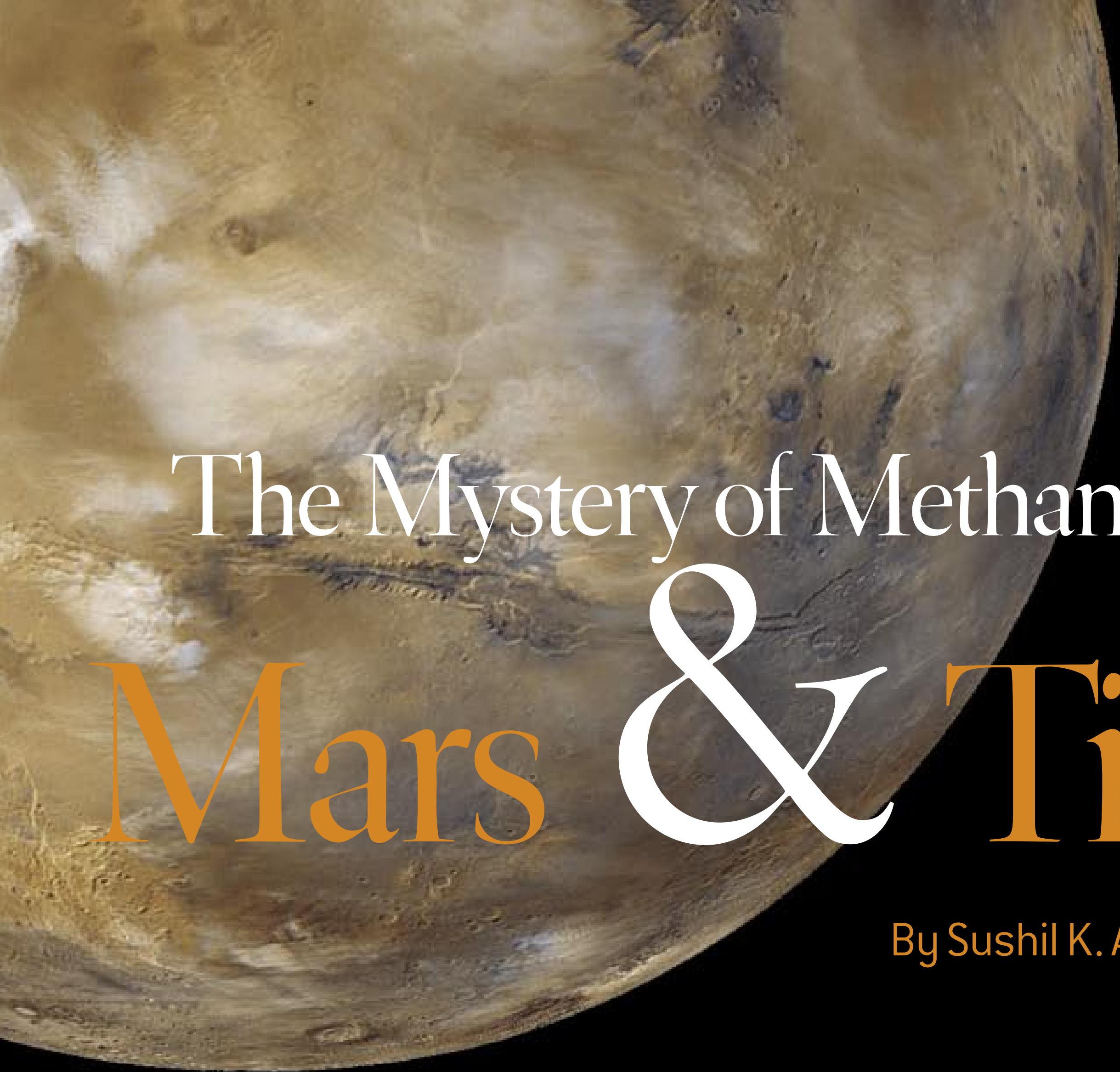


The Mystery of Methane on Mars & Titan

By Sushil K. Atreya

MARS has long been thought of as a possible abode of life. The discovery of methane in its atmosphere has rekindled those visions. The visible face of Mars looks nearly static, apart from a few wispy clouds (*white*). But the methane hints at a beehive of biological or geochemical activity underground.

Of all the planets in the solar system other than Earth, Mars has arguably the greatest potential for life, either extinct or extant. It resembles Earth in so many ways: its formation process, its early climate history, its reservoirs of water, its volcanoes and other geologic processes. Microorganisms would fit right in. Another planetary body, Saturn's largest moon Titan, also routinely comes up in discussions of extraterrestrial biology. In its primordial past, Titan possessed conditions conducive to the formation of molecular precursors of life, and some scientists believe it may have been alive then and might even be alive now.

To add intrigue to these possibilities, astronomers studying both these worlds have detected a gas that is often associated with living things: methane. It exists in small but significant quantities on Mars, and Titan is literally awash with it. A biological source is at least as plausible as a geologic one, for Mars if not for Titan. Either explanation would be fascinating in its own way, revealing either that we are not alone in the universe or that both Mars and Titan harbor large underground bodies of water together with unexpected levels of geochemical activity. Understanding the origin and fate of methane on these bodies will provide crucial clues to the processes that shape the formation, evolution and habitability of terrestrial worlds in this solar system and possibly in others.

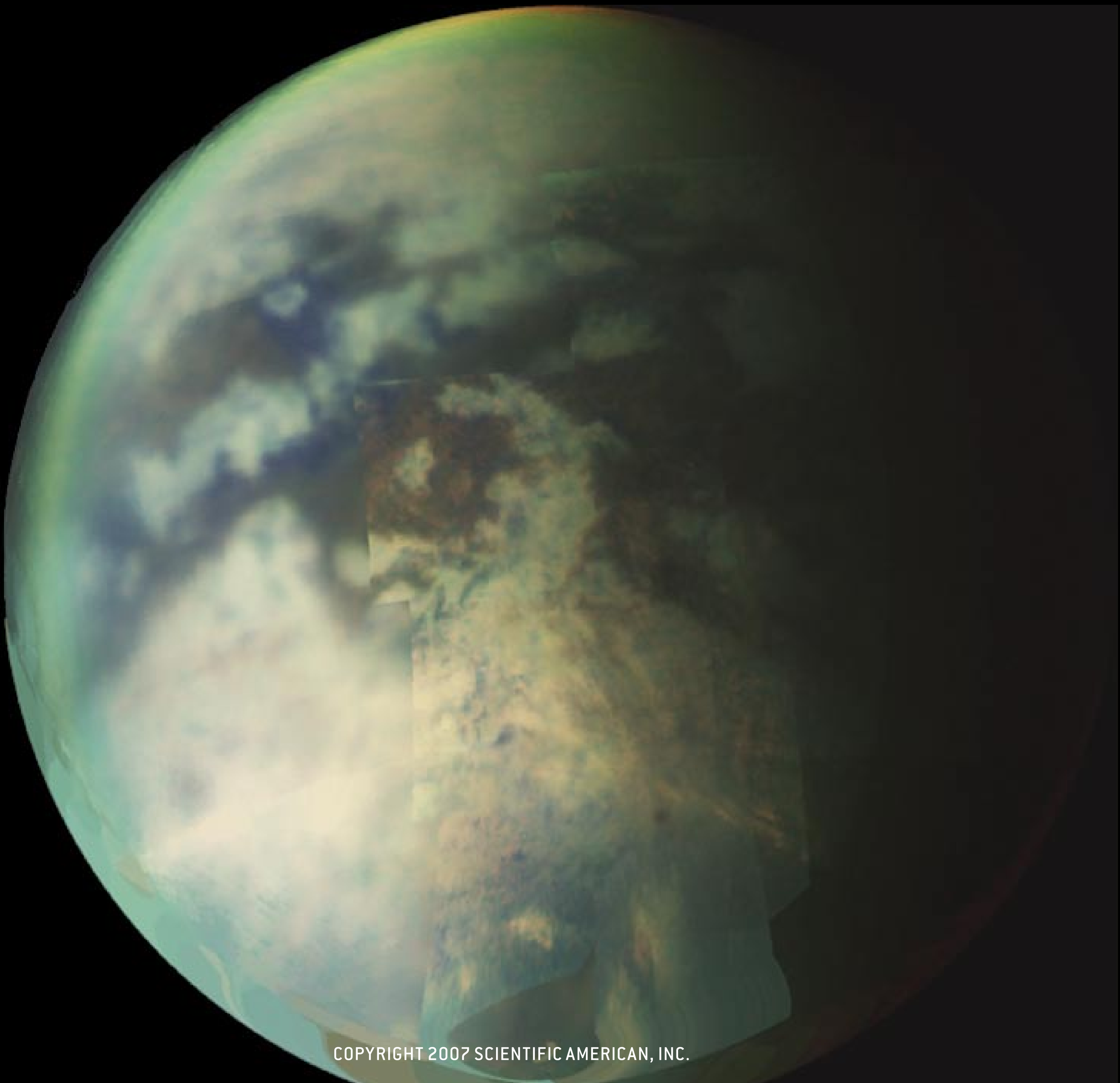
Methane (CH_4) is abundant on the giant planets—Jupiter, Saturn, Uranus and Neptune—where it was the product of chemical processing of primordial solar nebula material. On Earth, though, methane is special. Of the 1,750 parts per billion by volume (ppbv) of methane in Earth's atmosphere, 90 to 95 percent is biological in origin. Grass-eating ungulates such as cows, goats and yaks belch out one fifth of the annual global methane release; the gas is a metabolic by-product of the bacteria in their guts. Other significant sources include termites, rice paddies, swamps, *It might mean life,*

it might mean unusual geologic activity; whichever it is, the

presence of methane in the atmospheres

of Mars and Titan is one of the most tantalizing puzzles in our solar system

TITAN, technically a satellite of Saturn but for all intents and purposes a full-fledged planet, has a nitrogen atmosphere denser than Earth's and a surface sculpted by tectonic activity and rivers of liquid methane. Where the methane comes from, no one knows for sure. The Cassini space probe took this composite infrared image last year.



leakage of natural gas (itself a result of past life) and photosynthetic plants [see "Methane, Plants and Climate Change," by Frank Keppler and Thomas Röckmann; Scientific American, February 2007]. Volcanoes contribute less than 0.2 percent of the total methane budget on Earth, and even they may simply be venting methane produced by organisms in the past. Abiotic sources such as industrial processes are comparatively minor. Thus, detection of methane on another Earth-like object naturally raises the prospect of life on that body.

In the Air

That is what happened with Mars in 2003 and 2004, when three independent groups of scientists announced the discovery of methane in the atmosphere of that planet. Using a high-resolution spectrograph at the Infrared Telescope Facility in Hawaii and at the Gemini South Telescope in Chile, a team led by Michael Mumma of the NASA Goddard Space Flight Center detected methane concentrations in excess of 250 ppbv, varying over the planet and perhaps over time. Vittorio Formisano of the Institute of Physics and Interplanetary Science in Rome and his colleagues (including me) analyzed thousands of infrared spectra collected by the Mars Express orbiter. We found methane to be much less abundant, ranging from zero to about 35 ppbv, with a planetary average of approximately 10 ppbv. Finally, Vladimir Krasnopolsky of the Catholic University of America and his colleagues, using the Canada-France-Hawaii Telescope, measured a planetary average of about 10 ppbv. They could not determine the variation over the planet because of poor signal and spatial resolution.

Mumma's team is now reanalyzing its data to try to determine why its value is the outlier. For now, I will take the 10 ppbv value as the most likely. It corresponds to a concentration of methane (in molecules per unit volume) that is only 40 millionths of the concentration in Earth's atmosphere. Nevertheless, even the barest presence of the gas demands an explanation.

Although astronomers detected methane on Titan as early as 1944, it was only the additional discovery of nitrogen 36 years later that generated the immense interest in this cold and distant moon [see "Titan," by Tobias Owen; Scientific American, February 1982]. Nitrogen is a key constituent of biological molecules such as amino acids and nucleic acids. A body with a nitrogen-methane atmosphere, where the ground-level pressure is one and a half times that of our home planet,

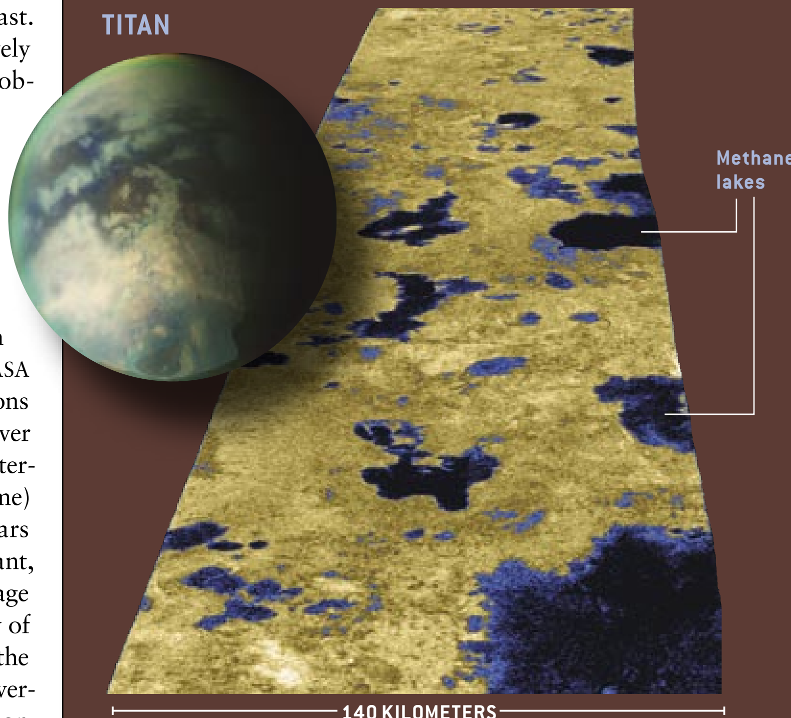
Overview/*Methane*

- Astronomers have been talking about life on Mars for a century or longer, but seldom with the benefit of hard data. That situation changed in 2003 with the discovery of methane in the atmosphere. Some ongoing process must pump it out to offset its steady destruction by sunlight.
- Researchers have narrowed the possibilities to two. The first is Martians—specifically, methane-belching bacteria like those in cows' guts on Earth. The second is a rock-water reaction called serpentinization, which occurs in the black smokers on Earth's seafloor. The latter possibility may seem like a letdown but would be a dramatic discovery in its own right. A new rover scheduled for launch in 2009 may be able to settle the issue.
- A similar debate swirls around Saturn's largest satellite, Titan. In 2005 the Huygens space probe showed that methane plays much the same role there as water does on Earth. The methane may come from geochemical reactions in a vast hidden ocean.

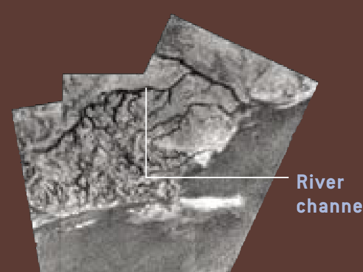
SNAPSHOTS FROM TITAN AND MARS

Astronomers discovered methane in Titan's atmosphere in the 1940s, but dense haze blocked their view of the surface. The Cassini-Huygens mission has now seen the extent to which methane shapes the terrain.

TITAN

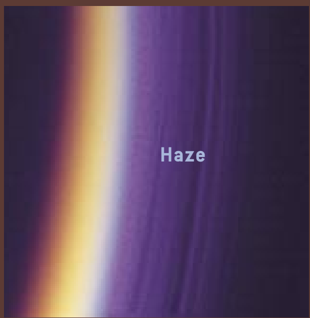


LARGE BODIES of liquid, probably methane, show up in these Cassini radar images of Titan's far northern hemisphere. Liquid appears dark (*colorized blue*) for the same reason that a wet road looks dark when you are driving at night: the smooth liquid surface reflects the headlight beams away from your eye. Conversely, dry, rough terrain appears bright (*tan*). This image has a resolution of 500 meters.



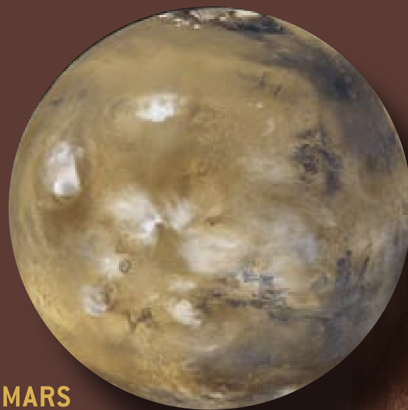
RIVER CHANNELS may have been carved by liquid methane flowing from a series of ridges (about 200 meters high) down to a lakebed (now dry). The pattern of tributaries suggests that the methane came from rainfall. The Huygens probe captured this image from an altitude of 6.5 kilometers as it descended through the atmosphere.

On the Red Planet, methane exists only at the parts-per-billion-by-volume (ppbv) level, so it cannot be seen as directly as on Titan. Various observed processes may destroy or create it.



HAZE in the upper atmosphere of Titan consists of hydrocarbons created when sunlight strikes methane. The haze resembles urban smog. This image has a resolution of 700 meters.

TITAN'S SURFACE had never been glimpsed before the Huygens probe landed in January 2005. It may look like a boring field of rocks, but the "rocks" are in fact fist-size chunks of ice and, on close examination, show signs of erosion by flowing liquid—probably methane. As the probe warmed the soil, methane oozed out.



MARS

DUST DEVILS, such as this one spied by the Mars Global Surveyor on May 21, 2002, rub dust grains together and thus create strong static-electric fields—which can tear apart water molecules and lead to the production of methane-destroying peroxides.

UNDERGROUND WATER FLOW in the Martian past would explain this whitish ridge (*arrow*) recently seen by the Mars Reconnaissance Orbiter. Water flowing through a rock fracture would have deposited minerals, much as hard water causes buildup in a household pipe. When surrounding rock eroded away, the minerals remained, leaving a ridge. Underground water might also have facilitated methane production.

METHANE DATA	EARTH	MARS	TITAN
Atmospheric concentration	1,750 ppbv	10 ppbv	5 percent
Molecular lifetime in atmosphere (years)	10	600	10 million
Production rate needed to sustain constant amount (tons per year)	515 million	125	25 million
Main sources	Cattle, termites, swamps, rice paddies, natural gas	Bacteria? Rock-water reactions in aquifer?	Rock-water reactions in under-ground ocean

NASA/JPL/UNIVERSITY OF ARIZONA (*Titan globe on opposite page and on preceding pages and ridge*); NASA/JPL/USGS (*lakes*); ESA/NASA/JPL/UNIVERSITY OF ARIZONA (*river and Titan surface*); NASA/JPL/MSSS (*Mars globe on this page and on preceding pages and dust devil*); NASA/JPL/SPACE SCIENCE INSTITUTE (*haze*)

may have the right ingredients for molecular precursors of life and, some have speculated, even life itself to form.

Methane plays a central, controlling role in maintaining Titan's thick nitrogen atmosphere. It is the source of hydrocarbon hazes, which absorb solar infrared radiation and warm the stratosphere by approximately 100 degrees Celsius, and of hydrogen, whose molecular collisions result in a 20-degree warming in the troposphere. If the methane ever ran out, temperatures would drop, nitrogen gas would condense into liquid droplets and the atmosphere would collapse. Titan's special character would change forever. Its smog and clouds would dissipate. The methane rain that seems to have carved its surface would stop. Lakes, puddles and streams would dry up. And, with its veil lifted, Titan's stark surface would lay bare and readily accessible to telescopes on Earth. Titan would lose its mystique and turn into just another satellite with thin air.

Could it be that methane on Mars and Titan has a biological origin, as on Earth, or does it have another explanation, such as volcanoes or impacts of comets and meteorites? Our understanding of geophysical, chemical and biological processes has helped narrow the field of possible sources on Mars, and many of the same arguments apply to Titan as well.

Split by Sunlight

THE FIRST STEP to answering the question is to determine the rate at which methane must be produced or delivered. That, in turn, depends on how fast the gas is being removed from the atmosphere. At altitudes of 60 kilometers and higher above the Martian surface, solar ultraviolet radiation splits methane molecules apart. Lower in the atmosphere, oxygen atoms and hydroxyl radicals (OH), which form when water molecules are broken apart by ultraviolet photons, oxidize methane. Without being resupplied, methane would gradually disappear from the atmosphere. The "lifetime" of methane—defined as the time it takes for the gas concentration to drop by a factor of the mathematical constant *e*, or roughly three—is 300 to 600 years, depending on the amount of water vapor, which undergoes seasonal changes, and on the strength of solar radiation, which varies during the solar cycle. On Earth, similar processes give methane a lifetime of about 10 years. On Titan, where solar ultraviolet radiation is much weaker and oxygen-bearing molecules are substantially less abundant, methane can last 10 million to 100 million years (which is still a short time in geologic terms).

Methane's lifetime on Mars is long enough for winds and diffusion to mix the gas into the atmosphere fairly uniformly. Thus, the observed variations of methane levels over the planet are puzzling. They may be a sign that the gas comes from localized sources or disappears into localized sinks. One possible sink is chemically reactive soil, which could accelerate the loss of methane. If such additional sinks operated, it would take an even larger source to maintain the observed abundance.

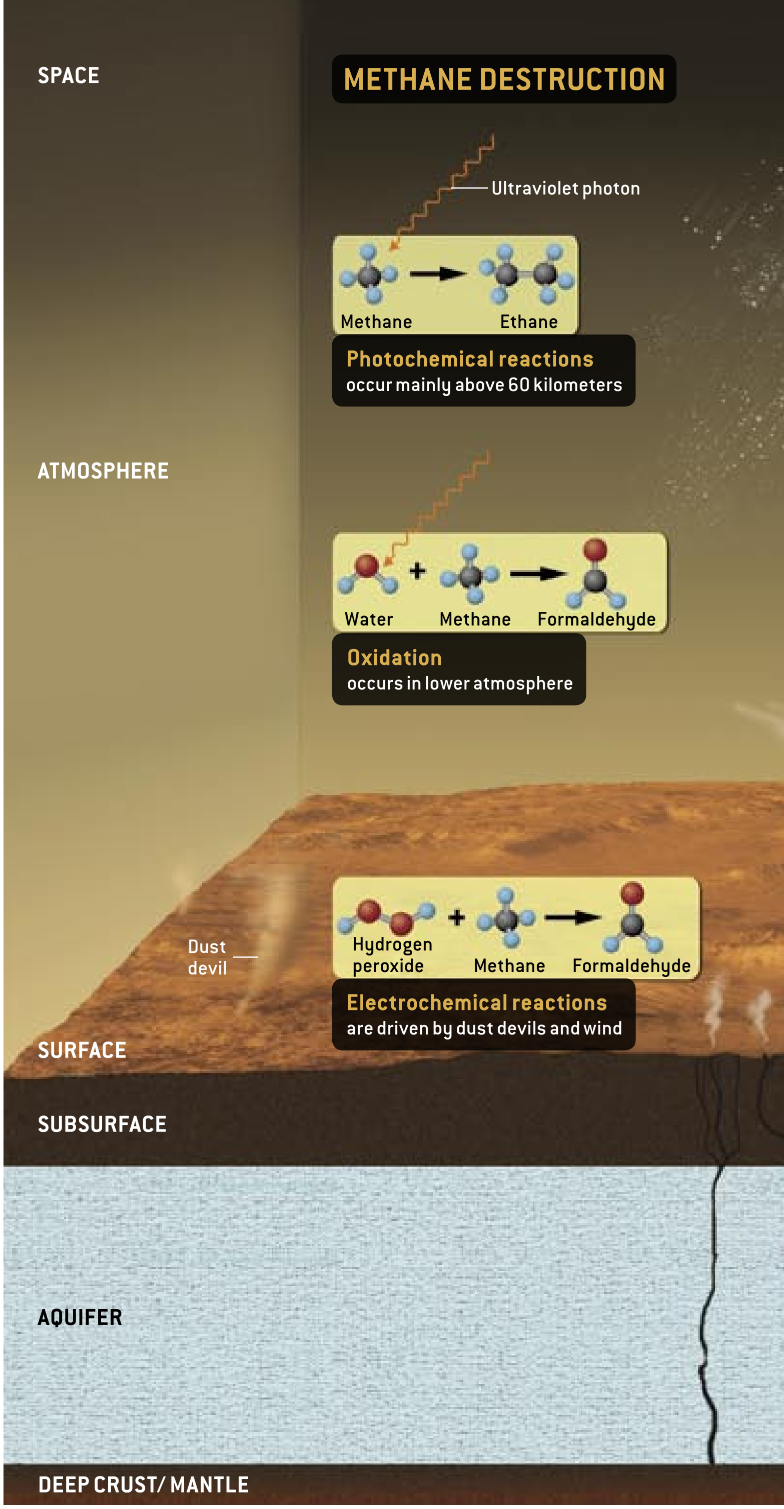
The next step is to consider potential scenarios for forming methane. The Red Planet is a good place to start because its methane abundance is so low. If a mechanism cannot explain even this small amount, it would be unlikely to account for Titan's much greater quantity. For a 600-year lifetime, a little over 100 metric tons of methane would have to be produced each year to maintain a constant global average of 10 ppbv. That is about a quarter-millionth the production rate on Earth.

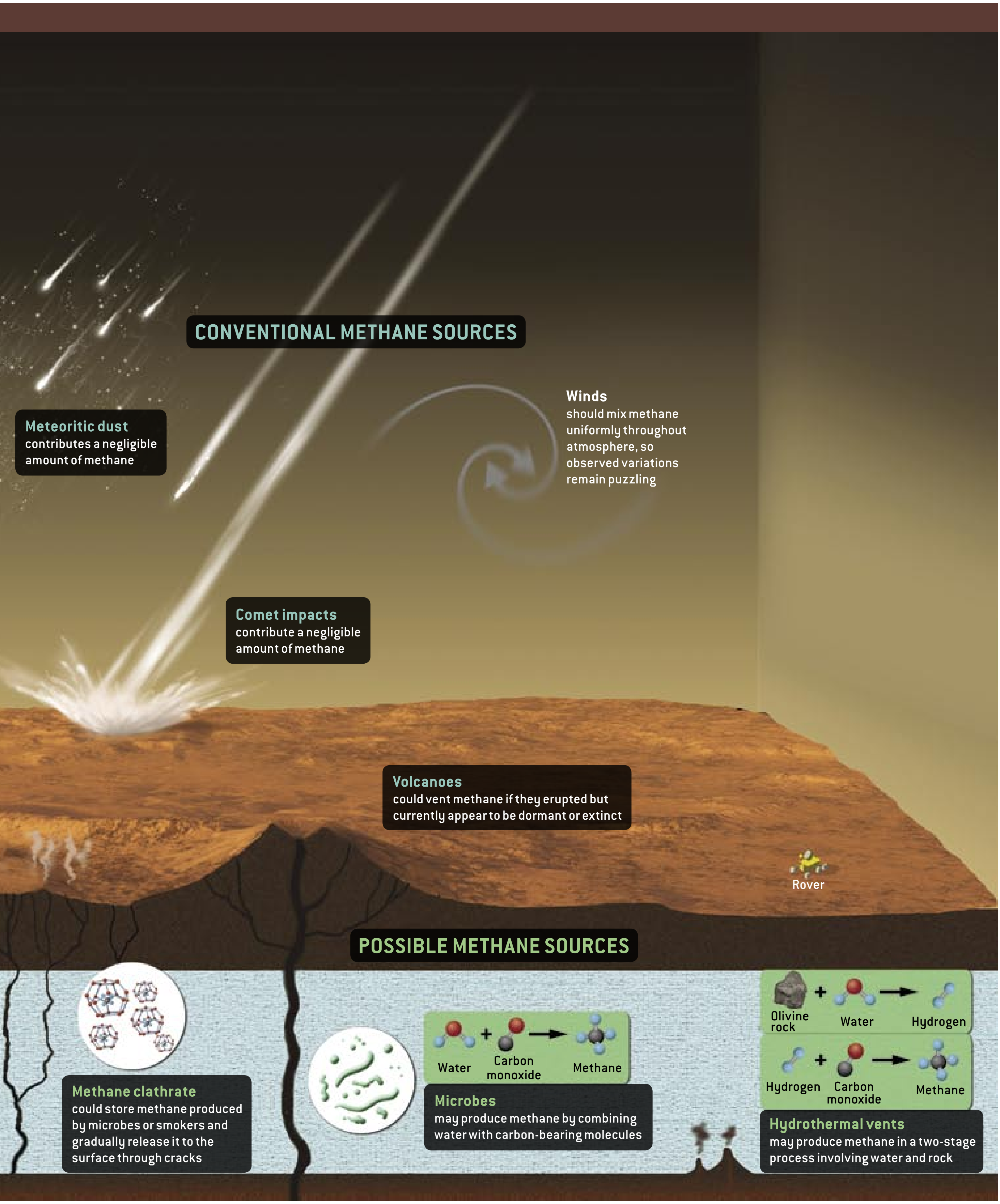
As on Earth, volcanoes are most likely not responsible. Martian volcanoes have been extinct for hundreds of millions of years. Furthermore, if a volcano had been responsible for the methane, it would also have pumped out enormous quantities of sulfur dioxide, and Mars's atmosphere is devoid of sulfur compounds. Extraplanetary contributions also appear minimal. Some 2,000 tons of micrometeoritic dust are estimated to reach the Martian surface every year. Less than 1 percent of their mass is carbon, and even this material is largely oxidized and hence an insignificant source of methane. Comets are about 1 percent methane by weight, but they strike Mars only once every 60 million years on average. Thus, the amount of methane delivered would be about one ton a year, or less than 1 percent of the required amount.

Could it be that a comet struck Mars in the recent past? It could have delivered a large amount of methane, and over time the abundance in the atmosphere would have declined to its present value. An impact of a comet 200 meters in diameter 100 years ago, or a comet 500 meters in diameter 2,000 years

METHANE ON MARS

By all rights, Mars should have zero methane. The gas is quickly cleansed from the air by chemical reactions driven by sunlight or weather patterns, and known geologic and astronomical processes cannot replenish it fast enough. Thus, the methane hints at unseen activity, such as black smokers or methane-creating microbes swimming in underground bodies of water.





RON MILLER; MELISSA THOMAS (*chemical reactions insets*) ago, could have supplied sufficient methane to account for the currently observed global average value of 10 ppbv. But this idea runs into a problem: the distribution of methane is not uniform over the planet. The time it takes to distribute methane uniformly vertically and horizontally is at most several months. Thus, a cometary source would result in a uniform methane distribution over Mars, contrary to observations.

Smoke in the Waters

THAT LEAVES US WITH two possible sources: hydrogeochemical and microbial. Either one would be fascinating. Hydrothermal vents, known as black smokers, were first discovered on Earth in 1977 on the Galápagos Rift [see "The Crest of the East Pacific Rise," by Ken C. Macdonald and Bruce P. Luyendyk; SCIENTIFIC AMERICAN, May 1981]. Since then, oceanographers have found them along many other mid-oceanic ridges. Laboratory experiments show that under the conditions prevailing at these vents, ultramafic silicates—rocks rich in iron or magnesium, such as olivine and pyroxene—can react to produce hydrogen in a process commonly referred to as serpentinization. In turn, reaction of hydrogen with carbon grains, carbon dioxide, carbon monoxide or carbonaceous minerals can produce methane.

The keys to this process are hydrogen, carbon, metals (which act as catalysts), and heat and pressure. All are available on Mars, too. The process of serpentinization can occur either at high temperatures (350 to 400 degrees C) or at milder ones (30 to 90 degrees C). These lower temperatures are estimated to occur within purported aquifers on Mars.

Although low-temperature serpentinization may be capable of producing the Martian methane, biology remains a serious possibility. On Earth, microorganisms known as methanogens produce methane as a by-product of consuming hydrogen, carbon dioxide or carbon monoxide. If such organisms lived on Mars, they would find a ready supply of nutrients: hydrogen (either produced in the serpentinization process or diffusing into the soil from the atmosphere) plus carbon dioxide and carbon monoxide (in the rocks or from the atmosphere).

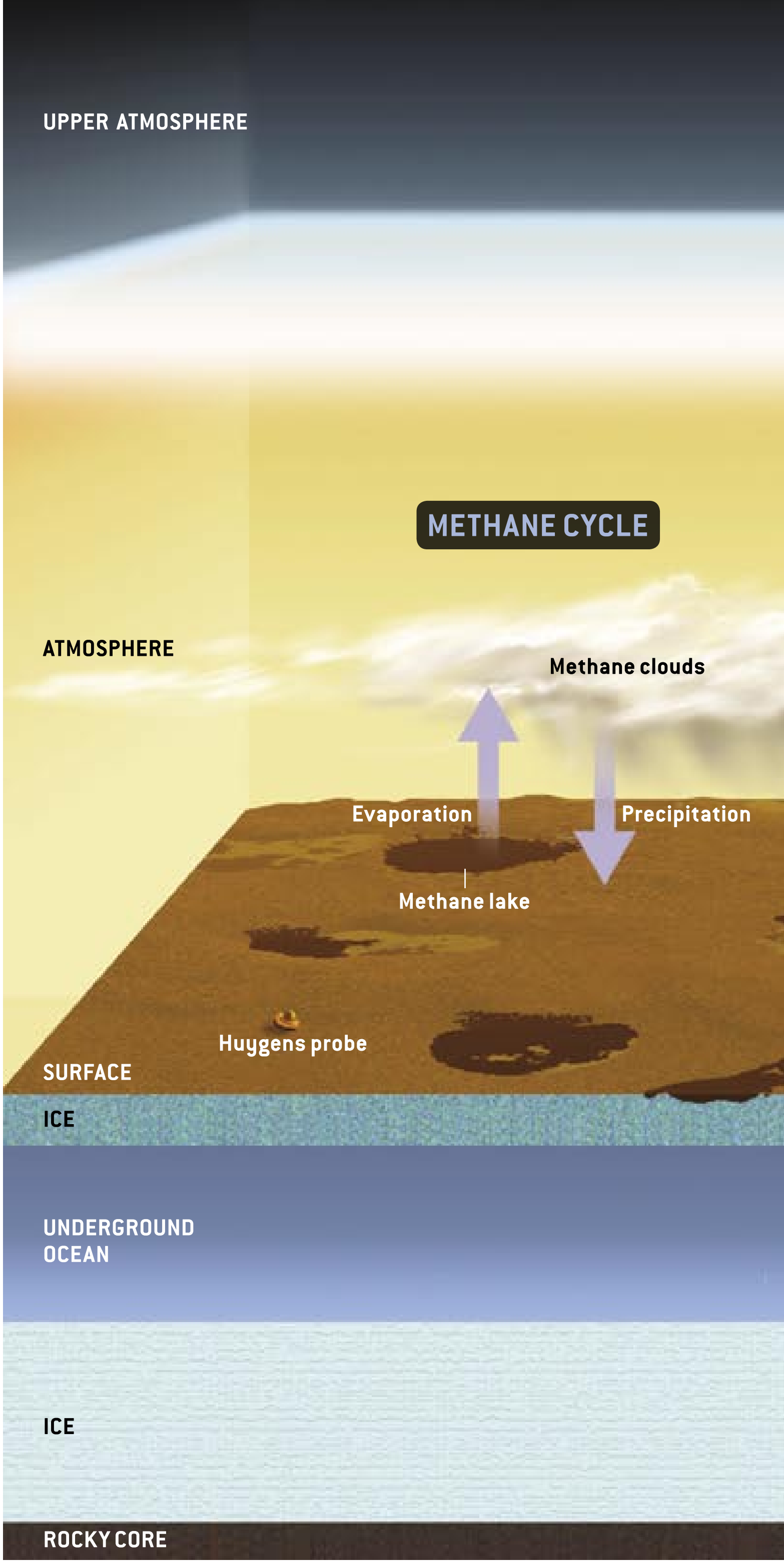
Once formed by either serpentinization or microbes, methane could be stored as a stable clathrate hydrate—a chemical

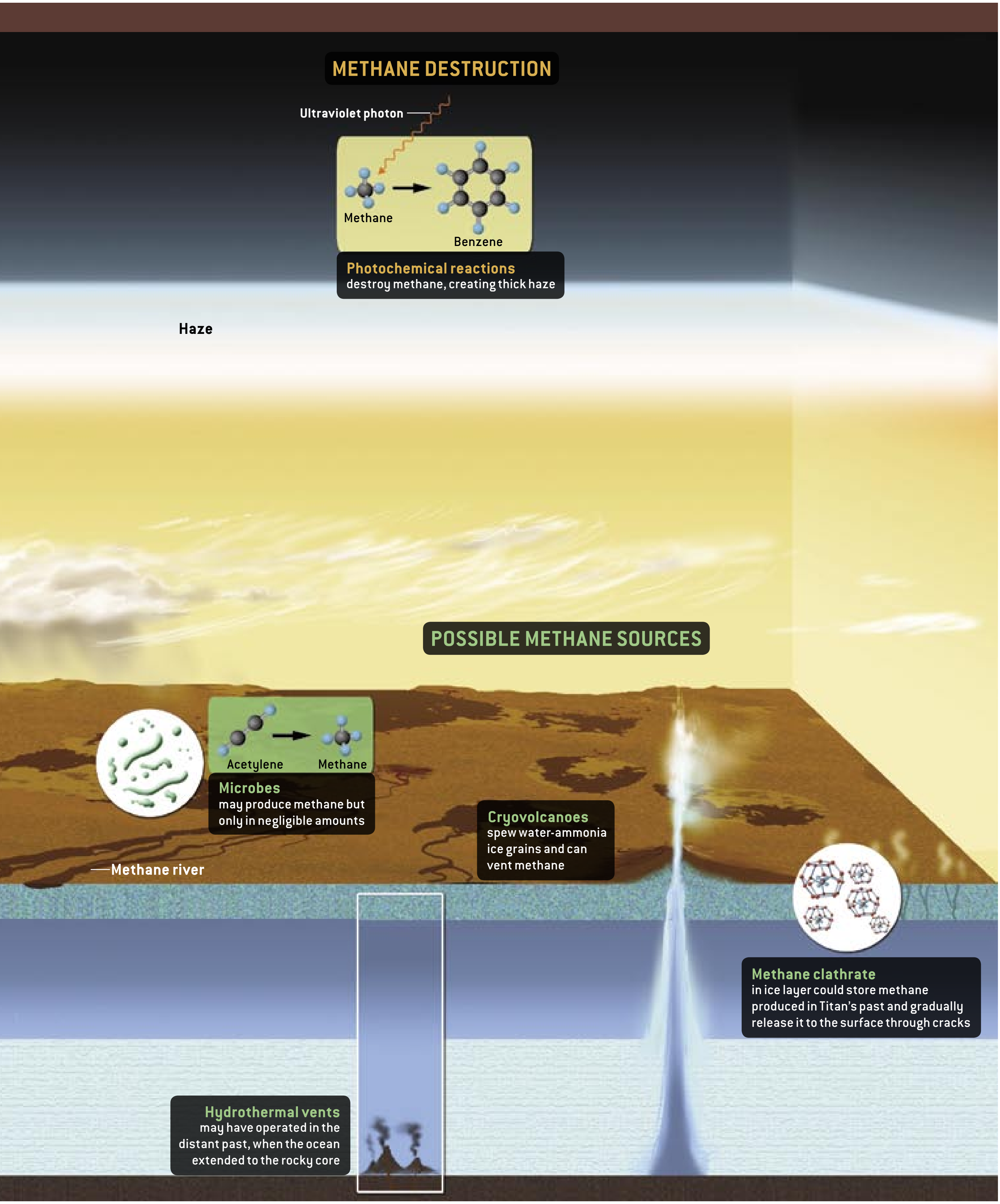
THE AUTHOR

SUSHIL K. ATREYA began his space career on the science teams of the Voyager missions to the giant planets, continuing with Galileo, Cassini-Huygens, Venus Express, Mars Express, Mars Science Laboratory (scheduled for launch in 2009) and Juno-Jupiter Polar Orbiter (2011). His research focuses on the origin and evolution of atmospheres and the formation of planetary systems. He is a professor at the University of Michigan at Ann Arbor, a Fellow of the American Association for the Advancement of Science, and a Distinguished Visiting Scientist at the Jet Propulsion Laboratory. When not exploring other worlds, Atreya likes to go hiking in the mountains and cycling. He expresses his gratitude to Chloé Atreya, Wesley Huntress, Paul Mahaffy, Inge ten Kate, Henry Pollack and Elena Adams for discussions and comments on the drafts of this article.

METHANE ON TITAN

Methane is to Titan what water is to Earth: a substance that cuts rivulets into the surface, pools in standing bodies, evaporates into the air and rains back down. As on Mars, chemical reactions deplete Titan's methane, so some geologic or biological activity must replenish it.





RON MILLER; MELISSA THOMAS (*chemical reactions insets*) structure that traps methane molecules like animals in a cage—for later release to the atmosphere, perhaps by gradual outgassing through cracks and fissures or by episodic bursts triggered by volcanism. No one is sure how efficiently the clathrates would form or how readily they would be destabilized.

The Mars Express observations hint at greater methane concentrations over areas containing subsurface water ice. Either the geologic or biological scenario would explain this correlation. Aquifers below the ice would provide a habitat for creatures or a venue for the hydrogeochemical production of methane. Without more data, the biological and geologic possibilities appear equally likely.

A Titanic Ocean

AT FIRST GLANCE, one might think that Titan's methane would be easier to understand: the moon formed in the subnebula of Saturn, whose atmosphere contains huge amounts of the gas. Yet the data argue for production of methane on Titan rather than delivery of methane to Titan. The Huygens probe of the joint NASA and European Space Agency's Cassini-Huygens Mission found no xenon or krypton in the moon's atmosphere. Had the planetesimals that formed Titan brought methane, they would have brought these heavy noble gases as well. The absence of such gases indicates that methane most likely formed on Titan.

Therefore, the presence of methane on Titan is as mysterious as it is on Mars—in some respects more so because of its sheer quantity (5 percent by volume). A plausible source, as on Mars, is serpentinization at relatively low temperatures. Christophe Sotin of the University of Nantes in France and his colleagues have argued that Titan might sustain an underground ocean of liquid water [*see box on two preceding pages*]. Dissolved ammonia, acting as an antifreeze, would help to keep it from freezing solid. In their model, the ocean is 100 kilometers underneath Titan's surface and 300 to 400 kilometers deep. In the past, the decay of radioactive elements and the leftover heat from Titan's formation might have melted nearly all the body's ice—so the ocean might have extended all the way down to the rocky core.

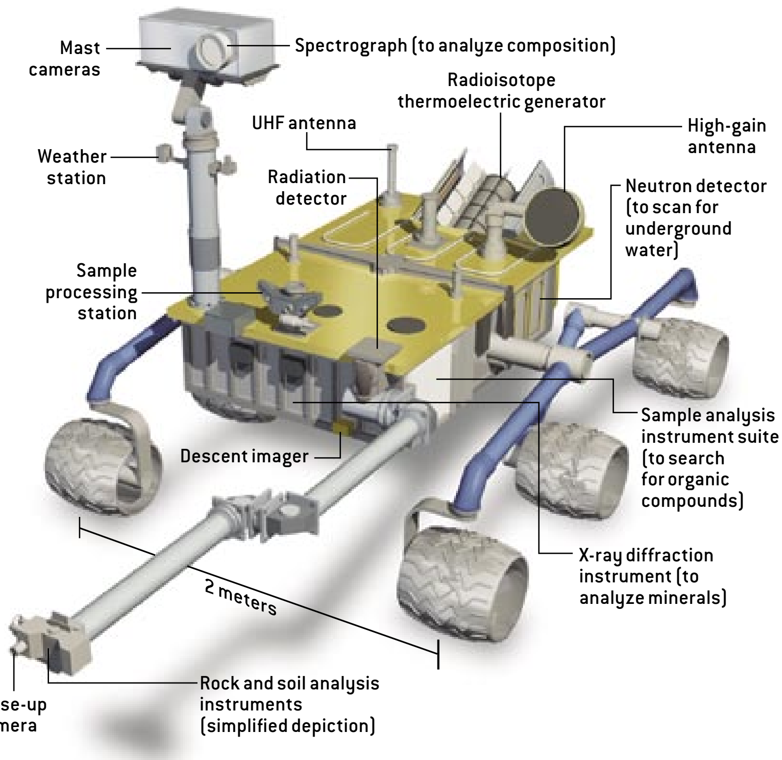
Under those conditions, reactions between the water and the rock would have liberated hydrogen gas, which in turn would have reacted with carbon dioxide, carbon monoxide, carbon grains or other carbonaceous material—producing methane. I estimate that this process would have been capable of explaining Titan's observed methane abundance. Once produced, methane could have been stored as a stable clathrate hydrate and released to the atmosphere either gradually, through volcanism, or in bursts, triggered by impacts.

An intriguing clue is the argon 40 gas detected by Huygens as it descended through Titan's atmosphere. This isotope forms by the radioactive decay of potassium 40, which is sequestered in the rocks deep in Titan's core. Because the radioactive half-life of potassium 40 is 1.3 billion years, the small amount of argon 40 in the atmosphere is evidence for slow release of gases from the interior. In addition, optical and radar images of the surface show signs of cryovolcanism—geyserlike eruptions of ammonia-water ice—which also indicates that material wells up from the interior. The surface appears relatively young and free of craters, which is a sign of resurfacing by material from the interior. The estimated resurfacing rate would release methane from the interior quickly enough to balance the photochemical loss. Methane on Titan plays the role of water on Earth, complete with liquid surface reservoirs, clouds and rain—a full-fledged methalogical cycle. Thus, a substantial body of evidence exists, even more so than for Mars, that methane stored in the interior would have no difficulty getting out to the surface and subsequently evaporating into the atmosphere.

Might biology also play a role in creating Titan's methane?

NASA'S NEXT ROVER

The next step to solving the problem of methane on Mars is NASA's Mars Science Laboratory, scheduled for launch in 2009. Its instruments should be able to measure the methane's isotopic makeup (a clue to its origin) and sift through soil looking for organic compounds (the composition of which would indicate which chemical or biological processes have created or destroyed methane).



DON FOLEY; SOURCE: NASA/JPL

Christopher McKay of the NASA Ames Research Center and Heather Smith of the International Space University in Strasbourg, France, as well as Dirk Schulze-Makuch of Washington State University and David Grinspoon of the Denver Museum of Nature and Science, have suggested that acetylene and hydrogen could serve as nutrients for methanogens even in the extreme cold of Titan's surface (–179 degrees C). This biogenic process differs from that employed by methanogens on Earth and their cousins, if any, on Mars in that no water is needed. Instead liquid hydrocarbons on Titan's surface serve as the medium.

Yet this hypothesis has a shortcoming. Huygens data rule out an underground source of acetylene; this compound must ultimately come from methane in the atmosphere. Thus, it seems like a circular argument: to produce methane (by microbes), one needs methane. Moreover, the sheer abundance of methane on Titan is so immense that methanogens would have to work in overdrive to produce it, severely depleting the available nutrients.

In view of these obstacles, a biological explanation for methane is much less attractive on Titan than on Mars. Nevertheless, the hypothesis of habitability bears investigating. Some scientists argue that this moon might have been or still be habitable. It receives enough sunlight to turn nitrogen and methane into molecules that are the precursors to biology. An underground water-ammonia brine, with some methane and other hydrocarbons thrown in, could be a friendly environment for complex molecules or even living organisms. In the distant past, when the young Titan was still cooling off, liquid water may even have flowed on the surface.

The Mars Science Laboratory rover will study solid and gaseous samples for **chemical signs of past or present life**.

Organic Food

ONE CRUCIAL MEASUREMENT that could help determine the sources of methane on Mars and Titan is the carbon isotope ratio. Life on Earth has evolved to prefer carbon 12, which requires less energy for bonding than carbon 13 does. When amino acids combine, the resulting proteins show a marked deficiency in the heavier isotope. Living organisms on Earth contain 92 to 97 times as much carbon 12 as carbon 13; for inorganic matter, the standard ratio is 89.4.

On Titan, however, the Huygens probe measured a ratio of 82.3 in methane, which is smaller, not larger, than the terrestrial inorganic standard value. This finding argues strongly against the presence of life as we know it. To be sure, some scientists suggest that life could have evolved differently on Titan than on Earth or that the inorganic isotope ratio may be different there.

No one has yet determined the carbon isotope ratio for Mars. This measurement is challenging when the concentration of the gas is so low (one billionth of that on Titan). NASA's Mars Science Laboratory (MSL) rover, scheduled to arrive at Mars in 2010, should be able to carry out precise measurements of the carbon isotopes in methane and possibly other organic materials. It will also study solid and gaseous samples for other chemical signs of past or present life, such as a very high abundance ratio of methane to heavier hydrocarbons (ethane, propane, butane) and chirality (a preference for either left-handed or right-handed organic molecules).

Tied up with these issues is the question of why organics seem to be missing from the surface of Mars. Even in the absence of life, meteorites, comets and interplanetary dust particles should have delivered organics over the past four and a half billion years. Perhaps the answer lies in Martian dust devils and storms and ordinary saltation (the hopscotching of windblown dust grains). These processes generate strong static electric fields, which can trigger the chemical synthesis of hydrogen peroxide. Being a potent antiseptic, hydrogen peroxide would quickly sterilize the surface and scrub out the organics. The oxidant would also accelerate the loss of methane locally from the atmosphere, thus requiring a larger source to explain the abundances observed in the Martian atmosphere.

In summary, methane serves as the glue that holds Titan together in some mysterious ways. The presence of methane on Mars is equally intriguing, not the least because it evokes visions of life on that planet. Future exploration of both bodies will seek to determine whether they were ever habitable. Although life as we know it can produce methane, the presence of methane does not necessarily signify the existence of life. So planetary scientists must investigate thoroughly the sources, sinks and isotopic composition of this gas, along with other organic molecules and trace constituents in both gaseous and solid samples. Even if methane is found to have no connection to life, studying it will reveal some of the most fundamental aspects of the formation, climate histories, geology and evolution of Mars and Titan. SA

MORE TO EXPLORE

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Sushil K. Atreya's Web page: **www.umich.edu/~atreya**