux[32]. Once sufficient evaporation has been achieved, the conditions at the equator would be several degrees warmer than at present because of the infrared opacity contributed by the methane. Convective storms would form in the equatorial and mid-latitudes, scouring the surface, but the absence of an ocean and the sluggish re-evaporation associated with the small solar flux would prevent the atmosphere from recharging its supply of moisture. Eventually the atmosphere would become dry enough, except at the colder poles, that convective storms would cease, and slow recharge of the atmosphere from the lakes would begin again.

If the lakes contain liquid methane, how are they recharged? It is possible that the lakes are deep enough that only a small fraction of their methane is evaporated into the atmosphere until conditions of convective instability are reached. Alternatively, the crust might be porous and/or heavily fractured, so that the methane flows gradually back to the coldest places in the crust — the poles. Finally, direct evaporation and transport by Hadley cell circulation might occur. Interestingly, at the landing site, methane (and possibly ethane and other organics) was detected by the Huygens probe mass spectrometer vaporizing out from under the warm underbelly of the probe[2,33], and it has been suggested that a slow drizzle might occur even today at the site[6]. Whether the detected methane is part of a larger reservoir under the plains where Huygens landed, or a local effect of drizzle, is not known.

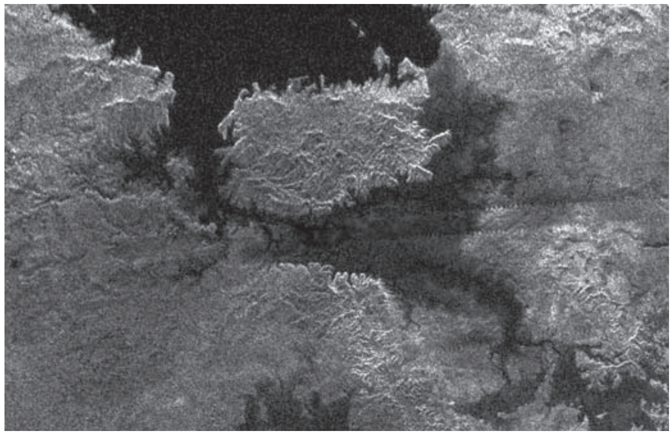

**Figure 2** The Cassini RADAR shows details of dendritic channels in high northern latitudes. The channels appear to be feeding dark areas that may contain liquid methane and/or ethane. The image is 90 × 150 km in size. The smallest features are 700 m across. Copyright NASA/JPL.

## LONG-TERM METHANE BALANCE

The cycles of methane depletion by rainfall and recharge by evaporation are not 100% closed. Photochemical destruction of methane on a timescale of $10^7$ years means that, in each cycle of (for arguments sake) $10^3$ years, on the order of 0.01% of the methane is lost. The lakes are not plausible candidates for a long-term resupply reservoir of the methane, unless they were tens of kilometres deep; this is implausible. An extensive methane (or methane-ethane) equivalent of an aquifer system — an 'alkanofer' — might circulate liquids, especially at high latitudes, where the lake and sea features are present. But the system would need to extend through tens of kilometres of the water ice crust of Titan, and be densely packed, in order to represent an equivalent global layer of methane a kilometre thick, which is what is needed to re-supply methane against photolysis over geologic time. There is no evidence in the Cassini remote sensing data for or against such a system.

More plausible is a source of methane from the deep interior. The fact that Titan has an atmosphere whereas its physical twin Ganymede (a moon of Jupiter nearly identical in mass and size) has none, is most likely an indicator of the lower temperatures in the satellite-forming disk from which Titan formed around Saturn compared with that in the disk around Jupiter. Higher temperatures at Jupiter would be reflective of a more massive disk, the higher luminosity of the planet and its closer proximity to the Sun (or, in the optically thick phase of the solar nebula, its presence in warmer, denser and more turbulent nebular gas)[34]. Conditions could plausibly have been cold enough in the disk around Saturn (but not at Jupiter) that ammonia, hydrogen-bonded to water ice as a stochiometric hydrate, and methane, trapped in ice as clathrate hydrate, were incorporated into Titan in significant amounts[35]. Alternatively[5], if the Saturnian nebula was too warm during Titan's formation to allow methane to be trapped, methane might not have been captured directly from Saturn's subnebula, but may have arrived in the form of carbon grains, carbon monoxide, carbon dioxide and refractory organic material. These could have been converted to methane by water-rock reactions ('serpentinization' at low temperatures) in Titan's interior during the moon's early geologic history, with methane subsequently being stored as a clathrate hydrate in Titan's interior and released over time.

Carbon dioxide has been detected on the surface by the Cassini VIMS instrument[36], and could well indicate outgassing of native $CO_2$ as photochemical production of this molecule is so limited[18] that the resulting surface deposits almost certainly would not be preserved. The lack of detection of the heavy noble gases, xenon and krypton, by the Huygens GCMS provides support to the $CO_2$ origin hypothesis, as these gases should have been delivered in large quantities together with methane if methane was captured directly. However, these gases might be trapped in the interior, for example as clathrate hydrates[37,38]. Further laboratory and planetary data are needed to determine whether there are plausible sinks of the heavy noble gases on Titan that might have removed them from the present-day atmosphere.

When constrained by the density of Titan, the equation of state of the relevant materials, and the available energy sources[39,40], Titan's interior includes a liquid water ocean with perhaps a few percent of ammonia, overlain by a crust (which today is mostly water ice but in the past was thin and largely composed of (methane) clathrate hydrate), a lower mantle of high-pressure phases of water ice, and a rock core[41]. A different model in which sulphur is leached from the core yields a thicker crust and a briny ocean containing dissolved ammonium sulphate[42]. In either case, substantial amounts of methane are stored in the interior — whether the gas arrived as methane or it was produced in the moon's interior — and are available for outgassing to the surface. The detection of small quantities of $^{40}$Ar in Titan's atmosphere by the Huygens GCMS provides evidence of outgassing from Titan's interior as $^{40}$Ar is produced in the decay of $^{40}$K in the rocky (or rocky–metallic) core. In the thin-crust model, the low thermal conductivity and high rigidity of the methane clathrate delay thickening of the crust, so that thermal events such as onset of convection in the core and later in the crust could result in methane outgassing to the surface — and hence re-supply to the surface–atmosphere methane cycle — late in Titan's history, perhaps through the involvement of ammonia–water cryovolcanism[41]. In the thick-crust model, the presence of briny cryomagmas allows explosive dissociation of entrained methane[42]. The latter model is potentially

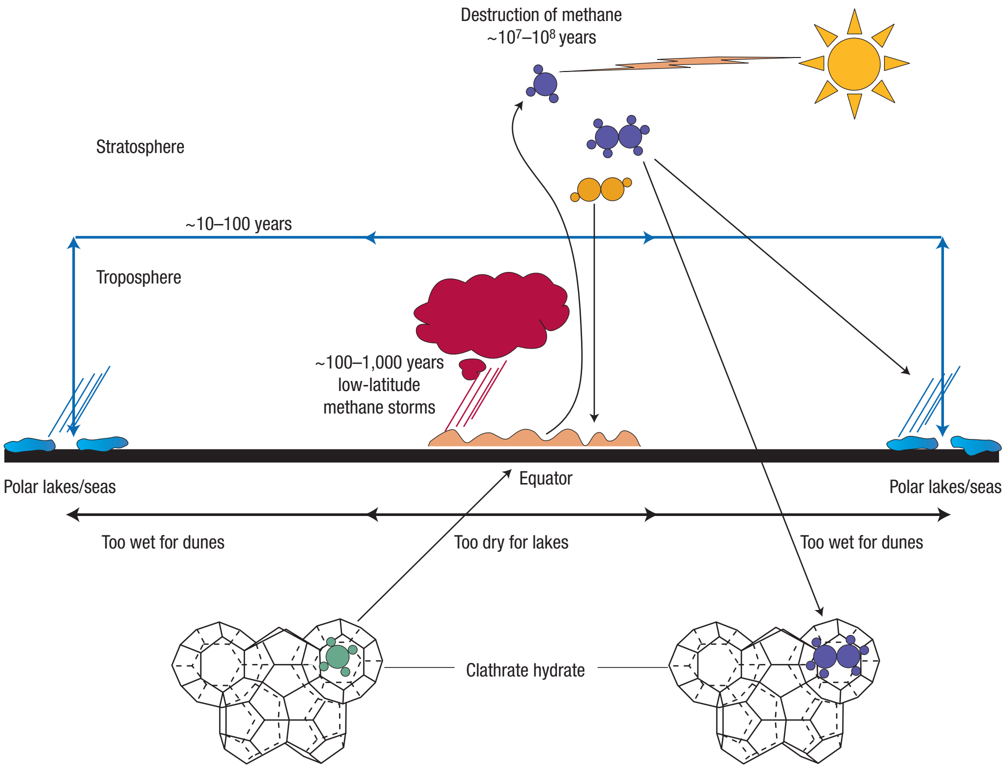


**Figure 3** A schematic view of the methane cycle on Titan is shown with rough timescales for the various processes. The introduction of methane (green) bound in clathrate hydrate into the surface–atmosphere system is shown; methane is either primordial or made in Titan's interior and then outgassed to the surface. It cycles from pole-to-pole, perhaps residing at high latitudes in lakes (blue). Periodically the equatorial humidity increases to the point that convective storms at low latitudes are possible (red), carving fluvial features. Photochemistry and charged particle chemistry produce higher hydrocarbons and nitriles, some of which end up in the hydrologic system as ethane (purple), and some as solids that agglomerate to form equatorial dunes (orange). Ethane might be lost to the crust in voids or as clathrate hydrate.

attractive if large amounts of carbon dioxide — which reacts with ammonia — was present in Titan's interior early in its history.

In both models, the methane cycle has been a persistent feature of the history of Titan over the age of the solar system, and both allow the possibility of long periods in which volcanism was absent so that Titan's surface–atmospheric methane was fully consumed, temporarily. This would have led to a nearly pure but somewhat thinner nitrogen atmosphere. Radiative balance studies of Titan's atmosphere suggest that for at least the last half of the solar system's history, the luminosity of the Sun was high enough that even in the absence of methane, nitrogen could have supported surface temperatures within 10 K of the present value[43]. Surface deposits of ethane might have been frozen continuously or periodically under such circumstances, leading to glacial erosion.

An outstanding problem in any evolutionary model is the disposition of ethane. Persistent photolysis of methane over the age of the solar system would have produced the equivalent of a global ocean of hundreds of metres deep[19], for which Cassini sees no evidence. Coupled photochemical–ionospheric models based on updated chemical kinetics[5,18] would reduce the depth by a factor of 4–5, down to ~100–200 m. It is also possible that methane has been present in the atmosphere for only a fraction of the 4.5 billion year history of Titan[44], further reducing the equivalent depth of photochemically produced ethane to an extent that is readily accommodated in subsurface voids, alkanofers, and surface high-latitude lakes[45]. On long geological timescales, ethane might become sequestered in clathrate hydrate in the crust, leading effectively to its permanent removal from the surface–atmosphere system[37,38].

Recent observations suggest that ethane may be reprocessed, at least at some levels in the atmosphere, again reducing the amount of ethane deposited on the surface over the age of the solar system. Benzene ($C_6H_6$) has been detected in Titan's stratosphere by the Infrared Space Observatory[46] and Cassini Composite Infrared Spectrometer[20], and in the ionosphere by the Cassini Ion and Neutral Mass Spectrometer[17]; positive ions of up to 350 AMU in size and heavy negative ions (>8,000 AMU) have been detected by Cassini Plasma Spectrometer[17]; and haze layers have been observed at high altitudes. For all of these features to be present, ethane (and acetylene) gas must be participating in further photochemical reactions. This will eventually produce highly complex heavy hydrocarbon molecules[47] in the form of sedimenting aerosols that will take the place of, or even adsorb[48], some of the liquid ethane on Titan's surface. The equivalent depth of the surface layer of ethane would consequently be reduced, but by how much is a poorly constrained matter in view of the currently available Cassini data. Future observations of Titan should be designed to address this critical issue about the methane cycle, but they will be challenging: clathrate hydrate resembles water ice at moderate spectral resolution, and subsurface sounding by long-wavelength radio may not be diagnostic of particular water ice phases such as clathrate versus ice I.

## COMPARISON WITH OTHER PLANETS

The methane cycle on Titan is summarized in Fig. 3. It differs from the Earth's hydrological cycle in four major respects: (1) temperatures on Titan are much lower and hence methane/ethane, rather than water, represents the working fluid; (2) Titan lacks a global ocean; (3) the ratio of latent heat capacity of the working fluid to available solar energy is much higher on Titan than on Earth; (4) Titan's tropopause is not much colder than the surface, allowing methane to leak into the ultraviolet-active stratosphere in larger amounts where it is rapidly destroyed. What characterizes the Titan environment then is a vast equatorial stretch of dunes — made of some or all of the solid products of the methane photochemistry — and possibly methane–ethane lakes in the high latitudes. The present-day dryness at the equator is not absolute — the relative humidity is ~45% — and periodically recharging the troposphere with methane unleashes an epoch of heavy rains and active erosion. The long-term loss of methane by stratospheric photolysis will eventually fail to be matched by resupply from the interior, and Titan's methane cycle will end.

In some respects the rapid loss of methane from the top of the atmosphere makes Titan a model for the future Earth, when the solar luminosity has increased by 10–20% from the present-day. At that time — still within the remaining 4 billion years of the Sun's main sequence lifetime — the rise in surface temperature may generate a positive feedback loop between the tropospheric temperature profile and the tropospheric abundance of water vapour. Under some models[49], but not all[50], this will warm the Earth's tropopause temperature sufficiently that water will begin to flow into the stratosphere in large quantities, to be broken apart by ultraviolet light into OH and hydrogen. Because much of the Earth's carbon dioxide will have been locked up as carbonates, the end result will look less like the massively hot and carbon dioxide-rich Venus atmosphere than it will like Titan, with dry equatorial regions and remnant water at the poles. Whether this will remain so indefinitely would depend on resupply of water from the interior and the cessation of plate tectonic recycling of carbon dioxide. Perhaps more conservatively, one might say that Titan's climate regime represents a distinct one from that of Venus, Mars, or Earth — but one that has something to teach us about an Earth in the throes of rapid water loss.

The ultimate end of the current Titan climate regime will come when the Sun becomes a red giant, at which point remaining methane will be lost with much of the atmosphere But the much higher red-giant luminosity will — if ammonia is present in the crust — melt the water ice crust leaving an exposed water ammonia ocean as a potential host for life[51]. However, even the present-day surface of Titan might not be ruled out as an environment for exotic forms of life[52].

## FUTURE OBSERVATIONS

Key remaining observations for Cassini include near-infrared observations of the lakes as Titan comes out of northern hemisphere winter, to search for spectral signatures of methane and ethane through the murk of the nitrogen–methane atmosphere; more complete mapping of surface features to search for cryovolcanic features and impact craters; and observations of cloud formation and dissipation as equinox progresses over that part of Titan's 29-year seasonal cycle. However, it is clear from existing observations that the 300 m resolution available from radar is not sufficient to globally map the small-scale fluvial features that are seen at the Huygens landing site. Furthermore, whether the lakes are filled with liquid methane–ethane, are frozen, or are something unexpected, may not be definitively determined with the instrumentation aboard the Cassini orbiter.

A future mission to Titan that might map fluvial features at the metre scale, put near-infrared spectrometers near the surface to eliminate the obscuration by gaseous methane over vast parts of the spectrum, sound the subsurface with long-wavelength radar to detect pockets of liquid and make precise gravity measurements to quantify the extent any putative ammonia-water or briny liquid 'ocean' beneath the ice crust, and characterize the chemical and isotopic nature of Titan's surface material, would put the study of Titan's methane cycle on a much firmer footing. Such a mission might consist of an orbiter and a semi-autonomous atmospheric platform such as a blimp or balloon[53]. In view of what Cassini–Huygens has taught us about Titan's methane cycle, future exploration of this planet-sized moon with active surface-atmosphere volatile cycling would be most rewarding.

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### References

1. Lebreton, J.-P. *et al.* An overview of the descent and landing of the Huygens probe on Titan. *Nature* **438,** 758–764 (2005).
2. Niemann, H. B. *et al.* The abundances of constituents of Titan's atmosphere from the GCMS instrument on the Huygens probe. *Nature* **438,** 779–784 (2005).
3. Tyler, G. L. *et al.* Radio science investigation of the Saturn System with Voyager 1: preliminary results. *Science* **212,** 201–206 (1981).
4. Fulchignoni, M. *et al.* Titan's physical characteristics measured by the Huygens Atmospheric structure instrument (HASI). *Nature* **438,** 785–791 (2005).
5. Atreya, S. K. *et al.* Titan's methane cycle. *Planet.Space Sci.* **54,** 1177–1187 (2006).
6. Tokano, T. *et al.* Methane drizzle on Titan. *Nature* **442,** 432–435 (2006).
7. Tomasko, M. G. *et al.* Rain, winds and haze during the Huygens probe's descent to Titan's surface. *Nature* **438,** 765–778 (2005).
8. Roe, H. G., Brown, M. E., Schaller, E. L., Bouchez, A. H. & Trujillo, C. A. Geographic control of Titan's mid-latitude clouds. *Science* **310,** 477–479 (2005).
9. Griffith, C. *et al.* The evolution of Titan's mid-latitude clouds. *Science* **310,** 474–476 (2005).
10. Griffith, C. A. Hall, J. L. & Geballe, T. R. Detection of daily clouds on Titan. *Science* **290,** 509–513 (2000).
11. Porco, C. C. *et al.* Imaging of Titan from the Cassini spacecraft. *Nature* **434,** 159–168 (2005).
12. Schaller, E. L. *et al.* Dissipation of Titan's south polar clouds. *Icarus* **184,** 517–523 (2006).
13. Griffith, C. A. *et al.* Evidence for a polar ethane cloud on Titan. *Science* **313,** 1620–1622 (2006).
14. Hueso, R. & Sanchez-Lavega, A. Methane storms on Saturn's moon Titan. *Nature* **442,** 428–431 (2006).
15. Yung, Y. L., Allen, M. A. & Pinto, J. P. Photochemistry of the atmosphere of Titan: comparison between model and observations. *Astrophys. J. Suppl. S.* **55,** 465–506 (1984).
16. Atreya, S. K. *Atmospheres and Ionospheres of the Outer Planets and Satellites*. (Springer-Verlag, Berlin, 1986).
17. Waite, J. H. *et al.* The process of tholin formation in Titan's atmosphere. *Science* **316,** 870–872 (2007).
18. Wilson, E. H. & Atreya, S. K. Current state of modelling the photochemistry of Titan's mutually dependent atmosphere and ionosphere. *J. Geophys. Res.* **109,** E06002 (2004).
19. Lunine, J. I., Stevenson, D. J. & Yung, Y. L. Ethane ocean on Titan. *Science* **222,** 1229–1230 (1983).
20. Coustenis, A. *et al.* The composition of Titan's stratosphere from Cassini/CIRS mid-infrared spectra. *Icarus* **189,** 35–62 (2007).
21. Dubouloz, N., Raulin, F., Lellouch, E. & Gautier, D. Titan's hypothesized ocean properties — The influence of surface temperature and atmospheric composition uncertainties. *Icarus* **82,** 81–96 (1989).
22. West, R., Brown, M. E., Salinas, S. V., Bouchez, A. H. & Roe, H. G. No oceans on Titan from the absence of a near-infrared specular reflection. *Nature* **436,** 670–672 (2005).
23. Stofan, E. R. *et al.* The lakes of Titan. *Nature* **445,** 61–64 (2007).
24. Elachi, C. *et al.* Cassini radar views the surface of Titan. *Science* **308,** 970–974 (2005).
25. Whiffen, D. H. Measurements on the absorption of microwaves. Part IV.— Non-polar liquids. *Trans. Faraday Soc.* **46,** 124–130 (1950).
26. Lellouch, E., Schmitt, B., Coustenis, A., Cuby, J.-G. Titan's 5-micron lightcurve. *Icarus* **168,** 209–214 (2003).
27. Rannou, P. Montmessin, F. Hourdin, F., Lebonnois, S. The latitudinal distribution of clouds on Titan. *Science* **311,** 201–205 (2006).
28. Mitri, G., Showman, A. P., Lunine, J. I. & Lorenz, R. D. Hydrocarbon lakes on Titan. *Icarus* **186,** 385–394 (2007).
29. Kirk, R. *et al.* in *AGU Fall Meeting* abstract P22B-01 (AGU, Washington DC, San Francisco, 2007).
30. Lorenz, R. D. Fluvial Channels on Titan: Initial Cassini Radar Observations. *Planet. Space Sci.* (in the press).
31. Soderblom, L. *et al.* Topography and Geomorphology of the Huygens landing site on Titan. *Planet. Space Sci.* **55,** 2015–2044 (2007).
32. Lorenz, R. D. Griffith, C., Lunine, J. I., McKay, C. P. & Renno, N. O. Convective plumes and the scarcity of Titan's clouds. *Geophys. Res. Lett.* **32,** L01201 (2005).
33. Lorenz, R. D. Niemann, H. B., Harpold, D. N., Way, S. H. & Zarnecki, J. C. Titan's damp ground: Constraints on Titan surface thermal properties from the temperature evolution of the Huygens GCMS inlet. *Meteorit. Planet. Sci.* **41,** 1705–1714 (2006).
34. Lunine, J. I. and D. J. Stevenson, D. J. Formation of the Galilean satellites in a gaseous nebula. *Icarus* **52,** 14–39 (1982).
35. Hersant, F., Gautier, D., Tobie, G. & Lunine, J. I. Interpretation of the carbon abundance in Saturn measured by Cassini. *Planet. Space Sci.* (submitted).
36. McCord, T. *et al.* Titan's surface: Search for spectral diversity and composition using the Cassini VIMS investigation. *Icarus* (in the press).
37. Osegovich, J. P. & Max, M. D. Compound clathrate hydrate on Titan's surface. *J. Geophys. Res.* **110,** E08005 (2005).
38. Fortes, A. D. & Stofan, E. in *36th Lunar Planet. Sci. Conference* Abstract 1123 (Lunar and Planetary Institute, 2005).

39. Tobie, G. Grasset, O., Lunine, J. I., Mocquet, A., Sotin, C. Titan's internal structure inferred from a coupled thermal-orbital model. *Icarus* **175,** 496–502 (2005).
40. Sohl, F., Hussman,n, H., Schwentker, B., Spohn, T., Lorenz, R. D. Interior structure models and tidal Love numbers of Titan. *J. Geophys. Res.* **108** (E12), 5130 (2003).
41. Tobie, G., Lunine, J. I. & Sotin, C. Episodic outgassing as the origin of atmospheric methane on Titan. *Nature* **440,** 61–64 (2006).
42. Fortes, A. D. Grinrod, P. M., Trickett, S. K., Vocadlo, L. Ammonium sulfate on Titan: Possible origin and role in cryvolcanism. *Icarus* **188,** 139–153 (2007).
43. Lorenz, R. D., McKay, C. P. & Lunine, J. I. Photochemically-induced collapse of Titan's atmosphere. *Science* **275,** 642–644 (1997).
44. Lorenz, R. D. *et al.* Titan's inventory of organic surface materials. *Geophys. Res. Lett.* **35,** L02206 (2008).
45. Stevenson, D. J. in *Proc. Symp. on Titan, Toulouse, September 1991* 29–33 (European Space Agency, Noordwijk, The Netherlands, 1992).
46. Coustenis, A. *et al.* Titan's atmosphere from ISO mid-infrared spectroscopy. *Icarus* **161,** 383 (2003).
47. Atreya, S. K. Titan's organic factory. *Science* **316,** 843–845 (2007).
48. Kasting, J. F. Runaway and moist greenhouse atmospheres and the evolution of Earth and Venus. *Icarus* **74,** 472–494 (1988).
49. Pujol, T. & North, G. R. Runaway greenhouse effect in a semigray radiative-convective model. *J. Atmospheric Sci.* **59,** 2801–2810 (2002).
50. Lorenz, R. D., Lunine, J. I. & McKay, C. P. Titan under a red giant sun: A new kind of "habitable" moon. *Geophys. Res. Lett.* **24,** 2905–2908 (1997).
51. *The Limits of Organic Life in Planetary Systems* (National Academies Press, Washington DC, 2007).
52. Lorenz, R. D., Lunine, J. & Zimmerman, W. Post-Cassini exploration of Titan: Science goals, instrumentation and mission concepts. *Adv. Space Res.* **36,** 281–285 (2005).
53. Lindal, G. F. *et al.* The atmosphere of Titan — an analysis of the Voyager 1 radio occulation measurements. *Icarus* **53,** 348–363 (1983).
54. Hunten, D. The sequestration of ethane on Titan in smog particles. *Nature* **443,** 669–670 (2006).



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