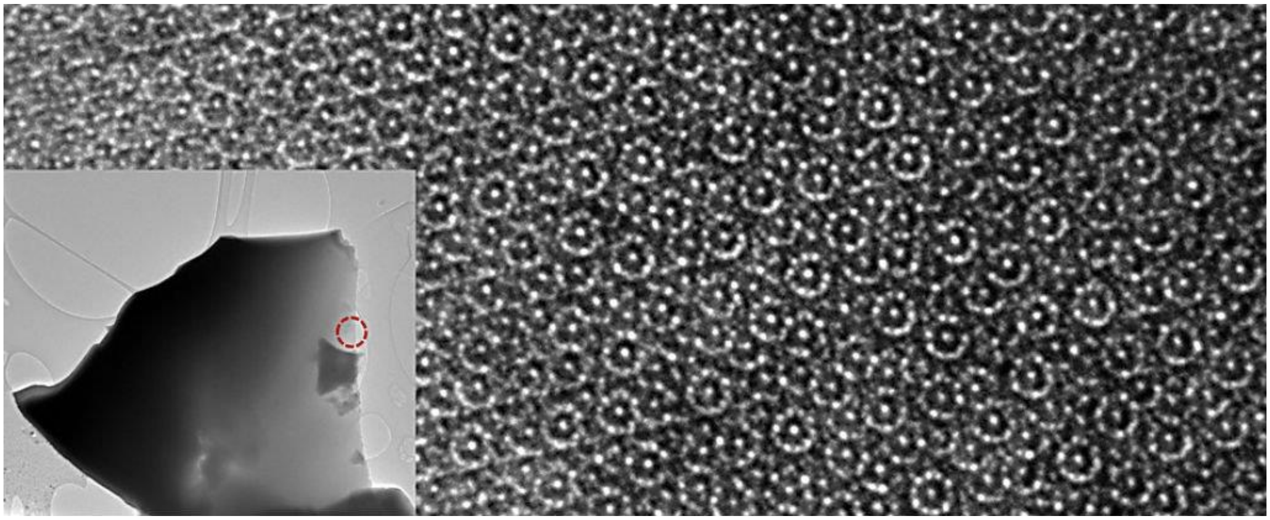
Scientists Might Have Finally Figured Out Where The Rarest Crystals on Earth Formed

by BEC CREW



Atomic image of a micron-sized grain of the natural Al71Ni24Fe5 quasicrystal (shown in the inset) from a Khatyrka meteorite.

Scientists have just come up with an explanation for how one of the rarest structures on Earth came to be, and it's got heads spinning.

Natural quasicrystals are exceptionally scarce, and have only been found in one place since their existence was first proposed back in 1982. Found inside a Russian meteorite with an 'impossible symmetry' that no one could explain, they cost the scientist who discovered them his job.

Now scientists have an explanation for why these things are so rare: quasicrystals appear to have come from outer space, where conditions are as strange as their atomic structure.

"If you had called me before the study and asked if this would work I would have said 'no way,'" Sarah Stewart, a planetary collision expert from the University of California, Davis, who reviewed the paper, told Robert Perkins at Phys.org. "The astounding thing is that they did it so easily. Nature is crazy."

Crystals are one of nature's most stunning formations, and they're pretty simple to wrap your head around - they're made up of atoms that are arranged in near-perfect symmetry to form tiny symmetrical wonders like snowflakes, diamonds, and table salt.

Other types of structures include polycrystals, such as most metals, rocks, and ice, and amorphous solids, including glass, wax, and many plastics.

Unlike crystals, which are both ordered and periodic, and have a perfectly defined geometric structure, polycrystalline and amorphous structures are disordered and random, and this gives them unique physical properties related to how to respond to things such as heat and pressure.

Back in 1982, Israeli chemist Daniel Shechtman proposed that another type of atomic structure exists, which he found in a sample of synthetic material he created in the lab.

Known as quasicrystals, these structures consist of a strange, semi-ordered form of matter, with an atomic structure that displays no repeating patterns anywhere you look. What he'd discovered was so strange, he reportedly told himself, "Eyn chaya kao," which translates to "There can be no such creature," in Hebrew.

Shechtman was awarded the 2011 Nobel Prize in Chemistry for his trouble, but not before being literally laughed out of his lab and ridiculed by his peers for decades for daring to suggest something so preposterous as a semi-ordered structure.

Science can be savage.

"The first sample, made in 1982, was so improbable that eventual Nobel prize winner Shechtman was ridiculed and ultimately asked to leave his lab," Nadia Drake reports for *Wired.*

"Then, for years, no one believed that quasicrystals could exist anywhere but the lab - assembling the strange, quasi-periodic structures was simply too tricky, requiring precise temperatures and strange conditions including vacuums and an argon atmosphere."

Fast forward to 2007, and the story of quasicrystals get even weirder.

Physicist Paul Steinhardt of Princeton University and geologist Luca Bindi from the University of Florence, Italy cracked open a meteorite found in the Koryak mountains of east Russia in the late 1970s, and found the first example of naturally formed quasicrystals.

"Bindi and Steinhardt eventually proved, in 2012, that the quasicrystals inside the rock had been forged in space, and were the natural result of an astrophysical process, and not the product of terrestrial furnaces or a consequence of the rock's collision with Earth," says Drake.

Another quasicrystal was discovered in this same meteorite in 2015, but this is still the only known natural source.

Around 100 different types of quasicrystals have been created in the lab, and they've been used in everything from non-stick cookware and LED lights to surgical instruments, but scientists have been trying to narrow down the origin of naturally occurring quasicrystals. Now we're finally getting close.

A new paper builds on Bindi and Steinhardt's discovery by pinpointing exactly where in space these quasicrystals likely originated.

Led by geochemist Paul Asimow from Caltech, the team proposes that the only natural quasicrystals we know about formed out of collisions in the asteroid belt - a floating disc of irregularly shaped asteroids or minor planets located between the Mars and Jupiter orbits - before falling to Earth as meteorites.

The reason quasicrystals are so unlikely is because perfect symmetry follows a very strict set of rules (or so we thought). Before their existence was confirmed, scientists assumed that for a structure to grow with a repeating, symmetrical structure, it could exhibit one of four types of rotational symmetry: two-fold, three-fold, four-fold, or six-fold.

Perkins explains for Phys.org:

"The number refers to how many times an object will look exactly the same within a full 360-degree rotation about an axis. For example, an object with two-fold symmetry appears the same twice, or every 180 degrees; an object with three-fold symmetry appears the same three times, or every 120 degrees; and an object with four-fold symmetry appears the same four times, or every 90 degrees."

Quasicrystals broke this rule, because they have crystal-like structure with a five-fold rotational symmetry. "The rules of crystallography had been around since 1820," Asimow told Jennifer Ouellette at Gizmodo. "So they were completely unexpected when they were discovered."

Asimow hypothesised that the strange structure was the result of massive cosmic collisions, because he noticed that textures of iron metallic beads inside the meteorite quasicrystals were similar to what he'd seen in previous shock compression experiments, which involves firing projectiles at various materials to see how they respond.

An analysis of the microscopic structure of the meteorite suggested that this collision happened before it slammed into Earth, and its outer space origin was made more likely by the fact that the Khatyrka meteorite contained a metallic copper-aluminium alloy that's not be found anywhere else on Earth.

Asimow's team performed new shock compression experiments on slivers of meteorite minerals, including a sample of a metallic copper-aluminium alloy, by blasted them with projectiles at nearly 1 kilometre per second.

"The impact smashed the sandwiched elements together and, in several spots, created microscopic quasicrystals," Perkins reports.

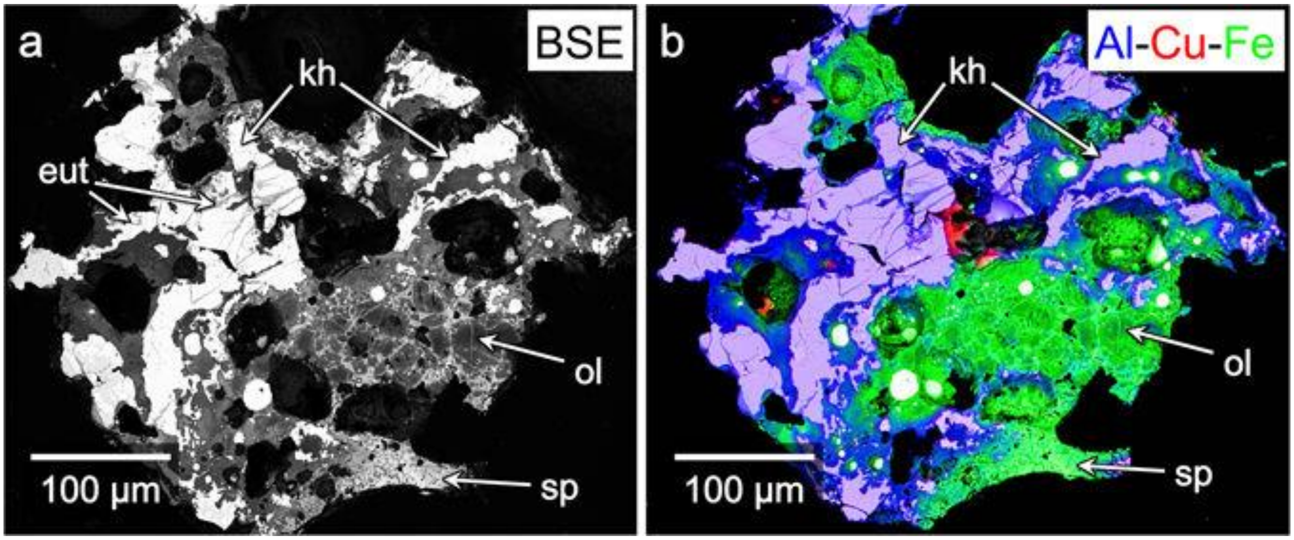
"We know that the Khatyrka meteorite was shocked," Asimow told him. "And now we know that when you shock the starting materials that were available in that meteorite, you get a quasicrystal."

The results, published in *Proceedings of the National Academy of Sciences*, strengthen Asimow's hypothesis that a collision between asteroids - most likely in the bustling asteroid belt - caused the quasicrystals inside to form inside the meteorite. Now he plans to collide different types of minerals together to see if something other than copper-aluminium alloy can produce natural quasicrystals.

"It explains the mechanism for making natural quasicrystals, and why we haven't found any others," Asimow told Gizmodo. "We have a unique starting material, and we have a unique environment. Now the biggest mystery is why there were copper aluminium alloys in that meteorite in the first place."

Written by Bec Crew 14 JUN 2016 and reprinted with permission of ScienceAlert Editor "Jacinta"

Source: https://www.sciencealert.com/scientists-might-have-finally-figured-out-where-the-rarest-crystals-on-earth-formed



Evidence of cross-cutting and redox reaction in Khatyrka meteorite reveals metallic-Al minerals formed in outer space

Overview of Khatyrka Grain 126A. (**a**) Backscattered electron (BSE) image of Grain 126A. Bright regions are mostly Al-Cu-Fe metal assemblages; they have an irregular, cuspate-lobate appearance and consist predominantly of khatyrkite (“kh”), stolperite, and eutectoid regions that contain a vermicular mixture of metallic Al (up to 13.3 weight% Cu) and khatyrkite. The darker regions mostly comprise crystals of olivine and spinel-group minerals with varying composition, which we call “spinel”—all surrounded by silicate glass. (**b**) Al-Cu-Fe combined X-ray area map, overlaid on a BSE image. Light purple regions are Al-Cu metal (khatyrkite, stolperite); blue/dark purple regions are predominantly glass and spinel; green regions are mainly the silicate glass and crystals that grew within the melt (olivine, spinel); the relatively large white grains are predominantly Fe-Ni (appearing white because of the underlying BSE image, despite containing Fe). The different compositions of spinel manifest here as different degrees of brightness (**a**) and different colors (**b**).

Source: http://www.nature.com/articles/s41598-017-01445-5/figures/1

Natural Quasicrystals & the Khatyrka Meteorite: FAQS

Grains from the Khatyrka meteorite (a complex CV3 (ox) breccia), recovered from the banks of the Listvenitovyi stream in the Chukotka Autonomous Okrug north of the Kamchatka peninsula, have been shown to contain two distinct quasicrystalline minerals (icosahedrite and decagonite) and at least seven crystalline phases bearing metallic aluminum. In five of these cases, the phases also include metallic Cu.

MOST FREQUENTLY ASKED QUESTIONS THAT WE DO NOT YET KNOW THE ANSWER TO:

What was the original source of copper and aluminum and what kind of natural processes combined for them to form the variety of mineral phases found in the Khatyrka meteorite that contain metallic aluminum and copper, where aluminum requires extraordinarily low oxygen fugacity and the two metals have profoundly distinct cosmochemical properties?

FAQS we can answer:

How can we be sure where the meteorite samples come from?

With the exception of the original sample that was found in the mineral collection of the Università di Firenze and marked as coming from the Koryak Mts., we recovered the rest of the grains ourselves on a geological expedition to Chukotka in 2011 from a stratified, glacial outwash clay layer along the Listevenitovyi stream. The clay layer is more than 7000 years old, based on radiocarbon dating of wood fragments in the clay, and hence the grains are neither anthropogenic nor salted.

If the samples have been there for > 7000 years, how could the metals have been preserved?

Alloyed copper, the cold temperature of clay (always close to freezing), impermeability of clay, and anoxicenvironment due to carbon material in clay may all have contributed to the preservation of the metals.

How do we know the samples are meteoritic in origin?

Measurements of oxygen isotopes of silicates and oxides show the meteorite is a CV3 carbonaceous chondrite that formed 4.5 million years ago in the early solar system. All reported grains have been tested and produce the same fit. Absence of any excesses of 26Mg (produced by the decay of the short-lived nuclide 26Al, with half-life~0.71 My, known to have existed in the early solar system) suggests the metal formed a few million years (or more) after the formation of calcium-aluminum-rich inclusions (CAIs) that represent the first solar system solids. Other evidence includes the presence in some samples of Allende-type matrix material and actual CAIs.

Is there any evidence of a chemical reaction between the metal and chondritic material?

Yes. In Grains 129 and 126, we have observed a redox reaction near the contact between metallic and nonmetallic phases that led to the formation of Fe beads in the chondritic phases, mostly spinel and glass.

Why are all the samples a few mm in size or less?

In tracing the origin of the Florence sample, we discovered that it had been found by panning clay recovered from undisturbed clay along the stream banks, and so the expedition to Chukotka followed the same procedure in searching for new grains, not knowing at the time if any would be found. Conceivably, larger samples could be found in a return trip to Chukotka using a different search procedure. We note, however, that the recovered grains of meteorite are very friable due to differential expansion of meteorite matrix material and CuAl compounds, which may make it difficult for larger samples to have survived.

What mineral phases have been found with metallic Al and which ones also have copper?

metallic Al + Cu:

Icosahedrite (Al63Cu24Fe13, Florence sample, grains from Chukotka) – SCIENCE 2009, MAPS 2013
Khatyrkite (CuAl2, Florence sample, grains from Chukotka) – SCIENCE 2009, MAPS 2013, NatComms 2014
Cupalite (CuAl, Florence sample, new 126) – SCIENCE 2009
β-phase AlCuFe (solid solution, Florence sample) – SCIENCE 2009

Al-Cu-bearing taenite (Fe44Ni26Al18Cu12; grain #126) – NatComms 2014

metallic Al w/o Cu:

Decagonite (Al71Ni24Fe5; grain #126) – SciRep 2015
Steinhardtite (Al38Ni32Fe30 to Al50Ni40Fe10; grain #126) NatComms 2014 and AmMin 2014
Al-bearing sulfide ((Fe0.84Al0.04)S1.12; grain #126) – NatComms 2014
Aluminum, in an eutectic (peritectic) texture with CuAl2 – NatComms 2014

What evidence do we have that the metal and conventional CV3 minerals were in contact?

Icosahedrite inclusions in stishovite – PNAS 2012, ROP 2012
Diopside in direct contact with icosahedrite – PNAS 2012
Cu-bearing troilite in contact with clinoenstatite (grain #126) – NatComms 2014
Khatyrkite in contact with forsterite (grain #129 and new grain #126) – to be published
Khatyrkite in contact with glassy pyroxene (grain #129) – to be published
Other contacts in Grain 129 and new 126, especially evidence of redox reaction producing Fe droplets

What do we know about the temperature and pressure conditions that the meteorite underwent?

We have found abundant evidence that the meteorite underwent an impact shock that produced a highly heterogeneous distribution of pressures (> 5 GPa) and temperatures (> 1500 K). The eutectic texture of the CuAl metal phases show that they solidified from a CuAl melt at around 1100K or so. The chondritic material was partially melted in some places, in some parts mostly melted. The CAI was partially melted, but some melilite was not melted. More specifically, we found:

Overall shocked texture: compressed barrels of olivine separate by veins – NatComms 2014
Ladder: injection into cracks of presumed liquid that rapidly quenched forming "ladders" (cotectic composition) of ahrensite (high P) interleaved with glassy silica– NatComms 2014
Veins of spinels and spinelloid (high P)– NatComms 2014
Magnetite grain surrounded by ladder; magnetite very likely existed in forsterite prior to impact and then melt injected that surrounded magnetite and formed ladders – NatComms 2014
Fe beads in grain 129 and new 126 –LPSC abstract

What other minerals have been identified aside from the ones named above?

Stishovite – PNAS 2012
Coesite – unpublished data
Spinel – MAPS 2013, NatComms 2014
Pentlandite – unpublished data
Melilite – MAPS 2013
Possible *cordierite*? – in progress
Ringwoodite-ahrensite solid sol. – NatComms 2014
Cu-bearing troilite (grain #126) – NatComms 2014
Spinelloid Fe3-xSixO4 (with x = 0.4) – NatComms 2014
Clinoenstatite – NatComms 2014
Nepheline – MAPS 2013
Sodalite – MAPS 2013
Taenite – NatComms 2014
Diopside – PNAS 2012, MAPS 2013
Possible (Fe1.8Cu0.2)Al5? – in progress

Source: http://wwwphy.princeton.edu/~steinh/KhatyrkaFAQs7.pdf