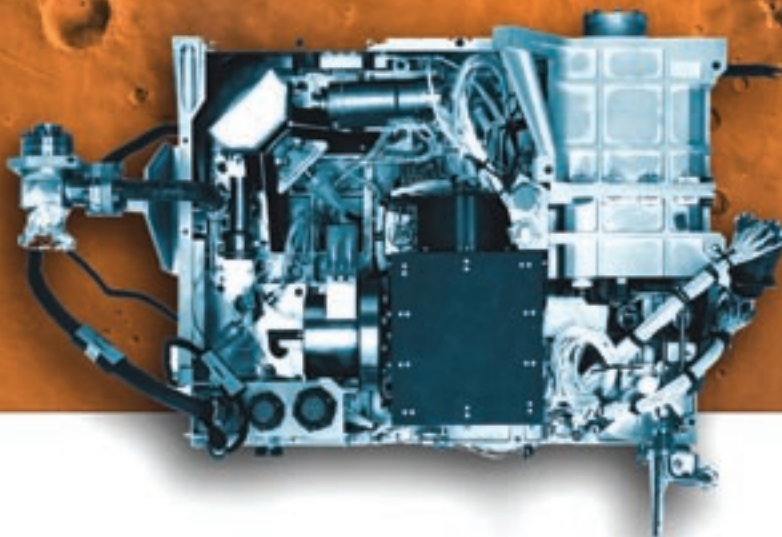


The VIKING GC/MS and the search for ORGANICS on MARS

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hirty-one years have gone by, but researchers still aren't done talking about the two GC/MS instruments that were sent to Mars in 1976. In the summer and early fall of that year, NASA landed Viking 1 and 2 on the red, dusty planet. The GC/MS systems, ensconced in the spacecraft with other kinds of instruments, carried out a series of experiments to get a detailed look, for the first time ever, at the conditions on another planet.

Viking 1 and 2 landed in the northern hemisphere on opposite sides of Mars, at Chryse Planitia and Utopia Planitia. The spacecraft each consisted of an orbiter and a lander. The identical suites of instruments on the landers gathered high-resolution images of the Martian surface, characterized the structure and composition of the atmosphere and surface, and conducted soil tests for organic material and signs of life.

**The instrument and mission
of the 1970s continue to influ-
ence scientific inquiry and
spark lively discourse.**

Although the detection of life and the search for organic material were meant to be separate experiments, they've become inextricably linked in people's minds. The life-detection tests gave conflicting results—only one of the three biological experiments yielded a seemingly positive outcome. Scientists weren't sure what to conclude. However, the test for organic material, carried out by the GC/MS on each lander, showed no signs of organics around the landing sites of the Viking spacecraft. The two GC/MS instruments saw only CO₂ and water (1).

After considering the results from both the biological and organic experiments, scientists involved in the Viking mission concluded that it was inconceivable to have a life-form without an organic counterpart—thus, there wasn't life on Mars. The vague results from the life-detection experiments were ascribed to chemical, not biological, phenomena. However,

some scientists haven't been satisfied with the conclusion and have questioned the ability of the Viking GC/MS to detect organic material. The questioning finally snowballed this year into a head-on confrontation.

Questioning the Viking GC/MS

In 2000 and 2001, different groups of scientists published papers that suggested that the GC/MS setups couldn't have detected highly cross-linked organics (kerogens) or low numbers of bacteria (2, 3). In 2006, Rafael Navarro-González, Christopher McKay, and colleagues at Ciudad Universitaria (Mexico), Université Paris (France), Instituto Nacional de Técnica Aeroespacial (Spain), and the NASA Ames Research Center published a paper in *Proceedings of the National Academy of Sciences U.S.A. (PNAS)*. The paper asserted that the Viking GC/MS instrument lacked the detection sensitivity to catch low levels of organic material in Martian soil (4). In their abstract, Navarro-González and colleagues stated that the pyrolysis-based Viking GC/MS "may be blind to low levels of organics on Mars."

The paper provoked a sharply worded commentary a few months later in the same journal by Klaus Biemann, the Massachusetts Institute of Technology professor who led the design and development of the Viking GC/MS instrument and experiment (5; box on p 7251). Biemann hadn't responded to earlier critiques of the experiment, such as the paper that suggested the instrument couldn't detect salts of mellitic acid, the nonvolatile oxidation products of kerogens (2). Biemann notes that the GC/MS would have seen phthalic anhydride and acetone, derived from two other oxidation products of kerogens. As for the paper that stated the GC/MS couldn't see low numbers of bacteria (3), it "just confirmed that we could not detect microorganisms, which the instrument was never intended to do," says Biemann.

But after publication of the paper by Navarro-González and colleagues, Biemann felt obliged to defend the experiment he and his team had carried out more than three decades ago. In addition to taking issue with the science in that paper, Biemann worried that the acknowledgment of thanks to him for commenting on a version of the unpublished manuscript gave the impression that he endorsed the authors' findings.

Experts in mass spectrometry and Mars research supported Biemann's decision to respond. None of those who were contacted by *Analytical Chemistry* found the arguments made by Navarro-González and colleagues in their paper to be compel-



A model of the Viking lander in which the GC/MS was installed.

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ling enough to throw the data from the Viking GC/MS into doubt. "I would take Biemann's side that his instrument did what it was asked to do. He's a very smart guy, and the instrument had a lot of fine engineering," says Robert Cotter at the Johns Hopkins School of Medicine. The instrument "worked beautifully," says David Des Marais of NASA Ames Research Center. "Anyone claiming that the instrument didn't work as planned

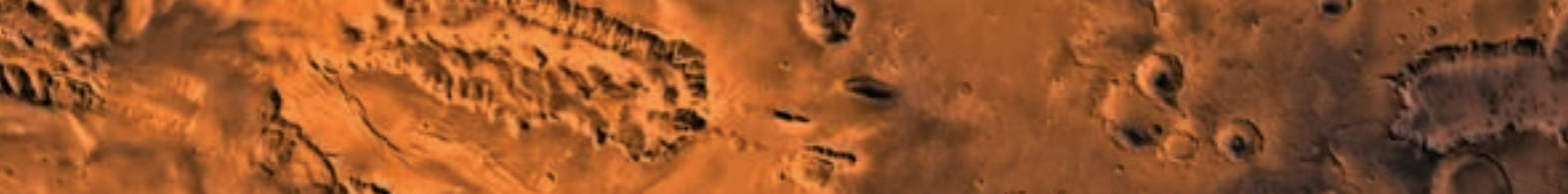
is wrong—that's not an accurate recapitulation."

"The Viking experiment was a huge success. It just didn't find organics. It also sampled the atmosphere and got just beautiful atmospheric measurements," says Paul Mahaffy of NASA Goddard Space Flight Center. When unusual meteorites (known as the SNC meteorites) were discovered in places such as Antarctica, India, and Egypt, "it really was the comparison between the gases released from glassy inclusions in those meteorites with the Viking atmospheric measurements that gave an incredible match and led everybody to conclude these meteorites were from Mars," points out Mahaffy.

The data from the Viking instruments helped scientists surmise that the surface of Mars was covered in an oxidizing soil. The oxidizing soil was probably created by the continuous bombardment of UV rays from the sun (Mars has a thin atmosphere and lacks an ozone layer) and strong winds, which make it difficult for any organic material to survive in the top few centimeters of soil.

Some experts say there are whispers in the space science community that funding for the search for life on Mars will be cut off because of the Viking results. But they point out that the accumulating evidence since the Viking mission for water on Mars gives NASA an excellent reason for returning to the planet for further exploration.

"The case for going back to Mars and looking hard at the chemistry of the volatile matter and searching for evidence for prebiotic or even biotic products is strong and very interesting," says John Hayes of Woods Hole Oceanographic Institution and a former student of Biemann's who played a role in selecting the GC column. "But nobody should be trying to strengthen the case by asserting that the Viking [GC/MS] actually missed organics. If they want to say Viking landers went to the wrong spots or the Viking robotic arm didn't dig deep enough for samples, that would be fine. But to say that the [GC/MS] instruments didn't work, I don't think that could be sustained."



In fact, Biemann says, the twin instruments operated so well that once they started to run on Mars, they picked up traces of the solvents that were used to clean them on Earth before they were packaged onto the spacecraft. The instruments had a detection sensitivity in the parts-per-billion range for organics with more than two carbons and in the parts-per-million range for organics with one or two carbons.

And finally, the Viking GC/MS wasn't meant for life detection. "The thing that most gets me annoyed is that people think we were looking for life," says Biemann. "That confusion came up even in the press conference during the Viking mission. In our *Science* paper of 1976 (6), in footnote 19, we calculated that we would need 1 million microorganisms per gram of soil to be able to detect the organic material that they represent. And still people say that we couldn't have

detected microorganisms—of course we couldn't because we weren't looking for them! In fact, if NASA had asked me to fly an experiment for life detection, I would have said, 'Go to someone else.'"

Lost in transmission

When contacted by *Analytical Chemistry*, the senior author of the Navarro-González et al. paper, McKay, said, "I think we did a bad job in writing our paper because it's come across as a criticism of the GC/MS. In fact, it's not. We believe that the GC/MS operated flawlessly, exactly as intended and exactly as it was built."

McKay says the point he and his coauthors wanted to make was that the extraction step used to pull organics out of the Viking GC/MS samples—a pyrolysis step—needs closer scrutiny.

Design of the Viking GC/MS

Experts say the Viking GC/MS was a masterpiece. The members of the GC/MS team "did all kinds of things that were utterly sensible but, until then, unprecedented," says Hayes. "The engineering that went into the instrument was just gorgeous." The engineering and construction of the instrument have been described in great detail (8).

In the 1970s, the GC/MS was a state-of-the-art instrument that was gaining traction in analytical chemistry. The Viking GC/MS "was revolutionary in that it took a level of analytical capability which was pretty close to the state of the art in a terrestrial laboratory and made it so robust that it could actually be loaded onto a spacecraft, sterilized, shipped at hard vacuum for 1½ years, landed on the surface of a planet, and work," says Hayes. "Nowadays, people say '[the] GC/MS works,' right? You buy one, plug it in, and, although it's not idiotproof, it's a pretty conventional instrument." In the days when Biemann and colleagues were developing the concept of gas chromatography/mass spectrometry, it was novel and technically challenging. Extraordinary care went into various parameters, such as what was injected into the instrument and the sizes of loads placed on the vacuum pumps. The setup for a GC/MS could take up an entire room.

The Viking instrument consisted of three sample ovens in which pyrolysis took place. Each oven could be heated to 50, 200, 350, or 500 °C in 1–8 seconds. The sample ovens were connected to the GC by valves. Any volatile materials that came off the samples in the heated ovens were swept into the GC. The GC contained a special liquid-modified organic adsorbent called Tenax as the stationary phase that was capable of resolving nanogram quantities of organics in a millionfold excess of water and CO₂ (9). Past the GC sat an effluent divider that protected the mass spectrometer from excessive gas loads and a palladium separator that removed the H₂ carrier gas.

According to experts, the palladium separator was one of the most elegant pieces of engineering. The carrier gas had to be removed from the sample before it entered the magnetic-sector MS. A tiny ion pump was packaged with the MS, but it couldn't do the work of the huge vacuum pumps that were readily available in terrestrial laboratories to remove the carrier gas. The palladium separator was designed so that the H₂ could dissolve into it but all the other remaining gases would continue on to the MS. On Earth, the hydrogen diffuses through the palladium and burns when it comes into contact with atmospheric oxygen. On Mars, there isn't any atmospheric oxygen. So Biemann and colleagues incorporated an electrochemical cell as the external oxidant.

"A little tank about the size of a baseball held enough H₂ for all the GC/MS experiments," says Ronald Hites. "The whole instrument fit into a box roughly the size of two shoeboxes side by side. You could carry it around in one hand. The lander had to supply power to all the instruments on board, and the way the lander supplied power was with two little nuclear generators."

Analytical chemists rave about the robustness of the 1976 instrument. It operated remotely 300 million miles away from Earth. It withstood huge variations in temperature, from the heat sterilization process to kill off all terrestrial microorganisms before launch to the low temperatures on Mars. The instrument was pumped down in January 1975 when it was put together at the Jet Propulsion Laboratory. It was then flown to a laboratory in Denver, Colo., to be installed inside the Viking lander. Once mounted into the lander, the GC/MS was flown to the Kennedy Space Center in Florida in June 1975. Viking 1 was launched in August 1975, and Viking 2 followed a month later, and the two spacecraft flew 10 months to get to Mars. In July and September 1976, the landers touched down on the surface of Mars. The GC/MS in each lander powered up, turned on, and worked.



tiny. In their opinion, pyrolysis does a poor job of removing low levels of organics, especially highly cross-linked, refractory ones from iron-rich soils (Martian soils are iron-rich, hence the rust-red color of the planet). They believe that liquid-based chemical extractions are the way to go.

"We have never criticized the quality of Biemann's work," says Navarro-González. "We only raised two limitations of the [pyrolysis] technique in our paper." The two limitations were that 500 °C wasn't hot enough for pyrolysis to extract low levels of organics from soil and that the oxidative iron in the Martian soil completely converted any low levels of organic materials into CO₂, helping the organics elude detection. The authors think their data indicated that the pyrolysis of iron-rich soils destroyed organics and reduced their concentrations by factors of 100–1000.

Pyrolysis is a popular method for quickly and easily extracting organic matter from soil. Experts say that NASA likes it, because it's a relatively cheap method and has already been tested on Mars by the Viking GC/MS systems. A GC/MS is being developed by a team led by Mahaffy for the Mars Science

There has been unwarranted criticism of the GC/MS over the years by researchers with an agenda of pushing for biological interpretations of the results from the Viking mission.

Lab (MSL) mission (box on p 7255), and Navarro-González and McKay are part of Mahaffy's team. "The original proposal had both pyrolysis and chemical extraction, but [NASA] headquarters wanted to drop the chemical extraction," says McKay. "Their argument was, 'Why do we need two methods? Pyrolysis is cheaper and more comparable to the Viking [setup] so let's just use that, drop chemical extractions, and save money.'"

The MSL mission is currently in the midst of a budget crisis, so McKay is worried that the liquid extraction will be cut. He is concerned that if pyrolysis is relied on as the sole extraction method, sophisticated and expensive analytical instrumentation such as a GC/MS won't detect trace levels of organic materials.

McKay feels the point he and his coauthors were trying to make in their *PNAS* paper got lost because they did a poor job of crystallizing their conclusions. "[Klaus] is a smart guy, and I respect his opinion. I think many of the points he raised [in his commentary] are correct," says McKay. "But none of the points that he raised go to the central argument that we're making. I think it's a failure of communication [on our part] because he doesn't come right out and say, 'Pyrolysis worked fine on Mars'. What he says is that the GC/MS worked fine on Mars. But we never really were debating that. To be fair to Klaus, there's been a lot of gratuitous criticism of the GC/MS over the years by people with an agenda for pushing for bio-

logical interpretations of the results from Viking."

But experts who read the Navarro-González et al. paper say they weren't even aware that the use of pyrolysis as a method for releasing organic material was being debated. "I haven't encountered anyone who read it in that way," says Hayes. "A rereading with the idea in mind might show how that message could be extracted, but it is certainly not the message that I got when I read the paper."

Pyrolysis as an extraction method

McKay says it's important to make the distinction between the method of extraction and the method of detection. He agrees that the method of detection, gas chromatography/mass spectrometry, worked flawlessly during the Viking mission. The adequacy of pyrolysis is another matter. "You can have the most sensitive instrument in the world, but if the way you're taking the organics out of the soil doesn't pull them out—because, for some reason, they are bound to the soil physically or react chemically as you try to extract them—then your instrument is not going to see them," he says.

McKay started to think about the efficiency of pyrolysis after being asked to review a paper by Richard Mathies of the University of California Berkeley and colleagues at the University of California San Diego, the Jet Propulsion Laboratory at the California Institute of Technology, and Leiden University (The Netherlands; 7). The authors described a microfluidic device, developed for Mars missions, that extracted amino acids from soil samples.

"In that paper, they mentioned that the extraction efficiency when they used chemical methods was 1000 times better than when they used pyrolysis," says McKay. "They just mentioned it in passing. They said, 'Oh, by the way, we find that the efficiency for chemical extractions is 1000 times more than [for] pyrolysis.' But it just blew me away."

McKay was puzzled by the factor of 1000 and started to wonder if the finding by Mathies and colleagues was going to be a serious consideration for future analytical endeavors on Mars as well as for the interpretation of the Viking GC/MS data. A month later, says McKay, Navarro-González told him about some samples, which he obtained from the Rio Tinto, a river in Spain, that contained jarosite, an iron sulfate mineral.

Navarro-González recounts that when he heard that the Mars rover Opportunity had discovered jarosite on the Martian surface, he immediately thought of the Rio Tinto and went there to collect samples to use as Martian soil analogs. After conducting some experiments, Navarro-González says, "I was surprised to see even though there was life in the sediments of the Rio Tinto, there was virtually no detection of organic compounds." He informed McKay that with pyrolysis, he couldn't detect organics or breakdown products of organics from the samples, but with the application of liquid extraction, he could detect them.

At that point, McKay and Navarro-González made a list of soils to test. "A lot of them were soils that are now good models for Mars but, at the time of Viking, would not have been considered models for Mars soils. At the time of Viking,

it was generally thought that the Mars soils were clay,” says McKay. “Now, the best models are weathered palagonite and jarosite-rich soils.”

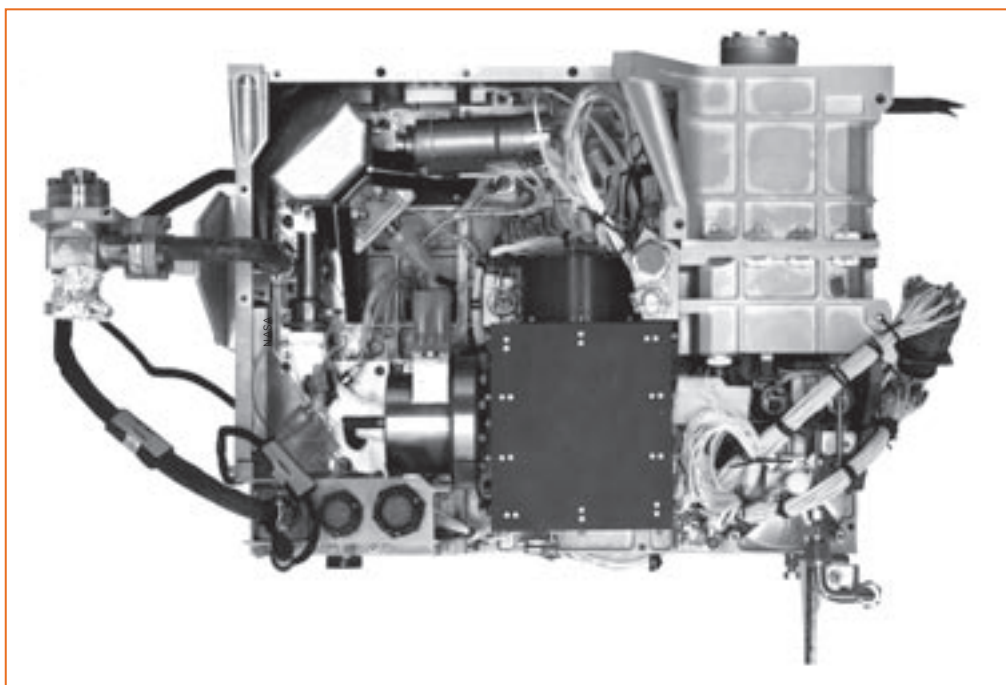
The investigators tested jarosite soils from the Rio Tinto, jarosite soils from California, and a palagonite soil—a so-called Mars soil simulant—from Hawaii. All the soils showed the same effect that Mathies and colleagues had reported in their paper—that pyrolysis was 1000× less efficient than chemical extractions for organics.

Mathies—who was stunned when informed that a single sentence in his paper had sparked the exchange of words over the Viking GC/MS detection capabilities—says that data collected by him and his colleagues leave no doubt that liquid extraction methods boost sensitivity. His interest in liquid extractions was also spurred by the discovery of jarosite by the Mars rovers. He and his colleagues went to the Panoche Valley in California to obtain jarosite-rich soil samples and began sample analysis by sublimation in their microfluidic device, the Mars Organic Analyzer.

“We picked up the sublimates, reacted [them] with fluorescamine, and ran them on the Mars Organic Analyzer. In that system, while valine gave very high numbers, up around 100 ppb, most of the other amino acids were significantly lower, in the few tens of parts per billion range,” Mathies says. “The interesting thing is, we took the same powdered samples that we sublimated and did an aqueous extraction on [them]. The valine signals came up from 100 to 300 ppb, but other amino acids came up nearly a factor of 100 or more, some of them a factor of 1000, as reported in [our] paper. That demonstrated a dramatic improvement in the efficiency of the extraction of the organics when you go to an aqueous phase.”

That pyrolysis isn’t as efficient as chemical extraction doesn’t surprise Hayes. He says when the goal is to get the most accurate view of the structures of molecules in a mixture of organic and inorganic materials, pyrolysis should be avoided. The high temperatures can cause alterations in molecular structure, and mineral surfaces can catalyze rearrangements or increase alterations in other ways. “For all of those reasons, organic geochemists working in earthbound laboratories—myself included—rely almost exclusively on liquid extraction techniques when making high-quality analyses,” he says.

But McKay and other experts are all quick to state that the Viking GC/MS isn’t to be faulted for using pyrolysis. Biemann



The Viking GC/MS photograph shows the GC column in the center above the effluent divider/separator box; double focusing MS is to the left; sample oven compartment is in the upper right; H₂ tank is the sphere below, behind the wire bundles. Tray dimensions: 28 × 38 cm. Electronics and data processing system are located behind. (Adapted with kind permission from *Origins Life* **1974**, 5, 417–430. Copyright 1974 Springer Science and Business Media.)

says he was well aware that pyrolysis wasn’t as effective as liquid extractions while he was designing the instrument and experiment in the 1970s. Given how little was known about Mars at the time, pyrolysis was the perfectly sensible thing to do.

Hayes paints the scenario the Viking GC/MS team faced in the late 1960s and the 1970s during the instrument’s development. “Imagine that you were designing an instrument that wouldn’t operate in an earthbound laboratory. Imagine that it would be used to analyze samples whose characteristics could only be estimated with great uncertainty. Your objectives were to maximize reliability, generality, and sensitivity. For the first, you kept it simple. For the second, you avoided procedures that would select one class of compounds over others. For the third, you preferred techniques that would at least attack all of the organic carbon in the sample, even if you got to see it only after it had been altered. All of those considerations led you away from liquid extraction,” he explains. “To a degree that has proven decisive for many sets of investigators on multiple planetary missions, the [considerations] lead you to pyrolysis, not because it is perfect but because it is the best compromise.”

Despite the engineering complexities and significant expense, experts echo McKay’s sentiment that NASA should include liquid extraction techniques. “I would say future missions ought to consider some sort of liquid extraction front end,” says Ronald Hites of Indiana University, who worked with Biemann for a few years on the development of the Vi-



The adequacy of pyrolysis
as an **extraction method**
for organic matter from
iron-rich soil **is debatable.**

king GC/MS. "In fact, since we tried pyrolysis and it didn't show much of anything, one could argue that it is appropriate to try something different. I think that's a valid point, but I don't think that is a valid criticism of the Viking instrument."

According to McKay, the fact that pyrolysis was used for the Viking GC/MS instrument is critical for understanding the results from the mission. "All we're saying is, because the GC/MS had a detection limit of 10^{-9} , it doesn't mean that there was a detection limit in the soil of 10^{-9} ," he states. "If you read the Viking GC/MS papers, they're careful to never say that it's the detection limit in the soil. They say the analytical precision of the instrument is in the parts per billion, and that's correct. But the rest of us have assumed that meant the soil detection sensitivity was parts per billion." McKay says he and his colleagues think that the amount of organic materials in the soil for the Viking experiments could be as high as in the parts-per-million range but that the organic materials were overwhelmed and oxidized by the jarosite in the Martian soil and thus were not seen by the Viking GC/MS systems.

Hayes questions McKay's interpretation, because the Viking GC/MS team had provided data that clearly supported sensitivities much better than 1 ppb for many compounds of interest. "If [McKay] were to say that the discussion of detection limits in the Viking GC/MS papers didn't really get into the possibility that some of the organic material might not be released or might be oxidized, rather than volatilized, and that quantitative treatment of that issue might reduce the quoted detection limit by as much as a factor of 10, I think he would have a point. But I still regard 1 ppb as a very realistic estimate of the overall sensitivity," says Hayes.

But "the real issue is not going back and reliving the Viking experiments after all these years but looking forward to those instruments going to Mars now, and [those instruments] are relying on pyrolysis as one of their methods for soil extraction," says McKay. "If I were rewriting that [PNAS] paper, I guess I would have titled it 'Efficiency of pyrolysis and implications for future Mars missions' and only mentioned the Viking GC/MS in the last paragraph—'Oh, by the way, our results also have implications for interpreting the Viking results.' I would have focused the paper entirely on what do we do in the future on Mars and how pyrolysis may not be the right method."

Temperature, oxidative iron, and low levels of organics

Despite the all-round agreement that pyrolysis has limitations and that other alternatives should be considered for future Mars missions, experts say the Navarro-González et al. paper doesn't make a convincing case. First, they all point out that the GC/MS Navarro-González and colleagues used was 1000× less sensitive than the Viking GC/MS. The investigators put together commercially available laboratory instruments—a pyrolyzer, a GC (with a column only suitable for low-polarity organic compounds with seven or fewer carbon atoms), and

a quadrupole MS—to create the GC/MS for their experiments.

"The instrumentation Navarro-González [and colleagues] put together was clearly quite inadequate," says Mathies. "They say the Viking GC/MS should have


heated the system more, gone to 750 °C instead of 500 °C, but that's obviously technically difficult to do on a spacecraft. But the fact is since Navarro-González [and colleagues] have a 1000 times lower sensitivity, who knows? They might have actually detected stuff at 500 °C had they built a more sensitive instrument!"

However, since publishing the PNAS paper and talking to *Analytical Chemistry*, Navarro-González has compared the performance of his instrument with that of the Viking GC/MS. He says he can't find any indications to suggest that the commercially available instrument that he and his coworkers used has a poorer sensitivity than the Viking one. Navarro-González says the sample size is a lot smaller in their setup compared with the Viking instrument, which could explain the detection limit they measured: micrograms of benzene per gram of soil.

But, more importantly, "we analyzed the samples using the highest sensitivity of our instrument and were not interested in modifying the design of the commercially available instrument to increase sample size and improve sensitivity," states Navarro-González. "That's not an issue. The problem is, regardless of your sensitivity, if you have refractory organic molecules in your sample, they will not be volatilized, and consequently, they will not be analyzed by your instrument. If there is iron present, then it will catalytically oxidize the organics into CO₂. If we find this problem in any instrument that isn't as highly sensitive as the Viking GC/MS, it means the problem is just [worsened]."

Experts agree with Navarro-González and colleagues that a higher temperature for pyrolysis occasionally generates more information about nonvolatile organics in a sample. "As you carry out early stages of pyrolysis, let's say at 400 °C, the non-volatile material sits there, cooks, and produces some really ugly tars. They don't break up until the temperature exceeds 500 °C or higher," says Hayes. "Navarro-González and colleagues are correct in saying that materials can come off above 500 °C. But I don't see that as relevant because when material does come off above 500 °C, it's because it got vulcanized at lower temperatures in the procedure. At those lower temperatures, inevitably in my experience, there is plenty of stuff that is volatile and which thus would have been detected by the Viking instrument."

The second issue that puzzled experts was that when Navarro-González and colleagues tried to make the point that 750 °C was more effective than 500 °C for pyrolysis, they only reported the amount of benzene released from the various Martian soil analogs. As Biemann points out, experiments he and his colleagues did in the 1970s with Antarctic soils as Martian analogs demonstrated that pyrolysis generates more



than just benzene. “At 500 °C, you get all kinds of compounds,” he says.

Hayes makes the same point. “When you pyrolyze organic material, you get a wide range of products,” he says. “There are literally hundreds of other components. In my experience—and I’ve pyrolyzed a lot of dirt—benzene is rarely the key product of pyrolysis. The exclusive focus on benzene [by the investigators], ignoring all other materials, is extremely strange.”

Navarro-González says he and his co-workers did see a range of pyrolytic products in their experiments. “You see compounds like benzene, toluene, silanes, nitriles, also oxygen-bearing compounds. You find a large variety,” he says. “But interestingly, the only compound we have found to be quite stable under all the pyrolysis conditions was benzene. This is why we used it as a proxy to understand what was happening in the various sediments.”

Another issue that prompted much discussion was Navarro-González and colleagues’ assertion that all traces of organic material were completely oxidized to CO₂ by the iron in the Martian analog soils. According to the investigators, that’s what presumably occurred when the Viking GC/MS ovens pyrolyzed the samples, causing the instrument to see only CO₂ and no other organic materials. But experts counter that the investigators didn’t consider the kinetics of the oxidative process and the fact that oxidation would compete with the rate of volatilization of organic materials.

“My experience in dealing with pyrolysis of organic material in soils and sediments is that the kinetics of oxidation are never fast enough to completely overwhelm the release of volatile organic material,” says Hayes. “By saying everything could have converted to CO₂, Navarro-González and colleagues are suggesting that the oxidation was quantitative and the speed of oxidation greatly exceeded the speed of volatilization. I don’t think there’s any evidence for that, certainly not in their paper and certainly not in any part of the literature or my own experience. In an open system, lots of organic materials are swept out of the reaction zone before they’re burnt, and those materials would have been seen in the Viking instruments.”

Biemann also makes the case that there can’t be sufficient oxidative iron in the Martian soil at the Viking landing sites to completely convert all organics into CO₂. Navarro-González and colleagues stated the Martian soil samples analyzed by the Viking instruments contained 19% ferric oxide, drawing the number from the X-ray fluorescence measurements done by another set of Viking instruments. “What they didn’t understand is that X-ray fluorescence doesn’t tell you the oxidation state” of the iron, says Biemann. He points out that the Viking X-ray fluorescence team just expressed the iron content (12–15%) as Fe₂O₃, as was common practice in those days. “But it’s just a paper calculation,” he says.

Mössbauer data from the recent Mars rovers showed ratios of 0.25–0.40 for Fe(III)/Fe(total) in the surface soil. Biemann says that’s 3–6% Fe(III) at the Viking landing sites, an insufficient amount to oxidize all traces of organic material, as is also shown by Navarro-González’s own experimental data (Figure

5 in Ref. 4). There would still be some organic material left over that would be detected by the Viking GC/MS. The low Fe(III) content at the Viking landing sites also indicates that it can’t be jarosite, which contains 33.9% Fe(III). Biemann says the fact eliminates the basis of Navarro-González and colleagues’ original reasoning.

“Navarro-González and colleagues’ argument and fixation is that iron oxide oxidized all the organics at 500 °C, and therefore one couldn’t find them because they were all burnt,” says Biemann. “I say that’s absolute nonsense.”

Navarro-González says he and his colleagues are only claiming that a small portion of the CO₂ that the Viking GC/MS did see was probably due to organics, and he stands by the data presented in his *PNAS* paper. “You have to take into account that these samples don’t have high levels of organics,” he says. “Compounds that are present are refractory or molecules that

Design of the MSL GC/MS

Mahaffy and his colleagues are developing the first GC/MS to go to Mars since the Viking mission as part of the Sample Analysis at Mars (SAM) suite of instruments. The SAM will be on the MSL mission, which is slated to launch in 2009 and to land on Mars in 2010. Another GC/MS instrument is planned for the European Space Agency’s 2013 ExoMars mission.

Unlike the Viking GC/MS, which stayed put in a lander, the MSL will be housed on a rover to gain better access to samples. The rover will have a rotary percussive drill. “Not only can we rove and look for outcrops, we can go into fairly hard rocks,” says Mahaffy. He adds that a rocky environment might be more impermeable to the oxidants that might destroy organics. “Going down even a few centimeters might expose very old preserved organics that the UV and the oxidants didn’t get to.”

Mahaffy says they are taking advantage of all the technical progress that has taken place since the days of Viking. “For example, we’re developing turbomolecular pumps so we can get by with much higher throughput of gas and do the GC/MS experiments in a more analogous way to what we would do in a terrestrial laboratory. The experiment we do with MSL should be much more similar to what analytical chemists are used to in the lab,” he says.

The 2010 mission has the room to fly six GC columns so that a range of molecules with a variety of polarities can be captured. And this time, helium—the chromatography standard—will be the carrier gas. For pyrolysis, the ovens will go up to 1000 °C because the capability is now available. The MS part of the instrument will cover a larger mass range than the Viking counterpart—the Viking scanned from *m/z* 12 to 200, but the MSL MS will be able to go up to *m/z* 535.



are not easily cleaved. Consequently, when you heat them, they don't volatilize. They are beginning to react on the surfaces of the soil, and iron oxidizes them more readily. In addition to experimental data, we also did thermochemical calculations in the *PNAS* paper, and in all cases these theoretical calculations predict a complete oxidation of the organic matter. That's what we observed."

McKay says the amount of iron in the analog soils for Mars outweighs the organics, allowing the iron to dominate its reaction with organics. "If the soil is rich in organics, like typical soils here in North America or even in the Mojave Desert, where the percentage of organics in the soil is 1% or something, then the organics will win out. They will come out in the pyrolysis. But if the organic concentration is very small, say 1 ppm, then the iron will win out. It's a stoichiometry issue," he says. "Whichever reactant is in excess is the one that remains at the end of the reaction."

As for the kinetics of the reaction, McKay says they don't have an explanation for why they don't see anything other than CO₂. "We're talking about an actual measured result," he says. "We hypothesized there was a reaction of the organics with iron, and we did a model of the kinetics of it. . . . You would think there would be some release of organics even at low levels, and maybe there is. But with soils with very low organics in the parts-per-million level, we found only CO₂."

The influence on future missions

Despite the trail left by the two *PNAS* papers, there's a consensus that the Viking GC/MS worked the way it had been designed to. All the experts agree that the instrument has left a lasting legacy. Besides teaching subsequent generations of researchers what works well, experts say they've learnt what to take note of and correct. Pyrolysis is one of those factors to reconsider—experts say other extraction methods that don't rely on volatility of organic matter can dramatically improve the efficiency of sample release and detection by GC/MS and other analytical instruments.

Experts involved in current Mars exploration missions say the weakness of the Viking mission was that the instruments had a very limited range of sample types available to them. The landers had robotic arms that could only scoop up the loose Martian soil available on the surface around the landing sites. "You know the old adage—a chain is only as strong as its weakest link. The weak link in the Viking mission was its access to samples," says Des Marais.

The limited access was partially related to the way the landers touched down on the planet. "The Vikings landed blind," says Mahaffy. "With the quality of imaging available then, all



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they could do was try to get to a spot where they could land safely."

Because of the blind landing and restricted access to samples, the Viking mission has taught researchers to think more critically about regions to explore on Mars. Des Marais says, "Since the Viking mission, the Mars program has achieved much more orbital reconnaissance—finding where are the good places to land, performing measurements from orbit that can determine if ancient habitable environments might have existed, and determining whether certain materials that can effectively preserve a record of life or organic matter are present, such as clay minerals, silica, sulfates. Once we locate some highly promising sites, we send a

rover with a capable instrument, like the GC/MS, and try to make those direct detections."

With detailed data from rovers like Opportunity and Spirit, scientists now say they have a better idea of what to expect. The time has come to send sophisticated instruments. As a result of evidence of vast amounts of water at a point in Mars's history, several researchers have great expectations of finding organic materials, maybe even life-forms, on Mars in future missions.

And all the discussion over the 31-year-old Viking data, with its indisputable influence on subsequent planetary missions, makes one thing obvious. "Analytical chemists have a big contribution to make here," says Hayes. "Our understanding of the Earth system and planetary systems has to be based on good chemical data and correct interpretations. There is just a lot of detailed chemistry in those processes, and for analytical chemists to take an interest and make a contribution is very much in order. It can only help to clarify the situation. A lot of the people who come to this subject are biologists and geologists, and if analytical chemists show up at the party, it can only help."

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