

Pretty, but real? Colors denote concentrations of atmospheric methane on Mars in 2003 as reported by Mumma and colleagues.

PLANETARY SCIENCE

Could a Whiff of Methane Revive The Exploration of Mars?

The controversy over claimed detections of martian methane—a possible product of life on Mars—could be settled come August once the Curiosity rover arrives at the Red Planet

How many cows are there on Mars? That depends on which planetary scientist you're asking. Some would say there have been thousands of head of cattle, judging by how much methane three independent groups reported detecting in the atmosphere of Mars in 2003. Earthly cows belch the digestive gas all day long, so a bovine equivalent for Mars is a convenient, if playful, way to quantify martian methane. Whether the reported methane is from microbes eking out a living beneath the surface or from deep stirrings of the geologically moribund planet, no one can say. Either would excite scientists, but only martian biology could rejuvenate a troubled NASA Mars program.

Despite the playful units, planetary researchers are quite serious about their meth-

ane on Mars. "I'm shocked by these results," said planetary scientist Michael Mumma of NASA's Goddard Space Flight Center in Greenbelt, Maryland, when he first announced his team's methane detection at a meeting in 2004, but "our results are certain." The researchers reported that they had detected a few tens of parts per billion (ppb) by volume of martian methane. They found it by reading the squiggly lines of infrared spectra recorded by ground-based telescopes. Two other independent groups backed up Mumma with their own reported spectroscopic detections.

But some planetary scientists now see no credible signs that there ever was any methane on Mars. Last October, planetary scientist Kevin Zahnle of NASA's Ames Research Center at Moffett Field in California called

his invited seminar on the subject "Lack of Evidence for Animal Husbandry on Mars." Zahnle has never done spectroscopy of any sort. But he and more spectroscopically inclined colleagues have scrutinized Mumma's results, noting that the reported parts-per-billion detection relied on instruments looking through the 2000-times-more-abundant methane of Earth's atmosphere. Correcting for that earthly methane "is just really, really hard," Zahnle says. "I don't think they can possibly do it."

The right head count of martian livestock could have multibillion-dollar implications for the exploration of Mars. NASA's Mars science program took a severe hit in President Barack Obama's 2013 budget request this past February (*Science*, 24 February, p. 900). But once before, in the 1990s, hints of ancient martian life—that time in a meteorite from Mars—helped resuscitate NASA's Mars program. So within weeks after its arrival this August, NASA's rover Curiosity could again fan the flames of life on Mars if it detects uncontested martian methane.

Methane, methane everywhere?

Martian methane burst on the scene in March 2004 at a press conference in Paris (*Science*, 26 March 2004, p. 1953), and was soon followed by two more independent claims in a meeting and its press conference. All three research groups reported at least 10 ppb of methane in the atmosphere of Mars in 2003. That's just 10 cubic centimeters of methane dispersed in the thousand cubic meters of a 10-meter cube of thin martian air. The three claimed detections—all since published in leading peer-reviewed journals—are still often cited as reinforcing one another, implying some measure of consensus. But they have not fared equally well among experts.

All three reported detections rely on recognizing methane's signature in the sun's infrared radiation reflected from the surface of Mars. As solar radiation passes through the martian atmosphere, methane molecules—carbon atoms studded with four hydrogen atoms—absorb infrared energy at specific wavelengths. A spectrometer's optics break the reflected radiation into a rainbowlike spectrum in which scientists can recognize the narrow "lines" of absorption unique to methane.

First to announce the detection of methane was Vittorio Formisano of the Institute of Physics and Interplanetary Space in Rome and the orbiting Mars Express spectrometer

team. After the announcement at that Paris press conference, Formisano told *Science* that he and his team “have seen methane on Mars. A very little amount, but the result is clear.” The group’s paper appeared in the 3 December 2004 issue of *Science* (p. 1758), but its reported detection of 10 ppb averaged across Mars has fared the worst of the three claims.

Sushil Atreya, an atmospheric chemist at the University of Michigan, Ann Arbor, and second author on the Mars Express paper in *Science*, says the Mars Express result was not a true “detection.” The spectrometer’s ability to separate methane’s absorption lines from interfering lines, its spectral resolution, was not up to snuff, he says, adding, “I would put more stock in ground-based” results.

The two ground-based claims of martian methane in fact look somewhat better. At times working with colleagues, planetary astronomer Vladimir Krasnopolsky of the Catholic University of America in Washington, D.C., has used spectrometers mounted on large telescopes to search for methane. In three papers in *Icarus*, the first in 2004, Krasnopolsky reported methane detections.

But Mumma, who has published with Krasnopolsky and supervised him at Goddard, has his doubts. Krasnopolsky’s first two reported detections suffered from technical problems in processing the data, Mumma says. In a third paper, in the January 2012 issue of *Icarus*, Krasnopolsky reports detecting 10 ppb of methane over the Valles Marineris canyon region of Mars in 2006. Mumma calls the result “interesting,” although his own group’s observations a few weeks before and after Krasnopolsky’s found no detectable methane over Valles Marineris.

The Cadillac of data reductions

By all accounts, Mumma’s observations have fared the best. For one thing, Mumma is highly regarded in the planetary observing community. He has measured 10 different volatile compounds, including methane, spewing from 30 active comets. Mumma and his group are also seen as having most thoroughly accounted for the bugaboo of ground-based observers: Earth’s own methane. An absorption line from Earth’s methane should be 2000 times as strong as a line from 20 ppb of methane on Mars would be. (After all, Earth has actual belching cows.)

Mumma first reported detection of martian methane at the annual meeting of the Division for Planetary Science (DPS) in November 2004. In his talk, Mumma reported finding 86 ppb of methane using one absorption line and 66 ppb using another line. That rough agreement from two independent

absorption lines remains the backbone of the Goddard group’s defense of their numbers. “The methane is secure,” he said. At a press briefing later the same day, however, he mentioned a methane concentration of 250 ppb. Over the next year or two, Mumma continued to report readings as high as 700 ppb, Atreya recalls. But none of the numbers appeared in DPS abstracts because Mumma considered them still preliminary.

After almost 4 years of increasingly thorough processing of the raw data, including accounting for terrestrial methane, Mumma and colleagues published their 2003 observations in the 20 February 2009 issue of *Science* (p. 1041). The group reported much lower final values for the 2003 methane detections—20 to 45 ppb—along with a detection of 5 ppb from 2006. Methane was concentrated in the vicinity of Syrtis Major and Nili Fossae near the equator and varied in abundance from season to season and year to year.

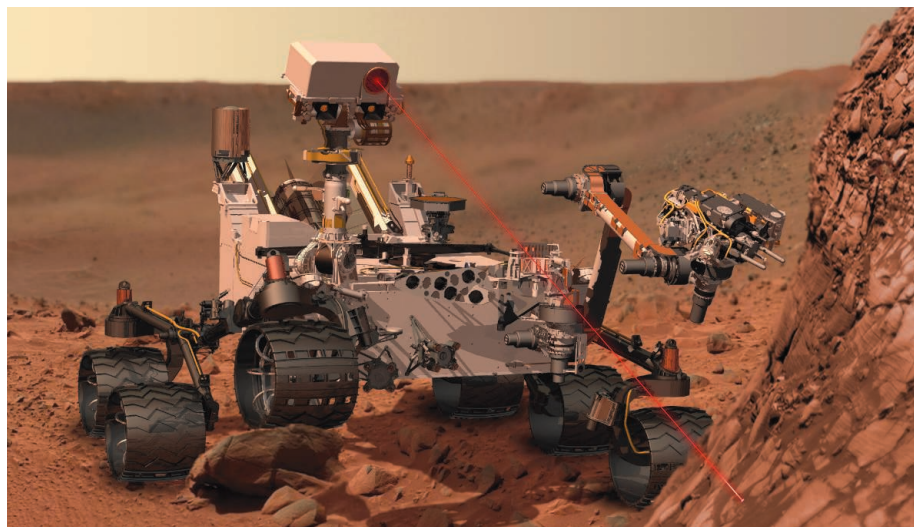
To Mumma’s group, that evanescent, plume-like behavior of methane suggested that shortly before the 2003 observations—and perhaps at other times—the planet had

the interference by observing Mars when it is moving toward or away from Earth. That’s when the Doppler effect shifts a given martian methane absorption line away from the same line created by terrestrial absorption, making the two lines distinguishable.

Mumma thinks that he and his co-authors—most of whom are at Goddard—have reliably accounted for any remaining methane interference using a sophisticated model of Earth’s atmosphere. The 20-person spectroscopy group he directs at Goddard is “a powerhouse in the world community,” he says. That view is widely shared. “Mumma has given [his data] about as good a look as can be,” says atmospheric chemist Paul Wennberg of the California Institute of Technology (Caltech) in Pasadena.

Not so fast

Zahnle wasn’t having any of it. With 30 years of experience modeling the atmospheric chemistry of the planets, he “just couldn’t imagine anyone taking [methane on Mars] seriously,” he says. “Methane doesn’t behave like this. It was such an obvious joke.



Methane sniffer. Before the Curiosity rover samples any rocks with its arm-mounted drill or rock-zapping laser, it will test the air for signs of methane, a possible product of any martian life.

been spewing a couple of tons of methane an hour from the ground. The methane might have been microbial, trapped kilometers beneath the frozen crust and released occasionally through crustal cracks. Or it could have been geological, escaping from volcanic or geothermal vents. No one can say what the source would have been, and no one has reported detecting any methane since 2006.

Key to determining whether the martian methane plumes were real is the procedure for removing the spectral signal of Earth’s methane. Ground-based observers avoid most of

I was upset that the community wasn’t taking an interest” in critically evaluating detection claims. Instead, methane claims were propelling a proposed orbital mission to Mars, NASA’s Trace Gas Observer, on its way to launching in 2016.

So Zahnle looked at methane on Mars the best way he knew how: from a chemical perspective. He concluded that the proposed scenario—repeated injections of methane into the atmosphere, followed by the methane’s rapid destruction—would wreak havoc on the composition of the martian atmosphere.

As Zahnle lays out in an April 2011 *Icarus* paper, destroying that much methane that quickly would consume the atmosphere's meager endowment of oxygen in 7000 years. That might not happen if exotic processes had been overlooked—say, chemical oxidizing agents generated on the dust of self-electrifying dust devils.

But that doesn't seem to be the case, Zahnle says. The standard model of how solar energy creates and destroys chemical compounds already neatly explains the trace gas composition of the martian atmosphere without invoking any such hidden methane-busters. And nonphotochemical means of removing methane, such as adsorbing it onto soil, don't work either if theory, lab experimentation, and the trace gas composition of Mars are any indication, he says. Even microbes feeding on the methane probably couldn't cause the proposed disappearing plumes, Zahnle says. That's because the martian atmosphere abounds in carbon monoxide—a molecule that microorganisms with anything like earthly metabolisms would finish off before starting to consume methane.

Zahnle concludes that there is no support for claims that martian methane plumes were popping up repeatedly almost a decade ago. However, he can't exclude the possibility that a single plume appeared in 2003. "If it's one time in 100 years, it's not a problem," he says. That relieves atmospheric chemists' great unease with the idea of methane coming and going on Mars. "The photochemical argument Kevin made seems to be pretty solid," Atreya says.

About that spectroscopy

Next, Zahnle looked for possible problems in Mumma's spectroscopic methane detection. As an atmospheric chemist, he needed lots of help. So he brought in Richard Freedman of Ames, an astrophysicist and stellar spectroscopist, and David Catling of the University of Washington, Seattle, "somebody who knows something about Mars."

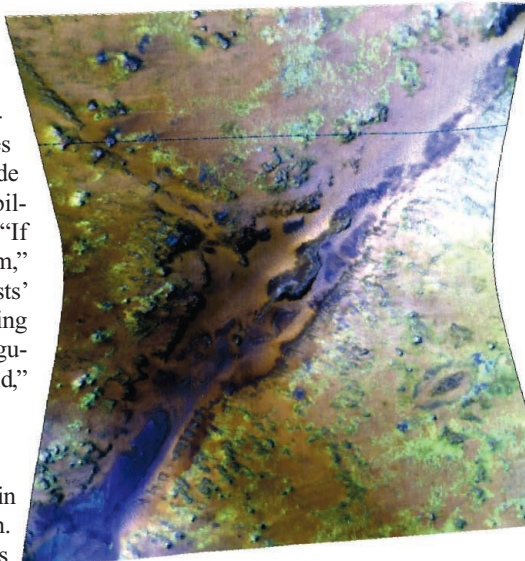
The trio found several possible problems with both the space- and ground-based spectroscopy, as they reported in the *Icarus* paper. But the focus of their criticism became the two absorption lines at the core of Mumma and colleagues' reported detections. Mumma, they note, is relying on only two methane lines and can see only one of them on any given observing night.

More worrisome, they say, is their suspicion that the same Doppler shift that conveniently brings Mars methane lines into view, by moving them away from Earth's methane lines, also moves a Mars line to where

a minor Earth methane line can impersonate the Mars line. The Mumma group has never seen methane when Mars is moving away from Earth; it is only seen when Mars is moving toward Earth, and the lines are shifted toward the blue end of the spectrum. Zahnle and colleagues suggest that in such a blue shift, the line of methane that contains the heavy carbon-13 isotope comes into coincidence with the martian line of normal methane. The heavy-carbon methane line is about 25 times as strong as the line of martian methane at 20 ppb would be. So the Earth line, the group contends, could appear to signify abundant methane on Mars.

"I'm no spectroscopist, but it's going to be challenging to correct for that," Zahnle says. "The point is not to slam Mike Mumma. This is just really, really hard; it's ridiculously difficult."

Mumma disagrees. "I respect Kevin as a colleague," he says, but "there are so many



Methanogenic? Water-altered Nili Fossae (color-coded by mineral) may have gushed methane in 2003.

errors" in the Zahnle *et al.* paper, some of which "were egregious." He points to three sorts of consistent behavior in the spectroscopic data that support martian methane. One involves the nonappearance of the terrestrial carbon-13 methane line when, as he sees it, Zahnle's reasoning would have it there. "We've got carbon-13 methane modeled correctly," Mumma says.

All this debate, which has not gotten much of a public airing, has left the larger planetary community a bit adrift. With 50 years working in the Mars community, geologist Michael Carr of the U.S. Geological Survey in Menlo Park, California, finds methane on Mars "such an iffy thing." John Mustard of Brown Univer-

sity does spectroscopy of the martian surface from orbiters. "It looks really problematic for Mumma's [detections]," he says. All the variability "just doesn't make sense. I'm thinking it's not there."

David Crisp of NASA's Jet Propulsion Laboratory (JPL) in Pasadena, California, does atmospheric spectroscopy. "My intuition is there's methane there," he says, "but it's not clear [Mumma] is seeing time and spatial variations." Interfering atmospheric dust is just too variable on Mars, he says. "If anything, I would trust the detection of methane more than the [reported] absolute amount," says Mark Allen of Caltech, who was the principal investigator of the now-canceled Trace Gas Orbiter mission. Mumma "is really doing differences of [two] large numbers to get a small number," Allen says, always a tricky bit of arithmetic.

Last chance?

Confirming such contentious claims will require getting up close and personal with Mars. The Trace Gas Orbiter was going to carry a capable spectrometer that "could detect three cows on Mars," Allen says. But NASA killed the mission when it restarted its Mars program in the wake of the Obama Administration's lowered budget request. Next up is NASA's Curiosity rover, arriving at Mars on 6 August. It carries a different sort of spectrometer, the Tunable Laser Spectrometer (TLS). It has two lasers whose beams bounce back and forth 81 times through a sample cell filled with martian atmosphere. The lasers scan across infrared wavelengths in which methane has not one or two but three absorption lines that form a distinctive fingerprint for methane. "It's a very simple, direct, and unambiguous measurement," says TLS developer Christopher Webster of JPL.

TLS will also be extremely sensitive. Its first quick measurement, scheduled for the first few weeks of the mission, should be able to detect as little as 1 ppb of methane. Mumma calculated that the 2003 release of methane would have amounted to 6 ppb once it spread around the planet. Although Mumma sees his observations as suggesting that methane on Mars has a lifetime of a few years, atmospheric chemists still think martian methane would last several centuries. If they are right, almost all of 6-ppb methane should still be there. And even if it is destroyed faster, when TLS takes a longer look at atmospheric samples, it will be able to detect 50 to 100 parts per trillion of methane, according to Webster. If methane really is long-lived on Mars, Zahnle says, Curiosity "is going to crush this."

—RICHARD A. KERR