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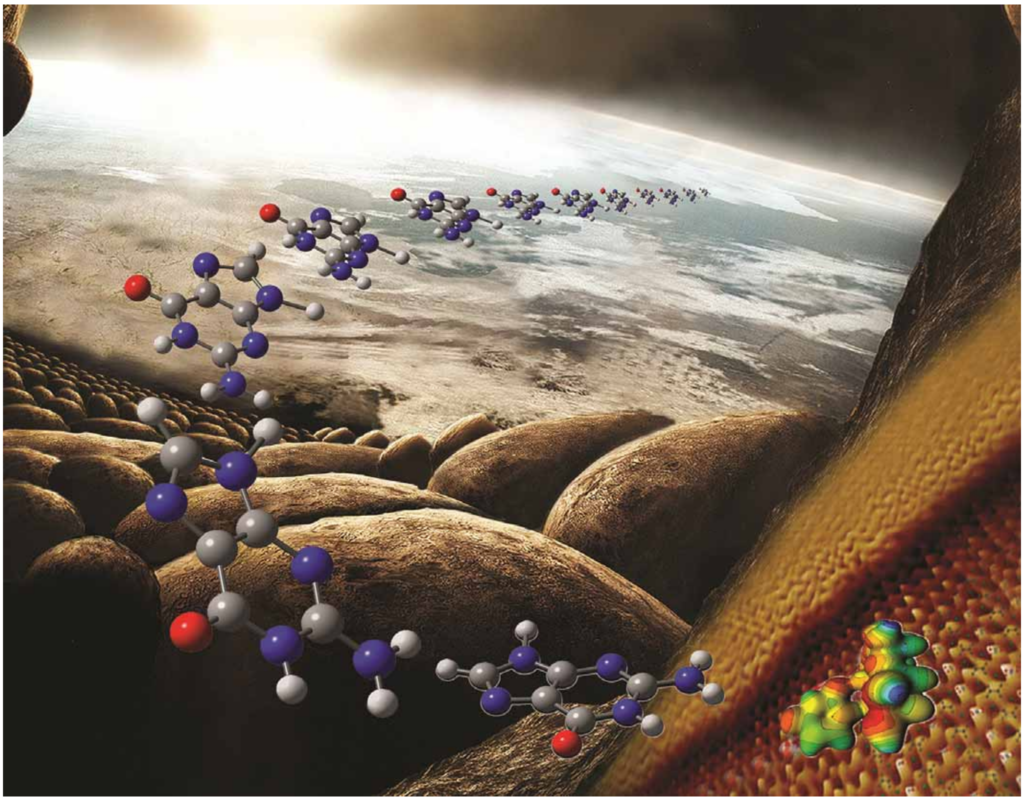

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TUTORIAL REVIEW

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Prebiotic-like chemistry on Titan†

François Raulin,* Coralie Brassé, Olivier Poch and Patrice Coll

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Titan, the largest satellite of Saturn, is the only one in the solar system with a dense atmosphere. Mainly composed of dinitrogen with several % of methane, this atmosphere experiences complex organic processes, both in the gas and aerosol phases, which are of prebiotic interest and within an environment of astrobiological interest. This *tutorial review* presents the different approaches which can be followed to study such an exotic place and its chemistry: observation, theoretical modeling and experimental simulation. It describes the Cassini–Huygens mission, as an example of observational tools, and gives the new astrobiologically oriented vision of Titan which is now available by coupling the three approaches. This includes the many analogies between Titan and the Earth, in spite of the much lower temperature in the Saturn system, the complex organic chemistry in the atmosphere, from the gas to the aerosol phases, but also the potential organic chemistry on Titan's surface, and in its possible internal water ocean.

Introduction

From the theory of so called "Chemical Evolution", it is assumed that life emerged on our planet from a prebiotic chemistry involving organic matter in the presence of liquid water and under energy fluxes. One of the main goals of exobiology (or astrobiology), the study of life in the universe, is to understand the processes involved in the origin of life on our planet and to search for extraterrestrial life.

An important approach of this scientific field is to look for extraterrestrial environments where some of those processes may have occurred or may occur today. Indeed, since the emergence of life on Earth, about 4 billion years ago, our planet has drastically changed, in particular because of life itself. Most geological characteristics of the primitive Earth (its oceans, its atmosphere, its surface) have disappeared as well as the traces of the early living systems. Thus it is also important for exobiology to look for other planetary bodies

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† Part of the prebiotic chemistry themed issue.

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Coralie Brassé achieved her bachelor degree in Chemistry in 2009 and her master's degree in Chemistry and Physics of the atmosphere in 2011 from the University Paris Diderot. She is presently studying for a PhD in Chemistry under the supervision of Prof. François Raulin and Prof. Patrice Coll at the University Paris Est Créteil. Her PhD research, as her bachelor and master internship, is developed at LISA and is related to the physical–chemical properties of Titan's aerosols including their possible evolution when they reach Titan's surface.

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having similarities with the early Earth. Consequently there are different kinds of extraterrestrial planetary bodies of prime interest for this field.

The first category corresponds to planetary bodies where life, either extinct or extant, may be present. Mars is considered as one of the best targets of that kind in the Solar System. The second category includes planetary bodies where a complex organic chemistry is taking place, such as the cometary environment, although life is not expected to be present on comets. And the third category corresponds to planetary bodies, which may show some similarities with our own planet, particularly with the early Earth, before the emergence of life. This is the case with Titan, the largest satellite of Saturn, which belongs clearly to the second category and also maybe to the first one.

Titan is the largest moon of Saturn. It was discovered in 1655 by the Dutch astronomer Christiaan Huygens who was even able to determine that this satellite orbits Saturn slowly, within 16 terrestrial days. Two centuries later, John Herschel proposed to name it "Titan", as one of the siblings of Saturn, the god of agriculture in the Roman mythology. In 1908 the Spanish astronomer José Comas-Sola, observing limb darkening around the disk of this satellite, proposed that an appreciable atmosphere could be present around Titan. This was clearly confirmed in 1944 by the American-Dutch astronomer Gerard Kuiper who detected the absorption bands of gaseous methane in the near infrared spectrum of Titan. Kuiper was also able to derive the methane abundance from his observations and estimated the partial pressure of methane at Titan's surface to be about 0.1 bar. The presence of gaseous methane in abundance around Titan—evidence for the presence of an atmosphere—was also confirmed later on by many observations from ground based telescopes, and then by data from NASA's Pioneer 11 in 1979, NASA's Voyager 1 in 1980.

Table 1 Some general characteristics of Titan

Surface radius	2.575 km
Distance from Saturn	20 Saturn radius ($\sim 1.2 \times 10^6$ km)
Orbit period around Saturn	~16 days
Orbit period around Sun	~30 years
Orbital inclination (Saturn obliquity: 27°)	0.33°
Mean volumic mass	1.88 kg dm^{-3} (= 0.34 Earth's value)
Surface gravity	1.35 m s^{-2} (= 0.14 Earth's value)

Atmospheric data (from Huygens HASI measurements)

	Altitude/km	Temperature/K	Pressure/mbar
Surface	0	93.7	1470
Tropopause	42	70.4	135
Stratopause	~250	~187	$\sim 1.5 \times 10^{-1}$
Mesopause	~490	~152	$\sim 2 \times 10^{-3}$

In fact, with a surface radius (Table 1) of 2575 km (~40% that of the Earth), Titan is bigger than the planet Mercury and is the second satellite of the solar system by its size, after Ganymede. But if we take into account the atmosphere, which extends up to more than 1000 km above the solid surface, then Titan becomes the largest satellite of the solar system. It is also the only one with a noticeable atmosphere (Fig. 1).

The presence of this atmosphere is probably linked to the relatively large distance (20 times the radius of Saturn) of Titan to the giant planet. Since the Voyager mission, Titan's atmosphere is known to be mainly composed of dinitrogen with several % of methane, with a surface pressure of 1.5 bar and a surface temperature of around 94 K. Compared to the terrestrial values (~1 bar and ~300 K) this makes the density of Titan's atmosphere at the surface level about 4.5 times

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Patrice Coll

Patrice Coll did his undergraduate (1994) and PhD studies (1997) in chemistry at the Paris Val de Marne University in France. His PhD studies were performed under the supervision of Prof. François Raulin and Dr Marie-Claire Gazeau. After doing his postdoctoral research at the Service d'Aéronomie, France, where he developed analytical systems devoted to Mars exploration, he worked at the Chemistry Department of Paris Diderot University (LISA laboratory, http://www.lisa.u-pec.fr), where he was promoted to Professor in 2008. His major research interests include the evolution of organic matter in the Solar System (Mars, Titan, Asteroids, Europe…), which he studies using laboratory simulations or by participating in exploration missions of planetary environments. Prof. Coll was recently selected as a member of Institut Universitaire de France (http://iuf.amue.fr); this new status is devoted to support a research project on Past, Present and Future Habitability of Mars.

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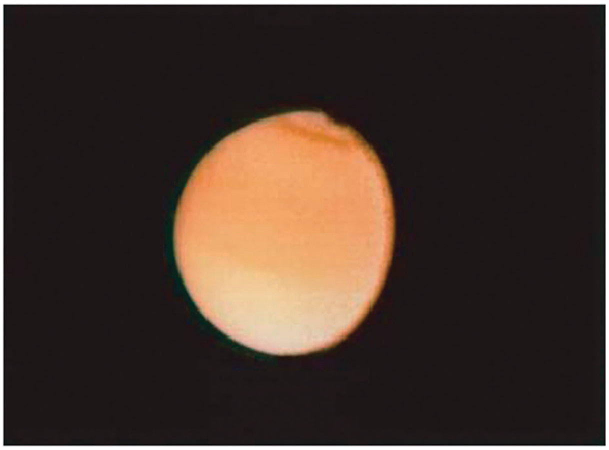

Fig. 1 Titan as seen on August 1981 from a distance of approximately 2.3 million kilometres, by the camera of the Voyager 2 spacecraft. The atmospheric hazes, photoproducts of the atmospheric constituents, mask the surface of Titan in the visible wavelengths and form a distinct dark zone in the high north latitudinal region. Credit: NASA/JPL-Caltech.

larger than that of the Earth. Titan's troposphere extends up to about 40 km (compared to $\sim$10 km for the Earth) with a tropopause temperature of about 70 K, and its stratosphere extends up to 250 km (Table 1).

As for Saturn, it takes Titan 30 terrestrial years to turn around the sun. Since the inclination of Titan's orbit around Saturn is almost merged with that of Saturn's orbit around the sun, and since the obliquity of the giant planet (the angle between its axis of rotation and axis perpendicular to the orbital plane) is 27°, Titan, like Saturn, has seasons. And those seasons are 7.5 terrestrial years long!

Although, as mentioned above, the solid surface of the satellite rotates slowly (16 terrestrial days for a complete rotation) Titan exhibits a super-rotation of its atmosphere due to strong zonal winds (similarly to the case of Venus with its very dense atmosphere).

The mean density of Titan, 1.88 g cm^{-3}, indicates that it is made of low density materials like water (in solid and possibly liquid phases) and, other ices of a mean density around 1 g cm^{-3}, mixed with higher density materials, such as silicates (mean density of about 3 g cm^{-3}). This is a key information to model the internal structure of the satellite, its formation and evolution.

With a mean distance to the sun, like Saturn, of 10 astronomical units (1 au is the mean distance of the Earth to the sun), Titan gets only 1% of the solar flux received by the Earth. Nevertheless thanks to the greenhouse gases of its atmosphere (CH_4, N_2 and H_2), producing an increase of about 20 K, and in spite of the antigreenhouse effect ($\sim$10 K) of the atmospheric haze, Titan's surface temperature is about 94 K, higher by more than 10 K than that of a related black body.[1] This solar flux is also high enough to induce an active photochemistry in Titan's atmosphere. One of the key products of this chemistry seems to be haze particles which are abundant in the atmosphere and mask the surface of the satellite in the visible spectral domain (Fig. 1).

Indeed, long before the Cassini–Huygens mission arrived in the Saturn system and explored Titan in great detail, several hydrocarbons in addition to methane were detected in Titan's atmosphere. Later on, when the Voyager spacecrafts were able to flyby Titan in early 1980s, several nitriles were also detected. Detailed photochemical models of Titan's atmosphere were then developed to provide an interpretation of the complex chemical processes occurring in this exotic environment. In parallel, laboratory experiments trying to mimic experimentally those processes were carried out.

In this paper we present briefly these three different but complementary approaches—observation, theoretical modeling and experimental simulations—which have been and are still followed to explore the environment of Titan and to study its chemistry. Then, the various aspects of Titan's properties and especially its atmosphere, surface and sub-surface chemistry are described, on the basis of the results obtained from the three main approaches. We show the many analogies appearing between Titan and the Earth, and the complexity of Titan's organic chemistry. Such chemistry, even in the absence of permanent bodies of liquid water on Titan's surface, looks also similar in many aspects to the likely early Earth prebiotic chemistry.

The tools to study Titan's chemistry

As in many scientific fields, there are three main approaches to study a planetary environment and in particular its chemistry. These are observation, theoretical modeling and experimental simulation.

Observation

Generally observation is the starting point. It can use ground based or Earth orbiting observatories, or observation from spacecrafts flybying or orbiting the target, without or with *in situ* measurements capabilities. This last way has been the most successful one to get detailed information on Titan. This was particularly the case with the Voyager mission in the early eighties. Although the optical remote sensing instruments on the two Voyager spacecrafts were not able to see the surface of Titan because of the thick atmospheric haze layers not transparent in the studied wavelength range, they provided the first determination of the main composition of Titan's atmosphere, of its vertical profile from 200 km to the surface and the detection of many trace species, especially hydrocarbons and nitriles.

Those important discoveries drastically enhanced the interest of the scientific community, planetologists as well as cosmochemists and exobiologists for this still mysterious planetary object. The need to return to the Saturn system with a dedicated space mission equipped with powerful scientific instruments able, in particular, to explore the only moon in the solar system having an atmosphere and lift Titan's veil, became clear. Only one year after the flyby of Titan by Voyager 2, the concept of such a new mission was considered.

It took 15 years before the idea became reality with the Cassini–Huygens mission and its launch in October 1997. It took then seven more years for the NASA Cassini spacecraft, after two flyby of Venus, one of the Earth, and one of Jupiter, to reach the Saturn system. On July 1st, 2004, Cassini was put into orbit around Saturn and became its first artificial satellite. On December 25th Cassini released the Huygens probe. It penetrated into Titan's atmosphere on January 14th, 2005, and

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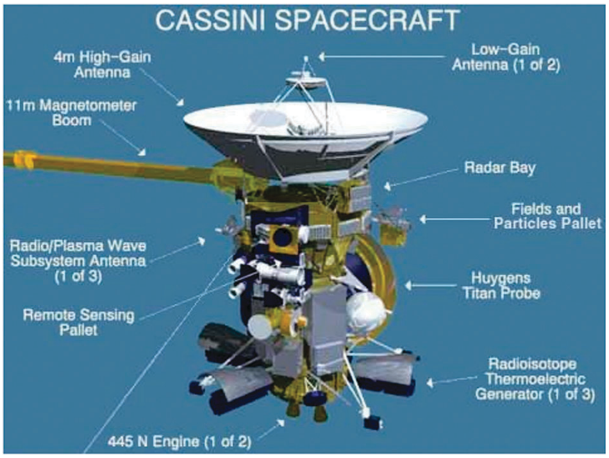

Fig. 2 The Cassini Spacecraft carrying the Huygens probe. Credit NASA/JPL/Caltech.

was able to explore this exotic environment and to provide data on its atmosphere and surface during 2 hours and 20 minutes of descent and more than one hour after it touched down.

With a height of almost 7 metres and a total mass of 5600 kg (including the 373 kg of the Huygens probe and 3100 kg of propellant) Cassini (Fig. 2) was the largest spacecraft ever sent to the outer solar system.[2,3] Cassini was (and is still) carrying 12 scientific instruments (Table 2). The remote sensing instrumentation covers a large spectral range, from IR to UV with 4 instruments: ISS, the Imaging Sciences System, with a spectral coverage extending from the near IR to the near UV, VIMS, the Visual and Mapping Spectrometer, a mapper able to observe Titan's surface in the near IR, CIRS, the Composite InfraRed Spectrometer, a high resolution Fourier Transform IR spectrometer for determination of atmospheric composition and temperature, and UVIS, the Ultraviolet Imaging Spectrometer able to study the high atmosphere. The Cassini Radar and the Radio Science Subsystem (RSS) are observing in the radio wavelength ranges. The other instruments are performing field particle and wave measurements. They include INMS, an Ion and Neutral Mass Spectrometer, which performs *in situ* measurements of neutral molecules and positive and negative ions at very low concentration.

Such a very complementary and powerful scientific payload is able to probe the different parts of Titan from its high atmosphere to its surface, and even its subsurface with RSS, and to provide data on the structure and composition of the atmosphere, surface and subsurface and the different processes involved.

The Huygens probe (Table 2) included six scientific experiments.[4,5] The GC-MS instrument combined a 3 columns gas chromatograph and a quadrupole mass spectrometer (with a mass range of 2–141 Daltons). The MS was equipped with 5 ion sources (one for direct atmospheric MS analysis, one for

Table 2 Scientific instruments and interdisciplinary investigations on Cassini and Huygens

Instrument or interdisciplinary investigations	P.I.,T.L. or IDS	Country
CASSINI		
Optical remote sensing instruments		
Composite infrared spectrometer (CIRS)	V. Kunde/M. Flasar	USA
Imaging science subsystem (ISS)	C. Porco	USA
Ultraviolet imaging spectrograph (UVIS)	L. Esposito	USA
VIS/IR mapping spectrometer (VIMS)	R. Brown	USA
Field particles and wave instruments		
Cassini plasma spectrometer (CAPS)	D. Young	USA
Cosmic dust analysis (CDA)	E. Grün	Germany
Ion & neutral mass spectrometer (INMS)	H. Waite	USA
Magnetometer (MAG)	D. Southwood/M. Dougherty	U.K.
Magnetospheric imaging instrument (MIMI)	S. Krimigis	USA
Radio & plasma wave spectrometer (RPWS)	D. Gurnett	USA
Microwave remote sensing		
Cassini radar (Radar)	C. Elachi	USA
Radio science subsystem (RSS)	A. Kliore	USA
Interdisciplinary program		
Magnetosphere and plasma	M. Blanc	France
Rings and dust	J.N. Cuzzi	USA
Magnetosphere and plasma	T.I. Gombosi	USA
Atmospheres	T. Owen	USA
Satellites and asteroids	L.A. Soderblom	USA
Aeronomy & solar wind interaction	D.F. Strobel	USA
HUYGENS		
Gas chromatograph-mass Spectrometer (GCMS)	H. Niemann	USA
Aerosol collector & pyrolyser (ACP)	G. Israël	France
Huygens atmospheric structure instrument	M. Fulchignoni	Italy
Descent imager/spectral radiometer (DISR)	M. Tomasko	USA
Doppler wind experiment (DWE)	M. Bird	Germany
Surface science package (SSP)	J. Zarnecki	UK
Interdisciplinary program		
Aeronomy	D. Gautier	France
Atmosphere–surface interactions	J.I. Lunine	USA
Chemistry and exobiology	F. Raulin	France

P.I. = Principal investigator; T.L. = Team leader; IDS = Interdisciplinary scientist.

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each GC column, and one for the samples provided by the ACP experiment). ACP, an Aerosol Collector and Pyrolyzer, was designed to collect the atmospheric aerosols in two different zones from the low atmosphere. Then collected particles are transferred into an oven and heated at different temperatures, including a pyrolysis at 600 °C. The resulting gases are then transferred into the GC-MS instrument for molecular analysis.

DISR was an optical remote sensing instrument composed of an imager (in particular for Titan's surface) and a spectral radiometer. Its goals were to study the main composition of Titan's atmosphere, its dynamics, the properties of the aerosols, and the nature of the surface. HASI, The Huygens Atmosphere Structure Instrument, was designed to measure the physical properties of Titan's atmosphere (temperature, pressure, lightning) using a variety of sensors. SSP, the Surface Science Package, was dedicated to surface measurements to determine its physical nature. DWE, the Doppler Wind Experiment, was devoted to the study of Titan's zonal winds. In addition several InterDisciplinary Scientists (IDS) were selected by NASA and ESA, to carry out scientific investigation using data from various instruments of the Cassini–Huygens mission, on a synergic way.

After a nominal 40 year duration, the Cassini–Huygens mission has been extended for 2 years in July 2008, as the "Cassini Equinox" mission. It was then extended again for 7 more years with the "Cassini Solstice mission", allowing to explore Titan during its summer season, and to look for seasonal variations in spite of the difficulties induced by the long period (7.5 years, as mentioned above) of these seasons.

All together this mission is a fantastic example of the great power and richness of the observational approach. Observations from the orbiter provide global survey of the studied environment, information on different locations within similar or very different time periods and using different but complementary instruments. This allows, in particular, to look for spatial changes as well as temporal changes in chemical composition, to better understand the chemical mechanisms involved in the formation and evolution of atmosphere or surface species. Observation from an atmospheric probe such as Huygens provides detailed information on a very localised region, of the atmosphere or the surface, complementing the more global view offered by the orbiter. Those observational data can then be used to constrain, confirm or reject theoretical models.

Theoretical modeling

Modeling is indeed another essential approach to the understanding of a planetary environment. Since the discovery of hydrocarbons in Titan's atmosphere, and especially that of N_2 as its main constituent, many photochemical models, from 0 to 3D models, have been published[6–8] to describe the chemical behaviour of this planetary atmosphere under solar photons and saturnian magnetospheric electron fluxes (Fig. 3). Initially limited to gas phase processes, the published models tried progressively to incorporate heterogeneous processes, likely to play an important role in Titan's atmosphere with the presence of aerosols.[9] One of the main end-products of these models is generally the vertical concentration profile of minor species which can then be compared to observed values to test the validity of the model. Bad fits are usually due to the lack of important reactions in the model, the lack of reliable entry data (especially the rate constant within the right temperature, and/or pressure conditions), or the uncertainties in the

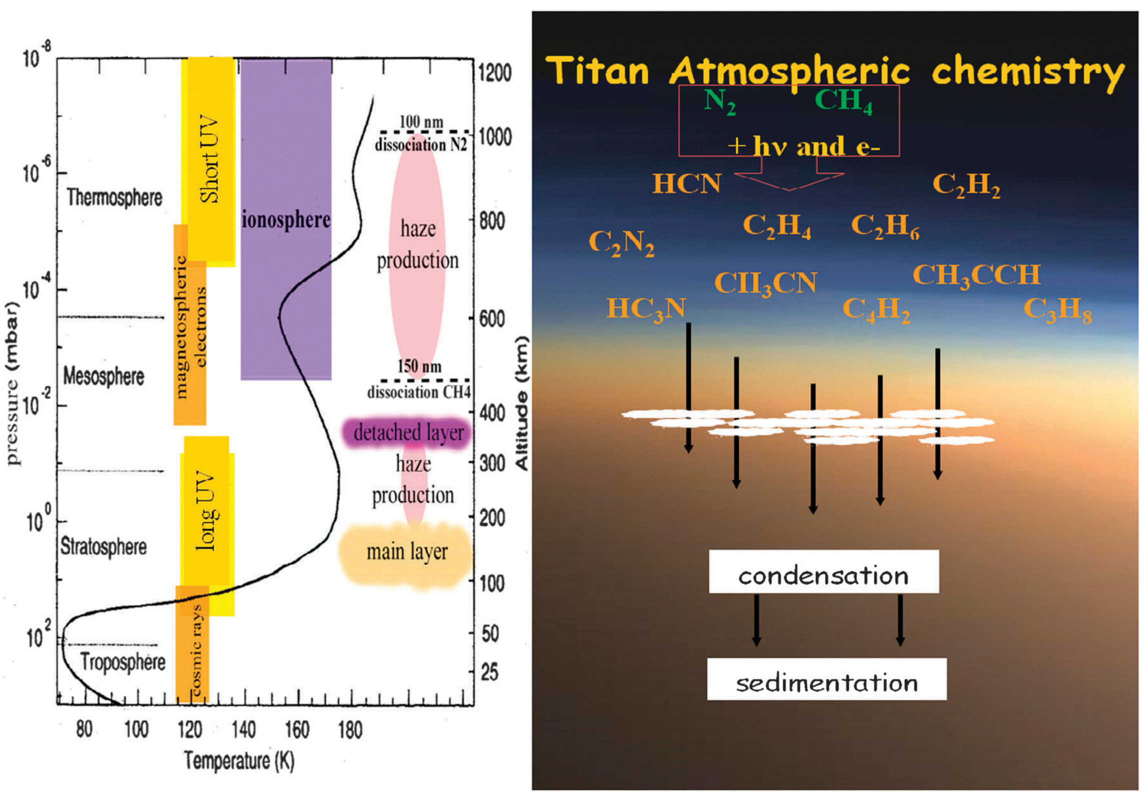

Fig. 3 Temperature profile, energy deposition and atmospheric processes.

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atmospheric transport parameters (such as the eddy diffusion vertical profile).[10,11] The question of Titan's organic haze origin has been partially solved by the numerical Global Circulation Model of Titan (GCM), putting in evidence that aerosols generated in the upper Titan's atmosphere, form and drift toward the winter pole.[12]

Theoretical modeling can also be used to study the interaction between the atmosphere and the surface. For instance, this approach, assuming thermodynamic equilibrium in the system, has been followed to estimate the chemical composition of the liquid bodies present on Titan.[13–16] A very recent GCM model[17] provides some explanation of the difference in lakes and seas abundances between the north and south polar regions, and foresees seasonal variation of their levels of liquid.

Another, although quite different, example of theoretical modeling is the determination of the internal structure of Titan, based on models of formation and evolution of the planetary body. Several models of the internal structure of Titan have been published, based on such an approach, before Cassini arrives in the Saturn system. They predict the presence of an internal water–ammonia ocean, between two thick water ice layers.[18–20]

Experimental simulation

A third approach is the use of so called "simulation experiment". It has also been largely followed to study Titan, and especially its atmospheric organic chemistry. Here one tries to mimic the chemical processes occurring in Titan's atmosphere by subjecting a gas mixture to an energy source, both representative of Titan's atmosphere.[21–28] In these experiments, a mixture of methane diluted in dinitrogen is introduced into a chemical reactor and irradiated by UV photons and/or electrons.

Photodissociation of dinitrogen requires VUV photons of wavelength shorter than 100 nm, conditions which are difficult to get in the laboratory. Thus most UV simulation experiments done with a photochemical reactor used a starting gas mixture including *N*-containing organics such as HCN or HC_3N, which have been detected in Titan's atmosphere, although as trace constituents, and can then be dissociated by usual UV lamps, such as Lyman alpha lamps. Only recently photochemical experiments simulating Titan's atmospheric chemistry were carried out with VUV photons (λ = 82.5 and 60 nm), able to dissociate N_2, provided by a synchrotron accelerator.[27]

In fact the majority of simulation experiments have been using electrons as an energy source. The reactor (Fig. 4) can be operated at low pressure (around 1 mbar), low temperature (100–150 K) to mimic Titan's stratospheric conditions.[21–26,28] All trace organics detected in Titan's stratosphere have been obtained as gas phase products in these experiments. Many other gas phase compounds not yet detected in Titan's stratosphere although likely to be present have also been obtained. These are essentially hydrocarbons and nitriles, in particular polyynes $C_{2n}H_2$ (with n = 3 and 4) and cyanopolyynes $HC_{2n}CN$ with n = 2. These compounds seem to play a key role in the chemical processes involved in Titan's atmosphere.

In addition to the volatile products, these simulation experiments also form refractory organic compounds. The non-volatile solid products obtained from laboratory experiments

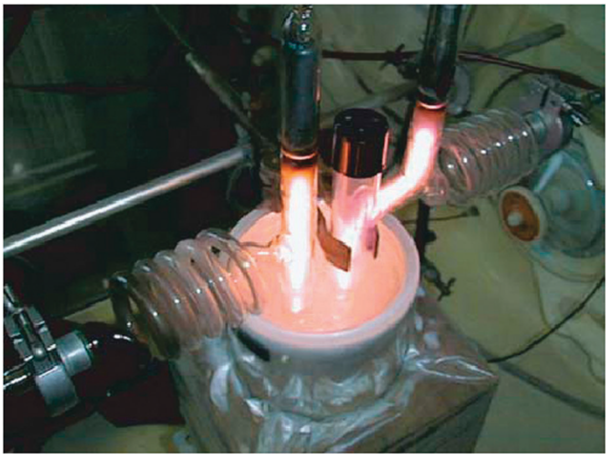

Fig. 4 Titan simulation experiment "PLASMA" used at LISA (Credit: Patrice Coll).

irradiating gas mixtures of astrophysical interest have been named "tholins" from the Greek word "tholos", meaning "muddy" by Carl Sagan and Bishun Khare[29,30] in the late 70s. Titan's tholins are thus the solid products obtained during experiments simulating Titan's atmospheric chemistry. They are supposed to be laboratory analogs of Titan's aerosols. The Cassini–Huygens data recently supported this hypothesis and Titan tholins are even now more systematically used to interpret observational data of Titan or to get information on processes involving Titan's aerosols. Titan's tholins appear to be very reactive with the atmosphere of the laboratory (they probably react with water and dioxygen). Some experiments have been developed in a glove box allowing to recover these products without air contamination.[21–24,31,32]

The tholin case nicely illustrates the complementarity of the three main approaches. In the following sections we describe different aspects of Titan as seen from the Cassini–Huygens

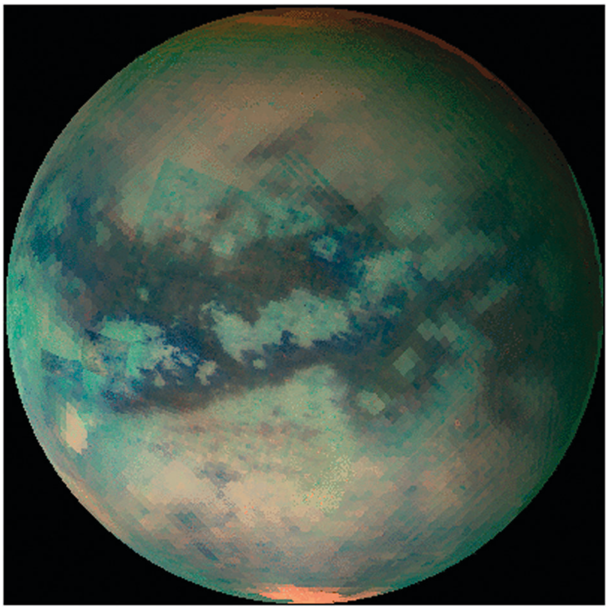

Fig. 5 Titan seen by Cassini-VIMS at 1.6 microns (blue), 2.01 microns (green) and 5 microns (red). Credit NASA/JPL/Univ. of Arizona.

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observations[33–35] (Fig. 5), coupled to laboratory simulations and theoretical modeling. These include the description of the many analogies between Titan and the Earth, and the active Titan atmospheric organic chemistry involving a complex methane cycle. This prebiotic-like chemistry occurs in the atmosphere in the gas phase and in the solid phase. It is also likely to occur on the surface of Titan. The model of the internal structure of the satellite also suggests the possibility of a prebiotic subsurface chemistry.

Analogies between Titan and the Earth

Although there are many differences between Titan and the Earth, due to the temperature difference, there are many similarities between these two planetary objects.

The first ones are related to their atmosphere, mainly made of N_2. Titan has an atmospheric structure qualitatively similar to that of the Earth, with a troposphere, a stratosphere and a thermosphere. With a surface pressure of 1.5 bar, its atmosphere is the closest one to the Earth, much closer than Venus (90 bars) or Mars (7–9 mbars). As shown by the Cassini–Huygens data (INMS in the ionosphere and GC-MS in the low atmosphere), the most abundant noble gas in Titan's atmosphere is, similarly to the Earth, ^{40}Ar.[33,36] Its abundance in the stratosphere[36] is 34 ppm, that of ^{36}Ar, primordial Argon is only 0.2 ppm. Since ^{40}Ar is produced by the radioactive decay of ^{40}K, this observation shows that, like for the Earth's atmosphere, Titan's atmosphere is of secondary origin, produced by a degassing from its internal structure.

From its distance to the sun, Titan's surface temperature should be 82 K. The values measured by Cassini–Huygens ($\sim$90–94 K, depending on the latitude) indicate the presence of a noticeable greenhouse effect. Indeed this is due to the presence of methane but also of dinitrogen and dihydrogen, which can absorb, due the collision induced absorption in the far IR, in particular of N_2–N_2 and H_2–N_2, the radiation emitted by Titan's cold surface.[1] In fact, these two atmospheric gases play the role, respectively, of water and carbon dioxide in the Earth atmosphere, the first been able to condense, but not the second.

There are several geological structures and processes on Titan which have similarities with what is seen on Earth. Although still debated, there seem to be volcanoes on Titan.[37–40] Those are in fact cryo-volcanoes, where water ice replaces the fused rock of terrestrial lava.[38,39] There are mountains,[41] of more than 1 km altitude, indicating that there is some tectonic activity, but again involving a mantle/crust made of water ice instead of rocky materials.

There are complex eolian processes of Titan which are involved in the formation of huge dune fields[42] (Fig. 6) located mainly in the low latitude regions. The shape and structure of Titan's dunes are very similar to those of some terrestrial ones. The main difference is their chemical composition: Titan's dunes are very likely made of organics mixed with water ice,[43] which, consequently, seems to play the role of silica on Earth. Indeed, the dramatic close images of Titan's surface taken by DISR[33] show the presence of pebbles on Huygens landing site (Fig. 7). Those are water ice pebbles shaped by running liquid methane.

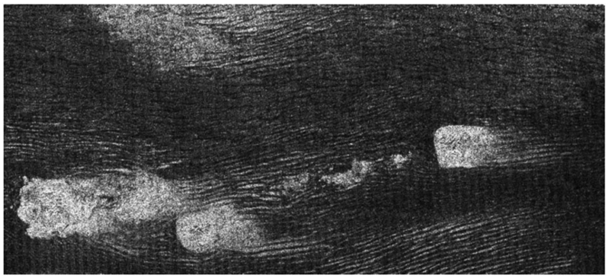

Fig. 6 Titan's dunes (up to 3 km spaced) pattern in equatorial regions seen by the Cassini radar. Credit NASA/JPL.

Fig. 7 Titan's surface at Huygens landing site as seen by DISR. Credit NASA/Univ. Arizona.

This analogy between methane on Titan and water on Earth is observed in many other examples. The GCMS on Huygens has clearly shown that methane is saturated in the low troposphere (below $\sim$7.5 km), indicating the likely presence of methane clouds in these atmospheric zones. Indeed ISS and VIMS images of Titan on the Cassini orbiter provide evidence of many complex cloud systems on Titan, analogs of the water clouds on Earth. Some of these clouds present extraordinary shapes, covering large fractions of the tropical zones of Titan and organized by planetary-scale waves. The associated storms may engender huge methane–ethane rain precipitation on Titan's surface.[44,45]

As for liquid water on Earth, there are evidence of liquid methane on Titan. The images taken by the Huygens probe (Fig. 8) before the end of its descent in Titan's troposphere highlight the presence of dendritic structures on the surface of the satellite[33] which look very much like river beds on Earth. After Huygens landed, the GCMS instrument measured an important increase of methane abundance, which remains constant during the 70 minutes of surface data.[33,36] Similar behavior was also observed for ethane.[36] The simplest explanation is the presence of liquid methane mixed with methane in Titan's soil.

Even more spectacular are the radar images of the many lakes in the high latitude regions (Fig. 9). Some of these have the size of terrestrial seas, especially when taking into account the size of Titan compared to that of the Earth. The detection

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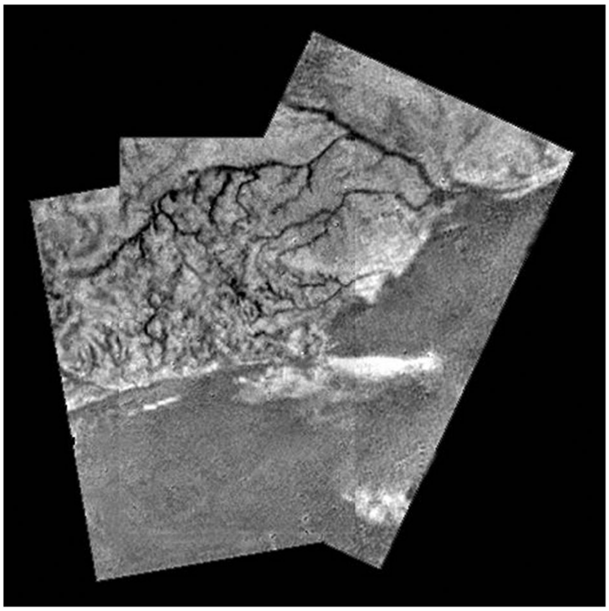

Fig. 8 Channel networks seen by Huygens-DISR at 6.5 km altitude (Credit: ESA/NASA/JPL/University of Arizona).

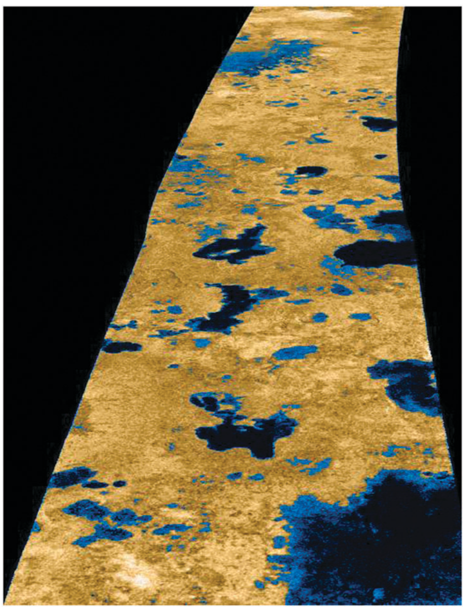

Fig. 9 Lakes and seas in north polar regions of the Titan seen (in blue) on a false color Cassini Radar image (credit: NASA/JPL/USGS).

of a specular reflection beam from one of these lakes/seas demonstrates that it is filled with liquid.[45] VIMS infrared spectra of some of those lakes show that one of the main constituents is liquid ethane. They must also include liquid methane, because of the several percent of gaseous methane in the atmosphere above the liquid, although the IR signature of liquid methane cannot be distinguished on these VIMS spectra due to the strong spectral contribution of atmospheric methane. VIMS images also show the presence of a shore line around those lakes/seas, indicating a seasonal variation of the level of liquid, again similar to what is seen on Earth.[46] This is also suggested from recent global circulation modeling of Titan.[17]

Thus Titan appears to be the only planetary body in the solar system with the Earth having large liquid bodies on its surface. But on Titan liquid methane replaces liquid water. Methane on Titan presents a complex cycle, analogous to that of water on Earth, involving a complex organic chemistry which also exhibits some similarities with the likely terrestrial prebiotic chemistry.

Titan atmospheric organic chemistry

The presence of a noticeable fraction of methane in Titan's atmosphere (5% in the near surface troposphere, 1.5% in the stratosphere and around 2% in the high atmospheric zones) is the source of an active atmospheric organic chemistry on Titan.

This chemistry starts indeed in the ionosphere with the direct dissociation of methane and dinitrogen by high energy solar UV ($\lambda < 100$ nm for N_2 dissociation) and Saturn magnetospheric electrons (Fig. 3). Most of the detailed chemical models published so far involved radical chemistry and photochemistry, with the formation of primary species, CH_3, CH_2, CH and N radicals resulting from CH_4 and N_2 dissociation leading to the production of simple hydrocarbons and *N*-compounds through the coupling of dinitrogen and methane chemistries.[6–11]

Among those products, C_2H_2 and HCN play a key role in the chemical scheme. After their formation in the high atmospheric zone, these two products are transported, through diffusion processes, downward lower atmospheric levels, where the UV photons capable of methane direct photodissociation are not available, being absorbed by the atmosphere above. However, acetylene and hydrogen cyanide have a UV spectrum extending toward the near UV range, they can absorb the UV photons available in those lower atmospheric levels and be photodissociated, yielding more complex organic species.

Some of the radicals produced by these photochemical processes are energetic enough to dissociate methane. This is the case, for instance, with the C_2H radical resulting from the photodissociation of acetylene. The bulk reaction appears as the dissociation of methane photocatalyzed by acetylene:

$$\begin{array}{lllll} & C_2H_2 + h\nu & \rightarrow & C_2H + & H \\ & C_2H + CH_4 & \rightarrow & C_2H_2 + & CH_3 \\ \hline \text{net:} & CH_4 & (h\nu, C_2H_2) \rightarrow & CH_3 + & H \end{array}$$

Higher acetylenic compounds, especially polyynes such as C_4H_2, already detected in Titan's atmosphere, and C_6H_2 or C_8H_2, likely to be present, could play the same catalytic role. In addition to HCN, a large variety of nitriles are also produced by these processes. Indeed several nitriles (Table 3)[36,47–52] have been detected in the stratosphere: CH_3CN, HC_3N, C_2N_2 and—in the condensed form—C_4N_2, and additional ones in the ionosphere. Many others which are observed in simulation experiments should be present, in particular cyanopolyynes, analogues of HC_3N, such as HC_5N, which could be involved in the formation of high molecular weight organics present in the haze particles.

Only three different oxygen-containing molecules have been detected in Titan's atmosphere: CO, CO_2 and H_2O. The most

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Table 3 Compounds detected in Titan's atmosphere

Compounds	Mixing ratio	Location with[reference#]
Main constituents		
Dinitrogen N_2	0.98	Mid stratosphere, mid latitude[36]
Methane CH_4	0.0148	
Dihydrogen	~0.001	
Other hydrocarbons		
Ethane C_2H_6	1.1×10^{-5}	Mid stratosphere, 70°N[47]
Ethene C_2H_4	5.5×10^{-7}	
Ethyne C_2H_2	5.1×10^{-6}	
C_2HD	2.0×10^{-9}	
Propane C_3H_8	6.9×10^{-7}	
Propene C_3H_6	$\sim 3 \times 10^{-6}$	Ionosphere[48]
Propyne C_3H_4	2.4×10^{-8}	Mid stratosphere, 70°N[47]
Butadiyne C_4H_2	2.3×10^{-8}	
Benzene C_6H_6	4.2×10^{-9}	
Toluene C_7H_8	Inferred	Ionosphere[48]
Anthracene $C_{14}H_{10}$	Inferred	
N-organics		
Methanenitrile HCN	9.7×10^{-7}	Mid stratosphere, 70°N[47]
Propynenitrile HC_3N	4.6×10^{-8}	
Ethanedinitrile C_2N_2	1.4×10^{-8}	
Ethanenitrile CH_3CN	2.0×10^{-8}	300 km disk-average[49]
Butynedinitrile C_4N_2	Solid phase	Stratosphere[50]
Propanenitrile C_2H_5CN	$\sim 2 \times 10^{-7}$	Ionosphere[48]
Propenenitrile C_2H_3CN	$\sim 4 \times 10^{-7}$	
O-compounds		
Carbon monoxide CO	4.7×10^{-5}	Stratosphere[51]
Carbon dioxide CO_2	1.4×10^{-8}	Stratosphere[47]
Water H_2O	4.0×10^{-10}	Stratosphere[52]
Rare gases		
Argon ^{40}Ar	3.4×10^{-5}	Mid stratosphere, mid latitude[36]
Argon ^{36}Ar	2.1×10^{-7}	
Neon ^{22}Ne	2.8×10^{-7}	

abundant is CO, present at a concentration of about 50 ppm. H_2O is supposed to be imported from meteoritic fluxes in the atmosphere. Its photodissociation into H and OH, followed by the reaction between OH and CH_3 radical could be the source of atmospheric CO and CO_2. Although the abundance of CO is relatively low, other sources are requested to explain its value. Moreover, CO could be a noticeable source of O atoms in Titan's atmosphere, inducing the formation of some O-organics, at low concentration, such as oxyrane.[22,23]

The INMS instrument on Cassini has detected many organic species, neutral as well as ions in its mass range (1–100 Daltons) at altitudes around 1000 km.[48,53] They include additional nitriles, both with saturated carbon chain (C_2H_5CN) and unsaturated one ($CH_2{=}CH–CN$) and ions up to C_7. The distribution of the INMS ion mass spectra strongly suggests that ions with much higher masses (of several hundred Daltons) are also present at similar concentrations in these ionospheric levels. Indeed, the data of the Ion Beam Spectrometer (IBS) and the Electron Spectrometer (ELS) of the Cassini CAPS instrument indicate the presence of high mass positive and negative ions. The IBS spectra—which are in very good agreement with INMS in the 1–100 Dalton INMS range—show the presence of positive ions with significant density up to more than 300 Da, and a maximum density around 150 Da. The ELS spectra show the presence of negative ions with noticeable concentration up to almost 10 000 Da. Several possibilities have been proposed for the molecular composition of these high molecular weight negative ions, such as PAH's clusters, fullerenes, and more generally tholin-like materials.[34] Detailed chemical models including these high mass ions and the ion-chemistry involved in their formation are now obviously needed.

One of the major end products of this atmospheric organic chemistry is indeed a macromolecular material, close to laboratory Titan tholins. This refractory material constitutes the core of the aerosols present in the several haze layers present in the atmosphere. These layers exhibit a complex structure, with a so-called "detached haze layer" observed around 500 km, by Voyager and by Cassini at the beginning of its prime mission, in 2004–2006, and at much lower altitudes (around 380 km) 5 years later, in 2010. The aerosol concentration in the various layers[34] varies from about 10^2 particle cm^{-3} around 1000 km altitude to 10^5 near the surface. Interpretation of the DISR observation of the aerosols in the low atmosphere (140–0 km altitude) indicates that the particles are made of an aggregate of about 3000 monomers of 0.05 to 0.1 μm mean radii.

The ACP instrument on Huygens was able to perform the first *in situ* chemical analysis of the particles in the low stratosphere and mid-troposphere. ACP was equipped with a filter, installed at the end of a movable tubing, to collect the aerosols during the descent of the Huygens probe. The aerosols were collected first in 130–35 km, then in the 25–20 km altitude levels. After each collection, the filter was transferred into an oven, which was then closed and heated at different temperatures. The gases produced at each temperature were transferred into the Huygens GC-MS instrument and analyzed essentially by mass spectrometry. The obtained results[33] show that the collected particles are made of a refractory nucleus covered by volatile, mainly organic, species. After evaporation of the volatile constituents at low temperatures, the particles release HCN and NH_3 when heated at 600 °C. This demonstrates that the aerosols include a nucleus of refractory macromolecular material made of C, H and N atoms. Their molecular composition should be close to that of the laboratory tholins which release HCN and NH_3 when pyrolyzed at 600 °C, and should include CN groups and amino groups (primary, secondary and/or tertiary) in the molecular structure. This clearly supports the hypothesis that Titan tholins are good laboratory analogues of Titan atmospheric aerosols. Nevertheless, many questions remain about the chemical and physical properties of the haze particles. This is particularly the case with their molecular composition, and even their elemental composition, since ACP did not provide the relative abundances of the different chemical elements constituting the particles. Thus so far, the interpretation of many observations of Titan's atmosphere which needs quantitative data on the aerosols, not yet available, uses the corresponding data of the aerosol analogues, the laboratory Titan's tholins. For example the index of refraction of tholins[30,31] which has been determined by several teams in a large range of wavelength, or their UV or IR spectral properties are often used to interpret the observed reflectance spectra of Titan's surface.

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Another main product of methane chemistry in Titan's atmosphere is ethane. It is the most abundant volatile organic compound in the atmosphere after methane, with a mole fraction of more than 10 ppm in the mid-stratosphere. Ethane condenses in the cold lower part of the stratosphere, this process is induced by the aerosols acting as condensation nuclei. In the troposphere, these particles are probably involved in the formation of clouds and the precipitation of methane–ethane rains and hails down to the surface. Thus these precipitations carry the produced ethane to the surface, where it accumulates, contrary to methane which can evaporate and return into the atmosphere. A fraction of this surface ethane feeds the lakes and seas which are observed in the high latitude zones, both at south and north polar regions. But only a minor part of ethane is involved in those lakes, and the sink for the major part is not fully understood yet. One possibility is to suppose that ethane is trapped as clathrates or is adsorbed with other organics in porous materials present in the subsurface near Titan's surface.

Methane thus exhibits a complex cycle on Titan[54] which presents similarities with the water cycle on Earth. It is dissociated directly by energetic electrons or photons in the high atmosphere, or through photocatalytic pathways in the lower atmospheric regions. In the troposphere, it condenses and precipitates to the Titan surface as rain or hail, eventually mixed with ethane and other organics produced by its atmospheric chemistry. Part of this surface methane fills the many lakes and seas present in the polar regions, mainly mixed with ethane and propane. Other part produces the liquid flows observed in several regions of Titan, in particular in the equatorial regions, like the dentritic structures seen by DISR on Huygens (Fig. 8). Taking into account the present total amount of methane in Titan's atmosphere and the global destruction rate of methane (about 5×10^9 cm^{-2} s^{-1}) the life time of methane in the atmosphere is of the order of 10–100 My.[55] The presence of an abundant fraction of methane in the atmosphere after ~4.5 Gy of Titan's history suggests that there is a large reservoir of methane on or in the satellite. Before Cassini's observation of the surface of Titan it was proposed that this reservoir could be large and deep seas on the surface, acting simultaneously as sink for ethane. There are high latitude seas on Titan, but not large and deep enough to play such a role. The main reservoir of methane is likely to be located in the subsurface of Titan as methane clathrates, able to release regularly their methane content in the atmosphere through degassing, with the possible involvement of cryovolcanism. Another potential source is the *in situ* formation of methane from the chemical reduction of water and carbonates by minerals which may be present in the subsurface: this is the serpentinization process, the occurrence of which is well known on Earth.

The main products of methane chemistry are the macromolecular organics formed in the high atmosphere. The estimated haze production[55] and deposition on the surface resulting from methane evolution is around 0.5–3 $\times$ 10^{-14} g cm^{-2} s^{-1}. If we assume that methane has been present since the early history of Titan in the atmosphere of the satellite at the few % concentration levels, with atmospheric profiles close to the present one, these polymeric materials should have formed a layer of several metres to ten metres thick on the surface. Macromolecular organics, similar to laboratory Titan's tholins, have not been clearly identified on Titan's surface, although they could be involved in the grains constituting the many dune fields observed in the equatorial regions, or in the surface soil analyzed by the DISR instrument in the Huygens landing area. However, several organic compounds have been identified on Titan's surface by GCMS, after Huygens landing, and by a VIMS instrument on Cassini, from near infrared spectroscopy, such as C_2-hydrocarbons and benzene.[56] Study of Titan's inventory of organic surface materials indicates that there are more organics in solid phase than in liquid phase.[57]

This potential large accumulation of organic products on Titan's surface is also in good agreement with the isotopic ratio of various chemical elements in the atmosphere. The mole fraction of ^{36}Ar in Titan's atmosphere[36] is much lower than the solar value (Ar/N_2 = 0.11). This suggests that N was initially present as NH_3 which was then photolyzed into N_2. Moreover the nitrogen isotopic ratio measured by Huygens GCMS[36] in Titan's troposphere: $^{14}N/^{15}N$ = 183, is about 0.6 the terrestrial value. This indicates an important loss of N by escape processes and the renewing of the atmosphere with the accumulation of organics on the surface.

Titan's surface chemistry

The many observations of Titan from Cassini show the wide diversity of its surface (Fig. 10). Dunes, volcanoes, impact craters, mountains, dark and bright terrains, complex flow networks, and many lakes and seas.[58] These geological features are continuously covered by the organics sedimenting and precipitating from the atmosphere. Rain and hail bring the most volatile organic compounds, mainly methane, ethane and propane to the surface. Aerosols carry both volatile and refractory organics to the surface. Depending on the location, the precipitated material will follow different evolution.

In the high latitude regions, this atmospheric material feeds the lakes and seas. The most volatile compounds, methane, ethane and propane, are also the main constituents of these surface liquid bodies and are totally dissolved in it. The other compounds, depending on their solubility in such an exotic solvent and on their atmospheric flux, totally or only partly dissolve[13–16] in it. All alkanes are indeed very soluble and are totally dissolved. Alkenes and alkynes are less soluble and their flux is high enough to allow these compounds to reach the saturation in the liquid. The non-dissolved part, depending on its density relative to the liquid either floats, or sinks, or remains in suspension. Modeling of these processes, assuming quasi thermal equilibrium between the liquid surface and the atmosphere just above it, allows us to predict the chemical composition of these lakes and seas.[15,16] The results indicate that the liquid is mainly composed of ethane (around 65%) and methane (around 30%), with several percents of propane, ethylene and dissolved N_2.

The solution (Table 4) should also include many minor compounds C_4–C_7 alkanes, alkenes and benzene in the concentration range 1000–1 ppm, acetylene several 100 ppm, diacetylene ~1 ppm, and nitriles such as HCN and HC_3N in the range 50–1 ppm. Several inorganic compounds should be

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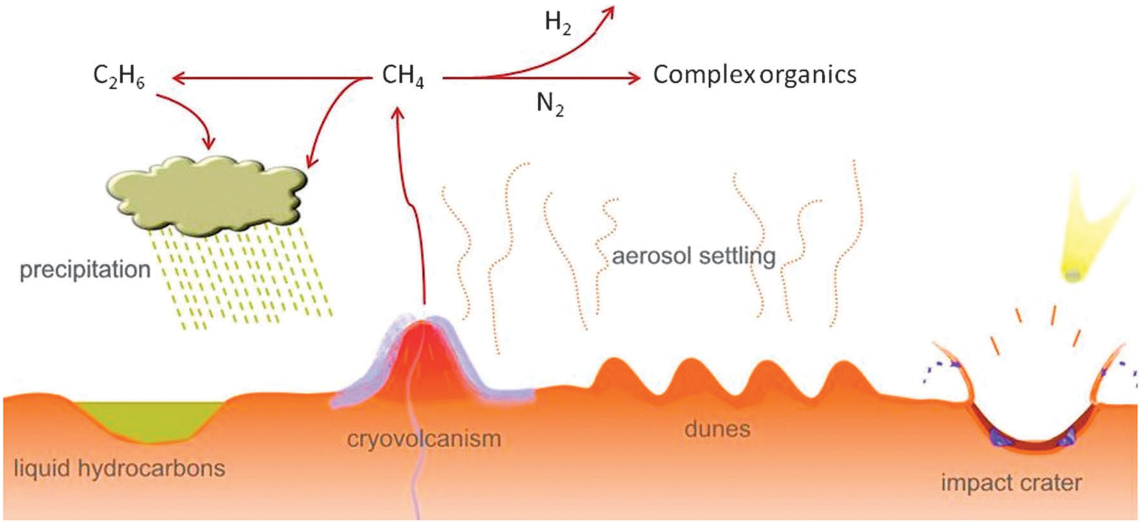

Fig. 10 Methane cycle and variety of surface features able to participate in surface chemistry (adapted from *Planetary and Space Science*, 2012, **61**, 114–123; O. Poch *et al.*). Production yields of organics of astrobiological interest from $H_2O–NH_3$ hydrolysis of Titan's tholins (ref. 64) (Copyright 2011, with permission from Elsevier)

Table 4 Composition of Titan's lakes from thermodynamical equilibrium modeling (adapted from ref. 16)

Titan's lakes : made of ~65% ethane and ~30% methane, with many minor species dissolved

- Other hydrocarbons : ethylene and propane : several%
  C_3-C_7 alkanes, alkenes and benzene : several‰-1 ppm
  acetylene : 400 ppm diacetylene: ~1 ppm
- Nitriles : 50 - 1 ppm
  HCN : 3 ppm - HC_3N : 5 ppm
- Heterocyclic bases : Pyrimidine 2 ppm - Adenine 10 ppb
- Inorganics : CO_2 : 10 ppm
  NH_3 : 5 ppm
  H_2O : 0.2 ppt !!
  CO: ~4 ppm
  Ar, other noble gases very soluble

also present, in particular noble gases very soluble, and CO_2, NH_3 and CO at the 10–1 ppm level. Extrapolating the very low solubility of Titan tholins in such a solvent to the aerosols, it is likely that the macromolecular fraction of the particle is not dissolved in the surface liquid bodies where it mainly remains in suspension or sinks.[16]

The solar photons reaching Titan's surface are not energetic enough to allow further chemical evolution of these lakes. However, cycles of evaporation, refilling of the lakes, may induce some chemical changes, in spite of the very low temperature of the system (around 90–94 K), especially if the particles in suspension could exhibit some catalytic properties. Another possibility of evolution could be induced by very high energy (30 GeV or more) cosmic rays reaching Titan's surface[59] although their flux is quite low (of the order of 1 particle cm^{-2} per day). This has not been studied experimentally in detail so far. There is a need currently for more data on the solubility of Titan tholins in cryogenic mixtures representative of Titan's lakes, and on the possible chemical evolution of these mixtures under high energy particle fluxes. In these processes, oxygen chemistry plays a minor role, although the presence of CO and CO_2 at a several ppm concentration may induce some O chemistry.

Interpretation of combined Cassini INMS and VIMS observation of the north polar lakes indicates the possible presence of organic sedimentary deposits in dry lakebeds.[60] This is another analogy with our planet: this looks like the evaporated deposits seen on the surface of the Earth.

The involvement of oxygen atoms may be more important in places which could episodically experience the presence of liquid water. Models show that large cometary impacts could melt surface water ice and provide for short time periods (but as long as several 1000 years) liquid water bodies,[61] allowing further chemical evolution at temperatures more favorable than the surrounding 90–94 K and with a favorable solvent. Another possibility, also quite interesting for prebiotic chemistry, is the release of water–ammonia slush coming from the deep surface layers, during cryovolcanism episodes. Although ammonia has not been clearly and directly detected on Titan's surface yet, it has been suggested by Cassini-VIMS observations[40] though the interpretation of these observations is still under debate.[62] Those events, which could be more frequent than the large impacts, would bring to the surface a reactive $H_2O–NH_3$ medium, which, even at low temperature, could allow the chemical transformation of the organics present on the surface, especially the macromolecular organic materials with an important incorporation of O-atoms, through hydrolysis processes, in the resulting products.

During the past few years, many experimental works have been carried out in the laboratory to study those processes, using Titan's tholins within conditions trying to mimic these Titan's surface conditions.[32,63–65] In these experiments, after their synthesis (including within conditions avoiding air contamination), the tholins are put in suspension in water–ammonia solutions and kept for several weeks at different temperatures, including low temperatures. Then the solution is filtered, dried out and the obtained solid residue is analysed. Different techniques have been used, in particular chemical derivatization-gas

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Table 5 Amino acids, nucleobases and urea produced from hydrolysis of tholins with water–ammonia solutions at different temperatures (reprinted from *Planetary and Space Science*, 2012, **61**, 114–213; O. Poch *et al.*, Production yields of organics of astrobiological interest from H_2O–NH_3 hydrolysis of Titan's tholins (ref. 64) (Copyright 2011, with permission from Elsevier). *See ref. 64 for details on the calculation of these yields

	Tholins no. 1 + water at 279 K	Tholins no. 2 + NH_3 at 279 K	Tholins no. 2 + NH_3 at 253 K
Alanine	No data	2–3 × 10^{-2}%	0%*
Glycine	4–6 × 10^{-2}%	3–4 × 10^{-1}%	0–4 × 10^{-3}%*
Urea	0–3%	6–12%	0–2%*
Uracil	0%	6–9 × 10^{-4}%	0%*
Aspartic acid	1.6–2 × 10^{-3}%	3–4 × 10^{-3}%	0–3 × 10^{-4}%*
Adenine	0%	1–2 × 10^{-2}%	0%*

chromatography-mass spectrometry (Deriv-GC-MS).[32,64] The results (Table 5) show the formation of several hydrolysis products of biological interest, amino acids and nucleobases, as well as urea, even at low temperatures. The corresponding yields (w/w, related to tholins) are of the order of a few 10^{-4}% to several 0.1%.[32,64] High Resolution Mass Spectroscopy (HRMS) of Titan tholins obtained from N_2–CH_4 gas mixtures including CO suggests that the amino acids and heterocyclic bases may be already present in the starting macromolecule, before hydrolysis.[65]

Extrapolation of the obtained quantitative data[33,64] can allow to estimate the possible concentration of these compounds in a Titan little pond, dissolved or in suspension (whatever the liquid is). With a flux of aerosols to Titan's surface $\sim 2 \times 10^{-14}$ g cm^{-2} s^{-1}, if 0.1% of the particle is transformed into amino acids, within 1000 years this gives ~1 μg amino acids per cm^2. In a 10 m deep little pond, this corresponds to 1 μg L^{-1} equivalent to ~10 nmole L^{-1}. Such a concentration is reachable by analytical techniques, including by *in situ* space instrumentation.

Because of the presence of such an active chemistry in Titan's environment and of liquid bodies, the possibility of biological activity on its surface has been considered by a few exo/astrobiologists.[66,67] In particular, it has been suggested[67] that an exotic life in the hydrocarbon lakes could derive its energy from the reduction of acetylene to methane:

$$C_2H_2 + 3H_2 \rightarrow 2CH_4$$

This hypothesis has been looked at very closely, since Cassini observations have revealed an H_2 deficiency near Titan's surface, which, together with the non-detection of acetylene on its surface, is in agreement with the hypothesis. However, the very low temperature of Titan's surface remains a strong energy barrier for biological processes.

A subsurface organic chemistry?

Although we have no direct information on the subsurface composition of Titan, models predict the presence of a water (mixed with a few % ammonia) ocean below a thick water ice layer, covering a layer of high pressure water ice. Huygens DISR data support this model and suggest the presence of a salty water ocean ~55–80 km below the surface.[68] Recent observation by the RSS experiment on Cassini indicates that Titan icy mantle is not totally differentiated, and is a mix of water ice and silicates.[69]

From models of the formation and evolution of Titan[18–20,34] in the very early Titan's history the ocean would have been in direct contact with the atmosphere and above a rocky surface. Those conditions are close to the terrestrial ones, compatible with the presence of submarine volcanic activities, and the presence of deep sea vents. The latter is a location favourable for prebiotic syntheses. Moreover, it is likely that such a Titan's primordial ocean could have included organic matter, coming in particular from chondritic materials which were involved in the formation of the satellite. Consequently, such an early ocean may have experienced an active prebiotic chemistry and one cannot exclude that life may have emerged on Titan within those conditions. One cannot exclude that life could have survived until now, since the subsurface oceans may be still suitable for life. It has indeed been described that the current conditions are not incompatible with the presence of extant life.[18] Fortes[18] has shown that there are no insurmountable obstacles. The temperature of the ocean could reach ~300 K in the vicinity of hypothetical cryovolcanic hotspots, compatible with the development of living systems. The high pressures in this ocean (several kbars) do not seem to be a real obstacle for life since we know piezophile micro-organisms on Earth can live under such conditions. Similar remarks apply for pH: a water ocean containing 15% w/w ammonia would have a pH of 11.5, less alkaline than the pH of some milieu where alkalophiles are living on Earth. Even the possible available energy resources in Titan's ocean—although limited—do not allow to exclude the presence of life. Indeed it has been estimated from the possible radiogenic heat flow[18] that the energy flux available in Titan's ocean could be about 5×10^8 W, corresponding to the production of $\sim 4 \times 10^{11}$ mole y^{-1} of ATP. Such a value would correspond to the production of $\sim 2 \times 10^{13}$ g y^{-1} of biomass and to a biomass density of ~1 g m^{-2}, assuming a turn over of 1 year. Although much lower than the terrestrial biomass (10^3 to 10^4 g m^{-2}) this indicates the possible presence of a noticeable bioactivity on Titan. Several chemical red-ox reactions which can be used as potential metabolism processes such as nitrate–nitrite reduction or nitrate–dinitrogen reduction, sulfate reduction, methanogenesis have been postulated[70] and, as already mentioned but for the more exotic surface life, catalytic hydrogenation of acetylene.[66,67]

Conclusions

Since the arrival of the Cassini–Huygens mission in the Saturn system, our knowledge of its larger satellite, and particularly of its chemistry has been drastically increased.[34] Titan looks like an organic chemical reactor allowing to study prebiotic-like chemistry at the planetary scale. This chemistry plays a major role in a complex methane cycle and is present in the atmosphere, both in the gas and condensed phases, but also on the surface and even in the subsurface. Titan's organic chemistry may be more complex than what has been observed so far, with the potential involvement of oxygen, and even other biogenic elements like phosphorus, recently discussed,[71] or sulfur. The Cassini mission has been extended twice: the current mission—called the Solstice mission—is planned to end in 2017. It allows to observe Titan during its summer and to study the seasonal variations, in particular in the chemical processes, especially in the atmosphere. Future missions are already considered in particular to explore in more detail the surface of the satellite, and to analyse the chemical composition of one of the lakes as proposed through the TANDEM mission[72] (Titan AND Enceladus Mission) or the TiME[73] (Titan Mare Explorer) mission. This would be the first *in situ* study of an extraterrestrial surface liquid body, where a complex and exotic organic chemistry is going on, at low temperature.

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