Today methane-producing microbes are confined to oxygen-free settings,

When Methane


METHANE-INDUCED HAZE on Earth two billion years ago.

such as the guts of cows, but in Earth's distant past, they ruled the world

Made Climate

By James F. Kasting

About 2.3 billion years ago

unusual microbes breathed new life into young Planet Earth by filling its skies with oxygen. Without those prolific organisms, called cyanobacteria, most of the life that we see around us would never have evolved.

Now many scientists think another group of single-celled microbes were making the planet habitable long before that time. In this view, oxygen-detesting methanogens reigned supreme during the first two billion years of Earth's history, and the greenhouse effect of the methane they produced had profound consequences for climate.

Scientists first began to suspect methane's dramatic role more than 20 years ago, but only during the past four years have the various pieces of the ancient methane story come together. Computer simulations now reveal that the gas—which survives about 10 years in today's atmosphere—could have endured for as long as 10,000 years in an oxygen-free world. No fossil remains exist from that time, but many microbiologists believe that methanogens were some of the first life-forms to evolve. In their prime, these microbes could have generated methane in quantities large enough to stave off a global deep freeze. The sun was considerably dimmer then, so the added greenhouse influence of methane could have been exactly what the planet needed to keep warm. But the methanogens did not dominate forever. The plummeting temperatures associated with their fading glory could explain Earth's first global ice age and perhaps others as well.

The prevalence of methane also means that a pinkish-orange haze may have shrouded the planet, as it does Saturn's largest moon, Titan. Although Titan's methane almost certainly comes from a nonbiological source, that moon's similarities to the early Earth could help reveal how greenhouse gases regulated climate in our planet's distant past.

Faint Sun Foiled

WHEN EARTH FORMED some 4.6 billion years ago, the sun burned only 70 percent as brightly as it does today [see "How Climate Evolved on the Terrestrial Planets," by James F. Kasting, Owen B. Toon and James B. Pollack; SCIENTIFIC AMERICAN, February 1988]. Yet the geologic record contains no convincing evidence for widespread glaciation until about 2.3 billion years ago, which means that the planet was probably even warmer than during the modern cycle of ice ages of the past 100,000 years. Thus, not only did greenhouse gases have to make up for a fainter sun, they also had to maintain average temperatures considerably higher than today's.

Methane was far from scientists' first choice as an explanation of how the young Earth avoided a deep freeze. Because ammonia is a much stronger greenhouse gas than methane, Carl Sagan and George H. Mullen of Cornell University suggested in the early 1970s that it was the culprit. But later research showed that the sun's ultraviolet rays rapidly destroy ammonia in an oxygen-free atmosphere. So this explanation did not work.

Another obvious candidate was carbon dioxide (CO_2), one of the primary gases spewing from the volcanoes abundant at that time. Although they debated the details, most scientists assumed for more than 20 years that this gas played the dominant role. In 1995, however, Harvard University researchers uncovered evidence that convinced many people that CO_2 levels were too low to have kept the early Earth warm.

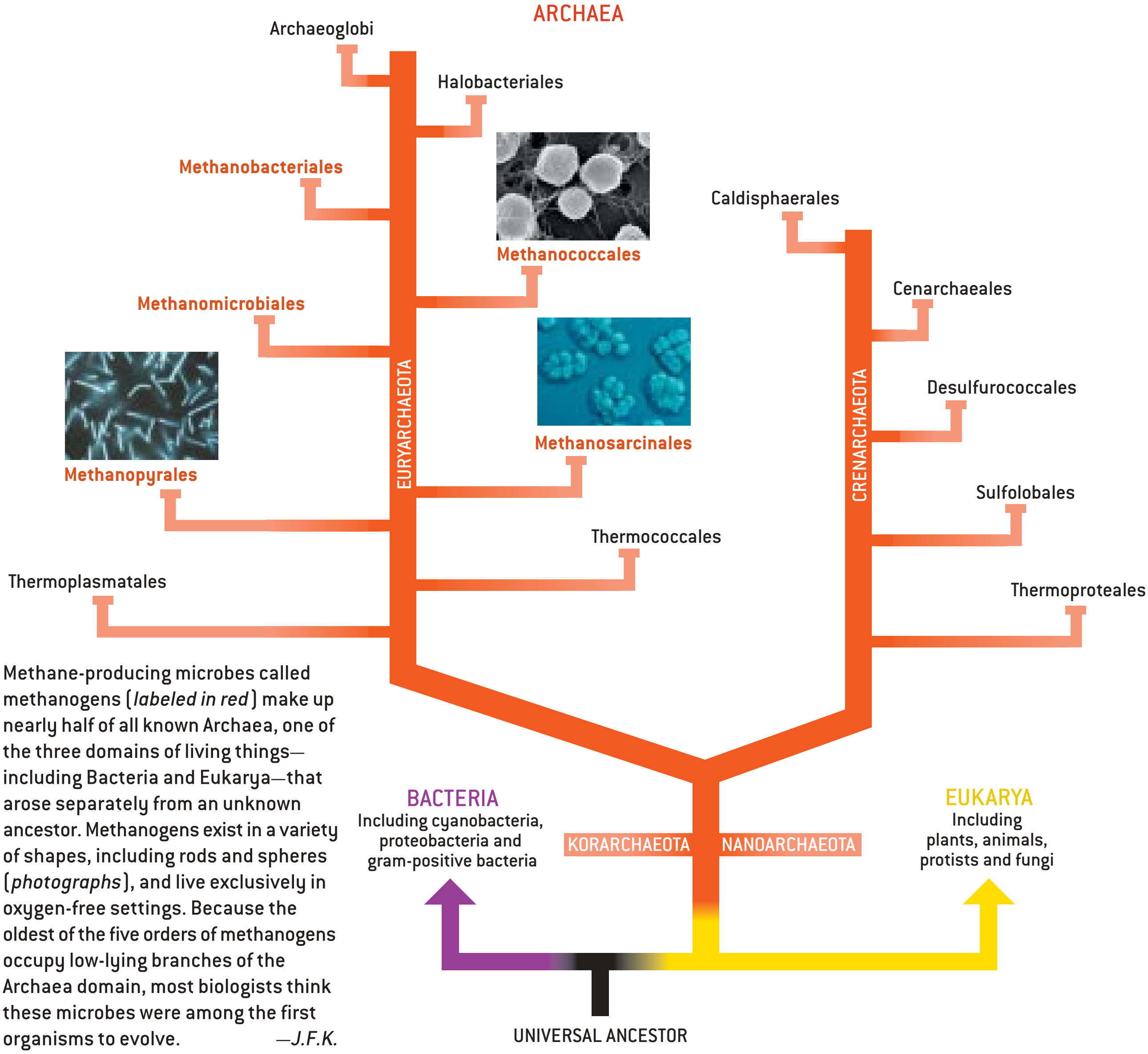
The Harvard team, led by Rob Rye, knew from previous studies that if the atmospheric concentrations of CO_2 had ex-

Overview/*The Microbe That Roared*

- Before about 2.3 billion years ago, Earth's atmosphere and oceans were virtually devoid of oxygen, making the world a nirvana for oxygen-detesting microbes such as methanogens.
- Scientists now think that methanogens—so named because they give off methane gas as a waste product—could have filled the ancient skies with nearly 600 times as much methane as they do today.
- That extra methane would have produced a greenhouse effect powerful enough to warm the planet even though the sun burned less brightly at that time. Such was the case until the atmosphere filled with oxygen and drove the methanogens into seclusion.

DON DIXON (*preceding pages*)

METHANE MAKERS ON THE TREE OF LIFE



Methane-producing microbes called methanogens (*labeled in red*) make up nearly half of all known Archaea, one of the three domains of living things—including Bacteria and Eukarya—that arose separately from an unknown ancestor. Methanogens exist in a variety of shapes, including rods and spheres (*photographs*), and live exclusively in oxygen-free settings. Because the oldest of the five orders of methanogens occupy low-lying branches of the Archaea domain, most biologists think these microbes were among the first organisms to evolve. *—J.F.K.*

JOHNNY JOHNSON

ceeded about eight times the present-day value of around 380 parts per million (ppm), the mineral siderite ($FeCO_3$) would have formed in the top layers of the soil as iron reacted with CO_2 in the oxygen-free air. But when the investigators studied samples of ancient soils from between 2.8 billion and 2.2 billion years ago, they found no trace of siderite. Its absence implied that the CO_2 concentration must have been far less than would have been needed to keep the planet's surface from freezing.

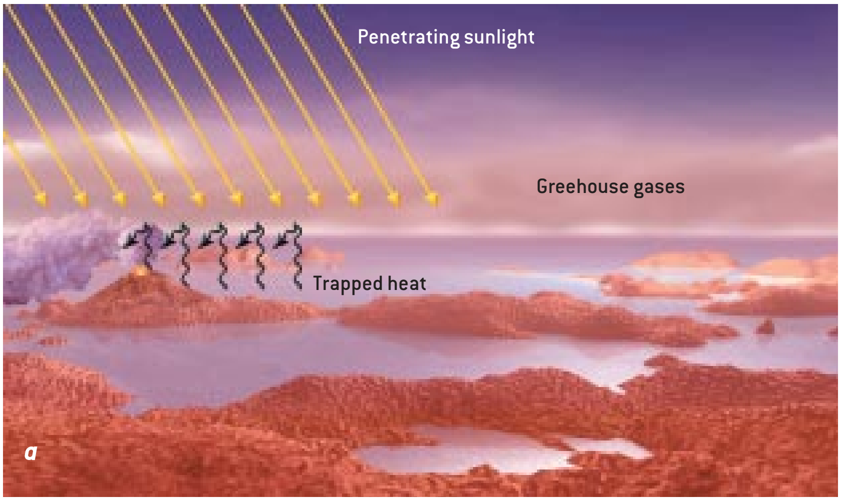
Even before CO_2 lost top billing as the key greenhouse gas, researchers had begun to explore an alternative explanation. By the late 1980s, scientists had learned that methane traps more heat than an equivalent concentration of CO_2 because it absorbs a wider range of wavelengths of Earth's outgoing radiation. But those early studies underestimated methane's influence. My group at Pennsylvania State University turned to methane because we knew that it would have had a much longer lifetime in the ancient atmosphere.

In today's oxygen-rich atmosphere, the carbon in methane is much happier teaming up with the oxygen in hydroxyl radicals to produce CO_2 and carbon monoxide (CO), releasing water vapor in the process. Consequently, methane remains in the atmosphere a mere 10 years and plays just a bit part in warming the planet. Indeed, the gas exists in minuscule concentrations of only about 1.7 ppm; CO_2 is roughly 220 times as concentrated at the planet's surface and water vapor 6,000 times.

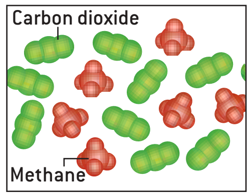
To determine how much higher those methane concentrations must have been to warm the early Earth, my students and

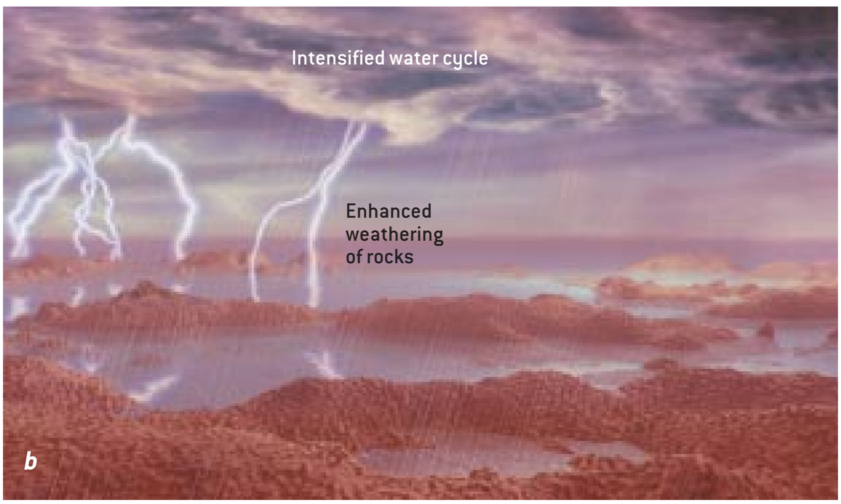
HOW HAZE FORMS

A methane-induced haze of hydrocarbon particles may have held the ancient Earth in a delicate balance between a hothouse and a deep freeze. The concentration of methane would have increased (*a*)—thereby intensifying the greenhouse effect (*b*)—for no more than a few tens of thousands of years before the climate-cooling haze would have developed (*c*).

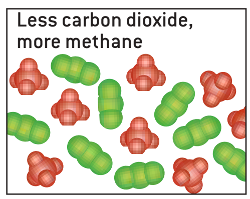


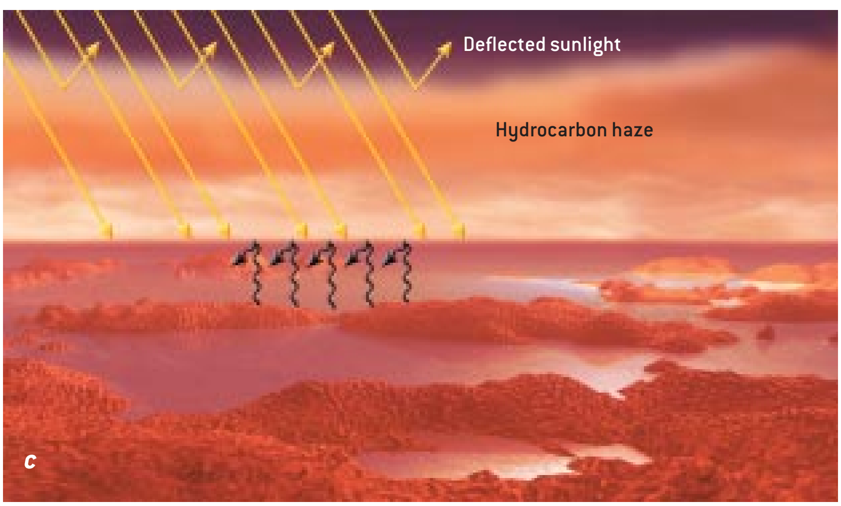
METHANE'S STARRING ROLE in Earth's atmosphere may have begun almost as soon as life originated more than 3.5 billion years ago. Single-celled ocean dwellers called methanogens would have thrived in a world virtually devoid of oxygen—as Earth was at that time—and the methane they produced would have survived in the atmosphere much longer than it does today. This methane—along with another, more abundant greenhouse gas, carbon dioxide (CO_2) from volcanoes (*inset*)—would have warmed the planet's surface by trapping Earth's outgoing heat (*black arrows*) while allowing sunlight (*yellow arrows*) to pass through.



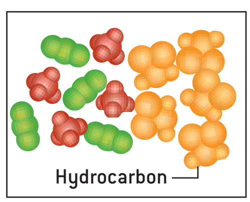


A HUMID GREENHOUSE is the preferred climate for many methanogens; the warmer the world became, the more methane they would have produced. This positive feedback loop would have strengthened the greenhouse effect, pushing surface temperatures even higher. Warmer conditions would have intensified the water cycle and, consequently, enhanced the weathering of rocks on the continents—a process that pulls CO_2 out of the atmosphere. Concentrations of CO_2 would have dropped as those of methane continued to rise, until the two gases existed in nearly equal amounts (*inset*). Under such conditions, the behavior of methane in the atmosphere would have altered dramatically.





CHANGING CHEMISTRY would have kept the rising methane levels from turning Earth into a hothouse. Some of the methane would have linked together to form complex hydrocarbons (*inset*) that then condensed into dustlike particles. A high-altitude haze of these particles would have offset the intense greenhouse effect by absorbing incoming sunlight at visible wavelengths and reradiating it back to space, thereby reducing the total amount of warmth that reached the planet's surface. Fewer heat-loving methanogens could have survived in the cooler climate; the haze would thus have put a cap on overall methane production.



DON DIXON

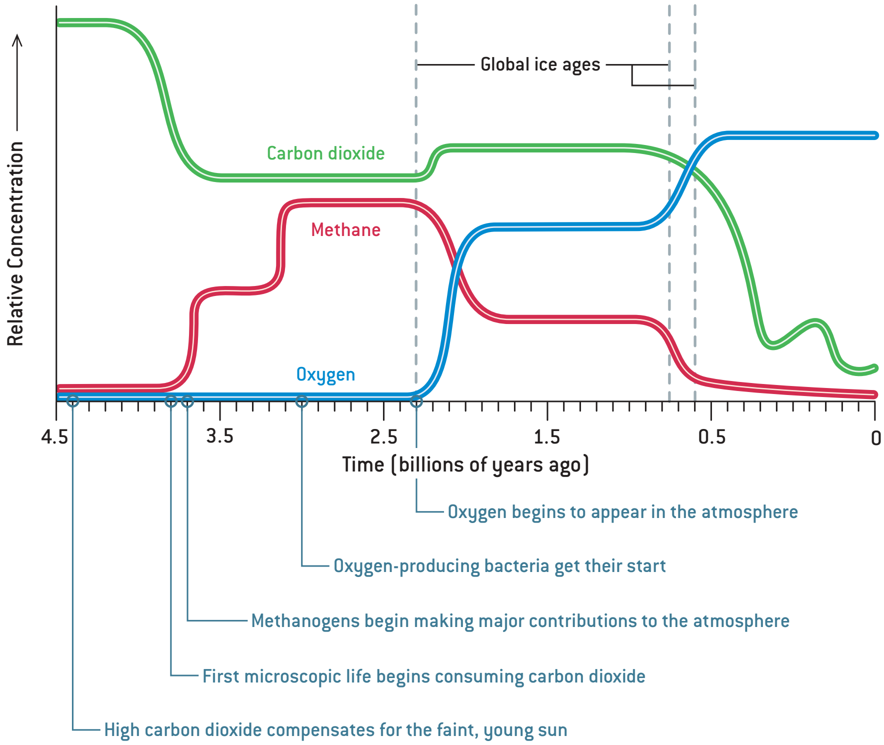
I collaborated with researchers from the NASA Ames Research Center to simulate the ancient climate. When we assumed that the sun was 80 percent as bright as today, which is the value expected 2.8 billion years ago, an atmosphere with no methane at all would have had to contain a whopping 20,000 ppm of CO_2 to keep the surface temperature above freezing. That concentration is 50 times as high as modern values and seven times as high as the upper limit on CO_2 that the studies of ancient soils revealed. When the simulations calculated CO_2 at its maximum possible value, the atmosphere required the help of 1,000 ppm of methane to keep the mean surface temperature above freezing—in other words, 0.1 percent of the atmosphere needed to be methane.

Up to the Task?

THE EARLY ATMOSPHERE could have maintained such high concentrations only if methane was being produced at rates comparable to today. Were primordial methanogens up to the task? My colleagues and I teamed up with microbiologist Janet L. Siefert of Rice University to try to find out.

Biologists have several reasons to suspect that such high methane levels could have been maintained. Siefert and others think that methane-producing microbes were some of the first microorganisms to evolve. They also suggest that methanogens would have filled niches that oxygen producers and sulfate reducers now occupy, giving them a much more prominent biological and climatic role than they have in the modern world.

Methanogens would have thrived in an environment fueled by volcanic eruptions. Many methanogens feed directly on hydrogen gas (H_2) and CO_2 and belch methane as a waste product; others consume acetate and other compounds that form as organic matter decays in the absence of oxygen. That is why today's methanogens can live only in oxygen-free environments such as the stomachs of cows and the mud under flooded rice paddies. On the early Earth, however, the entire atmosphere was devoid of oxygen, volcanoes released significant amounts of H_2. With no oxygen available to form water, the hydrogen probably accumulated in the atmosphere and oceans in concentrations high enough for methanogens to use.



RELATIVE CONCENTRATIONS of major atmospheric gases may explain why global ice ages (*dashed lines*) occurred in Earth's distant past. Methane-producing microorganisms flourished initially, but as oxygen skyrocketed about 2.3 billion years ago, these microbes suddenly found few environments where they could survive. The accompanying decrease in methane—a potent greenhouse gas—could have chilled the entire planet. The role of carbon dioxide, the most notable greenhouse gas in today's atmosphere, was probably much less dramatic.

Based on these and other considerations, some scientists have proposed that methanogens living on geologically derived hydrogen might form the base of underground microbial ecosystems on Mars and on Jupiter's ice-covered moon, Europa. Indeed, a recent report from the European Space Agency's Mars Express spacecraft suggests that the present Martian atmosphere may contain approximately 10 parts per billion of methane. If verified, this finding would be consistent with having methanogens living below the surface of Mars.

Geochemists estimate that on the early Earth H_2 reached concentrations of hundreds to thousands of parts per million—that is, until methanogens evolved and converted most of it to methane. Thermodynamic calculations reveal that if other essential nutrients, such as phosphorus and nitrogen, were available, methanogens would have used most of the available H_2 to make methane. (Most scientists agree that sufficient phosphorus would have come from the chemical breakdown of rocks and that various

THE AUTHOR

JAMES F. KASTING studies the origin and evolution of planetary atmospheres, especially those of Earth and its nearest neighbors, Venus and Mars. Since earning his Ph.D. in atmospheric science at the University of Michigan at Ann Arbor in 1979, he has used theoretical computer models to investigate atmospheric chemistry and to calculate the greenhouse effect of different gases and particles in both the present day and the distant past. Recently Kasting has begun exploring the question of whether Earth-like planets might exist around other stars in our galaxy. He is working with several other scientists to design the theoretical foundation for NASA's Terrestrial Planet Finder, a space-based telescope designed to locate planets around other stars and scan their atmospheres for signs of life.

JOHNNY JOHNSON

Methane would never again

exert a dominating effect on climate, but it could still have been an important influence at later times.

ocean-dwelling microorganisms were producing plenty of nitrogen.) In this scenario, the methanogens would have yielded the roughly 1,000 ppm of methane called for by the computer models to keep the planet warm.

Even more evidence for the primordial dominance of methanogens surfaced when microbiologists considered how today's methanogens would have reacted to a steamy climate. Most methanogens grow best at temperatures above 40 degrees Celsius; some even prefer at least 85 degrees C. Those that thrive at higher temperatures grow faster, so as the intensifying greenhouse effect raised temperatures at the planet's surface, more of these faster-growing, heat-loving specialists would have survived. As they made up a larger proportion of the methanogen population, more methane molecules would have accumulated in the atmosphere, making the surface temperature still warmer—in fact, hotter than today's climate, despite the dimmer sun.

Smog Saves the Day

AS A RESULT of that positive feedback loop, the world could have eventually become such a hothouse that life itself would have been difficult for all but the most extreme heat–loving microbes. This upward spiral could not have continued indefinitely, however. Once atmospheric methane becomes more abundant than CO_2, methane's reaction to sunlight changes. Instead of being oxidized to CO or CO_2, it polymerizes, or links together, to form complex hydrocarbons that then condense into particles, forming an organic haze. Planetary scientists observe a similar haze in the atmosphere of Saturn's largest moon: Titan's atmosphere consists primarily of molecular nitrogen, N_2, along with a small percentage of methane [*see box on opposite page*]. The scientists hope to learn more when NASA's Cassini spacecraft arrives at Saturn in July [see "Saturn at Last!" by Jonathan I. Lunine; SCIENTIFIC AMERICAN, June].

The possible formation of organic haze in Earth's young atmosphere adds a new wrinkle to the climate story. Because they form at high altitudes, these particles have the opposite effect on climate that greenhouse gases do. A greenhouse gas allows most visible solar radiation to pass through, but it absorbs and reradiates outgoing infrared radiation, thereby warming the surface. In contrast, high-altitude organic haze absorbs incoming sunlight and reradiates it back into space, thereby reducing the total amount of radiation that reaches the surface. On Titan, this so-called antigreenhouse effect cools the surface by seven degrees C or so. A similar haze layer on the ancient Earth would have also cooled the climate, thus shifting the methanogen population back toward those slower-growing species that prefer cooler weather and thereby limiting further increases in methane production. This powerful negative feedback loop would have tended to stabilize Earth's temperature and atmospheric composition at exactly the point at which the layer of organic haze began to form.

Nothing Lasts Forever

METHANE-INDUCED SMOG kept the young Earth comfortably warm—but not forever. Global ice ages occurred at least three times in the period known as the Proterozoic eon, first at 2.3 billion years ago and again at 750 million and 600 million years ago. The circumstances surrounding these glaciations were long unexplained, but the methane hypothesis provides compelling answers here as well.

The first of these glacial periods is often called the Huronian glaciation because it is well exposed in rocks just north of Lake Huron in southern Canada. Like the better-studied late Proterozoic glaciations, the Huronian event appears to have been global, based on interpretations that some of the continents were near the equator at the time ice covered them.

This cold snap formed layers of jumbled rocks and other materials that a glacier carried in and then dropped to the ground when the ice melted sometime between 2.45 billion and 2.2 billion years ago. In the older rocks below these glacial deposits are detrital uraninite and pyrite, two minerals considered evidence for very low levels of atmospheric oxygen. Above the glacial layers sits a red sandstone containing hematite—a mineral that forms only under oxygen-rich skies. (Hematite has also been found at the landing site of the Mars rover Opportunity. This hematite is gray, however, because the grain size is larger.) The layering of these distinct rock types indicates that the Huronian glaciations occurred precisely when atmospheric oxygen levels first rose.

This apparent coincidence remained unexplained until recently: if we hypothesize that methane kept the ancient climate warm, then we can predict a global ice age at 2.3 billion years ago because it would have been a natural consequence of the rise of oxygen. Many of the methanogens and other anaerobic organisms that dominated the planet before the rise of oxygen would have either perished in this revolution or found themselves confined to increasingly restricted habitats.

Although this finale sounds as if it is the end of the methane story, that is not necessarily the case. Methane never again exerted a dominating effect on climate, but it could still have been an important influence at later times—during the late Proterozoic, for example, when some scientists suggest that the oceans froze over entirely during a series of so-called snowball Earth episodes [see "Snowball Earth," by Paul F. Hoffman and Daniel P. Schrag; SCIENTIFIC AMERICAN, January 2000].

Indeed, methane concentrations could have remained significantly higher than today's during much of the Proterozoic

Hazy Comparison

Saturn's moon Titan gets its characteristic orange glow from a dense layer of hydrocarbon particles that forms as sunlight destroys methane high in its atmosphere. Scientists have recently begun to think that a comparable haze cloaked Earth before 2.3 billion years ago. But fortunately for the planet's earliest inhabitants, the similarity stops there.

A chilling –179 degrees Celsius, Titan's atmosphere is dramatically colder than Earth's has ever been. On Earth an organic haze as thick as Titan's would have deflected enough sunlight to counteract the warming effect of methane—a potent greenhouse gas. The planet's surface would have frozen solid, thereby killing the single-celled microbes that created the methane in the first place.

Researchers speculate that Titan's haze grows thick because methane gas evaporates readily from an abundant ocean of liquid methane, nitrogen and ethane. Earth's ancient microbes released a mere puff of the gas by comparison, which helped to keep its haze layer relatively thin.

What the primordial Earth lacked in methane it made up for in carbon dioxide and liquid water—two ingredients that made possible the evolution of life. Because scientists have seen no sign of either compound on Titan, they conclude that life as we know it could not have evolved there. But that does not mean Saturn's largest moon cannot tell us something about biological evolution.

Much of the same chemistry that takes place in Titan's atmosphere probably also occurred on the young Earth. The European Space Agency plans to test that theory with its Huygens probe, which is scheduled to arrive at Saturn onboard NASA's Cassini spacecraft in July. If the probe enters Titan's atmosphere successfully next year, investigators will obtain the first direct evidence of what methane-induced smog is really like. Such observations could provide clues about how Earth maintained its delicate balance between the climate-cooling haze and the methane-dominated greenhouse that kept the planet habitable for well over a billion years. *—J.F.K.*

NASA/JPL-CALTECH

eon, which ended about 600 million years ago, if atmospheric oxygen had continued to be somewhat lower and the deep oceans were still anoxic and low in sulfate, a dissolved salt common in modern seawater. The rate at which methane escaped from the seas to the atmosphere could still have been up to 10 times as high as it is now, and the concentration of methane in the atmosphere could have been as high as 100 ppm. This scenario might explain why the Proterozoic remained ice-free for almost a billion and a half years despite the fact that the sun was still relatively dim. My colleagues and I have speculated that a second rise in atmospheric oxygen, or in dissolved sulfate, could conceivably have triggered the snowball Earth episodes as well—once again by decreasing the warming presence of methane.

Extraterrestrial Methane

AS COMPELLING AS this story of methanogens once ruling the world may sound, scientists are forced to be content with no direct evidence to back it up. Finding a rock that contains bubbles of ancient atmosphere would provide absolute proof, but such a revelation is unlikely. The best we can say is that the hypothesis is consistent with several indirect pieces of evidence—most notably, the low atmospheric CO_2 levels inferred from ancient soils and the timing of the first planet-encompassing ice age.

Although we may never be able to verify this hypothesis on Earth, we may be able to test it indirectly by observing Earth-like planets orbiting other stars. Both NASA and the European Space Agency are designing large space-based telescopes to search for Earth-size planets orbiting some 120 nearby stars. If such planets exist, these missions—NASA's Terrestrial Planet Finder and ESA's Darwin—should be able to scan their atmospheres for the presence of gases that would indicate the existence of life.

Oxygen at any appreciable abundance would almost certainly indicate biology comparable to that of modern Earth, provided that the planet was also endowed with the liquid water necessary for life. High levels of methane, too, would suggest some form of life. As far as we know, on planets with Earth-like surface temperatures only living organisms can produce methane at high levels. The latter discovery might be one of the best ways for scientists to gain a better understanding of what our own planet was like during the nascent stages of its history. SA

MORE TO EXPLORE

Greenhouse Warming by CH_4 in the Atmosphere of Early Earth. Alexander A. Pavlov, James F. Kasting, Lisa L. Brown, Kathy A. Rages and Richard Freedman in *Journal of Geophysical Research—Planets,* Vol. 105, No. E5, pages 11,981–11,990; May 2000.

Life and the Evolution of Earth's Atmosphere. James F. Kasting and Janet L. Siefert in *Science,* Vol. 296, pages 1066–1068; May 10, 2002.

Methane-Rich Proterozoic Atmosphere? Alexander A. Pavlov, Matthew T. Hurtgen, James F. Kasting and Michael A. Arthur in *Geology,* Vol. 31, No. 1, pages 87–90; January 2003.