

The new Titan: an astrobiological perspective

F. Raulin, Y. Bénilan, P. Coll, D. Coscia, M.-C. Gazeau, E. Hébrard, A. Jolly, M.-J. Nguyen,
C. Romanzin and R. Sternberg
LISA, CNRS & Universités Paris 7 & Paris12, 61 Avenue Général de Gaulle, F-94000 Créteil,
France

ABSTRACT

Since the first Voyager data, Titan, the largest satellite of Saturn and only satellite in the solar system having a dense atmosphere, became one of the key planetary bodies for astrobiological studies, due to: i) its many analogies with planet Earth, in spite of much lower temperatures, ii) the already well observed presence of an active organic chemistry, involving several of the key compounds of prebiotic chemistry, in the gas phase but also assumed to occur in the solid phase through the haze particles. And the potential development of a prebiotic chemistry in liquid water, with a possible water ocean in its internal structure, and the possible episodic formation of small liquid water bodies for short but not negligible time duration at the surface (from the melting of surface water ice by impact), iii) the resulting possibility that life may have emerged on or in Titan and may have been able to adapt and to persist. These aspects are examined with some of the associated questions on the basis of the already available Cassini-Huygens data.

Keywords: astrobiology, Cassini-Huygens, prebiotic chemistry, primitive Earth, Tholins, Titan

1. INTRODUCTION

Beyond the Earth, which is still the only planetary body where we are sure that life is present, there are many other bodies of astrobiological interest in the solar system. There are those where extraterrestrial life (extinct or extant) may be present, and which thus would offer the possibility of discovering a second genesis, and studying the nature and properties of these extraterrestrial living systems, and the environmental conditions which allowed their origin, development and persistence. Mars and Europa seem to be the best places for such a quest. On the other hand, there are planetary bodies where a complex organic chemistry is going on. The study of such chemistry can help us to better understand the general chemical evolution in the universe and more precisely the prebiotic chemical evolution on the primitive Earth. Comets are probably the best example, specially considering that their organic content may have been also involved in the prebiotic chemistry on the primitive Earth.

Titan, the largest satellite of Saturn may cover these two complementary aspects and is thus a key target for astrobiological researches. Moreover, with an environment very rich in organics, it is one of the best planetary environments to study prebiotic-like chemistry at a full planetary scale. Moreover, Titan presents many analogies with Earth and studying Titan today may give us information on the conditions and processes which occurred on Earth four billion years ago. In addition, models of the internal structure of Titan strongly suggest the presence of a large permanent subsurface water ocean, and the potential for extant life.

Since the Voyager flyby's of Titan in the early 1980's, our knowledge of this exotic place, the only satellite of the solar system having a dense atmosphere, has indeed been improved. The vertical atmospheric structure has been determined, and the primary chemical composition, trace compounds, and especially organics constituents described. Additional organics have also been identified later on by ground based observation and by the European Infrared Space Observatory satellite. Other ground based and Hubble observations have also allowed a first mapping of the surface, showing a heterogeneous milieu. However, at the beginning of the millennium, many questions still remained concerning Titan and its astrobiological aspects. What is the origin of its dense atmosphere? What is the source of methane? How complex is the organic chemistry? What is the chemical composition of the aerosols which are clearly present in the atmosphere (and even mask the surface in the visible wavelengths)? What is the chemical composition of Titan's surface? What is the nature of the various potential couplings between the gas phase the aerosol phase and the surface and their role in the

chemical evolution of the satellite and its organic chemistry? How close are the analogies between Titan and the primitive Earth? Is there life on Titan?

Table 1. Cassini-Huygens Science Instruments and IDS's and the potential astrobiological return of their investigation

Cassini Instruments and InterDisciplinary Programs	P.I., Team Leader or IDS		Astrobiological Return
<u>Optical Remote Sensing Instruments</u>			
Composite Infrared Spectrometer (CIRS)	V. Kunde/M. Flasar	USA	+++
Imaging Science Subsystem	C. Porco	USA	+++
Ultraviolet Imaging Spectrograph (UVIS)	L. Esposito	USA	++
Visual & I.R. Mapping Spectrometer	R. Brown	USA	++
<u>Fields Particles and Waves Instruments</u>			
Cassini Plasma Spectrometer	D. Young	USA	+
Cosmic Dust Analysis	E. Grün	Germa.	+
Ion & Neutral Mass Spectrometer	H. Waite	USA	+++
Magnetometer	D. Southwood /M. Dougherty	U.K.	
Magnetospheric Imaging Instrument	S. Krimigis	USA	
Radio & Plasma Wave Spectrometer	D. Gurnett	USA	
<u>Microwave Remote Sensing</u>			
Cassini Radar	C. Elachi	USA	+++
Radio Science Subsystem	A. Kliore	USA	++
<u>Interdisciplinary Scientists</u>			
Magnetosphere and Plasma Rings and Dust	M. Blanc	France	+
Magnetosphere and Plasma Atmospheres	J.N. Cuzzi	USA	+
Satellites and Asteroids	T.I. Gombosi	USA	+
Aeronomy & Solar Wind Interaction	T. Owen	USA	+++
	L.A. Soderblom	USA	++
	D.F. Strobel	USA	++
Huygens Instruments and InterDisciplinary Programs	P.I. or IDS		Astrobiological Return
<u>Interdisciplinary Scientists</u>			
Gas Chromatograph-Mass Spectrometer	H. Niemann	USA	+++
Aerosol Collector & Pyrolyser	G. Israël	France	+++
Huygens Atmospheric Structure Instrument	M. Fulchignoni	Italy	++
Descent Imager/Spectral Radiometer	M. Tomasko	USA	+++
Doppler Wind Experiment	M. Bird	Germany	+
Surface Science Package	J. Zarnecki	U.K.	+++
<u>Interdisciplinary Scientists</u>			
Aeronomy	D. Gautier	France	++
Atmosphere/Surface Interactions	J.I. Lunine	USA	++
Chemistry and Exobiology	F. Raulin	France	+++

The NASA-ESA Cassini-Huygens mission was designed to explore the Saturn system in great detail, with a particular focus on Titan, and to bring answers to these questions. Indeed, since the successful Saturn orbital insertion of Cassini on July 1st, 2004, and the release of the Huygens probe in Titan's atmosphere on January 14th, 2005 (Lebreton et al, 2005) many new data have already been obtained which are essential for our vision and understanding of Titan's

astrobiological characteristics. This paper reviews three aspects of Titan with astrobiological importance of Titan, on the basis of these new data provided by Cassini-Huygens (Table 1), and complemented by theoretical modelling and laboratory experimental studies.

2. ANALOGIES BETWEEN TITAN AND THE EARTH

With a diameter of more than 5100 km, Titan is the largest moon of Saturn and the second largest moon of the solar system. It is also the only one to have a dense atmosphere. This atmosphere, clearly evidenced by the presence of haze layers, extends to approximately 1500 km (Fulchignoni et al, 2005). Like the Earth, Titan's atmosphere is mainly composed of dinitrogen, N₂. The other main constituents are methane, (CH₄, about 1.6% to 2.0% in the stratosphere, as measured by CIRS on Cassini (Flasar et al, 2005) and GC-MS on Huygens (Niemann et al, 2005) and dihydrogen (H₂, approximate 0.1%). With surface temperatures of approximately 94 K, and an average surface pressure of 1.5 bar, Titan's atmosphere is nearly five times denser than the Earth's. Despite of these differences between Titan and the Earth, there are several analogies that can be drawn between the two planetary bodies.

The first resemblances concern the vertical atmospheric structure (see Table 2). Although Titan is much colder, with a troposphere (~94~70 K), a tropopause (70.4 K) and a stratosphere (~70-175 K) its atmosphere presents a similar complex structure to that of the Earth, and also includes, as recently evidence by Cassini-Huygens, a mesosphere and a thermosphere. Because of a much higher density, in the case of Titan, the mesosphere extends to altitudes higher than 400 km (instead of only 100 km for the Earth), but the shape looks very much the same.

These analogies are linked to the presence in both atmospheres of greenhouse gases and antigreenhouse elements. Methane has strong absorption bands in the medium and far infrared regions corresponding to the maximum of the infrared emission spectrum of Titan and is transparent in the near UV and visible spectral regions. It thus can be a very efficient greenhouse gas in Titan's atmosphere. Dihydrogen, which is also absorbing in the far IR (through bimolecular interaction) plays a similar role. In the pressure-temperature conditions of Titan's atmosphere, methane can condense but not dihydrogen. Thus, on Titan, CH₄ and H₂ are equivalent respectively to terrestrial condensable H₂O and non-condensable CO₂. In addition the haze particles and clouds in Titan's atmosphere play an antigreenhouse effect similar to that of the terrestrial atmospheric aerosols and clouds (McKay et al, 1991).

Table 2 Main Characteristics of Titan (including the HASI-Huygens data)

Surface radius	2.575 km		
Surface gravity	1.35 m s ⁻² (0.14 Earth's value)		
Mean volumic mass	1.88 kg dm ⁻³ (0.34 Earth's value)		
Distance from Saturn	20 Saturn radius (~1.2 x 10 ⁶ km)		
Orbit period around Saturn	~16 days		
Orbit period around Sun	~30 years		
Atmospheric data	Altitude (km)	Temperature (K)	Pressure (mbar)
Surface	0	93.7	1470
Tropopause	42	70.4	135
Stratopause	~250	~187	~1.5 x 10 ⁻¹
Mesopause	~490	~152	~2 x 10 ⁻³

Indeed, methane on Titan seems to play the role of water on the Earth, with a complex cycle, which still has to be understood. Although the possibility that Titan is covered with hydrocarbon oceans (Lunine, 1993), is now ruled out (West et al, 2005), it is still possible that Titan's surface includes lakes of methane and ethane, although they have not yet been detected by Cassini. Nevertheless, the ISS camera on Cassini has detected dark surface features near the south

pole which could be such liquid bodies. Moreover, the DISR instrument on Huygens has provided pictures of Titan's surface which clearly show dendritic structures (Figure 1) which look like fluvial net, in a relatively young terrain, fresh of crater impacts, strongly suggesting recent liquid flow on the surface of Titan (Tomasko et al, 2005). In addition, the Huygens GC-MS data show that methane mole fraction increases in the low troposphere (up to 5%) and reaches the saturation level at approximately 8 km altitude, allowing the possible formation of clouds and rain (Niemann et al, 2005). Furthermore, GC-MS analyses recorded a ~50% increase in the methane mole fraction at Titan's surface, suggesting the presence of condensed methane on the surface near the landed probe.

Other observations from the Cassini instruments clearly show a very diversified surface (Figure 2) with the presence of various surface features of different origins indicative of volcanic, tectonic, sedimentological and meteorological processes as we find on Earth. INMS on Cassini and GC-MS on Huygens have detected the presence of argon in the atmosphere. Similarly to the Earth atmosphere, the most abundant isotope is ^{40}Ar , which comes from the radioactive decay of ^{40}K . Its stratospheric mole fraction is about 4×10^{-5} , as measured by GC-MS (Niemann et al 2005). This strongly suggests that Titan's atmosphere is a secondary atmosphere, produced by the degassing of trapped gases. Since N_2 cannot be efficiently trapped in the icy planetesimals which accreted and formed Titan, contrary to NH_3 , this also indicates that its primordial atmosphere was initially made of NH_3 . Ammonia was then transformed into N_2 by photolysis and/or impact driven chemical processes (Owen, 2000; Gautier and Owen, 2002). The $^{14}\text{N}/^{15}\text{N}$ ratio measured in the atmosphere by INMS and GC-MS (183 in the stratosphere) is 1.5 times less than the primordial N and indicates that the present mass of the atmosphere was probably lost several times during the history of the satellite (Niemann et al, 2005). Since such evolution may also imply methane transformation into organics, this may be also the indication of large deposits of organics on Titan's surface.

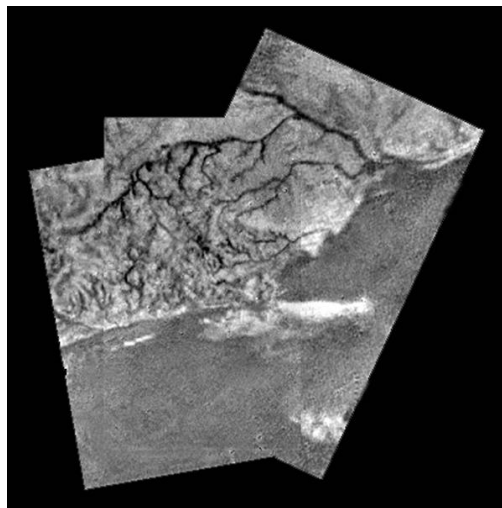


Figure 1. Channel networks, highlands and dark-bright interface seen by the DISR instrument on Huygens at 6.5 km altitude. Credit: ESA/NASA/JPL/University of Arizona

Analogies can also be made between the organic chemistry which is very active now on Titan and the prebiotic chemistry which was active on the primitive Earth. In spite of the absence of permanent bodies of liquid water on Titan's surface, both chemistries are similar. Several of the organic processes which are occurring today on Titan imply some of the organic compounds which are considered as key molecules in the terrestrial prebiotic chemistry, such as hydrogen cyanide (HCN), cyanoacetylene (HC_3N) and cyanogen (C_2N_2).

In fact, with several % of methane in dinitrogen, the atmosphere of Titan is one of the most favourable atmospheres for prebiotic synthesis, as shown by Miller's experiments. Until recently, such atmosphere composition was supposed to be far from that of the primitive Earth. However, new modelling of the hydrogen escape in the primitive atmosphere of the Earth suggests that it may have been much richer in hydrogen and methane than previously thought (Feng et al, 2005). This suggests that Titan maybe even more similar to the primitive Earth than we thought.

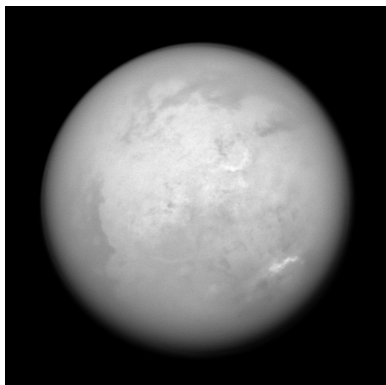


Figure 2. Titan, seen by Cassini narrow-angle camera shows a very diversified surface, with bright (like the so-called “Xanadu” region in the middle of the picture) and darker areas. Image Credit: NASA/JPL/Space Science Institute

3. A COMPLEX PREBIOTIC-LIKE CHEMISTRY

In the atmosphere of Titan, CH_4 chemistry is coupled with N_2 chemistry producing the formation of many organics – hydrocarbons and N-containing organic compounds - in gas and particulate phase. Those are hydrocarbons, nitriles and complex refractory organics. Several photochemical models describing the chemical and physical pathways involved in the chemical evolution of the atmosphere of Titan and estimating the resulting vertical concentration profiles of the different involved molecules have been published for the last 20 years. For a review, see the most recent publications and the included references (Lebonnois et al, 2001; Wilson & Atreya, 2004; Hébrard et al, 2005). The whole chemistry starts with the dissociation of N_2 and CH_4 through electron and photon impacts. The primary processes allow the formation of C_2H_2 and HCN in the high atmosphere. These molecules play a key role in the general chemical scheme: once they are formed, they diffuse down to the lower levels where they allow the formation of higher hydrocarbons and nitriles. Additional CH_4 dissociation probably also occurs in the low stratosphere through photocatalytic processes involving C_2H_2 and polyynes.

Another approach, very complementary of photochemical modelling, to study Titan’s organic chemistry is to develop simulation experiments in the laboratory. These experiments seem to well mimic the real processes since recent experiments, carried out in particular at LISA, produce all the gas phase organic species already detected in Titan’s atmosphere, within the right orders of magnitude of relative concentration for most of them. Such observation demonstrates the validity of these recent experimental simulations. The experiments also produce many other organics which can be assumed to be also present in Titan’s atmosphere. Thus, simulation experiments appear as a very useful guide for further searches (both by remote sensing & in situ observations). The gas phase but also the aerosol phases are concerned by such an extrapolation.

In the gas phase, more than 150 different organic molecules have been detected in the simulation experiments (Coll et al, 1998, 1999a). These global simulations of Titan’s atmospheric chemistry use an open reactor flown by a low pressure N_2 - CH_4 gas mixture. The energy source is a cold plasma discharge producing mid-energy electrons (around 1-10 eV). The gas phase end products (molecules) are analyzed by IRFTS (InfraRed Fourier Transform Spectroscopy) and GC-MS (Gas Chromatography and Mass Spectrometry) techniques; the transient species (radicals and ions) are determined by on line UV-visible spectroscopy. The evolution of the system is also theoretically described using coupled physical and chemical (ions and neutrals) models. The identified organic products are mainly hydrocarbons and nitriles. The absence at a detectable level of molecules carrying amino groups, like amines, with the exception of ammonia, must be highlighted. These experiments allowed the detection of all gaseous organic species observed on Titan, including C_4N_2 , (Coll et al. 1999b). Among the other organics formed in these experiments and not yet detected in Titan’s atmosphere, one should note the presence of polyynes (C_4H_2 , C_6H_2 , C_8H_2) and probably cyanopolyne $\text{HC}_4\text{-CN}$. These compounds are also included in photochemical models of Titan’s atmosphere, where they could play a key role in the chemical schemes allowing the transition from the gas phase products to the aerosols. Recent experiments on N_2 - CH_4 mixtures including CO at the 100 ppm level (Bernard et al, 2003; Coll et al, 2003) show the incorporation of O atoms in the produced organics, with an increasing diversity of the products (more than 200 were identified). The main O-containing

organic compound is oxirane (also named ethylene oxide), (CH₂)₂O which appears as a good candidate to search for in Titan's atmosphere. These studies also show the formation of ammonia at noticeable concentration, opening new avenues in the chemical schemes of Titan's atmosphere.

Table 3. Main composition of Titan's stratosphere, trace components already detected and comparison with the products of laboratory simulation experiments (Maj= major product ; ++: abundance smaller by one order of magnitude ; +: abundance smaller by two orders of magnitude).

Compounds	Stratosphere Mixing Ratio (E=Equ.; N=North Pole)		Production in Simulation Experiments
<u>Main constituents</u>			
Nitrogen N ₂	0.98		
Methane CH ₄	0.02		
Hydrogen H ₂	~0.001		
<u>Hydrocarbons</u>			
Ethane C ₂ H ₆	1.3 x 10 ⁻⁵	E	Maj.
Acetylene C ₂ H ₂	2.2 x 10 ⁻⁶	E	Maj.
Propane C ₃ H ₈	7.0 x 10 ⁻⁷	E	++
Ethylene C ₂ H ₄	9.0 x 10 ⁻⁸	E	++
Propyne C ₃ H ₄	1.7 x 10 ⁻⁸	N	+
Diacetylene C ₄ H ₂	2.2 x 10 ⁻⁸	N	+
Benzene C ₆ H ₆	few 10 ⁻⁹		+
<u>N-Organics</u>			
Hydrogen cyanide, HCN	6.0 x 10 ⁻⁷	N	Maj.
Cyanoacetylene HC ₃ N	7.0 x 10 ⁻⁸	N	++
Cyanogen C ₂ N ₂	4.5 x 10 ⁻⁹	N	+
Acetonitrile CH ₃ CN	few 10 ⁻⁹		++
Dicyanoacetylene C ₄ N ₂	Solid Phase	N	+
<u>O-Compounds /Noble gases</u>			
Carbon monoxide CO	2.0 x 10 ⁻⁵		
Carbon dioxide CO ₂	1.4 x 10 ⁻⁸	E	
Water H ₂ O	few 10 ⁻⁹		
Argon ⁴⁰ Ar	~ 4x10 ⁻⁵		
³⁶ Ar	~ 2x10 ⁻⁷		

Simulation experiments also produce solid organics, as mentioned above, usually named tholins (Sagan and Khare, 1979). These "Titan tholins" are supposed to be laboratory analogues of Titan's aerosols. They have been extensively studied since the first work by Sagan & Khare more than 20 years ago (Khare & Sagan, 1984; 1986 & refs. included). These laboratory analogues show very different properties depending on the experimental conditions (Cruikshank et al, 2005). For instance, the average C/N ratio of the product varies between less than 1 to more than 11, in the published reports. More recently, dedicated experimental protocols allowing a simulation closer to the real conditions have been developed at LISA using low pressure and low temperature (Coll et al, 1998; 1999a) and recovering the laboratory tholins without oxygen contamination (from the air of the laboratory) in a glove box purged with pure N₂. Representative laboratory analogues of Titan's aerosols have thus been obtained and their complex refractive indices have been determined (Ramirez et al, 2002), with – for the first time - error bars. These data can be seen as a new point of reference to modelers who compute the properties of Titan's aerosols. Systematic studies have been carried out on the influence of the pressure of the starting gas mixture on the elemental composition of the tholins. They show that two different chemical-physical regimes are involved in the processes, depending on the pressure, with a transition pressure around 1 mbar (Bernard et al, 2002; Imanaka et al, 2004).

The molecular composition of the Titan tholins is still poorly known. Several possibilities have been considered such as HCN polymers or oligomers, HCN-C₂H₂ co-oligomers, HC₃N polymers, HC₃N-HCN co-oligomers (Tran et al, 2003 & refs. included). However it is well established that they are made of macromolecules of largely irregular structure. Gel filtration chromatography of the water soluble fraction of Titan tholins shows an average molecular mass of about 500 to 1000 Dalton ((McDonald et al., 1994). Information on the chemical groups included in their structure has been obtained from their IR and UV spectra and from analysis by pyrolysis-GC-MS techniques (Ehrenfreund et al., 1995; Coll et al, 1998; Imanaka et al., 2004; and refs; included). The data show the presence of aliphatic & benzenic hydrocarbon groups, of CN, NH₂ and C=NH groups. Direct analysis by chemical derivatization techniques before and after hydrolysis allowed the identification of amino-acids or their precursors (Khare et al., 1986). Their optical properties have been determined (Khare et al, 1984; McKay, 1996; Ramirez et al, 2002; Tran et al, 2003; Imanaka et al., 2004), because of their importance for retrieving observational data related to Titan. Finally, it is obviously of astrobiological interest to mention that Stoker et al. (1990) demonstrated the nutritious properties of Titan tholins for microorganisms. Nevertheless, there is still a need for better experimental simulations, where the primary processes are well mimicked including the dissociation of dinitrogen by electron impact with energies close to the case of Titan's atmosphere, and the dissociation of methane through photolysis processes. Such an experiment is currently under development at LISA, with the SETUP (Simulation Expérimentale et Théorique Utile à la Planétologie) programme which, in a dedicated low temperature flow reactor, couples N₂ dissociation by electron and CH₄ photodissociation by 2-photon (248 nm) laser irradiation, and theoretical studies, in order to improve the chemical schemes (Romanzin et al, 2005).

Several organic compounds have already been detected in Titan's stratosphere (Table 3). The list includes hydrocarbons (both with saturated and unsaturated chains) and nitrogen-containing organic compounds, exclusively nitriles, as expected from laboratory simulation experiments. Most of these detections were performed by Voyager observations, at the exception of the C₂ hydrocarbons which were observed before, acetonitrile which was detected by ground observation in the millimetre wavelength and water and benzene which were tentatively detected by ISO. Since the Cassini arrival in the Saturn system, the presence of water and benzene has been unambiguously confirmed by the CIRS instrument. In addition, the direct analysis of the ionosphere by the INMS instrument during the low altitude Cassini fly-bys of Titan shows the presence of many organic species at detectable levels (Figure 3), in spite of the very high altitude (1100-1300 km).

Surprisingly, GC-MS on board Huygens has not detected a large variety of organic compounds in the low atmosphere. The mass spectra collected during the descent show that the medium and low stratosphere and the troposphere are poor in volatile organic species, at the exception of methane. Condensation of these species on the aerosol particles is a probable explanation for these atmospheric characteristics (Niemann et al, 2005). These particles, for which no direct data on the chemical composition were available before, have been analyzed by the ACP instrument. ACP was designed to collect the aerosols during the descent of the Huygens probe on a filter in two different regions of the atmosphere. Then the filter was heated in a closed oven at different temperatures and the produced gases were analysed by the GC-MS instrument. The results show that the aerosol particles are made of refractory organics which release HCN and NH₃ during pyrolysis (Israel et al, 2005). This strongly supports the tholin hypothesis: from these new and first *in situ* measurement data it seems very likely that the aerosol particles are made of a refractory organic nucleus, covered with condensed volatile compounds (figure 4). The nature of the pyrolysates provides information on the molecular structure of the refractory complex organics: it indicates the potential presence of nitrile groups (-CN), amino groups (-NH₂, -NH- and -N<) and/or imino groups (-C=N-).

Furthermore comparison of the data obtained for the first (mainly stratospheric particles) and second (mid troposphere) samplings indicate that the aerosol composition is homogeneous (Israel et al, 2005). This also fits with some of the data obtained by DISR relative to the aerosol particle which indicates a relatively constant size distribution of the particles with altitude (with a mean dimension of the order of one micron). These particles sediment down to the surface where they likely form a deposit of complex refractory organics and frozen volatiles. DISR collected the infrared reflectance spectra of the surface with the help of a lamp, illuminating the surface before the Huygens probe touched down.

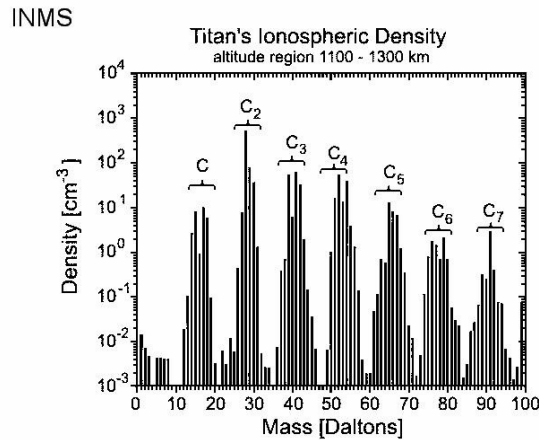


Figure 3. Mass spectrum of Titan's ionosphere near 1,200 km altitude. The spectrum shows signature of organic compounds including up to 7 carbon atoms. Image Credit: NASA/JPL/University of Michigan.

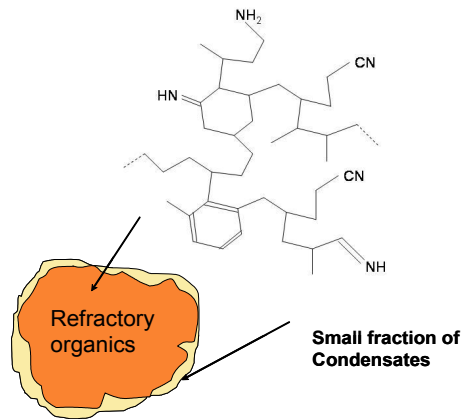


Figure 4. Model example of the chemical composition of Titan's aerosol from the Huygens-ACP data

The retrieving of these infrared data show the presence of water ice, but no clear evidence – so far – of tholins. The presence of water ice is also suggested by the data of the SSP instrument (Zarnecki et al, 2005). Its accelerometer measurements can be interpreted as the presence of small water ice pebbles on the surface where Huygens has landed, in agreement with the DISR surface pictures. On the other hand, GC-MS was able to analyse the atmosphere near the surface for more than one hour after the touch down. The corresponding mass spectra show the clear signature of many organics, including cyanogen, C3 – and C4 hydrocarbons and benzene:, indicating that the surface is much richer in volatile organics than the low stratosphere and the troposphere (Niemann et al, 2005). These observations are in agreement with the hypothesis that in the low atmosphere of Titan, most of the organic compounds are in the condensed phase.

Thus, altogether, these new data show the diversity of the locations where organic chemistry is taking place on Titan. Surprisingly the high atmosphere looks very active, with neutral and ion organic processes; the high stratosphere, where many organic compounds have already been detected before Cassini and since Cassini arrived in the Saturn system, also shows an active organic chemistry in the gas phase. In the lower atmosphere this chemistry seems mainly concentrated in the condensed phase. Titan's surface is probably covered with frozen volatile organics together with refractory, tholin-like, organic materials.

Irradiating effects of cosmic rays reaching Titan's surface may induce additional organic syntheses, particularly if part of these materials are dissolved in some small liquid bodies made of low molecular weight hydrocarbons (mainly methane and ethane). This could indeed allow the additional formation of reactive compounds such as azides as well as the polymerization of HCN (Raulin et al, 1995). Moreover, the interface between the liquid phase and the solid deposits at the surface may include sites of catalytic activity favourable to these additional chemical reactions.

In spite of the surface temperatures, even the presence of liquid water is not excluded. Cometary impacts on Titan may melt surface water ice, offering possible episodes as long as ~1000 years of liquid water (Artemieva and Lunine, 2003). This provides conditions for short terrestrial-like prebiotic syntheses at relatively low temperatures. Low temperatures reduce the rate constants of prebiotic chemical reactions, but may increase the concentration of reacting organics by eutectic effect which increases the rate of the reaction. In addition, the possible presence of a water-ammonia ocean in the depths of Titan, as expected from models of its internal structure (Tobie et al, 2005, and refs. included), may also provide an efficient way to convert simple organics into complex molecules, and to reprocess chondritic organic matter into prebiotic compounds. These processes may have very efficiently occurred at the beginning of Titan's history (with even the possibility of the water-ammonia ocean exposed to the surface) allowing a CHNO prebiotic chemistry evolving to compounds of terrestrial biological interest.

Even if these liquid water scenarii are false, the possibility of a pseudo biochemistry, evolving in the absence of a noticeable amount of O atoms cannot be ruled out, with a N-chemistry, based on "ammono" analogues replacing the O-chemistry (Raulin and Owen, 2002). Such alternatives of terrestrial biochemistry where, in particular the water solvent could be replaced by ammonia or other N-compounds, have also been recently re-examined by Benner (2002) and by Schulze-Makuch and Irwin (2004).

4. LIFE ON TITAN?

Several ways can thus be considered in Titan's environment to drive chemistry to prebiotic chemistry and even to biotic systems on Titan. But if life emerged on Titan, are Titan's conditions compatible with the sustaining of life? The surface is too cold and not energetic enough to provide the right conditions. However, the (still hypothetical) subsurface oceans may be suitable for life. Fortes (2000) has shown that there are no insurmountable obstacles. With a possible temperature of this ocean as high as about 260 K and the possible occurrence of cryovolcanic hotspots allowing 300 K, the temperature conditions in Titan's subsurface oceans could allow the development of living systems. Even at depth of 200 km, the expected pressure of about 5 kbar is not incompatible with life, as shown by terrestrial examples. The expected pH of an aqueous medium made of 15 % by weight of NH₃ is equivalent to a pH of 11.5. Some bacteria can grow on Earth at pH 12. Even the limited energy resources do not exclude the sustaining of life.

Taking into account only the potential radiogenic heat flow ($\sim 5 \times 10^{11}$ W) and assuming that 1% of that is used for volcanic activity and 10% of the later is available for living system metabolism, Fortes (2000) estimates an energy flux available in the subsurface oceans of about 5×10^8 W. Such a flux corresponds to the production of about 4×10^{11} mol of ATP per year and about 2×10^{13} g of biomass per year. If we assume an average turn over for the living systems in the order of one year, the biomass density would be 1 g/m^2 . This is very small compared to the lower limit of the value of the biomass for the Earth (about 1000 to 10000 g m^{-2}). Nevertheless, this indicates the possible presence of a limited but not negligible bioactivity on the satellite. The biota on Titan, if any, assuming that the living systems are similar to the ones we know on Earth, and based on the chemistry of carbon and the use of liquid water as solvent, would thus be localised in the subsurface deep ocean. Several possible metabolic processes such as nitrate/nitrite reduction or nitrate/dinitrogen reduction, sulphate reduction and methanogenesis have been postulated (Simakov, 2001) as well as the catalytic hydrogenation of acetylene (Abbas & Schulze-Makuch, 2002; McKay & Smith, 2005).

As expected, no sign of macroscopic life has been detected by Huygens when approaching the surface or after it landed. This can be concluded in particular from the many pictures taken by DISR of the same location on Titan during more than one hour after landing. But this does not exclude the possibility of the presence of a microscopic life. The metabolic activity of the corresponding biota, even if it is localized far from the surface, in the deep internal structure of Titan, may produced chemical species which diffuse through the ice mantle covering the hypothetical internal ocean and feed the atmosphere. It has even been speculated in several publications that the methane present in the atmosphere today is the

product of biological activity (include a citation/reference here). If this was the case, the atmospheric methane would be notably enriched in light carbon. Indeed, on Earth, biological processes induce an isotopic fractionation producing an enrichment in ^{12}C . Indeed, $^{12}\text{C}/^{13}\text{C}$ increases from 89 (the reference value, in the Belemnite of the Pee Dee Formation) to about 91-94 depending on the biosynthesis processes. The $^{12}\text{C}/^{13}\text{C}$ ratio in atmospheric methane on Titan, as determined by the GC-MS instrument on Huygens is 82 (Niemann et al, 2005). Although we do not have a reference for $^{12}\text{C}/^{13}\text{C}$ on Titan, this low value suggests that the origin of methane is likely to be abiotic.

4. CONCLUSIONS

Although exotic life, like methanogenic life in liquid methane cannot be fully ruled out (McKay and Smith, 2005), the presence of extant or extinct life on Titan seems very unlikely. Nevertheless, with the new observational data provided by the Cassini-Huygens mission, the largest satellite of Saturn looks more than ever as a very interesting object for astrobiology. The several analogies of this exotic and cold planetary body with the Earth and the complex organic chemical processes which are going on now on Titan provide a fantastic means to better understand the prebiotic processes which are not reachable anymore on the Earth, at the scale and within the whole complexity of a planetary environment.

The origin and cycle of methane on Titan illustrate the whole complexity of the Titan's system. Methane may be stored in large amount in the interior of the satellite, under the form of clathrates (methane hydrates) trapped during the formation of the satellite from the Saturnian subnebula where it was formed by Fisher-Tropsch processes (Sekine et al, 2005). It may also be produced through high pressure processes, like serpentinization allowing the formation of H_2 by reaction of H_2O with ultramafic rocks, or by cometary impact (Kress and McKay, 2004). Interestingly, those processes have rarely been considered in the case of the primitive Earth, although they may have contributed to a possible reducing character of the primordial atmosphere of our planet, a possibility which is currently being re-examined (Feng et al, 2005). This is an example of how Titan's study is indeed providing new insights into terrestrial chemical evolution.

In Titan's atmosphere, methane is photolysed by solar UV, producing mainly ethane and tholins-like organic matter. The resulting life time of methane in Titan's atmosphere is relatively short (about 10 to 30 myr). Thus methane stored in Titan's interior may be continuously replenishing the atmosphere, through degassing induced by cryovolcanism which has been clearly evidenced from the first images of Titan's surface provided by the VIMS, ISS and Radar instrument on Cassini (Sotin et al, 2005). In any case, the methane cycle should result in the accumulation of large amounts of complex organics on the surface and large amounts of ethane, which mixed with the dissolved atmospheric methane should form liquid bodies on the surface or in the near sub-surface of the satellite.

The Cassini-Huygens mission is far from complete. It will continue its systematic exploration of the Saturnian system up to 2008, and probably 2011 if the extended mission is accepted. Numerous data of paramount importance for astrobiology are still expected from several of its instruments (Table 1). The CIRS spectrometer should be able to detect new organic species in the atmosphere during the future limb observation of Titan, especially at the pole. ISS and VIMS should provide a detailed picture of Titan's surface revealing the complexity but also the physical and chemical nature of this surface and its diversity. Radar observation will also continue the systematic coverage of Titan's surface which shows contrasted regions of smooth and rough areas, suggesting a possible shoreline. The coupled observation of the same regions by these instruments will be essential to better understand the geology of Titan's surface. The already available data of this new, exotic and astonishing world already show that a future mission to Titan is needed if we want to understand the prebiotic-like chemistry which is occurring, in particular on Titan's surface. Such a mission, with surface mobility (using ballooning) and surface sampling and chemical analysis is now under study.

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