

ROCK FROM A HARD PLACE

It was a mineral so remarkable
it shouldn't have existed.
So what on earth had made it,
asks Lisa Grossman



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BY THE time Paul Steinhardt was sure the rock was what he thought it was, there was barely more than a grain of it left. He had to stick the remainder to the end of a glass rod so it wouldn't get lost.

It had taken long enough to get that far. But uncovering this unique rock's true story would take Steinhardt on a journey almost literally to the ends of the earth – and in some sense, beyond.

Neatly dressed, bespectacled and balding, Steinhardt makes an unlikely Indiana Jones figure. His day job is theoretical cosmology. In 2011, he was 58 and had never even been camping.

The obsession that led to his suddenly upping sticks had begun in the early 1980s as a mathematical game. Think of choosing bathroom tiles. Regular, repeating patterns of squares, triangles, parallelograms or hexagons joined edge to edge will fill the wall or floor just fine. But any other shape will leave gaps.

Or you can relax the rules a little. Allow the tiles to make patterns that are ordered, but don't repeat, and you can fill a wall completely with pentagons, trapezoids and any manner of other regular shapes. Mosques built as early as the 15th century use this sort of "quasi-periodic" tiling pattern. The tilings invented by the physicist Roger Penrose are a famous modern example (see diagram, page 41).

Steinhardt wondered whether similar patterns were possible in three dimensions. It wasn't an entirely idle speculation. Viewed through an electron microscope, any crystalline solid, from diamond to silica to graphite, produces characteristic diffraction patterns corresponding to atoms regimented in regularly repeating arrays, where joining them like dots would create squares, triangles, parallelograms and hexagons. But could you also arrange atoms quasi-periodically?

Eventually, Steinhardt proved theoretically at least that you could, and showed that any such material would make beautiful diffraction patterns utterly distinct from those of regular crystals. He recognised the signature immediately in November 1984, when he read a paper from Dan Shechtman, an Israeli physicist who had been tinkering with making new metallic alloys. "The paper had this pattern, and sitting on my desk we had the same pattern," says Steinhardt. The following month, he and his student Dov Levine published their theoretical findings, including a reference to Shechtman's material, in a paper they called *Quasicrystals: A New Class of Ordered Structures*.

Not everyone was best pleased with the findings. Most notoriously, the Nobel prizewinning chemist Linus Pauling declared that "there is no such thing as quasicrystals, only quasi-scientists". It was only in 1987 that the tide began to turn, when a group at the Massachusetts Institute of

Technology created an alloy of aluminium, copper and iron with an incontrovertibly quasicrystalline diffraction pattern. By 2011, when Shechtman was finally awarded his own Nobel prize, more than 100 different synthetic quasicrystals were known.

They are more than just oddities: the arrangement of atoms within quasicrystals gives them an array of tantalising properties. They are very hard, have low friction and are good thermal insulators. Possible uses include protective coatings on everything from airplanes to non-stick cookware to thermoelectric materials that convert waste heat to electricity. "There are all sorts of potential applications if you could understand more about how these things are made, and how to make them easily," says Paul's son Will Steinhardt, a graduate student in geology at Harvard University.

That was the problem. When researchers tried making quasicrystals in the lab, small fluctuations in temperature or pressure easily nudged the atoms from their delicately arranged pattern into a more conventional crystal structure. They had to be manufactured in finely controlled conditions, which is a slow and expensive process.

Steinhardt senior had a hunch that it didn't have to be that way – and an idea of how to prove it. Finding quasicrystals in nature would indicate there must be a simpler way to make them, one that we might learn to exploit.

Daily grind

It was a quest he had little time for at first. In the early 1980s, he had played a central part in developing a radical picture of the earliest instants of the universe – the theory of cosmic inflation – and that had expanded to fill most of his time. Rather haphazardly, in spare moments, he would request rock samples from museums and evaluate them by eye for signs of quasicrystallinity.

On moving to Princeton in 1998, though, he had access to a new piece of kit: an electron diffraction microscope. With some colleagues, he began to use an algorithm to comb through a database of thousands of diffraction patterns from powdered rocks. Obtaining samples of promising candidates from collections and museums, the team sliced and diced them and pored over them under the microscope to check for quasicrystallinity. "And we failed," says Steinhardt. "Again and again and again."

In 2001, they published a paper announcing their failures, in the hope that someone would step forward with more rocks (*Physical Review Letters*, vol 87, p 275507). For six years, no one did – until Steinhardt got an email from Luca Bindi.

Bindi was head of mineralogy at the Natural History Museum of the University of Florence, Italy, and his specialism was structural >



The quest for quasicrystals led Luca Bindi, Valery Kryachko and Paul Steinhardt (top left, left to right) into the Siberian wilderness

complexity in natural minerals. “The fact that he is the person who answered our call, out of all the mineralogists in the world, was a fantastic piece of luck,” Steinhardt says. “He immediately became fanatically attached to this project. As fanatical as I was.”

Bindi started grinding his way through the rocks in his museum that were already in the database, followed by some that weren’t. One was a mottled mix of white, grey, black and yellow grains about 3 millimetres across – according to its label, a mineral called khatyrkite, from the Koryak mountains in the far east of Siberia.

Khatyrkite had promising chemistry: it contained aluminium and copper, like some of the first lab-made quasicrystals. When ground up, it scored well on the algorithm. Early in 2009, Bindi sent some grains, perhaps a tenth of a millimetre in size, for Steinhardt to test under the electron microscope. Finally, they had a result (*Science*, vol 324, p 1306). “It was absolutely spectacular – as perfect as any quasicrystal I had ever seen,” says Steinhardt.

Unfortunately, the discovery had come at a cost. Bindi’s grinding had consumed most of the tiny sample, and with it vital clues as to its origin. This was much to the disgust of Lincoln Hollister, a Princeton geologist whom

Steinhardt roped into the search. “To discover it, he had to destroy the evidence of how it was made. To me that was blasphemy,” he says.

Over the following year, Steinhardt and his associates examined every remaining particle of the rock to glean what they could, assessing increasingly wild hypotheses for its origin: lightning strikes, hydrothermal vents, volcanoes, slag from industrial aluminium smelting, nuclear explosions. None fitted.

Out of this world

It was a grain they sent away to the California Institute of Technology, Pasadena, to have its oxygen isotopes analysed that provided an inkling of an answer. The isotopic mix precisely matched that of a class of meteorites called CV3 carbonaceous chondrites that date back some 4.5 billion years, to the solar system’s beginnings. That, plus the presence of a silica mineral called stishovite, which forms only at high temperatures and pressures, strongly suggested the mineral had formed in the high-speed collision of two asteroids in space, and subsequently fallen to Earth. It seemed the quasicrystal was indeed natural – but not of this world.

And that was where Steinhardt was in 2011,

with a grain of rock on the end of a stick and a load of unanswered questions. How old was the sample? How had it survived? Was it one of a kind, or was there much more of it? To find out, he would have to go camping.

But first he had to work out where. A label saying “Koryak mountains” wasn’t exactly much help – the range is one of the biggest in Siberia. And a note in Bindi’s records that the rock was one of 10,000 sold to his museum in 1990 by a collector called Niko Koekkoek from Amsterdam was initially no better – the man couldn’t be traced.

Exhaustive investigations did reveal one other sample of khatyrkite. Part of a museum collection in St Petersburg, it was off limits for running through the diffraction microscope. It had been donated by Leonid Razin, a former head of the Soviet Platinum Institute who had subsequently emigrated to Israel. When Steinhardt called him up with the help of a translator, Razin claimed to know nothing about the khatyrkite. Another trail went cold.

Then came a stroke of spectacular luck. Bindi recounted the quasicrystal quest to an acquaintance from Amsterdam. He lived down the street from a lady named Koekkoek – and she turned out to be none other than Niko Koekkoek’s widow. Visiting her in Amsterdam,

Bindi was able to persuade her to share her husband's secret diary – and then a second, even more secret diary. They traced the khatyrkite to a Romanian rock dealer named Tim, who sold it to Koekkoek in 1987. Tim, in turn, had received the khatyrkite from... Razin.

So it seemed their rock and the one in St Petersburg were related. Buoyed by that finding, a bit more detective work led them to the only person in the world who knew where the rock had come from, because he had found it: Valery Kryachko.

The mother lode

Now in his 60s, Kryachko had been working for the Platinum Institute in 1979 when Razin had sent him to the Listvenitovyi stream in the Koryak mountains to pan for platinum. Kryachko had spent days sifting through the blue-green clay, finding gold, mud and other strange, shiny rocks – but no platinum. To prove he really had been panning while he was out there, he had brought some of the strange rocks back with him.

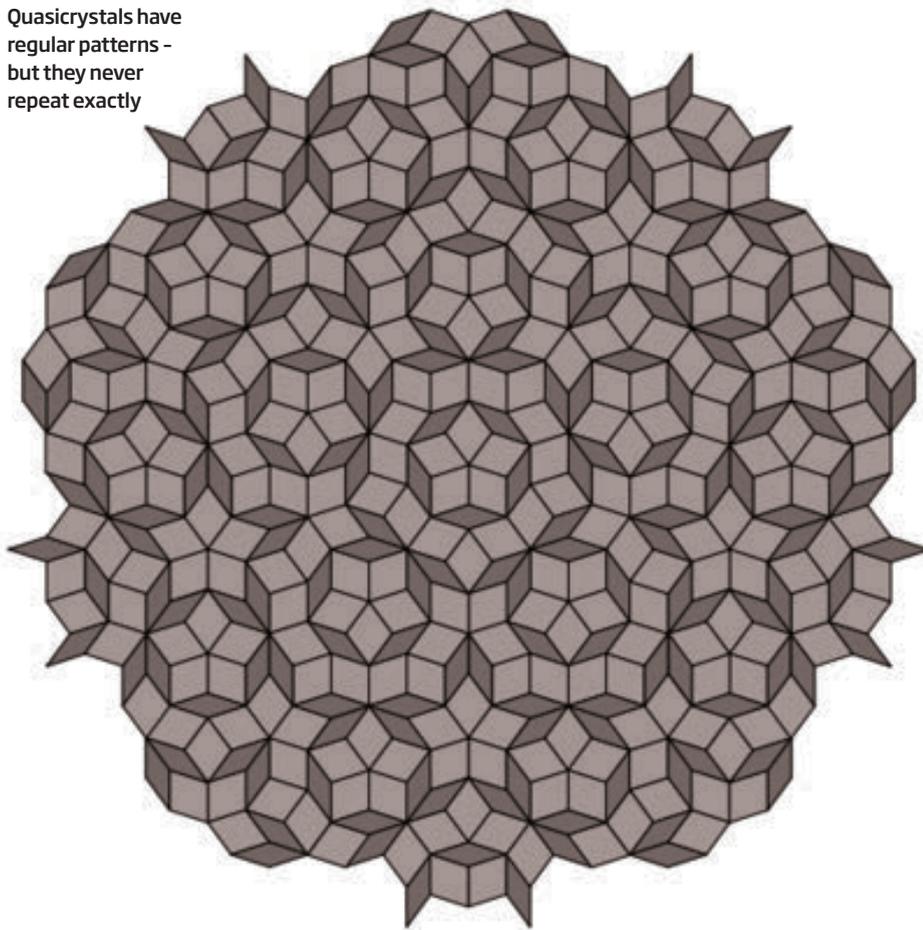
That was the last he saw or heard of them. Razin had taken the rocks to St Petersburg and then sold them on to collectors. "Razin probably thought he was pretty darn clever," says Steinhardt, "but he missed the big lode" – unsurprisingly, given that at the time no one had ever heard of quasicrystals.

At last they had a destination for their camping trip – and soon the money to go there. "It turns out with wealthy people there are two subjects they're interested in: dinosaurs and meteors," says Steinhardt. "We just had to find the meteorite people." And so on 22 July 2011, Steinhardt, Bindi and Kryachko found themselves in Anadyr, an isolated town at the easternmost tip of Siberia, accompanied by Will Steinhardt, six other scientists from Russia and the US, two truck drivers, a lawyer who helped them clear a barrage of legal hurdles and also did the cooking, and the lawyer's cat, Bucks.

Steinhardt senior hadn't expect to go on the trip personally. "Everyone knew the chances of getting even one sample were minuscule," he says. "But at some point, you just have to say, I'm all in. I really didn't know what I was getting into." If they were able to map the region and understand the geological context of the original rock, that would be a success.

They had time to appreciate the context in four days of off-road, mosquito-clouded driving, heading south and west from Anadyr on snowcats, retired military tanks fitted with caterpillar-like treads. They ate mushrooms, canned meat and fish caught from rivers they passed along the way. Finally, they reached the site where Kryachko had found the rocks more than three decades earlier. "We were camping in the middle of nowhere, digging in the mud, but also eating fresh salmon and caviar," says

Quasicrystals have regular patterns – but they never repeat exactly



Will Steinhardt. "It was surreal."

Surreal – and hard work. The dense mud broke two of their shovels on the first day, and they ended up sawing it out of the freezing river with trowels and knives. Boiling and panning through the mud to get rid of the water and the larger rocks left about a thimbleful of fine-grained dust at the end of each day. It fell to Bindi to play the optimist. "I was totally convinced from the beginning that we could be lucky again," he says. "I remember them saying, 'Luca, you see quasicrystals everywhere!'"

Only back in Princeton was he vindicated. The haul of likely suspects included nine grains of meteorite material that had hit Earth's atmosphere between 15,000 and 8000 years ago – and four or five of them contained quasicrystals.

That just raises more mysteries. Besides quasicrystals, the meteorite material contains aluminium on its own, a rare occurrence in nature owing to the metal's deep attraction to

"Boiling and panning through the mud left a thimbleful of dust at the end of each day"

oxygen. Stranger still, it also contains metallic copper, which generally forms in very different conditions from aluminium.

"The quasicrystal is an established part of the story, but how did all its friends get there?" says Steinhardt. One possibility is they came from a large asteroid that was pummelled by smaller rocks, heating parts of it enough to melt aluminium and copper-bearing minerals, liberating them and creating the quasicrystal grains. In the frigid temperatures of space, the rock cooled so quickly that these shock-formed grains survived.

In that sense, Steinhardt's quest so far has failed. The story of that tiny speck – a cosmic collision, a searing trip through Earth's atmosphere and a few millennia nestled in permafrost – hardly qualifies as an easy way to make a quasicrystal. But like all good obsessives, he has no plans to give up – albeit now, a little less like Indiana Jones and a little more like Bilbo Baggins at the end of *The Hobbit*, staying closer to home.

"Now that we know it's a meteorite, it could have landed in my backyard," he says. "We have one natural quasicrystal," he says. "So there's gotta be two." n

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