
Remote Sensing of Hydrocarbons on Titan

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ABSTRACT

Hydrocarbon reservoirs at Titan come in many forms—as gases and condensates in the atmosphere; as surface accumulations of liquid in lakes, slushy soils, and solid sediments; and in the subsurface, perhaps caged within clathrate hydrates and/or as part of a global hydrocarbon aquifer. Because Titan is so far from the Sun and contains multiple atmospheric haze layers, information on its surface features and their composition is extremely difficult to obtain and is acquired via imaging instruments that operate at wavelengths less affected by the haze. Unfortunately, the data are commonly of low resolution, and divergent interpretations abound. However, with the multinational Cassini spacecraft currently orbiting Saturn on its extended Solstice mission, Titan's surface composition is slowly coming into focus. This review will attempt to synthesize the current state of knowledge of hydrocarbon presence and distribution at Titan, emphasizing those observations that have direct compositional relevance to compounds in the atmosphere and on the surface.

INTRODUCTION

The search for hydrocarbons on Titan is far easier than here on Earth, where most oil and gas are found hidden deep within subsurface reservoirs. At Titan, hydrocarbons exist as haze particles, liquid cloud droplets, and gases in the atmosphere; as particulates composing sand dunes, as liquid in lakes and small seas on the surface; and probably as a major bound (or fluid) constituent of a porous and icy regolith. The real challenge for the petroleum geologist at Titan is

to identify the specific type and amount of each compound present, the function each takes in a global cycling of various hydrocarbon components, and how the size and distribution of the many reservoirs change through time.

This is a tall order for a summary paper at this point in our exploration of Titan. But ever since an atmosphere was inferred by the Spanish astronomer Sola in 1907 (Lorenz, 2008) and confirmed as containing methane more than 65 years ago (Kuiper, 1944), Titan science has been a heady mix of hard data and

(mostly serious) speculation. And with the Cassini Solstice Mission currently making Titan flybys approximately every six weeks, the data continue to inform and surprise. In this Introduction, the remote sensing of hydrocarbons will be more fully explained before looking at Titan as a world, and then getting on with the search.

Since its discovery in 1655 by Christiaan Huygens, very little was known about Titan, except its orbital distance and orbital period (Table 1) for more than 300 years. It remained essentially a bright point of light orbiting Saturn even after methane was discovered, until a series of spacecraft flybys in 1979 (Pioneer 11), 1980 (Voyager 1), and 1981 (Voyager 2). The close Voyager 1 flyby established the presence of many hydrocarbons in the upper Titan atmosphere (Table 2) but was unable to image the surface because of an opaque orange haze at multiple levels throughout its 1000 km+ (620 mi+) thickness. Imaging Titan's unseen surface was such a high priority that Voyager 1's close flyby required a trajectory that sent it out of the plane of the solar system, unable to visit the outer planets as did Voyager 2. But with only visible light optics, Voyager 1's cameras were apparently unable to penetrate the globe-encircling haze, although recent reprocessing of some images do show surface features faintly (Richardson et al., 2004). Voyager 1 also carried an infrared radiometer interferometer and spectrometer (IRIS) that identified more than 15 different organic compounds in Titan's upper atmosphere (Table 2). It is because of this hazy smog that remote sensing techniques are needed to determine the chemical composition of the atmospheric gases, liquids, and particles (from Earth and from space), as well as penetrate the highly absorbing atmosphere to image (and analyze) the surface.

Following Voyager 1 and Voyager 2, the fully instrumented Cassini-Huygens spacecraft arrived at Saturn in July 2004 and has been orbiting with multiple targeted Titan flybys ever since. Soon after arrival of this international mission, it separated into two craft—the Cassini Saturn orbiter and the Huygens probe—that entered Titan's atmosphere and survived landing on the surface on January 14, 2005. The data acquired during descent and on the surface are the only ground truth available from Titan and probably will be for quite some time, and are discussed in detail below.

All remote sensing of Titan, whether from Saturn orbit, Earth orbit, or Earth's surface, takes advantage of windows in the highly absorbing nitrogen-methane atmosphere (Figure 1). Although visible light

only reveals a hazy orange orb, seven wavelengths of infrared (IR) light can reach (and reflect from) the surface at varying efficiencies. In addition, electromagnetic radiation of centimeter to meter wavelengths can also penetrate the haze, meaning that radar can be used to determine surface brightness (in effect, a function of surface roughness, composition, and grain size). Hence, it turns out that remote sensing of hydrocarbons on Titan is not so unlike searches conducted on Earth using seismic methods: an input signal (here sunlight, with its own source spectrum) is convolved with a complex stratified fluid medium (Titan's atmosphere) and is received by instruments designed to maximize signal detection and reduce noise (particularly the visual and infrared mapping spectrometer [VIMS], the Imaging Subsystem for Science [ISS], and RADAR instruments aboard Cassini, Section IV). Interpretation, as all geophysicists know, is both an art and a science, and much debate exists over the meaning of data presently being acquired. This reviewer will attempt to remain within the realm of general consensus, but the inverse problem cannot be avoided. Only future missions will validate or refute our current understanding of Titan's complex hydrocarbon chemistry.

A final word on how the term hydrocarbon will be used here is necessary. Because Titan's atmosphere is so rich in nitrogen, in addition to the complex hydrocarbon photochemistry discussed in the Titan's Atmosphere section, nitriles (hydrocarbons containing a nitrogen functional group), cyanides (-CN compounds), and cyanopolyynes (essentially cyanide/acetylene compounds) are also generated and therefore included. For a full listing of all organic compounds considered in this chapter with their chemical formulas, refer to the Titan's Hydrocarbon Inventory section. For naming purposes, the International Union of Pure and Applied Chemistry (IUPAC) convention will be followed, except for a few better known compounds, for example, acetylene for ethyne (C_2H_2) and ethylene for ethene (C_2H_4). Wade (2003) has been used extensively to guide the organic chemistry discussion herein.

TITAN AS A WORLD

By far the largest moon of Saturn, if Titan were circling the Sun solo, it certainly would be called a planet, regardless of how that definition changes. Larger than Mercury, it has a surface gravity slightly weaker than the Moon's but with an atmosphere

Table 1. Titan physical parameters.

Mass	1.35×10^{23} kg (0.022 Earth mass)
Radius	2575 km
Bulk density	1.88 gm/cm^3 (1880 kg/m^3)
Surface gravity	1.35 m/s^2
Surface temperature	94 K (-179°C)
Surface atmospheric pressure	1.44 bar
Distance from Saturn	1.23×10^6 km (~ 20 Saturn radii)
Distance from Sun	9.5 AU (~ 1 billion mi)
Length of day (orbital period around Saturn)	15.95 Earth days
Length of year (orbital period around Sun)	29.5 Earth yr
Obliquity (tilt of rotational axis relative to ecliptic)	26.7°

AU = astronomical unit.

four times thicker and a surface pressure 50% greater than Earth's. Because Titan orbits Saturn nearly in its equatorial plane, which is tilted almost 27° to the plane of the solar system, it experiences seasons that vary regularly during the Saturnian year of 29.5 Earth years (Table 1). In addition, Titan's approximately 16-day rotation period is synchronously locked to its revolution around Saturn—it always shows the same face to Saturn as does Earth's Moon to Earth.

Put all this together and about 170 Titan days (a Titan day being slightly less than 400 hr long) occur in each of Titan's four seasons, or seasonal change at about half the relative pace of Earth. As discussed more fully later, the atmosphere is thermally stratified, has a significant component near its triple point, and experiences mid- and high-latitude (possibly convective) clouds, a polar vortex, and planetary-scale Hadley circulation (Coustenis, 2005)—all in common with Earth's atmosphere despite extreme differences in temperature and chemistry. Stratospheric haze layers are also present, which have now been penetrated at high spatial resolution by the Huygens probe and at medium resolution (over far greater areas) by three of Cassini's instruments. These reveal a surface of hilly regions with integrated drainage networks (Jaumann et al., 2008, 2009), occasional volcanic domes (Sotin et al., 2005; Lopes et al., 2007), local channels draining highland areas into now-dry river beds containing rounded cobbles and pebbles (Tomasko et al., 2005), vast plains of windblown sand dunes (Lorenz et al., 2006a), and dark polar lakes and small seas (Stofan et al., 2007). Very few impact craters have been identified, meaning that most of these features are relatively young (Lorenz and Mitton, 2008). This is a world with a thick dynamic atmosphere that interacts at many scales with the surface

and interior far more than its Martian equivalent, if not as actively as at Earth. The medium of much of this action is methane.

Models of formation for outer solar system satellites include methane for several reasons. The primary volatile (gaseous compound) in the early solar nebula from Jupiter's orbit (5 astronomical units [AU], or 5 times the Earth–Sun distance) outward was H_2O , and it dominates the surface of three of the four Galilean moons around Jupiter (Johnson and McCord, 1971, and many others). However, farther out where Saturn formed, at 9 to 10 AU, the solar nebula was sufficiently cold that other volatiles present could condense in the planetary subnebulae, and the most likely candidates are methane (CH_4) and ammonia (NH_3) (Cameron, 1973). Combined with other species, H_2O tends to form an interesting hydrate when freezing that isn't pure crystalline ice. Instead, it forms a cagelike network, or clathrate, that can encapsulate many small compounds, and methane fits into it particularly well (Sloan and Koh, 2007). The growing Titan may have acquired vast quantities of methane and other volatiles from icy planetesimal clathrates in the proto-Saturnian nebula.

As Titan accreted material from the methane-ammonia rich icytesimals—those loosely bound icy objects composed of water, carbon dioxide, ammonia, and other ices—that surround Saturn, collisions in the final stages were energetic enough to melt its outer layers, if not the entire moon. Early Titan, therefore, would have been a differentiated body with about one half its mass in a rocky-metallic core (releasing more heat from short-lived radionuclides) and the other half in an ice-rich mantle and crust (Sohl, 2010). Although Titan's icy part may have started out as completely liquid, models of current structure suggest an outer solid crust composed of pure ice I or

Table 2. Titan atmosphere composition and abundance.

<i>Compound</i>	<i>Location and Abundance</i>	<i>Best Observation; Group and Year</i>
Nitrogen, N ₂	95% near surface	HASI,* Huygens; Fulchignoni et al. (2005)
	98+% in stratosphere	GCMS,* Huygens; Niemann et al. (2005)
	~97% near 1000 km	INMS,* Cassini; Waite et al. (2007)
Methane, CH ₄	~4% near surface	HASI,* Huygens; Fulchignoni et al. (2005)
	1.4% in stratosphere	GCMS,* Huygens; Niemann et al. (2005)
	~2% above 1000 km	INMS,* Cassini; Waite et al. (2005)
Hydrogen, H ₂	0.2% in lower atmosphere	IRIS,* Voyager; Hunten et al. (1984)
	0.4% above 1000 km	INMS,* Cassini; Waite et al. (2005)
Argon, Ar	0.003% in stratosphere (⁴⁰ Ar)	GCMS,* Huygens; Niemann et al. (2005)
	0.00002% (0.2 ppm) in stratosphere (³⁶ Ar)	GCMS,* Huygens; Niemann et al. (2005)
Ethane, C ₂ H ₆	0.001–0.002% (10–20 ppm) in stratosphere	CIRS,* Cassini; Coustenis et al. (2007)
	120 ppm above 1000 km	INMS,* Cassini; Waite et al. (2005)
	8–20 ppm near 1000 km	INMS,* Cassini; Waite et al. (2007)
Propane, C ₃ H ₈	0.5–0.8 ppm in stratosphere	CIRS,* Cassini; Coustenis et al. (2007)
	<5 ppm above 1000 km	INMS,* Cassini; Waite et al. (2005)
Ethylene, C ₂ H ₄	0.1–0.2 ppm in stratosphere	CIRS,* Cassini; Coustenis et al. (2007)
	200–500 ppm above 1000 km	INMS,* Cassini; Waite et al. (2005)
	680–1000 ppm near 1000 km	INMS,* Cassini; Waite et al. (2007)
Acetylene, C ₂ H ₂	3–4 ppm in stratosphere	CIRS,* Cassini; Coustenis et al. (2007)
	190 ppm above 1000 km	INMS,* Cassini; Waite et al. (2005)
	200–260 ppm near 1000 km	INMS,* Cassini; Waite et al. (2007)
2-Propyne, C ₃ H ₄ (methyl acetylene)	5–20 ppb north winter stratosphere	CIRS,* Cassini; Coustenis et al. (2007)
	4 ppm above 1000 km	INMS,* Cassini; Waite et al. (2005)
	7–12 ppm near 1000 km	INMS,* Cassini; Waite et al. (2007)
1,3-Butadiyne, C ₄ H ₂ (diacetylene)	1–15 ppb north winter stratosphere	CIRS,* Cassini; Coustenis et al. (2007)
	0.5 ppm above 1000 km	INMS,* Cassini; Waite et al. (2005)
	2–6 ppm near 1000 km	INMS,* Cassini; Waite et al. (2007)
Propene, C ₃ H ₆ (propylene)	1–4 ppm near 1000 km	INMS,* Cassini; Waite et al. (2007)
Benzene, C ₆ H ₆	up to 3 ppb at north winter stratosphere; ~0.1 ppb everywhere else	CIRS,* Cassini; Coustenis et al. (2007)
	<5 ppm above 1000 km	INMS,* Cassini; Waite et al. (2005)
	1–5 ppm near 1000 km	INMS,* Cassini; Waite et al. (2007)
Toluene, C ₇ H ₈ (methylbenzene)	<1 ppm inferred near 1000 km	INMS,* Cassini; Waite et al. (2007)
	Possible presence at M/Z = 92 (this author's interpretation of Figure 1)	GCMS,* Huygens; Niemann et al. (2005)
Hydrogen cyanide, HCN	50 ppb in summer stratosphere to 500+ ppb in winter stratosphere	CIRS,* Cassini; Coustenis et al. (2007)
	<5 ppm above 1000 km	INMS,* Cassini; Waite et al. (2005)
Cyanoacetylene, HC ₃ N	80–250 ppb north winter stratosphere	IRIS,* Voyager; Coustenis et al. (1989)
	<5 ppm near 1000 km	INMS,* Cassini; Waite et al. (2007)
	0.1 ppb (summer stratosphere) to 25 ppb (winter stratosphere)	CIRS,* Cassini; Coustenis et al. (2007)
Acetonitrile, CH ₃ CN (methyl cyanide)	a few ppb in upper atmosphere	IRAM,* 30 m; Marten et al. (2002)
Acrylonitrile, C ₂ H ₃ CN (ethyl cyanide)	<2 ppb in stratosphere	IRAM,* 30 m; Marten et al. (2002)
	(estimate inferred from data)	
Cyanogen, C ₂ N ₂	5–16 ppb north winter stratosphere	IRIS,* Voyager; Coustenis et al. (1989)

Table 2. (cont.).

<i>Compound</i>	<i>Location and Abundance</i>	<i>Best Observation; Group and Year</i>
	5 ppb in stratosphere	INMS,* Cassini; Waite et al. (2005)
	2–6 ppm above 1000 km	INMS,* Cassini; Waite et al. (2007)
Dicyanoacetylene, C_4N_2	0.4 ppb inferred at 90 km	IRIS,* Voyager; Coustenis et al. (1989)
Cyanodiacetylene, HC_5N	<0.4 ppb in stratosphere	IRAM,* 30 m; Marten et al. (2002)
Propionitrile, C_2H_5CN	<2 ppb in stratosphere	IRAM,* 30 m; Marten et al. (2002)
Water, H_2O	8 ppb near 1000 km	INMS,* Cassini; Waite et al. (2007)
	<0.9 ppb in stratosphere	CIRS,* Cassini; De Kok et al. (2007)
Carbon monoxide, CO	45 ppm in stratosphere	CIRS,* Cassini; De Kok et al. (2007)
Carbon dioxide, CO_2	15 ppb in stratosphere	CIRS,* Cassini; De Kok et al. (2007)
Ammonia, NH_3	trace component of haze aerosols	ACP,* Cassini; Israel et al. (2005)

*GCMS = gas chromatograph and mass spectrometer; INMS = ion and neutral mass spectrometer; ACP = aerosol collector and pyrolyser; HASI = Huygens Atmospheric Structure Instrument; IRIS = infrared radiometer interferometer and spectrometer; CIRS = composite infrared spectrometer; IRAM = Institut de Radioastronomie Millimétrique radiotelescope.

methane clathrate hydrate to a depth of 50 to 100 km (31–62 mi); a subsurface liquid water ocean rich in dissolved ammonia (acting as an antifreeze) several hundred kilometers deep, overlying another high-pressure crystalline ice layer surrounding the rock and/or metal core (Tobie et al., 2005; Lunine et al., 2009; Iess et al., 2010) (Figure 2).

Note that in many spheres of the Titan system, methane plays an important, if not dominant, function. Because methane is the simplest and most abundant hydrocarbon, it forms the basis of a rich and still poorly understood dynamic atmosphere chemistry, which has been producing, circulating, precipitating, coating, eroding, transporting, and redepositing organics on (and within) the surface of Titan for more than 4 b.y. To better understand the function hydrocarbons have on Titan, this exotic and highly toxic atmosphere first must be considered in more detail.

TITAN'S ATMOSPHERE

Composition, Structure, and Dynamics

Like all planetary atmospheres, Titan's is understood from an evolving and intricate mix of observation and theoretical modeling (Yung and DeMore, 1999). Interestingly, among the eight worlds in this solar system with atmospheres, Titan's is most similar to Earth's, especially in overall structure (based on thermal gradient, Figure 3) and the presence of a minor component near its triple point. On both worlds, the layer nearest the surface is termed the troposphere (the active or turbulent layer), where temperatures decrease upward to a minimum at the tropopause. On Earth, this can be an unstable situation if a rising air mass cools more slowly than its surroundings, keeping it buoyant and able to rise farther. If the parcel contains water vapor, it may

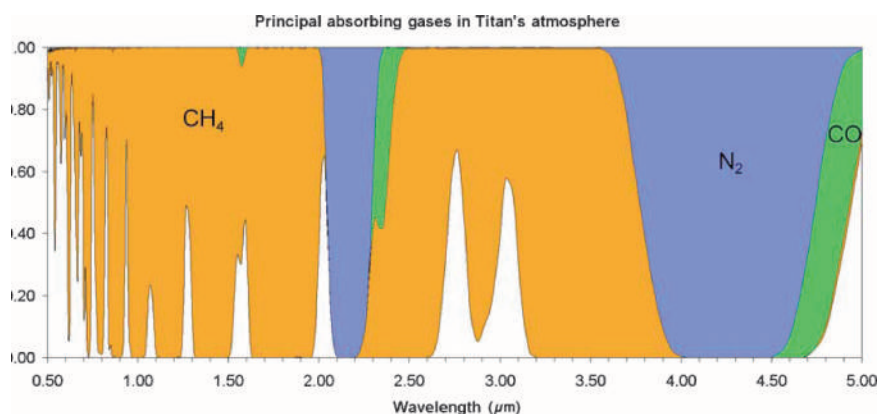


FIGURE 1. Titan atmospheric windows. Methane (CH_4 , orange), nitrogen (N_2 , blue), and carbon monoxide (CO , green) gases in Titan's atmosphere are highly absorbing and block the surface from most wavelengths of sunlight. In the near infrared, from $0.94\ \mu m$ to $5\ \mu m$, there are seven windows in the atmosphere (white regions), including the double window at $2.8\ \mu m$, that allow infrared light to reach the surface. The visible and infrared imaging spectrometer aboard Cassini takes advantage of all seven to obtain compositional information as well as surface images (modified from Clark et al., 2010).

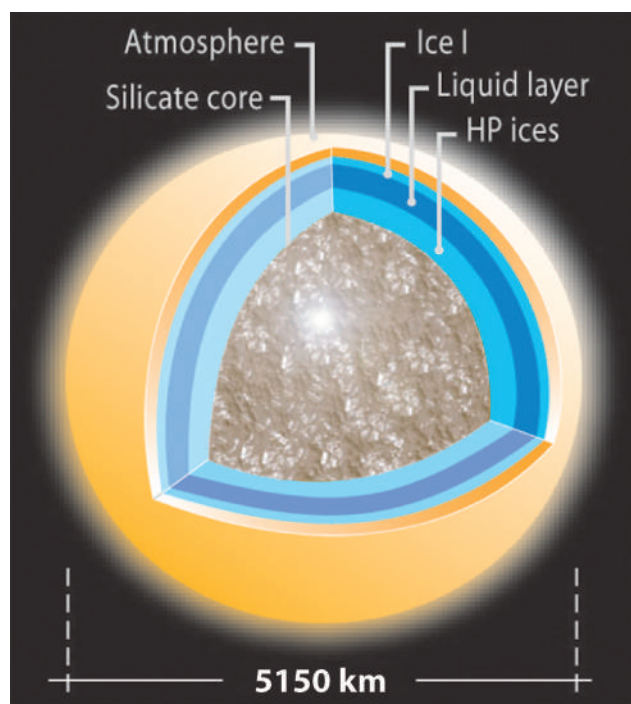


FIGURE 2. Pre-Cassini model of Titan's interior (modified from Sotin and Tobie, 2004) suggested that approximately one-half the moon's radius is a core of rock and metal. Surrounding that is a sphere many hundreds of kilometers thick of high-pressure crystalline ice, a liquid layer of water and dissolved ammonia perhaps 100 km (62 mi) thick, and an outer crust of ice I or possibly methane hydrate clathrate. An atmosphere extending more than 1000 km (>621 mi) into space is rich in nitrogen, methane, and many other simple organic compounds. HP = High-pressure.

reach a level at which condensation occurs, and clouds, possibly with rain or snowfall, will form (Danielson et al., 2003).

At Titan, methane is the tropospheric component near its triple point, and its abundance is relatively far greater in the Titan atmosphere than H_2O is in Earth's (Yung and DeMore, 1999). Near the surface at 94 K (-197°C), the 5% abundance measured by Huygens in a 1.5-bar atmosphere translates to 45% humidity, only half the 80% necessary to rain out under current conditions (Tokano et al., 2006). At lower temperatures higher up, however, Titan air is less capable of holding onto its methane moisture, and by 8 km (5 mi) above the surface, its relative humidity should reach 100%. Models of Titan's methane cycle predicted a low-level tropospheric saturation (Wilson and Atreya, 2004, and references therein), and in fact, evidence for methane cloud formation in the equatorial region was seen by the Huygens gas chromatograph and mass spectrometer (GCMS) (Niemann et al., 2005) at 16 km (10 mi) and in the Huygens descent imager and spectral radiometer (DISR) (Tomasko et al., 2005) data beginning at approximately 20 km (~ 12.4 mi) height. Other observations from Earth suggest that methane saturation and/or condensation include transient mid-latitude clouds (Griffith et al., 2005) and more pervasive, possible convective, clouds near the South Pole during the Southern Hemisphere summer (Schaller et al., 2008).

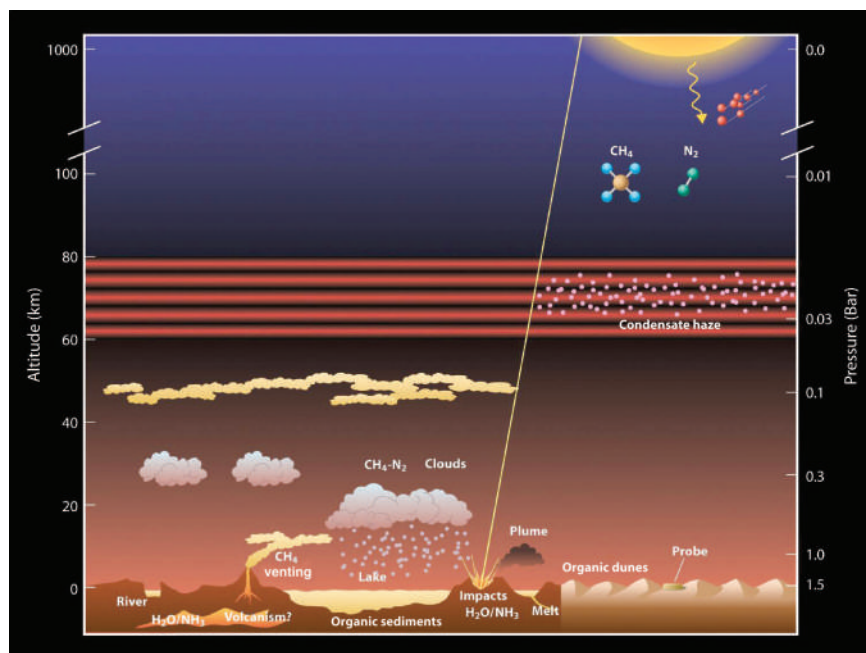


FIGURE 3. Titan atmospheric structure and dynamics. Titan's atmosphere is similar to Earth's in its temperature profile and overall structure, although far colder, and composed of an entirely different mix of secondary compounds. Above the tropopause, between 60 and 80 km (37–50 mi), methane leaks into the stratosphere and is broken apart by ultraviolet radiation. The radicals generated recombine into higher molecular weight hydrocarbons that may fall to the surface or be involved in the formation of condensate hazes; the hydrogen is lost to space. Nitrogen is also ionized in the upper atmosphere by higher energy solar radiation and cosmic rays and is likely involved in the creation of atmospheric hazes as well as surface organic particulates in sand dunes and river and lake sediments (modified from Teanby et al., 2009).

Under current atmospheric conditions, any light rainfall generated in the dense midtroposphere would likely evaporate on its leisurely journey to the surface under the weak Titan gravity, although rare but intense cloudbursts in which methane rainfall would reach the surface are possible (Tokano et al., 2006) and may have been observed recently (Schaller et al., 2009). The likely scale of such storms in terms of volume released and recurrence intervals is discussed below in the context of a broader hydrocarbon cycle linking the atmosphere, surface, and interior (Figure 3). But with so many lines of evidence from the Cassini-Huygens mission of recent fluvial activity (Tomasko et al., 2005; Perron et al., 2006; Barnes et al., 2007a; Stofan et al., 2007; Lorenz et al., 2008a; Jaumann et al., 2008, 2009), it seems inescapable that atmospheric hydrocarbons have an important and integrated function in the geologic activity on Titan (Figure 4A–C).

The temperature in the Titan troposphere continues to decrease with height, and it reaches a minimum of 72 K (–201°C) between 40 and 50 km (25–31 mi), the tropopause (Lindal et al., 1983). Here, the differences with the terrestrial atmosphere are important. Besides being much colder than its troposphere, Earth's tropopause at 10 km (6.2 mi) height is far drier: 0.001% H₂O versus nearly 1.5% CH₄ at the Titan tropopause. This and the fact that Titan's tropopause is not much cooler than the surface means that methane easily leaks into the overlying stratosphere and above, where it can be destroyed by solar ultraviolet (UV) radiation. This leads to a whole cascade of photochemical reactions that are discussed in the next section. But first, to truly understand the function of methane and other hydrocarbons on Titan, the destruction of methane in the upper atmosphere must be considered in more detail.

In Earth's upper atmospheric layers, not only is there very little water vapor, but other gases, notably oxygen, shield the water molecules from being broken when solar UV radiation vibrates in tune with the O–H bonds, tearing them apart in a process known as photodissociation. Titan's atmosphere lacks this UV shielding, and the similarly susceptible C–H bonds in methane are easily destroyed, initiating extremely complex atmospheric photochemistry (Yung et al., 1984). As the Voyager data were being digested, it was realized that (according to models), photodissociation of methane above the tropopause and subsequent loss to interplanetary space would deplete the current atmospheric methane in 10 to 100 m.y., a far shorter time scale than the age of the solar system. Methane also provides a mild greenhouse ef-

fect, and its loss would mean cooling, followed by possible condensation and precipitation of most of the nitrogen too, initiating total atmospheric collapse (Atreya et al., 2006). This means that either Titan is currently being observed at a unique time in its history or methane is being resupplied in some way. Both exogenic and endogenic sources were considered, but the abundance of the heavy noble gases xenon and krypton in Titan's atmosphere as measured by Cassini (Niemann et al., 2005) essentially rules out a cometary or asteroidal input. Models now focus on interior interactions to resupply the methane, including the one described in the Discussion section.

Above the tropopause, the atmosphere (on both Titan and Earth) begins to warm again with height. This situation is far more stable against thermal overturn, and it becomes horizontally stratified with little vertical motion—the stratosphere. On Titan, the stratosphere extends to nearly 300 km (186 mi) in elevation (vs. 40 km [25 mi] on Earth) and reaches a temperature of 186 K (–87°C). It is here in the stratosphere that at least two separate haze layers blocked the Voyager cameras from viewing the surface. The exact composition of the haze particles is unknown and highly debated, although their pyrolysis products are ammonia and hydrogen cyanide (HCN), which were measured by the aerosol collector and pyrolyser (ACP) aboard Huygens as it descended, indicating a solid organic refractory component (Israel et al., 2005). From the way they scatter UV, visible, and IR light, the haze particles appear to be smoke size, dominantly 0.1 to 0.3 μ m in diameter (Tomasko et al., 2005).

One interesting observation of this haze that has implications for hydrocarbon accumulation: it is pushed around the Titan globe by seasonal stratospheric circulation patterns. An atmosphere with thick layers of sunlight-absorbing haze coupled to a slowly rotating world means such a gradual exchange of heat that it can be accommodated in a single pole-to-pole circulation—a planetary scale Hadley cell (Lorenz, 2008). Every 15 (terrestrial) yr, one of Titan's poles enters deep winter, and observations by Voyager 1, the Hubble telescope, and the Cassini spacecraft have each confirmed the darkening of the winter polar stratosphere as organic haze is pushed toward the sinking part of the system (Lorenz and Mitton, 2008). It is only a matter of speculation as to whether some of these microscopic organic haze particulates aggregate further into particles sufficiently massive to fall to the polar surface or become entrained in the occasional methane rainfall (Discussion

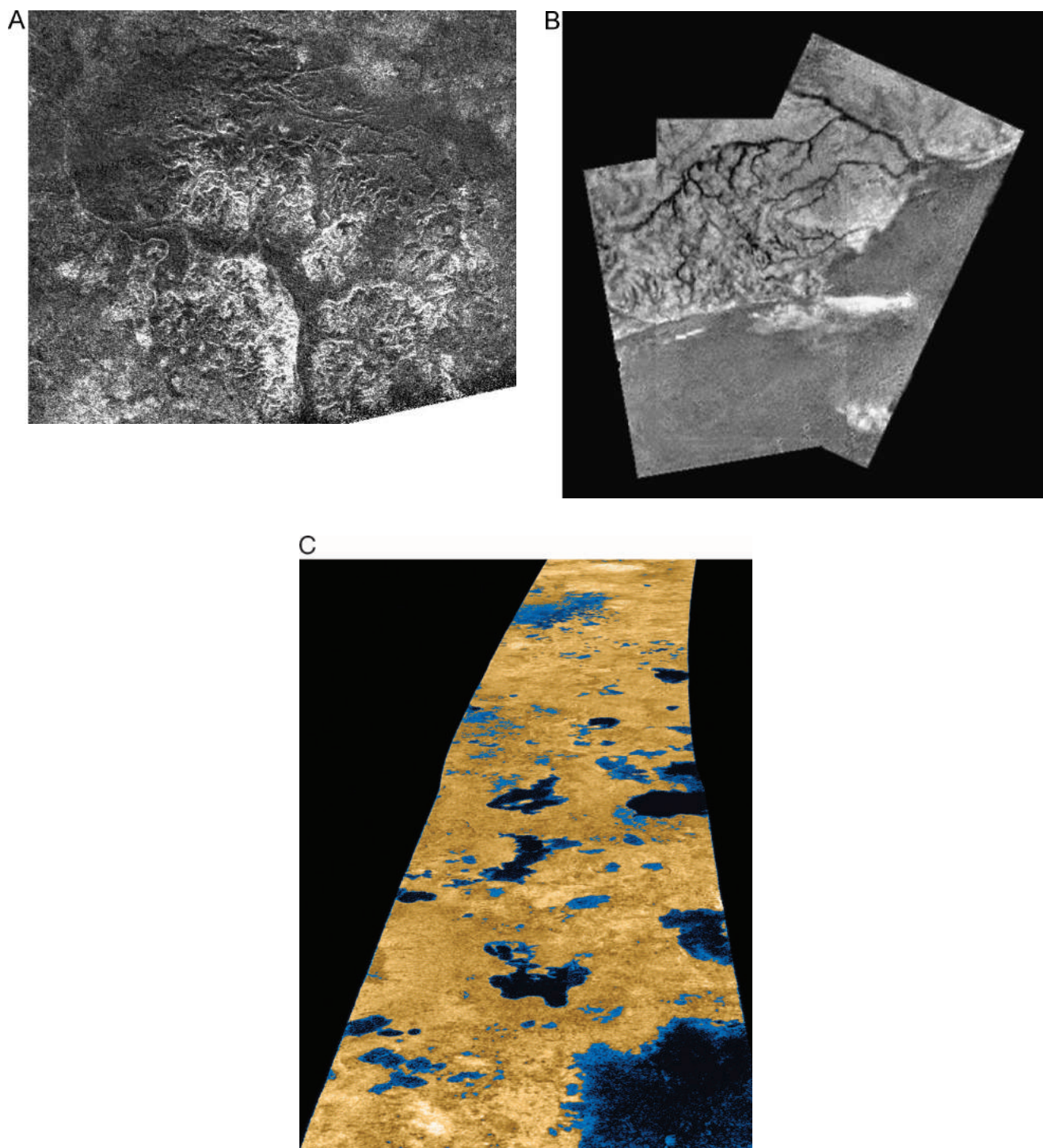


FIGURE 4. (A) Southern canyons of Titan. A complex and integrated drainage network in the southern highlands of Titan is revealed by Cassini RADAR on May 21, 2009. This image is centered at lat. 71°S and long. 240°W and exhibits no impact craters, suggesting this drainage system has been active recently. The trunk channel into which smaller tributaries flow is dark to synthetic aperture radar (SAR), meaning smooth, and probably filled with fine-grained materials. The erosive agent is probably liquid methane. Image size is 335 × 288 km (208 × 179 mi) and is modified from Jaumann et al., 2009. (B) Composite of Huygens probe images taken from approximately 16 km (~10 mi) above its landing site, in the western Shangri-La dark equatorial lowlands. The adjacent brighter highlands display a dendritic drainage pattern suggesting channelization by flowing liquid from rainfall; the channels themselves are probably empty and covered with a layer of fine organic sediments. The drainage empties into the dark lowlands where Huygens landed (Figure 11), only 20 km (12 mi) from a dune field (modified from Tomasko et al., 2005). (C) Titan lakes. Images taken by Cassini RADAR of the north polar region of Titan are combined and color-shaded to show a surface dotted with lakes of various sizes and morphologies. Noticeably, many show scalloped lakeshores with variable radar darkness that suggest changing lake levels in undulating terrain (modified from Stofan et al., 2007).

section), although one intriguing observation suggests that aggregation is indeed possible. Clark et al. (2010) report identification of a Northern Hemisphere aerosol cloud of HCN that shows a specular, or mirrorlike, response from the aerosol particles by VIMS at a wavelength of 5 μm . This can only occur if the particles themselves are greater than 5 μm in diameter, far larger volumetrically than those identified by Tomasko et al. (2005). Laboratory work with HCN at Titan surface temperatures indicates that it is a sticky and malleable substance, one very likely to accumulate other aerosols and coalesce into larger particulates as it descends to the surface through a thick Titan atmosphere, where polar lakes provide many a catchment basin for any rivulets and streams transporting atmosphere-derived organic sediments.

The middle atmospheric layer, or mesosphere, begins at an elevation of 280 to 300 km (174–186 mi), where the temperature again begins to fall with height (Fulchignoni et al., 2005). No hazes are observed in Titan's mesosphere, and the pressure falls to 1/10,000th of the surface. Measured at 1.4%, CH_4 remains the second most abundant atmospheric constituent behind nitrogen (N_2) (Lunine and Atreya, 2008). The mesosphere extends up to about 500 km (~ 311 mi) where the temperature reaches a minimum of 152 K (-121°C). It starts to rise again in the thermosphere, where the few molecules present can move about freely, meaning very little actual heat, but high temperatures (>200 K). Cassini's lower flybys actually dip into the extended thermosphere 1000 km (620 mi) above the surface, although the atmosphere could be detected to more than 1300 km (808 mi) height—fully one-half the solid moon's radius!

The dynamics of the Titan atmosphere with likely scales of weather patterns are illustrated in Figure 3. Again, terrestrial patterns are used as likely analogs, but a few primary differences between the two must be kept in mind: (1) temperatures are much colder on Titan; (2) the working fluid is a probable methane/ethane mixture, not water; (3) time scales are much longer (a single season is 7.5 Earth yr long); and (4) the surface-troposphere temperature gradient is so shallow at Titan that it allows a significant and ongoing leakage of methane into the upper layers (Lunine and Atreya, 2008).

Under current surface conditions of 45% humidity, frequent methane rainfall is unlikely, although some Huygens data suggest a light drizzle at the time of the landing in January 2005 (Tokano et al., 2006). Even in the presence of a dry equatorial region (the Huygens landing site was at 10°S), many global circu-

lation models predict seasonal clouds above lat. 70°S , although the amount of convective growth and subsequent precipitation depend heavily on the model (Rannou et al., 2006, and references therein). Indeed, seemingly convective clouds did form during the Southern Hemisphere summer (Griffith et al., 2005; Roe et al., 2005; Schaller et al., 2008) and dissipated as the equinox approached in August 2009 (Schaller et al., 2009).

If methane clouds do form seasonally from surface evaporation at high latitudes, how much methane would be needed to maintain the current atmospheric levels, and could seasonal rainfalls/cloudbursts (Perron et al., 2006) supply enough liquids for the observed polar lakes and seemingly global fluvial features? Recent calculations suggest that given reasonable estimates of total polar lake surface area (based on current RADAR coverage of 20% of the polar regions), the lakes are just sufficient to maintain global relative humidity, if they are at least a few tens of meters deep (Mitri et al., 2007). Youthful fluvial features (all crater free) reinforce the idea of a recently active methanological cycle, at least in equatorial regions.

The time scale of a methane cycle, beginning with surface evaporation from pooled liquids (and perhaps a saturated regolith—see below), followed by atmospheric accumulation and eventual saturation, and completed with condensation and rainout, may be on the order of hundreds of years (Lorenz et al., 2005). Converted to Titan years, of course, this would be once every decade or two and may occur as a cold and sustained drizzle or as brief and intense cloudbursts (Hueso and Sanchez-Lavega, 2006), but all possibilities at this point are highly model dependent.

In the short term, then, a methanological cycle seems plausible. Now, the issue of long-term atmospheric resupply shifts to near-surface sources—lakes, rivers, and/or a porous regolith. The somewhat limited number of lakes would need to be tens to hundreds of kilometers deep to maintain atmospheric methane levels during the life of the solar system, which seems unlikely (Lunine and Atreya, 2008). Currently, the most logical source of dwindling atmospheric methane is the interior, leaking out through a fractured and porous regolith, perhaps itself recharged with methane from yet deeper in the interior. Based on two prevailing theories, the presence of prodigious quantities of deep methane can be attributed to the Titan surface - primeval methane acquired from the original cold and volatile-rich sub-Saturn nebula in which Titan accreted and incorporated directly into a clathrate hydrate crust (Lunine, 1993) or generated

Hydrocarbon photochemistry	Nitrile photochemistry
$\text{CH}_4 + h\nu \rightarrow \text{CH}_3 \text{ (methyl radical)} + \text{H}$	$\text{N}_2 + h\nu \rightarrow \text{N}^*$
$\text{CH}_3 + h\nu \rightarrow \text{CH}_2 \text{ (methylene radical)} + \text{H}$	$\text{N}^* + \text{CH}_3 \rightarrow \text{H}_2\text{CN} + \text{H}$
$\text{CH}_2 + h\nu \rightarrow \text{CH} \text{ (methynyl radical)} + \text{H}$	$\text{H}_2\text{CN} + \text{H} \rightarrow \text{HCN} \text{ (hydrogen cyanide)} + \text{H}_2$
$\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6 \text{ (ethane)}$	$\text{HCN} + h\nu \rightarrow \text{CN} \text{ (cyanide radical)} + \text{H}$
$\text{CH} + \text{CH}_4 \rightarrow \text{C}_2\text{H}_4 \text{ (ethylene)} + \text{H}$	$\text{CN} + \text{C}_2\text{H}_2 \rightarrow \text{HC}_3\text{N} \text{ (cyanoacetylene)} + \text{H}$
$\text{CH}_2 + \text{CH}_2 \rightarrow \text{C}_2\text{H}_2 \text{ (acetylene)} + 2\text{H}$	$\text{CN} + \text{HC}_3\text{N} \rightarrow \text{C}_4\text{N}_2 \text{ (dicyanoacetylene)} + \text{H}$
$\text{C}_2\text{H}_4 + \text{H} \rightarrow \text{C}_2\text{H}_5 \text{ (ethyl radical)}$	$\text{N}^* + \text{C}_2\text{H}_4 \rightarrow \text{CH}_3\text{CN} \text{ (acetonitrile)} + \text{H}$
$\text{C}_2\text{H}_5 + \text{CH}_3 \rightarrow \text{C}_3\text{H}_8 \text{ (propane)}$	$\text{N}^* + \text{C}_2\text{H}_2 \rightarrow \text{CHCN} + \text{H}$
$\text{CH} + \text{C}_2\text{H}_4 \rightarrow \text{C}_3\text{H}_4 \text{ (propyne)} + \text{H}$	$\text{N}^* + \text{CHCN} \rightarrow \text{C}_2\text{N}_2 \text{ (cyanogen)} + \text{H}$
$\text{CH}_2 + \text{C}_2\text{H}_2 \rightarrow \text{C}_3\text{H}_3 + \text{H}$	$\text{HCN} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_3\text{CN} \text{ (acrylonitrile)} + 2\text{H}$
$\text{C}_3\text{H}_3 + \text{C}_3\text{H}_3 \rightarrow \text{C}_6\text{H}_6 \text{ (benzene)}$	$\text{CN} + \text{C}_2\text{N}_2 \rightarrow \text{Nitrile polymers}$
$\text{C}_6\text{H}_6 + \text{C}_6\text{H}_6 \rightarrow \text{PAH polymer}$	$\text{CN} + \text{C}_4\text{N}_2 \rightarrow \text{Nitrile polymers}$

FIGURE 5. Titan photochemistry. A sampling of chemical reactions that illustrate how higher molecular weight hydrocarbons and nitriles are generated in Titan's atmosphere. The ionization state of each radical has been left out for simplicity except for N^* , which represents a number of ionization states for nitrogen (adapted from Wilson and Atreya, 2004).

via serpentinization of silicates at the base of an internal Titan ocean after release of hydrogen and carbon from various interior mineral and icy phases (Atreya et al., 2006).

Photochemistry and Hydrocarbon Generation

The continuous loss of methane from an atmosphere that nonetheless remains methane rich has one other important implication in terms of Titan hydrocarbons. Not only would there be a geologically active surface atmosphere cycle providing methane from the interior, but photochemical models also predict abundant conversion of the methyl (CH_3) and

methylene (CH_2) radicals produced into ethane and to a smaller extent, ethylene, propane, propyne, acetylene, and others (Yung et al., 1984) (Figure 5). Ethane, like methane, would condense at the tropopause, and possibly fall to the surface as ethane rain, or more likely, a methane-ethane mixture, because ethane is completely miscible in methane under Titan atmospheric conditions (Yung et al., 1984). Stratospheric ethane clouds seem to have been observed (Griffith et al., 2006), and the polar lakes' spectra, as interpreted by the VIMS team, are consistent with liquid ethane or a liquid methane-ethane mixture (Brown et al., 2008). The early post-Voyager

models predicted that so much ethane would be converted from methane and subsequently rain to the surface that a global ethane ocean hundreds of meters deep (Lunine et al., 1983) seemed likely; hence, Huygens was the only probe sent to another world designed to float. However, Cassini observations have clearly ruled out the global ocean hypothesis, and sequestration of predicted ethane deposits remains an open issue. Three possibilities emerge: (1) methane has not been present in Titan's atmosphere during geologic time scales (currently impossible to assess); (2) ethane is reprocessed in the atmosphere before reaching the surface (in disagreement with most photochemical models); and/or (3) ethane is concentrated on or within the surface. Ethane has been identified as a component in one south polar lake (Brown et al., 2008), but most of the predicted vast quantities are as yet unidentified (next section).

Photodissociation of methane is not the only destructive process in Titan's upper atmosphere. Energetic particles and ions, higher energy solar radiation, and even interstellar cosmic rays can ionize N_2 into highly reactive N^{+3} and N^{+5} ions, initiating a second major cascade of hydrocarbon chemistry (Yung et al., 1984). The end product of methyl/methylene reactions with ionized nitrogen are nitriles, polyynes, cyanopolyynes, polycyclic aromatic hydrocarbons (PAHs), and larger complexes of these compounds, all of which are solid phases throughout Titan's atmosphere and plausible components of the haze. A few representative chemical reactions are shown in Figure 5; the pre-Cassini photochemical model synthesis of Wilson and Atreya (2004), beginning with just a dozen or so organic compounds identified by the Voyager IRIS instrument, considers no less than 116 neutral and ionic species among possible Titan atmospheric reaction pathways.

Earth-based remote sensing with the European Space Agency's orbital Infrared Space Observatory (ISO) and ground-based IR-sensitive telescopes (e.g., the 10 m [33 ft] Keck) also added to the inventory following Voyager, ensuring that Cassini and Huygens were well instrumented to further investigate Titan's atmospheric chemistry. One instrument in particular, the Cassini plasma spectrometer, sampled the upper atmosphere between 950 and 1150 km (590–715 mi) during numerous flybys early in the mission. Its three particle spectrometers have identified many aromatic intermediates from these models, including benzene, toluene, naphthalene, and anthracene derivatives, and one instrument has inferred the presence of even larger PAH-nitrile complexes

(Waite et al., 2005, 2007). In one plausible scenario, the dissociated methyl and nitrogen ions progress beyond one and two carbon compounds to benzene via ion-neutral chemical pathways that were developed to understand terrestrial soot formation and interstellar PAH formation. Benzene is quickly photolyzed to phenyl ($C_6H_5^+$) that can recombine with a methyl group leading to toluene or with another phenyl group leading to naphthalene and anthracene, the two simplest PAHs. Subsequently, these can aggregate into larger PAHs and PAH-nitrile complexes that float down to the stratosphere to become components of the aerosol hazes (Waite et al., 2007). Table 2 shows the variety in type and abundance of Titan's atmospheric constituents. To date, 21 individual hydrocarbons and nitriles have been identified, even at the parts-per-billion (ppb) level. Clearly, many of the predicted chemical pathways are occurring. Now that Titan's atmosphere dynamics and chemistry have been reviewed, it is time to consider the surface.

CASSINI-HUYGENS SURFACE OBSERVATIONS

After five years of periodic flybys with the Cassini spacecraft, a clearer image of the surface of this icy enigmatic moon is emerging. A complete description of Titan's diverse physiography is beyond the scope of this review, and the reader is referred to the many publications cited at the end. Here, the focus will be on the few Cassini instruments that not only penetrate the haze, but also collect data relevant to surface composition: the VIMS and Cassini RADAR. Although the ISS instrument is revealing Titan's surface albedo variations (bright vs. dark terrain), atmospheric haze scattering is greater in the short-wavelength IR window (0.94 μm) it uses, particularly at high phase angles. At great distances, ISS can resolve details on Titan better than VIMS, which has only one-fortieth to one-eightieth of the spatial resolution of the ISS, but during close flybys, the view with ISS is limited by aerosol scattering, whereas VIMS, working further into the IR, penetrates the haze. Viewing at a wavelength of 5 μm , the haze is almost invisible and images from VIMS reveal the full contrast of the surface. Unfortunately, at wavelengths shorter than about 1.6 μm , clear views are obtained only when looking straight down.

Images by ISS in windows near 1 μm reveal light and dark areas that seem to indicate not composition, but topographic differences: dark and smooth, meaning gentle slopes and lower surfaces; bright, meaning elevated areas that are commonly dissected

in some way (Porco et al., 2005). The VIMS cannot only see these topographic changes in the same window, but it can also image Titan's surface through six other longer wavelength IR windows, where the haze becomes far more transparent. At wavelengths of about 2 μm and longer, VIMS has found the atmosphere is clear enough to show shading cast by sunlight on mountains, whereas at shorter wavelengths, aerosol scattering diffuses sunlight, making discerning topographic shading difficult to impossible (see Barnes et al., 2007b, for images and discussion). The 5 μm window is particularly illuminating because it spans no less than 15 separate channels or individual detector wavelengths in the VIMS instrument, allowing microspectra to be generated in just this one window. These can then be compared with laboratory reference spectra of organic ice that have complex absorption bands spanning the entire IR range, particularly in the 4.9+ μm region (Clark et al., 2010). As discussed below, VIMS now has documented the high spectral diversity of Titan's surface in the 5 μm window and has begun to identify the specific compounds present and their spatial distribution.

The Cassini RADAR instrument is proving to be the workhorse of detailed surface imaging. In its active synthetic aperture (SAR) mode, it emits bursts of atmosphere-penetrating, high-frequency (13.8 GHz; 2.2 cm [0.9 in.] wavelength) radiation at the surface (Elachi et al., 2006). Reflected energy is collected by the primary 4 m [13 ft] Cassini communication antenna, requiring the spacecraft to orient itself so that optical remote sensing instruments like VIMS and ISS cannot be used simultaneously. At closest approach, radar echoes yield spatial resolution of 300 m (984 ft)/pixel, which increases to 1200 m (3937 ft)/pixel at each end. The images thus constructed reveal the stunning richness and variety of the Titan terrain in long thin swaths approximately every third flyby (Lorenz and Mitton, 2008). By themselves, these narrow radar images speak little of surface composition, although the magnificent vistas of mountains, valleys, lakes, and seas attest to dynamic atmospheric interaction (Figure 4A, C). However, the RADAR instrument also operates in a passive mode that collects data on how the surface interacts with microwave radiation: radiometric properties known as microwave emissivity, radar reflectivity, and dielectric constant (Zebker et al., 2008). Without all the attendant theory, these properties are (somewhat) related to each other, and at Titan, seemingly related more to surface physical properties (roughness, porosity, slope steepness) than to composition, although

in a few smoother areas (high emissivity, low reflectivity) that sample the equatorial dark terrains and polar lakes, composition does play a more dominant function in the response (Janssen et al., 2009).

Consequently, the primary remote sensing tools with which to ascertain surface composition are the select VIMS IR wavelength windows and SAR mode of the Cassini RADAR instrument. These are especially useful when combined VIMS + SAR mapping products are made from overlapping observations. The SAR brings into clear focus the regional albedo variations observed but unexplained by low-resolution Hubble, ISO, and even Cassini ISS images. The VIMS also provides compositional information unparalleled by any instrument, although as will be seen, spectral and spatial resolution trade-offs limit interpretation.

Two classes of surface features discovered and identified in SAR swaths are directly relevant to surface hydrocarbon accumulations: (1) vast longitudinal sand dunes, initially termed cat scratches (Lorenz et al., 2006a) and (2) north polar lakes and seas (Figure 4C) (Stofan et al., 2007). Although the post-Voyager vision of a vast Titan ocean has not materialized, RADAR observations of Titan's north polar regions show that 10% of it is covered by what are most likely lakes of liquid methane-ethane, enough to maintain methane's current humidity according to the latest models (Mitri et al., 2007). The lakes range in size from a few kilometers wide to small seas that are thousands of kilometers across (Hayes et al., 2008). They also show a variety of coastline morphologies and albedo transitions that suggest variable lake levels and perhaps a few dry lake beds (Stofan et al., 2007; Barnes et al., 2009). Radiometric properties of the radar-dark lake interiors are consistent with smooth liquid hydrocarbons, perhaps containing fine particulates (Stofan et al., 2007; Janssen et al., 2009). Confirming these hints of surface liquid hydrocarbons was a global image taken by the VIMS instrument on July 8, 2009, and released by the National Aeronautics and Space Administration (NASA) that December (Figure 6). It shows the unmistakable glint of sunlight, known as a specular reflection, from Kraken Mare, a Caspian Sea-size lake at lat. 71°N.

Unfortunately, the northern polar region remained in winter shadow and unobserved by VIMS at high resolution at the time of this writing. However, a south polar lake, Ontario Lacus, was observed by VIMS on T38 (the 38th targeted Titan flyby) during late southern summer in December 2007. Brown et al. (2008) report absorptions in the 2 μm lake spectrum unique to

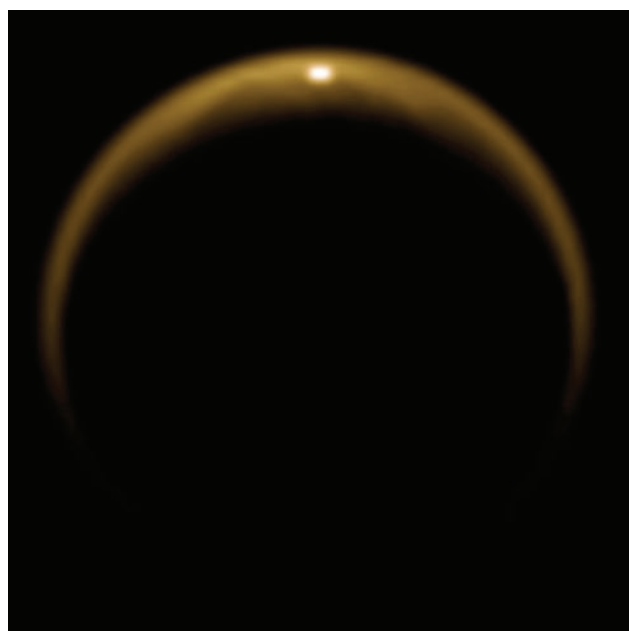


FIGURE 6. As Titan approached equinox in the summer of 2009, the visual and infrared mapping spectrometer (VIMS) instrument could begin to image its far Northern Hemisphere. Seen here at a wavelength of $5\text{ }\mu\text{m}$, the specular (or mirrorlike) reflection of the sun shines back into the instrument from Kraken Mare, a Caspian Sea-size hydrocarbon lake at lat. 71°N . This image was released by the National Aeronautics and Space Administration (NASA) in December 2009 and is modified from Stephan et al., 2010.

liquid ethane. Additional features in the $5\text{ }\mu\text{m}$ window suggest the presence of propane and butane and, significantly, rule out water ice, ammonia or ammonia hydrate, and frozen carbon dioxide. As mentioned in the discussion on the atmosphere, the ethane is most likely part of a methane-ethane liquid mixture, but liquid methane has nearly identical absorption bands to its vapor phase, so its presence in Ontario Lacus cannot be established firmly. By extension, however, the northern polar lakes are assumed to be composed of similar liquids, and the formation of ethane clouds there (Griffith et al., 2006) seems to confirm this.

The other set of physiographic features discovered by Cassini RADAR are vast equatorial dune fields composed of apparently sand-size organic particles. Nearly one-half of Titan's surface between 30°N and 30°S is covered by long linear sand dunes averaging tens of kilometers in length, 150 m (492 ft) in height, and with a 1 to 2 km (0.6 to 1.2 mi) interdune spacing—surprisingly similar to terrestrial analogs in the Namib or Arabian deserts (Lorenz, 2008). Both are examples of longitudinal dunes, which are aligned with an av-

erage wind direction that alternates between two primary regimes, clearly east-west on Titan. The particles composing the dunes average $200\text{ }\mu\text{m}$ in diameter (0.2 mm or medium-size sand on Earth), assuming they display cohesive properties similar to terrestrial sand. They lie exclusively within the dark-brown spectral unit of Barnes et al. (2007b), which is incompatible with water ice. They are most likely composed of simple organic ice, although little more can be said because of the low resolution (both spatial and spectral) of the VIMS data set (Barnes et al., 2008). Therefore, if Titan's regolith is water-ice rich, this implies that the dune particles are not physical breakdown products of crustal weathering, unless some process acts to concentrate organic materials independently of the water ice, from which dune sands can then be derived. Alternatively, the grains could be aggregates of smaller organic particulates grown into larger sand-size particles, a possibility that is discussed further in the Discussion section. The near global equatorial coverage of these dunes has led to one reservoir estimate: 200,000 to 800,000 km^3 (47,983–191,930 mi^2) of active sediment, a carbon equivalent to many hundreds of times the proven coal reserves on Earth (Lorenz et al., 2008b).

The difficulty of determining a precise chemical composition for a local feature like longitudinal dunes is amplified when attempting regional or global maps with VIMS data. For instance, because of the limited IR solar radiation available at Saturn, the ability to discriminate spectral details, particularly in the $5\text{ }\mu\text{m}$ window, requires long integration times (exposures greater than 160 ms/pixel), but this can only occur for small areas of the surface. Because flyby encounter times are brief, mission scientists prefer more regional fields of view versus long exposure times on smaller areas, thereby reducing typical observation times and decreasing the signal-to-noise ratio so that unique compositional information in the $5\text{ }\mu\text{m}$ window is lost. At best, albedo variations in other windows can be used to construct maps of spectral diversity (Barnes et al., 2007b, 2008; Soderblom et al., 2007; Le Mouelic et al., 2008; Clark et al., 2009, 2010), which, although colorful, only illuminate compositional variants of a general organic theme (Figure 7A, B). Although Barnes et al. (2008) established that all known dune locations were within the spectrally defined dark-brown unit of Soderblom et al. (2007), all that could be said a year later of this unit compositionally is that it is water-ice poor, at least more so than nearby dark-blue and bright units (Barnes et al., 2009). However, as discussed below, more recent analysis of VIMS pixels in some

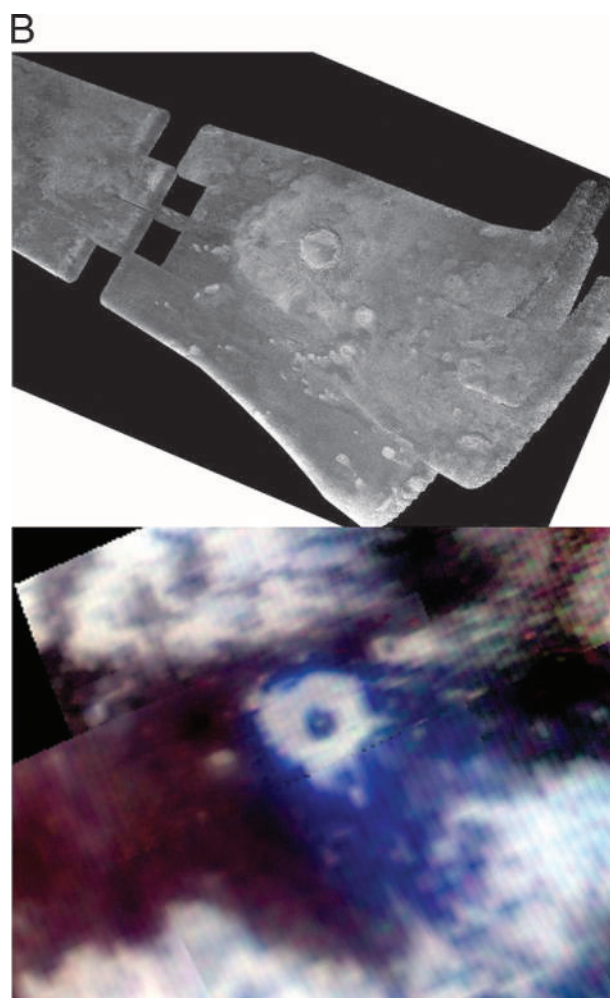


FIGURE 7. (cont.). (B) Sinlap crater at lat. 10°N and long. 15°W . Two views of a rare Titan impact crater, Sinlap: the upper RADAR image shows the morphology of this 100 km (62 mi)-wide impact structure with surrounding ejecta blanket, and the lower VIMS image shows spectral variations related to composition. The dark-blue spectral unit of the interior and outer wind-dispersed materials surrounding Sinlap to the southeast are more water-ice rich than the dark-brown (organic-rich) spectral unit of the plains; the bright inner ejecta blanket and nearby highlands may be exposed pure water ice or an unidentified organic compound (from LeMouélic et al., 2008).

dune-rich areas show that benzene is present on the surface at those locations (Clark et al., 2010).

A small subset of VIMS image cubes (two spatial dimensions and one spectral, or wavelength, dimension; Figure 8) does have sufficient integration time to identify not just spectral variations but specific absorptions within the $5\text{ }\mu\text{m}$ window (Figure 9A), which actually extends well beyond the VIMS spectral range of $5.2\text{ }\mu\text{m}$ to approximately $5.6\text{ }\mu\text{m}$. At $15+$ VIMS channels wide, absorption band location, width, and depth can all be measured and compared with

available laboratory reference spectra taken under similar conditions and in the same wavelength range (Figure 9B) (Clark et al., 2003, 2009, 2010). This is in contrast to most other windows, which reveal the surface at only one or two detector channels, or wavelengths (again, see Barnes et al., 2007b, for a more detailed discussion and images). The spectrum constructed from those windows is really just a set of five or six isolated points that, when connected, indicate spectral slopes of imaged materials, but no actual absorptions and thus no true compositional information. This has led to heated debates about the presence or absence of water ice in surface materials, as yet an unresolved issue that will be left aside here (Soderblom et al., 2009).

In an examination of long integration time, VIMS image cubes located primarily in the Sotra Facula region of Figure 10A, Clark et al. (2010) find four unique spectral features in different pixel averages: at 4.91 , 4.97 , 5.01 , and $5.05\text{ }\mu\text{m}$. A robust comparison of selected Titan surface spectra exhibiting each of these absorption features with available library spectra (Figure 9B) was performed following the procedure of Clark et al. (2003, 2007) to identify compositional candidates. A similar algorithm was then used to identify all surface pixels (within 1% error), displaying each feature and as a check to see whether its surface distribution was geologically sensible; a random surface distribution might indicate a detector

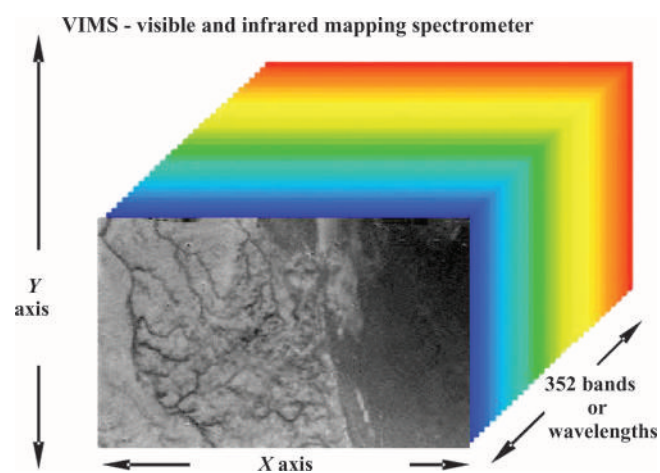


FIGURE 8. Representation of a VIMS (visual and infrared mapping spectrometer) image cube. The VIMS acquires images in 352 contiguous spectral channels, or wavelengths, between 0.3 and $5.2\text{ }\mu\text{m}$. Stacked x - y images for each wavelength, or detector channel, results in a cube of recovered VIMS images. Consequently, each pixel in a VIMS image is really a spectrum with 352 data points, parts of which are shown in Figure 9A.

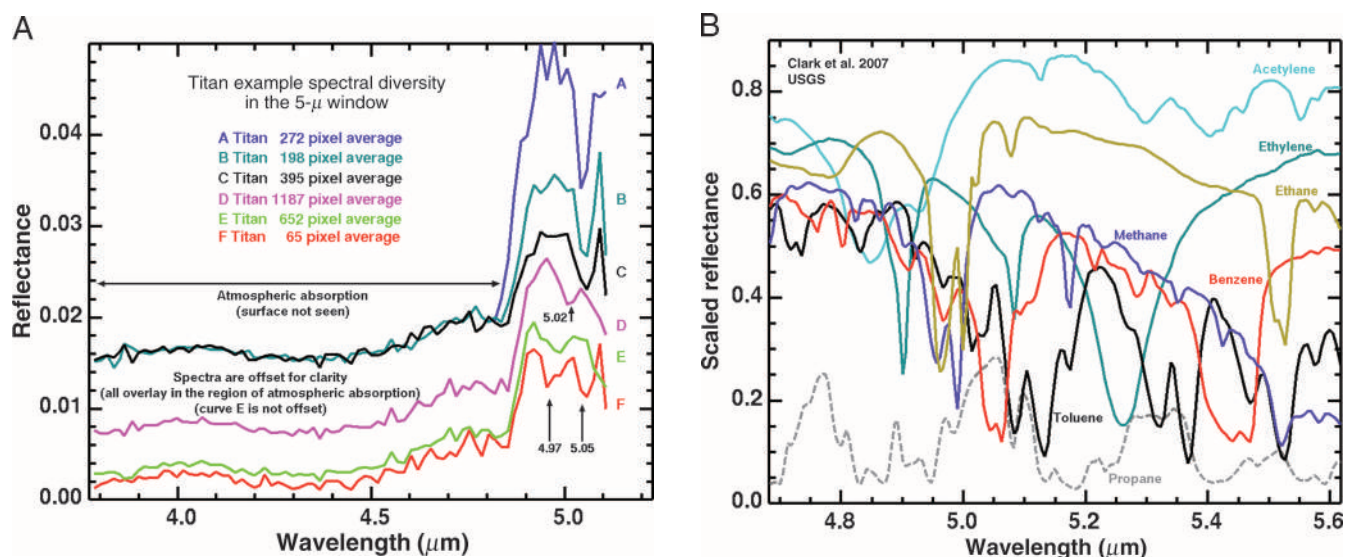


FIGURE 9. (A) Titan spectral diversity in the 5 μm window (from Clark et al., 2010). Visual and infrared mapping spectrometer (VIMS) image cubes with long integration times acquired through 2009, primarily in the Fensal-Aztlan region, display several spectral features in the 15-channel-wide 5 μm window. In particular, absorptions can be identified at 5.02 μm (5.01 μm in the text), at 4.97 μm, and at 5.05 μm. These appear to be associated with nitriles, low molecular weight alkanes, and benzene, respectively. (B) Hydrocarbon spectral diversity in the 5 μm window (from Clark et al., 2009). In this one limited wavelength range, most organic compounds exhibit a remarkable variety of absorptions. This has enabled identification of a number of compounds on Titan's surface with VIMS aboard the Cassini spacecraft, including methane, ethane, benzene, and possibly toluene.

spike or calibration error and would be meaningless compositionally.

The most confident identification is the 5.05 μm absorption feature: in shape, depth, and location, it precisely matches that of benzene, C₆H₆ (compare Figure 9A, B). It also maps spatially to the dark Fensal-Aztlan terrain (Figure 10A), where Coustenis et al. (2006b) recognized a 2.74 μm absorption, also present in the laboratory benzene spectrum (Clark et al., 2010). This terrain includes predominantly low-lying smooth plains between the brighter, more dissected, and elevated highlands, although locations in the elevated drainage systems and even a possible lakebed can be seen where benzene-rich pixels are concentrated (Figure 10B).

The 4.97 μm feature also maps primarily to dark terrain (Figure 10B), and it appears to be a low molecular weight alkane absorption, probably methane or ethane (Clark et al., 2010) (Figure 9B). Because of laboratory experience with ultracold methane and ethane, Clark et al. (2010) go on to suggest that the VIMS spectra indicate a slushy substrate, saturated with a liquid alkane solution, similar to the Huygens results (Zarnecki et al., 2005; see below).

The 5.01 μm absorption band—in size, shape, and position—has no match with any available laboratory reference spectrum, although alkynes and ni-

triles have similar spectral structures. The acetonitrile (CH₃CN) spectrum is most similar to the subset of Titan surface spectra displaying the 5.01 μm absorption, but it is not an exact fit (Clark et al., 2010).

The fourth feature, at 4.91 μm, is associated with a 5 μm bright region in the southern midlatitude highlands known as Tui Regio (Barnes et al., 2005). It has been interpreted as CO₂ absorption by McCord et al. (2008). Further analyses by Clark et al. (2010) and Curchin et al. (2010) find a better fit with the 4.91 μm absorption band of cyanoacetylene (HC₃N) ice, a previously recognized component of Titan's stratosphere and ionosphere (Coustenis et al., 2006a, b, and references therein). Cyanoacetylene also provides a better fit to an absorption seen through the 2.8 μm window in the same region, making it a primary candidate for Titan high alpine snows.

The net result, then, of long integration time and high spatial and spectral imaging (at very few locations) by VIMS reveals that the dark lowland equatorial patches of Titan's surface are probably composed of an ultracold organic mush of benzene and nitrile solids distributed within a wet mixture of methane-ethane (and probably nitrogen).

For all the capabilities of spacecraft remote sensing, ground truth is vital for both the geologist and spectroscopist. Cassini's atmospheric probe and lander,

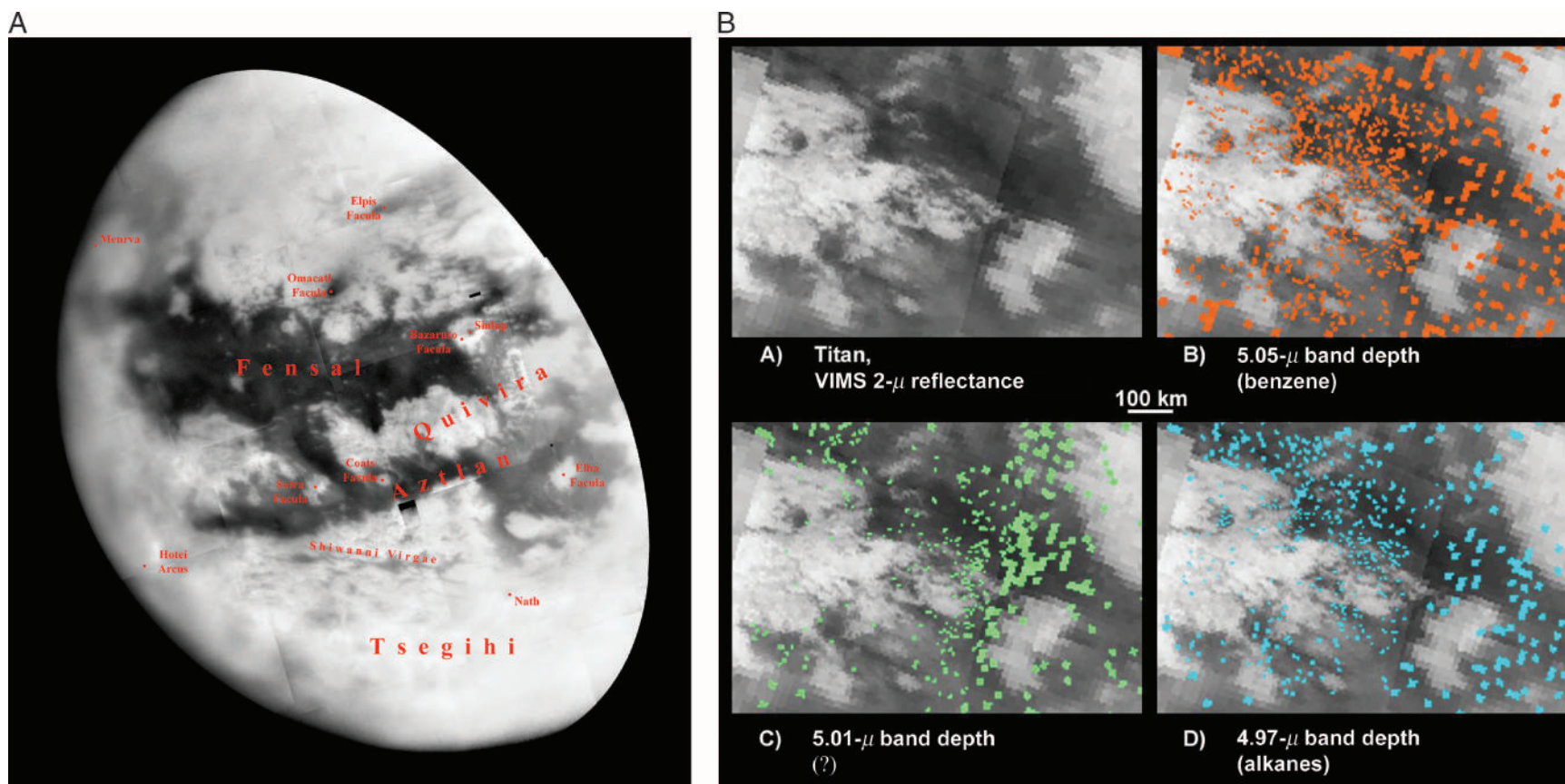


FIGURE 10. (A) Composite image of Titan's sub-Saturn hemisphere taken by the Imaging Subsystem for Science (ISS) through the atmospheric window at 0.94 μm . Shown is the equatorial dark terrain known as Fensal-Aztlan, with Sinlap crater (Figure 7B) in its northeastern corner, and Sotra Facula, the focus of high-resolution VIMS imaging in Figure 10B, in its south-central area (modified from Porco et al., 2005). (B) Compositional mapping of Sotra Facula (from Clark et al., 2010). Long integration time VIMS image cubes in the Sotra Facula region of the Fensal-Aztlan dark terrain have been used to identify specific spectral absorptions in the 5 μm window. Pixels containing a spectrum with the absorption identified are flagged, and colored orange, green, or blue, showing not just spectral diversity but also the location of actual compounds in the surface. In the Sotra Facula region, three absorptions at 5.05 μm (benzene), 5.01 μm (unidentified, probably a nitrile), and 4.97 μm (low weight alkane-methane or ethane) are primarily associated with the dark terrain—interpreted as low-lying smooth areas. Benzene in particular is concentrated in the 2 μm dark terrain and may be part of an icy coating on a lake in the highlands to the northwest in panel B. VIMS = visual and infrared mapping spectrometer.

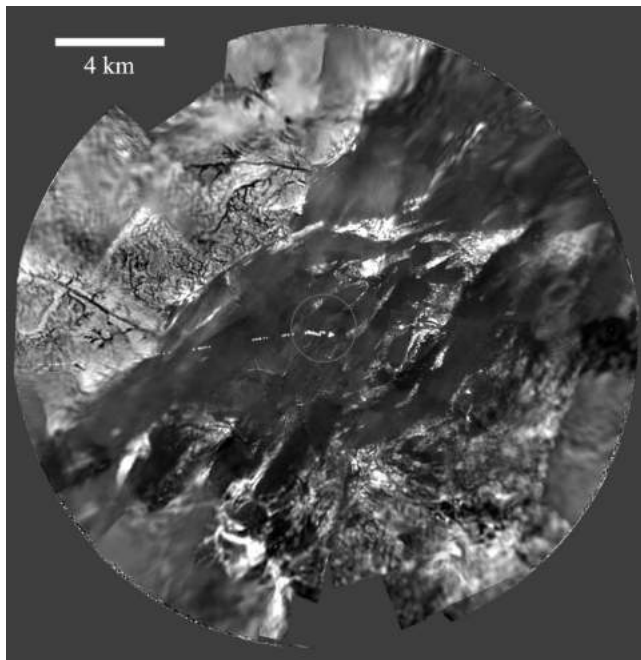


FIGURE 11. Composite photograph made from Huygens probe images taken during its atmospheric descent on January 14, 2005, at about 20 km (~12 mi) above the encircled landing site (tracking shown with white dots). This appears to be a dry lake or riverbed adjacent to well-drained highlands. No impact craters are visible, suggesting recent erosional activity; the highland tributary channels appear dendritic (attributed to channelized rainfall) although the two main trunk drainages are straight enough to suggest tectonic control (modified from Stephan et al., 2009).

Huygens, provided precisely such observations on January 14, 2005. Transmitting for nearly 4 hr, Huygens imaged the surface and analyzed lower atmospheric chemistry during its 2.5 hr descent (Figure 11) and sampled surface vaporization products while viewing them from knee height after landing (Figure 12). It is now established that Huygens settled on a dry riverbed (equivalent to dark terrain in $0.94\ \mu\text{m}$ ISS imaging) near well-drained hilly uplands (ISS bright regions). Surface imaging by the DISR shows rounded cobbles in the absence of smaller pebbles, which suggests that the most recent flow draining the landing site was quite rapid, possibly following a methane downpour (Tomasko et al., 2005). Surface rheology was tested with a surface penetrometer (Lorenz et al., 2006b) that indicated a crusty top layer overlying a wet sandy or slushy subsurface (comparable to *crème brûlée* as described by R. Lorenz [2005] at a press conference televised the day after the Huygens's transmissions, on January 15—from Paris).

Fortuitously, the impact also buried the heated GCMS inlet used to sample the atmosphere on

Huygens's way down. It proceeded to identify five gases released from surface materials warmed by the probe impact: methane, ethane, carbon dioxide, cyanogen, and benzene—the first two “firmly”; the last three “tentatively” (Niemann et al., 2005, page 782). Numerous other observations were made, notably, that haze layers extend all the way to the surface (Tomasko et al., 2005), but the agreement between two such different

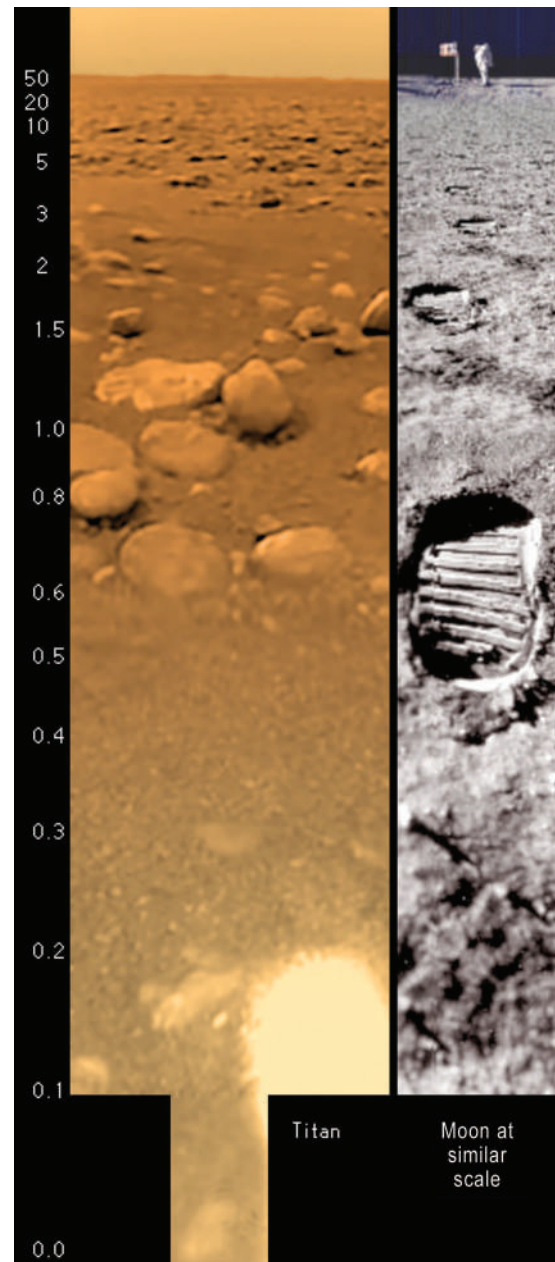


FIGURE 12. View from Titan's surface. The imager aboard the Huygens probe took this photograph from about knee height, showing 5 to 15 cm (2 to 4 in.)-wide rounded cobbles at a distance of 1 m (3.3 ft), off to a horizon a few tens of meters away. The famous Apollo 11 flag shot is shown next to it and foreshortened for a sense of scale (taken from Stephan et al., 2009; their figure 19.8).

data sets as VIMS and Huygens regarding the physiochemical nature of the Titan surface does seem to point in one direction—the outer few millimeters to centimeters (and possibly meters) of Titan’s equatorial lowland surface is a water-ice-free, ultracold, slushy mix of simple hydrocarbons and nitriles.

TITAN’S HYDROCARBON INVENTORY

The presence of such a diverse suite of hydrocarbons and nitriles in so many geologic settings at Titan lends itself to a listing compound by compound. Discussed first will be the most common: aliphatic hydrocarbons. This group includes both straight- and branched chain hydrocarbons with exclusively single C-C bonds (the alkanes), with one or more double C = C bonds (the alkenes), and those containing one or more triple C $\equiv$ C bonds (the alkynes and polyynes). The other major group of hydrocarbons at Titan is the aromatics, which are based on the six-carbon benzene ring, and these will be discussed next. Finally, a brief discussion of the nitriles (including cyanides and cyanopolyynes) will conclude this inventory of hydrocarbons at Titan.

Aliphatic Hydrocarbons: Alkanes

Methane

Ubiquitous at Titan, methane (CH₄) is a significant atmospheric component that currently ranges between 1.4 and 5%, depending on altitude, latitude, and season. In Titan’s nitrogen-rich lower atmosphere, methane’s relative humidity is about 45%, which means unlikely and/or infrequent cloud formation and rainfall today, but this may change at time scales of terrestrial centuries to millennia (Titan decades). Its atmospheric presence has been confirmed by multiple observations, and it appears to be resupplied from surface sources on the time scale of megayears (millions of years).

Methane’s presence on the surface is difficult to establish, given its highly absorbing function in the atmosphere. The best evidence for it in the near surface is the GCMS reading by the Huygens probe, which landed in the dark-blue spectral unit defined by Barnes et al. (2007b) and Soderblom et al. (2007). This is the same unit investigated by high-spectral/spatial resolution 5 μ m data in Clark et al. (2010), and it appears to contain essentially the same compounds, including methane (Figure 10B). By inference, the soil or upper regolith of large areas of equatorial and mid-latitude Titan contains a significant percentage of methane, likely a slushy liquid.



FIGURE 13. Shown here at the same scale, Titan’s far northern sea, Ligeia Mare, is larger than Lake Superior, although probably much shallower, and covers 0.12% of Titan’s surface. Note the changing Cassini RADAR response from the lake interior toward the shoreline, possibly indicative of a shallowing lake depth with perhaps methane mud flats along the perimeter (modified from Stofan et al., 2007).

Polar regions of Titan are dotted with hydrocarbon lakes, some of them quite large and officially termed seas (Figure 13), but they are not fully characterized chemically. Models (and physical conditions at the surface) suggest a major methane component, but as discussed, it is impossible to determine with present observations. Knowledge of subsurface structure is limited to interior models, some of which allow for vast quantities of methane encaged in a global, porous, icy lithosphere (cryosphere) tens of kilometers thick (Lunine et al., 2009, and references therein). If methane is present in the upper few meters to kilometers, the latest models suggest that convective overturn of the methane liquid in this layer is possible, depending on regolith permeability (Czechowski and Kossacki, 2009). One estimate puts the total atmospheric and lacustrine methane inventory at approximately 1,000,000 km³ (~200,000 mi³) (~1000 times Earth’s estimated oil and gas reserves), an incredible amount that itself would be dwarfed by a hypothetical cryospheric methane reservoir (Lorenz et al., 2008b). The amount of available methane at Titan is truly titanic, but technological challenges under such extreme conditions so far from Earth render thoughts of possible exploitation for use here to the distant (centuries to millennia) future—perhaps when Titan’s atmosphere is once again fully recharged with this abundant natural gas.

Ethane

Ethane (C₂H₆) is the second most common hydrocarbon in Titan’s atmosphere, but at 10 to 100 ppm at various levels (Table 2), it is 100 to 1000 times less

common than methane. It does seem to form infrequent polar clouds (Griffith et al., 2006) and is the current best candidate for some part of the dark smooth liquids identified by Cassini RADAR in north polar lakes and is included in the estimated inventory for lacustrine methane above.

Ethane was also firmly identified by the Huygens GCMS on the surface and, therefore, is probably a major component of the soil in the Barnes/Soderblom-defined dark-blue spectral unit covering the Huygens landing site (Barnes et al., 2007b; Soderblom et al., 2007). Recall also that methane and/or ethane may account for the 4.97 μm absorption in the Fensal-Aztlan dark terrains; as such, its global distribution in the near-surface regolith from the equator to mid-latitudes is also likely. Still, the hundreds of meters thick surface deposits predicted in post-Voyager models have not been identified, unless ethane's presence in parts of the near-surface regolith extends far deeper.

Propane and Butane

Propane (C_3H_8) gas has been identified in trace amounts in Titan's stratosphere and ionosphere above 1000 km (620 mi) (Table 2); butane (C_4H_{10}) has not been detected. At the surface, propane would be a liquid and butane a solid, and their laboratory spectra, particularly at 5 μm , could contribute to the 4.91 μm absorption band associated with the Fensal-Aztlan dark terrain (Clark et al., 2010). This band is shifted to longer wavelengths in higher molecular weight aliphatics (Clark et al., 2009), so none of them could contribute to this alkane feature. Most atmospheric models predict propane as a product (and reactant) in various chemical reaction pathways (e.g., Wilson and Atreya, 2004) and as a condensed species followed by precipitation with the methane-ethane mix near the surface. Although the GCMS inlet valve did not detect propane, its presence at the parts-per-million (ppm) level in the slushy soil remains unconfirmed, but likely.

Aliphatic Hydrocarbons: Alkenes

Ethylene

Also known as ethene (IUPAC nomenclature), ethylene (C_2H_4) was a commonly predicted photochemical by-product, and it has been detected at the ppb level throughout Titan's atmosphere (Table 2). The laboratory spectrum of its solid phase (as it would exist at the surface) exhibits such a distinctive set of absorptions in the 5 μm window that its presence at

any significant level (greater than a few percent in the upper few millimeters) at the surface in the regions investigated would have resulted in detection (Clark et al., 2009, 2010). Hence, no process seems to be concentrating and depositing ethylene at the surface, at least at a few localities in the equatorial dark terrains. However, its relative abundance in the atmosphere and likely formation as a condensed phase in polar downwelling currents (Discussion section) suggest that its surface presence is likely. Perhaps ethylene is combined with other organic sediments at the bottom of north polar lakes. If indeed the lakes go through an evaporation-refilling cycle on a seasonal time scale, the Cassini spacecraft may have the opportunity to observe recently exposed north polar lake-bottom sediments in its extended Solstice mission as those lakes dry out in the coming Titan summer.

Propene

Also known commonly as propylene, propene (C_3H_6) was not detected in Titan's atmosphere by Voyager and has just recently been identified at the ppm level by Cassini's ion and neutral mass spectrometer (INMS) (Waite et al., 2007). Measured laboratory spectra display such a unique fingerprint of absorptions in the 5 μm range that significant quantities at the surface in the areas investigated would have resulted in detection (Clark et al., 2009, 2010). It may be a polar lake constituent, but further observations are needed. Higher molecular weight alkenes have neither been identified in the atmosphere, nor have their spectra been measured in the solid phase in the laboratory as of this writing.

Aliphatic Hydrocarbons: Alkynes

Acetylene

Known as ethyne in IUPAC nomenclature, acetylene (C_2H_2) is the simplest of the triple carbon-bonded compounds. Predicted to be present and detected at the ppm level in Titan's stratosphere, Cassini measurements have found a surprisingly high abundance in the upper atmosphere (Table 2). Just as surprisingly, acetylene was expected to be in abundance on Titan's surface (at least, relative to benzene), but a careful search with appropriate VIMS data could find none, at least at a detection level of less than 1% (Clark et al., 2010). This remains a puzzle, awaiting future observations and improved models (e.g., Vuitton et al., 2008).

Methyl Acetylene

Known as 2-propyne in IUPAC nomenclature, methyl acetylene ($\text{CH}_3\text{C}_2\text{H}$) is another common constituent of the Titan stratosphere and upper atmosphere (Table 2). It has not been detected at the surface, although like most alkenes, higher molecular weight alkynes have not been measured as ice by laboratory spectrometers.

Diacetylene

Known as 1,3-butadiyne in IUPAC nomenclature, diacetylene (C_4H_2) is an extremely toxic compound measured in Titan's stratosphere and upper atmosphere in trace amounts by both Voyager and Cassini (Table 2). Because of its toxicity, its manufacture is illegal in the United States, and no cryogenic spectra of its solid are available to compare with Titan surface spectra. It is yet another hydrocarbon whose surface presence is likely, but unknown.

Aromatic Hydrocarbons

Benzene

Benzene (C_6H_6) is the simplest aromatic and a frequent component of Titan photochemical models, although not identified in the atmosphere until Cassini's arrival (Table 2). Its relatively high abundance in the upper atmosphere was unanticipated, and it is a possible major player in the methane cycle (Waite et al., 2007; Vuitton et al., 2008). Benzene was also tentatively identified in the surface by the Huygens GCMS (Niemann et al., 2005) and seems to have a distinctive presence in the dark terrains and drainage systems of the Fensal-Aztlan region (Clark et al., 2010) (Figure 10B). Therefore, benzene is considered a confirmed component of the surface, and future deposits likely will be found—in lake bottoms, within dune sand particles, and/or as part of the mushy mix of surface organic materials.

Toluene

Also known as methylbenzene, toluene (C_7H_8) is one of the compounds seemingly present just at various detection thresholds. The Cassini INMS inferred its presence at 1000 km (620 mi) (Waite et al., 2007), and its surface presence remains unknown. However, the Huygens GCMS recorded a small spike at $M/Z = 92$ at about 125 and 75 km (~ 78 and 47 mi) in the atmosphere (figure 1A, B in Niemann et al., 2005) that was not fully discussed. One possible compound whose M/Z is 92 would be toluene.

Naphthalene

The simplest PAH, naphthalene (C_{10}H_8) is composed of two benzene rings fused along an edge. It was also identified by Waite et al. (2007) at approximately 1000 km (620 mi) from a mass peak near 130 d in the Cassini plasma spectrometer (ion beam spectrometer [IBS]) data.

Anthracene

Also identified by the IBS at 1000 km (620 mi) altitude (Waite et al., 2007), a derivative of anthracene ($\text{C}_{14}\text{H}_{10}$) is associated with a mass peak at 170 d and its dimer with a peak at 335 d. Higher molecular weight aromatic hydrocarbons have been neither identified in the atmosphere, nor measured as ice in the laboratory, and are not considered further here.

Nitriles and Cyanides

Hydrogen Cyanide

The simplest cyanide, hydrogen cyanide (HCN) is another compound that is so toxic, its manufacture is highly regulated in the United States. Given the primary components of Titan's atmosphere, however, its presence there was expected—the real questions now are its vertical and latitudinal distribution and how they change seasonally (Table 2). The winter stratosphere seems particularly rich in hydrogen cyanide (and other cyanides/nitriles), and an integral function for this aerosol in seasonal circulation patterns is likely. As noted, Clark et al. (2010) find that in its solid state, it is a very sticky substance and may provide surfaces to which other aerosol particulates (and eventually, surface particles) could adhere, especially during winter polar downwelling currents.

Cyanoacetylene

Both a cyanide and cyanopolyne, cyanoacetylene (HC_3N) in Titan's atmosphere has been detected from Earth by Voyager and by Cassini (Table 2). Its abundance and distribution also seems to follow seasonal patterns, and its noticeable enrichment in the winter stratosphere suggests that it is a part of the global Hadley circulation and that surface accumulations at the poles might be expected. Currently, a variously interpreted absorption band at $4.91\ \mu\text{m}$ is the best evidence for its presence at the surface (McCord et al., 2008; Clark et al., 2010), but higher spectral and spatial resolution data will be needed to

resolve whatever seems to be coating the Tui Regio highlands.

Cyanodiacetylene

Detected by Earth-based IR spectrometry (Marten et al., 2002) in Titan's atmosphere, cyanodiacetylene (HC_5N) is not available in the United States. Hence, its spectrum is not known, nor is its surface presence on Titan. If so, there may be small amounts with acetylene and other organic deposits in polar lacustrine deposits.

Cyanogen

Probably the most toxic chemical on this list, cyanogen (C_2N_2) is another compound whose abundance seems to increase in the winter stratosphere (Coustenis et al., 2003). It is also another common component of photochemical models and may well be accumulating with the other organic solids at the bottom of Titan lakes and seas. Along with carbon dioxide and benzene, cyanogen was tentatively identified in the surface Huygens GCMS data (Niemann et al., 2005).

Dicyanoacetylene

Nearly as toxic as cyanogen, dicyanoacetylene (C_4N_2) is another illegal-to-manufacture compound (in the United States) that is present in trace amounts in the Titan atmosphere (Table 2). Whether or not it would condense and/or be entrained in any methane rainfall to the surface is unknown and, again, currently pure conjecture.

Acetonitrile

Also known as methyl cyanide, acetonitrile (CH_3CN) was not detected in Titan's atmosphere until well after Voyager by Earth-based IR telescopes (Bezard et al., 1993; Marten et al., 2002) and only in trace amounts (Table 2). It is, however, a very good candidate for producing the unidentified $5.01\text{ }\mu\text{m}$ absorption band, in which case, it would be a significant component of the equatorial Fensal-Aztlan dark terrain (Figure 10B) (Clark et al., 2010). This would be the first nitrile found on the surface, if its presence is confirmed with future imaging.

Acrylonitrile

Also known as ethyl cyanide, trace amounts of acrylonitrile ($\text{C}_2\text{H}_3\text{CN}$) have been identified in Titan's

stratosphere from the Earth-based 30 m (98 ft) radio-telescope located at the Institut de Radioastronomie Millimétrique (IRAM) (Marten et al., 2002) (Table 2). Its solid ice has been measured spectroscopically in the laboratory, but in a search of appropriate VIMS image cubes of the surface, no unique acrylonitrile absorptions were found (Clark et al., 2010). Still, it is considered a likely surface component, especially at the poles.

Propionitrile

Also known as propyl cyanide, minute amounts of propionitrile ($\text{C}_2\text{H}_5\text{CN}$) in the atmosphere (<2 ppb) were inferred from the IRAM data of Marten et al. (2002). Its solid ice has not been measured spectroscopically in the laboratory over the VIMS wavelength range, and a surface search for its presence is not possible at this time. This would be another winter stratospheric condensate that may fall to the polar surface as part of the seasonal Titan carbon cycle and may be another component of lake-bottom sediments and, perhaps, dune sands.

DISCUSSION AND FUTURE OBSERVATIONS

Even this list of compounds leaves many hydrocarbons and other organic reservoirs among the various Titan regimes unidentified. Neither of the known condensate reservoirs, haze particles and dune sands, are characterized chemically, aside from being probably organic and probably not water ice. There appears to be a liquid methane-ethane component in clouds, lakes, and the upper porous regolith (soil), but it also contains many other compounds, some tentatively identified, but most not. The atmosphere is the best-understood part of the Titan system, and it is here that any comprehensive model of hydrocarbon cycling begins.

The emerging picture of Titan's atmosphere is one that is physically and chemically dynamic at many spatial and temporal scales. Despite the marked differences with Earth's atmosphere, it interacts at the surface via many of the same processes, yielding some very familiar landscapes. With Cassini observations opening a new era of Titan science, a model begins to present itself. On the time scale of days (all time units relative to Titan), the atmosphere follows its planetary Hadley circulation, beginning with ascending air currents at the summer pole, which begin to move toward the equator. Along the way, during most of a Titan century, evaporation of surface methane reservoirs continuously replenishes losses from upper

atmospheric photodissociation and energetic particle bombardment.

The summer pole provides the thermal energy driving this circulation, and by the time the air reaches the winter pole (days to weeks), it is somewhat cooler and enriched not only in methane and ethane but also in higher order hydrocarbon and nitrile condensates (those considered in Figure 5 and Titan's Hydrocarbon Inventory section). The winter pole is a location of descending currents, and it is here that Titan's rich surface chemistry may be the most active. Of course, occasional storms and even localized drizzle, as already mentioned, may rain out their share of organics in equatorial and midlatitude regions. But polar regions are where the atmospheric concentration of many nitrile and cyanide compounds increases by up to 100 times (Table 2), where a polar hood or high haze layer appears (Flasar, 2006) and where cloud compositions other than methane, including ethane (Griffith et al., 2006) and hydrogen cyanide (Clark et al., 2010), have been identified.

Therefore, the model proposed here suggests that descending haze particles, entrained in this organic-rich polar methane-ethane-propane rain, act as nucleation sites to which other hydrocarbon-nitrile-cyanide condensates can attach. As noted, solid hydrogen cyanide is particularly sticky and may continue to enhance particle growth once at the surface and moved around by the winds there. This is one mechanism to produce the much larger dune sands, although eolian or fluvial transport to lower latitudes would be necessary, during which aggregation may continue over time.

Accumulation of organic solids entrained in rain and surface fluids may result also in extensive deposits of polar lake-bottom sediments, especially acetylene and larger nitriles, as noted above. Each summer, the lakes would shrink as methane is evaporated from lake surfaces, and some nearshore sediments would be exposed to the Titan surface regime that becomes increasingly dry as the summer goes on. If Earth and Mars are any guides, this would lead to physical weathering of possibly lithified layers—clearly, physical breakdown and transport of surface materials occurred at the Huygens landing site (Figure 12). At the poles, once physical weathering of these sediments does occur, the lighter particles can be picked up by the frequent winds and transported around the globe. Either way that sand-size particles are generated, the polar regions are too wet with methane for enough dry sediments to accumulate into dunes, but as the surface becomes drier toward the equator, fewer

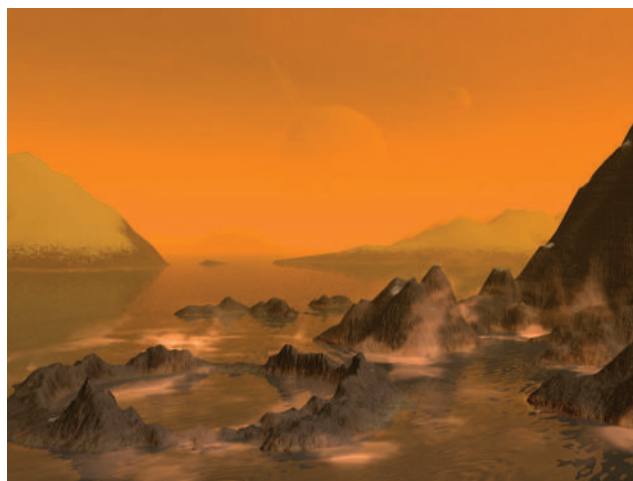


FIGURE 14. Artist's concept of methane-ethane lakes and cyanoacetylene snow-capped hills as viewed from the surface of Titan, with Saturn and Rhea in the background (modified from Stephan et al., 2009).

sediments bond with or sink into the regolith. This allows for surface accumulations in midlatitude and equatorial regions, where the sediments have been winnowed to a fairly uniform size (larger ones left at the poles; smaller ones entrained back into the atmosphere). These sands might be one long-sought ethane reservoir; they do form globe-encircling dune seas.

The mantling of the surface with atmospheric organics may be a global process, and the occasional low-latitude thunderstorm each century washes the upland deposits to lower elevations where the same erosional and winnowing processes occur. Indeed, as illustrated in Figures 7A and 10B, it is at the bright-dark terrain boundaries, interpreted to be changes in topographic slope, that the most spectral diversity in the 5 μm window is seen, and these locations are probably additional sites of organic sediment accumulation. The long-term atmospheric methane loss and conversion to higher weight carbon compounds mean that a deeper and abundant source of methane is resupplying the atmosphere for millions of years. Current models suggest convective overturn in the upper few hundreds of meters of a porous, possibly methane-enclathrated, upper regolith. But Titan's carbon cycle, as presented here and elsewhere (Atreya et al., 2006), may well turn out to be the most complex and dynamic one in the solar system (Figure 14).

Even with results from the Cassini mission, several future observations can be considered. Most importantly, a dedicated Titan orbiter is needed, but the only currently approved outer solar system mission by either NASA or ESA (European Space Agency) is to

the Jupiter/Europa system, and that will have a higher priority in the near future (a Saturn/Titan mission was the second choice). Ideally, a dedicated Titan mission would consist of an orbiter (including navigation and communication bus) coupled with a lander (and possibly rover or lake sampler) and a long-term atmospheric probe, perhaps a Montgolfier hot-air balloon, a highly efficient strategy in such a cold, dense, windy atmosphere (Lorenz, 2008). Tethered to the balloon would be an atmospheric monitor, continuously recording wind speed, direction, composition, etc., whereas the lander and/or rover and orbiter observe specific targets.

Essential to all these components would be an integrated observation strategy—similar instruments working over equivalent wavelength ranges so that all data sets could be rectified, coadded, and easily compared. Martian exploration is analogous here. It seems that each new set of observations at different wavelengths and/or resolution reveals a new and unknown Mars. Unlike travel to the red planet, multiple missions to Titan are even less likely than a single dedicated one; sending the most useful suite of instruments the first time is crucial. For instance, the 5 μm window through Titan's atmosphere is wide enough that a high-spectral resolution IR spectrometer spanning 4.8 to 5.6 μm could distinguish among most organic compounds, whose spectral responses are so variable in this wavelength region. A lander could simultaneously test the soils with a GCMS-type instrument that the orbiter uses while also drilling below the outer few centimeters to sample the crust not explored by IR imaging. The atmospheric balloon-tether probe would continuously monitor methane abundance, temperature, wind speed, etc., while imaging the surface with a similar spectrometer and sampling the atmosphere with its own mini-GCMS. Ideally, the orbiter also would continuously map the surface with radar from changing geometrical perspectives to build up global three-dimensional surface profiles with stereo imagery. In this way, a coordinated suite of observations could fully characterize Titan chemically and physically at many scales and truly assess the types and abundance of hydrocarbons and other organic compounds as they cycle among the multiple Titan reservoirs.

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