Volatile Origin and Cycles: Nitrogen and Methane,

S. K. Atreya, R. D. Lorenz, and J. H. Waite, in *Titan from Cassini-Huygens* (R.H. Brown et al., eds.), Chapter 7, pp 177-199, 2009, DOI 10.1007/978-1-4020-9215-2_7, Springer Dordrecht, Heidelberg-London-New York.

Chapter 7
Volatile Origin and Cycles: Nitrogen and Methane

Sushil K. Atreya, Ralph D. Lorenz, and J. Hunter Waite

Abstract The story of Titan's two most abundant volatile constituents, nitrogen and methane, is intertwined. The focus of this paper is the origin and evolution of Titan's nitrogen atmosphere and the cycle of methane from its production to destruction to replenishment. Relevant observational results from Cassini–Huygens, Voyager and the Earth as well as various hypotheses and models are reviewed. The origin of nitrogen by direct capture, and from dissociation of primordial nitrogen-bearing molecules, especially ammonia, by impact, photolysis, thermal and other processes is evaluated. Similarly, the origin of methane from Saturn's sub-nebula or by water-rock reactions in Titan's interior is reviewed. The role of methane in regulating Titan's climate is noted, and similarities and differences between the methane cycle in Titan's troposphere and the hydrological cycle on Earth are discussed. The fate of methane in the stratosphere and the upper atmosphere/ionosphere is examined in order to evaluate the possibility and extent of an ocean of ethane, requirement of methane replenishment, and the role of product aerosols in maintaining Titan's nitrogen atmosphere.

7.1 Historical Perspective: From Christiaan Huygens to Cassini–Huygens

Titan is unique in the solar system. Whereas satellites in general are not known for atmospheres, Titan is not only endowed with an atmosphere, it has a massive atmosphere with surface pressure exceeding that on Earth by 50%. Moreover, its atmosphere is largely made up of nitrogen (N_2). Its second most abundant constituent, methane (CH_4), displays a meteorological cycle similar to the hydrological cycle on Earth, complete with surface reservoirs, evaporation, clouds, rain, and dendritic channels presumably carved by the rain of methane. In Titan's stratosphere and the ionosphere, the two volatiles, nitrogen and methane, together create a complex web of chemical reactions. The resulting trace species condense or otherwise produce multiple layers of aerosols, filling Titan's atmosphere with photochemical smog and haze. The aerosols play a crucial role on Titan, however. They provide stratospheric warming, which is critical in preventing nitrogen from condensing.

The above modern-day view of Titan had its origins in 1655 when Christiaan Huygens discovered Titan – a large satellite, in geosynchronous orbit at 20.25 Saturn radii from the planet Saturn. First indication of an atmosphere around Titan began to emerge in 1908. José Comas Solá recorded limb darkening, which he attributed to the "existence of a strongly absorbing atmosphere around Titan". This was a remarkable finding for the time, considering Titan's angular size is only 0.1 arc sec, which is at the limit of the seeing capability of best ground-based telescopes. Yet Comas Solá was gifted with exceptional acuity, and his sketches (e.g. Lorenz 1997) of the Galilean satellites are broadly accurate, and he knew that Mars had no canals.

The first quantitative spectroscopic observations of Titan began in earnest in 1944 with Gerard Kuiper's detection of methane at 6190 Å in the visible and in the near-infrared. Kuiper (1944) derived 0.2 km-am for the methane abundance. Trafton (1972) detected methane in the $3\nu_3$ band of CH_4 at 1.1 μm, and arrived at a much greater abundance of 1.6 km-am, or 16 mb, considering self-broadening in a pure CH_4 atmosphere. An even greater surface pressure of 200 mb was suggested by Lutz et al. (1976) from their analysis of the weak methane bands in the visible where pressure broadening is not a complicating factor. However, they concluded that methane is a minor constituent of the atmosphere, with any number of cosmogonically abundant and stable constituents such as Ar, Ne or N_2 as possible candidates for the background gas. Lewis (1971) had previously speculated on the possibility of a nitrogen atmosphere on Titan, result-

---

S.K. Atreya (✉)
University of Michigan, Ann Arbor, MI, 48109-2143, USA
e-mail: atreya@umich.edu

R.D. Lorenz
Johns Hopkins University, Applied Physics Laboratory,
Laurel, MD, 20723, USA

J. Hunter Waite
South West Research Institute, San Antonio, TX, 78228, USA

R.H. Brown et al. (eds.), *Titan from Cassini-Huygens*,

ing from the photolysis of ammonia outgassed from the ices that were needed to explain Titan's low density. Danielson et al. (1973) analyzed the spectroscopic observations also, and concluded that the atmosphere was thin, comprising only a few millibars of CH_4. In the late 1970s, results of Titan's surface temperature began to emerge. Conklin et al. (1977) interpreted their 3 mm observations to imply a surface temperature of 200 K, which was surprisingly greater than Titan's black body radiation temperature of 82 K. This led Hunten (1978) to propose an atmosphere of 20 bar of N_2, whose pressure-induced opacity could explain the high surface temperature. In their pre-Voyager model, Atreya et al. (1978) calculated that approximately 20 bar of N_2 could be produced *initially* on primordial Titan, from the photolysis of ammonia (NH_3) during the satellite's accretionary heating phase. Ground-based observations could not detect nitrogen, as N_2 has no rotational-vibrational spectral lines due to dipole transitions. Thus, by the end of the 1970s the situation with Titan's basic characteristics was less than satisfactory – surface temperature ranged from 82 K to 200 K, surface pressure ranged from a few millibars to 20 bar, and the make up of the atmosphere from pure CH_4 to N_2 with traces of CH_4 and/or H_2 thrown in. This broad range defined the envelope of the engineering models used for guiding the Voyager 1 encounter with Titan.

On 12 November 1980, Voyager 1 flew past Titan at a distance of 6490 km (3915 km from surface). For the first time, it detected nitrogen, found trace quantities of methane in the stratosphere, a thick haze blanketing the satellite – which prevented composition and most other measurements below the lower stratosphere – a pressure of 1496 ± 20 mb and a temperature of 94 ± 0.7 K at the surface, as well as numerous minor constituents in the stratosphere, including C_2-hydrocarbons and nitriles (for a complete summary of the Voyager 1 and Voyager 2 findings, see Atreya 1986; Coustenis and Taylor 1999; Lorenz and Mitton 2008). N_2 was identified in its Rydberg, Lyman-Birge, and Lyman-Birge-Hopfield bands by the ultraviolet spectrometer (Broadfoot et al. 1981; Strobel and Shemansky 1982) but placed only an upper limit on the argon abundance (see Section 7.2.1).

The Voyager radio occultation experiment derived a mean molecular weight that was "consistent" with a pure nitrogen atmosphere, but the possibility of a small non-zero argon component could not be ruled out either (Eshleman 1982). This is because the radio occultation experiment derives the mean molecular weight, not composition. By itself, it yields only a *relative* pressure–temperature profile from a determination of the atmospheric refractivity. The refractivity of the atmosphere as a function of time (height) during occultation is derived from the angle of refraction of the received frequency of the radio signal (S and X bands, respectively at 2.293 GHz or 13 cm, and 8.6 GHz or 3.6 cm on Voyager). The relative pressure–temperature profile can then be obtained from refractivity, which is related to the atmospheric composition (mean molecular weight). In order to obtain the absolute pressure–temperature profile, an *independent* knowledge of either the temperature or the composition is required (Eshleman et al. 1977). The composition of the troposphere was not constrained at the time of the Voyager measurements. Therefore, the radio occultation experiments relied on the temperature measured by the Voyager infrared spectrometer at 1 mb in the stratosphere as a reference temperature. Any uncertainty in the reference value would propagate to the lower levels. This resulted in a slight uncertainty in the tropospheric and the surface temperatures of Titan. The resulting surface temperature had a range from 93 K to 95 K. The corresponding mean molecular weights were 27.8 and 28.3, respectively (Eshleman et al. 1983; Lindal et al. 1983). The average of the two values led Eshleman (1982) to conclude that the mean molecular weight was consistent with a pure N_2 atmosphere. On the other hand, the higher value (28.3) could accommodate up to 4% Ar, whereas the smaller value (27.8) could be explained by including 2% CH_4. Since the composition of the troposphere was unknown, even the average value of the mean molecular weight (28) could accommodate within a small range various proportions of Ar (36 AMU) and CH_4 (16 AMU). Less than a year after the Voyager 1 flyby of Titan, Voyager 2 observed Titan on 26 August 1981, but from a much greater distance of 666,190 km. Despite its remoteness, Voyager 2 yielded valuable data on Titan's multiple haze layers and the photochemical species.

The Voyager flybys gave a fleeting but tantalizing glimpse into the unusual and complex world of Titan. Their findings were instrumental in establishing the importance of studying Titan in detail, for it may even provide clues to the way Earth was before life emerged. The detailed composition of the gases and the aerosols, what lay beneath the thick haze, and the nature and composition of the surface were some of the mysteries of the time that could be revealed only by returning to Titan with an orbiter and an entry probe. A grass-roots effort by scientists in the United States and Europe in the mid 1980s culminated in what we know now as the Cassini–Huygens mission, a joint undertaking of NASA, ESA and ASI (Italian Space Agency). The first ever in situ exploration of Titan was carried out by the ESA-furnished Huygens probe. After its release from the Cassini orbiter on 25 December 2004, the Huygens probe reached Titan on 14 January 2005, and began a historic 148-min descent through the moon's atmosphere and landed on the surface. Although not designed as a lander mission, the probe continued to send the composition data to the Cassini orbiter for another 72 min upon reaching the surface, and the carrier signal from the probe was recorded by ground-based radio telescopes for yet another 2 h and 2 min. This was a remarkable feat, considering the Huygens probe was expected to send data from the surface for only 3 min. Titan is also being explored remotely by the Cassini orbiter in the multiple close flybys of the moon since the arrival of the spacecraft at the Saturn System on 1 July 2004. As a consequence of these in situ and remote observations, new and vastly improved data have become available which form much of the basis of the discussions in this chapter.

7.2 Origin and Evolution of Titan's Nitrogen Atmosphere

Two distinct possibilities existed for the origin of Titan's nitrogen before the Voyager observations: (1) N_2 is primordial, i.e. it was captured directly as N_2, or (2) N_2 is secondary, formed from the dissociation of ammonia, i.e. NH_3, not N_2, is primordial. The Voyager observations did not yield the data that could unambiguously answer the question of the origin of nitrogen on Titan. We had to wait another 25 years for Cassini–Huygens to settle the issue. In the following paragraphs, we review the various possibilities and present the current status of the origin of nitrogen on Titan.

7.2.1 Direct Capture of N_2

Lewis and Prinn (1980) suggested that the dominant form of nitrogen in the solar nebula was N_2. Owen (1982) initially proposed that Titan's atmosphere resulted from the direct capture of the nebular material. In that case, its Ne/N_2 should be solar, or 6.2 (using $N/H = 6.76 \times 10^{-5}$ for the solar nitrogen from Grevesse et al. 2005, but scaling the neon value up by 2.7 to account for the newer x-ray stellar data of Drake and Testa 2005, so that solar $Ne/H = 2.10 \times 10^{-4}$, as discussed in Table 1 of Atreya 2007b). However, neon has never been detected in Titan's atmosphere. The Voyager ultraviolet spectrometer (UVS) observations of Ne at 736 Å yielded a very low *upper limit* of 0.01 for Ne/N_2 above Titan's homopause (Strobel and Shemansky 1982). In the well-mixed homosphere, the Ne/N_2 would be even smaller, not greater, than this upper limit of 0.01. This is because the concentration of species in the diffusive separation region above the homopause is controlled by their individual molecular weights (or, scale heights). This would result in greater mixing ratio of a lighter species, such as Ne (20 AMU, compared to the heavier background of ~28 AMU) above the homopause than in the well-mixed atmosphere below. Thus the Voyager UVS data imply that the Ne/N_2 mixing ratio on Titan is well below the solar value of 6.2. The same conclusion is reached by examining the tropospheric mean molecular weight, M. As determined by the Voyager radio occultation experiment, M is very close to 28 (Eshleman 1982), which also does not permit any significant quantities of neon to be present in the atmosphere. Owen (1982) surmised that the way out of the neon dilemma is that N_2 was initially trapped in a hydrate, together with CH_4 and Ar. This idea was based on an earlier work of Miller (1961) who proposed that the ice in Saturn's moons is largely in the form of a methane hydrate ($CH_4 \cdot 6H_2O$), and of Lewis (1973) who suggested that the methane hydrate in the cooling solar nebula goes to completion at 60 K. Neon is highly volatile, and even at that temperature its vapor pressure is 40 bar, so that it could not have been trapped in the hydrate. Thus the non-detection of neon was not surprising, according to Owen (1982).

If the above scenario of Titan's nitrogen atmosphere forming from the degassing of N_2-CH_4-Ar containing hydrate is correct, it would imply that solar proportions of argon and carbon must be present. The solar $^{36}Ar/N_2$ ratio is 0.11 (solar $N/H = 6.76 \times 10^{-5}$ from Grevesse et al. (2005), but $Ar/H = 3.62 \times 10^{-6}$ from Anders and Grevesse (1989), as the former used oxygen as proxy to derive Ar, and Ne whose correction is given in the previous paragraph). The Voyager UVS observations near a resonance feature of argon at 1048 Å yield an upper limit of 0.06 for $^{36}Ar/N_2$ above the homopause (Strobel and Shemansky 1982). Unlike neon, the argon mole fraction could be larger in the homosphere. This is because ^{36}Ar is heavier than the background atmosphere of N_2, which would lead to a drop in the mole fraction of ^{36}Ar above the homopause due to molecular diffusive separation. Thus, the Voyager data on argon could neither support nor discard the direct capture of N_2 hypothesis of the origin of Titan's atmosphere. The interpretation based on CH_4/N_2 was similarly ambiguous. The solar C/N is 4.07 (based on solar C/H and N/H from Grevesse et al. (2005)). The primordial carbon could be in the form of CO, CO_2, carbon grains or organic material. CO and CO_2 were found to be quite small in the atmosphere by Voyager. If most of the carbon were tied up in methane, then CH_4/N_2 would be solar, or ~8. If indeed methane was so abundant on Titan, a huge reservoir of liquid methane would be present on the surface (the methane triple point of 90.67 K is close to Titan's surface temperature of 94 K). This would lead to the collapse of the atmosphere, as nitrogen gas readily dissolves in liquid methane. The Voyager Infrared Interferometer Spectrometer Radiometer (IRIS) observations yielded $CH_4/N_2 = 0.02$ at 100 mbar in the lower stratosphere (Hanel et al. 1981). Although no direct measurements of methane could be made below the tropopause, using the IRIS data and the Voyager radio refractivity data Samuelson et al. (1997) derived a 50% supersaturation of CH_4 in the upper troposphere and a CH_4 mole fraction close to 6% near the surface.

Lacking the critical data on the distribution of methane in the troposphere and the mole fraction of primordial argon in the homosphere, the Voyager observations were not able to settle the question of the origin of nitrogen on Titan. There were still two competing hypotheses (a) the pre-Voyager model of Atreya et al. (1978) and Hunten (1978) where nitrogen was acquired from the Saturnian subnebula in the form of NH_3, whose subsequent photolysis led to the formation of an N_2 atmosphere in Titan's warmer past, and (b) the post-Voyager model of Owen (1982) according to which nitrogen was captured directly. In a later publication, Owen (2000), however, agreed with the model of the formation of N_2 from NH_3 photolysis, considering that direct trapping of N_2 requires the temperature of planetesimals to be below 30 K, which is far too low for the Saturn subnebula where Titan formed.

7.2.2 N_2 as a Secondary Atmosphere from Primordial NH_3

Speculations of a nitrogen atmosphere resulting from the photolysis of ammonia were made as early as 1971 (Lewis 1971). Considering Titan's density of 1.8 g/cm^3, it is believed that Titan is made of roughly 40% ice by mass, and the rest rock. A small fraction of the ice is expected to have been in the form of ammonia ice initially. Prinn and Fegley (1981) argued that kinetic inhibition to the conversion of N_2 to NH_3 in the nebula and the subnebulae of the outer planets was minimal. Thus, NH_3, not N_2, was the dominant form of nitrogen in the Saturnian subnebula where Titan formed. Even before this reaffirmation, the idea of Titan's nitrogen as being a secondary atmosphere had caught on (Section 7.1). Three possibilities exist for producing N_2 from the dissociation of NH_3: photolysis, impact, and endogenic.

7.2.2.1 N_2 from NH_3 Photolysis

During the accretionary heating phase the volatiles were released from the ices to the atmosphere of Titan. Lunine and Stevenson (1987) suggested an atmosphere that contained copious quantities of methane, ammonia and water vapor. Atreya et al. (1978) developed a photochemical model, according to which the photodissociation of NH_3 takes place at wavelengths below 300 nm, and peaking at ~195 nm. Their photochemical scheme for ammonia is shown in Fig. 7.1. The photolysis of ammonia produces amidogen radicals (NH_2). About a third of ammonia so destroyed is recycled by the reaction of these radicals with hydrogen atoms. Nearly two-thirds of the NH_2 radicals recombine to form hydrazine (N_2H_4) molecules (Fig. 7.1). Hydrazine acts essentially as the rate limiting step in the subsequent production of N_2. If the temperature is sufficiently warm, N_2H_4 remains in the vapor phase and is dissociated by the solar ultraviolet flux to form hydrazyl radicals (N_2H_3). The self-recombination reaction of N_2H_3 leads to the production of N_2 on Titan (Fig. 7.1). If the temperature is too low, little NH_3 would be present in the form of vapor, and whatever small amount of hydrazine is formed from it would condense and snow out of the atmosphere, preventing further chemistry and production of N_2 (impacts are ineffective in converting NH_3 or N_2H_4 in any phase to N_2, as discussed in the next section). Atreya et al. (1978) found that the ideal temperature range is determined not just by the thermodynamic phase of N_2H_4, but also the relative humidities of water and ammonia. At relatively high temperatures, a large quantity of water vapor coexists with the ammonia vapor. The photolysis of H_2O vapor results in the highly reactive hydroxyl molecules (OH). The latter react with NH_2, severely limiting the formation of N_2H_4 and the subsequent production of N_2. At low temperatures, hydrazine condenses and N_2 does not form, as discussed above. With these considerations, Atreya et al. (1978) determined that the ideal range of temperatures is 150–200 K for the production of nitrogen from ammonia on Titan. Allowing for the increased solar ultraviolet flux in the pre-main sequence of the Sun (Zahnle and Walker 1982), Atreya et al. (1978) and Atreya (1986) calculated that up to 20 bar of N_2 could be produced in less than 2 Myr on primordial Titan initially, i.e. not accounting for subsequent N_2 escape.

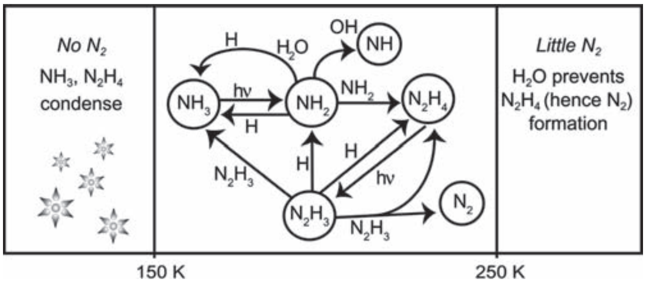

Fig. 7.1 Photochemical production of N_2 from NH_3 in Titan's primordial atmosphere (updated from Atreya et al. 1978). Below 150 K, little NH_3 is in vapor phase, and whatever small intermediate product hydrazine (N_2H_4) forms from it condenses, thus preventing N_2 formation. Above 250 K, water vapor has sufficiently large vapor pressure, so that OH from its photolysis reacts with NH_2 and NH_3 drastically decreasing the subsequent yield of N_2, despite some recycling of NH_3 by H from H_2O

Atreya et al. (1978) assumed an isothermal primordial atmosphere in their nitrogen evolution model. For more realistic time scales for the formation of nitrogen, possible vertical gradients in the atmospheric temperature should be taken into account. Considering a range of possible abundances of H_2O, CH_4 and NH_3 on primordial Titan (Lunine and Stevenson 1987), Adams (2006) developed a radiative transfer model for primordial Titan. Additional constraints on the pre-main sequence solar flux from x-ray to the infrared were included, based on the work of Ribas et al. (2005) and Zahnle and Walker (1982). The NH_3 photochemical scheme used was similar to the one used by Atreya et al. (1978). The use of the atmospheric temperature structure derived from radiative transfer led to longer time scales for the generation of nitrogen than the isothermal model of Atreya et al. (1978). The longer time scales are a consequence of the much smaller abundance of ammonia available in the photochemical regime of Titan's stratosphere because of cold trapping of the gas at the tropopause, which was not an issue for the isothermal models with temperatures far greater than the tropopause values. For example, current models require a little over 30 Myr to produce 10 bar of N_2 on primordial Titan. This will be discussed further in Section 7.2.2.4.

7.2.2.2 N_2 from Impacts

High velocity impacts were suggested by Jones and Lewis (1987) and McKay et al. (1988) as a probable cause of Titan's atmosphere. Considering the possibility of shock-induced dissociation of ammonia from high velocity impacts during Titan's accretion, McKay et al. (1988) carried out a laboratory simulation experiment using a 1.06-µm Nd-YAG laser on a mixture of NH_3 and CH_4. This process generated relatively large quantities of N_2. For a simplified accretion scenario, they could produce up to 25 bar on N_2 in the late stage of Titan's accretion. Although an attractive idea, the shock-induced production of N_2 encounters several difficulties. Nitrogen was not the only molecule produced in their experiment. The total yield of numerous hydrocarbons was even greater than N_2, i.e. up to 100 bar. H_2 production was nearly 4 bar. The H_2 amounts are so enormous that they exceed the present H_2 abundance a thousand-fold, unless the hydrogen escape rate throughout Titan's geologic history was also improbably large, exceeding 1000 times the present value (Waite et al. 2005) of 6×10^9 cm^{-2} s^{-1} from the Ion and Neutral Mass Spectrometer (INMS). We are not aware of any mechanisms that could sustain such a rapid loss rate of H_2 from Titan. The large hydrocarbon production may also pose a further challenge, as most of them would end on the surface, depositing a layer 15 km thick. There is little direct evidence of such a thick aerosol layer on Titan's surface, although a substantial organic component to the surface material on Titan cannot be ruled out. Finally, the shock experiment did not include water vapor. As we discussed in the context of NH_3 photolysis, presence of water vapor would inhibit N_2 production (Section 7.2.1.1), especially in the cooling phase of the shock.

A variation on the impact-induced delivery of Titan's atmosphere was proposed by Griffith and Zahnle (1995). These authors suggested that cometary impacts resulted in Titan's nitrogen atmosphere. In this scenario, the source of nitrogen lies in the comets that condense out of the solar nebula, not in the planetesimals that condensed from the Saturnian subnebula to accrete Titan. In the cometary hypothesis, nitrogen is believed to have been supplied originally in the form of complex organic molecules or molecular nitrogen. If comets were indeed the source of Titan's atmosphere, the D/H ratio on Titan should resemble that in comets. Although the D/H ratio has been determined in the ice of only a handful of comets (Halley – Eberhardt et al. 1995; Balsiger et al. 1995; Hyakutake – Bockelee-Morvan et al. 1998; and Hale-Bopp – Meier et al. 1998a), in each case its value was found to be larger than that in Titan's hydrogen reservoirs. The average value is found to be $(3.16 \pm 0.34) \times 10^{-4}$, which is greater than the D/H ratio either from CH_3D $(1.3\ (+0.15, -0.11) \times 10^{-4}$; Bézard et al. 2007; Coustenis et al. 2007) or H_2 ($(2.3 \pm 0.5) \times 10^{-4}$, Niemann et al. 2005) in Titan's troposphere. The cometary D/H has also been determined in one organic compound, HCN, and the value $(2.3 \pm 0.4) \times 10^{-3}$ (Meier et al. 1998b) is more than ten times greater than the above values on Titan. Thus, comets do not appear to be the main source of Titan's atmosphere. Finally, direct infusion of N_2 by comets is unlikely, as comets are deficient in N_2 since the temperature in the region of their condensation between the orbits of Uranus and Neptune was too high (50–60 K) for trapping nitrogen. We discuss the cometary hypothesis further in Section 7.2.2.4.

7.2.2.3 Endogenic N_2

Matson et al. (2007) have surmised that the dissociation of ammonia in Titan's interior may have produced some, if not all, of Titan's nitrogen, especially if catalyzed by clay or metals. If Titan formed 2.5 to 5.0 Myr after the calcium–aluminum inclusions (CAIs) were created (as suggested for Iapetus, Castillo-Rogez et al. 2007) then differentiation occurred early and a stable core formed. During differentiation, heat from short-lived radioisotope decay and gravitational energy enabled rapid serpentinization of most of the silicate phase. (In serpentinization, water-rock reactions comprising oxidation and hydrolysis of low-silica and ultramafic silicate rocks such as olivine or pyroxene occurs, resulting in large quantities of heat, together with molecular hydrogen, serpentine, brucite and other minerals, as discussed in more detail in Section 7.3.5.) Water and chemical reactants were trapped by the hydrated silicate that accumulates into the core. After a few hundred million years, temperatures become high enough for ammonia decomposition to take place, producing molecular nitrogen and hydrogen. As Titan cooled, nitrogen was trapped in ice as a clathrate-hydrate. The outgassing of nitrogen occurred from time to time when the clathrates were destabilized. This scenario predicts that nitrogen is still being released from the interior. This would lead to a replenishment of nitrogen lost to space, and resetting of the $^{14}N/^{15}N$ isotope ratio to terrestrial or near-terrestrial value, as is the case with $^{12}C/^{13}C$ in the CH_4

that is also believed to be released from Titan's interior to replenish the methane destroyed photochemically. The present data yield near-terrestrial $^{12}C/^{13}C$, whereas $^{14}N/^{15}N$ is severely depleted. At the moment, there is no simple solution to the isotope dilemma. In view of the above, the endogenic production of N_2 should be considered as tentative for the time being until further research is carried out. It is important to recognize also that any endogenic source would only supplement, not replace, the photolytic origin of nitrogen. This is because warmer Titan in the past would have certainly put large quantities of NH_3 vapor into the atmosphere, which could not have escaped photochemical destruction to produce nitrogen.

7.2.2.4 Origin and Evolution of Titan's Nitrogen Atmosphere: The Cassini–Huygens Perspective

The Cassini–Huygens Mission collected the data that finally helped settle the question of the origin and evolution of the atmosphere on Titan. Two sets of measurements are particularly relevant: the primordial argon abundance, and the abundance of the nitrogen and carbon isotopes. None were available until they were done by Cassini–Huygens in 2005. The abundance of primordial argon, ^{36}Ar, can shed light on the form of nitrogen acquired by Titan originally. The nitrogen isotope ratio is important for determining the mass of N_2 that must be formed originally to explain the present N_2 amount in the atmosphere. And, the comparison of the nitrogen isotope abundances along with the carbon isotope abundances provides clues to the evolutionary history of the gas. The Gas Chromatograph Mass Spectrometer (GCMS) on the Huygens probe measured the $^{14}N/^{15}N$ ratio in the troposphere of Titan by analyzing the N_2 data at 28 and 29 Da, i.e. $^{14}N^{14}N$ and $^{15}N^{14}N$ (Niemann et al. 2005). Similarly, the Ion and Neutral Mass Spectrometer on the Cassini orbiter measured the ratio at ~1000 km altitude in the thermosphere (Waite et al. 2005). Likewise, the $^{12}C/^{13}C$ was measured by both instruments from $^{12}CH_4$ and $^{13}CH_4$. Primordial argon, ^{36}Ar, as well as radiogenic argon, ^{40}Ar, produced from the radioactive decay of potassium, ^{40}K, in the rocks in the core, were also measured by the INMS and the GCMS. Table 7.1 lists these values. A comparison to the terrestrial values is given also, using the GCMS data. We use the GCMS data for the mixed atmosphere for this comparison instead of the INMS data, as the latter were measured in the thermosphere (~1000 km) where they are diffusively separated, so their extrapolation to well-mixed atmosphere is somewhat model-dependent.

The mole fraction of ^{36}Ar is 2.8×10^{-7} (Table 7.1), which is well below the solar $^{36}Ar/N_2$ value of 0.11 (Section 7.2.1.1), and ^{38}Ar was not even detected. This implies that nitrogen was not captured directly as N_2, nor did it arrive as N_2 from the subnebula, but as another nitrogen compound, most likely ammonia (NH_3). Had Titan acquired its nitrogen in the form of N_2, it would have also accreted large (i.e., solar) quantities of primordial argon, i.e. nearly 11% by volume, or over 300,000 times greater than measured, and over 1 million times greater when N_2 escape is included – see below. During the accretionary heating phase, ammonia should have been present as vapor in the atmosphere of Titan. Subsequent photolysis of this ammonia then led to the nitrogen we find on Titan today, as discussed in Section 7.2.2.1. The $^{14}N/^{15}N$ is found to be 183 in Titan's troposphere, which is ~0.67 times the value in the terrestrial atmosphere (Table 7.1). This implies loss of nitrogen from the atmosphere to space

Table 7.1 $^{12}C/^{13}C$, $^{14}N/^{15}N$, D/H ratios, and the ^{36}Ar, ^{40}Ar, Kr, and Xe mole fractions (f)

Ratio	GCMS[a] in homosphere	INMS[b] in heterosphere	Titan/Earth(c) using GCMS
$^{14}N/^{15}N$	183 ± 5 (from N_2)	240 ± 20 (1,450 km) 155 ± 5 (1,000 km) 143 ± 5 (extrapolated to surface)	0.67
$^{12}C/^{13}C$	82.3 ± 1	118 ± 10 (1,450 km) 83 ± 5 (1,000 km) 81.0 (extrapolated to surface)	0.92
D/H	$(2.3 \pm 0.5) \times 10^{-4}$		1.44
$f\,^{36}Ar$	$(2.8 \pm 0.3) \times 10^{-7}$	$<(4 \pm 1) \times 10^{-7}$	7.0×10^{-3}
$f\,^{40}Ar$	$(4.3 \pm 0.1) \times 10^{-5}$	$(1.26 \pm 0.05) \times 10^{-5}$ (1050 km)	3.6×10^{-3}
f Kr, and f Xe	$<10^{-8}$	Not measured	

[a] GCMS measurements are from the Huygens probe from 146 km to the surface. Errors quoted represent 1 standard deviation (Niemann et al. 2005). The GCMS determined the D/H from HD and H_2. The value derived from the Cassini CIRS data using CH_3D and CH_4 is D/H = 1.3×10^{-4} (Bézard et al. 2007; Coustenis et al. 2007). The $^{14}N/^{15}N$ from ground-based submillimeter observation of HCN is 60 ± 6 (Marten et al. 2002), confirmed by Cassini/CIRS HCN data (Vinatier et al. 2007). This is or about a factor of four less than the terrestrial value of 272, most likely due to the fractionation in photochemical production of HCN (Niemann et al. 2005).

[b] INMS values are from Mandt et al. (2009), except for ^{40}Ar (Magee et al. 2009), revised from the values published by Waite et al. (2005) from the first flyby of the Cassini orbiter between 1174 km and 3000 km above Titan's surface.

[c] The terrestrial inorganic $^{12}C/^{13}C$ = 89.45, is the Vienna Pee Dee Belemnite Standard.

in Titan's past. Lammer et al. (2000) found that non-thermal escape due to solar wind ion pick-up and atmospheric sputtering could have resulted in a loss of up to 40 bar of N_2. However, this conclusion was based on a pre-Cassini–Huygens $^{14}N/^{15}N = 60 \pm 6$ derived from HCN (Marten et al. 2002). That nitrogen isotope ratio is a factor of three smaller than that in the principal reservoir of nitrogen, N_2 (Table 7.1), most likely due to fractionation in the process of photochemical formation of HCN.

From a comparison of the current $^{14}N/^{15}N = 183$ in N_2 in Titan's atmosphere measured by the Huygens GCMS with the terrestrial $^{14}N/^{15}N$, Niemann et al. (2005) estimate that the mass of primitive atmosphere of Titan was between two and ten times today's value and perhaps several times the present mass was lost over geologic time, based on a model of diffusive separation of ^{15}N from ^{14}N by Lunine et al. (1999). Lammer et al. (2000) concur that diffusive separation is an important process, but ion pick-up and atmospheric sputtering caused by a high solar wind outflow during a Post T-Tauri phase of the Sun is required to explain the large nitrogen isotope anomaly. They estimate a loss of roughly 10 bar of atmosphere from Titan due to this process in the first 500 Myr, in general agreement with the earlier finding (Lunine et al. 1999). (Note that the mass loss estimates in both Lunine et al. and Lammer et al. were based on the then available smaller $^{14}N/^{15}N = 60 \pm 6$ from HCN, but the mass loss numbers given here have been scaled to reflect the larger GCMS value of 183.) Comparing the GCMS nitrogen isotope ratio with the terrestrial value implies that Titan would have started out with a nitrogen pressure of between 5 and 10 bar in its primordial atmosphere, in order to explain the present surface pressure of 1.5 bar. Considering a radiative transfer model for the primordial atmosphere of Titan, prevalent solar fluxes, and the photochemical scheme of Atreya et al. (1978) and Atreya (1986) for the production of N_2 from NH_3 (Section 7.2.2.1), Adams (2006) calculated that it would take, respectively, 17 and 33 Myr to accumulate 5 and 10 bar of N_2 on primordial Titan. The time scale could be as low as 13–25 Myr for 5–10 bar, if the methane abundance was 30% lower, because of the role of CH_4 in radiative transfer. As we discussed in Section 7.2.2.1, the ideal temperature range for photochemical conversion of NH_3 to N_2 is between 150 and 250 K. Post-accretionary evolution models show that Titan's temperature was in this range for 100–200 Myr (Lunine and Stevenson 1985), which is more than adequate for producing the above initial inventory of nitrogen, even allowing for uncertainties in the primordial atmosphere models. If needed, the ammonia photolysis model is also capable of accommodating even much greater loss of nitrogen than the above 3–8 bar, considering the long duration of ideal temperatures for photolysis on primordial Titan.

The nitrogen isotope ratio in Titan's atmosphere is also remarkable from another point of view. It seems to place Titan in the same family of solar system objects as the terrestrial planets, in so far as the origin of nitrogen is concerned. Later we will see the similarities extend beyond nitrogen. In the right panel of Fig. 7.2, we illustrate this point by showing a comparison between Titan's $^{15}N/^{14}N$ isotope ratio with that of Venus, Mars and the Earth. The $^{15}N/^{14}N$ ratio in the atmosphere of Mars is larger than the solid Mars value as measured in the AL84001 meteorite, but is consistent with it after escape of nitrogen from the atmosphere is accounted for. Thus, the three terrestrial planets, Venus, Earth and (solid) Mars, have very similar $^{15}N/^{14}N$ ratios. The $^{15}N/^{14}N$ ratio of Titan would also be similar to the terrestrial planet value if Titan lost some nitrogen as discussed above. The nitrogen in the atmospheres of Venus (3.5% by volume), Mars (2.7%) and the Earth (78%) is also secondary, i.e. it formed from the dissociation of a nitrogen molecule, most likely ammonia, in the early stages of planetary evolution. The Cassini–Huygens observations show that similar to the terrestrial planets, Titan's nitrogen atmosphere is also secondary.

Finally, a comparison of Titan's nitrogen isotope abundance with that on comets, solar wind and other primordial sources (left panel of Fig. 7.2) provides further constraints to the origin of nitrogen. Very few measurements exist for the comets, however. Furthermore, the nitrogen isotopes in more

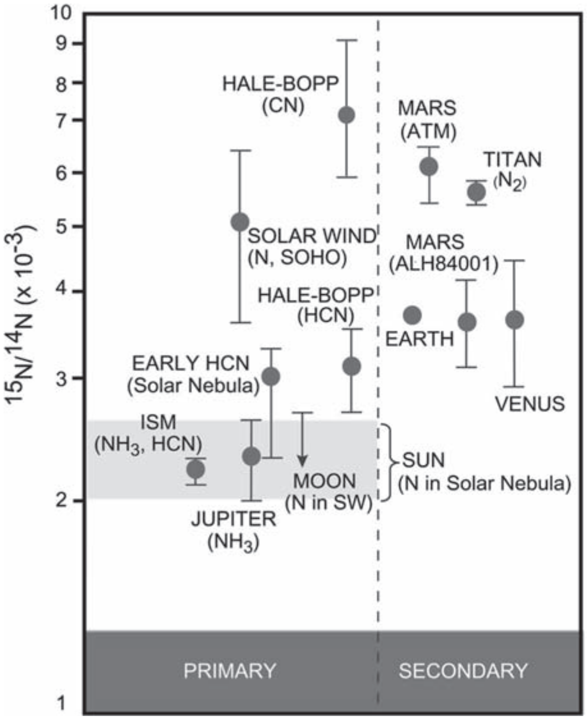

Fig. 7.2 Nitrogen isotope ratio in Titan's atmosphere compared with those on the terrestrial planets, and primary sources, including the interstellar medium (ISM), Sun (SW: solar wind, SOHO: Solar and Heliospheric Observatory), Jupiter (which represents the protosolar value) and comet Hale-Bopp. For Mars, two values are shown, in the atmosphere (ATM) and Allan Hills meteorite (ALH84001); the latter presumably represents the solid Mars value (prepared in consultation with Paul R. Mahaffy)

than one molecule (two) nitrogen containing molecules have been determined for only one comet so far. Submillimeter observations of HCN in comet Hale-Bopp yield $^{14}N/^{15}N = 323 \pm 46$, or $^{15}N/^{14}N = 3.10 \times 10^{-3}$ for the central value (Jewitt et al. 1997). Another observation of the same comet gives a nearly identical value of 330 for $^{14}N/^{15}N$ (or, 3.03×10^{-3} for $^{15}N/^{14}N$) from HCN (Ziurys et al. 1999), which is close to the terrestrial value of $^{14}N/^{15}N = 272$ (or, 3.68×10^{-3} for $^{15}N/^{14}N$). On the other hand, optical data yield an $^{14}N/^{15}N = 140 \pm 30$ from CN in comets Hale-Bopp, LINEAR and a dozen other comets (Arpigny et al. 2003; Hutsemékers et al. 2005). Waite et al. (2009) and Mandt et al. (2009) propose a cometary, rather than the subnebular (NH_3), origin for Titan's N_2, considering that the revised INMS value of $^{14}N/^{15}N = 143 \pm 5$ in the homosphere of Titan matches the value of this ratio in the CN of a dozen comets. This is an interesting alternative, but several caveats should be noted. First, the INMS value of $^{14}N/^{15}N$ in the homosphere (143) is model-dependent, as it is derived by extrapolating the value measured in the heterosphere (above 900 km, where $^{14}N/^{15}N = 188$), where diffusive separation dominates. Second, the derived INMS value for the homosphere (143) differs from the in situ determination of $^{14}N/^{15}N = 183$ directly in the homosphere by the Huygens GCMS. The GCMS value does not resemble the cometary $^{14}N/^{15}N$, being greater than that from CN and less than that from HCN. Third, the cometary $^{14}N/^{15}N$ ratio used for comparing the INMS derived $^{14}N/^{15}N$ for Titan's homosphere is not from the principal reservoir of nitrogen on comets, ammonia, or even the next most abundant one, HCN, but from a tertiary product, CN. The $^{14}N/^{15}N$ in HCN is more than twice that from CN in comet Hale-Bopp, the only comet for which the ratio has been determined in both HCN and CN ($^{14}N/^{15}N$ from NH_3 is not yet available, but may be greater than that in HCN due to photofractionation). Fourth, it would take an unrealistically large number of impacts of comets to deliver the amount of nitrogen present on Titan. Finally, such impacts, or impacts of smaller number of larger comets delivering equivalent amount of N_2, would introduce excessive amounts of H_2 into Titan's atmosphere and result in a D/H value different from that observed on Titan, as discussed in Section 7.2.2.2. The cometary nitrogen reservoir and its potential for delivering N_2 to Titan (third and fourth points above) are further elaborated in the following paragraphs.

The dominant nitrogen bearing molecule on comets is ammonia, whose abundance is 0.5–1.5% relative to water (Bockelee-Morvan et al. 2004). The nitrogen isotope ratio in NH_3 is not measured. However, experience shows that $^{14}N/^{15}N$ fractionation occurs in photochemistry, so that the ratio is smaller in the product than in the parent. This would imply that the $^{14}N/^{15}N$ in NH_3 of comets might be greater than that in HCN, a product of the chemistry between NH_3 and CH_4 of comets. $^{14}N/^{15}N = 323$ from HCN in comet Hale-Bopp, the only comet in which the ratio has been determined. The cometary $^{14}N/^{15}N$ ratio from HCN is a factor of 2.3 *greater* than the INMS value for Titan's homosphere (143). On the other hand, $^{14}N/^{15}N = 140 \pm 30$ in CN of certain comets is similar to the extrapolated INMS value for the homosphere of Titan. Incidentally, photochemical fractionation of nitrogen isotopes is evident in comets as it is on Titan. The $^{14}N/^{15}N$ ratio in the cometary CN is a factor of 2.3 smaller than that in HCN; CN being a photoproduct of HCN (Hutsemékers et al. 2005; Ziurys et al. 1999). Similarly, the $^{14}N/^{15}N$ ratio in Titan's main (parent) nitrogen reservoir, N_2 (143, using the revised INMS value), is also 2.3 times the value derived from HCN (60), a photochemical product of the N_2-CH_4 chemistry. If comets were indeed the source of Titan's nitrogen, the nitrogen isotope ratio in its atmosphere should reflect that in the dominant nitrogen bearing molecules in the comet, NH_3 and HCN, not CN. The INMS $^{14}N/^{15}N$ ratio is a factor of 2.3 smaller than that in the cometary HCN, and probably even less compared to that in the cometary NH_3. If, for some mysterious reason, CN of comets were still responsible for producing Titan's N_2, the paragraph below gives an estimate of the magnitude of required cometary impacts.

In comets, the abundance of HCN is 0.1% relative to H_2O (Bockelee-Morvan et al. 2004). The abundance of CN has not been determined, but is expected to be much smaller than this, being a product of HCN. For example, Wilson and Atreya (2004) find $CN/HCN = 10^{-3}$ from their photochemical model of Titan's atmosphere. In the most optimistic, but clearly unrealistic, scenario where *all* of the cometary HCN was converted to CN, the abundance of CN would be same as HCN, or 0.1% relative to water. A typical comet of 2 km diameter would then deliver 4×10^9 kg of CN to Titan, taking the comet density to be same as that of water ice. The amount of N_2 in Titan's atmosphere today is 9×10^{18} kg, based on a 1500 mbar atmosphere containing 95% N_2 and 5% CH_4. Assuming that *all* of the cometary CN was converted to N_2 upon the comet's impact, again a stretch, it would take a staggering two billion 2 km diameter comets to deliver the amount of nitrogen currently present on Titan. In reality the number would be far greater. Since CN is expected to be only a small fraction of HCN, that not all of the CN is going to end up in N_2, and that the starting inventory of nitrogen was perhaps three to five times greater than that present on Titan today, the number of comets would easily exceed a trillion comets. Fewer, but bigger (than 2-km), comets delivering an equivalent amount of N_2 could be envisioned also. However, cometary impacts, whether in the form of large comets or smaller ones, whether recent or in the past, including those in the purported Late Heavy Bombardment between 3.8 and 4.1 Gyr ago, etc., would also deliver excessive H_2 and produce too large a D/H ratio, etc., as mentioned previously in this section and discussed in Section 7.2.2.2. It should be noted also that the probability of a comet striking

Titan is low. For example, the probability of a comet striking Mars, a somewhat larger object, is only once in 62 Myr.

In summary, photolysis of ammonia on primordial Titan is found to be the most robust mechanism for producing Titan's nitrogen atmosphere. Nevertheless, further measurement of the chemical composition and isotope abundances of nitrogen and other elements in a multitude of comets together with modeling will benefit our understanding of the contribution of comets to the make-up of the planets and satellites in the solar system.

7.3 The Cycle of Methane on Titan

The maintenance of a stable atmosphere of nitrogen on Titan is critically dependent on the warming resulting from the presence of its second most abundant atmospheric constituent, methane. In the absence of methane, Titan's nitrogen would condense and the atmosphere would collapse (Lorenz et al. 1997a, 1999). The photochemistry of methane produces hazes and molecular hydrogen, amongst other products. The hazes absorb the incoming solar infrared radiation and heat the stratosphere. The collision-induced opacity due to the H_2-N_2, CH_4-N_2 and N_2-N_2 collisions raises the temperature below. The resulting methane initiated warming of the atmosphere is crucial for preventing nitrogen from condensing out from the atmosphere as droplets. On the other hand, the stability of methane itself is not a given. Methane has a meteorological cycle in the troposphere that could lead to its loss to the interior, if only temporarily. In the stratosphere and the ionosphere, photochemistry destroys methane irreversibly. Episodic resupply of methane from its possible storage in the interior of Titan is necessary to restore it to levels where it can participate in the atmospheric radiative balance and photochemistry, although the amount available to condense on to the surface in reservoirs such as the polar lakes may be highly variable. In this section, we will review this complex meteorological–photochemical–hydrogeochemical cycle of methane on Titan that is somewhat similar to the terrestrial hydrological cycle, and was referred to as the "methalogical cycle" by Atreya et al. (2006).

7.3.1 The Meteorology of Methane

For the first time, the vertical distribution of methane in Titan's troposphere was available following the in situ measurements made by the Huygens Gas Chromatograph Mass Spectrometer (Niemann et al. 2005). The GCMS determined the CH_4 mole fraction at a high spatial resolution starting at an altitude of 146 km altitude above the surface, and on the surface after the probe's landing. The distribution, shown in Fig. 7.3, is remarkable in many respects. First, the CH_4 mole fraction is uniform, with a value of $1.4 \pm 0.07 \times 10^{-2}$ from the lower stratosphere (146 km) to ~32 km altitude which is just below the tropopause (40 km). Second, the mole fraction gradually increased in the troposphere until it reached a maximum value of $4.9 \pm 0.25 \times 10^{-2}$ at 8 km, below which it remained constant down to a level just above the surface. Third, the methane signal suddenly increased as the probe descended through the 16 km altitude and remained high for a couple of km (see inset in Fig. 7.3). Finally, the methane mole fraction began to increase again after the probe landed on Titan, reaching a plateau within 2 min to a value that was ~50% greater than that just above the surface (not shown). The methane mole fraction then remained constant essen-

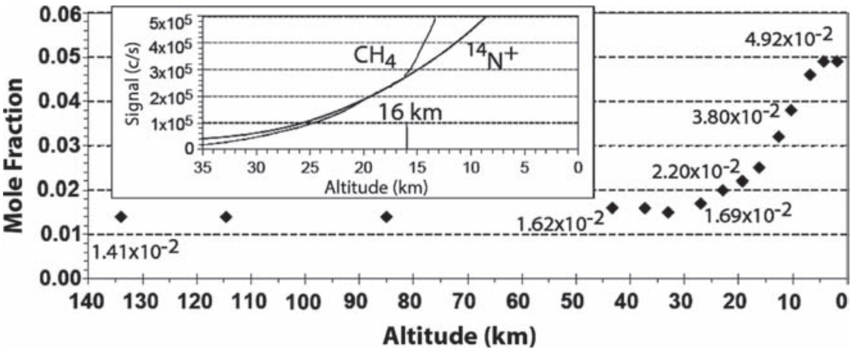

Fig. 7.3 Methane mole fraction in Titan's atmosphere from the GCMS. The CH_4 mole fraction is $1.4 \pm 0.07 \times 10^{-2}$ in the stratosphere. It increased below 32 km, reaching a plateau of $4.9 \pm 0.25 \times 10^{-2}$ at about 8 km. The inset shows the behavior of CH_4 as the probe descended through 16–14 km region. A sudden increase in the methane counting rate relative to N_2 (in this case $^{14}N^+$, which is used as a proxy for N_2 to get around the problem of saturation in the N_2 counts) was detected starting at 16 km and lasting over about 2 km. This was presumably caused by a droplet (or frozen droplet) entering the heated inlet of the GCMS as the probe descended through a cloudy/hazy region (Niemann et al. 2005). The haze apparently extended to at least 21 km where it was detected by the Huygens Descent Imager (DISR), but was first registered by the GCMS at ~16 km where its concentration was large enough for detection by the GCMS

tially to the end of data transmission from the probe 1 h and 12 min later.

The uniform mixing ratio of methane in the lower stratosphere is due to the fact that the unit optical depth, where photolysis destroys most of the methane, is much higher, i.e. between 700 and 800 km. The increase in the methane signal at 16 km indicates that the probe descended through a cloud or haze of methane that evaporated in the heated inlet of the GCMS. The increase of signal at 16 km does not imply either the beginning or end of the cloud/haze layer; it is just where the mass of CH_4 condensate – most likely, a liquid or frozen droplet – was large enough for it to be noticed by the GCMS. The increase in the CH_4 mole fraction after landing indicates moist soil from which methane was evaporated by the heated underbelly of the probe. A slight decrease in the methane mole fraction toward the end of the surface measurements was noticed also, indicating the pool of methane in the Huygens landing site was limited. The above behavior of methane is similar to the familiar behavior of water on the Earth. In both cases, convective ascent of a subsaturated air parcel from the surface to the lifting condensation level (LCL) results in saturation and condensation of the condensible species – methane on Titan and water vapor on the Earth. Clouds form. Precipitation takes place. The surface becomes wet. Above the LCL, the mole fraction of the condensible species is limited to its saturation value, reaching the lowest point at the tropopause, and not rising above it in the warmer stratosphere.

The relative humidity of methane in the Huygens landing site (10.3° S, 192.37° W) was found to be ~50% just above the surface (temperature 93.8 K, CH_4 triple point 90.67 K). The measured CH_4 mole fraction was constant to ~8 km altitude, as is expected in equilibrium. If the LCL were indeed at 8 km, the methane relative humidity should reach 100% at ~8 km. However, the relative humidity turns out to be only 80% considering CH_4 in equilibrium above pure liquid methane, as shown by solid line in Fig. 7.4. On the other hand, since nitrogen gas dissolves in liquid methane, the CH_4 saturation vapor pressure is lower over this binary mixture (Kouvaris and Flasar 1991; Thompson et al. 1992). As a consequence, methane in fact reaches 100% relative humidity at 8 km (dashed line in Fig. 7.4, Atreya et al. 2006), not 80%. This is where the condensation of methane is expected to begin. Above this altitude, methane would remain at 100% relative humidity, if equilibrium prevailed. This is just what is found up to ~15 km altitude (Fig. 7.4). The departure of the CH_4 data from the saturated CH_4 mole fraction above ~15–16 km is due to the transition of methane condensate from the liquid to the solid phase above this altitude, to which the formulation of Kouvaris and Flasar does not apply.

The above discussion illustrates classic textbook example of equilibrium thermodynamics at work in Titan's atmosphere. The methane cloud/haze could actually extend well beyond the 16 km altitude where the GCMS first detected it. In fact, the Descent Imager (DISR) on the probe detected haze at ~21 km level (Tomasko et al. 2005), which is most likely the upper extent of the solid methane particles. Such a transition from liquid methane droplets below ~15–16 km to solid particles above is entirely consistent with the principles of equilibrium thermodynamics (Atreya et al 2006; Tokano et al. 2006). The detection of both an upper ice cloud of methane and a drizzle of liquid methane below has been reported by Adamkovics (2007) from their infrared obser-

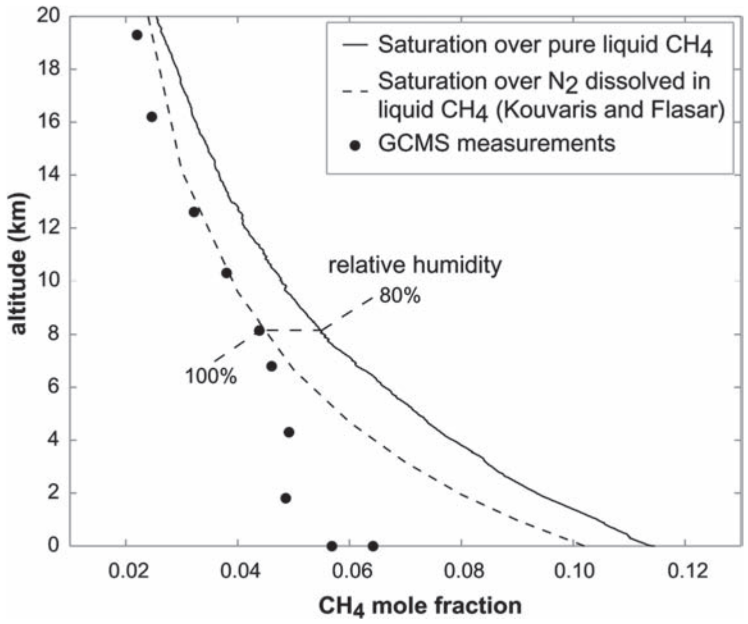

Fig. 7.4 GCMS measurements of the CH_4 mole fraction (*dots*) are shown against the saturation mole fraction curves for the CH_4 vapor over pure CH_4 liquid (*solid line*) and for the N_2 dissolved in the CH_4 liquid (*dashed line*; Kouvaris and Flasar 1991). The relative humidity of CH_4 is ~50% just above the surface. CH_4 is subsaturated up to 8 km, but reaches 100% relative humidity at this altitude, indicating the onset of condensation. The discrepancy between the data and model (*dashed curve*) above ~15 km is because of the change to solid phase of methane (after Atreya et al. 2006)

vations in the equatorial region covering the continent of Xanadu.

Based on the above cycle the average annual rainfall of methane in the equatorial region, such as the landing site of the Huygens probe, would amount to less than 10 cm per year, similar to the annual rainfall in terrestrial deserts. From time to time, convective storms could take place. Lorenz (2000) poses a global average energy limit on re-saturation of the atmosphere if a storm locally depletes it. The time interval between storms is estimated to be 100–1000 years, and could be much longer at a given location. Greater and more frequent precipitation is expected in the polar regions. Lakes have been inferred from the Cassini radar observations, largely at high northern latitudes of 78°N and higher (Stofan et al. 2007). The larger surface reservoir of liquid methane and the 2-4 K colder temperatures in the polar regions than the equatorial region (Flasar et al. 1981) result in ideal thermodynamic conditions for greater condensation and subsequent rainfall at the polar latitudes. The pole-to-pole circulation of methane is expected to occur on time scales of 10–100 years (Lunine and Atreya 2008).

7.3.1.1 Clouds

While it was speculated, largely on the near-coincidence of the Voyager-determined surface temperature with the triple point of methane, that methane might participate in a hydrological cycle as water does on Earth, there was no evidence to suggest an ongoing hydrometeorology on Titan until the late 1990s. Griffith et al. (1998) inferred the existence of clouds in Titan's upper troposphere from near-infrared ground-based spectroscopy acquired in 1995. This cloud system covered some 10% of Titan's disk, and may well be related to a cloud observed at nearly the same time at around 40° N by the Hubble Space Telescope (Lorenz and Mitton 2008; Lorenz 2008). No direct compositional determination of the cloud was made, but its altitude was consistent with that at which methane convective clouds might be expected to form. Further observations (Griffith et al. 2000) showed that the cloud cover varied on hourly timescales, suggesting that the clouds were actively convecting and/or precipitating.

In Titan's thick atmosphere and low gravity, even the largest raindrops fall gently. Lorenz (1993) showed that drops – controlled by the balance of surface tension and aerodynamic forces – could grow to about 9.5 mm in diameter (compared with about 6.5 mm for water drops on Earth; this is a statistical limit, occasional giants can exist for short periods) but would fall at only 1.6 m s^{-1}, compared with 9 m s^{-1} on Earth. Furthermore, the heat flux available to drive convection and evaporation from the surface in McKay et al.'s (1989, 1991) radiative–convective model is only ~1% of the incident sunlight, or about 0.04 Wm^{-2} on average (Fig. 7.5). Dividing by the latent heat of methane yields an average rainfall rate of only 1 cm per Earth year (the corresponding calculation for Earth yields, correctly, the typical rainfall of about 100 cm per year). These factors initially suggested (Lorenz and Lunine 1996) that rainfall would not be a major agent of erosion on Titan. However, Lorenz (2000) cautioned that, as with desert regions on Earth, landscapes can be fluvially dominated even with low average rates of precipitation, if that average rate is manifested by rare, but violent, rainstorms. Griffith et al. (1998) had noted that the Titan atmosphere holds several meters liquid equivalent of precipitable methane.

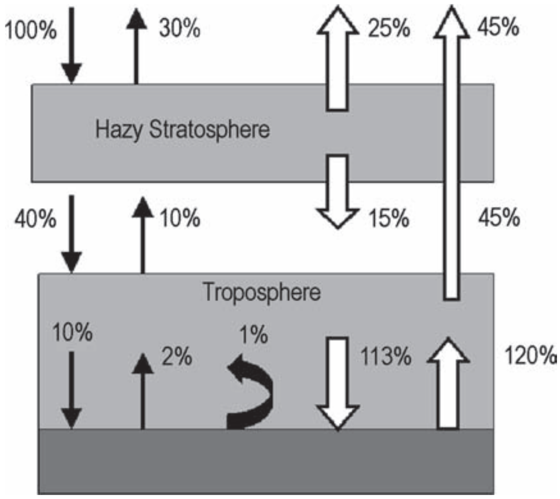

Fig. 7.5 Globally-averaged, annually-averaged energy balance of Titan's surface and atmosphere (original data from McKay et al. 1991). Fluxes are expressed as a percentage of the top-of-atmosphere insolation of 3.7 Wm^{-2}. Solid arrows are shortwave (solar) fluxes; open arrows are the longwave (thermal) fluxes. Curved solid arrow indicates convective flux driving weather and clouds of ~0.04 Wm^{-2}

Clouds began to be observed consistently on Titan from about 2001, as a result of several factors. Not least was the increased intensity of observation – several large telescopes able to image Titan became available around this time, and the performance of their adaptive optics systems got progressively better. Compounding the telescopes' availability was the establishment that Titan had time-variable weather, making it worthwhile to observe. Another factor was Titan itself, which cooperated by providing regular displays of large clouds around the south pole, which was at that time approaching midsummer. The association of the clouds with those latitudes where solar heating was strongest suggested that these clouds are at least driven by convection.

Griffith et al. (2005) observed the cloud tops of evolving clouds at southern midlatitudes (41°–61° S) in December 2005 (TB) using VIMS. Spectral data (the fit of the 2.1–2.2 μm spectral region) indicate cloud-top heights and overall opacity. The evolution of the cloud-top heights suggest that small centers of vigorous updraft existed in the clouds, in some cases observed to be rising at 2–4 m s^{-1} in larger cloud systems, and 8–10 m s^{-1} in more compact (perhaps less well-mixed or younger) clouds.

Spectra from Cassini's Visual and Infrared Mapping Spectrometer in 2005 revealed the presence of a vast tropospheric cloud on Titan at latitudes 51° to 68° N (Griffith et al. 2006) and the feature likely extended to the pole, although winter darkness prevented its observation. The derived characteristics indicate that this cloud is composed of ethane and forms as a result of stratospheric subsidence and the particularly cool conditions near the moon's north pole during the winter season. Preferential condensation of ethane, perhaps as ice, at Titan's poles during the winters may partially explain the lack of liquid ethane oceans on Titan's surface at middle and lower latitudes.

Tokano et al. (2001) modeled the methane transport in the troposphere with a global circulation model including condensation. They suggest that the latitudinal distribution of methane humidity indicated by Voyager (2% mole fraction at high latitude, about 5% at low latitude, Samuelson et al. 1997) could not be reproduced by purely atmospheric processes, and that the surface must somehow influence the humidity. Cloud data were not given in this paper.

A similar conclusion was reached by Rannou et al. (2006) who noted that the circulation would tend to desiccate low latitudes, yet the Huygens data had by this time confirmed the Voyager indication of ~5% methane mixing ratio at low latitude and thus a humidity of ~50%. Rannou et al. (2006) suggested that a low-latitude methane source was required. This model predicted cloud opacity as a function of latitude and season, notably suggesting persistent clouds at both poles in all seasons, and a seasonal midlatitude cloud in fall (e.g. at 40°N between 1985 and 1995).

Ongoing Cassini and ground-based observations show that the south polar convective clouds seem to have ceased towards the end of 2005. Sporadic clouds have been seen since at a variety of latitudes – these are discussed in the companion chapter by Lorenz et al. (2009).

7.3.2 Methane and the Climate on Titan

The climate of a planetary body reflects the balance between the absorption of sunlight, and the emission of thermal radiation to space. In the absence of atmospheric effects, these in turn depend on the body's distance from the Sun, and the optical reflectivity or albedo of the surface; the deviation from unity of the emissivity of most planetary surfaces is small and usually ignored. An atmosphere complicates the picture considerably, typically by reflecting and absorbing sunlight, and by blocking thermal emission. These factors are all significant at Titan, and were first quantified, analytically, by Samuelson (1983), who showed that the main roles of Titan's haze are to absorb blue light, while red and near-infrared light is scattered and penetrates to the surface, and the gas in the dense atmosphere acts as a powerful greenhouse, absorbing thermal infrared radiation. A further analytic investigation of these effects for Titan and for the early Earth was made by McKay et al. (1999).

The radiative balance was evaluated in much more detail with a numerical radiative–convective model constructed by McKay et al. (1989) – this considered 24 spectral intervals in the visible and near-infrared and some 46 intervals in the thermal infrared, including opacities for nitrogen, methane and hydrogen. The atmosphere was divided into 30 plane-parallel layers, and a microphysics code calculated the optical properties of spherical tholin haze particles in each level. The effects of the haze profile, and methane absorption, allowed the model to be adjusted to fit the visible/near-IR spectrum of Titan measured from the ground, and the temperature profile was adjusted to achieve radiative balance. Convective adjustment was applied where the profile exceeded the local adiabat. The resultant profile could be compared with the temperature profile measured by the Voyager radio-occultation experiment. This model was used to show that condensation clouds of methane played a minimal role in Titan's overall radiative balance, a conclusion that has been borne out with time.

This model, albeit a globally averaged one, allowed the competing effects (McKay et al. 1991) of antigreenhouse cooling by stratospheric haze (analogous to the hypothetical 'nuclear winter' scenario for the Earth) and greenhouse warming in the troposphere to be evaluated in familiar terms. In essence, the effective temperature of Titan, which is determined by the distance from the Sun and the planetary albedo, is 82 K – the antigreenhouse effect drops the temperature by 9 K, whereas the greenhouse increases it by 21 K, giving a net overall greenhouse warming of 12 K.

Meanwhile it was recognized that several effects would drive Titan's climate with time. Not only did the solar luminosity change, forcing the climate directly, but also since methane is a condensible gas at Titan's conditions, a feedback exists wherein the amount of gas (and thus the strength of the greenhouse thermal opacity) depends on the temperature, and this feedback can magnify the effects of the solar forcing. Furthermore, over time, the relative amounts of methane and ethane in a surface-atmosphere reservoir would change as photolysis progressively converted methane to ethane. Additional radiative effects, depending on the photolysis rate, would include the amount of haze in the atmosphere, and the small but significant opacity due to molecular hydrogen, also produced by photolysis.

An initial attempt to explore the solar forcing and volatile greenhouse effects was made by Lunine and Rizk (1989) who used a semianalytic grey radiative model. This effort found that temperatures on Titan several gigayears ago could have been rather lower, by 10–15 K, than present, largely due to the photochemical evolution of the greenhouse inventory and slightly amplified by the solar luminosity variation. These effects were explored in more detail by McKay et al. (1993) who noted that the sensitivity of Titan's climate to solar luminosity and possible surface heating was considerably amplified by the existence of a large surface volatile reservoir. In other words, if Titan just had a few surface lakes, the surface temperature and pressure would change only modestly over the age of the solar system, while if there was a massive ocean, the pressure could have been much lower in the past (~0.2 bar 4 Gyr ago) than at the present (Fig. 7.6). Under these conditions, the ocean would have been frozen at about 74 K. McKay et al. (1993) kept present-day hydrogen greenhouse and haze production rates, and noted, but did not study, the further complication that under these cold early conditions, nitrogen ice clouds would form in the atmosphere and affect the radiative balance.

The possibility that Titan's atmosphere may have been appreciably thinner in the past prompted consideration of possible geomorphological signatures of such history (e.g. Lorenz et al. 1995), in particular the increased abundance of small craters whose formation would be inhibited by atmospheric shielding at the present epoch (Engel et al. 1995). Further studies with the McKay et al. radiative–convective model explored a couple of additional scenarios. The situation of Titan around a red-giant star (either our own, some 5 Gyr from now, or perhaps some Titan-like body around a Saturn-like planet around a red giant elsewhere in the galaxy) was explored in Lorenz et al. (1997a). Here, strong heating causes the atmosphere to 'puff up' – higher temperatures give a large scale height, and since haze is assumed to form at a fixed low pressure the haze column becomes very large and surface temperatures are not substantially enhanced. However, as the solar spectrum changes to admit more penetrating red light, and to produce less UV and thus produce less haze, surface temperatures can increase profoundly – well above the ammonia-water melting point of 176 K – even without invoking the enhanced greenhouse due to a large volatile reservoir.

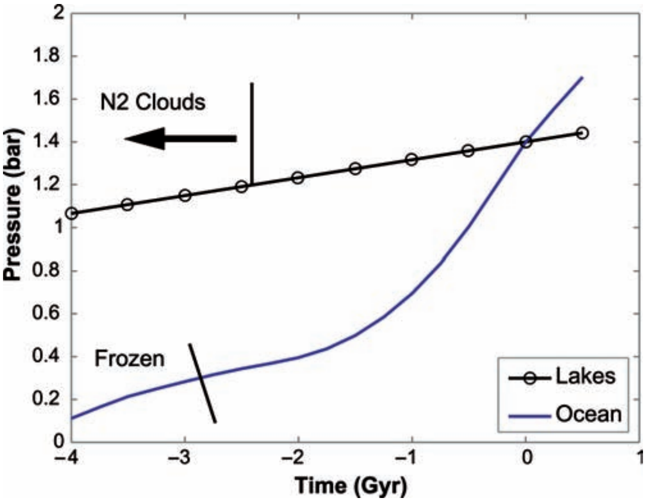

Fig. 7.6 Possible history of Titan's atmospheric pressure over the age of the solar system, assuming photolytic conversion of a methane ocean and the production of haze and hydrogen at present rates (data from McKay et al. 1993). If there are only lakes of methane (with insufficient volume to dissolve much of the atmospheric inventory of N_2) the evolution is modest, but if a large ocean of methane existed, the pressure could have been much lower when the Sun was fainter several Gyr ago

Lorenz et al. (1997b) also explored the climate in another direction – with present-day and reduced solar luminosities, but with the methane abundance as an adjustable parameter to allow for the possibility that methane supply to the surface-atmosphere system might be episodic, while its photochemical destruction is continuous. Thus there may have been episodes, perhaps many and sometimes long, when there was no methane available. This not only removes the CH_4–CH_4 and CH_4–N_2 collision-induced thermal opacity, but also (as hydrogen escapes over a subsequent period) would remove the N_2–H_2 greenhouse. These cooling effects are only partly offset by the loss of near-infrared CH_4 solar absorption and the clearing of the atmospheric haze: removal of methane drops the present-day surface temperature by about 5 K, although stratospheric temperatures fall dramatically from about 180 K today to around 60 K.

Lorenz et al. (1999) made a set of convenient–analytic fits to an ensemble of several hundred runs of the McKay et al. radiative-convective model, and reported the joint sensitivity of surface temperature to methane humidity and surface albedo: under present conditions, equilibrium surface temperatures rise by about 1 K for every 0.1 decrease in surface reflectivity, which might lead to some variation of surface temperatures across Titan's variegated surface. A drop of 0.1 in surface relative humidity from the present value of ~0.5 similarly results in a 1 K surface temperature drop. Also, temperatures drop by about 1 K for every 1 km increase in elevation. These analytic fits allowed further exploration of the evolution of the coupled surface-atmosphere climate system. Such a system (and the effect applies also to the Martian climate, where a substantial fraction of the total CO_2 inventory seasonally freezes onto the surface, as well as the water greenhouses on Earth and paleo-Venus) will have an equilibrium where the surface temperature and the resultant atmosphere are self-consistent, in that the surface-atmosphere thermodynamic equilibrium $P = f(T)$ and the radiative equilibrium $T = f(P)$ curves cross, where T represents the surface temperature and P represents the partial pressures of the various gases. As first noted by McKay et al. (1993) a small inventory ('lakes') is well behaved, having only one equilibrium (Fig. 7.7). However, if the volatile inventory of methane, ethane and nitrogen is large, there is the potential for strong positive feedback and the two curves form three equilibria of

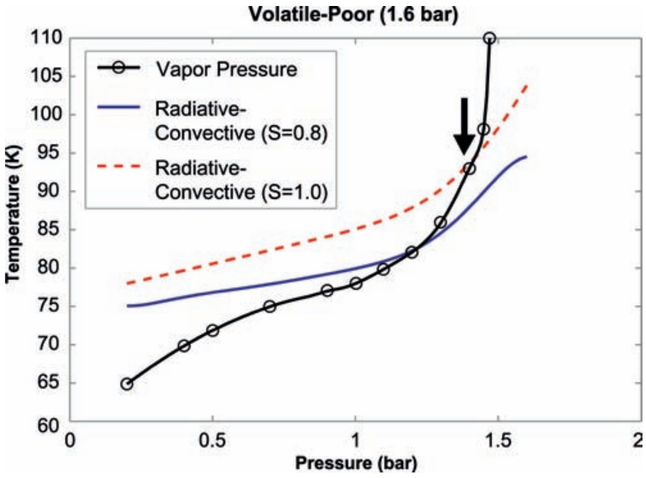

Fig. 7.7 Well-behaved surface-atmosphere equilibrium for a volatile-poor Titan (with ~0.1 bar of liquid at the present day, plus 1.5 bar atmosphere). The solid black curve with circles represents the surface-atmosphere thermodynamic equilibrium, in effect the vapor pressure of the ocean as a function of temperature. The red dashed curve represents the radiative–convective equilibrium, i.e. the temperature as a function of the greenhouse effect in the atmosphere for the present solar constant. Where the red and black curves cross (*marked with an arrow*) indicates a stable self-consistent equilibrium. The stippled blue curve shows the same for a solar constant of 80% the present value – because the greenhouse curves are much shallower than the thermodynamic equilibrium curve, the crossing point moves only gradually as the solar constant increases (data from Lorenz et al. 1999)

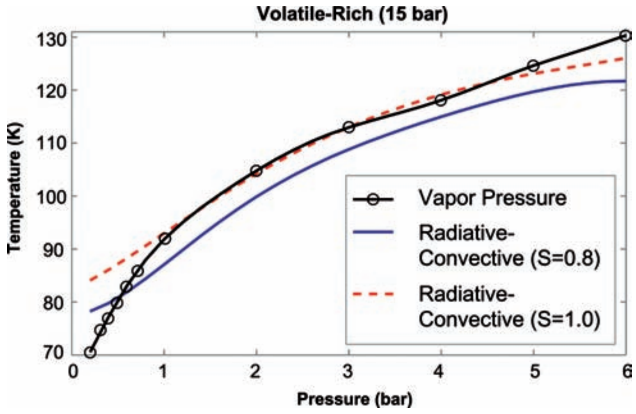

Fig. 7.8 Extreme climate sensitivity in a volatile-rich Titan (with 16 bar of volatiles). This figure is the same as figure 7.7, but with a larger volatile inventory. The corresponding vapor pressure curve (*black*) yields a thicker atmosphere for a given temperature, and the slope of the curve is very similar to the greenhouse curves. For a low solar constant (*blue*) there is a single stable self-consistent equilibrium. However, for the present solar constant (*red*) there are three equilibria. The central crossing is unstable, but two stable equilibria (*arrowed*) exist – one at present conditions, the other with a much higher temperature and pressure. Small perturbations may cause the climate to flip between these conditions (data from Lorenz et al. 1999)

which only the outer two are stable (Fig. 7.8). The choice of which of these two climates will Titan be in would depend on the history of the system, and indeed discontinuous jumps between them can occur – a runaway greenhouse, or equivalently in the opposite direction, atmospheric collapse. This hysteresis makes climate prediction forward or backwards a significant challenge.

Up to this point we have not considered variations of temperature with latitude. Such variations are important in the surface-atmosphere equilibrium, in that the planetwide strength of the greenhouse effect depends on the partial pressure of the various greenhouse gases, which will be close to thermodynamic equilibrium with the coldest part of the planet. Therefore, it is the coldest parts of the planet, and thus to a large extent the effectiveness of equator-pole heat transport that controls the planetary average temperature.

In simple 1-D energy balance climate models used in the 1970s to study the stability of the terrestrial climate to lower insolation (so-called Budyko–Sellers models) the heat transport – embodying ocean as well as atmospheric motions – is represented by a single heat transfer parameter D, which empirically today has a value of ~1 Wm^{-2} K^{-1}. For Martian paleoclimate studies, the terrestrial value has been scaled by atmospheric pressure. For Titan, however, this approach yields a transport that is too high (Lorenz et al. 2001), and results in an equator-to-pole temperature gradient that is orders of magnitude lower than the 3–4 K suggested by Voyager observations. A much lower value, D~0.02 Wm^{-2} K^{-1} is required, and appears consistent with the idea that some climates, including the Earth's, may select combinations of heat transport modes in order to maximize the entropy production by the turbulent heat flux. While this idea is controversial, it is of interest that both the dimensions and the value itself of the heat transport parameter D are the same as the planetary entropy production dS/dt – absorbed solar flux divided by absolute temperature. For the Earth, this is ~300 Wm^{-2}/300 K = 1 Wm^{-2} K^{-1}, while for Titan the flux is ~3 Wm^{-2} and the temperature ~100 K, yielding dS/dt~0.03 Wm^{-2} K^{-1}.

Even though its thermal inertia is such that the bulk of Titan's atmosphere does not warm and cool with the seasons, the surface temperature may see seasonal variations. These were first explored by Stevenson and Potter (1986) who suggested an analogy with the seasonal frost cycle on Mars. Under their scenario, some meters of methane might condense onto the cold winter pole (i.e. forming a transient liquid polar cap – or seasonal lakes) before re-evaporating in spring. In reality, the seasonal variations (see chapter by Lorenz) are rather more complex, involving varying winds and humidity, as well as the availability of condensation nuclei. Nonetheless, the possibility of seasonal evaporation of surface methane lakes has been underscored by Mitri et al. (2007).

Global circulation models of growing sophistication are being applied to understanding Titan's winds and, in particular, the seasonal and latitudinal variations in methane amount, clouds and precipitation. While these models are able to produce some basic features of the Titan climate such as dry conditions at low latitudes where dunes are seen (e.g. Mitchell 2008) and more abundant clouds at high latitudes (e.g. Rannou et al. 2006), many details remain to be resolved. Further, to date, there has been no latitudinally-resolved modeling of Titan paleoclimates with conditions different from the present.

7.3.3 *Photochemical Destruction of Methane in the Stratosphere: The Ethane Ocean Dilemma*

The cycle of methane discussed in the above subsections represents at best a closed cycle of surface reservoirs, volatile evaporation, cloud formation, followed by precipitation, similar to the hydrological cycle on the Earth. In the worst case scenario, it may represent a net loss of methane due to surface runoff and loss to the interior of Titan through cracks and fissures in the surface. Any such loss is expected to be temporary, however, as various geological processes are likely to pump the methane back out to the surface over time. On the other hand, photochemistry destroys atmospheric methane irreversibly due to the escape of its product, hydrogen, as shown first by Strobel (1974). Consequently, the lifetime of methane in the atmosphere is ~30 Myr (Wilson and Atreya 2004; Yung et al. 1984). The UV photolysis occurs primarily above ~600 km in the stratosphere and is responsible for about one-third of the total CH_4 destruction rate of 4.8×10^9 cm^{-2} s^{-1} (8.7×10^9 cm^{-2} s^{-1} when referenced to the surface, E.H. Wilson, personal communication 2008), whereas the catalytic destruction by acetylene (C_2H_2) – itself a product of the CH_4 photochemistry – in the lower atmosphere accounts for the rest (Wilson and Atreya 2004). In each case, ethane (C_2H_6) is the principal product, as seen in the chemical scheme below. (About 10–15% of the methane is destroyed in the ionosphere above 900 km, but little ethane is produced.)

$$\begin{array}{ll} 2(CH_4 + h\nu \rightarrow CH_3 + H) \quad \text{and} & 2(C_2H_2 + h\nu \rightarrow C_2H + H) \\ CH_3 + CH_3 + M \rightarrow C_2H_6 + M & 2(C_2H + CH_4 \rightarrow C_2H_2 + CH_3) \\ & CH_3 + CH_3 + M \rightarrow C_2H_6 + M \\ \text{Net: } 2CH_4 \rightarrow C_2H_6 + 2H & \\ & \text{Net: } 2CH_4 \rightarrow C_2H_6 + 2H \end{array}$$

[M is the concentration of the background atmosphere]

Based on the above photochemical fate of methane, Lunine et al. (1983) predicted that over geologic time, a kilometer-deep ocean of ethane is expected to cover Titan's surface. This was a bold but reasonable prediction for its time, considering the limited state of knowledge about the composition and structure of Titan's atmosphere. A quarter century later, observations made from the Cassini–Huygens give no evidence of a global ethane ocean, however. The lack of ethane oceans may be attributed to a much more complex cycle of methane including photochemistry and geology than was previously envisioned and a better understanding of atmospheric vertical mixing. Current photochemical models show that many other products either compete with or are formed from ethane itself. Of special significance to the question of ethane oceans is the detection of benzene (C_6H_6), which was not included in the model of Yung et al. (1984), which was the basis of Lunine et al.'s prediction of global ethane oceans.

Benzene was identified tentatively by the Infrared Space Observatory (ISO, Coustenis et al. 2003). Its presence at 1–4 ppbv levels in the stratosphere was confirmed by the Cassini Composite Infrared Spectrometer (CIRS, Coustenis et al. 2007), and at much higher mixing ratio of 1–5 ppmv above 900 km by the Ion and Neutral Mass Spectrometer (Waite et al. 2005, 2007). Despite these differences in the mixing ratio, the column abundance of C_6H_6 in these two parts of the atmosphere is similar (Atreya 2007a), indicating potent production mechanisms throughout the atmosphere. Several pathways have been proposed for the formation of benzene in the neutral atmosphere and the upper ionosphere, but all can eventually be traced back to ethane. Benzene is the precursor to the formation of polycyclic aromatic hydrocarbons, PAH's, whose polymerization may result in some of Titan's most abundant haze layers. Both the ionosphere and the stratosphere contribute significantly to the haze.

Thus, contrary to the earlier notions, ethane is not the end product (or even close to it) of the methane photochemistry, but it goes on to produce heavier hydrocarbons that subsequently form the multitude of haze and soot layers in Titan's stratosphere and higher (Wilson and Atreya 2004; Waite et al. 2007). Wilson and Atreya (2004) found that the inclusion of benzene and other chemical pathways in a coupled atmosphere-ionosphere photochemical model led to a reduction in the downward flux of ethane at the tropopause by a factor of 4–6 from a value of ~6×10^9 cm^{-2} s^{-1} in the model that did not include them (Yung et al. 1984) and was the basis of earlier ethane ocean predictions. The new models thus predict much less condensation of ethane, reducing the depth of a global ethane ocean to 150–250 m from the previous predictions of a kilometer.

Atreya et al. (2006) found that the vertical distribution of ethane is also significant factor in determining the amount of ethane condensation. They found the best fit to the CIRS data on ethane requires substantially smaller eddy diffusion below 200 km than that in the previous models. The smaller stratospheric mixing seems consistent also with the conclusion of Yelle et al. (2008) who found a value of 2–5 × 10^7 cm^2 s^{-1} for the eddy diffusion coefficient at the homopause, using

^{40}Ar as the observational constraint, or about an order of magnitude smaller than in pre-Cassini models where the analysis was based on the CH_4 distribution alone (see chapter by Strobel et al. (2009) for a comprehensive discussion of composition and structure). Since the eddy diffusion coefficient varies inversely with some power of the atmospheric density, the lower values assumed by Atreya et al. (2006) for the lower atmosphere are reasonable. The reduced eddy mixing results in a further reduction in the downward condensation flux of ethane, by 30–50%. The reduction factor is probably larger, as the Atreya et al. (2006) model was done prior to the complete analysis of the upper atmospheric mixing from the INMS data (Yelle et al. 2008) that indicated a more severe reduction of eddy mixing in the upper atmosphere. Thus, with the above new constraints on atmospheric mixing and the composition from Cassini, the depth of a global ethane ocean is expected to be no greater than 100–150 m, not a kilometer.

Finally, geologic considerations indicate that the depth could be even smaller. Models of the interior show that methane on Titan may be outgassed only episodically, with the last such episode occurring 600 Myr ago (Tobie et al. 2006). This would further reduce the possible depth of the ethane ocean to less than 10 m over the geologic time. Since any ethane condensation would be gradual, it is quite likely that even a good fraction of this last bit may be largely sequestered as ethane clathrate in Titan's regolith (Atreya et al. 2008; Lunine and Atreya 2008). Mousis and Schmitt (2008) estimate that a cryovolcanic icy crust of less than 2.3 km thick is required to bury all the ethane (and other less abundant hydrocarbon liquids) produced over the geologic time. Since the ethane rain ultimately originates in the stratosphere (Sections 7.3.1.1 and 7.3.3), its sequestration as ethane-clathrate is expected to be at shallow depths just below the surface, unlike the methane clathrates that are predicted to be present in the high pressure ice some 50–100 km below Titan's surface (Section 7.3.4).

In conclusion, although roughly 40% of Titan's methane is expected to be converted to ethane over geologic time, global oceans of ethane are no longer predicted by current photochemical–geological models, nor are they seen in the Cassini data. On smaller time scales, ethane may still condense in the atmosphere, especially at mid-high latitudes, and form lakes. Thermodynamic considerations predict a relative humidity of ethane ranging from 80% to 100% in the equatorial region, as shown in Fig. 7.9 (Atreya et al. 2008). Thus the condensation of ethane there would be at best marginal, and moreover any ethane drizzle may be sequestered in shallow subsurface clathrates. This seems to be the case in the Huygens landing site (10.3° S, 192.37° W), where the probe mass spectrometer detected a slow evaporation of ethane from Titan's moist surface (Niemann et al. 2005). On the other hand, at polar latitudes, where the temperatures are 2–4°cooler, ethane would almost certainly condense (Fig. 7.9). Since ethane liquid is fully miscible in the methane liquid, Titan's polar lakes are expected to be composed largely of a methane–ethane mixture (Atreya et al. 2008; Lunine and Atreya 2008). Brown et al. (2008) have, in fact, identified spectral features of ethane in Ontario Lacus (72° S, 183° W), which was observed by VIMS through Titan's atmospheric windows at 2.0, 2.7 and 5.0 µm during Cassini's 38th close flyby of the satellite. The authors conclude that "ethane, probably in liquid solution with methane, nitrogen and other low-molecular mass hydrocarbons, is contained in Ontario Lacus". (The very large abundance of methane gas in the atmosphere prevents the identification of methane liquid on the surface.) Since the stratospheric mole fraction of ethane vapor is about a factor of 10^4 smaller than the CH_4 mole fraction, ethane liquid may constitute a small fraction of the methane–ethane lakes at any given time. However, a realistic assessment of eventual fraction of the ethane liquid in the lakes is a complicated matter. Lorenz (1993) suggested that pure methane droplets may not survive their descent through Titan's troposphere. Even the survival of a ternary mixture of CH_4-N_2-C_2H_6 droplets against evaporation depends on the relative humidity of C_2H_6 (Graves et al. 2008). Until the distribution of ethane is determined from the lower stratosphere down to the surface, the fractional amount of ethane in the polar lakes will continue to remain highly uncertain.

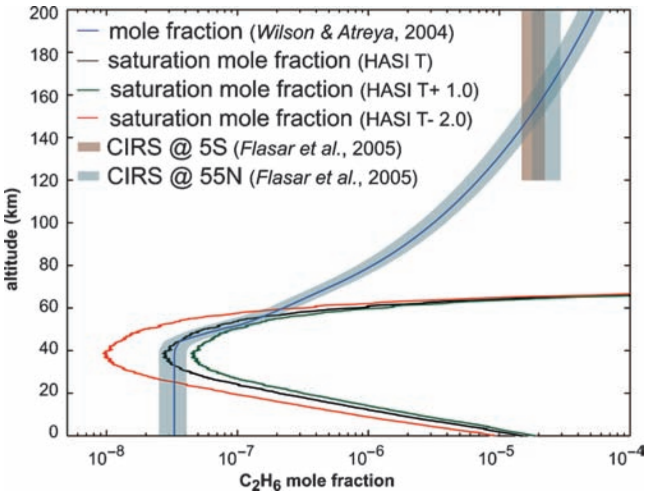

Fig. 7.9 Photochemical profile of ethane with uncertainty envelope (*blue curve*) and its comparison with (**a**) the CIRS data at 5°S and 55°N (*vertical bars, with uncertainty envelopes*), and (**b**) C_2H_6 saturation vapor pressures, using the central HASI temperatures near the equator (*black curve*), HASI temperatures increased by 1° to accommodate the uncertainty in the temperature determination (*green curve*), and temperatures reduced by 2° relative to the HASI equatorial temperatures, to mimic high polar latitude conditions (*red curve*). The resulting C_2H_6 relative humidity at the tropopause is 75–100% in the equatorial region, and over 200% at the polar latitudes (after Atreya et al. 2008)

7.3.4 Methane Replenishment – The Source of Methane

The time scale for the photochemical conversion of the present atmospheric abundance of methane to heavier hydrocarbons, nitriles and hazes on Titan is ~30 Myr, as discussed above. In the absence of recycling or replenishment, Titan would have lost its methane, and therefore much of its nitrogen atmosphere, a long time ago. It is conceivable that the level of methane in the atmosphere has fluctuated over geologic time. However, it seems unlikely that Titan could lose all of its methane at some point in time and then some process would trigger a re-supply of the entire atmosphere at another epoch, considering the sheer amount of methane and nitrogen involved. The most plausible scenario is that the methane destroyed in the atmosphere is somehow replenished from time to time. The $^{12}C/^{13}C$ isotope ratio provides evidence that this must be happening. On Titan, the measured $^{12}C/^{13}C$ ratio of 82.3 (Table 7.1) is only slightly below the terrestrial inorganic value (89.45), or 92% terrestrial, whereas the $^{14}N/^{15}N$ ratio is only 67% terrestrial (Table 7.1), or less if the INMS extrapolation from thermosphere to the homosphere is used (the slight excess of the ^{13}C isotope on Titan could result from methane escape or geology in Titan's interior). This implies irreversible escape of nitrogen from the atmosphere, but replenishment of methane. Unlike the giant planets where the products of the methane chemistry can be recycled back to methane by thermochemical reactions in the planets' H_2-rich, hot and dense interiors, the hydrocarbon and nitrile aerosols cannot be turned back into methane in Titan's cold interior even if the aerosols could all wash into the interior of this solid object. Therefore, a direct source of methane itself is required, irrespective of where the methane came from in the first place. No significant source of methane exterior to the satellite can be identified, so the resupply needs to occur from within. Indeed, if methane is stored as a clathrate-hydrate ($CH_4.6H_2O$) in the high pressure ice in Titan's interior, as has been suggested by Lunine and Stevenson (1985, 1987), Tobie et al. (2006) and others, it could be the source of atmospheric methane, irrespective of its ultimate origin. Any number of processes, including impacts and cryovolcanism (Lunine et al. 2009; Tobie et al. 2006; Sotin et al. 2005) can destabilize the clathrates and release the stored methane to the atmosphere. It is important to ask whether Titan's methane cache is large enough to replenish the amount destroyed by photochemistry in the atmosphere. We address this question below.

Originally, Titan should have accreted approximately four times more carbon (C) than nitrogen (N) (using the solar elemental abundances of Grevesse et al. 2005), considering that the inter-elemental abundance ratios in Titan should reflect the solar composition of the Saturnian subnebula where Titan was formed. Assuming that most of the carbon ended up as methane, and that the primordial atmosphere of Titan contained 5–10 bar of N_2 (Section 7.2.2.4), the partial pressure of methane then should have been 30–80 bar. Thus, the average partial pressure of CH_4 on primordial Titan is expected to be ~55 bar, or 750 times its present partial pressure using the present CH_4 mole fraction of ~5%. Using the current photochemical destruction rate of 4.8×10^9 cm^{-2} s^{-1} for CH_4 from Wilson and Atreya (2004), we find that only 4%, or roughly 2.5 bar, of the original methane has been destroyed over geologic time. Today, the atmosphere contains ~75 mbar of CH_4. Therefore, most of the original methane should still be present on Titan, presumably stored as clathrate in Titan's interior with a small fraction as liquid in the lakes. This implies that Titan should have plenty of methane storage to replenish the gas destroyed in the atmosphere. It would take up to 100 billion years to destroy the entire methane inventory of Titan!

The above conclusion is based on several simplifying assumptions, including a constant rate of photochemical destruction throughout the geologic time, and that all of the carbon was sequestered in methane. Nevertheless, it is fairly robust, considering that the solar UV flux has remained nearly uniform after the Sun entered its main sequence and methane is by far the dominant carbon compound formed, irrespective of whether it was produced in the Saturn subnebula or in the interior of Titan. Somewhat larger or smaller amounts than given above could have been destroyed depending on the past history of methane, but it is not likely to change the basic conclusion, considering the wide margin between the amount destroyed and the potential reservoir. As discussed later in this section, ~2% of the original ^{40}Ar has escaped (Waite et al. 2005), which is comparable to the 4% of the CH_4 destroyed (and replaced). This indicates comparable rates of release considering that ^{40}Ar is released from the core whereas CH_4 is released from only 50–100 km below the surface. Related to the question of the replenishment of methane is whether the liquid contained in the lakes alone is sufficient to replace the methane destroyed in the atmosphere. An estimate of methane in the lakes can be obtained by considering the available radar observations and using terrestrial analogy.

Above 55° N latitude, imaging radar observations have covered 55.4% of the terrain through Titan's 30th close encounter in May 2007. A variety of lake types covering almost 10% of that terrain are seen (Hayes et al. 2008; Lorenz et al. 2008a) ranging in size from a few kilometers, which is the smallest recognizable in data of ~300 m/pixel, to several hundred kilometers. The combination of low radar reflectivity and high microwave brightness, thus implying high emissivity, and the feature morphology and association with channels all point to present-day liquid, presumably methane and ethane. Lorenz et al. (2008b) attempted to estimate the liquid volume in the lakes. Using terrestrial analogs as a guide (e.g. typical lake depth in meters equals its dimension in kilometers), the typical 20-km wide lake may be expected to have a depth on the order of 10–20 m. Multiplying by the radar-observed lake area of 400,000 km^2 and assuming similar contributions from the rest of the Northern hemisphere as yet unobserved by radar yields an inventory of $\sim 2 \times 10^4$ km^3 of liquid – some hundreds of times the known oil and gas reserves on Earth (BP 2007). However, if depth scales with size, the inventory (e.g. Lorenz 1998) is dominated by the single largest lake, and such an average approach may underestimate the inventory – e.g. Ligeia Mare and Kraken Mare are on the order of 200 and 400 km across, and thus may have average depths ten times higher than that above, with a correspondingly higher total inventory, in other words $>2 \times 10^4$ km^3 of liquid.

The discussion above pertains only to the North. While radar coverage of the south polar regions is presently very limited with only the 39th close flyby observing beyond 70° south latitude so far, southern coverage in the Cassini Equinox Mission will become comparable with the present north polar coverage. From this small southern sampling a couple of lake features are evident, and a couple of years earlier a likely lake candidate Lacus Ontario (~235 km across) was identified in ISS images (Turtle et al. 2009). However, the overall impression (Lunine et al. 2008) is of rather less lake coverage than in the north, and thus a complete inventory of Titan's bulk liquid reservoir as more data emerge is likely to increase by no more than a few tens of percent from the estimate given above for the north only. Therefore, for the time being we take the total volume of methane liquid in all of Titan's lakes to be $\sim 3 \times 10^4$ km^3, keeping in mind that it could be ten times higher as discussed above.

As discussed above, ~2.5 bar, or 1.4×10^{19} kg of methane is estimated to have been destroyed over geologic time, whereas the total CH_4 inventory in the lakes is 1.3×10^{16} kg using the lower limit of the lake volume and 1.3×10^{17} kg if the lake volume were ten times higher. Thus, the lakes are capable of replenishing no more than 1% of the methane destroyed by photochemistry in the atmosphere. This means that if methane was present in Titan's atmosphere throughout most of its geologic history, it had to be supplied from Titan's interior from time to time. Episodic outgassing of methane was proposed by Tobie et al. (2006) whose model indicates that the last such episode took place 600 Myr ago. Evidence of outgassing from the interior was provided by the Huygens GCMS that measured smaller than expected abundance of ^{40}Ar (Table 7.1) in the atmosphere (Niemann et al. 2005) and from INMS (Waite et al. 2005, 2007). ^{40}Ar is a product of radioactive decay of ^{40}K whose half-life of 1.3 Gyr is much shorter than the geologic time of 4.5 Gyr, yet not all of the ^{40}Ar has apparently leaked out to the atmosphere. Waite et al. (2005) estimate that ~2% of the ^{40}Ar that was produced originally has escaped to date. Since ^{40}K is a component of the rocks in the core of Titan, detection of its product, ^{40}Ar in the atmosphere, indicates that outgassing is taking place from even a couple of thousand kilometers below the surface. Hence methane, which is believed to be stored as clathrate in the ice shell above a water-ammonia ocean presumed to be present at a depth of perhaps 50–100 km below the surface, should have no difficulty getting out when the clathrates are destabilized. When it does, it would be in the form of liquid at the surface, re-charging the lakes and the atmosphere in turn with methane.

7.3.5 Origin of Methane

Though methane is believed to be stored in Titan's interior, it requires an explanation as to where it came from in the first place. Kinetic models of the Saturnian subnebula have wavered between methane and non-methane carbon-bearing compounds including CO_2, CO, etc. as the principal form of carbon in the subnebula. As a result, two distinct possibilities for the origin of methane were envisioned (a) methane was delivered *to* Titan by the planetesimals during accretion, or (b) methane formed in situ *on* Titan, from non-methane molecules, such as CO, CO_2, etc. A possible test of the hypotheses was expected to be provided by the measurement of the abundance of the heavy noble gases, argon (^{36}Ar), krypton (Kr) and xenon (Xe). Mousis et al. (2002) predicted nearly solar ratios of $^{36}Ar/C$, Kr/C and Xe/C in Titan's atmosphere if the conversion of CO to CH_4 (and N_2 to NH_3) occurred in the subnebula, as in the model of Prinn and Fegley (1981). In this scenario, CH_4 was produced in the subnebula and delivered as CH_4 to Titan during accretion. Mousis et al. (2002) argued, however, that instead of forming in the subnebula, CH_4 is trapped, along with NH_3 and Xe as clathrate-hydrates from the feeding zone of Saturn. Their pre-Cassini–Huygens model predicted six times solar Xe/C ratio in Titan's atmosphere, and four and five times solar $^{36}Ar/C$ and Kr/C, respectively, if these latter gases were fully trapped (Ar and Kr require 10–15 K lower trapping temperatures than Xe). In this scenario also, methane was delivered to Titan during accretion.

The Huygens GCMS made the first measurements of the noble gases, and found $^{36}Ar/CH_4$ to be a factor of 10,000 times less than the predictions of the Mousis et al. model. Moreover, Xe and Kr were not even detected, with their mixing ratios below the 10^{-8} detection limit of the GCMS. This seems to imply that methane was not delivered to Titan directly as CH_4, otherwise the heavy noble gases, especially Xe which forms clathrates at similar temperatures as CH_4, would certainly be present in Titan's atmosphere. The unexpected non-detection of Xe and Kr and the extremely low abundance of ^{36}Ar has spawned a number of possible explanations, including gradual absorption of Xe and Kr, but not argon, into clathrates near the surface (Thomas et al. 2007), burial of Xe and Kr as clathrates in Titan's interior below the water-ammonia ocean (Lunine et al. 2009; Tobie et al. 2008), and sequestration of Xe and Kr in aerosols (Jacovi and Bar-Nun 2008). The surface clathrate model fails to explain the highly subsolar argon in the atmosphere. The aerosol hypothesis fails to explain why the heavy noble gases were not detected by the GCMS when the surface material was vaporized. The trapping below the ocean hypothesis is somewhat selective and does not allow for the possibility of any destabilization of noble gas clathrates at all during the entire geologic time, but is arguably one of two current leading hypotheses for the origin of Titan's methane, the other being serpentinization as discussed below. In the final section of this chapter, we discuss future measurements that could help discriminate between the various hypotheses for the origin of Titan's methane.

An alternative hypothesis for the origin of methane is that methane did not arrive at Titan as CH_4, but was actually formed on Titan. The process involves water-rock reactions – serpentinization – in which hydration of Fe, Mg or Cr-rich ultramafic silicate minerals, such as olivine [$(Mg, Fe)_2SiO_4$] or pyroxene [$(Mg, Fe)SiO_3$], first liberates hydrogen ($H_{2(aq)}$), which reacts in turn with the primordial carbon in the form of CO_2, CO, carbon grains or organic material to produce CH_4, as below:

$$CO_{2(aq)} + [2 + (m/2n)]H_{2(aq)} \rightarrow (1/n)\ C_nH_m + 2H_2O$$
$$CO_{2(aq)} + 4H_{2(aq)} \rightarrow CH_4 + 2H_2O$$
$$C + 2H_{2(aq)} \rightarrow CH_4$$

Atreya et al. (2006) have estimated that the yield of methane from the above process is adequate to explain Titan's methane, and the most plausible period for the production of methane is in the early stages of the formation of Titan when the accretionary heating and heating due to decay of short-lived radioactive elements allowed the water-ammonia ocean to extend all the way to the rocky core. Black Smokers (hydrothermal vents) in terrestrial oceans are known to produce methane and other hydrocarbons by serpentinization, but at relatively high temperatures of 350–400°C. On the other hand, copious quantities of methane are also produced by serpentinization in Lost City, some 15–20 km from spreading centers, where the temperatures are 40–90°C, much lower than in Black Smokers (Kelley et al. 2005). Such low-temperature serpentinization may have occurred over a long period in Titan's interior in the past. The methane produced in the interior could then be stored in the high pressure ice in Titan's interior as Titan cooled. The separation of the rocky core from the water ocean by intervening ice on present day Titan prevents current production of methane.

Finally, McKay and Smith (2005) and Schulze-Makuch and Grinspoon (2005) have proposed microbial production of methane on Titan. In their scenario, acetylene and hydrogen, resulting from the action of sunlight on methane in Titan's atmosphere, serve as nutrients, and methane is produced in turn as a byproduct of metabolism: $C_2H_2 + 3H_2 \rightarrow 2CH_4$. Unlike life on Earth that depends on (liquid) water as solvent or medium, the non-aqueous, non-polar methane liquid in Titan's surface serves as solvent or medium for Titan's methanogens. If indeed Titan's methane were produced by such microbes, one would expect the $^{12}C/^{13}C$ to be greater than the inorganic value of 89.5, as is the case for all living things on Earth. However, the $^{12}C/^{13}C$ ratio on Titan was measured to be 82.3, which is smaller, not larger, than the terrestrial inorganic standard. This argues against a biological origin for Titan's methane. One could imagine that Titan's microbes are "exotic", different from life as we know it (see, e.g. NRC 2007), but at this time we have no evidence that is the case. Moreover, if methanogens were responsible for producing even a fraction of Titan's two hundred and fifty trillion tons of methane in the atmosphere today, they would have put a serious dent in Titan's hydrogen and acetylene inventory. We have no evidence of that either. Nevertheless, life as we *don't* know it is an intriguing thought that deserves further inquiry in any future exploration of the satellite.

7.4 Summary and Future Observations

In many ways, Saturn's moon, Titan, seems so similar to the Earth – its cycle of methane is akin to Earth's hydrological cycle, its dominant atmospheric constituent is nitrogen, as on Earth, its nitrogen atmosphere is secondary, most likely a product of ammonia, as on Earth, and in its past, it had all the right conditions –liquid water, methane and ammonia in a warm environment – necessary for forming pre-biotic, perhaps even biogenic species, as on Earth. Yet there are notable differences. Being ten times farther from the Sun than the Earth, Titan receives only one percent of the solar energy compared to Earth, so that the satellite has remained perpetually frozen for 4 billion years. A purported ocean beneath the frozen ice shell can remain liquid only due to an admixture of 5–10% ammonia, an antifreeze, with water. Ammonia is toxic to life as we know it. The average annual rainfall of methane pales in comparison with the annual average rainfall of water on Earth. Titan's atmosphere is full of smog created by chemistry between its two most abundant constituents, nitrogen and methane, and the smog is persistent unlike the Earth. It is these differences and similarities between Titan and the Earth that make Titan such a unique and intriguing object in the solar system. The Cassini–Huygens Mission has opened new vistas into Titan's past and present, but the view is limited. As is the nature of every new endeavor, Cassini–Huygens' tantalizing findings have only whetted our appetites to return to this fascinating object to investigate more probing issues that are beyond the scope of even the extended Cassini mission.

In particular, the origin, fate, and cycle of Titan's methane require further exploration. The missing isotope ratios, particularly D/H in the surface H_2O ice, $^{16}O/^{18}O$ in CO, CO_2 and H_2O, $^{36}Ar/^{38}Ar$, $^{12}C/^{13}C$ in CO, CO_2 and abundant surface organics, determination of Xe and Kr to at least the 10^{-10} mole fraction level in the atmosphere, together with a thorough analysis of the surface material are important for discriminating between various hypotheses of the origin of methane. Long term, synoptic observations of the atmospheric phenomena including clouds and precipitation are essential supporting data. Identification and quantification of complex organic molecules in the vapor, condensed and solid forms from the ionosphere to the surface will be crucial. The composition and evolution of the lakes and the dune material is critical. Monitoring for signs of sudden or episodic events such as cryovolcanoes, fumaroles and impacts will provide an insight into the existence and nature of the purported subsurface ocean, its potential for habitability, as well as the origin of Titan's nitrogen. These and other outstanding questions can best be addressed by exploring Titan as a coupled system of the interior, surface and the atmosphere-ionosphere, employing diverse platforms including balloons, orbiters and landers. In future missions to Titan, a concerted effort should be made to fully characterize Titan's surface, since this is where the atmospheric products reside, but in higher concentration, and this is where the material from Titan's interior would end up in any cryovolcanic eruptions (Atreya 2007a). The surface is key to Titan's mysteries.

Acknowledgments SKA and JHW acknowledge support by the NASA Planetary Atmospheres Program and the Cassini–Huygens Mission. RDL acknowledges the support of Cassini. Patricia Egeler Dowd provided expert help with editing and figures.

References

Adamkovics M, Wong MH, Laver C, DePater I (2007) Widespread morning drizzle on Titan. Science 318:962–965

Adams EY (2006) Titan's thermal structure and the formation of a nitrogen atmosphere. Thesis, The University of Michigan, Ann Arbor

Anders E, Grevesse N (1989) Abundances of the elements – meteoritic and solar. Geochim Cosmochim Acta 53:197–214

Arpigny C, Jehin E, Manfroid J, Hutsemekers D, Schulz R, Stuwe JA, Zucconi J-M, Ilyin I (2003) Anomalous nitrogen isotope ratio in comets. Science 301:1522–1524

Atreya SK (1986) Atmospheres and ionospheres of the outer planets and their satellites. Springer, New York-Berlin

Atreya SK (2007a) Titan's organic factory. Science 316:843–845

Atreya SK (2007b) Saturn probes: why, where, how? Proceedings of the International Planetary Probe Workshop, NASA Jet Propulsion Laboratory Document, Table 1, Chapter 4_6ATREY in http://ippw.jpl.nasa.gov/20070607_doc/

Atreya SK, Donahue TM, Kuhn WR (1978) Evolution of a nitrogen atmosphere on Titan. Science 201:611–613

Atreya SK, Adams EY, Niemann HB, Demick-Montelara JE, Owen TC, Fulchignoni M, Ferri F, Wilson EH (2006) Titan's methane cycle. Planet Space Sci 54:1177–1187

Atreya SK, Lunine JI, Niemann HB, Wilson EH (2008) Where have Titan's ethane oceans gone? Geophys Res Abst 10, EGU2008-A-04876

BP (2007) BP statistical review of world energy. BP, London, UK

Balsiger H, Altwegg K, Geiss J (1995) D/H and $^{18}O/^{16}O$ ratio in the hydronium ions and neutral water from in situ measurements in comet Halley. J Geophys Res 100:5827–5834

Bézard B, Nixon CA, Kleiner I, Jennings DE (2007) Detection of $^{13}CH_3D$ on Titan. Icarus 191:397–400

Bockelee-Morvan D, Gautier D, Lis DC, Young K, Keene J, Phillips T, Owen T, Crovisier J, Goldsmith PF, Bergin EA, Despois D, Wootten A (1998) Deuterated water in Comet C/1996 B2 (Hyakutake) and its implication for the origin of comets. Icarus 133:147–162

Bockelee-Morvan D, Mumma MJ, Weaver HA (2004) The composition of cometary volatiles. In: Festou MC, Keller HU, Weaver HA (eds) Comets II. The University of Arizona Press, Tucson, pp 391–423

Broadfoot AL, Sandel BR, Shemansky DE, Holberg JB, Smith GR, Strobel DF, McConnell JC, Kumar S, Hunten DM, Atreya SK, Donahue TM, Moos HW, Bertaux JL, Blamont JE, Pomphrey RB, Linick S (1981) Extreme ultraviolet observations from Voyager 1 encounter with Saturn. Science 212:206–211

Brown RH, Soderblom LA, Soderblom JM, Clark RN, Jaumann R, Barnes JW, Sotin C, Buratti B, Baines KH, Nicholson PD (2008) The identification of liquid ethane in Titan's Ontario Lacus. Nature 454:607–610. doi:10.1038/nature07100

Castillo-Rogez JC, Matson DL, Sotin C, Johnson TV, Lunine JE, Thomas PC (2007) Iapetus' geophysics: Rotation rate, shape, and equatorial ridge. Icarus 190:179–202

Conklin EK, Ulich BL, Dickel JR (1977) 3mm observations of Titan. Bull Am Astron Soc 9:471

Coustenis A, Taylor F (1999) Titan: the earth-like moon. World Scientific, Singapore

Coustenis A, Salama A, Schultz B, Ott S, Lellouch E, Encrenaz Th, Gautier D, Feuchtgruber H (2003) Titan's atmosphere from ISO mid-infrared spectroscopy. Icarus 161:383–403

Coustenis A, Achterberg RK, Conrath BJ, Jennings DE, Marten A, Gautier D, Nixon CA, Flasar FM, Teanby NA, Bézard B, Samuelson RE, Carlson RC, Lellouch E, Bjoraker GL, Romani PN, Taylor FW, Irwin PGJ, Fouchet T, Hubert A, Orton GS, Kunde VG, Vinatier S, Mondellini J, Abbas MM, Courtin R (2007) The composition of Titan's stratosphere from Cassini/CIRS mid-infrared spectra. Icarus 189:35–62

Danielson RE, Caldwell JJ, Larach DR (1973) An inversion in the atmosphere of Titan. Icarus 20:437–443

Drake JJ, Testa P (2005) The 'solar model problem' solved by the abundance of neon in nearby stars. Nature 436:525–528

Eberhardt P, Reber M, Krankowsky D, Hodges R (1995) The D/H and $^{18}O/^{16}O$ ratios in water from comet P/Halley. Astron Astrophys 302:301–316

Engel S, Lunine JI, Hartmann WK (1995) Cratering on Titan and implications for Titan's atmospheric history. Planet Space Sci 43: 1059–1066

Eshleman VR (1982) Argon in Titan's atmosphere? Science 217:200

Eshleman VR, Tyler GL, Anderson JD, Fjeldbo G, Levy GS, Wood GE (1977) Radio science investigation with Voyager. Space Sci Rev 21:207–232

Eshleman VR, Lindal GF, Tyler GL (1983) Is Titan wet or dry? Science 221:53–55

Flasar FM, Samuelson RE, Conrath BJ (1981) Titan's atmosphere: temperature and dynamics. Nature 292:693–698

Flasar FM and the CIRS Team (2005) Titan's atmospheric temperatures, winds, and composition. Science 308:975–978

Graves SD, McKay CP, Griffith CA, Ferri F (2008) Rain and hail can reach the surface of Titan. Planet Space Sci 56:346–357

Grevesse N, Asplund M, Sauval J (2005) The new solar composition. In: Alecian G, Richard O, Vauclair S (eds) Element stratification in stars: 40 years of atomic diffusion, EAS Publications Series pp 21–30

Griffith CA, Zahnle K (1995) Influx of cometary volatiles to planetary moons: the atmospheres of 1000 possible Titan's. J Geophys Res 100:16907–16922

Griffith CA, Owen T, Miller GA, Geballe T (1998) Transient clouds in Titan's lower atmosphere. Nature 395:575–578

Griffith CA, Hall JL, Geballe TR (2000) Detection of daily clouds on Titan. Science 290:509–513

Griffith CA, Penteado P, Baines K, Drossart P, Barnes J, Bellucci G, Bibring J, Brown R, Buratti B, Capaccioni F, Cerroni P, Clark R, Combes M, Coradini A, Cruikshank D, Formisano V, Jaumann R, Langevin Y, Matson D, McCord T, Mennella V, Nelson R, Nicholson P, Sicardy B, Sotin C, Soderblom LA, Kursinski R (2005) The evolution of Titan's mid-latitude clouds. Science 310:474–477

Griffith CA, Penteado P, Rannou P, Brown R, Boudon V, Baines KH, Clark R, Drossart P, Buratti B, Nicholson P, McKay CP, Coustenis A, Negrao A, Jaumann R (2006) Evidence for a polar ethane cloud on Titan. Science 313:1620–1622

Hanel RA, Conrath B, Flasar FM, Kunde V, Maguire W, Pearl JC, Pirraglia J, Samuelson R, Herath L, Allison M, Cruikshank DP, Gautier D, Gierasch PJ, Horn L, Koppany R, Ponnamperuma C (1981) Infrared observations of the Saturnian system from Voyager 1. Science 212:192–200

Hayes A and the Cassini RADAR Team (2008) Hydrocarbon lakes on Titan: distribution and interaction with a porous regolith. Geophys Res Lett 35:L09204

Hunten DM (1978) A Titan atmosphere with a surface of 200 K. In: Hunten DM, Morrison D (eds) The Saturn System, NASA Conference Publication 2068, pp. 127–140

Hutsemékers D, Manfroid J, Jehin E, Arpigny C, Cochran A, Schulz R, Stüwe JA, Zucconi J-M (2005) Isotopic abundances of carbon and nitrogen in Jupiter-family and Oort Cloud comets. Astron Astrophys 440:L21–L24

Jacovi R, Bar-Nun A (2008) Removal of Titan's noble gases by their trapping in its haze. Icarus 196:302–304

Jewitt DC, Matthews HE, Owen T, Meier R (1997) Measurements of $^{12}C/^{13}C$, $^{14}N/^{15}N$ and $^{32}S/^{34}S$ ratios in comet Hale-Bopp (C/1995 01). Science 278:90–93

Jones TD, Lewis JS (1987) Estimated shock production of N_2 and organic compounds on early Titan. Icarus 72:381–393

Kelley DS, Karson JA, Früh-Green GL, Yoerger DR, Shank TM, Butterfield DA, Hayes JM, Schrenk MO, Olson EJ, Proskurowski G, Jakuba M, Bradley A, Larson B, Ludwig K, Glickson D, Buckman K, Bradley AS, Brazelton WJ, Roe K, Elend MJ, Delacour A, Bernasconi SM, Lilley MD, Baross JA, Summons RE, Sylva SP (2005) A serpentinite-hosted ecosystem: the lost city hydrothermal field. Science 307:1428–1434

Kouvaris LC, Flasar FM (1991) Phase equilibrium of methane and nitrogen at low temperatures – application to Titan. Icarus 91: 112–124

Kuiper GP (1944) Titan: a satellite with an atmosphere. Astrophys J 100:378–383

Lammer H, Stumptner W, Molina-Cuberos GJ, Bauer SJ, Owen T (2000) Nitrogen isotope fractionation and its consequence for Titan's atmospheric evolution. Planet Space Sci 48:529–543

Lewis JS (1971) Satellites of the outer planets: their physical and chemical nature. Icarus 15:174–185

Lewis JS (1973) Chemistry of the outer solar system. Space Sci Rev 14:401–410

Lewis JS, Prinn RG (1980) Kinetic inhibition of CO and N_2 reduction in the solar nebula. Astrophys J 238:357–364

Lindal GF, Wood GE, Hotz HB, Sweetnam DN, Eshleman VR, Tyler GL (1983) The atmosphere of Titan – an analysis of the Voyager 1 radio occultation measurements. Icarus 53:348–363

Lorenz RD (1993) The life, death and afterlife of a raindrop on Titan. Planet Space Sci 41:647–655

Lorenz RD (1997) Did Comas Solá discover Titan's atmosphere? Astron Geophys 8:16–18

Lorenz RD (1998) Many lakes make an ocean. Abstract #1689, XIXth Lunar and Planetary Science Conference, Houston, TX

Lorenz RD (2000) The weather on Titan. Science 290:467–468

Lorenz RD (2008) The changing face of Titan. Physics Today 61:34–39

Lorenz RD, Lunine JI (1996) Erosion on Titan: past and present. Icarus 122:79–91

Lorenz R, Mitton J (2008) Titan unveiled: Saturn's mysterious moon explored. Princeton University Press, Princeton

Lorenz RD, Lunine JI, Grier JA, Fisher MA (1995) Prediction of aeolian features on planets: application to Titan paleoclimatology. J Geophys Res (Planets) 88:26377–26386

Lorenz RD, Lunine JI, McKay CP (1997a) Titan under a red giant sun: a new kind of "habitable" moon. Geophys Res Lett 24(22): 2905–2908

Lorenz RD, McKay CP, Lunine JI (1997b) Photochemically driven collapse of Titan's atmosphere. Science 275:642–644

Lorenz RD, McKay CP, Lunine JI (1999) Analytical investigation of climate stability on Titan: sensitivity to volatile inventory. Planet Space Sci 47:1503–1515

Lorenz RD and Lunine JI, McKay CP, Withers PG (2001) Entropy production by latitudinal heat flow on Titan. Mars and Earth. Geophys Res Lett 28:415–418

Lorenz RD and the Cassini RADAR Team (2008a) Fluvial channels on Titan: initial Cassini radar observations. Planet Space Sci 56: 1132–1144

Lorenz RD and the Cassini RADAR Team (2008b) Titan's inventory of organic surface materials. Geophys Res Lett 35:L02206

Lorenz RD, Flasar FM, Brown ME (2009) Seasonal cycles. In: Brown RH, Lebreton J-P, Waite JH (eds) Titan From Cassini–Huygens. Springer, Dordrecht

Lunine JI, Atreya SK (2008) The methane cycle on Titan. Nat Geosci 1:159–164

Lunine JI, Rizk B (1989) Thermal evolution of Titan's atmosphere. Icarus 80:370–389

Lunine JI, Stevenson DJ (1985) Thermodynamics of clathrate hydrate at low and high pressures with application to the outer solar system. Astrophys J Suppl 58:493–531

Lunine JI, Stevenson DJ (1987) Clathrate and ammonia hydrates at high pressure – application to the origin of methane on Titan. Icarus 70:61–77

Lunine JI, Stevenson DJ, Yung YL (1983) Ethane ocean on Titan. Science 222:1229–1230

Lunine JI, Yung YL, Lorenz RD (1999) On the volatile inventory of Titan from isotopic abundances in nitrogen and methane. Planet Space Sci 47:1291–1303

Lunine JI and the RADAR Science Team (2008) Lack of south polar methane lakes on Titan. Abstract #1637, XXIXth Lunar and Planetary Society Conference, Houston, TX

Lunine JI Choukroun M, Stevenson DJ, Tobie G (2009) The origin and evolution of Titan. In: Brown RH, Lebreton J-P, Waite JH (eds) Titan from Cassini–Huygens. Springer, Dordrecht

Lutz BL, Owen T, Cess RD (1976) Laboratory band strengths of methane and their applications to the atmospheres of Jupiter, Saturn, Uranus, Neptune and Titan. Astrophys J 203:541–551

Magee BA, Mandt KE, Waite JH, Westlake J, Gell DA, De La Haye V (2009) INMS derived composition of Titan's upper atmosphere: analysis methods and model. Planet Space Sci in press

Mandt KE, Waite JH, Lewis W, Magee BA, Bell JM, Lunine J, Mousis O, Cordier D (2009) Isotopic evolution of the major constituents of Titan's atmosphere based on Cassini data. Planet Space Sci in press

Marten A, Hidayat T, Biraud Y, Moreno R (2002) New millimeter heterodyne observations of Titan: vertical distributions of nitriles HCN, HC_3N, CH_3CN, and the isotopic ratio $^{15}N/^{14}N$ in its atmosphere. Icarus 158:532–544

Matson DL, Atreya SK, Castillo-Rogez J, Johnson TV, Adams EY, Lunine JI (2007) Endogenic origin of Titan's N_2. Abstract 2007AGUFM.P21D.04M, American Geophysical Union Fall Meeting, San Francisco

McKay CP, Smith HD (2005) Possibilities for methanogenic life in liquid methane on the surface of Titan. Icarus 178:274–276

McKay CP, Scattergood TW, Pollack JB, Borucky WJ, van Ghyseghem HT (1988) High-temperature shock formation of N_2 and organics on primordial Titan. Nature 332:520–522

McKay CP, Pollack JB, Courtin R (1989) The thermal structure of Titan's atmosphere. Icarus 80:23–53

McKay CP, Pollack JB, Courtin R (1991) The greenhouse and antigreenhouse effect on Titan. Science 253:1118–1121

McKay CP, Pollack JB, Lunine JI, Courtin R (1993) Coupled atmosphere-ocean models of Titan's past. Icarus 102:88–98

McKay CP, Lorenz RD, Lunine JI (1999) Analytic models of the greenhouse and anti-greenhouse effects: application to Titan and the early Earth. Icarus 137:57–61

Meier R, Owen TC, Matthews HE, Jewitt DC, Bockelee-Morvan D, Biver N, Crovisier J, Gautier D (1998a) A determination of the HDO/H_2O ratio in Comet C/1995 01 (Hale-Bopp). Science 279: 842–844

Meier R, Owen TC, Jewitt DC, Matthews HE, Senay M, Biver N, Bockelee-Morvan D, Crovisier J, Gautier D (1998b) Deuterium in Comet C/1995 01 (Hale-Bopp): detection of DCN. Science 279:1707–1710

Miller SL (1961) The occurrence of gas hydrates in the solar system. Proc Natl Acad Sci USA 47:1798–1808

Mitchell J (2008) The drying of Titan's dunes: Titan's methane hydrology and its impact on atmospheric circulation. J Geophys Res 113:E08015, doi:10.1029/2007JE003017

Mitri GL, Showman AP, Lunine JI, Lorenz RD (2007) Hydrocarbon lakes on Titan. Icarus 186:385–394

Mousis O, Schmitt B (2008) Sequestration of ethane in the cryovolcanic subsurface of Titan. Astrophys J 677:L67–L70

Mousis O, Gautier D, Bockelée-Morvan D (2002) Turbulent model of the Saturn subnebula: implications for the origin of methane in Titan's atmosphere. Icarus 156:162–175

NRC (2007) The limits of organic life in planetary environments, National Research Council Publication, Washington DC

Niemann HB and the GCMS Team (2005) The abundances of constituents of Titan's atmosphere from the GCMS instrument on the Huygens probe. Nature 438:779–784

Owen TC (1982) The composition and origin of Titan's atmosphere. Planet Space Sci 30:833–838

Owen TC (2000) On the origin of Titan's atmosphere. Planet Space Sci 48:747–752

Prinn RG, Fegley B (1981) Kinetic inhibition of CO and N_2 reduction in circumplanetary nebulae: implications for satellite composition. Astrophys J 249:308–317

Rannou P, Montmessin F, Hourdin F, Lebonnois S (2006) The latitudinal distribution of clouds on Titan. Science 311:201–205

Ribas I, Guinan EF, Gudel M, Audard M (2005) Evolution of the solar activity over time and effects on planetary atmospheres. I. High-energy irradiances (1–1700 Å). Astrophys J 622:680–694

Samuelson RE (1983) Radiative equilibrium model of Titan's atmosphere. Icarus 53:364–387

Samuelson RE, Nath NR, Borysow A (1997) Gaseous abundances and methane supersaturation in Titan's troposphere. Planet Space Sci 45:959–980

Schulze-Makuch D, Grinspoon DH (2005) Biologically enhanced energy and carbon cycling on Titan? Astrobiology 5:560–567

Sotin C, Jaumann R, Buratti BJ, Brown RH, Clark RN, Soderblom LH, Baines KH, Bellucci G, Bibring JP, Capaccioni F, Cerroni P, Combes M, Coradini A, Cruikshank DP, Drossart P, Formisano V, Langevin Y, Matson DL, McCord TB, Nelson RM, Nicholson PD, Sicardy B, LeMouelic S, Rodriguez S, Stephan K, Scholz CK (2005) Release of volatiles from a possible cryovolcano from near-infrared imaging of Titan. Nature 435:786–789, doi:10.1038/nature03596

Stevenson DJ, Potter BE (1986) Titan's latitudinal temperature distribution on seasonal cycles. Geophys Res Lett 13:93–96

Stofan ER, Elachi C, Lunine JI, Lorenz RD, Stiles B, Mitchell KL, Ostro S, Soderblom L, Wood C, Zebker H, Wall S, Janssen M, Kirk R, Lopes R, Paganelli F, Radebaugh J, Wye L, Anderson Y, Allison M, Boehmer R, Callahan P, Encrenaz P, Flamini E, Franscescetti G, Gim Y, Hamilton G, Hensley S, Johnson WTK, Kelleher K, Muhleman D, Paillou P, Picardi G, Posa F, Roth L, Seu R, Shaffer S, Vetrella S, West R (2007) The lakes of Titan. Nature 445:61–64

Strobel DF (1974) The photochemistry of hydrocarbons in the atmosphere of Titan. Icarus 21:466–470

Strobel DF, Shemansky DE (1982) EUV emission from Titan's upper atmosphere: Voyager 1 encounter. J Geophys Res 87:1361–1368

Strobel DF, Atreya SK, Bézard B, Ferri F, Flasar FM, Fulchignoni M, Lellouch E, Muller-Wodarg I (2009) Atmospheric composition and structure. In: Brown RH, Lebreton J-P, Waite JH (eds) Titan from Cassini–Huygens. Springer, Dordrecht

Thomas C, Mousis O, Ballenegger V, Picaud S (2007) Clathrate hydrates as a sink of noble gases in Titan's atmosphere. Astron Astrophys 474:L17–L20

Thompson WR, Zollweg JA, Gabis DH (1992) Vapor-liquid equilibrium thermodynamics of $N_2 + CH_4$: model and Titan applications. Icarus 97:187–199

Tobie G, Lunine JI, Sotin C (2006) Episodic outgassing as the origin of atmospheric methane on Titan. Nature 440:61–64

Tobie G, Gautier D, Hersant F, Lunine JI (2008) Interpretation of Titan's atmospheric composition measured by Cassini–Huygens. EPSC Abstract, 3, EPSC2008-A-00325

Tokano T, Molina-Cuberos GL, Lammer H, Stumptner W (2001) Modelling of thunderclouds and lightning generation on Titan. Planet Space Sci 49:539–560

Tokano T, McKay CP, Neubauer FM, Atreya SK, Ferri F, Fulchignoni M, Niemann HB (2006) Methane drizzle on Titan. Nature 442: 432–435

Tomasko MG and the DISR Team (2005) Rain, winds and haze during the Huygens probe's descent to Titan's surface. Nature 438:765–778

Trafton LM (1972) The bulk composition of Titan's atmosphere. Astrophys J 175:295–306

Turtle EP, Perry JE, McEwen AS, DelGenio AD, Barbara J, West RA, Dawson DD, Porco CC (2009) Cassini imaging of Titan's high latitude lakes, clouds, and south polar surface changes. Geophys Res Lett 36:L02204, doi:10.1029/2008GL036186

Vinatier S, Bézard B, Nixon CA (2007) The Titan $^{14}N/^{15}N$ and $^{12}C/^{13}C$ isotopic ratios in HCN from Cassini/CIRS. Icarus 191:712–721

Waite JH, Niemann H, Yelle RV, Kasprzak WT, Cravens TE, Luhman JG, McNutt RL, Ip W-H, Gell D, De La Haye V, Müller-Wordag I, Magee B, Borggren N, Ledvina S, Fletcher G, Walter E, Miller R, Scherer S, Thorpe R, Xu J, Block B, Arnett K (2005) Ion neutral mass spectrometer results from the first flyby of Titan. Science 308:982–986

Waite JH, Young DT, Cravens TE, Coates AJ, Crary FJ, Magee B, Westlake J (2007) The process of tholin formation in Titan's upper atmosphere. Science 316:870–872

Waite HW, Lunine JI, Owen TC, Gautier D, Niemann HB, Strobel DF (2009) Conversion of methane and nitrogen to complex polymers on Titan. In: Brown RH, Lebreton J-P, Waite JH (eds) Titan from Cassini–Huygens. Springer, Dordrecht

Wilson EH, Atreya SK (2004) Current state of modeling the photochemistry of Titan's mutually dependent atmosphere and ionosphere. J Geophys Res 109:E06002, doi:10.1029/2003JE002181

Yelle RV, Cui J, Müller-Wodarg ICF (2008) Methane escape from Titan's atmosphere. J Geophys Res 113:E10003, doi:10.1029/2007JE003031

Yung YL, Allen MA, Pinto JP (1984) Photochemistry of the atmosphere of Titan: comparison between model and observations. Astrophys J Supp 55:465–506

Zahnle KJ, Walker JCG (1982) The evolution of solar luminosity. Rev Geophys Space Phys 20:280–292

Ziurys LM, Savage C, Brewster MA, Apponi AJ, Pesch TC, Wyckoff S (1999) Cyanide chemistry in comet Hale-Bopp (C/1995 O1). Astrophys J 527:L67–L71