SECRETS OF THE MARTIAN SOIL

For 30 years scientists have believed that there are no organic molecules in the martian soil. Will NASA's Phoenix probe prove them right or wrong, asks **Corinna Wu**.

L. GEORGIA/CORBIS

In the summer of 1976, humanity first got its surrogate hands on the soil of another planet. Two Viking probes scooped up samples from their landing sites and fed them into an array of instruments carried from Earth for the purpose. Perhaps the most technically sophisticated of those instruments were the gas chromatograph-mass spectrometers (GC-MS) designed to detect evidence of organic compounds in the soil. After months of operation they had found none at all. The Viking missions were accepted almost unanimously as showing that Mars was a sterile planet, and the GC-MS data were a crucial part of the evidence.

This month, another mass spectrometer is on its way to Mars. NASA's Phoenix mission was launched on 4 August, and if all goes according to plan, it will touch down 1,200 kilometres from the north pole of Mars on 28 May 2008. Phoenix is essentially a sister ship to the Mars Polar Lander (MPL) lost in December 1999 — hence the imagery of its name — and the first in NASA's new line of low-cost 'Scout' missions. It is a Buick to the Bentleys of the Viking missions, but some chemists are all but certain that it will find evidence for organic chemicals close to the martian surface even though the better equipped Vikings found none. If it does it will raise the hopes of those who cling tenaciously to the idea that there might be evidence for past, or even present, life somewhere on that frigid, radiation-battered and deeply inhospitable planet.

The Viking landers each carried a suite of three experiments designed to detect microorganisms in the dust and sand that, along with pumelled rocks, made up the surface at the landing sites. Their results were inconclusive. When watered and fed nutrients, the martian soil gave off gases in ways that had not been expected, some of which might be consistent with biological activity. But the GC-MS data were unequivocal.

The GC-MS is a workhorse lab instrument used to pick out the various components in mixtures of organic molecules. It works by first passing samples through a thin capillary column — the chromatograph. Small molecules move through quickly; heavier ones more slowly. When the compounds emerge from the column, sorted by size, they pass through the mass spectrometer, which measures the mass either of whole molecules or their fragments.

The Viking GC-MS team was led by Klaus Biemann, a chemistry professor at Massachusetts Institute of Technology (MIT), Cambridge, and a pioneer in the development of such instruments. Biemann was not a space scientist; his work concentrated on determining the structure of protein fragments — laying the foundations for today's 'proteomics'. He agreed to work on the Viking instrument only as an act of "scientific charity", he recalls. "I said if it needs to be done, it might as well be done well." And it was.

At the time, the GC-MS Biemann had in his laboratory was the size of a room. The instrument needed to analyse the compounds that might be given off when martian soil samples were heated had to fit into a box just thirty centimetres long on each side. Biemann's team produced a fully automated system that met the constraints in size and available power and yet was still sensitive to compounds present only at a parts-per-billion level. "To get two machines a hundred million miles out and both of them working is just a marvel of engineering," says Steven Benner of the Foundation for Applied Molecular Evolution in Gainesville, Florida, who has worked on chemical approaches to various astrobiological questions.

Organic ball game

Biemann's team expected to have organic compounds to analyse when its instrument reached Mars. Mars's cratered face showed it had been bombarded by meteorites, and by the 1960s some meteorites were known to contain organic compounds. So organic compounds were to be expected, even if Mars itself had produced none of them. "You should be sitting in a sea of this stuff," says Benner. Indeed, according to Benner some Viking developers worried that the GC-MS would be swamped by the sheer amount of organics.

Yet the only things that came out of the heated soil samples on Mars were water and carbon dioxide, which were taken to have been either physically trapped in soil particles or released from inorganic minerals. Although the experiments did see some organic compounds, they were those that had been used to clean the equipment back on Earth, and had already been detected when the instrument was tested in deep space during the probes' transit to Mars.

With no evidence for organic molecules in the soil, the results from the life detection

©2007 Nature Publishing Group

experiments were to some extent rendered moot. "That's the ball game," said Jerry Soffen, Viking's project scientist, at the time. "No organics on Mars, no life on Mars." The activity seen in the samples was subsequently interpreted as being due to chemistry, not biology. Bombardment by ultraviolet light would make the soil rich in oxidants such as peroxides, and also lead to some unusual — on Earth — compounds such as carbon suboxide (C_3O_2); scientists proposed various ways that reactions with such chemicals could have provided the results seen by the life detection experiments. Only one of the investigators, Gil Levin, continued to think that what they had seen was best explained by biology.

In 2000, though, Benner, then at the University of Florida, Gainesville, suggested that Mars might indeed have contained some organic material, but that Viking could have missed it. He proposed that the organics might take the form of mellitic acid, which is seen when the mess of polymerized carbon that makes up much of the organic component in meteorites is not completely oxidized. "It is readily formed under the oxidizing conditions you'd expect to find on Mars," Benner says. "It is quite stable to further oxidation, and it's also refractory — it doesn't dissolve in anything. And when you heat it, it doesn't give off anything volatile. So they could have been sitting in a sea of this stuff and not seen it." Benner's study estimated that this process could have generated 2 kilograms of mellitic acid per square metre of martian surface over the course of 3 billion years[1]. Unfortunately, it takes a lot of heat to break down mellitic acid — and when it breaks down, the primary product is benzene, says Benner, which was one of the solvents that had been used to clean the instrument. If the Viking experiments had heated their samples to 600 °C instead of 500 °C, they might have picked up traces of something distinctive. But they didn't reach 600 °C .

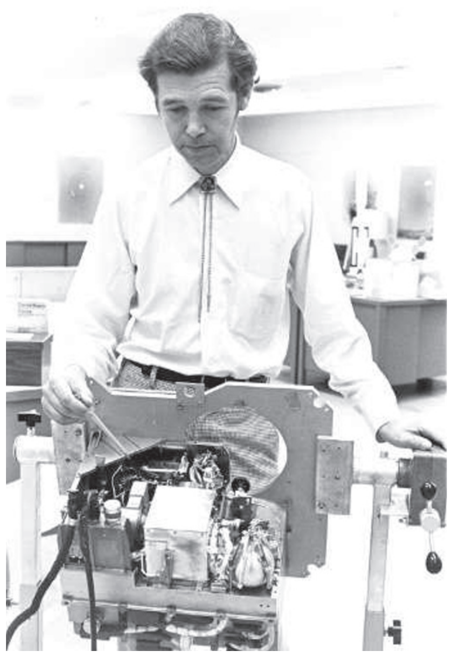
"That's the ball game. No organics on Mars, no life on Mars."
— Jerry Soffen

In October 2006, a team including chemist Rafael Navarro-González of the National Autonomous University of Mexico's Institute of Nuclear Science, Mexico City, and planetary scientist Christopher McKay of NASA's Ames Research Center in Mountain View, California, reported that the experiment might not have picked up some other types of organic compound in the soil[2].

Navarro-González was inspired to revisit the Viking tests for organic molecules after the Opportunity rover discovered jarosite, a hydrated iron sulphate that forms in the presence of water, on Mars in 2004. Studying jarosite-containing soils in the Rio Tinto area of Spain, he found that getting organic material out with chemical approaches was relatively easy — but getting it out just by heating was not. "When I repeated the Viking experiments," he says, "I was surprised to see that despite the huge amount of organic matter present, there was virtually no detection of organics in the sediments. This was quite strange."

Independently, McKay had been doing research on soils from the Atacama desert in Chile, and had also started to suspect that the Viking experiments weren't telling the whole story. Alison Skelley, a graduate student at the University of California, Berkeley, had asked McKay to review a paper on a device she had developed for detecting amino acids in soil[3]. McKay found the paper striking, noting that "it found that there were a thousand times more amino acids released by chemical extraction than pyrolysis" — the heating method used by the Viking experiments. Then McKay says, "Within a month, Rafael told me about his puzzling result with the jarosite. That's when I suggested that we ought to see if this effect was widespread."

In addition to the Rio Tinto sediments and Atacama desert samples, they tested soil samples from other inhospitable and vaguely martian environments — the Dry Valleys of Antarctica and the Libyan desert. Chemical extractions revealed low levels of organic compounds — between 20 and 90 micrograms of carbon per gram of soil, in Antarctica for example. But heating samples from most of the sites to 500 °C did not produce organic volatiles that their GC-MS setup — a combination of several commercially available instruments — could detect. Only at 750 °C did they start to get a signal from more than half the samples — a temperature the Viking systems were not designed to reach.


H.-P. BIEMANN

Klaus Biemann with a copy of the Viking GC-MS in 1975, the day before the mission landed.

Heated debate

Navarro-González and McKay think that during the heating step of the Viking experiment, any organics given off at moderate temperatures would have been turned into CO_2 before they reached the GC-MS, thanks to catalytic iron compounds in the martian soil. "We suggest that a small portion [of the carbon dioxide seen by the Viking experiments] could have resulted from the oxidation of organics," says Navarro-González. "Even if it's just a small percentage, this could mean levels of organics on the surface of Mars a thousand times higher than expected."

Before publication they sent the paper to Biemann for his feedback and "he was completely upset," says Navarro-González. "But he did bring up some interesting points that we had to resolve." Navarro-González says they sent further versions of parts of the paper; Biemann says he received no satisfactory answer to his questions. In the finished article, the authors thank Biemann "for comments on an earlier version of the manuscript".

Biemann, who denies he was upset, says he heard that the Navarro-González paper had finally been published only after his daughter read a story about it in the *Wall Street Journal*. Being thanked in the paper, he feels, implies that


R. NAVARRO-GONZALEZ
VIKING PROJECT/M. DALE-BANNISTER, WASHINGTON UNIV., ST. LOUIS/NASA

Spot the difference: the Atacama Desert in Chile (left) shares many features with the surface of Mars.

©2007 Nature Publishing Group

he agreed with their second version, which he says he never saw. And so in a strongly worded critique of the revisionist work, Biemann argued that the experimental setup used by the Navarro-González and McKay team was a thousand times less sensitive than the Viking device[4]. "To say in their experiment that they don't find things at 500 °C that they find at 750 °C doesn't mean anything," he says. If their instrumentation had corresponded more closely in its performance to the carefully-tailored Viking GC-MS, it would have been easily sensitive enough to detect what was going on at 500 °C, he says.

Biemann thinks that a misplaced zeal to find life on Mars has driven scientists, including the Navarro-González team, to try and prove the GC-MS results wrong; they want to "get rid of that obstacle", he says. McKay, for his part, expresses frustration over what he feels is a misunderstanding of the thrust of their paper. "If I were rewriting the paper, I would emphasize that the GC-MS operated flawlessly. The problem is the pyrolysis release of organics." He says the debate over the Viking results has been so narrowly focused on the GC-MS that the pyrolysis step has been ignored.

Even accepting the group's analysis that there might be some organic matter in the soil, "it's not a rich soil by any stretch of the imagination", says McKay. "When we say [the organic fraction] could be as high as a part per million, it's important to note that it could also still be zero." What's important, he says, is to take the new work into account on future missions.

"This could mean levels of organics on the surface of Mars a thousand times higher than expected." — Rafael Navarro-González

Indeed, the scientists in charge of the instruments on NASA's Phoenix lander have paid heed. The primary goal of the mission is to characterize ice and minerals in the martian soil, but the lander will also have the ability to detect organics. The Thermal and Evolved Gas Analyzer (TEGA), originally developed for MPL, heats soil samples at a constant rate, measuring changes in the rate of warming so as to detect phase changes — when things melt or evaporate they can absorb heat without changing temperature. But Phoenix's TEGA, unlike that on MPL, also boasts a small mass spectrometer which will be used on the output from samples heated as high as 1,000 °C — twice the temperature of Viking's ovens, and hot enough to decompose the most refractory compounds.

"If we don't see organic compounds, we will have at least answered the question that it's not because they are of a refractory nature," says William Boynton of the University of Arizona in Tucson, who is lead scientist for the TEGA

Take off: Phoenix begins its journey to Mars.

NASA

project. "It will also mean that this particular environment was not suitable for protecting organic molecules from being destroyed."

The search for life continues

Benner is more or less convinced that the Phoenix ovens will find the mellitic acid and associated salts he has predicted — which would make it third time lucky for him. He originally hoped to see evidence for the compounds from Raman spectrometers that would have been carried on the Spirit and Opportunity rovers, but a tight schedule saw the necessary lasers cut from the payload. The Beagle 2 mission should also have measured organics in the soil, and had a cunningly contrived device that would have let it take samples from underneath rocks, where the ultraviolet-induced oxidation might not be so bad. But contact with the spacecraft was never established after it left its mothership, the European Space Agency's (ESA) Mars Express.

If TEGA does detect organics that reveal themselves only at high temperatures, the chances are strong that they will be from meteorites, not native to Mars. But their persistence would show that the soil was not quite as powerful an oxidant as the post-Viking consensus supposed, which might offer hope that in some places native organic matter might be preserved. What's more, there is a possibility that the icy soil on which Phoenix is hoping to land might be such a place. If the source of the ice — the presence of which was confirmed by the gamma-ray spectrometer that Boynton flew on NASA's Mars Odyssey orbiter — is ground water that has welled up and then frozen, it might contain organics derived from reservoirs that are below the reach of the soil's harsh oxidizing properties and subsequently protected by the ice, Benner suggests. If such organics were detected it would not necessarily prove the Viking results wrong — it would just show that different environments in different parts of Mars offer different levels of comfort for such molecules.

Navarro-González and McKay are both working on the Sample Analysis at Mars (SAM) package that will be part of NASA's Mars Science Laboratory, scheduled for launch in 2009. SAM will contain the first GC-MS since Viking — Phoenix has no chromatograph — as well as a laser spectrometer, and it will use chemical extraction as well as pyrolysis, allowing the two techniques to be compared and to be used in a complementary way.

In the longer run, some scientists are wondering if there are robust ways to tell whether any organics found are the product of living beings, but they recognize it will be a hard problem. On Earth, it is possible to distinguish life's organic products by the ratio of different carbon isotopes they contain, and SAM should be able to do this — Phoenix might, too.

But scientists do not expect that interpretation of any such results from Mars would be straightforward, since non-biological processes can also have isotopic signatures. An instrument on the ESA's ExoMars mission, slated for launch in 2013, will have the capacity to measure the 'handedness' of any organic molecules it finds. On Earth, life uses left-handed amino acids and right-handed sugars, and samples that reflected a similar prejudice might be seen as good evidence of a living source. But if the molecules have been around for millions of years, they may well have spontaneously rearranged themselves into a random mess, and thus become indistinguishable from molecules created through non-biological processes.

Before that next level of uncertainty and debate can be reached, though, evidence is needed that there are organic molecules out there to study. If Phoenix, unlike its ill-fated sibling, survives and sends back data, it will at least have moved the debate on. "It's more important to be looking forward to future missions than to be stuck on a debate about Viking," McKay says. "If we get results from Phoenix and from SAM, then people will have something new to argue about." Benner, meanwhile, just looks forward to what he sees as the inevitable surprises: "Every time we go back, it's like going for the first time." ■

Corinna Wu is a freelance writer in Washington DC.

1. Benner, S. A., Devine, K. G., Matveeva, L. N. & Powell, D. H. *Proc. Natl. Acad. Sci. USA* **97,** 2425–2430 (2000).
2. Navarro-González, R. *et al. Proc. Natl. Acad. Sci. USA* **103,** 16089–16094 (2006).
3. Skelley, A. M. *et al. Proc. Natl. Acad. Sci. USA* **102,** 1041–1046 (2005).
4 .Biemann, K. *Proc. Natl. Acad. Sci. USA* **104,** 10310–10313 (2007).

©2007 Nature Publishing Group