PERSPECTIVE

THE DISCOVERY OF THE FIRST NATURAL QUASICRYSTAL

A New Era for Mineralogy?

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For nearly two centuries, a basic tenet of geology and solid state physics was that pure substances form crystals, periodic arrangements of atoms with a restricted set of possible symmetries. For example, the rigorous mathematical theorems of crystallography derived over 100 years ago strictly forbid solids with five-fold symmetry axes. Then, in 1984, Dan Shechtman, Ilan Blech, Denis Gratias, and John Cahn (Shechtman et al. 1984) reported the discovery of a puzzling man-made alloy of aluminum and manganese that produces a diffraction pattern of sharp spots like a crystal, but with the symmetry of an icosahedron.

Icosahedral symmetry is the most famous forbidden crystal symmetry because it incorporates the largest possible number (six) of independent axes of five-fold symmetry. As luck would have it, a theoretical explanation was waiting in the wings. Dov Levine and one of us (PJS) had been developing the idea of a new form of solid they dubbed *quasicrystals*, short for quasiperiodic crystals, where a *quasiperiodic* atomic arrangement means the atomic positions can be described by a sum of periodic functions whose periods have an irrational ratio (Levine and Steinhardt 1984). Quasiperiodic patterns have true point-like Bragg peak diffraction like a crystal, but are free to violate the theorems that constrain crystal symmetries. A two-dimensional example is the Penrose tiling (Penrose 1974), comprised of two tiles arranged quasiperiodically in a five-fold symmetric pattern. In fact, all forbidden crystal symmetries are allowed for quasicrystals, including icosahedral symmetry. Furthermore, the diffraction pattern Levine and Steinhardt predicted for icosahedral symmetry matched the Shechtman et al. observations. Several competing ideas emerged, including Linus Pauling's suggestion of multiple twinning (Pauling 1985) and Shechtman and Blech's proposal of a glassy arrangement of icosahedral clusters (Shechtman and Blech 1985). However, the subsequent discovery of other icosahedral alloys with more perfect diffraction (Tsai et al. 1987) disproved the alternatives, and the quasicrystal picture became accepted. The 2011 Nobel Prize in Chemistry was awarded to Dan Shechtman for his experimental breakthrough that changed our thinking about possible forms of matter.

But do quasicrystals truly merit the same status as crystals? Some have argued otherwise, contending that all quasicrystals are inherently delicate, metastable oddities that must be synthesized under highly controlled artificial conditions. By contrast, Levine and Steinhardt showed that, in principle, quasicrystals could be as stable and robust as crystals. According to the latter view, it is possible that Nature beat us to the punch by forming quasicrystals through geological processes long before they were made in the laboratory. Here was an opportunity for mineralogy to play a key role in resolving a fundamental question about the nature of solids. The results culminated in a discovery highlighted in the Nobel Committee's report.

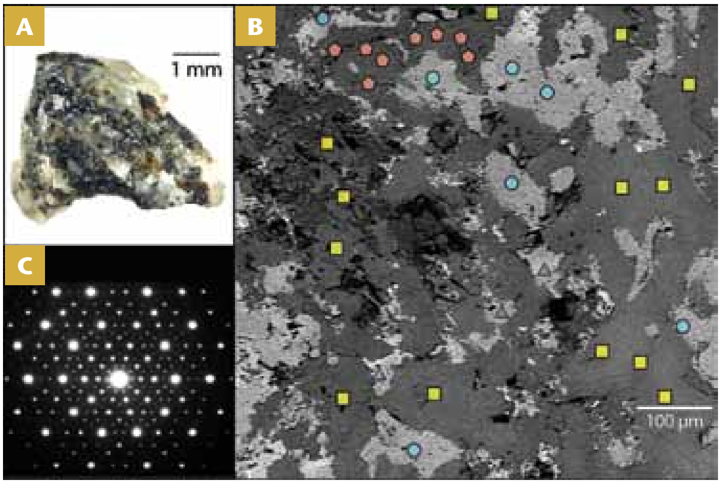

Figure 1 (**A**) The original khatyrkite-bearing sample used in the study. The lighter-colored material on the exterior contains a mixture of forsteritic olivine, diopsidic clinopyroxene, hedenbergite, nepheline, sodalite, and spinel. The dark material consists predominantly of khatyrkite and cupalite, but also includes granules of icosahedrite. (**B**) A BSE image from a thin polished slice of the khatyrkite sample shown in (A). Microprobe analyses revealed the following phases: khatyrkite, $CuAl_2$ (yellow squares); cupalite, CuAl (blue circles); unknown crystalline mineral, β-AlCuFe (purple triangles); and icosahedrite with composition $Al_{63}Cu_{24}Fe_{13}$ (red pentagons). (**C**) Diffraction pattern along the five-fold symmetry axis of icosahedrite. Note the rings of ten diffraction spots and pentagons, features impossible for ordinary crystals.

In 2009, the first natural quasicrystal was discovered in a rock sample found in the collection of the Museo di Storia Naturale of the Università degli Studi di Firenze (Bindi et al. 2009, 2011). The rock (Fig. 1a) was labelled "khatyrkite" and catalogued as coming from the Khatyrka region of the Koryak Mountains of Chukotka autonomous okrug in the northeastern part of the Kamchatka Peninsula. Khatyrkite ($CuAl_2$), a known crystalline mineral first reported by Razin et al. (1985), was only one component of a complex assemblage (Fig. 1b). The khatyrkite was intergrown with diopside, forsterite, other metallic crystal phases—cupalite (CuAl) and β-AlCuFe—and a few grains of a new phase whose X-ray powder diffraction pattern did not match that of any known mineral. When single grains of the new phase were examined using electron diffraction, the unmistakable signature of an icosahedral quasicrystal was found, including six different axes with point diffraction patterns characteristic of five-fold symmetry (Fig. 1c).

The new mineral, now officially accepted as the first natural quasicrystal and named *icosahedrite* (Bindi et al. 2011), was found to have the composition $Al_{63}Cu_{24}Fe_{13}$, a combination well known to quasicrystal researchers because it matches the composition of the first laboratory-synthesized quasicrystals that could be grown slowly without crystallizing and reach a high degree of perfection (Tsai et al. 1987). Remarkably, the same degree of structural perfection was observed in the natural icosahedrite, which grew without highly controlled conditions, something that seemed inconceivable based on laboratory experience.

A perplexing aspect of the rock sample is the presence of metallic aluminum in the quasicrystal grains and in some of the crystal mineral phases. Aluminum normally oxidizes unless placed in a highly reducing environment, as is done in the laboratory or in industry. Hence, serious consideration had to be given to the possibility that the sample was not natural at all but, rather, slag: a by-product of some anthropogenic process. At the outset, there was not even direct evidence that the sample from the Florence Museum actually came from the remote Koryak Mountains of Chukotka, as claimed in the Museo catalog. Over the next two years, however, through a forensic investigation worthy

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FIGURE 2 Scenes from the Koryak expedition are shown around a photo of the expedition team (left to right): Bogdan Makovskii (driver), Glenn MacPherson (Smithsonian Institution, USA), Will Steinhardt (Harvard, USA), Christopher Andronicos (Cornell, USA), Marina Yudovskaya (IGEM, Russia), Luca Bindi (University of Firenze, Italy), Victor Komelkov (driver), Olga Komelkova (cook), Paul Steinhardt (Princeton, USA), Alexander Kostin (BHP Billiton, USA), Valery Kryachko (Voronezh, IGEM), Michael Eddy (MIT, USA), and Vadim Distler (IGEM, Russia). DESIGN AND PHOTOS BY W. M. STEINHARDT

of a detective novel, the history of the sample was traced back to its original unearthing by V. V. Kryachko from a blue-green clay bed along the Listventovyi stream in the Koryak Mountains, a region far from industrial processing. Exhaustive examination of the rock fragments in the laboratory led to further evidence against the slag hypothesis. Most important was the observation of grains of quasicrystal included within stishovite, a polymorph of silicon dioxide that only forms at ultrahigh pressures (>10 Gpa), never approached in industrial processes (Bindi et al. 2012). Next, a series of ion microprobe measurements of the oxygen isotopes in the silicates intergrown with the metal were found to match precisely the known abundances in carbonaceous chondrite meteorites (Bindi et al. 2012), which probably formed >4.5 billion years ago, coincident with the formation of the Solar System. The evidence strongly indicates the quasicrystal intergrown with the silicates and oxides is extraterrestrial.

All this has been inferred from piecing together the story of the Florence sample. In 2011, a team of geologists from the US, Italy, and Russia was organized to conduct an expedition to Chukotka to search the clay bed along the Listventovyi stream for more samples and to explore the structural geology of the region (FIG. 2). The analysis of the 1.5 tons of material gathered there is not yet ready for publication, but it can be reported that new meteoritic grains have been discovered with icosahedrite and the other Cu–Al metallic phases attached.

The discovery of icosahedrite demonstrates that quasicrystals can form spontaneously under natural conditions and remain stable over geologic timescales, which supports the original proposal (Levine and Steinhardt 1984) suggesting that quasicrystals have equal status with crystals as a stable form of solid matter. From a geological standpoint, the occurrence of a natural quasicrystal opens a new age for mineralogy by expanding the catalog of possible structures formed by nature. The opportunity remains for mineralogy to play another important role: the search for new examples may lead to the discovery of classes of stable quasicrystals not yet observed in the laboratory.

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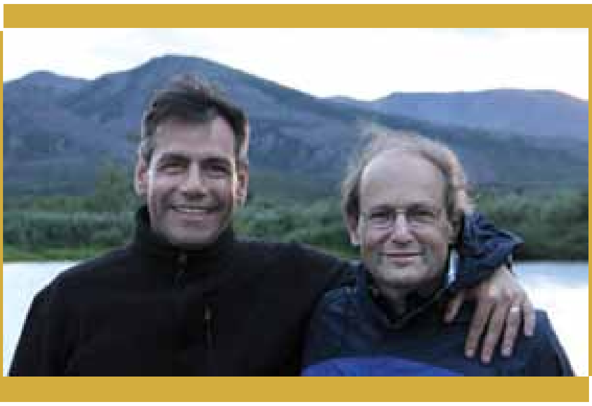

Luca Bindi (LEFT) has been the head of the Division of Mineralogy of the Natural History Museum of the University of Florence for the last five years. He is currently an associate professor of mineralogy at the Department of Earth Sciences of the same university. His research activity is mainly devoted to understanding the complexity of mineral structures, which he accomplishes by combining mineralogy with the most advanced fields of crystallography.

Paul J. Steinhardt is the Albert Einstein Professor in Science and director of the Princeton Center for Theoretical Science at Princeton University. With Dov Levine, he introduced the concept of quasicrystals in 1984 and has explored their physical properties since. He is also recognized for his contributions to particle physics and cosmology.