Spirit and *Opportunity*:

MÖSSBAUER ON MARS

The Red Planet rovers are the ultimate spectroscopic field instruments.

Michael J. Felton

The *Spirit* and *Opportunity* rovers, with their multiple spectrometers, are on one of the toughest science field missions ever: Mars.

Chemists and researchers are predominantly laboratory animals. They work and play at their benches with chemistry techniques and advanced instruments, analyzing samples synthesized within or delivered from around the globe. Geologists also often investigate rocks and minerals with the naked eye or with loupes in the field, generally bringing samples back to the lab for spectroscopic investigation. While rough crystal shape and likely compounds can be guessed in the field on the basis of experience, spectroscopic tools that are not usually portable can confirm the composition and crystal structure of samples.

But what happens when samples can't be returned to the lab for analysis? Say, for instance, the fieldwork is being conducted at least 30 million miles from the researchers. Putting rocks in Ziplock bags and FedEx-ing them to a lab for analysis are not yet an option when you're on Mars. Therefore, analysis needs to occur in the field without human help. NASA's latest missions to Mars are doing just this.

Two identical rovers, *Spirit* and *Opportunity*, are traversing opposite sides of the planet, conducting geochemical studies using a unique array of instruments, all without the help of human hands. Sure, researchers are telling the rovers where to go and what to examine, but the rovers carry out the orders on their own. The information gained has been phenomenal, and stories of Martian history are everywhere. How is this chemical and physical information obtained by the probe? What instruments are on board, and how do they work?

Instruments of Spirit and Opportunity

"In a chemistry lab, you don't use just one instrument," says Thomas Wdowiak, professor emeritus at the University of Alabama at Birmingham and a co-investigator on the Mössbauer instrument team. He adds, "That is the best way to do it on another world as well." The rovers' first instruments are its numerous cameras, but one of them is especially for its science mission. Called the microscopic imager, it is able to record images of microscopic objects, and it is similar in function to a geologist's loupe (hand-held lens). The imager is mounted on a robotic arm called the Instrument Deployment Device, which also holds several other science instruments: a rock abrasion tool for preparing samples, an alpha-particle X-ray spectrophotometer (APXS), and a Mössbauer spectrometer.

But it is not enough just to have a bunch of instruments on a mission. "It's got to be like an orchestra," says Wdowiak, "and the instruments we have on board work together very nicely. We have a device to measure an abundance of the elements (APXS), we have a device to understand the mineralogy of iron minerals (the Mössbauer spectrometer), and we have a device to let us get a view of what we are looking at (the microscopic imager)." The instruments on the topmast also include an infrared spectrometer, which differs from the arm because it is used as a

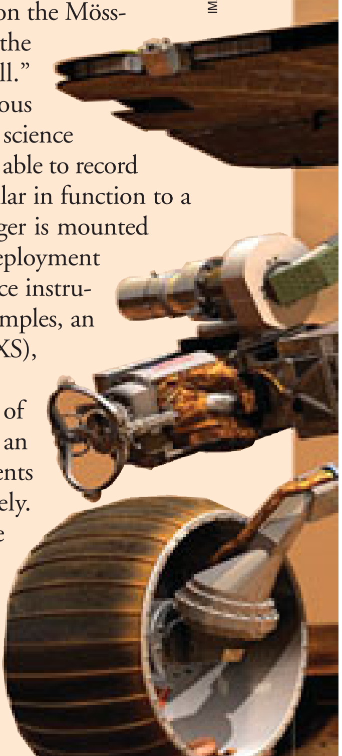
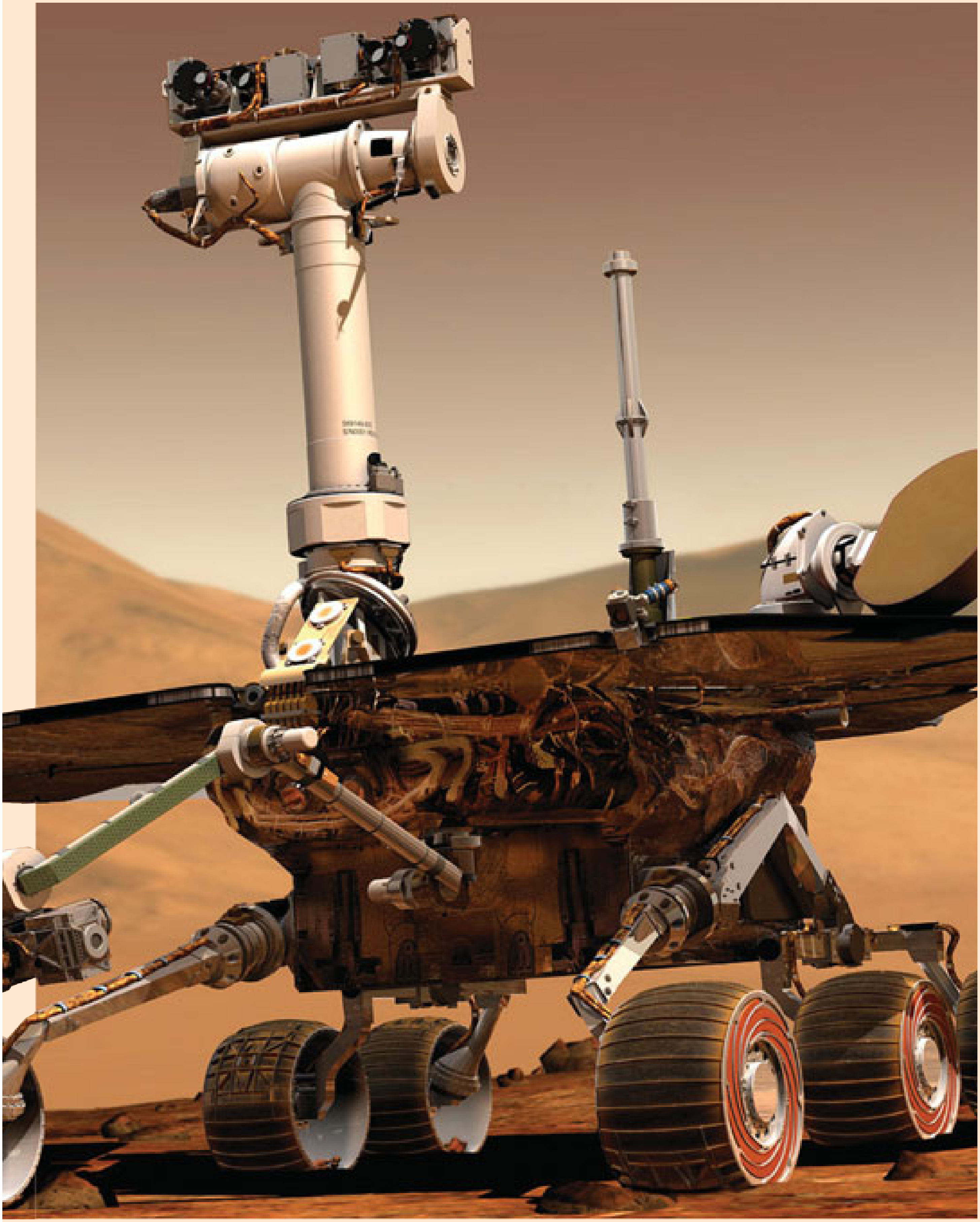


IMAGE: NASA/JPL/CORNELL



remote sensing device, to view temperatures of the surface surrounding the rover, to find locations of interest. But when the rover does get to a place of interest, how do these instruments work?

Figure 1. *Spirit*'s rock abrasion tool drilled a hole (left) and brushed the surface (right) off a rock nicknamed "Clovis".

RATs, Rocks, and APXS

When the rover approaches a target of interest, researchers, using images and thermal data, determine where to look and how to prepare the sample. And, because there is no one there to dig up the soil, clean off dust, or break rocks, various robotic techniques are being used.

One way to prepare a surface is with the rover itself. When *Opportunity* landed in the Meridiani Planum, small spheres were seen in the soil. To get better access, the rover spun one of its wheels, which dug up some Martian soil for examination. In addition, the landing of the spacecraft exposed some of the Martian subsurface.

However, when the rover approaches a rock, it cannot use these tricks to gain more sample diversity and access. The rock abrasion tool, or RAT, is then used. On *Spirit*'s first rock analysis, researchers suspected that the Adirondack rock was not covered in dust. However, after 5 min of cleaning with the RAT's brushes, a significant layer of dust was removed, leaving noticeably darker rock beneath (Figure 1). Stephen Gorevan of Honeybee Robotics, which made the RAT, said in a National Aeronautics and Space Administration (NASA) press release, "Ladies and gentlemen, I present you the greatest interplanetary brushing of all time." On August 12, the RAT's grinding ability was pressed to its farthest point so far, as Spirit ground a hole 8.9 mm deep and 4.5 cm in diameter into a rock called Clovis, in Endurance Crater (Figure 2).

Once the sample—whether a rock, the Martian surface, or subsurface—is prepared, the microscopic imager moves in. It is used to see the results of the surface preparations and to identify small structures. For instance, the microscopic imager was used extensively in Opportunity's first examination of a rock outcrop. The rock appeared to be finely layered. The microscopic imager showed little spherical grains being released from the rock as it was being eroded by the wind (Figure 3).

The rovers' spectrometers are what all this looking and sample prep have been about. "The APXS might have the longest history on in situ planetary exploration," says Ralf Gellert, who

Instrument Makers and NASA

Academic institutions are not the only parties who have become interested in NASA missions; commercial organizations also propose instrument and science payloads for projects like the Mars rovers. And like academic institutions, which partner with each other to provide skills for such ambitious missions, corporations partner as well.

An example is a Raman instrument development being proposed for a future Mars mission by Headwall Photonics and Hamilton Sundstrand. "Generally, what you have to pull together is a team of capabilities, and this may involve vendors," says Bruce McIntosh at Hamilton Sundstrand. "In our case, vendors such as Headwall Photonics and Infotonics." In addition, he says that people with specific scientific skills, typically researchers, also need to be involved in a project.

Industrial instrument makers, such as Hamilton, which produces process control instruments, may also bring expertise that traditional lab instruments may be missing. "There is sort of a continuum from laboratory instruments, which are pretty well pampered, to something that has to live for a year or so with no one closer than a few million miles away," says McIntosh. "And in-between, you have process control instruments that have to run 24-7 with very, very little involvement by human beings."

In fact, process control instruments have a great deal in common with instruments used for space exploration. Process control instruments need to be somewhat autonomous, making measurements with a few simple instructions, and they need to handle different kinds of samples. Process equipment also has to contend with extreme pressures, temperatures, and temperature fluctuations, all of which can also occur in space exploration.

However, size, weight, and power remain issues, and that is part of the challenge of space projects. But there are great benefits for companies that work with NASA projects, directly or indirectly. "We really go after NASA-type projects because they allow us the opportunity to accelerate out the technology development roadmap, since the space project requirements are typically more complex, requiring higher-performing instruments with a unique set of attributes," says David Bannon at Headwall Photonics. "There is obviously the need for small size, compactness, few moving parts, minimal alignment, and structural integrity," he adds. "Those types of things are great opportunities for us to design new products, because we have this vision of smaller and more portable high-performance instruments for field applications."

An instrument's use on a NASA mission is sometimes considered a stamp of approval, as the basic technology has progressed through rigorous scientific and technical investigation. And for companies there are also noncommercial factors. Bannon says, "There is a fair amount of glitter with having your product on a rocket."

IMAGE: NASA/JPL/CORNELL

helped develop the APXS for the rovers and is an investigator on the APXS team. In fact, APXS has been to Mars before and carried out in situ rock measurements as part of the Pathfinder mission in 1997. However, the instrument has been improved since it last visited Mars, and now carries an enhanced X-ray detector with better energy resolution, which allows superior measurement of lighter elements.

"In terrestrial laboratories, you would use more-standard methods like X-ray fluorescence (XRF), particle-induced X-ray emission (PIXE), energy-dispersive X-ray analysis (EDX), and so forth for chemistry determination," says Gellert. "But in space, you don't have the sample preparation, power, and weight available" A curium-244 radiation source basically replaces the proton beam sources (for PIXE) and X-ray tube sources (for XRF) that are used on Earth. With this alternate source, these three techniques can be combined on the Mars rover because they all use X-ray and alpha-particle detection.

Figure 2. An 8.9-mm-deep hole cut into a rock by *Opportunity*.

On Earth, XRF is used in industry to identify and quantify metals (heavier than Ti), and it does this by exposing the metal to X-rays, which cause the metal atoms to fluoresce and emit secondary X-rays with energies unique to the element. PIXE uses accelerated particles to cause atoms to emit X-rays, and it is used not only by geologists but also by archeologists and art conservationists.

After *Spirit* rolled onto the Martian soil, it tested its spectrometers on the soil. The APXS found soil that was strange to us Earthlings but typical for Mars: predominantly silicon and iron but also with significant levels of chlorine and sulfur. APXS has been used numerous times by each rover, but it is typically run during the night to take advantage of the colder temperatures that increase energy resolution. As *Opportunity* has used APXS to measure elements in the rocks lining the walls of Endurance Crater, the level of chlorine has increased, which may indicate the former presence of water.

Figure 3. Image of spherical grains being exposed by wind erosion, taken by the microscopic imager.

The one instrument that has been a surprising success has been the Mössbauer spectrometer. The spectrometer first identified olivine in the Martian soil in its test. This volcanically produced mineral is found on Earth but is easily weathered and therefore is typically found within rocks, but on Mars it is part of the soil. This is the first time a Mössbauer spectrometer has flown on a space mission, and although it has met with limited use on Earth, it is an exceptionally productive instrument for determining Martian soil composition.

Mössbauer Spectroscopy

In 1957, Rudolf Mössbauer discovered what came to be called the Mössbauer effect. Mössbauer was working on the question of why gases exhibited X-ray resonance but not gamma-ray resonance. Resonance, a somewhat deceptive term, occurs when the ray produced from one source is absorbed (or scattered) when it encounters a target that is in a specific state, usually extremely similar to or exactly the same as the source.

Mössbauer found that gamma-ray resonance worked in crystalline solids but not in gases, and he explained this phenomenon by using basic physics. He theorized that as a gamma ray is emitted from an atom's nucleus, it is akin to a cannonball, and the nucleus recoils. However, the recoil also affects the cannonball, shifting its energy. As numerous nuclei fire off their gamma rays, the gamma rays have a range of energies, broadening any peak that would be detected.

In gases, nothing holds the nuclei, so gamma rays of various energies are produced, and resonance couldn't be detected. However, in a crystal, the nuclei are held by other atoms in a crystal lattice. "Therefore, the recoil is absorbed, and the radiation comes off very monoenergetic," says Wdowiak. "In fact, it is more monoenergetic than any laser . . . and offers the most precise energy standard you can get."

When a monoenergetic gamma ray encounters an atom under the identical conditions as the atom from which it originated, it will be scattered.

On Mars, the rovers carry Mössbauer spectrometers containing cobalt-57 in a rhodium crystal lattice. This isotope of cobalt decays to iron-57 by emitting a gamma ray. When this gamma ray runs into another iron-57 atom in the same crystal lattice, it will scatter.

Although identifying iron-57 in rhodium crystals might be

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useful, it would be much more useful to identify a variety of other iron crystals as well. To do this, the source is moved rapidly, as fast as 13 mm/s, causing a Doppler shift in the gamma ray. This Doppler shift affects all the gamma rays emitted. By moving the source, a range of energies can be searched, giving a spectrum of iron nuclei under different conditions.

For instance, Mössbauer spectra can indicate if the iron atom is neutral, +2, or +3 and if the iron is in a magnetic field or not. "You can just look at Mössbauer spectra and see if a material is magnetic or not," Wdowiak says. "If you see a singlet or doublet, it is nonmagnetic, but if you see six peaks, it's magnetic." He adds, "The amount of quadrupole spinning for ferrous and ferric is very distinctly different, and just by eyeballing it you can see it" (see Figure 4). In addition, temperature changes can cause the Mössbauer spectra to change for certain minerals, providing another technique for their detection. For example, hematite goes through such a change at 260 K, which can occur on Mars, aiding in its identification.

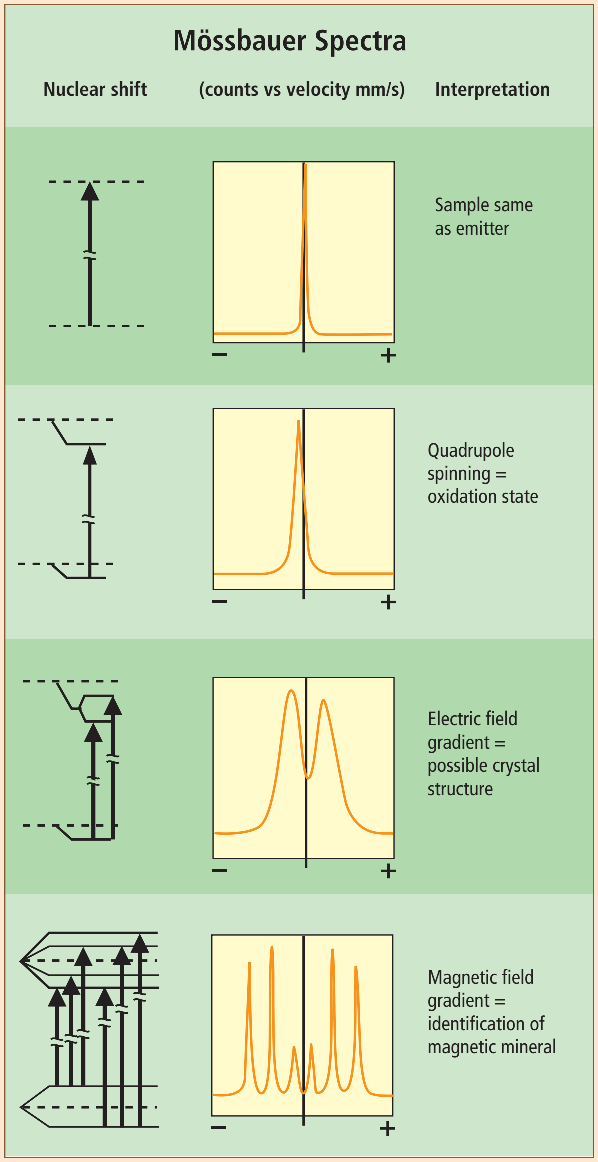

Figure 4. Different states of atomic nuclei cause various changes to the Mössbauer spectra, allowing many minerals to be identified.

Mössbauer, Hematite, and Magnetite

Using the Mössbauer spectrometer, *Spirit* found olivine on its first test in the Martian soil. *Opportunity* found hematite in the small spherical objects seen by the microscopic imager at its landing site on Meridiani Planum. Why is hematite important? Its infrared signature had been observed from Mars orbit with other instruments, but finding it on the surface with the Mössbauer was a mission success. Wdowiak answers, "You cannot make hematite without water. Maybe you could, but that would probably take intelligence, like a chemist, to do." Therefore, hematite almost certainly indicates that Mars had water.

Hematite and other important iron minerals have been found in numerous places, and some theories are being based on these findings. One is that there may have been water, in some form, on the Meridiani Planum, where the Opportunity landed, and some at NASA suggest there could have been an ancient body of saltwater because of the elemental concentrations provided by the APXS. *Spirit* encountered little evidence of water in the Gusev crater, but it has now found hematite and suggestions of water's presence at an outcrop above the crater's floor. The rocks are also soft, as seen by examination with the RAT, and are unlike the hard basaltic rocks that *Spirit* encountered in the rest of its journey through the crater.

The Future

The rovers look like they are in very good shape to survive the Martian winter and continue well beyond their intended life span. Hopefully, the instruments on board will continue to give researchers data to examine for the near future. But NASA and other space agencies are planning future missions with additional instruments, as the current ones have their limitations.

"For example," Wdowiak says, "Mössbauer does great mineralogy, but only for iron; the APXS does great abundances but can't tell you what the mineral is, but what you do is try and put these all together."

Future missions will likely incorporate instruments more familiar to modern chemists than the Mössbauer spectrometer. Raman will probably be an instrument that will go with future missions to Mars and other alien worlds. Several teams are currently submitting instrument- and science-based proposals for competition for payload and science space on NASA's 2009 *Mars Science Lab* rover.

Wdowiak and his colleagues at Washington University in St. Louis, as well as other investigators, are submitting Raman proposals. Academics are not the only ones involved; instrument companies are eager to be a part of future NASA missions (see box, "Instrument Makers and NASA").

And it is not just Raman. Wdowiak suggests that someday MALDI-TOF mass spectrometry may visit Jupiter's moon Europa, where it could study small organic molecules and search for possible biopolymers. Maybe someday, the missions will need chemists on board. But until then, unique sample prep and ingenious instruments will push our understanding beyond Earth. ◆

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