

The Secret Lives of Minerals

By Elisabeth Nadin

This rounded and polished rose quartz, mounted in a sculpture by silversmith John Marshall, hosts nanoparticles arrayed to scatter light into a six-pointed star. At 3.6 inches across, it's the world's largest rose quartz star. For over 100 years, scientists assumed both the color and the star pattern arose from inclusions of the mineral rutile. (They were wrong.) To see this and other jewels of gem collector Mike Scott's treasures, visit Orange County's Bowers Museum this summer. To see what really makes it shine, follow the pink path.

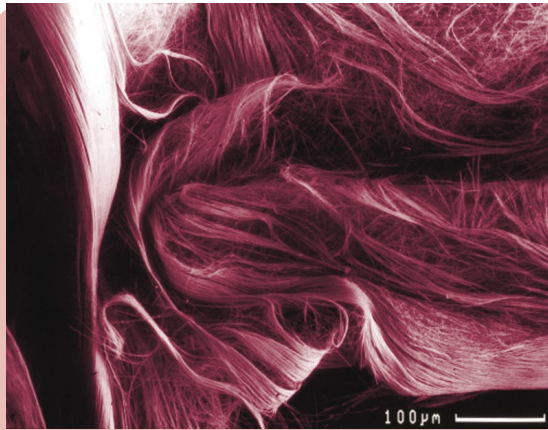


Since ancient times, colored stones have been enwrapped in mystery and intrigue, and assigned a worth far greater than their earthy origins imply. Some 4,000 years ago, ancient Egyptians decorated themselves and the walls of their tombs with green beryl—thought to symbolize immortality, and immortalized as emerald by the gem trade. Opal was the gemstone of love and hope for the Romans, who believed it could also render

its wearer invisible. Meanwhile, Australian aborigines suspected opal to be a devil luring men to their destruction. Minerals have assumed increasingly complex mythical properties over time. New Age practitioners wield rose quartz not only to treat physical maladies like kidney disease, sexual dysfunction, and migraines, but also to “stimulate the body’s love centers” to convert negative emotions to positive ones, calm hot tempers, and improve mental discipline and tranquility.

But these are not the myths that Caltech professor of mineralogy George Rossman (PhD ’71) and member of the professional staff Chi Ma, who manages the Geological and Planetary Sciences (GPS) Division

Analytical Facility, typically confront. Rather, they seek to dispel less obvious misapprehensions—speculations and inferences on optical phenomena in minerals that have become groundlessly entrenched in the scientific literature. To do so, they pursue the true origins of color, opalescence, and rare patterns like stars, flames, and rainbows. And, if they discover a new mineral while they’re at it, so much the better.



Take the rose quartz from the previous page (well, maybe a less attractive substitute), dissolve it in hydrofluoric acid at 100°C, and all that will remain is a nest of pink fibers. What are those fibers made of? Follow the pink to the next page to find out.

A BOYHOOD DREAM

Rossmann may be one of very few people who now does exactly what he first dreamed of doing, back when he was a kid picking shiny pebbles from the glacial outwash of the last great Ice Age. His love of nature and rocks in general became a fascination with minerals in particular when a grade-school friend gave him some clear, beautifully colored, glassy minerals. Rossmann turned to his teachers for information on these shiny objects, but got no answers. “I knew enough to know that I had to learn chemistry to understand,” he says. “It was a hobby interest; I wanted to know where the pretty colors came from.”

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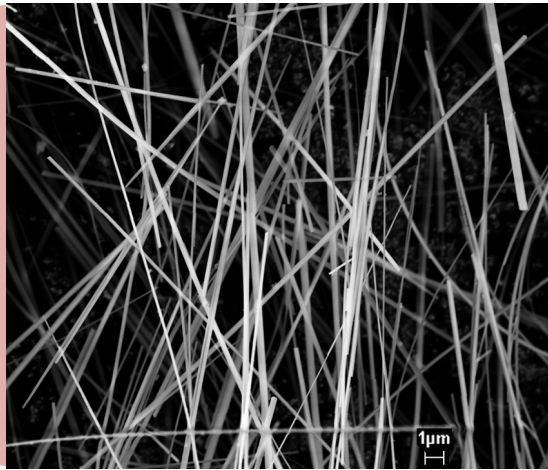
A high-school science project on the response of minerals to a metal detector led Rossmann to a summer NSF program during his undergraduate years at the University of Wisconsin–Eau Claire, in which he explored the oxidation state of one particular iron-bearing mineral. After finishing a double major in chemistry and math, he was caught between grad schools when a cult TV show changed the course of his life. “I had already accepted a famous eastern college,” Rossmann recalls. But then he saw an episode of *The Man from U.N.C.L.E.* in the winter of 1966. It featured the evil agents of THRUSH (Technological Hierarchy for the Removal of Undesirables and the Subjugation of Humanity), who captured young boy geniuses and sent them to a place called Caltech. Rossmann knew it was where he belonged. “My professors recommended it

[Caltech], of course,” recalls Rossmann. But “that stupid TV program” had a lot to do with his decision.

Rossmann became the first Caltech graduate student of Harry Gray, now Beckman Professor of Chemistry, then freshly arrived from Columbia University. Although his thesis molecule was a molybdenum cyanide, he made a more lasting contribution to a definitive understanding of iron-storage proteins in humans. “If you wanted to trivialize George’s work, you could say he figured out why iron rust is red-brown,” says Gray. “He laid out the spectroscopy of iron that allowed us to interpret the structure of iron proteins.” A model of the structure of ferritin stands in the Beckman Institute courtyard today. In a real molecule, which is colored rust brown, the body stores some five thousand iron atoms inside a spherical cavity.

“One of the best times of my life was being a graduate student at Caltech,” Rossmann says. “This is where I learned how to be a scientist.” While his thesis work was only indirectly related to minerals, he “came over and bugged people in geology to run minerals.” That was how the geology department got to know him, and how, soon after his defense in 1971, he came to accept the position offered him by GPS. At the time, most mineralogists were engrossed in crystallography, classifying how atoms are arranged to form minerals. As a chemist, Rossmann brought the tools to uncover how those atoms produced colors. According to one member of the hiring committee, professor emeritus Arden Albee, “I became convinced that spectroscopy, in its broadest sense, was the future of mineralogy and petrology. I think that the appointment of George has worked out very well.” The students seem to agree—they awarded him the Feynman Prize for Excellence in Teaching in 2004. To this day, Gray’s students run experiments in Rossmann’s lab, and Rossmann delivers a special lecture in Gray’s inorganic chemistry class on colors in gemstones.

The Rossmann of today seems to have retained



At 10,000 times magnification, fibers from the pink mat look like rods. But these rods are about one thousandth the thickness of a human hair, and they are made mostly of silicon, oxygen, aluminum, and boron. Further details on these borosilicate rods follows.

many of the traits of the Rossman of 50 years ago, among which is a bubbling, boyish enthusiasm for minerals. His office is cluttered with rare and common minerals—on shelves, on countertops, on the desk, and on newspapers on the floor. The wide, flat drawers that line one side of the room are crammed with minerals, arranged first in alphabetic order by mineral name, and then, within each drawer, in alphabetic order by locality of origin. “Can we find why G. Rossman became a scientist?” he mumbles while poking through one of these drawers. He’s searching for a thumbnail-sized, wedge-shaped slice of watermelon tourmaline also given to him when he was in grade school. He suspects it’s from Southern California, but can’t be sure. To the glassy wedge is glued the number 23, noting its place as the 23rd collectible of Rossman’s youth.

Behind Specimen 23 lie seemingly mythic connections linking the Rossman of yesteryear and today. Rossman’s first trespass of the world-famous tourmaline mines of San Diego-based Pala International—a gem mining, trading, and sales operation—in the waning days of his graduate years at Caltech led to the forging of a lifelong friendship and scientific exchange with the company’s president, Bill Larson. In the 37 years since they first met, Larson has supplied hundreds of various gem and mineral samples to the cause. “I would give him specific mineral specimens that I knew very well where they came from, and he would slice them and dice them and look at them,” says Larson. “A lot of it will go in the collections at Caltech, which will be there for any student that comes after.”

The second uncanny echo between tourmaline and Rossman the mineralogist is the mineral rossmanite. Yes, you read that correctly. Rossmanite is a rare, generally pale pink, translucent variety of tourmaline discovered in the Czech Republic by Canadian mineralogist Julie Selway, and named in honor of Rossman by the International Mineralogical Association in 1998 for his extensive spectro-

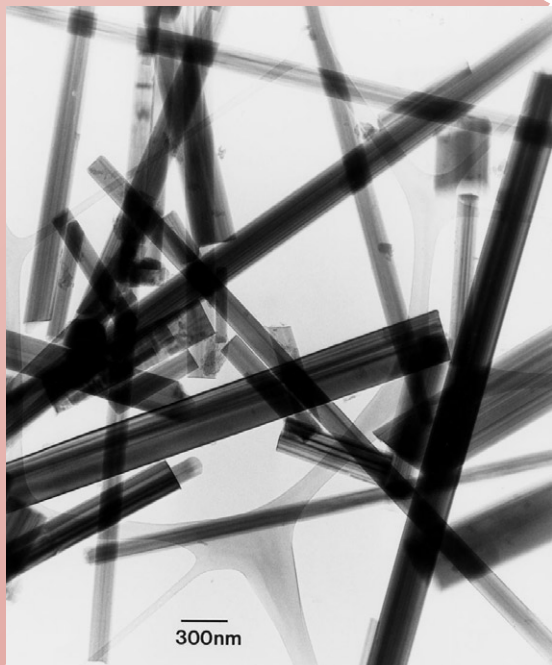
scopic work on this family of minerals. But despite his special affinity for tourmaline, Rossman is loath to name it his favorite. “Don’t you love all your children equally?” he retorts.

Although he has handled some of the rarest treasures of the mineral world, Rossman no longer collects. It might raise suspicions that he was angling to pad his private collection, compromising his fairly unrestricted access to unique samples for scientific testing. Instead, Rossman’s single-minded scientific curiosity—“I have no personal agenda for these things,” he says—has connected him with the world’s top mineral and gem traders, from whom he gets many of his samples. While he chooses his requests carefully, he concedes, “Anything I want from the Smithsonian, within reason, I could have.” Indeed, his former graduate student Liz Johnson (MS ’99, PhD ’03) handled the infamous Hope diamond during an extensive spectroscopic study of the Smithsonian’s diamond collection.

Rossman’s former postdoc Chi Ma says, “If you gave me a diamond, I won’t love it. I’d say, ‘Let’s crack it open and see if there’s a defect,’” but Rossman has a slightly more deferential attitude. “He’s very cautious not to ruin any good crystals,” says Larson. “He knows aesthetics, he knows what a nice mineral specimen is. Now that isn’t to say he wouldn’t break a piece off the back side, from where it’s not seen, and do research on it if he needed it. But he wouldn’t destroy a really good mineral specimen just for science.” Still, some techniques require destruction. “Let’s take one of my beautiful, gem-quality [insert mineral name here], and smash it with a hammer,” seems to be one of Rossman’s favorite phrases.

Larson considers Rossman to be one of the most intelligent men he has ever met, but Rossman is somewhat modest. Recently, when the two gem lovers were lunching at a symposium celebrating the 75th anniversary of the Gemological Institute of America, the guest speaker challenged audience members to rate their intelligence on a scale from

These borosilicate rods (note the scale bar!) are a rare pink variety of the mineral dumortierite, which underlies both the color and the star pattern in rose quartz. But every spectroscopic test performed by mineralogists George Rossman and Chi Ma yielded an imperfect match to the ideal structure of that mineral. Continue along the path for a view of its crystal structure.



one to 10. “And he said, ‘Don’t be shy,’” Larson remembers. “I happened to be at the table with George Rossman and George Harlow [Curator of Minerals and Gems at the American Museum of Natural History], and these guys are seriously intelligent. The guy calls out a 10, and we’re all staring at Rossman, waiting for him to raise his hand, because no one is going to say they’re smarter than George Rossman. He didn’t raise it at a 10. He raised his at a nine, so Harlow and I raised ours at eight, being only a little bit less humble than him.” As the story goes, after the lunch Larson and Harlow asked why he didn’t raise his hand at 10, and to this Rossman responded, “I know Mike Scott.”

Which brings us to the final member of a kind of mineral triumvirate. Michael Scott (BS ’65), the first president of Apple Computer, has amassed what has been called “the most important private gem collection in the United States.” His fascination with colors in minerals led him to Rossman, and his support of Rossman’s work led, in part, to the largest mineral spectroscopy and X-ray database on the Internet. Among Scott’s collection is what Rossman considers to be the finest specimen of star-patterned rose-colored quartz he has ever seen, and this particular piece spurred Scott to fund an epic investigation of the origins of its optical splendors.

MINERALS AND GEMS

What makes a mineral? It’s a fairly simple recipe, for the most part. Take quartz, for example—in this common mineral one silicon atom bonds to two oxygen atoms. SiO_2 molecules bind and repeat, forming interlocking rings that ideally build a hexagonal prism. The silicon-oxygen bond is the building block of 80 percent of all minerals on Earth’s surface—to it attach various other ions in orderly ratios and configurations, dictated by the properties of the elements themselves and by the conditions under which the minerals grow. Sometimes they grow with many other minerals to form rocks, and sometimes they fill fissures in these rocks, forming veins of rare composition that are turned by human hands into highly prized gems. Most minerals host trace amounts of rare elements that impart different colors. Garnet, for example, comes in all hues of the rainbow, the rarest of which is a blue-green found only in Madagascar.

ROSE STARS, SAPPHIRE STARS

Although colorless quartz is common, its rarer forms come in various hues: gray, purple, pink, or shot through with golden needles. The pink variety is rose quartz, and sometimes a sample of this, when polished and rounded into a sphere, will display a star pattern rising, ghostlike, from its center. The most recent edition of the *Manual of Mineralogy*—the manual of almost every undergraduate enrolled in a mineralogy course—reports “small amounts of Ti^{+4} [titanium] appear to be the coloring agent.” Indeed, the origin of rose coloration in quartz has been debated since the 1920s, when mineralogist Edward Holden reported that manganese [Mn^{+3}] was the pigmenting agent. Since then, various oxidation states of titanium and iron have also been called upon to explain the color. As for the star pattern, called asterism, since the 1920s

“When we saw this image, we knew we solved this. Unfortunately, the textbooks haven’t been updated yet.”

The crystal structure of rose quartz’s dumortierite (left), as captured by electron diffraction in a transmission electron microscope, is bigger than the mineral’s ideal structure (right). It’s a new find, which Rossman and Ma nicknamed “dididumortierite.” The numbers represent two of the crystal’s lattice planes.

mineralogists have agreed that it arises when light is scattered by inclusions of an oxide of titanium called rutile, which grows as golden needles, arrayed in three crystallographic directions. The *Manual* propagates this idea, and handily ascribes color and asterism to the same source. “It had been assumed, for 100 years, that the inclusions were rutile,” says Ma. It seemed like a safe assertion—rutile is observed and verified at macroscopic scales, after all, so why shouldn’t it also be present as microscopic inclusions in light-scattering arrays? Case closed.

But in the late 1980s, Kenneth Applin and Brian Hicks of the University of Missouri–Columbia analyzed some pink microfibers they found in rose quartz. Through the technique of X-ray diffraction (XRD), which essentially X-rays a crystal’s lattice structure, they established that the fibers were not rutile, but a boron- and aluminum-bearing silicate called dumortierite. This discovery spurred Rossman to reopen the case, which soon heated up. “I knew rutile was not the cause of the color,” says Rossman. “When I saw the article by Applin and Hicks, I immediately said ‘This has to be it!’” When graduate student Julia Goreva (MS ’97, PhD ’01) came along, they began to tackle the problem.

Together, they dissolved samples from around the world in hydrofluoric acid heated to 100°C, and sample after sample yielded the same thing: a mat of pink fibers.

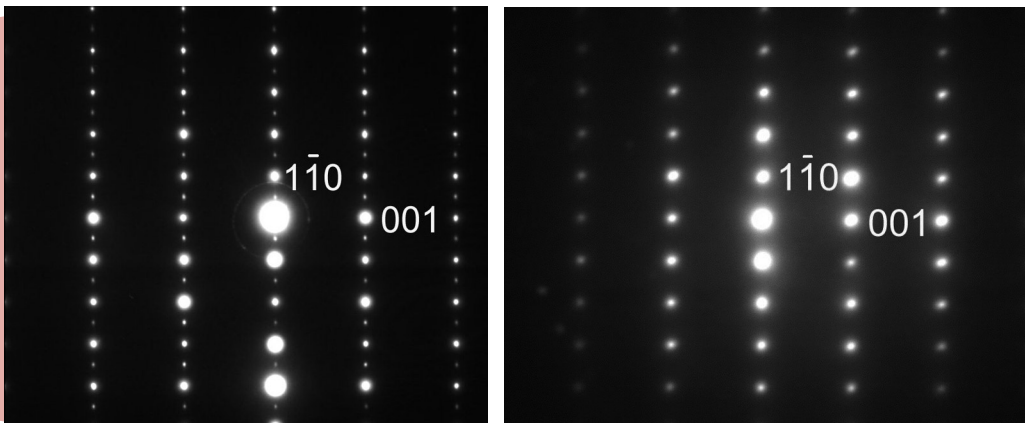
But were the fibers dumortierite? Rossman, Goreva, and Ma hit them with every spectroscopic tool in the arsenal. They imaged them with a Scanning Electron Microscope (SEM) capable of seeing down to 100 nanometers (100 billionths of a meter) in size. To put this into perspective, if you slice a human hair lengthwise into 1,000 strands you are operating at the scale of this instrument. Or, as Rossman puts it, “We’re talking things that are really, really tiny in size.” The SEM repeatedly pointed to the same thing: borosilicate fibers. Infrared spectra, Raman spectra, optical absorption spectra, and X-ray diffraction patterns all closely matched those of natural dumortierite. But the team was not satisfied—the tests showed a close, but not perfect, match.

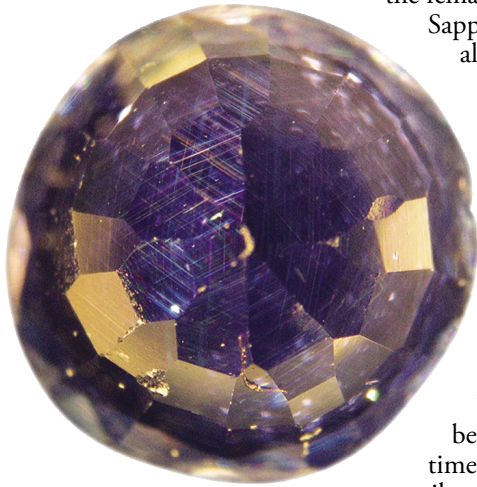
Through Transmission Electron Microscopy (TEM), in which a beam of electrons casts a glowing shadow of a specimen’s atomic structure onto a camera, they found extra spots in the diffraction pattern and finally established that the fibers’ crystal structure was actually bigger than the ideal structure of dumortierite. “We think we’ve found a global property of common, massive veins of rose quartz,” says Rossman, and “a phase previously unrecognized by science.”

“When we saw this image, we knew we solved this,” adds Ma. “Unfortunately, the textbooks haven’t been updated yet.”

You are probably wondering at this point why anyone besides a mineral collector might care about the true origin of color and asterism in rose quartz. If you have a cell phone or a TV, you might be interested to know that natural quartz is the source for the silicon wafers in those gadgets’ electronic brains. But the quartz must be ultrapure, because carefully controlled impurities, called “dopants,” are what make the chips work. Boron is a choice dopant, used to control the depths of junctions between which electricity flows across adjacent semiconductors, so the discovery of boron-bearing dumortierite in rose quartz ruled out this potential source of silicon.

Perhaps the best-known asterated gems are rubies and sapphires—names assigned to red and blue varieties of the same mineral, corundum. (After all, who wants to sport something called corundum on their finger?) Long ago, star sapphires were considered to be portable guide stars, protecting and guiding





A nearly half-carat sapphire from Burma, splayed with rainbowed needles. As with starry rose quartz, needles like these were always assumed to be inclusions of the mineral rutile.

travelers and seekers. More recently, the female supervillain Star Sapphire used the virtually limitless powers of the gem to battle the Green Lantern in the pages of DC comics. But mostly, people prize the jewels for their beauty and rarity. And, as with quartz, rutile needles are found in some corundum. So, says Rossman, “the assertion has been made, time and time and time again, that rutile needles cause asterism in sapphires.” Indeed, the online

encyclopedia Wikipedia reports that “star sapphires contain intersecting needlelike inclusions (often the mineral rutile) that cause the appearance of a six-rayed star-shaped pattern.” After the rose quartz adventure, Ma thought, “Why don’t we find a star ruby with the best effect and take a look?”

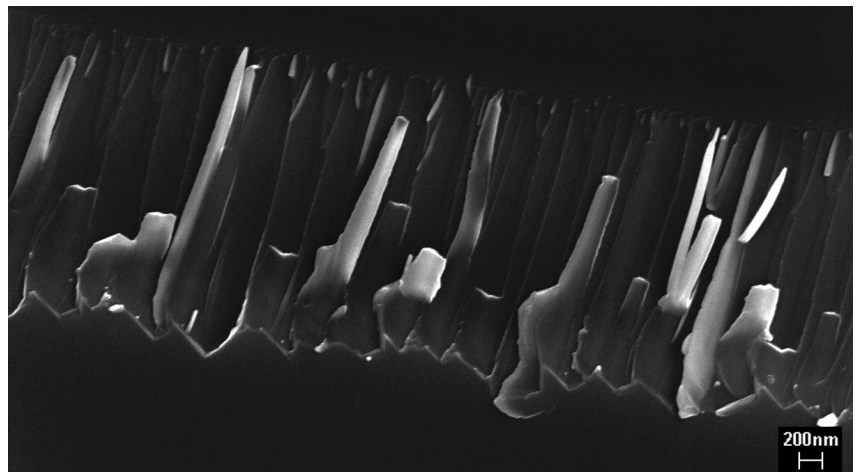
Corundum, like quartz, has an unassuming formula, consisting of two aluminum atoms bonded to three oxygen atoms. Brilliant reds, greens, purples, or blues arise when ions like iron, chromium, vanadium, or titanium join in. However, corundum is often naturally cloudy and therefore unmarketable. “Until about 30 years ago this stuff was virtually worthless, 50 cents a pound,” says Rossman. But then it was discovered that corundum from Sri Lanka clarified upon being heated to around 1,600°C, and that the oxidation state of the gases in the furnaces could be manipulated to control its color. This led to a flood of cheaper sapphires on the market.

It was presumed that heat treatment dissolved rutile inclusions, thereby destroying any possible hidden asterism. This was plausible for Asian gems, which responded well to heat treatment, but not for African stones, which remained stubbornly turbid. So Rossman and Ma cracked open untreated gems provided by dealers and by the Gemological

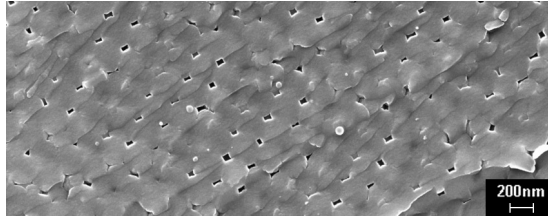
Institute of America from more than 10 different localities, including Vietnam, Burma, Tanzania, and Myanmar. The largest sample was just under one carat. “Ma Chi and I are destroyers. We take beautiful sapphires, and we smash them to pieces,” Rossman says with some glee. “We document it before we crush it,” adds Ma. They searched for rutile with the SEM, but found none, even in the samples that bore wispy rainbow trails. Instead, they found nanovoids in the Asian sapphires and nanoinclusions of something else in the African samples.

“Nanomineralogy—I like this term, so I keep using it,” says Ma. “We’re not like the nanotechnology people, we just use the same tools to look at minerals and find lots of new things,” in this case, nanoinclusions of a hydrous aluminum oxide mineral called diaspore. This discovery was made with yet another camera, the Electron BackScatter Diffractor (EBSD), which detects light diffracted by electrons beamed from the SEM and bouncing around the crystal’s lattice planes.

The pair concluded that the 200-nanometer-wide voids in Asian corundum heal, or anneal, upon heating. But in the African stones, the tiny diaspore inclusions persist through heat treatment, an observation that could save African sapphire dealers some money. “The fact that diaspore doesn’t redissolve when you heat it, like rutile does, is very consistent with the fact that these African rubies simply do not heat-treat, much to the great disgust of the dealers that mine these things,” says Rossman. He hopes this dispels the notion that rutile is the sole cause of optical patterns in gemstones. “To date, we haven’t found one single needle of nanorutile in all the material that’s been sent to us,” Rossman declares.



An inclusion-rich corundum, the aluminum oxide better known as sapphire, magnified 50,000 times. The pillar-like forms are nanorods of the mineral diaspore, made of aluminum, oxygen, and hydrogen. Just as with dumortierite in rose quartz, they are sometimes arrayed in a light-scattering star pattern.



Gemmy Australian opal (topmost) and a 50,000-time zoom-in. This magnified view reveals the origins of opal's iridescence. Regions of well-cemented silica spheres disperse white light into colors of the rainbow.

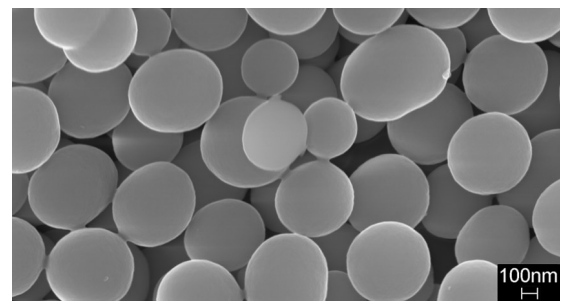
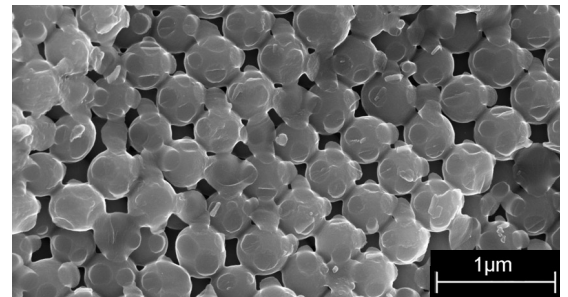
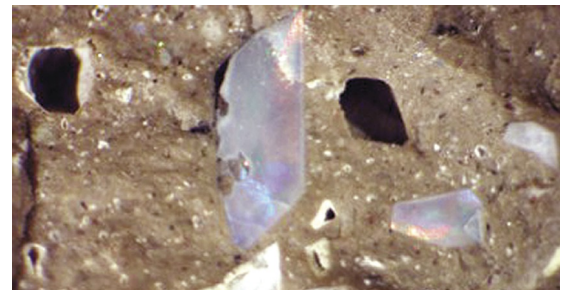
Less commercially appealing opal (below) is found in centimeter-scale pods in ash beds near Tecopa, California. Uniformly sized and regularly spaced silica beads (below middle, at 40,000 times magnification) yield some opalescence. But when the beads are loose and uneven (bottom, magnified 100,000 times), the result is creamy, dull opal.

OPALESCENCE

If a crystal arises from a fairly rigid ordering of atoms, what happens when the atoms are disordered? They form a glassy amorphous blob, which is the case for opal, the unruly twin of well-behaved quartz. Both are SiO_2 , but opal forms silica spheres with water in its structure. The process begins when silicic acid, which is insoluble in water, quickly polymerizes to form spaghetti-like chains of polysilicic acid. In time, these chains grow wide, forming ribbons, and the ribbons begin to wrap and intertwine to form spheres.

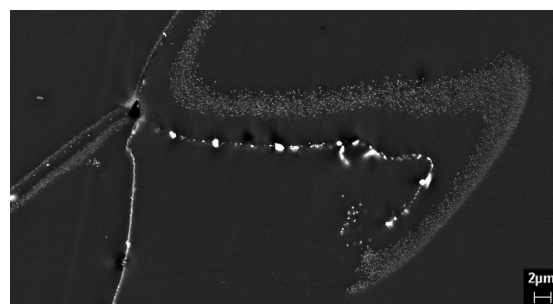
Opal comes in many different colors, and can be clear or creamy, but its most desirable form hosts a resplendent dance. When he was a graduate student in Australia, Ma bought such polychromatic opal earrings for his former girlfriend (now wife), and she lost one. Though he bought her a new pair, the surviving loner didn't last long—he cracked it open and ran it in the SEM at his Australian lab. When he got to Caltech, he showed the photos to Rossman, who wanted to see more. The result was a rigorous documentation of silica spheres in both common and gemmy, iridescent opal. The scientists have also been exploring the properties of the abundant opals in volcanic ash deposits around Tecopa, near Death Valley, which are often creamy but sometimes occur as gemmy centimeter-scale pods.

The play of light in gemmy opal arises when uniformly sized and packed silica spheres are cemented into centimeter-scale domains that act as diffraction gratings, dispersing white light into its spectral colors. In contrast, as Ma describes, “loose beads just give a kind of creamy color,” because the light scatters randomly among the irregularly distributed nanobeads of common opal. While this quickly became obvious with some of the first-ever SEM scans, Ma and Rossman recently shot what they are told are the best photos ever taken of opal, providing what Ross-

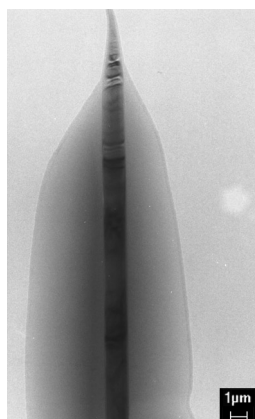
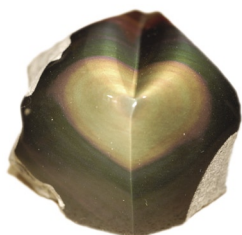


man reports as “an eye-opening view of the kinds of things you can see” with the SEM. Through a connection to the Ontario Science Centre in Toronto, Canada, thanks to student Shenda Baker (PhD '92), these images were commissioned for Zoom!, a recent exhibit highlighting views of the micro- and nanoworld.

Most obsidian in the field is pretty unattractive (top left, from Glass Buttes, Oregon), but sometimes a rare find is made. Fire obsidian, which shimmers colorfully under direct light (top right), is streaked with grey and brown “flames” under transmitted light (middle). What makes the flames? Nanoparticles of an iron oxide called magnetite, suspended in waves through the glass (bottom).



The author’s piece of rainbow obsidian, carved into a heart, is just a black blob until light is focused on it (top). The rainbows arise when nanorods of the mineral pyroxene align in just such a way as to set up light-interference.



RAINBOWS AND FIRE

Iridescence is simply the way colors dance about when light hits a surface at different angles. A rainbow emerges from a single drop of oil on a wet street—upon hitting the thin, greasy film, light splits into its individual components, from yellow to orange, red, violet, and blue, because a light wave moves slower in oil than it does in the underlying water. Depending on the thickness of the film, the wavelength of light shifts, so that yellow appears in the thinnest regions of the film and blue in the thickest.

The same process takes place in certain minerals, but the underlying causes have been somewhat mysterious. But Rossman and Ma are open to challenges from anyone who sends them samples, and from these interactions some remarkable discoveries have been made.

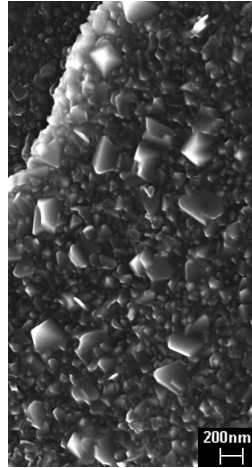
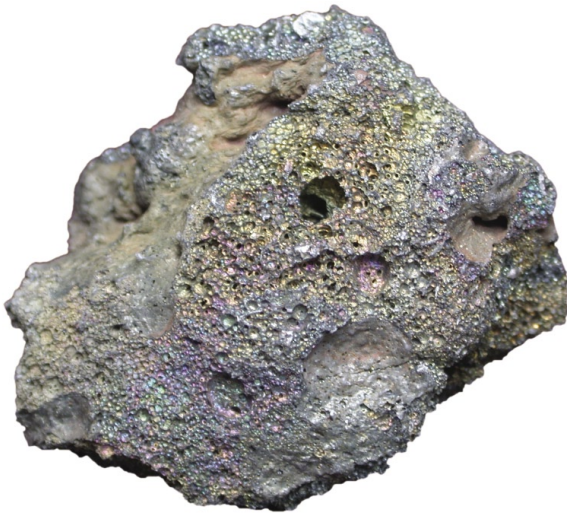
OBSIDIAN

One of their first challenges came in the form of obsidian. Obsidian is a glassy, silica-rich mass that erupts and solidifies almost instantaneously in the earliest stages of an explosive volcanic eruption. Because the material cools so quickly, it has no time to organize its elements into a lattice structure, and forms a noncrystalline glassy mass, which is typically black. But gem and mineral shops often sell worked pieces of Mexican obsidian displaying rainbows of pastel blue, green, purple, pink, and yellow. After SEM and TEM investigations, Rossman and Ma discovered that thin-film interference was at play. Within the glassy matrix of obsidian, nanorods of a calcium- and iron-bearing pyroxene mineral were oriented in just such a way as to set up light-interference.

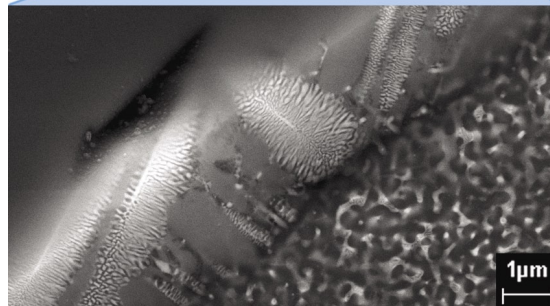
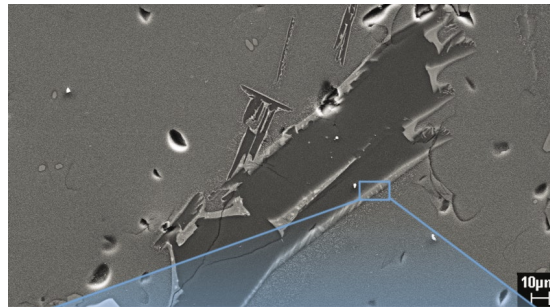
Their work on the rainbow obsidian sparked the interest of James Miller, a geologist with GeoEngineers Inc., based in Redmond, Washington. Miller

is an avid “knapper,” meaning he chips stone to make tools, the very old-fashioned way. And during a search for material, he came across some obsidian in Glass Buttes, Oregon, that shimmered colorfully in direct light. It didn’t look like rainbow obsidian, but instead hosted flame-like patterns in the glass. Wanting to know more, he sent a few samples to Ma; the result is an upcoming paper in the journal *The Canadian Mineralogist*.

Under bright light, fire obsidian reflects brilliantly colored streaks resembling an iridescent oil slick. When thinned to a translucent blade, dark, wispy flames can be seen through the glass. Rossman suspected the layers of “fire” were made of tiny particles that increased the refractive index in the layer, giving rise to another manifestation of thin-film interference. “Out of curiosity, we said, ‘Well, let’s take a look at it and find out what it is,’” he recalls. At 100,000 times magnification, they found their answer—a wave of white, snowflake-like nanoparticles were suspended in the glass. EBSD analyses revealed that these flakes were the mineral magnetite, an iron oxide. Prior to these studies on rainbows and flames, it had been assumed that both these effects were produced by bubbles of trapped air aligned in layers. Another scientific myth dispelled.



Iridescence covers basalt from Pisgah Volcano just as an oil slick on water does. The color comes from thin-film interference, in this case provided by 200-nanometer octahedral crystals of magnetite, seen here at 50,000 times magnification.



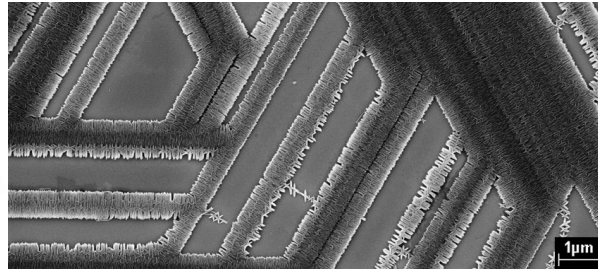
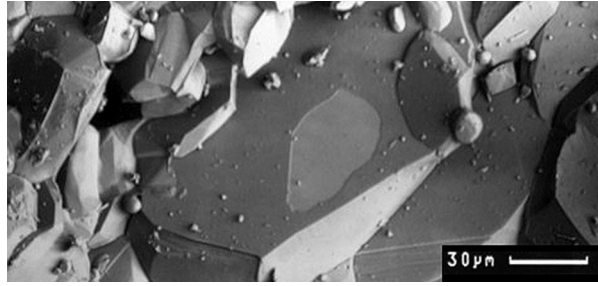
BASALT

Just last year, during a field trip to Pisgah Volcano in the Mojave Desert, Rossman picked up some solidified lava—called basalt—that was covered with an iridescent sheen. Under the tenfold magnification of his field lens he saw that the color was concentrated in some kind of surface froth coating the basalt. “And layers are what it takes to give rise to iridescent phenomena; layers on the order of a fraction of a micrometer,” he thought. So what was in those bubbles? At 50,000 times magnification, and with the help of an X-ray diffraction pattern, he got his answer. They were coated with 200-nanometer octahedral crystals of magnetite.

This discovery led to the next—the origin of the blue color in the “Blue Dragon” basalt of Craters of the Moon National Park in Idaho. At 20,000 times magnification under the SEM, bush-like patterns began to appear in the amorphous glass of the basalt. These proved to be crystals of titanium-bearing magnetite, just a few tens of nanometers thick, arrayed in branching patterns. The blue color arises from a charge transfer between iron and titanium, the same principle that colors sapphire blue. “Again, I’ve seen nothing comparable to this in the literature,” says Rossman. Ditto for the iridescent basalt.

Craters of the Moon National Park in Idaho is home to the rare “Blue Dragon” basalt (top). At 1,000 times magnification (middle), the origin of the blue color appears, in a thin layer coating the sample. Zooming in, to 20,000 times (bottom), reveals the layer consists of branching blobs. These are made of titanium-bearing magnetite, each branch a scant tens of nanometers thick.

Rainbow hematite (far left) is fairly common, but the root of its iridescence was a mystery, until recently. At fairly low magnification, a hole reveals that the specimen is coated with a very thin layer (top). The layer, magnified 20,000 times, resolves into a grid-like network of nanorods that clump together to form larger rods, sometimes aligned in rows and sometimes arrayed in star-like patterns (bottom, at 200,000 times magnification). At around 10 nanometers long, the nanoparticles are too small to determine an exact chemistry, but their rough compositions indicate a never-before-seen form of aluminum phosphate.



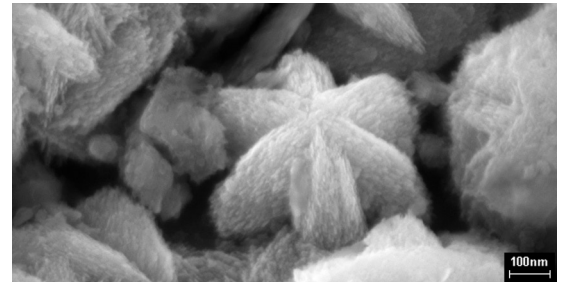
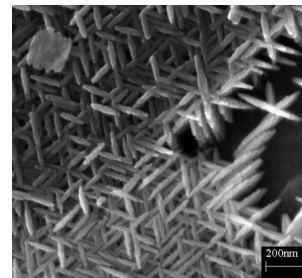
RAINBOW HEMATITE

Hematite, yet another iron-oxide mineral, is the main source for iron, and can also occur in a highly iridescent form. “We got pretty curious—what’s going on here?” Rossman recalls. “It’s so visually attractive, it was obvious that we should take a look at it.” At low magnification, Rossman and Ma found that the crystals of hematite had some sort of coating, with a hole through the coating clearly indicating its extreme thinness. The chemistry of the coating indicated an aluminum phosphate with “a very unusual aluminum-to-phosphorous ratio, unlike anything that’s known,” Rossman says. “So here we have an interference phenomenon, a thin layer of aluminum phosphate. End of story? No.”

At 20,000 times magnification, they found orderly lines of submicron-sized crystals arranged on the hematite like grids on a circuit board. At 85,000 times magnification, the grids resolved into individual rods, sometimes lined up in orderly rows, sometimes crisscrossing each other in star patterns. Their shapes are well defined, but the exact chemistry is difficult to determine, says Ma, because at 10–15 nanometers long and only five nanometers wide, they are “too damn small to get an XRD or EBSD pattern.” They have found the same nanocrystal growths in all the samples of rainbow hematite they have tested, from Georgia to Alaska to Brazil. And, says Rossman, “We believe that this is a new phase, previously unknown to science.”

DISCOVERIES

Many of Rossman’s and Ma’s discoveries have been made by pure chance with their powerful tools. “I don’t say, ‘Today, let’s try to find a new mineral,’” says Ma. But looking where no one has looked before often reveals things that have never been seen, and the pair are finding new



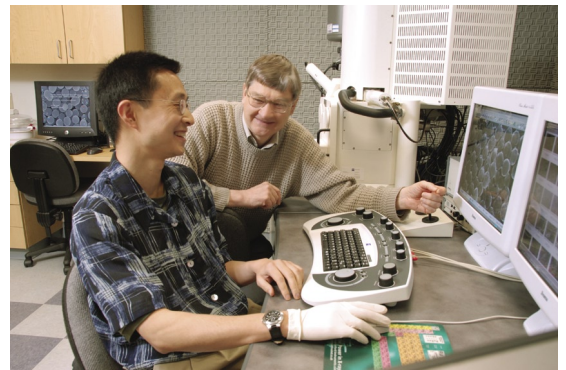
minerals with geological significance, one after the other. “Nanoscience opens up new possibilities in exploring the natural world,” Rossman says. When Ma was navigating the atomic structures of various forms of natural dumortierite in rose quartz, for example, he came across the most barium-rich specimen of a particular variety of the mineral mica. He has also recently discovered a natural occurrence of a mineral—just approved by the Mineralogical Society of America and pending public announcement by formal publication—whose only previously known form was a synthetic one fabricated for use in electronics like ultrasound machines. These discoveries speak to the broader appeal of nanodetectors, and a few years ago the GPS division, in collaboration with the materials science subdivision of Caltech’s engineering and applied science division, used part of their \$9.6 million NSF Materials Research Science and Engineering Center award to buy a brand new

SEM. One hundred times more powerful than the previous generation—it can see at the scale of one nanometer—and with various analytical attachments scrutinizing the material under observation, the machine is used by more than 200 scientists across the Caltech campus, from more than 40 research groups and from all disciplines except the social sciences and math. Materials scientists are particularly interested in nanodeposition and the study of electrical properties of synthetic materials at this scale.

These tools open all sorts of other intriguing avenues in research. In 1999, the White House invited Rossman to a conference (in the Old Executive Office Building) on “conflict” diamonds—those dubious diamonds that might have funded wars or terrorist activities and recently gained notoriety through the movie *Blood Diamond*. Instead of focusing on tracing techniques that invariably called for the gems’ destruction, he and Professor of Geochemistry John Eiler concentrated on looking at the isotopic properties of the dirt caught in microcracks in the stones. Although the program disappeared with the inauguration of the George W. Bush administration, Rossman remains interested in the problem.

But these days he’s focused on figuring out exactly how much water is bound up in minerals 100 kilometers below Earth’s crust, in the mantle. Scientists have long known that there is enough water down there to have serious implications for processes like how rock is moved around in the mantle and up to the surface, driving plate tectonics, but until now they have avoided tackling the issue of how much water there is. Rossman decided to take it on, and his studies brought him to the nuclear magnetic resonance imager in the sub-basement of the Sherman Fairchild Library. There he imaged the structure of miniscule amounts of water in what are considered basically dry minerals. What he found indicates that mantle-bound water could exceed that of all our oceans, which suggests

a deep-Earth reservoir for the entire global water system. “I took it upon myself to turn this into a quantitative problem, rather than a ‘here it is’ problem,” Rossman says. And this is, after all, how real scientific adventures begin. □



Chi Ma and George Rossman laugh as they invent fantasy lives for opal’s silica spheres, imaged by the scanning electron microscope behind Rossman. Before them is a nanoview of gemmy opal, while the background screen (behind Ma) displays the loose beads of creamy opal.

Mike Scott’s gems and minerals will be on display from June 2007 until August 2008 at the Bowers Museum of Cultural Art, 2002 N. Main St., Santa Ana, CA 92706. For more information, call them at (714) 567-3600 or visit their website, <http://www.bowers.org>.

PICTURE CREDITS: 10—Harold & Erica Van Pelt; 11-19—Chi Ma & George Rossman; 17—James Miller; 17, 19, 20—Bob Paz, 18—Teresa Petrykowski & Sterling Udell