Satellites of giant planets 2.

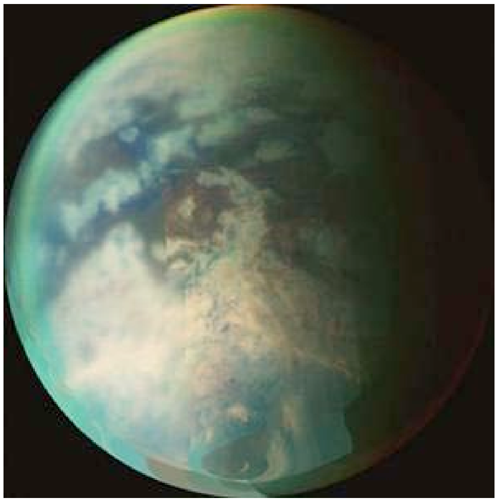
Titan

The direction of this reading is toward understanding how it was discovered whether or not there is liquid on the surface of Titan (and why it was so difficult to find), how that is related to clouds, what the liquid is, the crucial role of the atmospheric haze particles ("tholins"), and whether these particles can dissolve in this liquid. The "dissolving" aspect is crucial for completing a methane "hydrological cycle" to explain why the methane doesn't quickly disappear from the atmosphere, and is also crucial for many astrobiological schemes for an alternative Titan biochemistry. The latter view Titan as a big "Miller-Urey experiment," but with another liquid (ethane, it turns out), not water. These will become clearer as you read the folllowing discussion *and* the excellent (and only slightly out of date) discussion in your textbook (pp. 312-317).

This is meant to be a *supplement* to the discussion in the textbook. On the exam, I will want to find whether you understand the basic ideas, but of course not the details. I assume you are experienced enough, or have enough common sense, to recognize when I am including quantitative or technical results that are beyond the scope of this class, but may be of interest some of you. It also contains some more technical exerpts from recent papers, for those of you who might be interested in tracking down some of the current research.

Saturn's largest satellite, and the object that may be most interesting for astrobiology: It is massive (like Ganymede and Callisto in the Jupiter system), but Titan has an atmosphere. In fact, Titan is the *only* satellite in the Solar System to possess a substantial atmosphere. Surface pressure reaches around 1,5 bars, compared to an average of 1.0 bars on Earth. This is despite the fact that Titan itself is only 5,150 km in diameter compared tc Earth's 12,756 km.

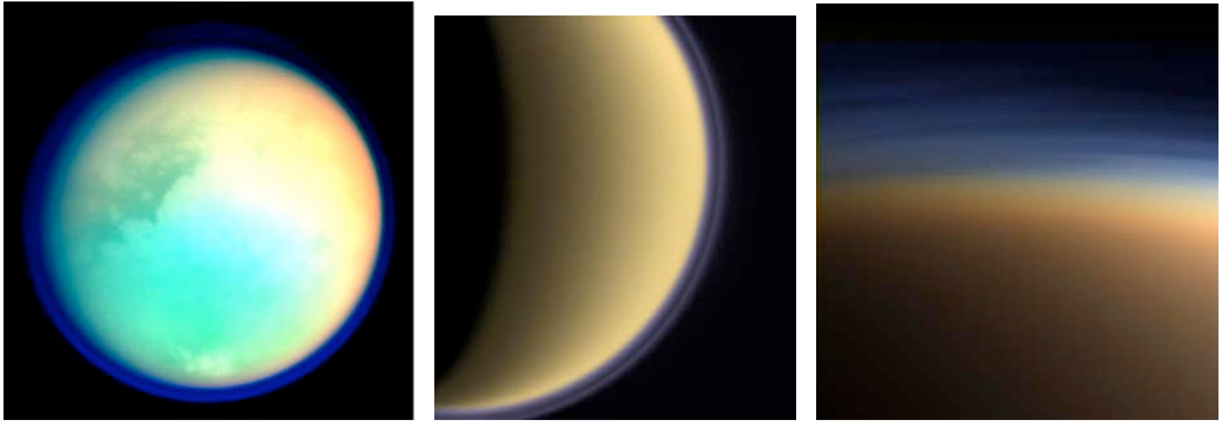
Why does Titan alone have an atmosphere ? Apparently the temperature at Jupiter was a little too warm to allow ices that formed the satellites to retain gases like nitrogen, methane, etc. But further away from the sun than Saturn, it is so cold that such compounds would be largely frozen, like on Triton (massive icy moon of Neptune). So Saturn's distance defines a sort of "habitable zone" for a satellite to retain an atmosphere.



This atmosphere must have arisen by outgassing of volcanoes on Titan, when it was young, not delivery by comets or asteroids or other "exogenous" sources. Can you explain how this is known? I will probably include a question about this on your exam. (It is in your textbook.)

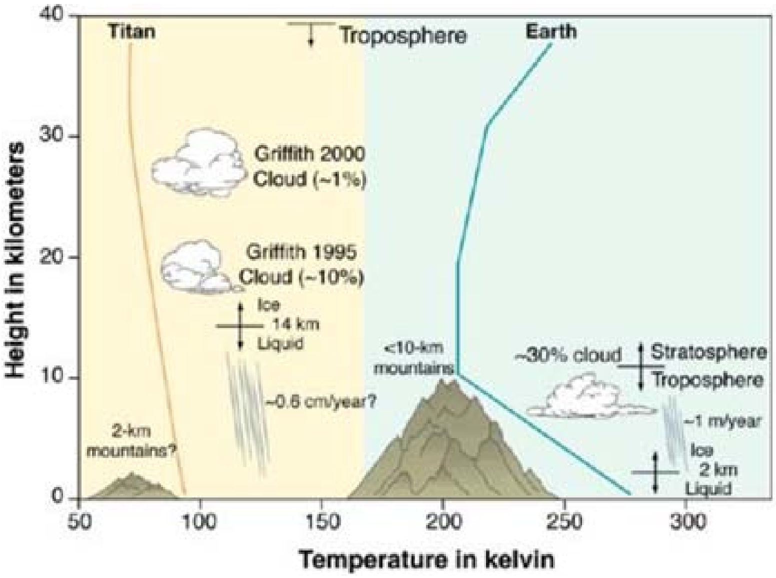
Yet Titan is not so massive that it could hold on to the lightest gases, like H_2 (compare with Jupiter). So it has an extremely interesting composition, with many organic molecules, as well as CO_2 and H_2O, observed through spectral lines. The hydrocarbons are formed either from methane (CH_4) or with nitrogen (such as HCN). Much more complex molecules must be present, but they are difficult to observe because of the smog layer that totally hides Titan's surface. This layer is often called the "**purple haze**" (see below), and is believed to be organic aerosols given the name "**tholins**." The haze hides the complex molecules from view, but, ironically, are good evidence that such molecules exist, since the only way to produce a tholin is by reactions of increasingly complex organics (again, see below).

Titan's day is 16 Earth days in length, and it also takes 16 days to complete one orbit of Saturn. This means that the same hemisphere of Titan always faces Saturn, much as the same hemisphere of the Moon always faces Earth. This is a result of Saturn's gravitational tidal effect (like Earth on Moon): It is **tidally locked**.



"Purple Haze" = aerosol layer, "tholins"

These play a crucial role in considerations of Titan's climate and its potential for a biochemistry.

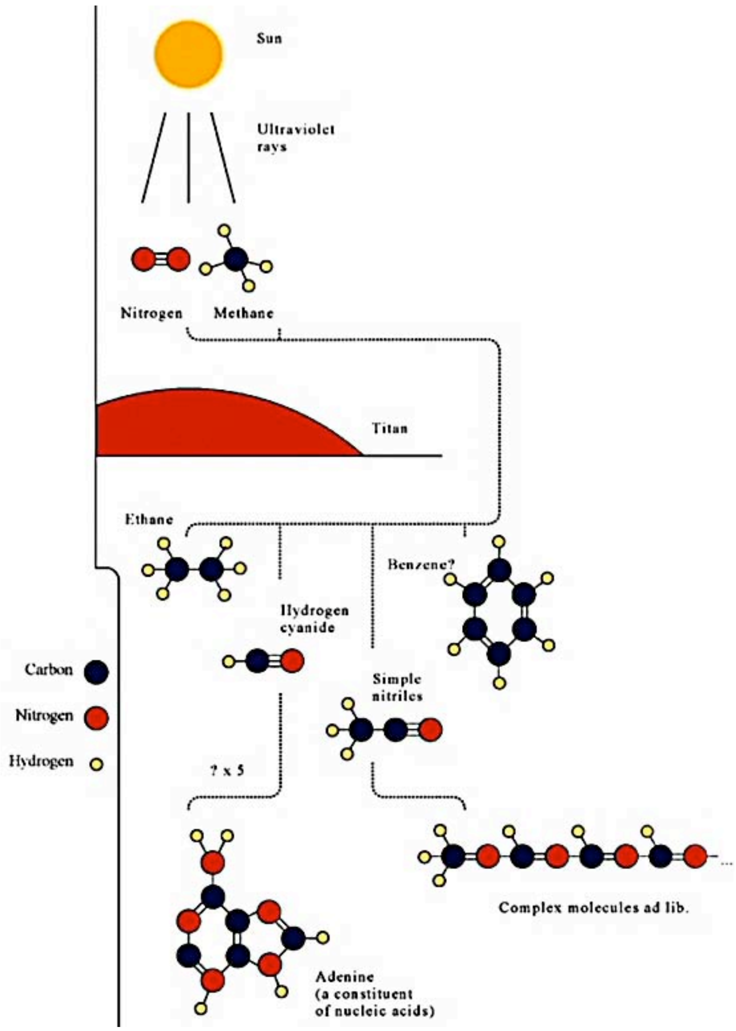


What is composition of Titan's interior?

Density = 1.9 g/cm^3 (compare—water=1, rock=3, iron=7), so must be composed largely of ices made from H_2O, CO_2, N_2, CH_4, NH_3, all with densities 1 to 1.5. *Note that there is little question that the interior is largely composed of water ice (among others), or that this water may be liquid **very deep in the interior**.*

Titan's atmosphere

At the surface, pressure is more than 1.5 bar (50% higher than Earth's). It is composed primarily of molecular nitrogen (as is Earth's) with a few percent methane (CH_4), ethane (C_2H_6), and carbon monoxide (CO).



There are also trace amounts of at least a dozen other organic compounds (i.e. ethane, hydrogen cyanide, carbon dioxide) and water. The organics are probably formed from **methane**, which dominates Titan's upper atmosphere, but is destroyed by sunlight. (Then how is it replenished? That has been *the* big question, because it may be a rainfall-evaporation cycle, discussed below.) These more complex chemicals in small quantities must be responsible for the orange color of Titan as seen from space.

A simple view of the *potential* photochemistry (picture to left). Notice the astrobiologically-optimistic molecules listed at the bottom.

There is clearly a lot of interesting and complex organic chemistry going on. Some of it is driven by **ultraviolet radiation from the Sun**, just as in the atmospheres of most planets. During part of its orbit Titan is inside Saturn's magnetosphere and so is subject to the **energetic charged particles** present there, which can drive interesting organic chemistry. Titan has no magnetic field and sometimes orbits outside Saturn's magnetosphere, so is therefore directly exposed to the **solar wind**, which may also drive some of Titan's peculiar chemistry.

The end result seems to be a lot like a very thick smog., similar in some ways to smog over large cities but much thicker, and dominated by hydrocarbon aerosol particles. These conditions may be similar to the conditions on Earth early in its history when life was first getting started. But this thick hazy atmosphere is also what makes it so difficult to see Titan's surface from Earth or even from orbit. Need *infrared observations* because the long wavelength radiation gets past the smog.

How do the haze particles form, and why don't they eliminate the methane?

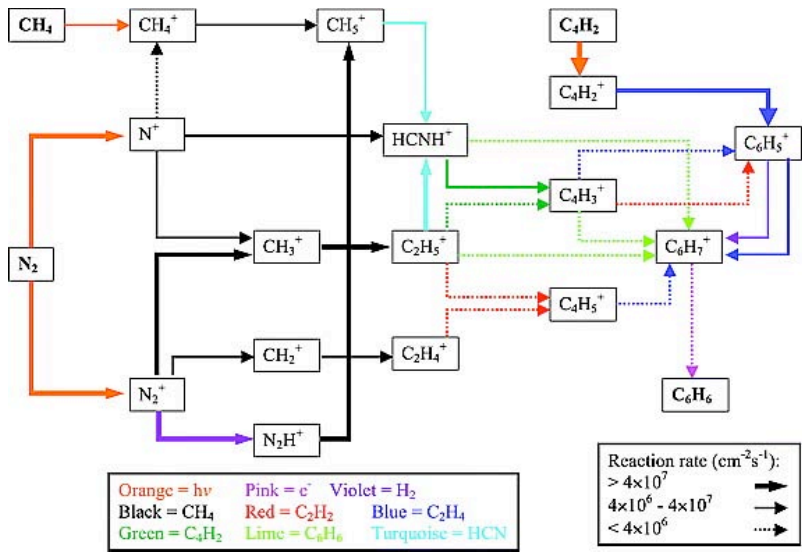
Actually, explanations of the formation of the Titan haze are fairly speculative, at least until recently, although everyone agreed that the particles obviously exist at high altitudes, and probably form (somehow) from the methane, which would then be depleted. ***That is one of the two most important aspects of the haze:*** the haze particles provide an *irreversible sink* that should rapidly eliminate the CH$_4$ (methane) from the atmosphere: **This is the big reason for assuming there must be liquid bodies of water whose evaporation can renew the methane to the**

atmosphere. ***Note that this will only occur if the haze particles can dissolve in the bodies of liquid on the surface, so they can release their methane.***

The chemistry calculations are very complicated (illustrated below for a *simple* set of reactions), so perhaps the problem was too difficult. After all, no one is really sure how aerosols form (in detail) in the Earth's atmosphere! (That is a major problem in understanding climate variations.)

Here is a typical description: Chemical processes are initiated by the break-up of methane (CH_4) and nitrogen (N_2) gas molecules by solar UV radiation and charged particle collisions (see the figure). Even though Titan receives only 1% of the solar ultraviolet flux that Earth does, and is bombarded by charged particles from Saturn's magnetosphere only some of the time, this energy is sufficient for photochemistry to proceed efficiently. Simple hydrocarbons--such as ethane, acetylene, and diacetylene--and nitriles, such as hydrogen cyanide (HCN) and cyanogen (C_2N_2) form readily. Somewhat more complex molecules such as propane, butane, polyacetylenes, and cyanoacetylene follow from these simpler units. Researchers believed that the haze seen on Titan by Voyager 1 and Voyager 2 during 1980-1981 and in later observations by HST and Cassini is the result of condensation of many of these molecules and polymers of polyynes and HCN, somewhat similar to the formation of urban photochemical smog on Earth.

Here is a simplified reaction network recently used to study these processes:



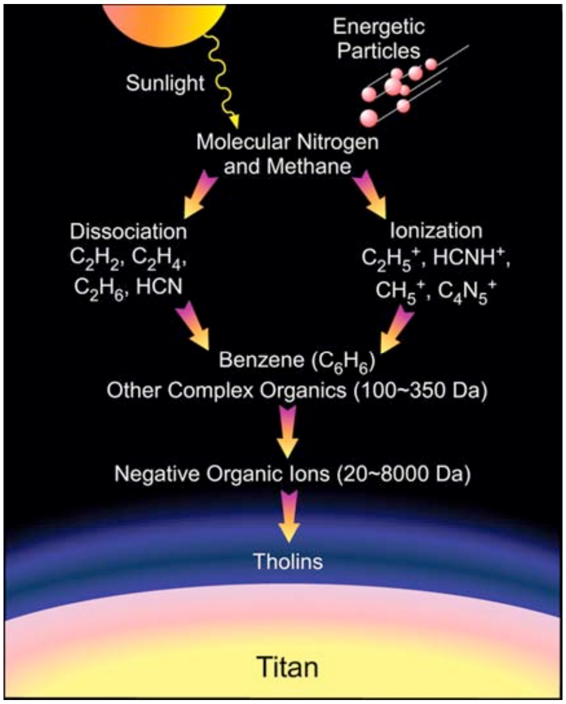
A current view of the process involves a surprising chemical process high in Titan's atmosphere, leading to the formation of benzene, and then PAH molecules. Below is the abstract of an important recent paper and a diagram showing the basics of the process:

Science 11 May 2007: Vol. 316. no. 5826, pp. 870

The Process of Tholin Formation in Titan's Upper Atmosphere

J. H. Waite, Jr.,[1]* D. T. Young,[1] T. E. Cravens,[2] A. J. Coates,[3] F. J. Crary,[1] B. Magee,[1]* J. Westlake[4]

Titan's lower atmosphere has long been known to harbor organic aerosols (tholins) presumed to have been formed from simple molecules, such as methane and nitrogen (CH_4 and N_2). Up to now, it has been assumed that tholins were formed at altitudes of several hundred kilometers by processes as yet unobserved. Using measurements from a combination of mass/charge and energy/charge spectrometers on the Cassini spacecraft, we have obtained evidence for tholin formation at high altitudes (1000 kilometers) in Titan's atmosphere. The observed chemical mix strongly implies a series of chemical reactions and physical processes that lead from simple molecules (CH_4 and N_2) to larger, more complex molecules (80 to 350 daltons) to negatively charged massive molecules (8000 daltons), which we identify as tholins. That the process involves massive negatively charged molecules and aerosols is completely unexpected.



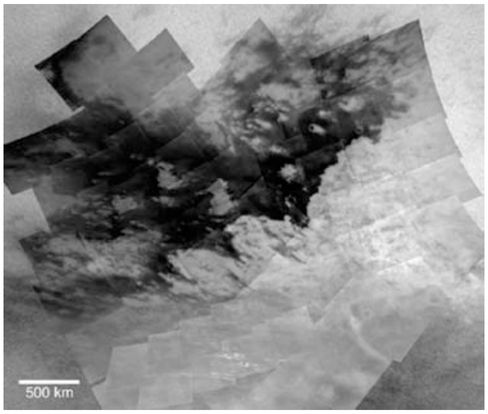
Cartoon showing the chemical process leading up to the formation of tholins in Titan's upper atmosphere. The process begins with free energy from solar UV radiation and energetic particles impinging on Titan's atmosphere. The most abundant constituents (CH_4 and N_2) combine through a number of reaction pathways to form larger organic and nitrile compounds (100 to 350 daltons) that eventually lead to the formation of negatively charged tholin aerosols (20 to 8000 daltons) observed at 1000 km.

The important result is that aerosols, however they are formed, **have been snowing down onto the surface of Titan over the past 4.5 billion years.** If left alone, they could accumulate to a depth of hundreds of meters. However, the rain of methane is expected to wash some of the deposit into lake beds or river basins. Nevertheless, relatively large quantities are expected to survive intact on the surface.

So now we have complex organics, in the form of these tholin haze particles, accumulating on the surface and in any bodies of liquid that exist on the surface, unabated during the history of the solar system, since the energy source powering the breakup of methane (cosmic rays, sunlight) has not changed, and we can see that the methane has not been used up. What happens when you put a microscopic glob of complex organics into a liquid? What liquid?

Liquid water? Combination of thick atmosphere and *some* clouds suggest significant greenhouse. But unlikely that it is enough to allow *liquid* water. Huygens lander confirms that at the surface, Titan's temperature is about 94 K (-290 F, -190 C, i.e. extremely cold). At this temperature water ice does not sublimate (vaporize) and so there is not even significant water *vapor* in the atmosphere. Direct imaging of lakes below did not show any water in lakes (they are ethane).

Clouds? There are occasional scattered variable clouds in Titan's atmosphere in addition to the overall deep haze. The detection and prevalence of clouds are a crucial first step in establishing if Titan has an ocean, or liquid bodies of any kind, on its surface (see below). These clouds are probably composed of methane, ethane or other simple organics. Analysis of the Cassini-Huygens data has given much more detail concerning all these questions. Here is a 2005 image of clouds on Titan, verifying they are methane (C. C. Porco et al. 2005 Nature).

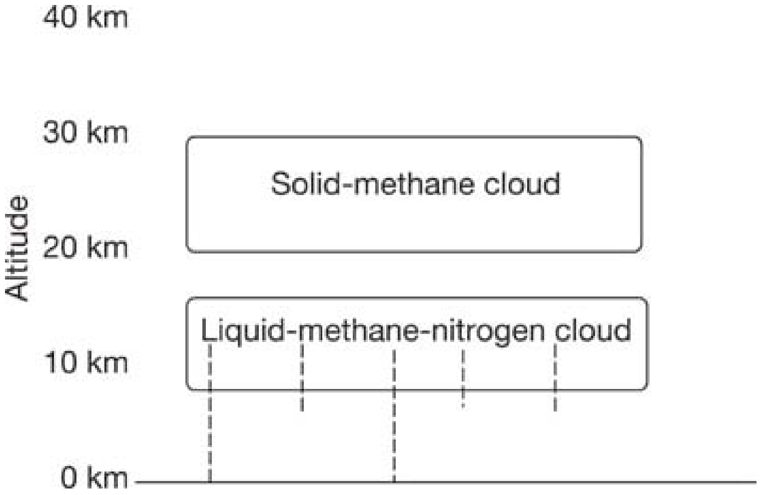


Oceans? The methane would be broken up by sunlight if not resupplied ⇒ *until recently, this supply was supposed to be <u>liquid methane</u> (or ethane—see below) oceans or lakes.* This can saturate the atmosphere, leading to methane clouds (just as H_2O clouds form on Earth).

Calculations showed that a likely chemical sequences is basically:
CH_4 + photon → CH_2 + CH → C_2H_4, C_2H_2, and H or H_2 which escape (because so light). So get irreversible conversion of methane into ethane, catalyzed by C_2H_2, so **expect <u>ocean of ethane</u> about a km thick.**

Is it a global ocean? **NO**—radar and Hubble Space Telescope infrared reflectivity show variations, suggesting fixed <u>continents</u>, but no ocean. Then astrobiologists and others worried that there might be no liquids at all, because methane could be supplied by volcanoes, not evaporation.

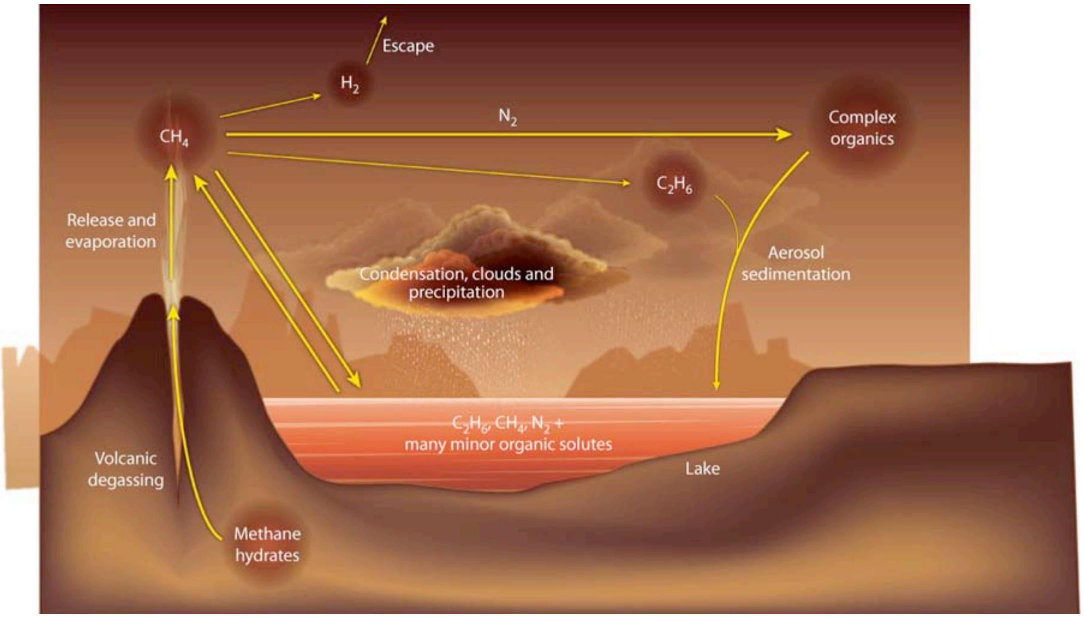
Several groups had shown that you could get clouds from processes that don't involve upward currents from bodies of water; Tokano et al. (2006 Nature) proposed that the methane clouds were of this nature and resulted only in a nearly constant weak "drizzle" of methane rain, but no bodies of liquid on the surface. They interpreted the data as in the following diagram.



The upper cloud consists of solid particles, mainly CH_4, and most resembles a terrestrial cirrostratus. The lower cloud consists of a liquid binary CH_4-N_2 mixture and resembles a terrestrial stratus. Either

cloud may or may not contain small amounts of C_2H_6 ice as condensation nuclei. CH_4 ice particles falling from the upper cloud passing this gap supply the lower cloud upon melting. Dashed lines indicate rainfall that partly arrives at the surface. Falling drizzle gradually becomes poorer in nitrogen by preferential evaporation of dissolved nitrogen.
Meanwhile other groups were finding evidence and building models in which volcanoes are the primary resupplier of methane for Titan's methane cycle.

The schematic diagram shows the cycles that are probably important in maintaining the chemistry and climate on Titan. Notice that methane has the equivalent of a "hydrological cycle" like Earth, with clouds and rain fed by evaporation from oceans (or lakes), but also an important source of methane from volcanoes, making it difficult to model. Note also the arrows connecting the methane with the "complex organics" through the good old nitrogen molecule, N_2.



Titan's methane/ethane cycle.
From: **Organic lakes on Titan** François Raulin *Nature* **454**, 587-589(31 July 2008)
Methane (CH_4) is released into the atmosphere from Titan's interior stores through volcanic action, and evaporates from the lakes of methane and ethane (C_2H_6) identified by the Cassini spacecraft on the satellite's surface[1]. Chemical reactions in the atmosphere convert it to ethane; complex organic aerosols consisting of carbon, hydrogen and nitrogen; and hydrogen gas (H_2), which escapes into space. Ethane and methane partly condense, forming clouds and hazes that precipitate, replenishing the lakes and bearing many organic species in solution.

But still, there was hope that there were liquid bodies of some sort. (Written in 2004): "The Cassini-Huygens mission will arrive at Saturn in 2004, and the Huygens probe will descend and either float on the ocean or land on solid surface. " This did *not* turn out to be the solution to the problem, but instead, the answer came from imaging from Cassini (the orbiter) as it passed repeatedly over Titan.

Lost Seas Found: Lakes.

On 26 October 2004, a couple of months before it did release Huygens, Cassini performed its first close fly-by of Titan, skimming its atmosphere 1,174 kilometres from the surface. Three remote-sensing instruments trained on the surface failed to detect a global ocean. What they detected instead was even more fascinating: impact craters, mountains, cryovolcanoes, dunes and river beds.

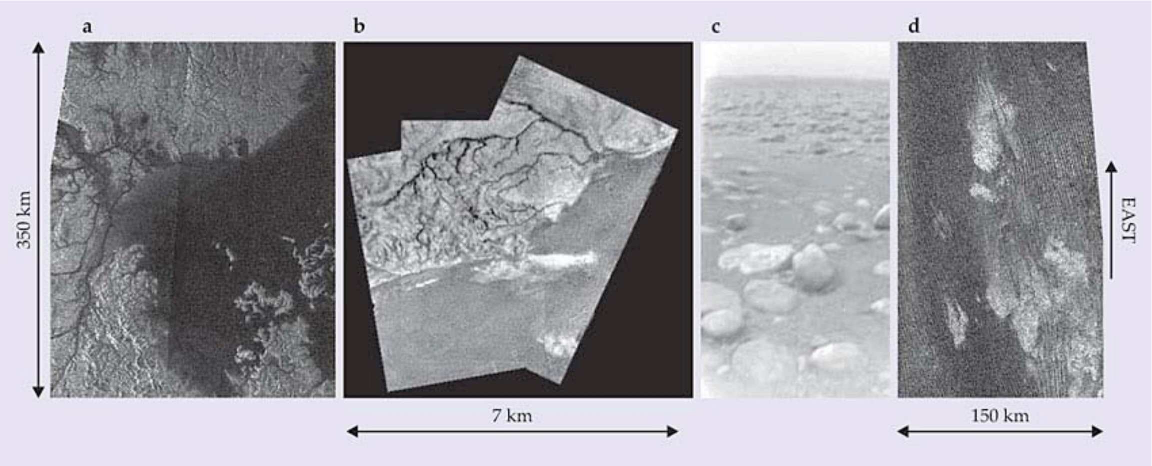
The lack of a global ocean and the discovery of these surface features, together with characteristics of Titan's atmosphere such as its nitrogen and carbon isotopic ratios, strongly implied that **the source of the atmospheric methane was internal. i.e. no liquid bodies.**

In 2005 Stofan et al. (Nature) presented fairly clear evidence of bodies that appeared to be lakes at northern latitudes, so the pendulum started to swing the other way once more. Stofan et al. speculated that the lakes contained frozen hydrocarbons.

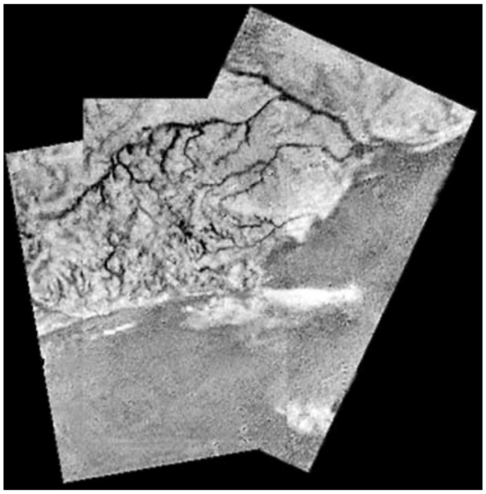
But no direct identification of composition of lakes (or that they were liquid) until July 2008.

The sequence of images below give summary of Cassini increasing evidence for lakes of ethane on Titan, from surface features, to “lakes” imaged by Cassini, but only resembling lakes by their form, and culminating with the direct detection of liquid ethane lakes by Brown et al. 2008 Nature (bottom right image)

Surface Features

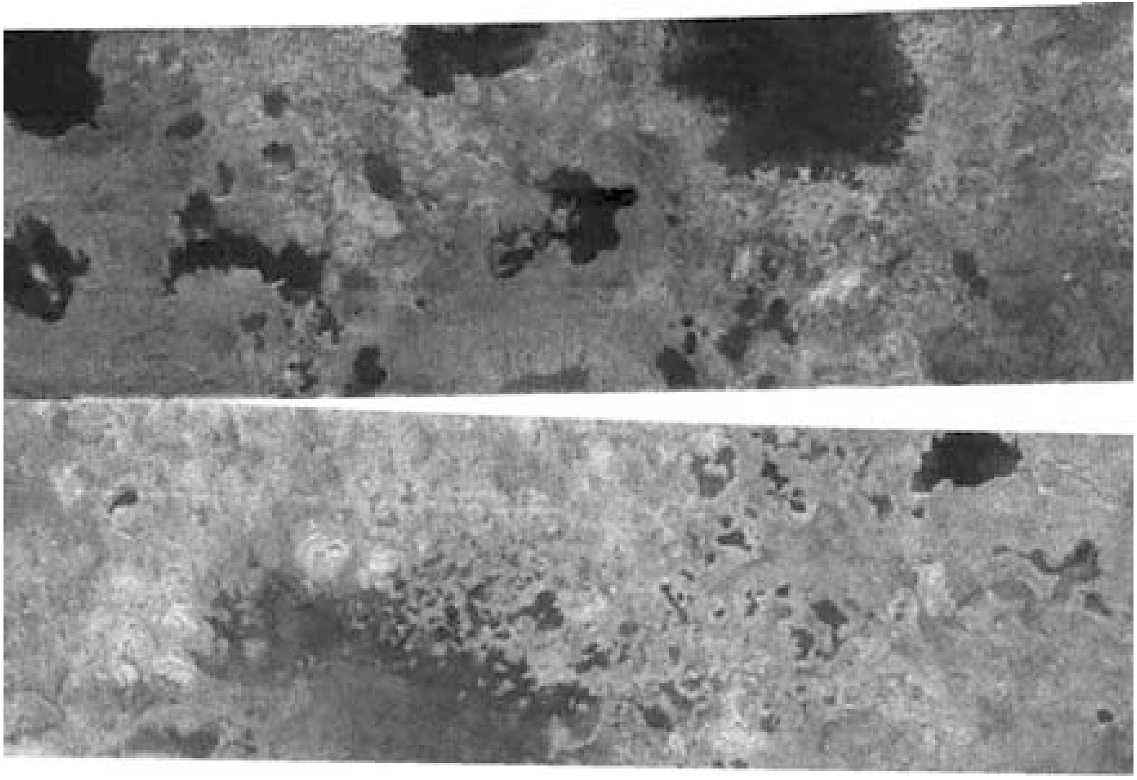


A surface modified by an atmosphere. (a) A *Cassini* radar image reveals a network of dark river channels draining into a hydrocarbon lake near Titan's north pole. **(b)** This view from the *Huygens* probe at about 8 km over Titan shows a network of smaller channels on highland terrain, evidently once fed by rainfall. **(c)** After the probe landed on the damp surface, its knee-high camera photographed rounded cobbles, up to about 15 cm across, on a streambed. **(d)** This radar image, taken by *Cassini*, shows a massive field of parallel sand dunes near Titan's equator.

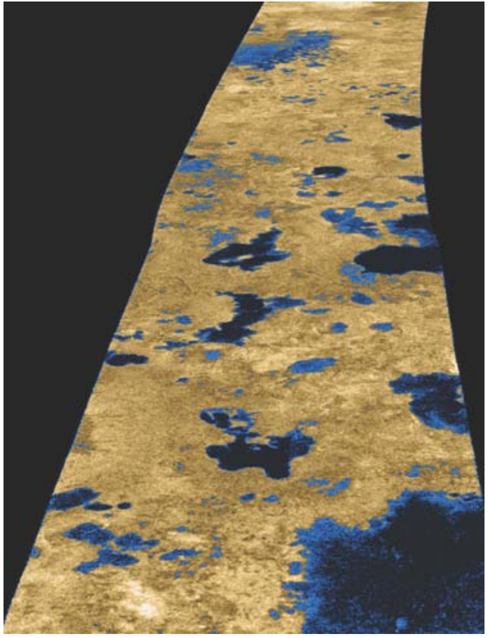


Above: Closer view of middle panel: Channel networks, highlands, and dark-bright interface seen by Huygens at 6.5 km altitude.

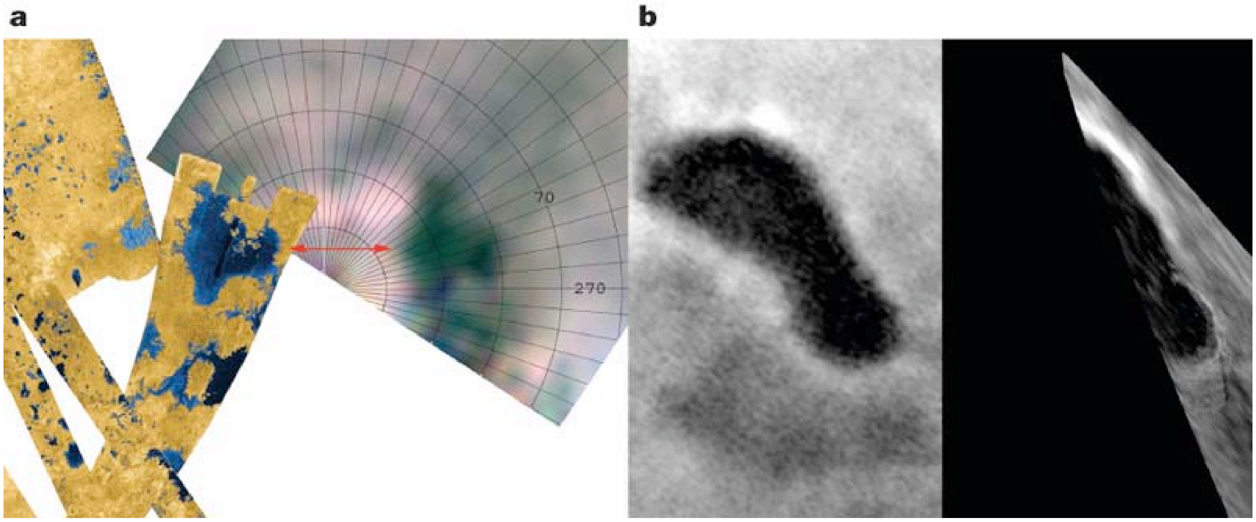
Below: Radar image of Titan North Pole region showing several dozen dark features which could be lakes. Smallest are about 1 km, several are more than 30 km wide. Biggest is about 100 miles long.



This is probably the most-seen version of the lake images (colorized):



July 2008: Paper by Brown et al. (2008) **finally directly detects ethane lakes by spectroscopic imaging** (see figure below—I will explain in class)



Left=visual images from Cassini imaging (2005). Right = VIMS (**Visual and Infrared Mapping Spectrometer**[11] **(VIMS) on board the Cassini spacecraft) on 38th flyby of Titan (2008)**

Note that they ruled out water ice or liquid water in this lake. Any liquid water must be beneath the crust, wherever the temperature has increased sufficiently.

Liquid water at earlier time? Too cold at surface now, but early planetesimal bombardment could have heated the early surface ice. But only get ~100 to 1000 yr before it refreezes after each impact, so most people think liquid water unlikely at any time in the past.

Liquid water under the icy crust? Most think it is there, since Titan is made of ices, including H_2O ice, and the temperature increases as you go into the interior. But if too far down, may not be astrobiologically important.

Notice that this discovery of ethane lakes is not quite the way most planetary astronomers would like things to have gone:

1. The lakes do not have enough area to replenish the methane in the atmosphere, so cryovolcanic emissions remain the prime candidate for the methane source.
2. The lakes are composed of liquids (ethane, methane) that are ***non-polar*** molecules (unlike water). It turns out that the tholin haze particles will not dissolve in these liquids.

Here is the abstract of a recent paper using the existence of cryovolcanoes to argue for the existence of subsurface water!! So please fund Cassini to keep investigating until 2012, and also give us a robotic lander to find the water that is "just under" the crust. Yes, astronomers are clever.

Nature **440**, 61-64 (2 March 2006)

Episodic outgassing as the origin of atmospheric methane on Titan

Gabriel Tobie[1,2], Jonathan I. Lunine[2,3] and Christophe Sotin[1]

Read→ Saturn's largest satellite, Titan, has a massive nitrogen atmosphere containing up to 5 per cent methane near its surface. Photochemistry in the stratosphere would remove the present-day atmospheric methane in a few tens of millions of years[1]. Before the Cassini-Huygens mission arrived at Saturn, widespread liquid methane or mixed hydrocarbon seas hundreds of metres in thickness were proposed as reservoirs from which methane could be resupplied to the atmosphere over geologic time[2]. Titan fly-by observations[3, 4, 5] and ground-based observations[6] rule out the presence of extensive bodies of liquid hydrocarbons at present, which means that methane must be derived from another source over Titan's history. Here we show that episodic outgassing of methane stored as clathrate hydrates within an icy shell above an ammonia-enriched water ocean is the most likely explanation for Titan's atmospheric methane. The other possible explanations all fail because they cannot explain the absence of surface liquid reservoirs and/or the low dissipative state of the interior. On the basis of our models, *we predict that future fly-bys should reveal the existence of both a subsurface water ocean* and a rocky core, and should detect more cryovolcanic edifices.

Life on Titan?

Some think Titan might be a near-ideal site for life's origin; others disagree. Here are some of the arguments.

<u>Against</u>:

a) Liquid methane and ethane don't dissolve compounds easily like water. Organic compounds formed in the atmosphere probably just settle to the bottom. This has now been verified for tholins (haze particles) in liquid ethane and methane, which are *nonpolar* (recall properties of liquid water tied to its polarized nature). It had been hoped that tholins, since they are probably composed of complex organics, would dissolve in the ethane or methane "oceans" (now lakes), like a big Miller-Urey experiment.

b) For the origin of life on Earth, many think that clays were necessary to catalyze polymerization. Recall that it is extremely difficult to produce even very short RNA strands or other polymers without the agency of a clay mineral surface. However there will be no clays (from silicates) without water. There is no water on Titan's surface. So how would you get polymerization on Titan?

c) Probably no silicates at surface anyway—they have almost certainly settled to the core (along with iron, phosphorus). So there may be a lack of biogenic elements (Si, Ca, Fe, P) at surface.

d) A persistent argument is that reaction rates will be very slow on Titan because of the drastically lower temperatures than on Earth. Most reaction rates increase *exponentially* (if you are not familiar with "exponential," you can translate as "extremely rapidly") with increasing temperature.

<u>For</u>:

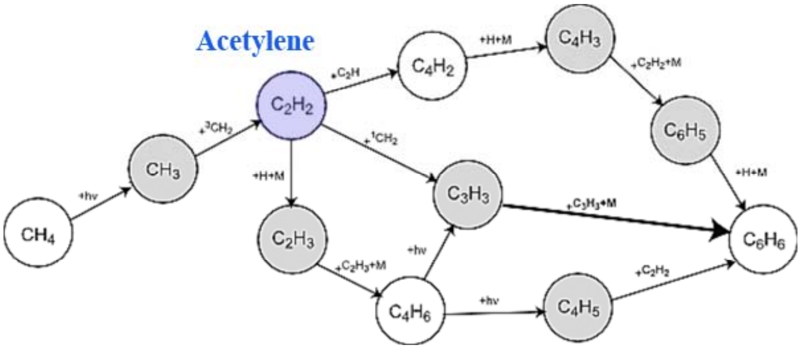
UV from the sun and high-energy charged particles from Saturn break bonds in CH_4 and and $N_2 \Rightarrow$ many hydrocarbons, including HCN and HC_3N (all observed by spectra).

These and more complicated molecules will saturate the atmosphere, producing haze (observed), and some will rain a layer of organic products on the surface ⇒ much of Titan may be covered by an "oil slick" 1 to 100 meters thick. (Wouldn't Huygens or Cassini have seen this? Or are they covering the lakes?)

With an energy source (lightning?) could get amino acids and organic polymers in high concentrations from this "oil slick." Note: One model for the origin of life on *Earth* is a "primordial oil slick," very similar! But current radar observations favor lakes rather than global oil slick.

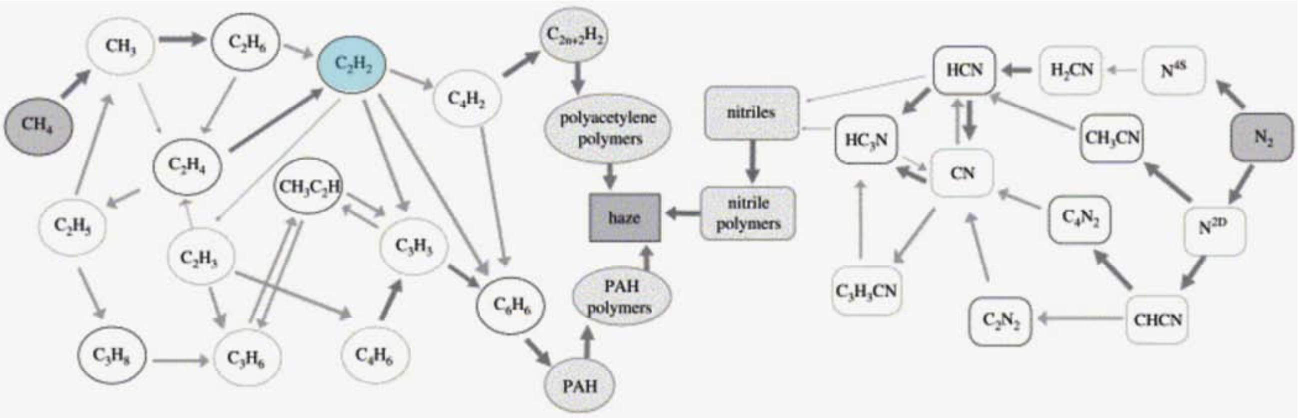
One possibly important important molecule is **acetylene** (C_2H_2), which turns out to be an energy-rich compound that might be a "food" source, releasing energy, and producing methane as a waste product, which could even help explain why there is still methane in the atmosphere (note that on Earth there is only methane because of biological processes—but on Titan you have cryovolcanoes too).

But look at the chemistry network shown earlier—where is the acetylene? Here are two others, showing how the C_2H_2 will depend on how rapidly it is supplied by and converted to other molecules. So even the abundance of acetylene, let alone whether it can be used biologically, is a complicated question.



Schematic diagram of the mechanisms for benzene formation.
The bold arrow represents the main pathway to benzene. From
Wilson et al. (2003). Acetylene is shaded blue.

Below is another, more detailed (but still simplified), reaction scheme for formation of hazes in Titan's atmosphere, with acetylene in blue. Here you can also see the nitrogen side of the chemistry (right), which is supposed to be crucial for producing prebiological polymers (see box "nitrile polymers").



(From Atreya and Wilson 2006). A **simplified** photochemical scheme for the formation of hazes in Titan's atmosphere is shown. The photolysis of methane leads to the formation of polycyclic aromatic hydrocarbon (PAH) and polyacetylene polymers, whereas the presence of nitrogen allows for the formation of the nitriles and nitrile polymers, all leading to the production of haze and the resulting loss of methane from the atmosphere. The species in bold have been detected in Titan's atmosphere to date. For full photochemical scheme, see Wilson and Atreya (2004).

The discussion of acetylene life is referring to the paper by McKay and Smith (2005), whose abstract is given below. A more recent and detailed investigation of the astrobiological potential of acetylene is given in the paper by Oremland and Voytek (2008), abstract also below (with 107 references—locate at UT link to ISI Web of Knowledge to access all references and citations for a given article in the (mostly) refereed literature). The latter paper is mostly concerned with early Earth, and microbial life, not origin of life—but you can still track to earlier references that are related to tholins, hydrocarbons, and origin of life on Titan.

Possibilities for methanogenic life in liquid methane on the surface of Titan

C.P. McKay[a, ,] and H.D. Smith[b, c]

Icarus Volume 178, Issue 1, 1 November 2005, Pages 274-276

Abstract

Photochemically produced compounds on Titan, principally **acetylene**, ethane and organic solids, would release energy when consumed with atmospheric hydrogen, at levels of 334, 57, and 54 kJ mol^{-1}, respectively. On Earth methanogenic bacteria can survive on this energy level. Here we speculate on the possibility of widespread methanogenic life in liquid methane on Titan. Hydrogen may be the best molecule to show the affects of such life because it does not condense at the tropopause and has no sources or sinks in the troposphere. If life is consuming atmospheric hydrogen it will have a measurable effect on the hydrogen mixing ratio in the troposphere if the biological consumption is greater than 10^8 cm^{-2} s^{-1} . *Life could develop strategies to overcome the low solubility of organics in liquid methane and use catalysts to accelerate biochemical reactions despite the low temperature*. The results of the recent Huygens probe could indicate the presence of such life by anomalous depletions of acetylene and ethane as well as hydrogen at the surface.

Acetylene as fast food: Implications for development of life on anoxic primordial earth and in the outer solar system

Oremland, Ronald S. and Voytek, Mary A. 2008 Astrobiology 8, Issue 1, pp. 45-58.

Abstract

Acetylene occurs, by photolysis of methane, in the atmospheres of jovian planets and Titan. In contrast, acetylene is only a trace component of Earth's current atmosphere. Nonetheless, a methane-rich atmosphere has been hypothesized for early Earth; this atmosphere would also have been rich in acetylene. This poses a paradox, because acetylene is a potent inhibitor of many key anaerobic microbial processes, including methanogenesis, anaerobic methane oxidation, nitrogen fixation, and hydrogen oxidation. Fermentation of acetylene was discovered similar to 25 years ago, and Pelobacter acetylenicus was shown to grow on acetylene by virtue of acetylene hydratase, which results in the formation of acetaldehyde. Acetaldehyde subsequently dismutates to ethanol and acetate (plus some hydrogen). However, acetylene hydratase is specific for acetylene and does not react with any analogous compounds. We hypothesize that microbes with acetylene hydratase played a key role in the evolution of Earth's early biosphere by exploiting an available source of carbon from the atmosphere and in so doing formed protective niches that allowed for other microbial processes to flourish. Furthermore, the presence of acetylene in the atmosphere of a planet or planetoid could possibly represent evidence for an extraterrestrial anaerobic ecosystem.

Will polymers of hydrocarbons or other complex organics be found? Note again the similarity between Titan as we now understand it, and the Miller-Urey experiment, with the crucial difference that ethane must replace water (and probably cannot—by now you should understand why). There are still other alternatives, but are even more speculative.