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Quasicrystals and the birth of the atomic age

Luca Bindi and Paul J. Steinhardt

The first nuclear bomb explosion led to the formation of a novel form of matter, known as a quasicrystal, with an elemental composition that had never been seen before.

At 05:29:45 Mountain War Time on 16 July 1945, a plutonium implosion device was detonated in New Mexico on the Alamogordo bombing range, about 330 km south of Los Alamos, and ushered in the atomic age. The experiment, known as the Trinity test, was part of the Manhattan Project, the US's top-secret effort to develop atomic weapons that was initiated after indications that German scientists were already pursuing their own atom bomb.

One of the Manhattan Project's designs, based on enriched radioactive uranium, was simple enough that it did not need to be tested in advance. The second design, based on plutonium, required a novel method of implosion to rapidly smash together enough plutonium to exceed the critical mass needed to set off a runaway nuclear chain reaction. (See the article by Cameron Reed, Physics Today, September 2017, page 42.) The Manhattan Project scientists decided that the Trinity test was essential for determining whether the implosion idea would work and, if so, provide them with firsthand data from an actual nuclear explosion.

The blast released 88 terajoules of energy—equivalent to 21 kilotons of TNT—which was enough to vaporize the 9 m test tower and surrounding copper transmission lines and create a crater about 1.4 m deep and 80 m wide. The fireball fused the desert sand, consisting mostly of quartz and feldspar, into crusts and droplets now known as trinitite. Most trinitite is greenish, but a rarer oxblood trinitite formed where sand fused with metals from the tower and copper cables.

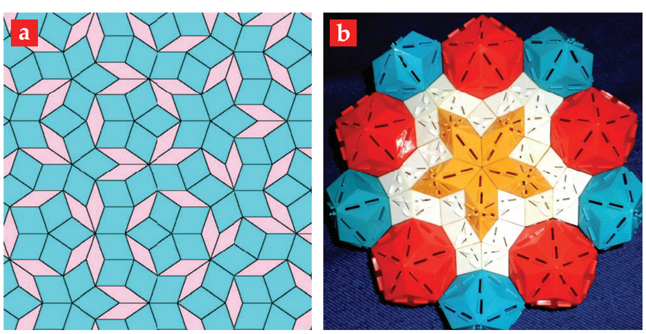

FIGURE 1. QUASICRYSTALS, whose structures are ordered but not periodic, can take different dimensionalities. **(a)** A two-dimensional Penrose tiling comprises two types of tiles (blue and pink) arranged in a quasiperiodic pattern with crystallographically forbidden fivefold symmetry. A 3D icosahedral quasicrystal **(b)** comprises four types of polyhedral units with holes and protrusions that constrain the way the units match such that all space-filling arrangements are quasicrystalline. (Photo courtesy of Lorenzo Bindi.)

Although the observers of the test recognized the explosion's awesome destructive power, they did not notice that it also created an unusual form of matter: a quasicrystal, hidden in a sample of red trinitite.

More than a repeating pattern

Before 1984 no one had ever seen or even conceived of a quasicrystal. Scientists thought they had a complete understanding of all the possible ways atoms and molecules can join to make a solid. That knowledge, established nearly two centuries earlier, was codified in a set of principles known as the laws of crystallography. The laws are essential for understanding and controlling the physical properties of matter, such as for making steel, cleaving the facets of a diamond, or manipulating the electronic properties of silicon for use in integrated circuits.

According to those laws, atomic arrangements either are random, as in glass, or are crystalline, as in sugar or table salt. In crystals, the atoms are organized in periodically repeating clusters that pack like building blocks to form a structure with a discrete rotational symmetry, analogous to a tessellation such as a checkerboard or a honeycomb.

A key fact about regular tessellations, noted even by the ancient Egyptians, is that they can comprise only certain tile shapes and possess only certain symmetries. The same rules apply to matter. Periodic materials are thus restricted to having one-, two-, three-, four-, or sixfold symmetry about an axis. Five-, seven-, eight-, and higher-fold symmetry axes are forbidden, as is icosahedral symmetry, which includes six independent fivefold symmetry axes.

About 40 years ago one of us (Steinhardt) and then-student Dov Levine first realized that a quasicrystal, which has ordered but not periodic structure, might be possible. We were inspired by a curious geometric pattern invented a few years earlier by Roger Penrose of Oxford University. He had identified a pair of shapes that fit together without gaps but only nonperiodically in a self-similar pattern of fivefold symmetric clusters of tiles, as shown in figure 1a.

Several theorists independently speculated that some analogous solids may exist, but what that would mean in actuality

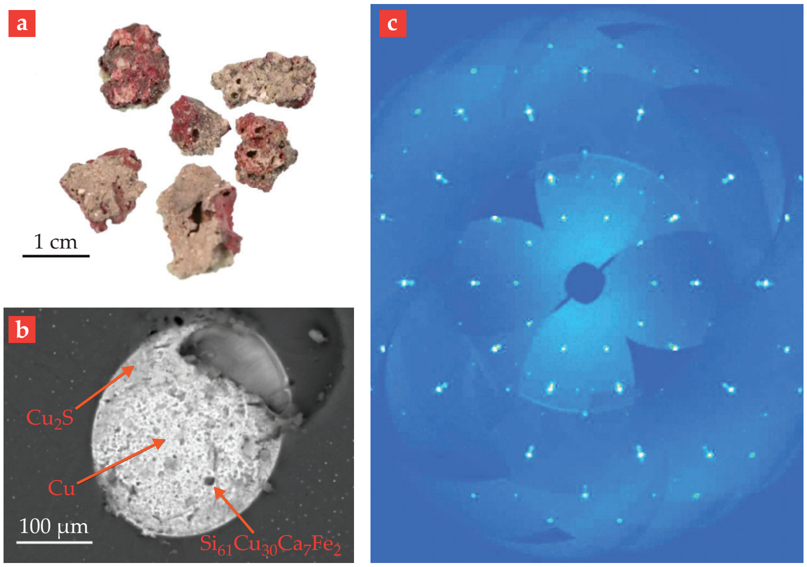

FIGURE 2. TRINITITE, which was created from the first nuclear bomb test, has trace amounts of quasicrystalline material. **(a)** Samples collected from the Trinity test site are reddish rather than trinitite's more common greenish hue. **(b)** Metal droplets from the trinitite sample were imaged with a backscattered scanning electron microscope. The quasicrystal is the small, dark gray fragment composed of silicon, copper, calcium, and iron $Si_{61}Cu_{30}Ca_7Fe_2$. **(c)** Once extracted from the metal droplet, the quasicrystal fragment was x-ray imaged along its fivefold symmetry axis. The 10-fold symmetric pattern is one of the signatures of an icosahedral quasicrystal. (Adapted from L. Bindi et al., *Proc. Natl. Acad. Sci. USA* **118**, e2101350118, 2021.)

wasn't clear. Levine and Steinhardt identified why the fivefold symmetry in Penrose's tiling was possible and then showed how to generalize the concept to other symmetries and to three-dimensional solids: by replacing periodic spacing between tiles or atoms with quasiperiodic spacings, in which at least two different spacings repeat with frequencies whose ratio is irrational. The theorists also demonstrated a possible 3D quasiperiodic solid composed of polyhedral units and with icosahedral symmetry, shown in figure 1b. They hypothesized that the same may be possible for some combinations of atoms, which they dubbed quasicrystals.

Materializing the concept

The idea of quasicrystals took off in 1984 when Dan Shechtman of the Technion–Israel Institute of Technology and his collaborators accidentally discovered a puzzling aluminum–manganese alloy with icosahedral symmetry. (See Physics Today, December 2011, page 17.) The interpretation of the discovery was controversial at first because the alloy's imperfections, such as defects and chemical disorder, left room for alternative explanations—for example, an intergrowth of multiple crystals or a glass made of icosahedral clusters. The issue was settled in 1987 when An-Pang Tsai of Tohoku University and his collaborators discovered what's generally considered to be the first definitive quasicrystal, made of aluminum, copper, and iron.

Since then, more than 100 quasicrystals have been synthesized in the laboratory by melting and mixing precise ratios of different elements and then cooling them. Those experiments incited new debates: Why do quasicrystals form? Are they truly stable forms of matter like crystals? If they are stable, shouldn't they be found somewhere in nature?

Those questions inspired our team's decade-long search for natural quasicrystals. It culminated in Chukotka in far eastern Russia where they were discovered in a 4.5-billion-year-old meteorite, as old as our solar system. Years of study revealed that the quasicrystals formed from a high-pressure shock in a collision between asteroids in outer space. To prove the hypothesis, researchers re-created the meteorite's minerals in the lab through high-pressure shocks produced by firing a high-speed projectile at a stack of materials.

That experiment led researchers to ask whether quasicrystals could lurk in remnants of other shock phenomena, such as an atomic blast. So the pursuit of quasicrystals led us to the Trinity test. One of us (Bindi) read an article by Nelson Eby of the University of Massachusetts Lowell and his collaborators that described red trinitite. That fusion of natural sand and human-made metals at high pressures and temperatures seemed a promising place to look for quasicrystals. Each red trinitite sample includes a mix of tiny grains with different compositions and structure. The challenge was to identify possible quasicrystal candidates in 10 μm fragments, extract them by hand, and search their x-ray diffraction patterns for a telltale fingerprint of a quasicrystal: sharp spots arranged in a pattern with the symmetries of an icosahedron.

After many failed attempts, we found the beautiful sample of icosahedral quasicrystal shown in figure 2. It had the same symmetry as the alloys in Shechtman's and Tsai's labs decades earlier and the quasicrystal discovered in the meteorite found in Russia. But the sample from the atomic blast had a composition of silicon, copper, calcium, and iron that had never been seen before and was not predicted to form a quasicrystal. It was also the oldest known human-made quasicrystal, with a precise time of creation that's indelibly etched in human history.

Finding quasicrystals in the material formed in the first atomic blast demonstrates that extreme conditions—for example, asteroidal collisions, shock waves, and atomic blasts—are able to produce novel compositions of quasicrystal. Those discoveries demonstrate that quasicrystals can be robust, possibly even stable, phases of matter. They also suggest new pathways to synthesize quasicrystals that may have useful electronic, phononic, and elastic properties derived from their unique sets of symmetries.

Additional resources

- Università degli Studi di Firenze, "Quasicrystals in the first nuclear explosion" (17 May 2021), www.youtube.com/watch?app=desktop&v=AkuLjTlUO7A&t=28s.
- P. J. Steinhardt, *The Second Kind of Impossible*, Harvard Science Book Talk (14 April 2020), www.youtube.com/watch?v=IZEiaF_-FeA.
- P. J. Steinhardt, "Natural Quasicrystals," article collection, https://paulsteinhardt.org/natural-quasicrystals-2. PT