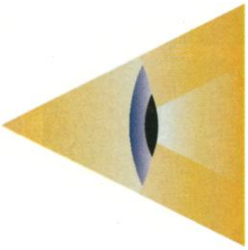
Candid Cameras for the Nanoworld

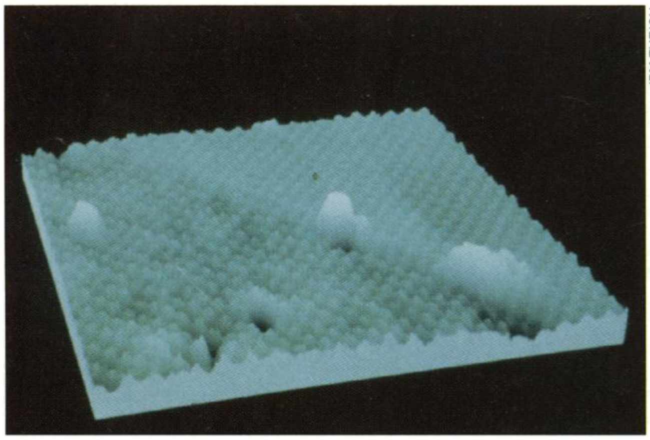
A 16-year-old atomic microscope has spawned a family of instruments that allow biologists, materials scientists, and chemists to see their fields from the bottom up



In 1982, a soft-spoken electrical engineer at Stanford University named Calvin Quate was flying 10 kilometers above the broad-brushstroke landscape on his way to a meeting in London. He was catching up on his technical reading when he came across a short article in the April issue of *Physics Today*. It is no exaggeration to say that what he read changed his life.

"I was going to stay for a week in London," he recalls, "but when I got there, I immediately flew to Zurich." He felt compelled to meet the protagonists of the article—Heinrich Rohrer and Gerd Binnig—at IBM's Zurich Research Center in Rüschlikon. Quate knew no one at the 200-researcher facility, but he managed to track down Christoph Gerber, a laboratory technician working for Rohrer and Binnig. "He showed me a notebook with all of these traces," Quate says. "I was absolutely astonished. I knew that something big was happening."

The traces were the first images from a new instrument called the scanning tunneling microscope (STM). They resembled topographic maps of gently wavelike territory, but the terrain was nothing like the vast expanses Quate had seen from his airplane; indeed, it would hardly have covered a protozoan's underbelly. The subtle rises and falls of the traces corresponded to atomic-scale steps and corrugations on the surfaces of gold and other metals. Isolated bumps might even have marked individual atoms that had settled onto the surfaces, although Binnig and Rohrer weren't quite ready to claim they were seeing atoms.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Landscape with clouds. In this cross section of a semiconductor laser, white patches of oxidation are forming near a junction between gallium arsenide atoms (upper right) and aluminum gallium arsenide.

Atomic resolution or not, Quate suspected that the STM, which builds an image by scanning an atomically sharp probe across a surface, was about to change researchers' perspective on materials as dramatically as a passenger's vantage changes when an airplane lands. Instead of getting broad-brush pictures of atomic landscapes—the best that techniques such as neutron diffraction, x-ray diffraction, and electron microscopy could do—Quate guessed that researchers using the STM might be able to crawl through every atomic nook and cranny.

Any uncertainties were dispelled a year later when Binnig, Rohrer, Gerber, and their colleague Edmund Wiebel published a now-classic *Physical Review Letters* paper that included an image showing a repeating pattern of atoms on what is known as the silicon 7-by-7 surface. As far back as 1957, scientists had used electron diffraction to probe this particular crystal surface, but the results were vague enough to be consistent with several different models for how the surface atoms are arranged. The STM image almost single-handedly settled the issue, dramatically illustrating the power of the new tool. Binnig was so moved, he says, that "it was a little too much to feel joy."

"That 7-by-7 image of silicon was the revolution," Quate says. Since then, the revolution has continued without letup. In 1986, Rohrer and Binnig shared the Nobel Prize for their invention. Quate's own laboratory back at Stanford soon became a key stage for the scientific and technological drama that opened at Rüschlikon. And for researchers in disciplines from surface science to cell biology, the STM and its progeny, collectively known as scanning probe microscopes (SPMs), are ending the need to infer the structure and behavior of ultratiny entities—atoms, molecules, unit cells of crystals, pores and channels in cell membranes—from measurements made on crowds. "Quite often, macroscopic measurements average over ensembles so you don't learn much about physics at small scales," says Donald Eigler, another of IBM's celebrity STM scientists. Now researchers can get downright personal with the tenants of the nanoworld, monitoring individual atoms or molecules and seeing how their particular environments affect them.

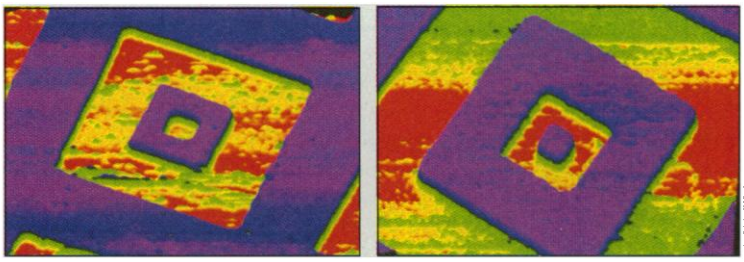
Just as light microscopes can see different properties of a material depending on how it is stained, SPMs can map such properties as magnetism, surface roughness, and electrical potential, depending on the kind of probe they are equipped with. They even allow researchers to reach into the nanoworld and change it, turning nanoscience into nanotechnology. Says Mark Ketchen, director of physical sciences at the IBM Thomas J. Watson Research Center in Yorktown Heights, New York, "Some 50 years from now, people will look back and say this was a major turning point."

Fine discrimination

Finesse was what made the STM possible. At the heart of today's version of the device is an electrically conductive tip (ideally tapered to a point a single atom across). When the tip is maneuvered to within a few atom-widths of a conductive surface, a quantum-mechanical phenomenon known as electron tunneling begins to occur. At these minuscule separations, the quantum-mechanically defined region of space that should contain an electron from an atom on the tip overlaps with the similarly defined region for electrons in the sample atoms just beneath the tip. This overlap behaves as a conduit through which electrons from the tip can tunnel into the sample. Because tiny changes in the overlap drastically speed or slow the electronic traffic through the conduit, the technique is exquisitely sensitive to surface relief.

To exploit these effects, Binnig and Rohrer developed a precise and stable control system for the stylus. Piezoelectric elements, based on ceramics that change size ever so slightly in response to an electric field, nudge the tip this way and that in increments of only a fraction of an atom-width. The piezoelectrics, in turn, are controlled by an electronic feedback system that lowers or raises the tip to maintain a constant tunneling current. The result is that the tip ends up tracing over a sample's surface contours at a constant, tiny altitude. A decade earlier, Russell Young, an engineer at the National Bureau of Standards—as the National Institute of Standards and Technology (NIST) was then known—had come close to inventing the STM when he devised the same basic scheme but fell short of perfecting a system for stabilizing the tip (see sidebar on p. 1984).

By scanning the tip in a tight, back-and-forth pattern while the feedback system maintains a constant current, the system can create arresting topographic maps of surfacescapes at resolutions all the way down to the level of individual atoms. Repeated images can be assembled into videos that show freshly exposed metal surfaces, in search of equilibrium, rearranging themselves into atomic steps or virus-sized islands. The STM can even identify different kinds of atoms by their electronic idiosyncrasies.



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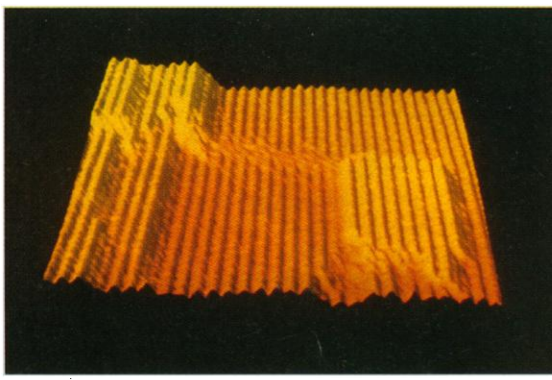
Chemical sensitivity. A 60-micrometer-wide pattern of water-loving methyl groups and water-shunning carboxyl groups. A methyl-bearing force microscope tip stuck to the methyl regions (red and green in image at left). With a carboxyl-bearing tip, the attraction was reversed.

This world didn't remain an exclusive preserve for materials scientists for long. The STM can image only electrically conductive samples, so its first devotees churned out surface images of gold, platinum, silicon, graphite, gallium arsenide, and pretty much any other metal, semiconductor, or superconductor they could lay their hands on. But that was not enough for Binnig, who says, "I always was a bit disappointed that this instrument could not work on insulators," which include the surfaces and molecules of the biological world.

Binnig brought this dissatisfaction with him when he and Gerber took a sabbatical from IBM's Zurich facility in 1985 to work with Quate at Stanford and at IBM's Almaden Research Center in nearby San Jose. There, Binnig says, he intuited the design of what became the most influential offspring of the STM, the atomic force microscope (AFM). The inspiration came one day when he was staring up from a sofa in his apartment at the stippled stucco ceiling and envisioned a fine stylus tracing its bumps. "I could have drawn out a design [of the AFM] with a pencil," Binnig recalls.



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Atomic rank and file. The contours of a gold surface.

Instead of a conductive tip interacting with a sample by way of tunneling electrons, the tip of Binnig's new instrument would be attached to a tiny cantilever—a wee diving board—that would bend and flex in response to the minute mechanical, electrostatic, and other atomic- or molecular-scale forces it encountered as it was scanned over a surface. A feedback system like the STM's would ensure that the force on the cantilever remained constant. Once Binnig and his colleagues had defined the principle of the AFM, it took only a few days for Gerber to build the first prototype. The AFM has since become the most popular type of scanning probe microscope.

Opening the floodgates

The AFM was just one of the STM's ever-enlarging brood of children, each specialized for mapping a different property across submicroscopic landscapes. Even before Binnig invented the AFM, Dieter Pohl, also at IBM Zurich, introduced the near-field scanning optical microscope, which replaces the probe with a special light-gathering optical fiber that can image surfaces optically, at resolutions smaller than the wavelength of light illuminating the sample.

The pace of innovation only accelerated after the AFM appeared. For one thing, the AFM's talent for imaging nonconductive materials served as a welcome mat to enormous research communities in areas such as polymer chemistry and molecular biology. For another, researchers quickly found that by modifying the AFM tip, say with a magnetic coating or a hydrophobic chemical coating, the basic instrument could be specialized for measuring almost any physical property on unprecedentedly fine scales.

Among its instrumental siblings are the magnetic force microscope, the frictional force microscope, the electrostatic force microscope, the scanning ion-conductance microscope, the scanning chemical-potential microscope, and the scanning plasmon near-field microscope, to name only some of them. "New ideas keep coming out—new things to scan, new detectors, new innovative ways of using these techniques," remarks IBM's Ketchen, who is part of a team developing yet another variation on the original: the scanning SQUID (superconducting quantum interference device) microscope, for imaging the minuscule magnetic fields that are the staple of data-storage technologies.

As a result, scanning probe microscopes are turning up in some surprising settings. Consider work by the husband-and-wife team of Paul and Helen Hansma, of the University of California in Santa Barbara, on biological molecules in solution. In 1989, they and six colleagues reported the first AFM-made video of a biological polymerization process. By making repeated scans and stitching them together, they visualized the linking and aggregation of fibrin, a blood-clotting protein, first into strands and ultimately into a netlike molecular fabric.

More recently, the Hansmas have spied on the progressive slicing and dicing of DNA molecules by the DNA-digesting enzyme DNaseI. They have also watched an RNA polymerase molecule bind to and travel along a DNA molecule, reading the code of its nucleotide bases one by one and transcribing them into messenger RNA. "One DNA polymerase molecule can replicate DNA at a rate hundreds of times that at which everyone in the genome project can decode DNA," says Paul Hansma, who dreams of using scanning probe microscopes "to learn the operating mechanism of these incredible little machines."

And last February in the *Biophysical Journal*, Helen Hansma, graduate student Daniel E. Laney, and two other colleagues reported that they had mapped not only the shapes but also the "feel" of individual synaptic vesicles—tiny sacs of neurotransmitter that release their cargo when one neuron communicates with its neighbor. By tapping the probe of an AFM across vesicles from the electric organ of the marine ray (*Torpedo californicus*), Hansma and her colleagues learned that the vesicles became turgid in the presence of calcium ions—the signal that triggers the vesicles to burst and release neurotransmitter. The feat could open the way for directly monitoring the biophysical changes that lead to the release of neu-

The Man Who Almost Saw Atoms

Heinrich Rohrer and Gerd Binnig were not the first to spy on the world of atoms when the two IBM scientists invented the scanning tunneling microscope (STM) in the early 1980s. In the late 1950s, for example, Erwin Mueller at Pennsylvania State University had invented an atom-resolving device called the field ion microscope. In a vacuum chamber, a strong electric field tore charged atoms from the surface of a sample, sending them careening into a detector in positions that reflected their arrangement in the sample. Field ion microscopy, however, was limited to metal samples drawn into very sharp points. But in the late 1960s, one of Mueller's former students invented a device that could have anticipated the STM directly—if only he had completed it.

Russell Young, then at the National Bureau of Standards (NBS, now the National Institute of Standards and Technology), called his instrument the "topografiner," after a Greek word meaning to describe a place. And to STM aficionados, its basic scheme has a familiar ring. Piezoelectric elements scanned its fine metal tip across a surface, with feedback and control systems maintaining the tip at a constant height. Young and colleagues John Ward and Fredric Scire even measured tunneling currents—the basis of the STM—when they brought the topografiner's tip sufficiently close to a metal sample. They published reports claiming that the effect could, in principle, be used to measure a surface position to within about 0.3 nanometer, or about atomic resolution. "One can honestly say that the instrument developed [at NBS] and the instrument that achieved atomic resolution [at the IBM Zurich Research Center] looked very similar," says Roland Wiesendanger of the University of Hamburg.

But Young ran into technical and bureaucratic difficulties. Vibrations and other perturbations were preventing the topografiner from seeing atoms. In a 1972 paper in the *Review of Scientific Instruments*, the NBS researchers gave some sense of the difficulties by pointing out that they were able to achieve tunneling currents only by running experiments during odd hours when their building's air conditioner was off and by operating the instrument remotely so that their own movements would not generate resolution-killing disturbances.

Binnig and Rohrer later solved these problems with multitiered isolation systems. Young never had a chance to try. In 1971, NBS management took him off the topografiner project in a resource-allocation decision. But Young never forgot that he was once on the verge of seeing atoms—and neither did the Royal Swedish Academy of Sciences. In awarding the 1986 Nobel Prize in physics to Binnig and Rohrer, the Nobel committee acknowledged Young's close approach to the STM and blamed his failure to beat Binnig and Rohrer on "exceptionally large experimental difficulties." **–I.A.**

rotransmitter, says Hansma.

Chemist Robert Dunn of the University of Kansas and his colleagues have been probing the workings of other cellular machinery: the channels and pores that riddle cellular membranes. These channels, made up of small bundles of molecules, open and close like locks on a canal to regulate the flow of substances into or out of the cytoplasm and nucleus. In one set of experiments, the Kansas researchers placed an AFM probe directly above so-called nuclear pore complexes in membranes from a frog egg cell to monitor their workings. "In the open state you see a channel, but after triggering the pore [with calcium ions] you see something like a piston stick up and block the central part of the channel," Dunn says. That's a mechanism some biophysicists had speculated about, but Dunn's images lend it direct support.

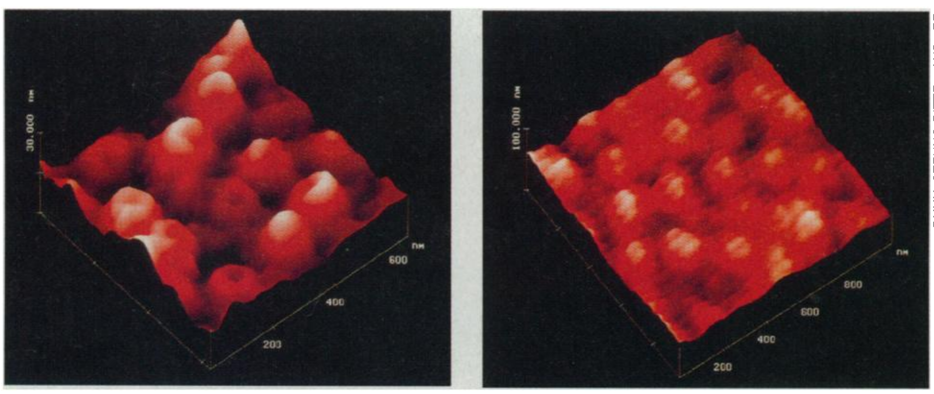
AFMs have made a foray into chemistry in the hands of chemist Charles Lieber of Harvard. He uses them to examine the molecular basis of phenomena that include adhesion, lubrication, and wear. "People were always making difficult arguments about what was going on [on the molecular level] when you couldn't see it," Lieber notes. "By attaching molecules to the force microscope tip, we can get chemical sensitivity" and tease apart those molecular interactions, he says. He and his co-workers scan the chemically coated AFM tip over surfaces micropatterned with different chemical toppings. They measure the forces the coated tip "feels" as it treks through chemically different neighborhoods, experiencing various amounts of hydrogen bonding and other chemical interplay.

One recent STM feat builds on its first: that famous silicon 7-by-7 surface. Phaedron Avouris and In-Whan Lyo at the T. J. Watson Research Center, with collaborator Yukio Hasegawa of the Institute for Materials Research at Tohoku University in Japan, used an STM to trace the movement of electrons through the silicon surface's "dangling bonds," where an atom isn't fully bound to its neighbors. By examining subtle variations in the tunneling current depending on whether the dangling bonds are occupied or not, the group was able to monitor the electron traffic through the bonds—information that could be critical for designers of ultrasmall circuits.

Remaking the nanoworld

Having opened these windows on the nanoworld, researchers are now reaching through them to modify that world to their liking, turning atoms into minuscule switches, batteries, and data-storage sites. In this effort, SPMs serve as both measuring devices and tools.

Two examples can be found in adjacent laboratories at NIST. One goes by the name Molecular Measuring Machine, or M^3, the handiwork of Clayton Teague of the precision engineering group. This onion-structured instrument, whose concentric layers isolate the STM nestled in the middle from physical perturbations, relies on a laser-based tip navigation system to measure the distance between any two points on a surface area centimeters across to within 1 billionth of a meter, or just a few atomic widths. That's a feat akin to locating two widely separated grains of sand in a 2500-square-kilometer patch of desert and then measuring the distance between them to within 1 millimeter.



DUNN, STEHNO-BITTEL, AND LEE

Open-and-shut case. In images from an atomic force microscope, doughnut-shaped channels in the membrane of a cell nucleus are open *(left)* when the membrane calcium content is high and closed when the calcium is released *(right)*.

Ordinary STMs, in contrast, are unable to map sites within such large areas.

This ability to survey the nanoworld should aid efforts to engineer it by planting or dislodging atoms with the tip of an STM or AFM. This interventionist brand of microscopy began in earnest with Eigler and his colleagues at IBM Almaden back in 1990. They made headlines by maneuvering 35 xenon atoms into Big Blue's famous company acronym atop a surface of crystalline nickel. Since then, Eigler and others have built more scientifically interesting structures; these include rings of iron atoms that behave like quantum corrals, constraining electronic motions on surfaces in accordance with the ways of quantum mechanics.

Now, across the hall from M^3 in an acoustically isolated room with a massive metal door, Joseph Stroscio and his colleagues are trying to take the next step in building atom-scale test-beds for quantum mechanics. Their instrument, not yet completed, should be able to modify and scan samples under ultrahigh vacuums, at 2 degrees above absolute zero, and in extreme magnetic fields. Stroscio and his colleagues expect that these experimental conditions will enable them to probe quantum effects to which standard STMs operating under less demanding conditions are blind. "We hope to make [ultrasmall] structures and then ask questions like ... what energy does it take to put an electron into the structure," Stroscio says. The answer could feed into the design of prototype data-storage devices that rely on the presence or absence of a single electron.

Costly, specialized devices such as Teague's and Stroscio's, however, are only a small part of what scanning probe microscopy has become since its invention. Thanks to large-scale production at companies including Digital Instruments, Park Scientific, and Topometrix, scanning probe microscopes can cost $50,000 or even less—complete with a computer package for creating wall-poster images of your favorite sample. Thousands of the instruments are now touring atomic landscapes.

After opening up the nanoworld, scanning probe microscopes have proceeded to democratize it. Without these tools, says Stroscio, "it would be like the Dark Ages."

–Ivan Amato

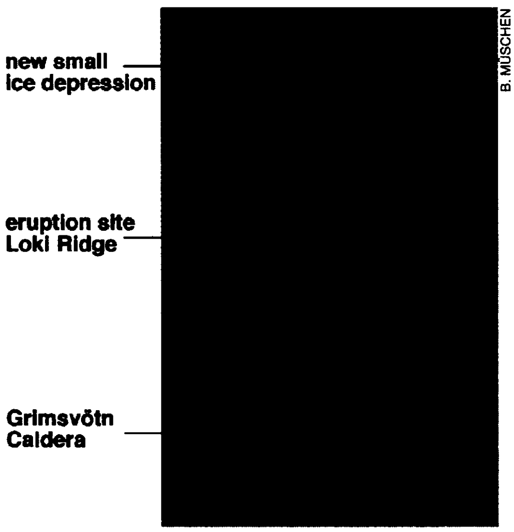
Ivan Amato's book on materials science, Stuff, *was just published by Basic Books.*

RADAR IMAGING

Monitoring a Killer Volcano Through Clouds and Ice

Late in the evening of 30 September last year, seismometers in Iceland detected the beginnings of a volcanic eruption beneath the Vatnajökull Glacier, the largest in Europe. By 2 October, the eruption had forced its way through the 500-meter-thick ice sheet—spewing steam and gas thousands of meters into the air. An estimated 2.3 cubic kilometers of meltwater was trapped beneath the ice and would soon burst out, threatening communities, roads, and communication links in this remote corner of southeast Iceland.

Because of the inaccessibility of the region and the constant cloud cover, which made aerial surveillance difficult, the Icelandic authorities could not tell which way the meltwater would go. They got some timely help, however, from an unlikely source: a cloud-piercing radar satellite and a new image-processing technique that allows researchers to see movements in Earth's surface down to a scale of a few centimeters.



University of Munich geographer Bettina Müschen and several colleagues at the German Aerospace Research Establishment (DLR) in Oberpfaffenhofen were involved in a project sponsored by the European Space Agency (ESA) to study radar images of Iceland from its ERS spacecraft. The team quickly realized that the satellites could help Iceland's disaster management by tracking the meltwater buildup. The synthetic aperture radar on ERS-2 had taken its first images of the Vatnajökull eruption in early October, but the Munich researchers believed that processing radar images of the eruption by a technique called SAR interferometry could generate even more valuable clues for disaster relief.

In this technique, two images are taken from the same vantage point, say, 24 hours apart, and superimposed. The resulting interferogram shows graphically any movement that has occurred in that 24-hour period. ERS mission managers agreed to provide the services of an older spacecraft, ERS-1, then in the process of having its systems checked. On 21, 22, 23, and 24 October, both ERS spacecraft passed over Iceland acquiring images that were then processed into interferograms at DLR. "We detected subsidence of just centimeters per day, which was not visible to the eye. A few days later, [these movements] were confirmed on the ground," says DLR's Achim Roth. "We could see the water going south," says Müschen.

As a result, the Icelandic authorities focused their monitoring and flood defenses to the south of the glacier. On 4 November, meltwater building up in a volcanic crater under the ice lifted the ice sheet and flooded southward. Over the next few days, floodwater and ice blocks of up to 1000 tons took out bridges and power and communication cables en route to the sea, but avoided a nearby village.

Tracking the Vatnajökull eruption was the most dramatic use yet of SAR interferometry, a technique pioneered by researchers at NASA's Jet Propulsion Laboratory in Pasadena, California, in the 1970s that has taken off since the launch of ERS-1 in 1991. "ERS-1 provided the first reliable source of data," says Steve Coulson, who coordinates SAR interferometry research for ESA. Besides making static topographical maps with unprecedented resolution, SAR interferometry is also being used to measure ground movement after earthquakes and volcanoes, the creep of glaciers, landslides, and subsidence caused by coal mining. According to Müschen, German insurance companies are looking into using SAR to assess the risk of natural disasters in different areas. Coulson says the latest application, still at the research stage, is to use interferometry to detect deforestation and different kinds of agricultural land use. SAR interferometry, he says, "seems to be the big thing at the moment."

–Daniel Clery