Pergamon

Planet. Space Sci., Vol. 46, No. 9/10, pp. 1099–1107, 1998

0032–0633/98/$—see front matter

PII: S0032–0633(97)00221–3

Some speculations on Titan's past, present and future

Jonathan I. Lunine,[1] **Ralph D. Lorenz**[1] **and William K. Hartmann**[2]

[1]Lunar and Planetary Laboratory, University of Arizona Tucson, Arizona 85721-0092, U.S.A.
[2]Planetary Sciences Institute, 620 N. 6th Ave, Tucson, Arizona, 85705, U.S.A.

Received 17 March 1997; revised 7 November 1997; accepted 11 November 1997

Abstract. The solar system's second largest natural satellite is shrouded by a thick nitrogen atmosphere, rich in methane, within which sunlight- and cosmic-ray-driven organic chemistry has gone on for some 4.5 billion years. The earliest history of Titan's atmosphere, and specifically its origin, remains unclear until the Cassini–Huygens probe measures the ratio of argon to nitrogen and the abundances of other noble gases and isotopes. However, the abundance of deuterated methane in the atmosphere today is consistent with an atmosphere that originated in the chemically-processed sub-nebula around Saturn, rather than in cometary material. Titan's overall atmospheric history is driven by the depletion of methane, and the mechanisms by which methane might be resupplied from surface or external sources. Remote sensing data mitigate against a large reservoir of methane at Titan's surface, leaving open the possibility that methane is periodically depleted from Titan's atmosphere on timescales of 10^7–10^8 years; under such conditions Titan might oscillate between thin and thick atmospheric epochs. Titan's surface may provide a repository for complex organic molecules that were synthesized during times when liquid water was temporarily available on the surface, such as after impacts or cryo-volcanic eruptions. Such molecules might provide clues to the resolution of some difficult issues associated with the origin of life. Identifying the presence and nature of such molecules is a difficult exploration problem that must be left to missions which follow-on from the Cassini–Huygens exploration of Titan. © 1998 Elsevier Science Ltd. All rights reserved

1. Introduction

The past several years have seen an increasing number of remote sensing observations of Titan's surface, which is hidden beneath a high altitude photochemical haze. Concurrent with such observations has been a renewed effort to understand the nature of Titan's surface, its interactions with Titan's atmosphere, and the resulting long-term evolution of this planet-sized moon.

The present article is a review and somewhat speculative synthesis of recent ideas and new data concerning the origin and earliest evolution of Titan's atmosphere, long-term stability of Titan's atmosphere, and the role this moon might play in helping exobiologists understand the chemical and physical origins of life. We do not attempt a review of current understanding of Titan's atmosphere; a very recent piece in this regard is that of Lunine (1996). A review of the remote sensing data and its implications for the nature of Titan's surface is provided by Lorenz and Lunine (1997).

We begin in Section 2 by considering recent data on deuterated methane and its implications for the origin of Titan's atmosphere and for the nature of Titan's interior. We then move in Section 3 to a discussion of recent models of long-term surface–atmosphere interactions, with particular emphasis on atmospheric stability. Finally, in Section 4 we examine one particular issue which is a conceptual sticking-point in understanding the origin of life, namely the origin of bimolecular-handedness, and consider the possibility that organic chemistry on Titan might provide a unique perspective on how such handedness arises.

2. Origin of Titan's atmosphere and implications for the interior

Titan's atmosphere may be a remnant of the circum-Saturnian gas and planetesimals from which the satellite itself was derived (Lunine *et al.*, 1989), or it could be a product of cometary impacts during or after accretion (Zahnle *et al.*, 1992). These are endmember cases, and it is possible that the present atmosphere contains contributions from both. The difficulty of quantifying how much atmosphere might be contributed from cometary

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Correspondence to: Jonathan I. Lunine, Lunar and Planetary Laboratory, 1629 East University Blvd., University of Arizona, Tucson, Arizona 85721-0092, U.S.A. Tel: (1) 520 621 2789; Fax: (1) 520 621 4933; E-mail: jlunine@lpl.arizona.edu

impacts lies in the wide range of cometary velocities associated with different dynamical states. Comets coming in from the Oort cloud have much higher velocities than Kuiper Belt comets, and hence would tend to erode atmosphere off of Titan, according to Griffith and Zahnle (1995), who tried a large number of different simulations of cometary population distributions. They found that typical runs yielded 10% of Titan's atmosphere being contributed from comets (the remainder assumed to be from the circum-Saturnian nebula), but that one out of six simulations yielded the entire atmosphere from comets.

One approach to understanding the origin of Titan's atmosphere is to measure the abundances of species that are diagnostic of different primordial chemical reservoirs. Owen (1982) suggested that the argon-to-nitrogen ratio would be diagnostic in this regard. Laboratory experiments and theoretical models (Bar-Nun *et al.*, 1988; Lunine *et al.*, 1991) indicate that argon is similar to that of molecular nitrogen in its tendency to incorporate into solid ice phases at temperatures typical of the Uranus–Neptune region during planet formation. Since comets appear to have much of their elemental nitrogen in the form of molecular nitrogen, a cometary source for Titan's nitrogen-dominated atmosphere would bring in large quantities of argon, as well. Hence, as Owen first pointed out, such an atmosphere would have a ratio of argon to nitrogen roughly solar, i.e., 0.1. Small differences in the propensity for trapping of these species in ice might lead to a variation of plus or minus an order of magnitude, i.e., argon-to-nitrogen ranging from 0.01–1.

Alternatively, if Titan's atmosphere were derived from circum-Saturnian gaseous and solid phases associated with the formation of the planet itself, molecular nitrogen might not be the principal form of nitrogen. Physical models of the circum-Saturnian nebula by Lunine and Stevenson (1982) support the chemical modeling of Prinn and Fegley (1981), who found that ammonia might dominate, or at least be comparable to molecular nitrogen, in a circum-Saturnian nebula with densities much higher than the surrounding solar nebula. The extent to which ammonia dominates depends upon the kinetics of the reactions converting N_2 to NH_3, because they determine the lowest temperature at which the reactions proceed in the lifetime of the circum-Saturnian nebula. (Note that the limiting temperature is well above that in the zone where Titan formed; the assumption is made that the ammonia is formed closer to Saturn and mixed outward by turbulent processes.) More rapid kinetics, made possible perhaps by heterogeneous catalysis, would strongly favor ammonia (Prinn and Fegley, 1981). Ammonia tends to hydrogen-bond with water ice, forming a number of stoichiometric compounds that remove almost all of the ammonia from the nebular gaseous phase. Molecular nitrogen, on the other hand, must rely on physical adsorption to be incorporated in the ice, and at plausible circum-Saturnian nebular temperatures near Titan's present position is mostly excluded from the solid phase. Thus, even if ammonia is merely comparable to molecular nitrogen in the gas phase of the nebula, it will dominate in the ice.

Argon, like molecular nitrogen, is incorporated inefficiently in the ice by adsorption. Thus, an origin of Titan's nitrogen atmosphere from ices condensed in a reducing nebula, with a high fraction of ammonia relative to the total nitrogen, would be reflected in a very small argon-to-nitrogen ratio—much less than 1%. (The conversion of ammonia to molecular nitrogen to form the present atmosphere of Titan is a separate problem; various models are reviewed in Lunine *et al.*, 1989.) Current Voyager-based upper limits on argon in Titan's atmosphere are too crude to apply this important test. However, the Huygens Gas Chromatograph Mass Spectrometer will be able to measure very small amounts of argon, and will enable the argon-to-nitrogen ratio to be very precisely determined during the descent scheduled for 2004.

A complimentary chemical test of the origin of Titan's atmosphere, focusing on the methane, lies in measuring the deuterium-to-hydrogen ratio, and can be applied today. Ion–molecule reactions in molecular clouds (Van Dishoeck *et al.*, 1993) lead to an enhancement of the D-to-H ratio in a variety of organic and other molecules, relative to the value predicted on the basis of thermodynamics and the rates of chemical reactions between neutral species. Insofar as comets contain ices that preserve much of this enhancement, a comet-derived atmosphere on Titan would be correspondingly enhanced in its D-to-H ratio. Alternatively, a Titan atmosphere derived primarily from circum-Saturnian material would exhibit little or no deuterium enhancement. Models for satellite-forming disks around Jupiter and Saturn predict that much or all of the material has undergone processing in fairly warm environments, i.e. above 200 K, such that strong D-to-H enhancements in molecular species would be erased by reequilibration with the molecular hydrogen gas. In contrast to enhancements of a factor of ten or more relative to the solar D-to-H value achieved by ion–molecule reactions in the molecular cloud, enhancements of only a factor of two over solar are possible in circumsatellite disks.

The predominant hydrogen-bearing species in Titan's atmosphere is methane, and it is in this species that deuterium enhancements—or lack thereof—are recorded for Titan. Pinto *et al.* (1986) developed a model in which the progressive photochemical destruction of methane over geologic time leads to an additional deuterium enhancement on top of any primordial enhancement. The effect derives from the greater magnitude of the binding energy of a deuterium atom to the carbon in methane, relative to the hydrogen–carbon binding energy. Thus, hydrogen has a greater probability of being removed from methane during absorption of ultraviolet radiation from the sun. If the current rates of photochemical destruction are typical over Titan's history, then the net tendency of methane to retain deuterium vs hydrogen leads to an enhancement of deuterated methane (CH_3D) relative to CH_4 of a factor of two. Hence if the primordial ratio of deuterium to hydrogen in methane was enhanced over solar by a factor of two, the current ratio would be four times solar.

Lecluse *et al.* (1996) have reexamined the observations of deuterium abundance in the sun, comets, the Earth and Titan. The observed value for Titan has decreased somewhat from determinations made in the late 1980's. The most recent measured value of CH_3D to CH_4 in Titan's atmosphere implies a D/H value of 7.75×10^{-5}, with an uncertainty of $\pm 30\%$ (Orton, 1992). This value is below the enhancement in comets and, as noted by Lecluse *et al.* (1996), consistent with the photochemical enrichment of deuterated methane proposed by Pinto *et al.* (1986), superimposed on at most a modest (factor of two or less) primordial enhancement relative to the solar D-to-H value. The lack of a strong primordial enhancement is consistent with the bulk of Titan's atmospheric methane having been derived locally, in a circum-Saturnian disk, rather than from collisions with cometary debris. However, earlier determinations of CH_3D are a factor of two higher (e.g., De Bergh *et al.*, 1986; Coustenis *et al.*, 1989), and therefore ambiguous with respect to constraining Titan's source region. It may be that we must await direct measurement by the Huygens probe to settle the question of Titan's atmospheric deuterium abundance.

If Titan's atmosphere had a local source, a high density disk of material formed as a by-product of the growth of Saturn, then carbon- and nitrogen-bearing molecules would have been dominated by reduced species (Prinn and Fegley, 1981) such as methane and ammonia. If the latter were the dominant nitrogen-bearing species, then the ammonia-to-water ratio in the planetesimals making up Titan would have been 15%. Plausibly some of the nitrogen was in the form of more oxidized species, but the main conclusion is that Titan is likely more ammonia-rich than an object composed of debris derived from the solar nebula or surrounding molecular cloud.

Is such a conclusion consistent with Titan's density, which at 1.87 g cm^{-3}, is larger than that predicted for a reducing disk, as reviewed by Lunine and Tittemore (1993)? Accretion models of satellites the mass of Titan, Ganymede and Callisto (Lunine and Stevenson, 1982) suggest that heating during late stages of formation was sufficient to vaporize incoming ices, leading to an enhancement in the silicate component (Stevenson *et al.*, 1986). Quantitative models of such water loss have yet to appear in the literature, a decade after this suggestion was made, but the direction of the effect, and the energetics, both support the notion that Titan lost water during accretion, as did Ganymede and Callisto.

If the deuterium abundance reflects the origin of Titan's atmosphere (and hence Titan itself), in a reducing environment, then the interior of the satellite should be relatively rich in ammonia. In turn, because ammonia lowers the melting point of water dramatically, Titan should have a liquid mantle of ammonia–water even up to the present day. Figure 1, modified from Stevenson (1992), illustrates such a model. The basic physics which allows such a mantle of ammonia–water liquid, but not liquid water, is the transport of heat outward from the satellite by subsolidus convection in the water ice. The ice self-regulates to a temperature below the ice melting point at which the viscosity is sufficiently low to allow flow and transport of accretional and radiogenic heat outward. This temperature happens to be above the liquidus for a compositionally-plausible solution of ammonia–water based on recent high-pressure experiments of Cynn *et al.* (1989). The most recent models of Titan's interior, by Grasset and Sotin (1996), also lead to the conclusion that a substantial liquid layer exists today if the satellite contains significant amounts of ammonia. In the absence of significant amounts of ammonia, Titan's interior structure today would be entirely solid, with Ice I atop several high pressure phases of water ice, below which is a rock core. The assumption that interior temperatures were warm enough, during or after accretion, to soften the ice and allow the rock to move to the center of Titan, is a fairly robust conclusion of thermal evolution models.

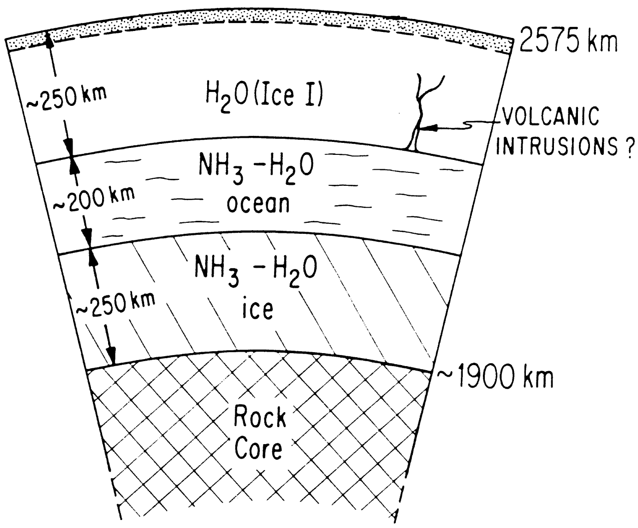

Fig. 1. Model of the present-day interior of Titan, assuming formation of the satellite in a reducing environment, adapted from Stevenson (1992). The Ice I layer might also contain methane clathrate hydrate, as well as trapped pockets of fluid methane. The uppermost thin layer is the portion of Titan's crust that might be in thermodynamic contact with the atmosphere, e.g., a porous ice layer suffused with liquid methane and other hydrocarbons

Density measurements suggest that near-peritectic (on the water-rich side) composition ammonia–water fluids are roughly neutrally buoyant relative to Ice I. This yields a situation in Titan's crust similar to that of the Earth with respect to magmas. In the case of Titan, the magma is ammonia–water fluid which may migrate, at some time and under some conditions, upward through the ice I crust to the surface (Stevenson, 1982; Lunine and Stevenson, 1987). Titan's surface and near-surface crust may contain ammonia–water solid compounds. There are exobiological implications to this statement which we discuss in a later section. Here, we point out that ammonia–water volcanism has both chemical and morphological implications.

Owen (1982) made the important point that the rare isotope argon-40, derived from the decay of potassium-40 in silicates, is potentially a measure of the amount of outgassing of a silicate core in Titan's interior, and computed that as much as 10^{-4} of the present Titan atmosphere could be argon-40, if the relative outgassing rate was equivalent to terrestrial. However, a problem is that diffusion of the argon-40 through the interior may be too slow to allow full outgassing over the age of the solar system. Therefore, the argon-40 content of Titan's atmosphere may be principally determined by the leaching of the parent potassium-40 from core silicates into adjacent ammonia–water liquid mantle, and the volume of that material subsequently erupted to Titan's surface. Engel *et al.* (1994) used thermodynamic modeling and experimental data to compute the solubility of potassium-40 in ammonia–water liquids under kilobar pressures, and used this result to determine the amount of argon-40 eventually released to the atmosphere as a function of surface flow volume. These numbers are not large; a kilometer-thick flow across Titan's surface would put into the atmosphere an argon-40 inventory equivalent to mole fractions of between 10^{-8} and 10^{-10} of the present atmosphere. This signature could be swamped by primordial argon-40, which is 1 part in 30,000 of the total argon abundance. If Titan formed of ices containing nitrogen in molecular form, the high argon abundance would imply a primordial argon-40 abundance (i.e. that not due to potassium-40 decay after Titan core formation) of order 10^{-6}. However, a Titan formed from ices containing nitrogen principally in the form of ammonia would lack this primordial component, allowing the outgassed component to show through. Rheological measurements indicate rather high viscosities in rapidly-cooled liquid ammonia–water flows (Kargel *et al.*, 1991), which could produce distinctive types of flow features detectable in Cassini orbiter radar and near-IR images, and particularly in the Huygens probe Descent Imager pictures (Lorenz, 1996), allowing for a determination of flow volumes independent of the argon-40 measurements. The combination of such flow volume estimates and measurement of atmospheric argon-40 from the Huygens probe thus provides a potentially interesting additional constraint on the origin of the atmospheric nitrogen.

3. Long-term stability of Titan's atmosphere

All post-Voyager published photochemical models (e.g. Yung *et al.*, 1984; Toublanc *et al.*, 1992; Lara *et al.*, 1994) of Titan's atmosphere agree that the current inventory of methane in Titan's atmosphere will be depleted by photolysis in less than 10^8 years. Various resupply mechanisms have been proposed, including a surface hydrocarbon ocean, methane hiding in a subsurface regolith, and cometary impacts (see the reviews cited in the introduction for the numerous references to these ideas). Because the thermal balance of Titan's atmosphere is dependant on infrared absorption during pairwise collisions of nitrogen, methane and hydrogen molecules (the last being a photochemical product of methane), a change in the methane abundance has a potentially significant effect on the atmosphere. In other words, photochemistry may drive climate change on Titan.

Various studies of the evolution of Titan's atmosphere coupled to different models of the surface have been conducted. McKay *et al.* (1993), for example, considered how the atmosphere would respond if the atmospheric methane abundance were controlled by surface reservoirs of methane. If a massive ocean were present (either on the surface or as a subsurface reservoir in thermodynamic contact with the atmosphere), then as methane is converted to heavier hydrocarbons in the atmosphere (whose fate is sedimentation), the surface reservoir would gradually become less methane-rich, reducing the near-surface methane relative humidity but allowing dissolved nitrogen to evaporate into the atmosphere. Under such conditions, and imposing the monotonically-increasing luminosity of the sun, a gradual warming of Titan's atmospheric temperatures would occur over geologic time. A similar result was obtained by McKay *et al.* (1993) in the situation where pools of methane only were present, such that the methane relative humidity was buffered at the surface, but no reservoir of nitrogen was available to exsolve to the atmosphere.

Remote sensing data (e.g., Muhleman *et al.*, 1991; Griffith, 1993; Lemmon *et al.*, 1995; Coustenis *et al.*, 1995; Smith *et al.*, 1996) fail to detect oceans that were hypothesized by Lunine *et al.* (1983) to both supply methane and store the major end product of methane photolysis (ethane). An alternative model must be considered, in which methane does periodically become depleted from Titan's atmosphere, until stochastic resupply mechanisms (such as cometary impacts or volcanism) restock the atmosphere with methane. Lorenz *et al.* (1997a) have examined the implications of such a depletion on Titan's atmosphere. They used the non-grey radiative–convective code developed by McKay *et al.* (1989) to model the present Titan atmosphere, with updated collision-induced absorption coefficients and a Mie scattering stratospheric haze. Moist convective transport of energy through the atmosphere was included for model atmospheres in which nitrogen saturates. Figure 2, adapted from their work, summarizes the surface temperature change. The results are rather sensitive to the behavior of the photochemically-produced haze in the stratosphere, on the surface albedo, and on the luminosity of the sun. Depletions of atmospheric methane early in Titan's history have a more severe effect on the atmosphere because the sun's luminosity was lower. In most of the cases studied the atmosphere becomes cold enough for the molecular nitrogen to condense out as rain or snow, leading to potentially complex scenarios of partial collapse of the atmosphere.

Although no single evolutionary timeline is implied by the calculations, Fig. 3 shows a possible schematic history of Titan's atmosphere which assumes no present-day massive surface reservoir of methane. The first few hundred million years after accretion of Titan are characterized by a massive primordial atmosphere of methane and ammonia, raised by accretional heating. Escape of primordial methane by early, rapid UV photolysis cools the atmosphere, forcing ammonia condensation and leaving behind an atmosphere of nitrogen (formed photochemically from the ammonia) and methane. As conditions cooled sufficiently for the crust of Titan (water ice and some ammonia) to freeze over, the atmospheric methane could have been supported by an ocean of methane which today is absent, but which could have left behind morphological signatures detectable by Cassini and Huygens (Lorenz and Lunine, 1996). There may have been a relatively stable time period during which the surface methane was slowly depleted, supplying the atmosphere with methane consumed by solar-ultraviolet-driven photolysis. As the surface reservoir depleted, and atmospheric methane was expended, the atmosphere cooled; in the first quarter of Titan's history when the sun's luminosity was less than 80% of the present-day value, the exhaustion of atmospheric methane could have led to complete freezeout of the atmosphere. The surface temperature after atmospheric freezeout is then determined principally by the albedo of surface frosts and the

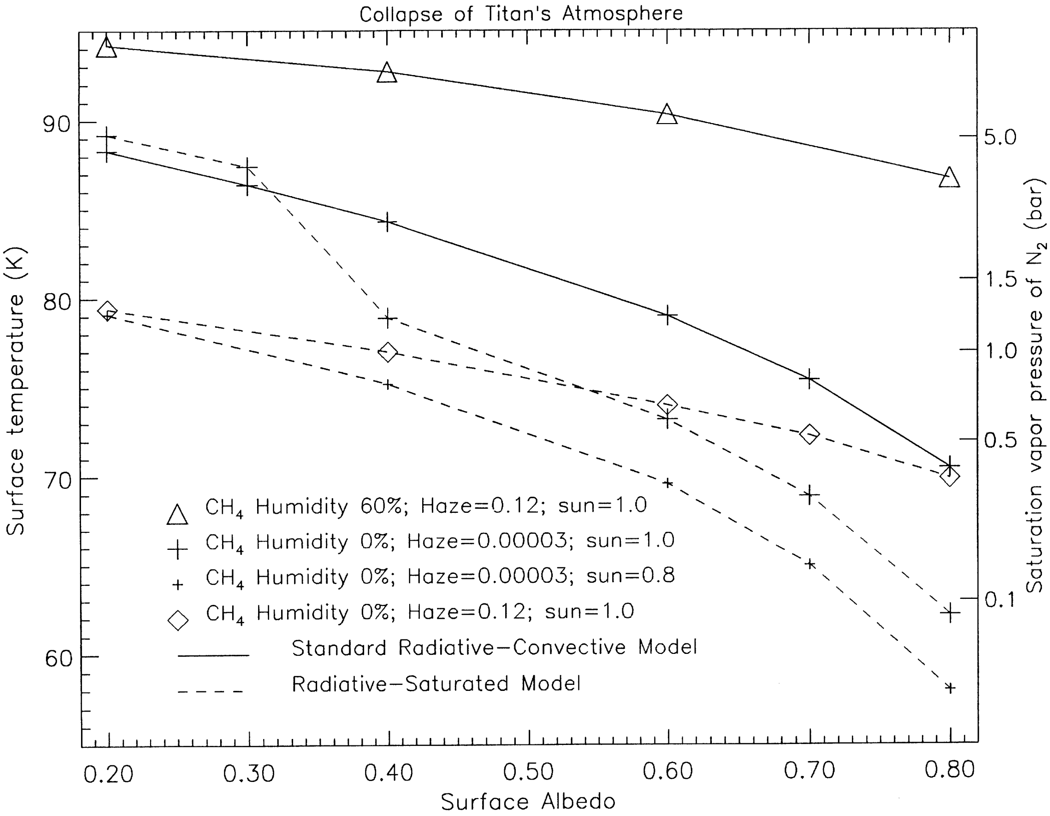

Fig. 2. The surface temperature of Titan as a function of albedo, methane gas phase abundance, solar luminosity and stratospheric haze properties, adapted from Lorenz *et al.* (1997a). Haze number are production rate (via methane photolysis) in units of 10^{-14} g cm^{-1} s^{-1}. Numbers for the sun are luminosity in units of the present-day value at Sun–Titan distance. Methane relative humidities refer to the value just above the surface. Dashed line includes the effect of moist convective transport of heat caused by nitrogen condensation. An auxiliary vertical scale on the right is the saturation vapor pressure of nitrogen, tied to the temperature axis on the left

luminosity of the sun at that time, since the remnant atmosphere is optically thin. Several cycles of atmospheric freezeout and resurrection, as new methane was supplied by volcanism or comet impact, might have occurred in the first half of Titan's history; only two are shown in the schematic history of Fig. 3.

Eventually, the luminosity of the sun increased sufficiently that, even when methane was depleted from Titan's atmosphere, atmospheric collapse was not as severe. The surface temperature during these modest collapse episodes is determined by the thermal structure of the essentially-pure nitrogen atmosphere and the value of the solar luminosity. The latter portion of Titan's geologic past might then have been characterized by episodes of modest atmospheric deflation and reinflation as methane was exhausted from, and then added back to, the atmosphere. The figure assumes that addition of methane endogenically or exogenically restores the atmosphere to a state similar to today's (normalized in temperature by the changing solar luminosity). It is conceivable that adding a very large quantity of methane during atmospheric reinflation might create a distended atmosphere with a surface temperature much higher than today's, but recent radiative-convective models by Lorenz *et al.* (1997b) suggest this is difficult to achieve for solar luminosities less than or comparable to the current value.

Such speculations would seem to have little hope of being tested, but the cratering record has the potential for providing evidence of epochs of thin atmosphere. As on Venus, where primary craters have a lower size cutoff, today's thick Titan atmosphere prevents smaller bolides from reaching the surface intact. Provided old, heavily cratered terrains exist on Titan and are not completely obscured by the hundreds of meters of photochemical detritus predicted to have fallen over geologic time, it should be possible to determine lower size cutoffs for cratered terrains. Engel *et al.* (1995) and more recently Ivanov *et al.* (1997), have quantified the shielding by Titan's atmosphere. Epochs of thin atmosphere on Titan, particularly during early times when cratering fluxes were enhanced, would show up in a crater size-frequency distribution extending below a cutoff of about 6 km to 8 km diameter dictated by the thickness of the present atmosphere, as well as in a preponderance of strewn fields that are less likely to form in the current atmospheric epoch (Ivanov *et al.*, 1997). Cassini–Huygens imaging of Titan, from orbiter and probe, extends over such a wide range of surface area and resolution, that analysis of impact crater fields could offer sensitive insight into Titan's atmospheric history. The combination of surface area and resolution suggests that Cassini–Huygens could detect crater densities on the order of a few percent those of the lunar mare surfaces. Thus, if the impact fluxes are comparable, we may detect measurable cratering records on surfaces

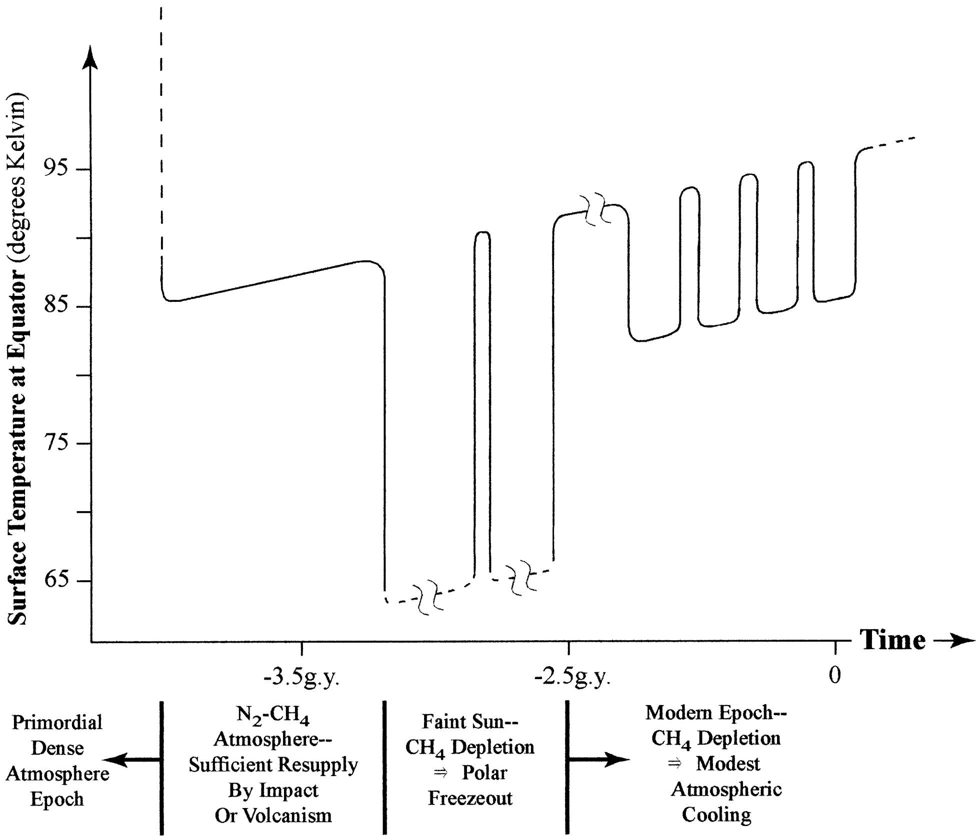

Fig. 3. One possible history of Titan surface temperature, drawn as equatorial surface temperature vs time; the present-day is labelled "0". Duration of collapsed or deflated atmospheric states depends on methane resupply mechanism and hence is uncertain. The sketch assumes a monotonically increasing solar luminosity beginning at 70% of the present-day value some four billion years ago

more than a few percent of the age of the lunar maria—e.g. Titan surfaces older than about 50–100 My. Of course, an independent measure of the impact flux, or crater production rate, would be needed to convert such data into an absolute age; Cassini mapping of the icy Saturnian satellites, added to the Voyager data base, would help accomplish this.

In addition, the Titan impact crater data base should allow a study of other aspects of the erosive and atmospheric history of this world. For example, absence of any craters would suggest a geologically very young surface, with active obliteration processes (either internal or atmosphere-driven). The shape of the size distribution and features of craters above the atmospheric cutoff diameter may be sensitive to specific aspects of erosive and impact processes. For example, the Martian crater population shows a loss of smaller craters apparently associated with aeolian erosion/transport processes, and dust infilling (e.g. Hartmann, 1971, 1974), while surface features around Venus impact craters appear to give evidence of atmosphere shock wave effects (Takata *et al.*, 1995). While Titan may well have aeolian erosion, an additional source of crater-fill is the accumulation of photochemical debris; examination of the morphology of craters over a range of sizes, the determination of the composition of the fill material itself by remote sensing spectroscopy on the Cassini orbiter will constrain regional and global variations in the depth of such deposits.

The ultimate fate of Titan's atmosphere is tied to the increasing luminosity of the sun. Lorenz *et al.* (1997b) have considered the habitability of Titan during the onset of the sun's red giant phase some six billion years hence. At a time when the Earth will lose its liquid water, driven off by enhanced solar luminosity, Titan surface temperatures will reach above the ammonia-water peritectic point of 176 K, and may exceed 200 K for several hundred million years. Mirroring a primordial, post-accretional warm epoch discussed above, this future Titan might evolve and support a modest biota until mass loss from the red giant Sun blows the satellite's atmosphere away.

4. Titan's surface and pre-biological organic chemistry

Much speculation has been written on the resemblance of the present atmospheric state of Titan to that of the Earth before life began. The current consensus is that the pre-biotic Earth's atmosphere was significantly more oxidizing than is the present Titan atmosphere, but much less so than the present Earth. Hence, terrestrial pre-biotic conditions might have been intermediate to the present state of the two bodies. Titan has a prodigious amount of organic material which participates in chemical cycles powered by sunlight and (at the 10% level relative to solar ultraviolet) by cosmic rays. It is worth asking what level of complexity might be achieved in Titan's organic chemistry over 4.5 billion years, particularly at the atmosphere–

surface interface. Some cosmic rays reach the surface, in contrast to solar ultraviolet radiation, but additional sources of surface energy include cryovolcanism and large impacts. Sagan and Thompson (1992) calculated that a large impact into an ammonia-water crust would produce pools of ammonia-water liquid lasting of order 10^3 years; even pure water pools might last hundreds of years.

Such timescales, while much less than the duration of liquid water on the pre-biotic Earth, are much longer than timescales available in terrestrial laboratories for pre-biotic chemical experiments. Therefore, the organic products of reactions in a transient liquid water pool on Titan might be of keen interest to exobiologists studying the transition between organic chemistry and biochemistry. Because the presence of liquid ammonia–water or water melts on Titan for long durations (compared to the laboratory) is a surprising result, a crude "reality-check" of the Sagan and Thompson (1992) calculation is presented here. They suggest around 1% of the crater volume may appear as impact melt. Melosh (1989) suggests the ratio of melt mass to projectile mass is $\sim 0.14 v_i^2/E_m$ with v_i the impact velocity and E_m the enthalpy of melting, about 2×10^6 J/kg for ice. Thus for a 500 m radius impactor at 10 km s^{-1}, which would produce a 10–20 km diameter crater, the melt volume is about 1 km^3 (factors of order unity are neglected in this analysis). Thus the 1% number is about right. The conduction-limited cooling time of a body of size D is roughly D^2/κ where κ is the thermal diffusivity, typically 10^{-6} m^2 s^{-1} for solid materials. Thus the conductive cooling time (ignoring the mutually-antagonistic effects of convection and latent-heat release) of a 1 km^3 melt body is about 10^{12} s, or about 10^5 years—in good agreement with Thompson and Sagan (1992). (There are terrestrial examples of chemical processing of impact melts: e.g. the economically-significant nickel and copper ore deposits at the Sudbury impact structure in Canada were produced by gravitational settling of the sulfide-rich component of the impact melt, see e.g. Grieve and Masaitis; 1994.)

A specific example of a problem in experimental exobiology is the formation of ribonucleic acid, or RNA. RNA is generally assumed to have preceded DNA as the storage molecule for the genetic code, and also acted as a catalyst in the absence of enzymes (for a review see Chyba and McDonald, 1995). The assembly of RNA without recourse to biologically-produced precursors requires a number of as yet poorly understood steps. One of these is the biological synthesis of the sugar ribose, which on the primitive Earth may have involved the so-called formose reaction, in which a wide variety of sugars are generated in an aqueous solution of formaldehyde (Shapiro, 1988). Producing a preponderance of ribose from out of this "sugar forest" (Chyba and McDonald, 1995) remains unsolved.

Beyond the synthesis of ribose itself is the constraint that for the construction of RNA there must be a significant predominance of a particular handedness of the molecule. Computer models and laboratory experiments show that functional RNA cannot be assembled from a mixture of left- and right-handed ribose molecules, yet the difference in formation energy of the two is exceedingly small (Joyce *et al.*, 1984). The non-biological natural world does not seem to select for a single handedness of the asymmetric sugars, and the same is generally true of amino acids (though there is very recent evidence from Cronin (1997) of a predominance of left-handed types in selected amino acids in the Murchison meteorite, which Engel and Macko (1997) argue from isotopic evidence is not due to terrestrial contamination).

The origin of selected handedness among the precursor molecules of biochemistry may involve trial-and-error whereby, for example, RNA assembly is truncated by the wrong-handed ribose, followed by fragmentation of the strand, assembly of a longer "homochiralic" (single-handed) strand, truncation by a wrong-handed ribose again, etc. Over long periods of time, some RNA molecules may by chance have been assembled out of homochiralic sugars and nucleic acids, but the timescales may exceed those accessible to the laboratory. Likewise, spatial scales larger than practical in the lab might provide a greater likelihood for such assembly. While this is speculation, it points to the issue that laboratory experiments in pre-biotic synthesis are limited in spatial and temporal scales relative to what is available in natural environments.

The record of such experiments on the pre-biotic Earth is completely erased, and the crust of Mars is so oxidizing that not much may be preserved there, either. Pre-biotic chemistry under the Europan crust is likely too hard to access for the foreseeable future (at least by direct sampling). The parent bodies of meteorites may have had pre-biotic aqueous chemistry occur which today is partly recorded in the meteorites themselves, but the degree of preservation of this record of very ancient chemistry is unknown, and the environment within which such chemistry occurred is poorly constrained.

Titan, on the other hand, is undergoing organic chemistry today throughout its atmosphere and on its surface. Periodic impacts could allow for aqueous organic chemistry on timescales much longer than those in the laboratory, and larger spatial scales. It is possible that the surface of Titan records numerous truncated experiments in pre-biotic aqueous chemistry, including the construction of homochiralic molecules of biological interest. While we do not propose here to examine whether ribose formation itself is even possible in transient aqueous solutions on Titan, the point is that the identification of asymmetry in the amount of left- and right-handed forms of any organic molecules found at Titan's surface would generate intense interest in the pre-biotic scientific community. Whether self-organizing chemical systems developed in certain environments on Titan is at present pure speculation, but Titan's surface has energy sources, raw organic materials, and a relative accessibility that together make it a worthy target for exobiological exploration.

The Huygens probe will be unable to do in depth exploration of organic chemistry at multiple sites on Titan's surface; its mission is to sample directly the atmosphere, take images and spectra of the surface, and conduct a limited range of direct experiments at the impact point. However, the mission will provide crucial information on the general nature of Titan's surface, both at the probe descent site and globally through Cassini remote sensing. The data returned should provide much better insight into the prospects for using Titan as a pre-biotic chemical laboratory. Should Titan prove promising, follow-on missions might include multiprobes covering a range of sites, or an "aerobot" with the capability to ascend and descend at several sites on Titan's surface (Lorenz and Nock, 1996). Regardless of the particular kind of delivery system chosen, careful consideration must be given to the kinds of advanced chemical experiments that could be carried to Titan. For example, the capability to detect optical activity (chirality) as the signature of molecules with the same sense of handedness would open up the possibility of discovering how and under what conditions a crucial bottleneck is overcome in the assembly of RNA. Such investigations represent a daunting challenge at present, but emphasize the need for continued development of analytic techniques that can be carried to other planetary surfaces.

5. Conclusion

This presentation is a mixture of review and speculations concerning the formation, history and significance of Titan's surface–atmosphere system. Much of the speculation is driven by relatively recent remote sensing data that suggests a diverse surface, while at the same time failing to provide a unique determination of surface physical state and composition. We are therefore driven back to a puzzle that surfaced at the time of the Voyager encounter—how methane is supplied long-term to Titan's atmosphere—and forced to consider the possibility that Titan's atmosphere and surface state have undergone repeated profound changes through their history. The other driver of the speculations contained herein is the issue of how chemical systems evolve into biochemical systems. While it is impossible to gauge the relevance of Titan's surface chemistry to addressing this question, we can at least point to Titan as a planet-sized system rich in the biogenic elements on which organic chemistry has proceeded for the age of the solar system, and still proceeds today. We have not previously explored a planet with such characteristics (leaving aside the Earth which surface is dominated by biology). Surprises must await us.

The Cassini–Huygens mission, a follow-on to the Voyager flybys, is at the same time a precursor to the kinds of in-depth chemical explorations that will be needed to understand fully the processes ongoing at the surface of this giant moon. Cassini–Huygens is superbly equipped to provide us with the information needed to assess whether Titan is a worthy target for further exploration of planetary evolution, climate change, and the processes that lead to the formation of life.

Acknowledgements. The authors acknowledge the support of the NASA Planetary Atmospheres and Geoscience Programs and the Cassini project in the preparation of this work.

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