

Hypothesis Paper

Biologically Enhanced Energy and Carbon Cycling on Titan?

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ABSTRACT

With the Cassini-Huygens Mission in orbit around Saturn, the large moon Titan, with its reducing atmosphere, rich organic chemistry, and heterogeneous surface, moves into the astrobiological spotlight. Environmental conditions on Titan and Earth were similar in many respects 4 billion years ago, the approximate time when life originated on Earth. Life may have originated on Titan during its warmer early history and then developed adaptation strategies to cope with the increasingly cold conditions. If organisms originated and persisted, metabolic strategies could exist that would provide sufficient energy for life to persist, even today. Metabolic reactions might include the catalytic hydrogenation of photochemically produced acetylene, or involve the recombination of radicals created in the atmosphere by ultraviolet radiation. Metabolic activity may even contribute to the apparent youth, smoothness, and high activity of Titan's surface via biothermal energy. **Key Words:** Titan—Life—Biomass—Metabolism—Environment. *Astrobiology* 5, 560–564.

ENVIRONMENTAL CONDITIONS AT TITAN

ENVIRONMENTAL CONDITIONS are generally thought to be conducive for life if it can be shown that (1) polymeric chemistry, (2) an energy source, and (3) a liquid solvent are present in appreciable quantities (Irwin and Schulze-Makuch, 2001). Polymeric chemistry has not been confirmed yet for Titan but is most likely present given the complex carbon chemistry in Titan's atmosphere and on its surface. Abundant energy sources are present at least in the form of ultra-

violet (UV) radiation and high-energy molecules produced from photochemistry, and probably also endogenic geological activity. If lightning exists in Titan's atmosphere it could provide an additional energy source (Tokano *et al.*, 2001a; Fischer *et al.*, 2004). Water as a liquid solvent may be limited, but liquid mixtures of water and ammonia are likely (Fortes, 2000), and the recent Cassini radar, visible and infrared images suggest the presence of a young surface and ongoing cryovolcanism (Lorenz and the Cassini RADAR Team, 2004; McEwen *et al.*, 2004; Porco and the Cassini Imaging Team, 2005; Elachi *et al.*, 2005),

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which points toward near-surface liquid reservoirs and strongly implies at least occasional surface flows of liquid water–ammonia. The presence of large methane and ethane reservoirs with traces of dissolved N_2 on Titan's surface has been suggested (Lunine, 1994), and their role as possible life-supporting solvents has been hypothesized (Schulze-Makuch and Irwin, 2004).

Titan's current surface temperature is very cold (~ 94 K) because of its distance from the sun and an optically thick, global atmospheric haze (*e.g.*, Lorenz *et al.*, 1997) that creates an anti-greenhouse effect (McKay *et al.*, 1999). However, early in its history, Titan would have likely been exposed to a large amount of greenhouse warming, with accretional and radiogenic heat having kept it much warmer than today. In fact, McKay *et al.* (1999) predicted a runaway greenhouse effect for Titan until the heat flux fell to 0.9 W m^{-2} . Even if temperatures on Titan's surface never reached the melting point of water for geological time spans, water–ammonia mixtures would have remained liquid to temperatures as low as 176 K (*e.g.*, Croft *et al.*, 1988), allowing amino acids and other macromolecules from space, as well as those produced by atmospheric photochemical processes, to interact with these solvents. Titan is considered as an important analogue to early (pre-biotic) Earth based on the chemistry of its atmosphere (Griffith *et al.*, 1998).

There are many apparent heterogeneities on Titan's surface (Smith *et al.*, 1996). Surface features observed at infrared and radar wavelengths appear to be of volcanic, tectonic, sedimentological, or meteorological origin (Lorenz and the Cassini RADAR Team, 2004; Turtle and the Cassini ISS Team, 2004; Porco and the Cassini Imaging Team, 2005). A methane cycle may exist on Titan with some similarities to the hydrological cycle on Earth. Methane clouds have recently been detected (Roe *et al.*, 2002; Coustenis *et al.*, 2004; Porco and the Cassini Imaging Team, 2005), and methane rain is consistent with modeling results (Tokano *et al.*, 2001b; Chanover *et al.*, 2003). Because of acetylene's higher specific gravity, solid acetylene may be present at the bottom of the ethane–methane reservoirs and available as an energy source for various chemical reactions that involve a multitude of organic compounds. The dearth of obvious impact features in early high-resolution Cassini imagery (Lorenz and the Cassini RADAR Team, 2004; McEwen *et al.*, 2004; Turtle and the Cassini ISS Team, 2004; Porco and

the Cassini Imaging Team, 2005) and inferred youth of the surface imply the possibility of active resurfacing and possible burial or subduction mechanisms that could supply subsurface liquid reservoirs with acetylene and other photochemical products. Fortes (2000) pointed out that given the extremely cold surface, some of the simplest prebiotic reactions on Titan would have half-lives on the order of 10^7 years. Perhaps, however, reactions could be accelerated by catalysis or localized warming. Regions of geothermal activity have been projected to exist on Titan (Lorenz, 2002), and early Cassini results suggest the presence of a young surface with widespread cryovolcanism (Lorenz and the Cassini RADAR Team, 2004; Porco and the Cassini Imaging Team, 2005). The most likely energy sources providing heat to the surface would be ammonia–water volcanism or meteorite impacts (Thompson and Sagan, 1992). Both mechanisms may have created episodes of aqueous chemistry in lakes on Titan's surface, perhaps lasting thousands of years before freezing over (Thompson and Sagan, 1992; Lorenz *et al.*, 2000; Artemieva and Lunine, 2003). An especially promising environment for life would thus be a hot spring or geothermal area at the bottom of a hydrocarbon reservoir, or an area where volatile overheated compounds intersect with such a reservoir (Fig. 1). This environment would not only provide a versatile suite of raw material for organic synthesis and some amount of molten water and ammonia for organic reactions, but also higher temperatures for reactions to occur more rapidly. A site such as this would be especially favorable for biological activity if it included microenvironments with zones of fluid accumulation or entrapment (*e.g.*, with fluid/solid interfaces) and areas enriched with material that could act as a catalyst (*e.g.*, zeolites, clay) (D. Schulze-Makuch and O. Abbas, unpublished data).

METABOLIC STRATEGIES ON TITAN

Primitive metabolism can be envisioned as a reaction or reaction sequence that yields free energy. Once produced, the energy is used by the organism to do work. The nature of the metabolic strategies employed depends largely upon the environmental constraints that affect an organism. For instance, anaerobic bacteria use metabolic pathways that do not depend on oxygen. Organisms usually adapt to environmental con-

ditions by evolving in a manner that allows them to utilize available raw materials. Because of the presence of a variety of carbon compounds in large quantities, any metabolic reaction pathway of a chemoautotrophic organism on Titan would probably involve the reduction or oxidation of at least one carbon compound.

Given the environmental conditions on Titan, a reasonable energy yielding reaction for a metabolizing microbe is the catalytic hydrogenation of photochemically produced acetylene:



The energy yield of this reaction is $107.7 \text{ kJ mol}^{-1}$ ($\Delta G = -107.7 \text{ kJ mol}^{-1}$ or $-25.7 \text{ kcal mol}^{-1}$) under standard conditions, and about 100 kJ mol^{-1} under Titan's surface conditions. Both acetylene and hydrogen are present in Titan's atmosphere at significant concentrations. Since acetylene is produced high in the stratosphere from solar UV radiation and then, for the most part, condenses and falls to the surface, it provides a potential means of transferring high-altitude solar UV energy to surface chemical reactions (Lorenz *et al.*, 2000). Spectroscopic evidence suggests that the product of this reaction, methane, is found to be isotopically lighter than would be expected from theories of Titan's formation (Lunine *et al.*, 1999), and thus may hint toward microbial fractionation (although, taken alone, this is certainly not evidence of biochemical activity). The energy released by this reaction may be captured by the organism and used to drive an endergonic reaction, or it may be directly utilized to perform cellular work (Abbas and Schulze-Makuch, 2002; Schulze-Makuch and Irwin, 2004).

Methane is unstable in Titan's atmosphere and destroyed on a short time scale of about 10^7 years by solar UV radiation (Raulin and Owen, 2002; Lorenz *et al.*, 2003). Without a constant re-supply, no significant amount of methane should be present in Titan's atmosphere. However, an atmospheric methane concentration of about 5% is observed in the troposphere (Lorenz *et al.*, 2000). The light carbon isotope ratio in methane ($^{12}\text{C}/^{13}\text{C} = 95 \pm 1$) found by Cassini's Neutral Ion Mass Spectrometer (INMS; Waite *et al.*, 2005) is consistent with a biological origin, since living systems preferentially incorporate lighter isotopes. Assuming that the re-supply is provided solely biologically via Reaction 1 with no inorganic input, an energy of $2.2 \times 10^{21} \text{ kJ}$ is pro-

duced over a period of 10 million years to keep the observed methane concentration constant. The free energy of the anaerobic formation of 1 unit carbon formula weight ($= 24 \text{ g mol}^{-1}$) for the yeast *Saccharomyces cerevisiae* has been determined to be 76.89 kJ (Battley, 1987), or 3.2 kJ g^{-1} . Assuming this energy demand and a generation time of 1 year, a biomass of $6.8 \times 10^{13} \text{ g}$ at an energy conversion efficiency of 100% would be required to keep the currently measured methane concentration at a constant level. Generation times for putative Titan organisms are assumed here to be much longer than for "average" terran organisms because of the slower kinetics in a colder environment. If the organisms were comparable in size to typical terran microorganisms with a dry mass of $2 \times 10^{-14} \text{ g}$ (Whitman *et al.*, 1998) and were envisioned to homogeneously populate the upper 1 m of the surface of Titan, the biomass density would be about 4.1×10^{13} microbes m^{-3} , a typical density for slightly nutrient-deprived environments on Earth. If there are significant inorganic sources of methane, the calculated biomass density would decrease accordingly, as would the isotopic fractionation rate observed.

On the other hand, the miniaturization of cellular life in water on Earth may be a misleading model for life in a non-aqueous environment (L.N. Irwin, e-mail to the Titan Study Group on 23 January 2002). In an extremely cold, hydrophobic (but liquid) environment, surface/volume ratio considerations may be less constraining than at higher temperatures in polar solvents. Thus, life on Titan could involve huge (by Earth standards) and very slowly metabolizing cells, in which case biomass densities would be higher than calculated above.

Other metabolic pathways are possible as well. An intriguing possibility is radical reactions as a basis for metabolism. Raulin (1998) suggested that Titan's stratosphere is an active site of complex carbon and nitrogen radical chemistry. Thus, energy-yielding reactions could be based on chemistry involving radicals. For, example, a chemoautotrophic organism may use the following reactions:



or



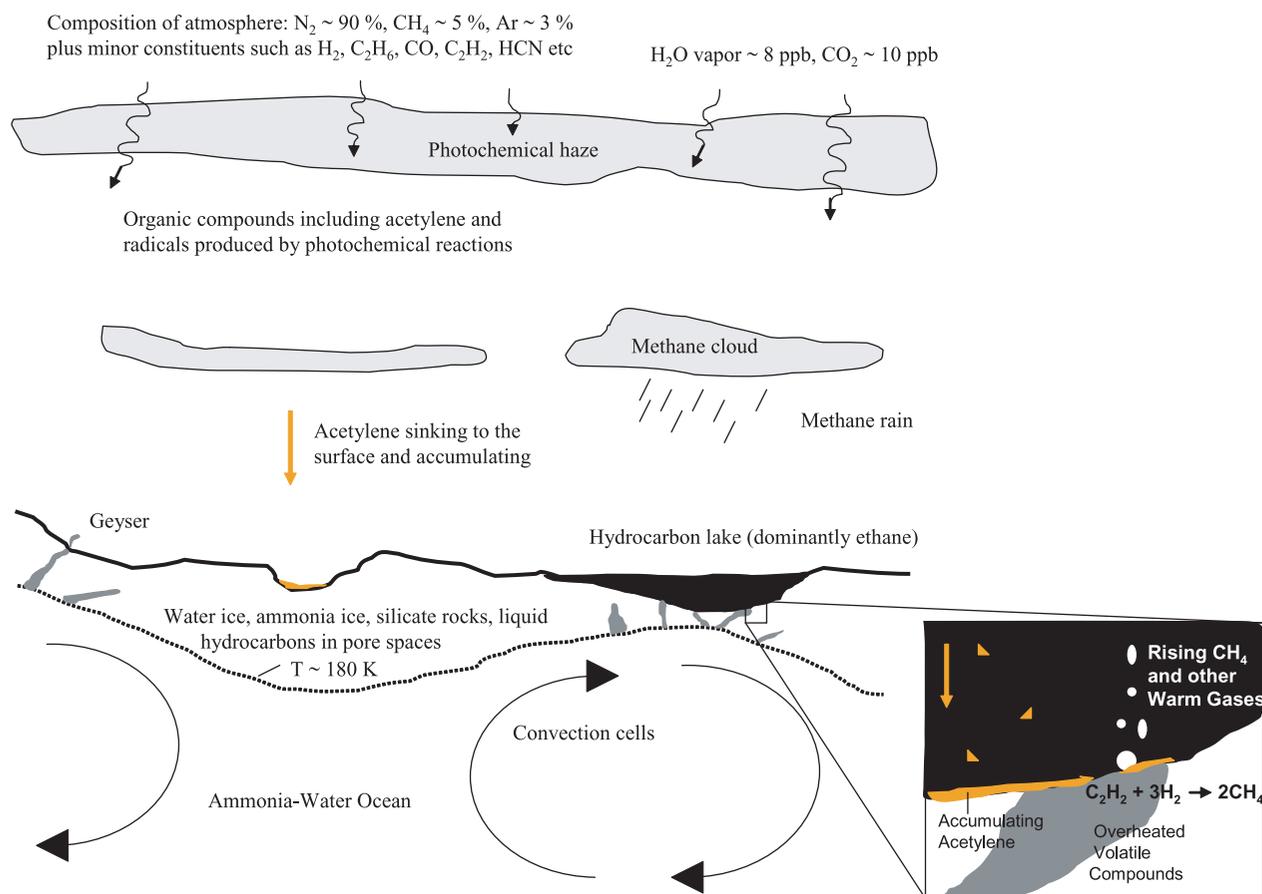


FIG. 1. Schematic of environmental conditions at Titan. Acetylene and radicals are produced by photochemical reactions in the atmosphere. Because of its high specific gravity acetylene will sink to Titan's surface and to the bottom of a hydrocarbon reservoir, where it can be used by putative organisms for metabolic reactions (inset). The metabolic end-product methane, which is isotopically lighter than predicted by Titan formation theories, rises to the atmosphere.

Reactions 2 and 3 produce a high yield of energy and may take place in the atmosphere or at the surface of Titan. All reactants have been detected in Titan's environment based on data from Voyager 1 (Kunde *et al.*, 1981; Smith *et al.*, 1982). On Earth, the energy-rich reactions involving radicals are very difficult to control and would cause internal damage to any organism. On Titan, however, at surface temperatures of less than 100 K, these reactions may proceed at a reasonable pace, and may constitute a feasible energy-yielding reaction for a metabolic pathway. An interesting consequence of the radical Reactions 2 and 3 is production of the biologically important compounds cyanamide and hydrocyanic acid, respectively (Schulze-Makuch and Irwin, 2004; D. Schulze-Makuch and O. Abbas, unpublished data).

BIOHERMAL ENERGY ON TITAN?

Initial Cassini results indicate that Titan has an extremely young and active surface, with preliminary crater counts (from incomplete surface imaging) that suggest a surface age of less than 300 Myr (Porco and the Cassini Imaging Team, 2005), and many features that suggest the likelihood of cryovolcanic activity. Titan has a low bulk density of 1.88 g cm^{-3} , which would imply that silicate substrate is quite rare at the surface. The relative lack of heavy elements may cause less radioactivity, volcanism, and heat. Nevertheless, the geothermal heat flow on Titan has been estimated as $4\text{--}6 \text{ mW m}^{-2}$ (Sotin *et al.*, 1998; Lorenz and Shandera, 2001). This may be sufficient to explain the apparent high level of volcanic and tectonic activity, especially if ammonia

is abundant in subsurface ices. Yet, an intriguing, though highly speculative, possibility is that biological heating could contribute to the surface activity and smoothness. Energy-rich organics, such as acetylene, are created in the upper atmosphere by the interaction with solar radiation and the electromagnetic field of Saturn, and fall to the surface. Through geological overturn and meteorological/fluvial processes [both of which seem to be quite active (Porco and the Cassini Imaging Team, 2005)], these compounds are transported to the subsurface where they can reach liquid reservoirs and serve as the basis for metabolism, using the reactions detailed above. Some of the energy from these highly exothermic metabolic reactions would be released to the surroundings and, in some circumstances, contribute to melting of water–ammonia ice. Glacial melting from biothermal energy released by algal metabolism has been reported previously (Gerdel and Drouet, 1960), as has been the influence of marine microorganisms on the melting of Arctic pack ice (Leck *et al.*, 2004). Microbial colonization occurs in cryoconite holes on glaciers (Wharton *et al.*, 1985) and in basal glacial melt waters, some of which are known to release methane as metabolic end product (Souchez *et al.*, 1995; Campen *et al.*, 2003). In an environment near the freezing point where availability of liquid microenvironments is a limiting factor on habitability, there may be selective pressure leading to a larger portion of the metabolic heat going into the environment. There may be places on Titan that are energy-rich but liquid-poor, with plenty of acetylene to metabolize, though it may be locked up in ice. In such a case, evolution would favor organisms that could use this energy to melt their own little watering holes.

However, the question is how significant the biomelting effect could be. Putative organisms would cause the reactions to occur locally over short time scales. In principle, using the suggested metabolic Reaction 1 and applying it to Titan's surface conditions, it is possible that a substantial amount of heating could be provided by biological means.

Given Titan's surface temperature of 94 K and the eutectic melting point of an ammonia–water mixture near Titan's surface pressure of 175 K, the energy needed for melting is calculated by adding the heat capacity of the water–ammonia mixture to the enthalpy, which results in approximately 11.5 kJ mol^{-1} . Of course, any puta-

tive organism would need some (really most) of the energy for its own metabolism. The energy used by the yeast organism *S. cerevisiae* is $76.89 \text{ kJ mol}^{-1}$ (see above), which compares with an estimated energy gain of 100 kJ mol^{-1} for Reaction 1 under Titan's environmental conditions. Further, assuming again that $2.2 \times 10^{21} \text{ kJ}$ of biological energy was produced over a period of 10 million years to keep the observed methane concentration constant with no inorganic input, an energy requirement of $2.2 \times 10^{14} \text{ kJ year}^{-1}$ would have been needed. Most of this energy would have gone toward the metabolism of the organism (~76.8% assuming an organism with the same energy need as *Saccharomyces*), but the remaining energy ($5.2 \times 10^{13} \text{ kJ year}^{-1}$) would have been available to heat the surrounding environment. Since 11.5 kJ is needed to melt 1 mol of water–ammonia rock, there is enough to melt $4.5 \times 10^{12} \text{ mol}$ of water–ammonia ice in one melting event per year. This would be sufficient to melt $7.9 \times 10^{10} \text{ kg}$ of water and ammonia ice once per year. These calculations indicate that biothermal melting would be possible.

Given the low temperatures on Titan, the biological effect, if it exists, should be larger than that on Earth. On the other hand, a great deal of energy would have to be expended to reach the liquid state. Volcanic activity or other energy sources, if present and significant, would increase the chances for life on Titan by elevating temperatures and providing potentially habitable geothermal areas and gases that could be used for metabolism. Any liquid water–ammonia mixture, which would be lighter than the surrounding ice, would float if produced at depth.

If life is present on Titan, it would likely use a different set of biomolecules than terran life. Nevertheless, life could be detected, and a checklist of search parameters for possible life applicable to Titan is provided in Table 1. No single search parameter is conclusive evidence of life, but the presence of a majority of the parameters listed here certainly would point in this direction. The more exotic life is (in the sense of being different from terran life), the more difficult it would be to arrive at a positive proof (for example, if life on Titan is not based on redox reactions, but radical reactions).

The best chances for obtaining an indication of life with the current Cassini-Huygens mission are probably based on measured isotope ratios. As discussed previously, the relatively light isotopic

composition of methane (measured as $\text{CH}_3\text{D}/\text{CH}_4$) compared with the isotopic composition of N (measured as $\text{HC}^{15}\text{N}/\text{HC}^{14}\text{N}$) is difficult to explain. Lunine *et al.* (1999) concluded that if methane were enhanced in a way similar to nitrogen during an era of early escape, it would produce the current $\text{CH}_3\text{D}/\text{CH}_4$ ratio without any photochemical enrichment. Little if any enrichment by photolysis could be tolerated and remain consistent with observations. However, it is known that current photochemical processes in the atmosphere led to a fractionation toward heavier methane. Lunine *et al.* (1999) explained this by suggesting that significant amounts of methane must have been out-gassed from Titan's interior after an early epoch of atmospheric loss, which led to the currently observed enrichment of heavy nitrogen relative to heavy methane isotopes. This is a reasonable explanation, but it raises the question as to how huge amounts of methane could have been stored on Titan in its early history and then released at a later time. Methane clathrates are one plausible explanation (*e.g.*, Mousis *et al.*, 2002). An alternative explanation would be that the observed isotopic ratio is caused by life processes that produce an enrichment of the lighter isotopic methane.

Detection abilities and sensitivities of the Huy-

gens probe are limited, and it is unclear as to whether the probe can obtain accurate enough measurements to distinguish between biological and chemical sources. However, the results of the Huygens probe and the Cassini orbiter will contribute to our understanding of Titan's environment and suitability for life. More elaborate instrumentation is needed for a next generation mission to be compatible with search parameters for life as listed in Table 1, and to reveal the molecular structures of complex organics at Titan's surface.

Given the current sample size of one biosphere upon which astrobiologists must base their theories and speculations, our ideas about life elsewhere must remain fluid and not too heavily based upon the specific metabolisms, strategies, and structures of terran organisms. The basic requirements of life, as they are understood today, are all present on Titan, including organic molecules, energy sources, and liquid media. If surface or subsurface organisms are able to take advantage of upper atmospheric photochemistry by way of the continuous downward transport of high-energy compounds such as acetylene, they would have vast energy reserves at their disposal that could be used, in part, to maintain the liquid environments conducive to life.

TABLE 1. LIST OF SEARCH PARAMETERS FOR POSSIBLE LIFE ON TITAN

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- Presence of complex organic compounds including polymeric compounds of high molecular weight of 1,000 or greater. This characteristic is based on the assumption that all life regardless of origin would have a macromolecular machinery and would be complex compared with the inorganic background.
 - Homochirality, based on the assumption that all life irrespective of its chemistry would employ well-structured, chiral, stereochemically pure macromolecules (>500 atoms) as their metabolic catalysts (Xu *et al.*, 2003). To fulfill the intricate functions of the molecular machinery of life, any organism regardless of origin would have to distinguish between molecules of different handedness and select a preferable handedness, thus enriching one enantiomer of chiral compounds.
 - Isotopic fractionation toward the lighter biogenic elements. On Earth we observe that organisms prefer lighter isotopes and thus produce as a net effect distinct fractionation rates of isotopic ratios in biological elements. Thus, this search parameter is based on the assumption that life elsewhere would also prefer isotopes that require less energy to process.
 - Cellular compartmentalization and boundaries, which prevent the living organism from equilibrating with its surrounding environment. A cellular compartmentalization may occur on different scales and employ different types of boundaries, but it would be expected to be based on the same biological principles as life on Earth.
 - Oxygenated compounds in significant quantity in Titan's reducing atmosphere and surface as evidence for life-sustaining redox reactions.
 - Presence of a metabolic by-product. Metabolism must be an intrinsic property of any living organism; otherwise that organism could not perform work. However, the exact metabolic by-product depends on the environment and the specific energy-harvesting mechanism an organism uses.
 - Presence of chemicals that could be the building block of a genetic code. Surely this chemical does not have to be DNA or RNA, or necessarily be composed of the bases of the known nucleic acids, but some type of chemical is necessary that would convey the information from one generation of organism to the next.
 - Morphological and mineralogical evidence consistent with the presence of life. Examples from Earth are the banded-iron formation and biogenic stromatolite deposits of early Earth, minerals that are precipitated by biological processes, or identified structures that are consistent with a biological origin.
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ACKNOWLEDGMENTS

We thank Jonathan Lunine, Norm Sleep, and two anonymous reviewers for constructive critiques that improved this paper. David Grinspoon's work was in part supported by grants from the NASA Exobiology Research Program and the NSF Program of Research into Life in Extreme Environments. We acknowledge the thoughtful discussions with all members of the Titan Study Group, which contributed to the ideas presented in this paper, especially Gustaf Arrhenius, John Bang, Penelope Boston, David Darling, Huade Guan, Victor Gusev, Robert Hazen, Remy Hennes, Jimmy Hincapie, Louis Irwin, Vladimir Kompanichenko, Jonathan Lunine, Anthonie Muller, François Raulin, Bart Rzonca, and Robert Shapiro.

ABBREVIATION

UV, ultraviolet.

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