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Véronique Vuitton

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Composition of Titan’s Atmosphere

Véronique [Vuitton](#)

veronique.vuitton@univ-grenoble-alpes.fr

Institut de Planétologie et d’Astrophysique de Grenoble Université Grenoble Alpes, Grenoble, France

Introduction

Titan, Saturn’s largest moon, occupies a special place in the study of planets and satellites in our solar system. The opaque atmosphere remained enigmatic until the Cassini-Huygens mission provided new information in 2004-17. Titan is the only moon known to have a dense atmosphere (1.5 bar, or 0.15 MPa at the surface). As on Earth, the main atmospheric compound is nitrogen (N₂). However, methane (CH₄, 1.4%), the second main compound, and the low amount of oxygen (mainly carried by carbon monoxide, CO, 50 ppmv) make the atmosphere chemically reducing. The induced chemistry is totally different from that currently developing on Earth—based on oxidative processes linked to the presence of molecular oxygen (O₂)—and ultimately leads to the formation of an extensive photochemical haze. Cold temperatures (70-94 K) prevail in the lower atmosphere and methane is at the origin of a cycle (evaporation, condensation, precipitation) similar to that of water on Earth. Strong interactions exist between the composition of the atmosphere, the atmospheric circulation, the temperature structure and the haze and clouds distributions. This chapter discusses the current understanding of the Titan system with a specific emphasis on the atmospheric composition and its seasonal variations.

Discovery and Exploration

Pre-Cassini Background

In 1655, Christiaan Huygens, a student of Jean-Dominique Cassini, discovered Saturn’s first satellite, which he named Luna Saturni, Saturn’s Moon. In 1850, John Herschel, son of William Herschel, proposed to assign to the many moons of Saturn discovered since Huygens the names of the brothers and sisters of Cronos (or Saturn in Roman mythology), the so-called Titans. Luna Saturni, the largest satellite in the Saturnian system, became Titan.

The question of the existence of an atmosphere around this satellite was first addressed through theory. The English astrophysicist Sir James Jeans applied his dynamic theory of gases (1904) to Titan in 1925. For an atmosphere to persist around a celestial body, it is necessary to have a massive body (with significant gravity to retain molecules in the atmosphere), [and](#) a cold atmosphere and heavy atmospheric molecules (i.e., with a lower thermal velocity, that would not reach the escape velocity). By his calculations, he argued that Titan could have an atmosphere, composed of molecules such as argon, neon, nitrogen and methane (hydrogen and helium would escape from the atmosphere).

On August 13, 1907, a Spanish astronomer named José Comas y Solá reported a spatial variability in luminosity on Titan: the edges were darker than the center, which highlighted the presence of an atmosphere. However, the discovery of Titan’s atmosphere is not attributed to José Comas y Solá and for good reason. Although the Spanish astronomer was known for his incredible visual acuity, he had been working at the sensitivity limit of his 38 cm diameter instrument and no other contemporary astronomer since has been able to see this phenomenon.

The final answer to the question of the presence of an atmosphere on Titan arrived in 1944. Gerard Kuiper placed a spectrograph behind his 2.08 m telescope, and acquired several photographic plates at different wavelengths. In his article, we can observe a slight white band around 726 nm on the Titan photographic plate, corresponding to a methane absorption band. This spectroscopic observation was the unambiguous evidence of the presence of an atmosphere on Titan.

At the beginning of space exploration, the first object to approach Titan was the Pioneer 11 (NASA) spacecraft in 1979, followed by the Voyager probes (NASA) in the early 1980s. Voyager 1 passed the closest to Titan (~ 4000 km) and established that the major constituent of the atmosphere is nitrogen, and more than a dozen minor hydrocarbons, nitriles, and oxygen-bearing species were identified. Finally, the suspected presence of haze layers around 300-400 km was confirmed ([Yung and DeMore, 1999](#)). It would nevertheless be necessary to wait until the end of the 20th century to have a space mission dedicated to the study of the Saturnian system: the Cassini-Huygens mission.

The Cassini-Huygens Mission

Following the keen interest for Titan promoted by Voyager 1 and 2's results, the American (NASA), European (ESA) and Italian (ASI) space agencies combined their financial resources and expertise to manufacture two space probes: an orbiter called Cassini (the discoverer of Saturn's ring divisions) and a descent module called Huygens (the discoverer of Titan). The purpose of the Cassini orbiter, with its 12 payload instruments, was to analyze over a long period of time the Saturnian system, and in particular Titan, while the Huygens module (six instruments) was intended to land on Titan to characterize its atmosphere during the descent, and its surface following landing.

The Cassini-Huygens mission was launched on October 15, 1997 and entered its orbit around Saturn on July 1, 2004, after a 7-year journey. On December 25, 2004, the Huygens module undertook a 2 h and 28 min descent before reaching the surface, allowing the in situ study of the atmosphere. The lander sent data from Titan's surface for an hour and 12 min before the Cassini orbiter set over the horizon. The Huygens module was (and is still the only one to date) the first human-made object to land on a body of the outer solar system. The Cassini orbiter continued to analyze the Saturnian system until September 15, 2017 before diving into the atmosphere of Saturn, after two mission extensions: the "Equinox mission" in 2008-10 and the "Solstice mission" in 2010-17 (Spilker, 2019). Ultimately, the Cassini orbiter completed 127 close Titan flybys and analyzed the moon for over half a Titan year, between mid-north winter and early north summer (Fig. 1).

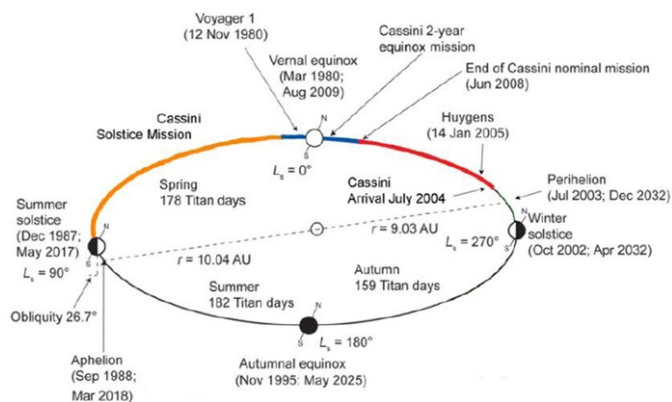


Fig. 1 Seasons on Titan.

Reproduced from Leary JC et al. (2008) Titan Explorer: Flagship Mission Study.

alt-text: Fig. 1

General Description

Orbit

Saturn's orbit is located on average at 9.54 AU (about 1.4 billion kilometers) from the Sun corresponding to a revolution around the Sun in 29.5 years. Titan orbits Saturn at an average distance of 1.22 million kilometers, or about 20 Saturn radii. It makes a revolution around Saturn in 15.9 days, always presenting the same face to Saturn (synchronous rotation), as the Moon with the Earth. Thus, a day on Titan lasts 15.9 Earth days. Saturn's obliquity of 26.7 degrees extends to the entire system of Saturn, including Titan. This obliquity leads to variations in sunlight on Titan for a revolution around the Sun, which induces seasons of a duration of about 7.4 years. Saturn and Titan orbital data are given in Table 1.

Table 1 Orbital parameters of Saturn and Titan.

alt-text: Table 1

Saturn's orbit	
Orbital period	29.5 years
Semi-major axis	1.43×10^9 km (9.58 AU)
Eccentricity	0.0565

Axial tilt	26.7 degrees
Titan's orbit	
Orbital period	15.9 days
Semi-major axis	1.22 × 10 ⁶ km (20.3 R _S)
Eccentricity	0.0288
Axial tilt	~ Zero

Interior

Titan is believed to have formed in Saturn's circumplanetary nebula. The accreted material formed the interior of Titan, whose composition is supposed to be a mixture of rock, ice and volatile compounds. The surface of Titan is covered with a layer of ice of a thickness of less than 30–40 km on average but that could be inhomogeneous in thickness in places (Béghin et al., 2012). This layer was deduced from gravity field data by radar sounding and from conductivity measurements of the Huygens Atmospheric Structure Instrument (HASI). Under the ice crust, an underground ocean of liquid water could be enriched with mineral salts or ammonia. There are two hypotheses for the layering structure below this underground ocean: either (i) a layer of pure ice, followed by a layer of a mixture of ice and rock overlying a core of pure (mainly anhydrous) rock; or (ii) a hydrated layer followed by a medium density rock core, composed mainly of hydrated silicate minerals. Both of these scenarios are consistent with the deduced normalized moment of inertia, which is between 0.33 and 0.34, which . This indicates that Titan is not fully differentiated and does not have a large iron core (Fortes, 2012). Titan's physical data are given in Table 2.

Table 2 Titan's physical characteristics.

alt-text: Table 2	
Mean radius	2574.73 ± 0.09 km (0.404 Earths)
Mass	(1.3452 ± 0.0002) × 10 ²³ kg (0.0225 Earths)
Mean density	1.8798 ± 0.0044 g.cm ^{−3}
Surface gravity	1.352 m s ^{−2} (0.138 g)

Surface

Visually, Titan is a sphere covered in an orange mist. However, the Huygens probe, during its descent in 2005, revealed a landscape that strongly resembles what we can see on Earth: drainage systems, lakes, dunes and mountains. At the time of its landing, the Descent Imager and Spectral Radiometer (DISR) instrument took an image of the surface of Titan showing the ground covered with dark organic compounds and small water ice rocks. There is morphological evidence of erosion at the base of the rocks, indicating possible fluvial activity. In the polar regions, Cassini radar measurements indicated the presence of lakes, particularly in the northern hemisphere. They are mainly composed of methane and ethane, brought in by fluvial networks and have depths of up to 200 m (Hayes, 2016). In the equatorial region, the Cassini radar (RADAR), Visual and Infrared Mapping Spectrometer (VIMS) and Imaging Science Subsystem (ISS) measurements showed 100 m high dune fields spaced ~ 3 km apart with a west-east orientation. Mountains can reach a height of 2 km with gentle slopes observed in the Xanadu region at the equator or in the Tsegihi region in the southern hemisphere (Lopes et al., 2020). Titan's surface also shows the presence of craters up to 80 km in diameter with a depth of 1.3 km like the Sinlap crater towards the equator. However, the presence of cryovolcanoes remains debated (Sotin et al., 2005).

Atmosphere

Origin

Despite its modest size, Titan is the only satellite in the solar system sustaining a massive atmosphere, and its origin has been an enduring mystery in planetary science. Titan's atmospheric data are given in Table 3. Based on nitrogen isotopes and the abundances of noble gases in Titan's atmosphere (see further below), the present paradigm argues that nitrogen was delivered in the form of NH₃ similar to cometary ices, and that photochemical and/or impact processes converted NH₃ to form present-day N₂. In light of new data from the Rosetta mission regarding the high abundance of refractory organic material on comet 67P/C-G and its similarity to other primitive extraterrestrial

organics, refractory organics as well as NH_3 may actually have been the dominant sources for Titan's atmospheric nitrogen. This mixture may be the result of accretion of material from a warm circumplanetary nebula followed by heating of organics in Titan's interior (Miller et al., 2019).

Table 3 Titan's atmospheric characteristics.

alt-text: Table 3

Surface temperature	93.7 K (− 179.5 °C)
Surface pressure	146.7 kPa (1.45 atm)
Stratospheric composition (by volume)	
Nitrogen (N_2)	98.4%
Methane (CH_4)	1.4%
Hydrogen (H_2)	0.2%

Main vertical structure

Like Earth, Titan has a well-defined troposphere, stratosphere, mesosphere and thermosphere (Hörst, 2017). Fig. 2 depicts a representative temperature profile. Titan receives about 1% of the solar flux that reaches Earth, and of that flux only 10% reaches the surface. The combination of the greenhouse effect provided by CH_4 and collision-induced absorption ($\text{N}_2\text{-N}_2$, $\text{N}_2\text{-CH}_4$, $\text{N}_2\text{-H}_2$, $\text{CH}_4\text{-CH}_4$) and the anti-greenhouse from the stratospheric haze layer results in a surface temperature of ~ 94 K. Interaction between surface and atmosphere occurs in the boundary layer (deepest 2 km) through convection. The upper atmosphere, located above 800 km altitude, is the transition region between the middle atmosphere and the magnetized environment of Saturn in which Titan is embedded. It includes the thermosphere, where significant extreme ultraviolet (EUV, 124–10 nm) heating rates are balanced by efficient cooling by HCN rotational lines, and a partially ionized region, the ionosphere. Titan's thermosphere shows an unexpectedly variable N_2 density that varies by more than an order of magnitude on timescales of a few Titan days (or less), accompanied by large wave-like perturbations in temperature profiles. The temperature variability does not seem to be controlled by solar input but rather appears to be related to the magnetospheric configuration.

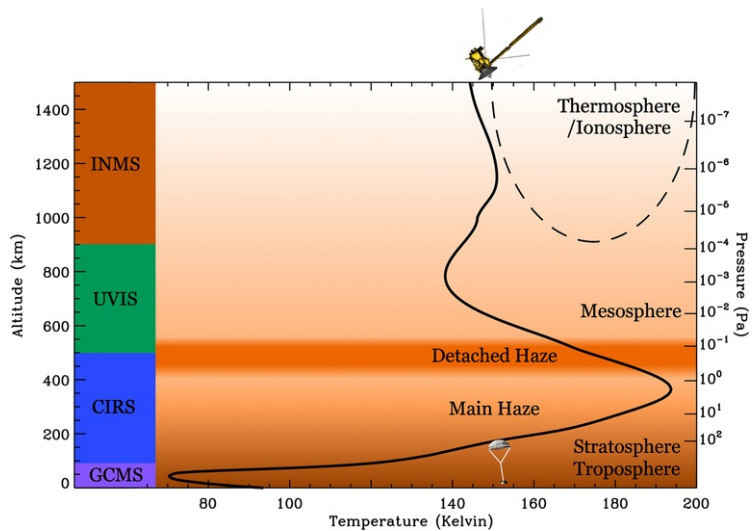


Fig. 2 Titan's atmospheric structure. The left side of the diagram shows the altitudes probed by different instruments onboard Cassini.

Copyright Sarah M. Hörst 2013.

alt-text: Fig. 2

Methane cycle

The temperature and pressure conditions at the surface of Titan, very close to the triple point of methane, allow for the presence of a hydrological methane cycle, very similar to the Earth's water cycle (Roe, 2012). Gaseous methane can condense to form clouds (liquid or ice) in the troposphere. However, the weak solar flux reaching Titan's surface, and the generally dry conditions in the lower troposphere, lead to relatively rare tropospheric cloud formation. Despite the scarcity of the observed clouds, Cassini revealed their diversity including small patchy convective clouds, and tropical storms associated with precipitation and stratospheric polar clouds. Large tropospheric clouds are thought to be composed of large methane droplets in ascending motions. These clouds precipitate methane as a rainfall, forming the channels and rivers observed at the surface, which are then discharged into the lakes located mainly in the polar regions.

However, the methane cycle on Titan is not a closed loop as a small amount of the liquid methane that evaporates back to the atmosphere leaks through the cold trap at the tropopause to the upper atmosphere, where it is irreversibly depleted by solar UV photolysis, producing gaseous byproducts and the complex organic material that makes up Titan's haze. These components irreversibly precipitate onto the surface such that the methane atmospheric content would be exhausted in ~ 30 million years (Yung et al., 1984). As a consequence, the abundance of methane in Titan's atmosphere and on the surface depends on whatever processes supply it from the interior. Potentially there have been dry, methane-free epochs, as well as wet and rainy methane-rich periods.

Complex Chemical Processes

Energy Sources

Chemical processes in the atmosphere of Titan begin with the ionization and dissociation of N₂ and CH₄, which provide the H, C, and N atoms necessary for the synthesis of complex organic molecules. Energy sources include solar extreme ultraviolet (EUV) and ultraviolet (UV) radiation, energetic photoelectrons (produced by solar X-ray and EUV radiation) and Saturnian magnetospheric electrons and ions. Energetic protons and oxygen ions can also ionize the neutral species between 1000 and 500 km altitude but their contribution is small under typical conditions. Meteors ablate in the altitude range 800–600 km and create long-lived metallic ions but this represents a weak source of ionization overall. Galactic cosmic rays (GCR) generate some ionization in the lower atmosphere, with a peak contribution around 100 km and a magnitude comparable to ionization by solar photons in the upper atmosphere.

Ionosphere

Cassini Ion Neutral Mass Spectrometer and Plasma Spectrometer (INMS and CAPS) performed the first and only in situ ion density measurements of Titan's upper atmosphere, which could not be obtained with any other technique. These instruments detected an extraordinarily complex ionospheric composition. In the positive ion mode, INMS recorded more than 50 mass channels with a density higher than 0.1 cm⁻³ in a mass range of 1–100 amu (Cravens et al., 2006). In comparison, CAPS provided evidence for heavy positively and negatively charged ions, with a mass-to-charge ratio reaching up to thousands of atomic mass units (Crary et al., 2009). This was one of the most outstanding observations of the Cassini mission as they revealed the dusty plasma nature of the upper atmosphere and its highly complex ion-neutral chemistry. Qualitatively, the dayside and nightside positive ion composition are similar, but quantitative differences exist, particularly for the species with relatively short chemical lifetimes (CH₅⁺, HCNH⁺, C₂H₅⁺) that are more abundant for the dayside (Cui et al., 2009). On the other hand, the day-to-night variations for terminal ion species with long lifetimes (NH₄⁺, C₆H₇⁺, C₂H₃CNH⁺) are rather small. Negative ions appear to be a permanent (yet variable) feature of Titan's highly complex ionosphere with the highest masses observed at the lowest sampled altitudes (950 km).

Solar radiation and associated photoelectrons, that are mostly deposited above 600 km, are at the origin of Titan's ion population. Energetic electrons from Saturn's magnetosphere contribute as a source of nightside short-lived ions but their contribution is always much lower than solar radiation on the dayside. In addition, day-to-night transport from the neutral atmosphere seems to be a significant source of the nightside long-lived ions. The nature of the positive and negative ions cannot be inferred directly from the observations and has been aided by numerical models based on two general principles: (i) radical ions are very reactive and only ions with a closed electronic shell are observed in large abundances; and (ii) charge flows to the species with the largest proton affinities (Vuitton et al., 2006). Results from these procedures for the lower mass ($m/z < 100$) positive ions are summarized in Fig. 3. Similarly, numerical models have attributed a few of the first negative ions as carbon-chain anions CN⁻/C₃N⁻ and C₂H⁻/C₄H⁻. The densities of numerous minor neutral species, especially nitrogen-bearing, have been estimated from the positive ion densities with a sensitivity higher than direct measurement of the neutral species. Nevertheless, the total positive ion density (essentially HCNH⁺) and the low mass negative ion densities (CN⁻, C₃N⁻/C₄H⁻) are not yet fully explained.

CH ₂ CCH ₂ (propadiene)	$(6.9 \pm 0.8) \times 10^{-10}$				
C ₃ H ₆ (propene)			$(7 \pm 3) \times 10^{-9}$		$(2.3 \pm 0.2) \times 10^{-6}$
C ₃ H ₈ (propane)	$(6.2 \pm 1.2) \times 10^{-7}$	$(2.0 \pm 1.0) \times 10^{-7}$	4.5×10^{-7}		$< 4.8 \times 10^{-5}$
C ₄ H ₂ (diacetylene)		$(2.0 \pm 0.5) \times 10^{-9}$	1.12×10^{-9}	$(7.6 \pm 0.9) \times 10^{-7}$	$(6.4 \pm 2.7) \times 10^{-5}$
C ₆ H ₆ (benzene)		$(4.0 \pm 3.0) \times 10^{-10}$	2.2×10^{-10}	$(2.3 \pm 0.3) \times 10^{-7}$	$(8.95 \pm 0.44) \times 10^{-7}$
HCN (hydrogen cyanide)	5×10^{-7}	$(3.0 \pm 0.5) \times 10^{-7}$	6.7×10^{-8}	$(1.6 \pm 0.7) \times 10^{-5}$	
HNC (hydrogen isocyanide)	$(4.9 \pm 0.3) \times 10^{-9}$	$(4.5 \pm 1.2) \times 10^{-9}$			
HC ₃ N (cyanoacetylene)	$(4.50 \pm 0.75) \times 10^{-9}$	$(5.0 \pm 3.5) \times 10^{-10}$	2.8×10^{-10}	$(2.4 \pm 0.3) \times 10^{-6}$	$(3.2 \pm 0.7) \times 10^{-5}$
CH ₃ CN (acetonitrile)	$(1.27 \pm 0.03) \times 10^{-8}$		$< 1.1 \times 10^{-7}$		$(3.1 \pm 0.7) \times 10^{-5}$
C ₂ H ₃ CN (acrylonitrile)	$(3.03 \pm 0.29) \times 10^{-9}$				$< 1.8 \times 10^{-5}$
C ₂ H ₅ CN (propionitrile)	$(7.37 \pm 0.32) \times 10^{-9}$				
C ₂ N ₂ (cyanogen)			9×10^{-10}		$(4.8 \pm 0.8) \times 10^{-5}$
NH ₃ (ammonia)		$< 1.9 \times 10^{-10}$	$< 1.3 \times 10^{-9}$		$(2.99 \pm 0.22) \times 10^{-5}$
H ₂ O (water)		$8 \times 10^{-9}/7 \times 10^{-10}$	$(4.5 \pm 1.5) \times 10^{-10}$		$< 3.42 \times 10^{-6}$
CO (carbon monoxide)	$(4.96 \pm 0.18) \times 10^{-5}$	$(4.0 \pm 5) \times 10^{-5}$	$(4.7 \pm 0.8) \times 10^{-5}$		
CO ₂ (carbon dioxide)		$(2.0 \pm 0.2) \times 10^{-8}$	1.1×10^{-8}		$< 8.49 \times 10^{-7}$

The completeness in observational coverage varies substantially by molecule and we focus on the equatorial and mid-latitudes as the observations allow.

The production of increasingly complex molecules is initiated by the destruction of methane and nitrogen to form reactive species. The process by which this occurs depends on the atmospheric level (Vuitton et al., 2019). Above 600 km, the driving mechanism is direct photolysis of methane and nitrogen, which ultimately leads to the production of numerous species, including benzene, ammonia and hydrogen isocyanide by positive ion chemistry, and acetylene, hydrogen cyanide and other nitriles by radical chemistry. These species are transported downward to the stratosphere where the photolysis of acetylene is indirectly responsible for the dissociation of methane, through catalytic processes. The peaks of radical production from these two processes are at ~ 800 and ~ 200 km, respectively. Radical-radical association efficiently forms alkanes in the stratosphere. Most of the photochemical molecules formed in the upper and middle atmosphere condense at the top of the troposphere, giving rise to vertical abundance profiles that have increasing volume mixing ratios with increasing altitude.

Molecular hydrogen is a by-product of methane photochemistry; the tropospheric/lower stratospheric mixing ratio derived from Voyager and Cassini infrared (IR) measurements and by direct measurement of Huygens mass spectrometer (GCMS) is 10^{-3} . This value is incompatible by a factor of two with the globally averaged thermospheric mole fraction of 4×10^{-3} from Cassini/INMS. This implies a downward H₂ integrated flux into Titan's troposphere comparable to the H₂ escape rate out of the atmosphere ($\sim 10^{28}$ H₂ s⁻¹).

The origin of the observed oxygen-bearing species (CO, CO₂, H₂O) is still a matter of debate. Unlike N₂ and CH₄, which are at the origin of all the minor nitriles and hydrocarbons detected on Titan, it became apparent from early on that CO, the main reservoir of oxygen on Titan, cannot be the single source of oxygen in this atmosphere. The detection of oxygen ions precipitating into Titan's atmosphere by the Cassini/CAPS instrument has offered a valid external source of oxygen, but it is unclear if Enceladus' current activity provides a flux large enough to be the ultimate source of water in the upper atmosphere of Titan (Vuitton et al., 2019). The difficulty of constraining the origin of Titan's water with the current known external sources supports the idea of a variable oxygen input (cf. next section about isotopes). These oxygen compounds increase Titan's astrobiological potential, as they could lead to the formation of amino acids and DNA nucleobases, as suggested from laboratory experiments that simulate Titan's chemistry (Hörst et al., 2012).

Isotopes

Isotopic species play an important role in helping to unravel the origin, evolution and present physical, chemical and biological processes acting on atmospheric gases. To date, five stable isotopes (D, ¹³C, ¹⁵N, ¹⁷O, ¹⁸O) along with radiogenic ⁴⁰Ar have been detected in Titan's atmosphere. The stable isotopes have been detected in a variety of compounds (see Table 5) whereas the noble gas ⁴⁰Ar was detected as a free atom.

Table 5 Titan's isotopic ratios.

alt-text: Table 5

Updated from Bézard B, Yelle RV and Nixon CA (2014) *The Composition of Titan's atmosphere, In: Titan: Interior, Surface, Atmosphere and Space Environment. Cambridge University Press, pp. 158-189.*

Species	Sub-mm		IR		MS	
	ALMA	Herschel SPIRE/PACS	IRTF TEXES/MPT Celeste	Cassini CIRS	Huygens GCMS	Cassini INMS
D/H (1.56×10^{-4})						
H ₂					$(1.35 \pm 0.30) \times 10^{-4}$	
CH ₄	$(1.033 \pm 0.081) \times 10^{-4}$		$(1.25 \pm 0.25) \times 10^{-4}$	$(1.59 \pm 0.27) \times 10^{-4}$		
C ₂ H ₂				$(1.63 \pm 0.27) \times 10^{-4}$		
HCN	$(2.5 \pm 0.2) \times 10^{-4}$			$(2.09 \pm 0.45) \times 10^{-4}$		
¹² C/ ¹³ C (89.3)						
CH ₄				86.5 ± 7.9	91.1 ± 1.4	88.5 ± 1.4
C ₂ H ₂				84.8 ± 3.2		
C ₂ H ₆			89 ± 8	89.8 ± 7.3		
C ₄ H ₂				90 ± 8		
HCN	89.8 ± 2.8	$96 \pm 13/66 \pm 35$		75 ± 12		
HC ₃ N				79 ± 17		
CO	89.9 ± 3.4	$87 \pm 6/124 \pm 58$				
CO ₂				84 ± 17		
¹⁴ N/ ¹⁵ N						
N ₂					167 ± 0.6	168-211
HCN	72.3 ± 2.2	76 ± 6		56 ± 8		
HC ₃ N	67 ± 14					
¹⁶ O/ ¹⁷ O (2680.6)						
CO	2917 ± 359					
¹⁶ O/ ¹⁸ O (498.8)						
CO	486 ± 22	380 ± 60				
CO ₂				380 ± 142		
³⁶ Ar/ ⁴⁰ Ar						
Ar						$(6.1 \pm 2.5) \times 10^{-3}$

Terrestrial values are enclosed in brackets.

D/H ratio

Four deuterated species have been measured in Titan's atmosphere: HD, CH₃D, C₂HD and DCN. The D/H in the first two species is some 10 times higher than that measured for Saturn, i.e., $(1.6 \pm 0.2) \times 10^{-5}$ (Fletcher et al., 2009). The enrichment in Titan's D/H relative to Saturn's appears to be primordial as no viable process has been found to generate the order-of-magnitude enrichment required. There is a factor of ~ 2 deuterium enrichment in acetylene and hydrogen cyanide compared to methane. The kinetic isotope effect may be responsible for this discrepancy, but numerical models constraining the photochemical and mass-dependent fractionation processes of hydrogen and deuterium on Titan remain to be developed.

¹²C/¹³C ratio

To date, the ¹²C/¹³C ratio has been measured in nine species and is compatible with the general trend observed throughout the solar system, with ¹²C/¹³C approximately 89 (Serigano et al., 2016). This value seems to indicate that methane is being continuously replenished at present, otherwise it should have evolved from this presumed starting value through isotope-selective chemistry and photolysis.

¹⁴N/¹⁵N ratio

¹⁴N/¹⁵N is the only isotopic ratio that varies strongly between molecules, being much lower in HCN and HC₃N than in N₂, and both ratios being substantially enhanced in ¹⁵N compared with N₂ in the protosolar nebula (¹⁴N/¹⁵N = 435(+ 65, - 50)) (Owen et al., 2001). The large difference between ¹⁴N/¹⁵N in nitriles and N₂ is explained by self-shielding of ¹⁴N₂ from solar UV, which leads to a relatively slower photolysis rate for ¹⁴N₂ than for ¹⁴N¹⁵N. Therefore, photochemistry preferentially removes the heavier isotope from N₂ and incorporates more ¹⁵N into HCN (and subsequently HC₃N) relative to ¹⁴N. Atmospheric escape processes cannot have significantly modified the ¹⁴N/¹⁵N ratio in N₂ over the satellite's history, implying a ratio for Titan's building blocks ≤ 190 , which agrees with the ¹⁴N/¹⁵N for NH₃ ice in the protosolar nebula based on cometary measurements (Mandt et al., 2014).

¹⁶O/¹⁷O/¹⁸O ratio

¹⁶O/¹⁸O has been measured in CO and CO₂, the latter with low signal-to-noise (Nixon et al., 2008). The detection of C¹⁷O represents the first detection of ¹⁷O in the outer solar system (Serigano et al., 2016). All five measurements suggest a slight enrichment in ¹⁸O, although the most precise measurement of C¹⁸O, obtained with ALMA, includes the terrestrial value within the 1 σ error. Different scenarios have been proposed to explain the abundance of oxygen on Titan, but there are no definitive arguments to discriminate between an external origin (e.g., micrometeorites, Enceladus' plumes) versus an internal origin (e.g., outgassing of primordial CO from the interior). Observations of C¹⁸O and CO¹⁸O are compatible with both scenarios as long as the various sources of oxygen have a cometary ¹⁶O/¹⁸O ratio (¹⁶O/¹⁸O ≈ 500). Improvement of the measurements of the ¹⁶O/¹⁸O ratio in both Enceladus' plumes and Titan's atmospheric CO₂ could give a valuable constraint on the origin of oxygen in Titan's atmosphere.

³⁶Ar/⁴⁰Ar ratio

The only radiogenic isotope detected on Titan, ⁴⁰Ar, is produced from decay of ⁴⁰K with a half-life of 1.28 Gyr (Niemann et al., 2005). The presence of this isotope in the atmosphere is a strong indication of endogenic activity, leading to the release of ⁴⁰Ar produced in the silicate fraction of the interior. This detection shows that trapping of highly volatile gases, including possibly N₂ and CO, was possible during Titan's formation.

Haze

Although there were hints of the presence of aerosols in Titan's atmosphere prior to space exploration, images and polarization measurements from Pioneer 11 and Voyager 1 and 2 revealed that the haze particles observed in the stratosphere were constituted of complex organic material. Stellar occultation measurements by Cassini/UVIS revealed particles up to altitudes of 1000 km while Cassini/VIMS reported an emission near 3.28 μm above 900 km that was tentatively attributed to Polycyclic Aromatic Hydrocarbons (PAHs). Analysis of VIMS solar occultation measurements from 700 to 250 km show a feature at 3.4 μm attributed to hydrocarbons (Bellucci et al., 2009). Below 300 km the haze is ubiquitous and measurements from Cassini/CIRS and VIMS find that the signature of C—H and C—C bonds dominate the spectra (Vinatier et al., 2010). A feature seen at 71.4 μm in CIRS corroborates that aromatic molecules are likely present in the haze (López-Puertas et al., 2013). The distribution of particles varies as a function of altitude and latitude albeit with no variation of their spectral characteristics in the far- and mid-IR. Huygens/DISR measurements of the absorption and scattering properties from 140 km to the surface are fit well by aerosol particles that are fractal aggregates composed of up to 4000 monomers with radii of 0.04 μm (Tomasko et al., 2009). Below 80 km, the measurements are consistent with aerosols being a combination of photochemically generated hazes and condensed organics. The Huygens Aerosol Collector and Pyrolyzer (ACP) collected samples in the stratosphere and troposphere that were subsequently heated, releasing HCN and NH₃ (Israël et al., 2005), which may indicate that the aerosols contain significant amounts of nitrogen, in apparent contradiction to the measurements from VIMS and CIRS (Bellucci et al., 2009; Vinatier et al., 2010).

Prior to the arrival of Cassini-Huygens, it was generally assumed that haze formed where it was observed, in the stratosphere. The discovery of large negative ions in the higher atmosphere was key to realizing that the initiation of aerosol formation, and the ensuing aerosol particle microphysical processes, extended higher up in Titan's atmosphere. An ionospheric mass flux of $\sim 3 \times 10^{-15} \text{ g cm}^{-2} \text{ s}^{-1}$ has been calculated (Wahlund et al., 2009), a significant fraction of the total aerosol production rate ($\sim 10^{-14} \text{ g cm}^{-2} \text{ s}^{-1}$). Macromolecules ($m/z > 100$) formed in the ionosphere attach electrons and therefore attract the abundant positive ions. At altitudes of 1000–500 km, aerosol

seed particles grow through coagulation and chemistry while they drift downward into the deep atmosphere. The resulting particles have a fractal dimension of 2, intermediate between linear and spherical aggregates. Fractal aggregates coagulate faster and fall slower because they have a larger cross-section than spherical particles of the same mass. Fractal aggregates have different optical properties because of their random structure; they absorb more in the UV versus visible light. Once the particles reach the stratosphere and troposphere, they are subject to dynamical processes and condensation, before being removed by sedimentation. If tectonic processes are occurring, they can be mixed downwards into the interior, undergoing further change and oxidation in the aqueous environment.

Laboratory experiments, with their ability to control conditions and access to state-of-the-art analytical techniques, play an important role in understanding Titan's haze. Titan haze analogues, deemed tholins, consist of refractory solid materials produced under exposition of Titan's most abundant gases to a representative energy source (Cable et al., 2012). Such experiments demonstrate common traits with the optical properties of the true haze aerosols along with a tremendous and daunting complexity of composition, as determined from very-high-resolution mass spectrometry and nuclear magnetic resonance spectroscopy. Notably, nitrogen appears to be very efficiently incorporated into the solid phase.

Coupling Between Atmospheric Dynamics, Composition and Haze Distributions

Atmospheric Dynamics

Meridional circulation

According to global circulation models (Lebonnois et al., 2012; Mitchell, 2009; Newman et al., 2011), the meridional circulation of the middle atmosphere of Titan, which is driven by thermal meridional gradients, varies seasonally because of Saturn's axial tilt. Fig. 4 summarizes the overall interpretation of dynamical processes occurring in Titan's midwinter stratosphere and mesosphere. During summer/winter, there is a global pole-to-pole Hadley circulation cell. Heated air in the summer polar region rises to higher altitudes and then moves to the winter polar region where air is transported to lower altitudes. Around the equinox, global circulation models predict a meridional circulation with two equator-to-pole atmospheric cells where the air rises at the equator and descends to the poles because the equatorial region is the most directly heated by the sun. The predicted transition lasts about three terrestrial years. Subsequently, the global pole-to-pole atmospheric circulation cell reverses. The descending branch of these different atmospheric cells has a strong impact on the polar region by: (i) adding an adiabatic heating contribution because the air is compressed as it descends into the atmosphere; and (ii) enriching the mesosphere with photochemical species (haze and molecules) that were formed at very high altitudes (> 800 km), which impact the radiative budget of the atmosphere and in turn affect the global dynamics. In addition to the main Hadley circulation, a number of these global circulation models find that a small tropospheric cell forms in the summer hemisphere.

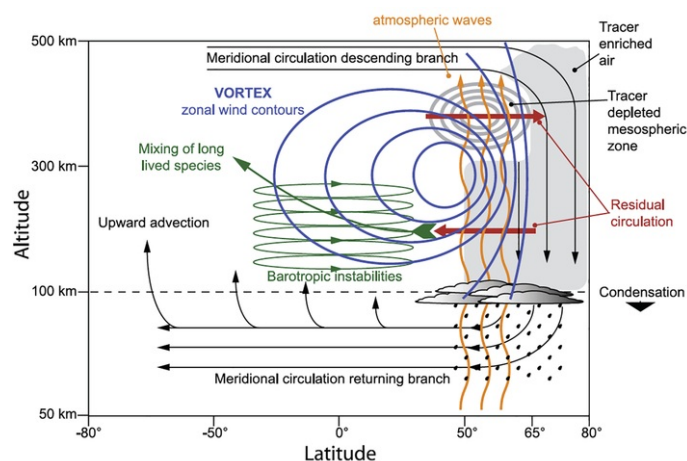


Fig. 4 Schematic of the dynamical processes occurring in Titan's winter polar region.

Reproduced from Teanby NA et al (2008) Titan's winter polar vortex structure revealed by chemical tracers. *Journal of Geophysical Research* 113(E12). doi: <https://doi.org/10.1029/2008JE003218>.

alt-text: Fig. 4

Zonal winds

Zonal winds are winds circulating at the same latitude, parallel to the equator, thermalizing the atmosphere longitudinally. They are mostly constrained from cloud tracking measurements (Porco et al., 2005), doppler shifts in the emission lines of atmospheric constituents like ethane (Kostiuk et al., 2001) and the Huygens Doppler Wind Experiment (DWE) (Bird et al., 2005). In the troposphere, wind speeds primarily eastward range from $< 1 \text{ m s}^{-1}$ at the surface, increasing to $\sim 40 \text{ m s}^{-1}$ near 60 km where they begin decreasing until they reach a sharp minimum ($\sim 5 \text{ m s}^{-1}$) around 70–80 km before increasing again in the middle atmosphere. This almost zero-wind layer decouples the tropospheric and stratospheric global dynamics. A stratospheric jet with wind speeds reaching 190 m s^{-1} at 50°N near 0.1 mbar (or 0.01 MPa; approximately 300 km altitude) was observed during the northern winter. A much lower wind speed on the order of 90 m s^{-1} , reaching lower latitudes ($< 40^\circ\text{S}$ in 2009), was observed in the southern hemisphere. The strong zonal winds in the northern hemisphere result from the significant thermal gradient between the north winter pole and the equatorial region. Titan is therefore one of two bodies in the solar system, along with Venus, to possess an atmosphere in global superrotation. It has been recently discovered from ALMA observations that the superrotation extends up to at least 1000 km with surprisingly high wind speeds up to 350 m s^{-1} .

Polar vortex

Another dynamic phenomenon that enters into play in the middle atmosphere is, like on Earth, the formation of a winter polar vortex (Fig. 5). A curious feature is the fact that the polar vortices appear to be tilted by a few degrees relative to the spin axis of Titan (West et al., 2016). Observations show that the air at high altitude is brought towards the winter pole by the atmospheric cell, due to the high temperature gradient at mid-latitudes in the winter hemisphere. As it approaches the planet's axis of rotation, the air is accelerated longitudinally to preserve the kinetic moment, which creates strong zonal winds. These strong zonal winds will dynamically isolate the latitudinal middle atmosphere and contain the polar vortex. The latitudinal extension of the polar vortex can be deduced by zonal wind speed maps, where the vortex boundary corresponds to a strong gradient of latitudinal temperature. The polar vortex forms during the winter and vanishes in early spring.

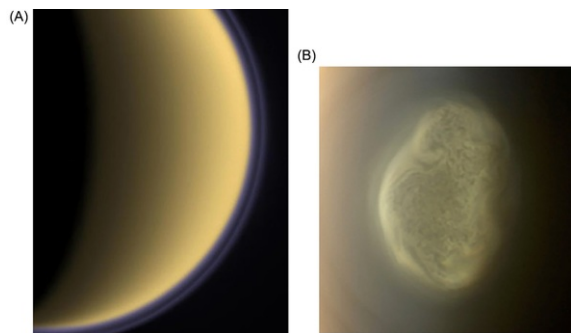


Fig. 5 Left: Titan's thick atmosphere, visible as a thin halo of purple light scattered by small haze particles. A thin, detached haze layer appears to float above the main atmospheric haze. Right: Vortex above Titan's south pole.

Credit: NASA, JPL, Space Science Institute.

alt-text: Fig. 5

Seasonal Change in Composition

Neutral species

Both Voyager and Cassini IR spectrometers measurements (Fig. 6) show strong variations with latitude for stratospheric mixing ratios, and there appears to be little, if any, inter-annual variability detected when comparing both datasets (Coustenis et al., 2016). In general, hydrocarbons and nitriles are more abundant at the winter pole than at other latitudes. This results from the winter polar vortex, which enhances abundances through subsidence of air from higher altitudes, where the molecules are produced and have larger mixing ratios, to altitudes closer to the surface. The strength of the latitudinal variation depends on the chemical lifetime of the species, with short-lived species being more locally enriched than long-lived species. This trend was observed when Cassini first arrived during northern winter (Vinatier et al., 2015), but has now been observed at the south pole as it moved into winter (Teanby et al., 2019), indicating the circulation has reversed and subsidence is now occurring at the south pole (Fig. 4). There is also compositional evidence for the transitional two-cell circulation predicted by global circulation models. Following equinox, enrichment at the south pole was greater than that observed in the north at the start of the mission. The south-polar stratosphere also achieved extremely cold temperatures that were not observed in the north and could be caused by extreme trace gas enrichments acting as infrared coolers, combined with slow initial subsidence producing only modest levels of adiabatic heating. This illustrates the importance of trace gases in Titan's overall atmospheric energy budget.

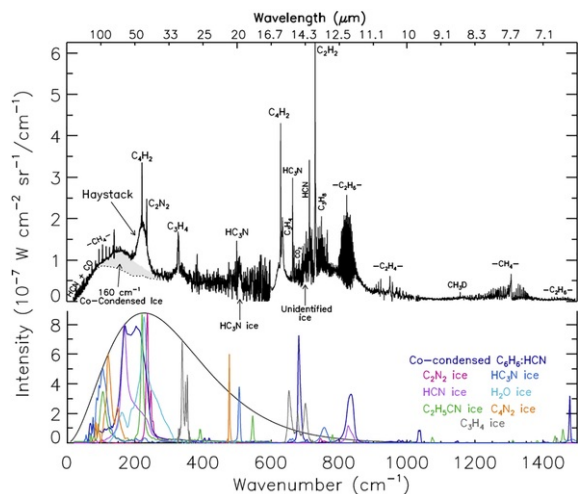


Fig. 6 Upper curve: CIRS far- and mid-IR limb spectra plotted as functions of wavenumber, recorded near 65°N during mid-northern winter and averaged over 100–150 km. Stratospheric ices and vapors are labeled. Lower curve: Laboratory-measured spectral dependence for various compounds that may contribute to ice clouds.

Reproduced from Anderson CM, Samuelson RE and Nna-Mvondo D (2018) Organic ices in Titan's stratosphere. *Space Science Reviews* 214. doi: <https://doi.org/10.1007/s11214-018-0559-5>.

alt-text: Fig. 6

Haze

Titan's photochemical haze exhibits features thought to be directly linked to seasonal behavior, particularly a hemispheric asymmetry in the main haze, a winter polar hood and a thin secondary "detached" haze above the main haze layer (Rannou et al., 2012).

Titan's haze is remarkably homogeneous across the globe, but images show that the winter hemisphere is darker at short wavelengths and brighter in the near-IR, and the winter pole has a layered structure that resembles a polar hood. The contrast can be accounted for by haze being more abundant in the winter hemisphere, increasing absorption in the UV and scattering in the near-IR. It seems clear that the seasonal reversal of the meridional circulation is ultimately responsible for the seasonal variations, with the polar hood being the result of downwelling of haze at the winter pole, but the details remain obscure.

During northern winter, the Cassini/ISS observed a detached haze at an altitude of 500 km (Fig. 5) and homogeneous in latitude south of the north polar hood (West et al., 2011). Around equinox the haze dropped to 380 km, where it was first observed by Voyager, one season earlier. After equinox, it disappeared for a few years, then reappeared sporadically and weakly at equatorial latitudes around 500 km (West et al., 2018). The origin of this haze layer is not yet well understood, but it seems likely that both dynamics and microphysics play a role in determining its structure and temporal evolution. According to global circulation models, in the summer hemisphere, particles are transported upward by winds at speeds greater than haze particle free-fall velocity and then transported horizontally to create the detached hazer layer (Larson et al., 2015; Lebonnois et al., 2012). Accordingly, the haze layer changes altitude because of the transient migration of the ascending branch of the Hadley cell. A significant correlation is observed between the detached haze layer position and a sharp transition in the temperature profile, marking the boundary with the thermosphere.

Stratospheric organic ice clouds

Numerous stratospheric ice clouds were observed by Cassini's remote sensing instruments. They are by far the most complex of any observed in the solar system, with over a dozen organic vapors condensing out to form a suite of pure and co-condensed ices, typically observed at high winter polar latitudes. Cassini/VIMS detected northern winter polar clouds with different morphologies, suggesting different cloud compositions later attributed to CH₄, C₂H₆ and HCN (Griffith et al., 2006). In Titan's mid southern fall season, the Cassini/ISS instrument observed the rapid onset of an unusually high (300 ± 70 km) particulate feature identified by VIMS to be HCN ice (de Kok et al., 2014). Cassini/CIRS observed numerous ice clouds (see Fig. 6) with varying chemical compositions such as HC₃N ice, C₄N₂ ice, co-condensed HC₃N:HCN ice, C₆H₆ ice, co-condensed C₆H₆:HCN ice (Anderson and Samuelson, 2011; Vinatier et al., 2018). Lastly, the *Haystack*, a spectrally broad and intense emission feature that spectrally peaks at 221 cm⁻¹, and an emission feature at 700 cm⁻¹ were also observed in Titan's northern polar stratosphere (Jennings et al., 2015; Vinatier et al., 2018); however, a definitive identification of these ice features still remains to be determined. Once the stratospheric ices are formed, they diffuse throughout Titan's lower atmosphere where most will eventually precipitate to the

surface and contribute to Titan's regolith.

Open Questions

The entry of the Cassini-Huygens spacecraft into orbit around Saturn in July 2004 marked the start of a golden era in the exploration of Titan. High-level scientific questions from the start of the mission have been answered, but others have not been satisfactorily resolved. At the same time, new questions have emerged from the discoveries that have been made, including the following:

Origin and evolution of the atmosphere

- What are the primordial building blocks that lead to such a massive atmosphere, and what can we learn on the solar system formation?
- What are the sources of oxygen in the atmosphere?
- What is controlling the H₂ profile and potential spatial variations?

Methane cycle

- Where is methane coming from, and is there a resupply from the interior into the atmosphere at the present day?
- How do clouds form and evolve, and what is the precipitation rate?
- How variable is the weather over long timescales (e.g., years? Decades? Millennia?)?

Chemical processes

- What is the chemical nature of the heavy ions (e.g., $m/z > 100$), and how do they form?
- What are the composition and optical properties of aerosols in the main haze layer?
- What is the composition and the structure of the massive stratospheric polar clouds?
- How do the haze and various condensates interact?
- To what level of complexity has prebiotic chemistry evolved in the Titan system?

Atmospheric dynamics

- What are the physical processes in the thermosphere that drive the density and temperature variabilities?
- What controls the global dynamics of the upper atmosphere? What are the effects on ion densities?
- What generates (and sustains) Titan's atmospheric superrotation?
- How do the polar vortices form, evolve and terminate?
- What is the wind regime near the surface?

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Biography



Véronique Vuitton is a CNRS Research Scientist at the Institut de Planétologie et d'Astrophysique de Grenoble, Université Grenoble Alpes, France. She obtained a PhD in Atmospheric Sciences from the University of Paris-Val-de-Marne. Her scientific fields of interest are related to planetary sciences and astrobiology. Her work focuses on the formation and evolution of complex organic matter in the solar system (and beyond). She focuses specifically on the chemical processes occurring in planetary atmospheres (Titan, Pluto, Super-Earths) and in the organic ices present at the surface of small bodies (comets, KBOs) through numerical modeling and analytical characterization of laboratory analogs. She was a participating scientist on the Cassini-Huygens mission.

Abstract

As a result of the 13-year exploration of the Saturn system by the Cassini-Huygens mission (2004–17), there has been a revolution in our understanding of Titan, Saturn's largest satellite. Titan's atmosphere shows the most complex chemistry in the solar system. A chain of chemical reactions is being initiated in the upper atmosphere by ionization and dissociation of the major species, nitrogen and methane, primarily by solar UV photons. The produced photochemical molecules and aerosols have a strong impact on the radiative budget of Titan's atmosphere, and hence on its temperature profile. Furthermore, transport by global dynamics which reverses each half Titan year, greatly affects the distribution of these compounds. These complex couplings between chemistry, radiation, and dynamics make Titan's atmosphere an ideal laboratory to understand physical and chemical processes at play in atmospheres in general, particularly those showing the presence of photochemical haze such as Pluto or the increasing number of detected exoplanets showing haz atmospheres. Finally, the study of Titan's chemistry has astrobiological implications as it naturally produces complex organic nitrogen species that settle to the surface to produce an organic soil. This material is postulated to be exposed to aqueous melt pools produced through meteoritic impact or cryovolcanism, or even to be transported to an underground ocean of liquid water. Therefore, we may entertain the idea that, in certain regions at the (sub-)surface of Titan, the results of chemistry leading to life as we know it may be present.

Keywords: Aerosol; Atmosphere; Cassini; Chemistry; Clouds; Composition; Dynamics; Huygens; Hydrocarbons; Methane; Nitriles; Nitrogen; Saturnian system; Titan

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