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PHYSICS

In a Grain, a Glimpse of the Cosmos

When scientists traced a museum rock back to its origins, they uncovered mysteries about the early solar system.

Yuta Onoda for Quanta Magazine

By: Natalie Wolchover

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Comments (4)

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One January afternoon five years ago, Princeton geologist Lincoln Hollister opened an email from a colleague he'd never met bearing the subject line, "Help! Help! Help!" Paul Steinhardt, a theoretical physicist and the director of Princeton's Center for Theoretical Science, wrote that he had an extraordinary rock on his hands, one that he thought was natural but whose origin and formation he could not identify. Hollister had examined tons of obscure rocks over his five-decade career and agreed to take a look.

Originally a dense grain two or three millimeters across that had been ground down into microscopic fragments, the rock was a mishmash of lustrous metal and matte mineral of a yellowish hue. It reminded Hollister of something from Oregon called

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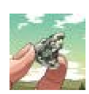
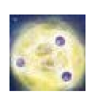

In a Grain, a Glimpse of the Cosmos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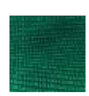
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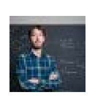

A New Physics Theory of Life

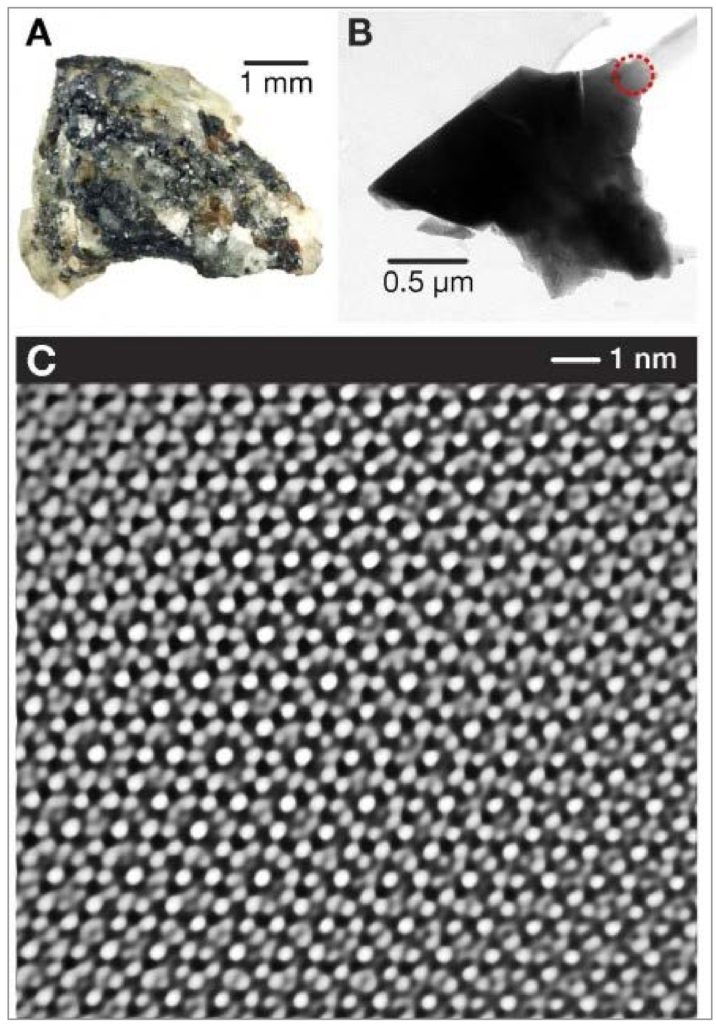
josephinite. He told Steinhardt that such rocks typically form deep underground at the boundary between Earth's core and mantle or near the surface due to a particular weathering phenomenon. "Of course, all of that ended up being a false path," said Hollister, 75. The more the scientists studied the rock, the stranger it seemed.

A Jewel at the Heart of Quantum Physics

After five years, approximately 5,000 Steinhardt-Hollister emails and a treacherous journey to the barren arctic tundra of northeastern Russia, the mystery has only deepened. Today, Steinhardt, Hollister and 15 collaborators reported the curious results of a long and improbable detective story. Their findings, detailed in the journal Nature Communications, reveal new aspects of the solar system as it was 4.5 billion years ago: chunks of incongruous metal inexplicably orbiting the newborn sun, a collision of extraordinary magnitude, and the creation of new minerals, including an entire class of matter never before seen in nature. It's a drama etched in the geochemistry of a truly singular rock.

"It is telling us there appear to be processes that took place in the early solar system that we were completely unaware of," said study co-author Glenn MacPherson, a senior geologist at the Smithsonian Institution in Washington, D.C. "It's going to be a burr under the skin of quite a few people, trying to understand this rather peculiar mystery."

Discovered in 2008 in the basement of a geology museum in Florence, Italy, in a box labeled "khatyrkite," the specimen boasted magnificent patches of quasicrystal, a special state of matter that had been created in laboratories but had never been seen in nature. From ice to diamonds, all crystals in the universe exhibit 14 types of symmetries — ways their atomic lattices can be rotated, translated or reflected into indistinguishable positions. Quasicrystals, in which atoms are arranged in orderly patterns that never exactly repeat, have an infinite number of possible symmetries. Until their highly disputed discovery in synthetic materials in 1982 (for which the Israeli scientist Dan Shechtman received derision and, 29 years later, the Nobel Prize in chemistry), such states of matter were widely deemed impossible. Even in 2009, they remained lab-grown curiosities. If the Florence specimen formed in nature, it would contain the first natural quasicrystal ever discovered — something Steinhardt has been doggedly pursuing for 10 years.



Bindi et al.

A khatyrkite-bearing rock sample (A) found in the collection of an Italian museum six years ago contains granules of icosahedrite (B), the only known natural quasicrystal. The quasi-periodic,

While analyzing the specimen, Hollister noticed that the dazzling pattern of the quasicrystal contained metallic aluminum, a substance that never occurs naturally on Earth because of how easily it binds with oxygen to form aluminum oxide. Metallic iron, also present, is almost as rare. Stranger still, the rock contained copper. Except for rare encounters in human-made alloys, aluminum and copper don't mix. Whereas aluminum bonds with oxygen and resists water, copper bonds with sulfur, dissolves in water and washes away. "Most known processes separate copper from aluminum," Hollister said. "Man can put these elements together, but nature takes them apart."

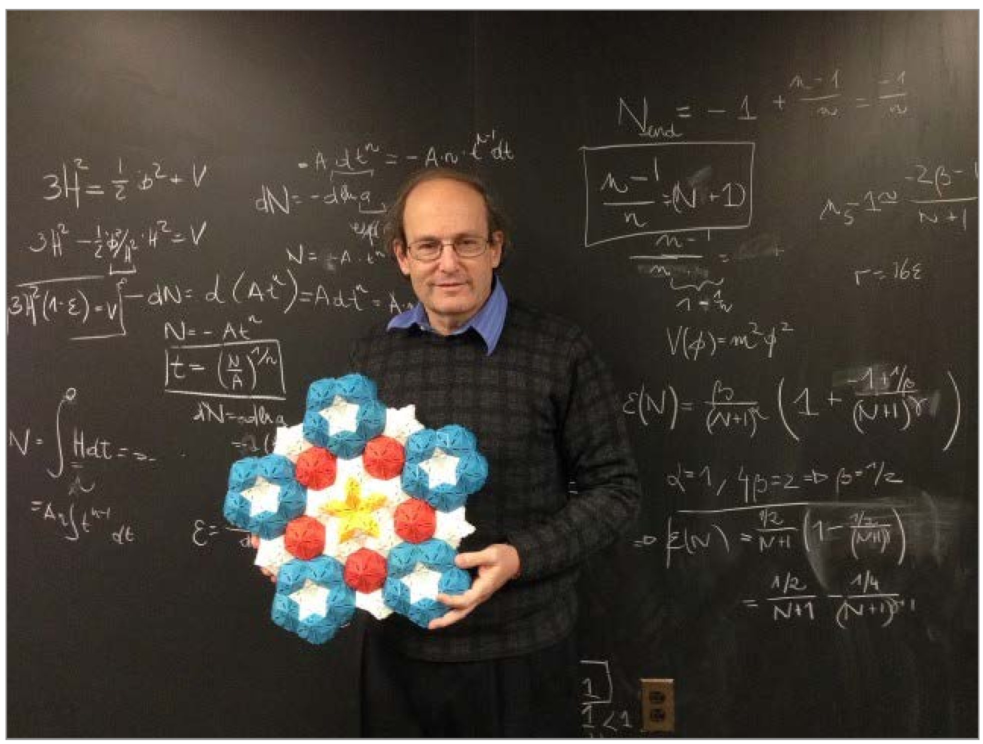
Like the many peculiar nuggets picked up near the iron furnaces in Trenton and delivered like offerings to his office, Hollister thought the sample must be slag, the solid waste that metal factories sometimes release into the environment. If it had come from an aluminum smelter, the presence of quasicrystals fivefold symmetric pattern of the atoms in the granule is shown in (C), generated from a high-resolution transmission electron microscope scan of a subregion of the granule.

wouldn't be so surprising. Since their discovery 30 years ago, more than a hundred types of quasicrystals have been forged in laboratory settings.

Steinhardt was devastated by Hollister's slag assessment. So was Luca Bindi, an Italian mineralogist who had spent years analyzing rocks in the collection of the Florence Museum of Natural History before shipping the promising khatyrkite sample to Princeton. If the rock couldn't have formed on Earth, then, they wondered, how about in space? Steinhardt paid a visit to MacPherson, a former student of Hollister's, who specialized in meteorites. But MacPherson immediately seconded Hollister's opinion that the sample was synthetic. It was like no meteorite he had ever seen.

Fazed but still not ready to give up on nature, Steinhardt and Bindi, with Hollister's assistance, spent the next few months analyzing trace minerals in the grain one by one and researching industrial processes that might have yielded them. To their delight, the rock grew less anthropogenic by the day. Strewn with funny islands of rare and even unknown minerals, it had evidently coalesced under extreme and tumultuous conditions. Finally, one mineral gave the scientists their answer. Surrounding a patch of quasicrystal was stishovite, an ultra-high-pressure form of quartz. "This is not something that is made in an aluminum smelter on the surface of the Earth," Hollister said. Stishovite could only have formed deep inside the mantle or during an outer-space impact.

A New Mineral



Natalie Wolchover/Quanta Magazine

Paul Steinhardt, a professor of physics at Princeton University, with a constructible model of a quasicrystal.

Steinhardt, a 61-year-old professor who radiates a quiet intensity, has studied the theory behind quasicrystals since before they were known to exist. Whereas a crystal can be understood as a motif of atoms repeating with a certain frequency in space, a quasicrystal involves two or more frequencies and their ratio is an irrational number, like the square root of two or the golden mean. The combination of the frequencies never exactly repeats and, therefore, neither does the pattern of atoms. "It's kind of a disharmony in space," Steinhardt explained this winter in Princeton, carefully handling a plastic model of a quasicrystal that he keeps on his desk. Like disharmonious musical notes conspiring to create a recurring but noncyclical progression of sounds, "you'll see arrangements of atoms that seem similar," he said, "but when you look at what's around those atoms, you'll see it's a little bit different here than there." The lack of exact repetition allows quasicrystals to have any possible rotational symmetry. The Florence specimen exhibited the symmetries of an icosahedron, a soccer-ball-like atomic arrangement that can be viewed from 60 different angles without any change to the structure's overall orientation.

It isn't clear why quasicrystals form. "We do not know how these atoms select such a complicated structure," said An Pang Tsai, a materials scientist at Tohoku University in Japan who has studied the question for more than 25 years. One idea, developed in the 1980s by Steinhardt and his student Dov Levine, now a theoretical physicist at Technion University in Israel, holds that the atoms in quasicrystals might first cluster together into pentagons, decagons, or a potentially infinite variety of other shapes, and that these clusters then follow specific rules governing how they align with their neighbors — analogous to the geometric rules that govern Penrose tilings — which lock them into irrational, non-repeating patterns. An alternative theory holds that quasicrystals assemble randomly: The atoms form symmetric clusters that then arrange themselves in arbitrary ways. If this theory is correct and there are no forces dictating how adjacent clusters must join together, this would mean that quasicrystals are not completely stable. “Over time they will decompose,” said Michael Widom, a physicist at Carnegie Mellon University in Pittsburgh, Pa., who helped develop this “entropic” theory.

Motivated largely by this debate, Steinhardt and a few colleagues began searching for a natural quasicrystal in 1999. The discovery of such an object would expand the list of classifications of minerals from 230 — the total possible combinations of those 14 crystalline symmetries — to infinity. It could point to exotic geologic processes involving unknown extremes of pressure or cooling. And most importantly, it would support Steinhardt’s view that quasicrystals are true, stable states of matter shaped by unknown interatomic forces rather than random assemblages of atoms that eventually decompose. “For Paul, it was crucial to know whether this material was stable for geologic periods of time,” Hollister said.

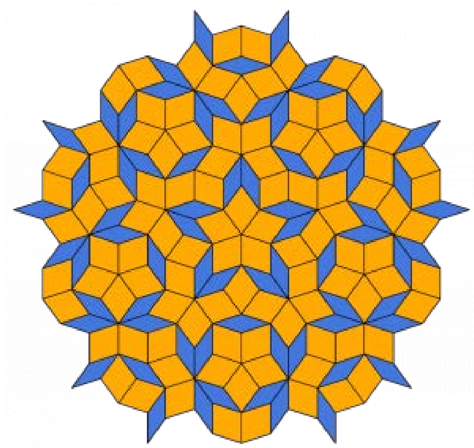
After years of failed searches punctuated with false positives, the presence of stishovite in the Florence specimen meant vindication: The rock and the quasicrystal it contained were natural, proving that at least some quasicrystals remain stable for far longer than physicists had been studying them in the lab. “The striking thing about it was it was perfect,” Steinhardt said. “A beautiful, unmistakable pattern.” In 2010, after the scientists spent months presenting their evidence to colleagues, the International Mineralogical Association accepted the Florence quasicrystal — $Al_{63}Cu_{24}Fe_{13}$, or icosahedrite — as a new mineral.

Still, a big question remained, Steinhardt said: “How did nature manage to do this?” He sent the sample to the California Institute of Technology for an analysis of its ratio of three isotopes of oxygen, which serves as a unique fingerprint of everything in the solar system. Sure enough, the rock had the oxygen fingerprint of a meteorite, and a rare and old kind, too: a CV3 carbonaceous chondrite. As the sole artifacts from the era of the sun’s birth more than 4.5 billion years ago, these meteorites “provide us with unique clues to that time and place” and are of “special interest” to experts, said Peter Buseck, a professor of chemistry at Arizona State University. A CV3 carbonaceous chondrite called the Allende meteorite that fell to Mexico in 1969, often described as the most studied meteorite in history, contained metal isotopes that suggested the gravitational collapse of gas and dust that created the sun may have been triggered by a shockwave from a nearby supernova.

But according to MacPherson, a leading expert on carbonaceous chondrites, the Florence sample was like none other known to science, even discounting the presence of quasicrystals. “This is the only meteorite that has any metallic aluminum in it, period,” he said. “We’re dealing with a statistic of one.”

Even that number was overstating the situation, as years of tests had reduced the sample to dust. “We had to get it in context in order to figure out how it formed, because that became the big question,” Hollister said. “First it was controversial if it

Penrose Tilings



In the 1970s, the British mathematical physicist Roger Penrose showed that it is possible to completely tessellate two-dimensional space with tiles of two different shapes arranged in non-repeating patterns. These “Penrose tilings” could be constructed by marking the edges of the tiles according to their shape and placing tiles next to one another only if their markings matched up. (The ratio of the two tile shapes was an irrational number; otherwise, the pattern would repeat.) Steinhardt and Levine later argued that clusters of atoms could behave the same way, exerting forces on neighboring clusters that are analogous to the tiles’ “matching rules.” The interatomic forces would lock the atoms into a quasi-periodic arrangement. This class of matter, dubbed quasicrystals, also gave rise to a new particle, a ripple of energy called a phason that momentarily inverts clusters of atoms, violating their matching rules, as it sweeps through the material.

was natural. Then we found unambiguous meteorite signs, but then the question is: What does it tell us about processes in outer space?"

The scientists needed more material, and so they had to retrace their sample's path back to its source. "We had to discover how the rock managed to get to the museum," Steinhardt said. "All we had was a box."

Secret Secret Diary

A letter in the museum archives explained that the box had been bought in a bulk allotment from an Amsterdam collector named Nicholas Koekoek — a man with no Internet presence and a common Dutch surname. It seemed like a dead end, until a fortuitous dinner in Florence three years ago. Bindi was regaling his companions with the quasicrystal story when an acquaintance at the table remembered that an older woman named Koekoek lived on her street in Amsterdam. When the acquaintance returned home, she asked her neighbor about the gem dealer who shared her last name. Remarkably, Nicholas Koekoek was the old woman's deceased husband. Bindi hopped on a plane to Amsterdam.

Courtesy of Paul Steinhardt

In 2011, a 13-person crew including MacPherson (second from left), Bindi (center), Steinhardt (fifth from right) and Kryachko (third from right) navigated a pair of snowcats across hundreds of miles of barren tundra in far-eastern Russia in search of a unique meteorite.

The widow knew nothing of khatyrkite, but she offered to let Bindi look through her husband's "secret diary." In it, Koekoek explained that he had purchased the mineral from a man named Tim during a trip to Romania in 1987. But where had Tim obtained the mineral? "We spent six weeks trying to find him and didn't get even a smidgen of a hint," Steinhardt said. "I sent Luca back to this woman to see if she knew anything about Tim the Romanian. She didn't. But she revealed that her husband used to keep a secret secret diary."

That diary revealed that Koekoek had actually purchased the mineral from Leonid Razin, then the director of the Institute of Platinum in St. Petersburg, Russia. It was a name Bindi recognized. In 1985, Razin had scientifically reported and characterized the only other genuine example of khatyrkite known to exist — the "holotype," or world standard, which was discovered near the Koryak Mountains in far eastern Russia and is kept in a museum in St. Petersburg. It seemed that the holotype and the Florence specimen were found together, and that Razin had studied the former and sold the latter. But when Steinhardt tracked down Razin and called him up at his new home in Israel, Razin said he didn't remember how he had acquired the khatyrkite.

Again, the trail went cold. Out of ideas, Steinhardt returned to the 1985 paper in which Razin reported the discovery of khatyrkite. The first paragraph mentioned a man named Valery Kryachko who seemed to have played a role in the discovery. Contacts told Steinhardt that Kryachko was probably an untraceable rural miner who had picked up the khatyrkite while panning for minerals on behalf of the Institute of Platinum. But not long after, while idly perusing Russian mineralogy journals in search of more leads, Steinhardt spotted Kryachko's name among the authors of a different paper from 1995. "Suddenly we went from nothing to maybe, maybe, maybe this is our guy," Steinhardt said.

The scientists found Kryachko in Moscow. An enthusiastic mineralogist in his 60s, he explained through Google Translate that Razin had indeed hired him to mine for platinum back when Kryachko was in graduate school. In 1979, he was deposited by helicopter at an obscure stream called Listvenitovyi hundreds of miles from the nearest village and spent several days digging through the blue-green clay. No platinum turned up in the several hundred kilograms of clay he panned, but Kryachko did find a few shiny little nuggets he couldn't identify. He delivered them to Razin and never heard about them again.

Courtesy of Paul Steinhardt

Valery Kryachko, the Russian mineralogist who found the only known specimens of khatyrkite while panning for platinum at the Listvenitovyi stream in 1979, returned to the stream three years ago to look for more of the mineral.

Remarkably, Kryachko could pinpoint the exact location of the stream on a map. It ran through a remote region called Chukotka, an autonomous province with a lower population density than the western Sahara and so far east that, as Hollister put it, "you can see Sarah Palin from there." Chukotka thaws out for just three weeks per year and is accessible during that time only by helicopter or custom-built snowcat trucks. Resembling army tanks, these vehicles can tread on snow, steamroller through dense thickets and float across rivers. "If you had asked most geologists, everyone would agree the chances of finding anything going back was tiny and it was probably a wild goose chase," Steinhardt said. "On the other hand the only way you had a chance was to go with Valery."

In the summer of 2011, a 13-person crew including Steinhardt, MacPherson, Bindi and Kryachko set off in a pair of snowcats from the remote mining town of Anadyr into the newly thawed tundra. As they lurched across the spongy, rugged landscape, the trucks took turns breaking down, and Steinhardt worried that the crew would not have enough time at the stream. After four long days, the caravan at last arrived at the scene Kryachko had described: a trickle of frigid water winding through strange blue-green clay in the foothills of the Koryak Mountains. MacPherson set up a makeshift lab to sort through candidate rocks, and the crew took turns digging and panning, and wielding a modified AK-47 assault rifle to protect the group from the enormous brown bears that roamed the region. That very first afternoon, a shiny rock fragment caught Bindi's eye — a piece of meteorite, he felt sure.

By the tenth day, the crew had panned a ton and a half of clay, which yielded a few kilograms of promising grains. As the scientists broke down their camp and loaded up the trucks, they could feel the air getting colder. "The next day we're driving out over the mountains and we look back and it's all white," Steinhardt said. "We got out literally the day before winter hit."

Freak of Nature

Hollister, who retired from Princeton in 2011 and cited age in staying home from Chukotka, likes to say that space rocks have bookended his career. He began in the 1970s analyzing moon rocks that had been collected by Apollo astronauts. Two years ago, in the very first grain he slid under a microscope from the Chukotka expedition, something reminded him of the Apollo rocks from decades earlier. Creeping through

Quasicrystal Questions

The stability of quasicrystals appears to result from a combination of the theories of entropy and matching rules. "In reality, both theories the sample were crystalline veins made of iron-rich ringwoodite, a high-pressure version of a more common mineral called olivine, much as stishovite is a high-pressure variant of quartz. Ringwoodite only forms from a shock equivalent to more than five million times atmospheric pressure — the kind of jolt moon rocks experienced when, in an event that is believed to have formed the moon, an asteroid impact knocked them loose from Earth. But this time, the presence of ringwoodite didn't make sense. Carbonaceous chondrites formed peacefully, slowly accreting as more and more material clumped together in orbit around the infant sun. "You don't find carbonaceous chondrites with evidence of shock," Hollister said — at least, never with battle wounds nearly this extreme.

The nine grains of meteorite that have been identified thus far among the Chukotka spoils, including Bindi's lucky find on the first day, contain an assortment of unlikely substances, including the natural quasicrystal icosahedrite, other rare aluminum-copper alloys, specks of pure aluminum, and ringwoodite riddling swathes of more common nickel and iron alloys. Hollister, MacPherson and the other scientists have spent the past two years working out a plausible backstory for the peculiar concoction. "That's how we build up our understanding of the evolution of the solar nebula, by looking at these materials and piecing together how they fit into the bigger story of the overall history of the solar system," Steinhardt explained.

Either an epic collision triggered the formation of icosahedrite and the other alloys, or the impact happened afterward. MacPherson is leaning toward the view that the metals formed first in some unknown way in the solar nebula and then experienced shock when the asteroid into which they later became incorporated collided with another. But, he admits, this would make the meteorite doubly remarkable, and "most of us are not real believers in coincidence."

Alternatively, the shock could have jolted the quasicrystal and other aluminum-copper alloys into being, which might also explain why they show telltale signs of rapid cooling (such as strips of aluminum metal extracted from surrounding crystals), as if the rock had suddenly been hurled into space. But it is still unclear how aluminum and copper came together inside iron-nickel alloys in the first place. "Aluminum was forming solids when copper was still a gas," MacPherson said. "That's why this quasicrystal is such a bizarre thing. It opens our eyes to things that we've not recognized before."

Then there is the unprecedented presence of aluminum metal. "No other meteorites have ever even suggested that there was metallic aluminum in the early solar system," said Hollister.

In general, the study authors say, further analysis is needed to understand the processes that led to the formation of the bizarre materials in the space rock, and their implications. "Although the quasicrystals are the big bling factor in this whole project," MacPherson said, "they're actually no longer the mystery. At least not to me. It's how the alloys formed."

Extensive studies in the laboratory by Tsai and others have shown that icosahedrite is almost certainly a stable state of matter, as Steinhardt and Levine have long argued, rather than a random, decomposing aggregate. With the discovery of an ancient example, the evidence is now overwhelming. It "adds an exclamation point to the fact that these are stable," Levine said. And yet, questions remain: Why are quasicrystals stable? What are the forces locking adjacent clusters together? The answers "will give

come into play," said Tsai, who laid out the evidence in a March 2013 review article. The law of increasing entropy drives some of the atoms in the quasicrystal to vibrate and rotate, randomly trying out various configurations and sometimes splitting their time between multiple positions. Nevertheless, most atoms are locked into one definite position. Atomic clusters also overlap each other according to forces that are the physical equivalent of matching rules. But what are these forces? Shared properties of all known quasicrystals suggest that their stability depends on their ratio of electrons to atoms, as if electrons somehow stabilize atomic clusters. "We still don't have a very good physical interpretation," Tsai said. In particular, it is not known why quasicrystal patterns can be described by irrational, competing frequencies. According to Tsai, the solution could be relevant to other peculiar phases of matter, like glass, which is rigid, but resembles a liquid frozen in place.

a new picture of physics," Tsai said, adding that they could have a bearing on the stability of other little-understood phases of matter.

Steinhardt is already thinking about where to look next for more examples of natural quasicrystals, perhaps ones never seen in the lab that could deepen scientists' understanding of their stability. "It could have turned out it was in my backyard and consisted of silicon and oxygen in some strange configuration," he said. "That could still be sitting in my backyard and I just don't know it."

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COMMENTS FOR THIS ENTRY

John Graybosch says:
June 13, 2014 at 9:30 am

Very cool article! An enthralling mystery... Pushing the boundaries of what we think we know is always the best way to learn more. I love the devotion these guys showed too.

Nico says:
June 14, 2014 at 4:00 am

Fantastic story of an improbable adventure!

Nishil Iyer says:
June 15, 2014 at 11:11 am

This story reaffirms the phrase"Man proposes , God disposes". It shows that in this age of technology and human achievemants... nature still manages to dumbfound us!

JJ says:
June 17, 2014 at 11:10 am

This is a wonderful read. I only wish it were longer with more details. What glorious vindication this must be for the scientists who have been arguing for thirty years.

I have been interested in the mathematical aspects of Penrose tiling, and it really astounds me that natural crystals form with similar patterns!

This Valery character seems worthy of a documentary. I love how the distinguished professor of the Institute of Platinum had zero memory of the specimen he sold on the black market years ago, but the mineralogist remembers the exact point in the stream where he found it.

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