Once Upon a Time in Kamchatka:

The Search for Natural Quasicrystals

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Abstract: We present evidence for a naturally occurring quasicrystal consisting of micron-sized grains of $Al_{63}Cu_{24}Fe_{13}$ with icosahedral symmetry embedded in a sample of khatyrkite (nominally, $(Cu,Zn)Al_2$) obtained from the Khatyrka ultramafic zone of the Koryak Mountains in the northern half of the Kamchatka Peninsula.

Keywords: Quasicrystals; X-ray diffraction; Geological materials; Alloys; Aperiodic materials; Inorganic materials

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1. Introduction

Throughout the history of geology spanning more than two millennia [1], all reported minerals with translational order have been crystals (or incommensurate crystals), with rotational symmetries restricted to a finite set of possibilities, as first established mathematically in the 19th century [2]. Until twenty-five years ago, this seemed to be the only logical possibility since no other kind of translational order was known. However, twenty-five years ago, the concept of solids with quasiperiodic translational order, quasicrystals, was introduced whose structure is characterized by rotational symmetries forbidden to crystals, including five-fold symmetry in the plane and icosahedral symmetry in three dimensions [3]. At the same time, the first examples of quasicrystals began to be found in the laboratory [4]. By now, well over one hundred quasicrystalline materials have been synthesized, typically by mixing precise ratios of selected elemental components in the liquid and quenching under controlled conditions ranging from rapid to moderately slow [5]. For the last twenty-five years, though, an open question has been whether Nature has beaten us to the punch: Were quasicrystals formed through natural geologic processes long before they were discovered in the laboratory?

There are numerous motivations for pursuing this question. In geology, the discovery of a natural quasicrystal would open a new chapter in the study of mineralogy, forever altering the conventional classification of mineral forms. In condensed matter physics, the discovery would push back the age of the oldest quasicrystals by orders of magnitude and have an impact on our view of how difficult it is for quasicrystals to form. Finding a natural quasicrystal is also a way of studying quasicrystal stability over annealing times and conditions not accessible in the laboratory. Identifying materials that form quasicrystals has always relied significantly on serendipity, and searching through Nature may prove to be an effective complement to laboratory methods. Finally, the discovery may suggest exotic new geologic or extra-terrestrial processes.

2. The search

A number of informal searches through major museum collections were attempted soon after quasicrystals were found in the laboratory, but they yielded no results. Then, nearly a decade ago, a systematic search [6] was initiated using a novel scheme for identifying quasicrystals based on powder diffraction data. The advantage of using powder diffraction data is that there exists a collection of over eighty thousand patterns in the powder diffraction file (ICDD-PDF) published by the International Center for Diffraction Data that includes some nine thousand mineral patterns in addition to a majority of synthetic inorganic and organic phases. The disadvantage of using powder patterns is that only the magnitude (and not the direction) of the wavevector $\boldsymbol{Q}$ is preserved and the distinctive noncrystallographic symmetry of quasicrystals cannot be observed directly. The key to the search strategy was to identify quantitative figures-of-merit that could be applied to powder patterns that would separate quasicrystals and promising quasicrystal candidates from the vast majority of powder patterns in the ICDD-PDF. The optimum figures-of-merit were found to be: (a) match the observed and optimal quasicrystal powder points such that the average deviation of $\boldsymbol{Q}^2$ between observed and ideal is minimal; the minimal deviation is the first figure-of-merit; (b) the second figure-of-merit is the intensity-weighted $\bar{Q}$, where $\bar{Q}$ is determined for each peak by the optimal match from (a). The results of the search through the ICCD-PDF catalog are shown in [6], from which there were identified the most promising quasicrystal candidates.

Samples of most of the top fifty candidates were located and explored with TEM and x-ray diffraction, but, in the end, no new quasicrystals, synthetic or natural, were discovered in the original study (6). A general call was made for others to submit powder patterns of other, yet untested materials from the list of promising candidates or other sources, which call was answered by one of us (LB) who began to examine candidates from the mineralogical collections of the Museo di Storia Naturale of the Università degli Studi di Firenze. After finding no success among candidates from the list of remaining promising candidates from the ICDD-PDF catalog, the search for natural quasicrystals turned to possibilities outside the catalog altogether, beginning with minerals that are metal alloys and using quasicrystals synthesized in the laboratory, such as i-AlCuFe, as a guide.

The search ultimately led to the consideration of a sample labeled khatyrkite (catalog number 46407/G; Fig. 1A) that was acquired by the Florence Museum in 1990 and cataloged as coming from the Khatyrka region of the Koryak mountains in the Chukotka oblast on the northeastern part of the Kamchatka peninsula [7]. Khatyrkite, nominally $(Cu,Zn)Al_2$, is a tetragonal mineral that was originally found in association with cupalite, nominally (Cu,Zn)Al, which is orthorhombic, both new minerals [8]. The sample label matched the location where the khatyrkite-cupalite holotype material (preserved at the St. Peterburg Mining Institute) was reported to be found by Razin et al. [8]. At first, there was no direct evidence that the sample in Fig. 1A came from a similar location. Over the course of the last year, through a remarkable investigation to be described elsewhere, we have traced the history to show that our sample was, in fact, originally attached to the holotype material; the rock was discovered by V.V. Kryachko in a blue-green claybed along the Listventovyi stream, off the Iomrautvaam tributary of the Khatryka River, a remote region in southeastern Chukotka. This locality in the Chetkinvaam tectonic mélange is a Triassic (about 200 million years old) ultramafic (silicon-poor) zone.

Although the holotype mineral in St. Petersburg has the appearance of a metal placer, our sample as a whole is a complex assemblage (Fig. 1A) that contains spinel, augite, forsteritic olivine, and diopsidic clinopyroxene, in addition to the metal alloy phases. We made polished thin sections and examined the microstructure using backscattered electron (BSE) imaging in a scanning electron microscope (Fig. 1B).

3. Natural quasicrystal candidate

Quantitative chemical compositions using wavelength dispersive x-ray analysis (WDX) revealed a number of grains rich in aluminum whose compositions are consistent with khatyrkite and cupalite, with only traces of Zn, confirming the museum identification. These grains were intergrown with forsteritic olivine and an unknown mineral, AlCuFe, corresponding to the β-phase [5] in synthetic Al-Cu-Fe alloys. In addition to these phases, we observed grains about 90-120 μm across (Fig. 1B) that, based on microprobe analyses, are approximately $Al_{63}Cu_{24}Fe_{13}$, with an uncertainty of less than 0.1 at%. This was promising since the icosahedral phase i-AlCuFe, first reported by Tsai et al. [9] and subsequently examined by many groups over a range of stoichiometries, temperatures, and quench conditions [10], has the optimal composition $Al_{62.5}Cu_{24.5}Fe_{13}$. Two small fragments were dug out from polished thin sections, mounted on glass fibers, and prepared for powder XRD study. The results [7] confirmed the grains to be promising quasicrystal candidates according the figures-of-merit in [6].

The next step was to remove from the glass fibers several of the granules, each a few microns across [7]. The diffraction patterns obtained with a transmission electron microscope were found to consist of sharp peaks arranged in an incommensurate lattice with five-, three- and two-fold symmetry, the characteristic signature of an icosahedral quasicrystal [1,5]; for example, the diffraction pattern along the five-fold symmetry axis is shown in Fig. 1C. In addition, the angles between the symmetry planes are consistent with icosahedral symmetry. For example, the angle between the two-and five-fold symmetry planes was measured to be 31.6 ± 0.5 degrees, which agrees with the ideal rotation angle between the two-fold and five-fold axes of an icosahedron ($\arctan \frac{1}{\tau} \approx 31.7$ degrees). TEM and XRD also demonstrated the high degree of structural perfection of the natural quasicrystal. For example, in the electron diffraction patterns in Figure 1C, there is no visible distortion, which can be observed by holding the diffraction patterns at a grazing angle and noting the deviation of the dimmer peaks from straight rows. Quasicrystals produced by rapid quenching or embedded in a matrix of another phase often exhibit measurable deviations from the ideal pattern due to phason strains [11,12]. However, the diffraction pattern in Figure 1C exhibits no discernible evidence of phason strain. Similarly, the score on the $\bar{Q}$ figure-of-merit test in [6], a sensitive test of phason strain, demonstrates that the natural quasicrystal has a degree of structural perfection comparable to the best laboratory specimens. Either the mineral samples formed without phason strain in the first place, or subsequent annealing was sufficient for phason strains to relax away.

Significantly more data has been gathered since the original evidence for a natural quasicrystals was reported in [7]. For example, Fig. 2A shows a larger (~100 μm) grain that consists primarily of quasicrystal with a visible interface with a thin layer of cupalite on top. In Figure 2B, the first single-crystal x-ray diffraction pattern of a natural quasicrystal is shown. The evidence that the grain is substantially single comes observing that the x-ray pattern consists of sharp spots and EBSD images, like that in Fig. 2C, which shows that the orientation of the quasicrystal grain is uniform across the sample. The extensive WDS scans taken over the entire grain confirm the homogeneity of the quasicrystal phase, but show a more subtle overall structure than is apparent in the image. Namely, between the cupalite layer and the quasicrystal portion there is a layer of khatyrkite (where both the khatyrkite and cupalite are Fe-bearing). The grain also contains a small notch of corundum (Al_2O_3), a rare sign of metal oxidation in the sample.

4. Implications

Although the evidence for the existence of the quasicrystal phase in the rock is overwhelmingly strong, a deeply puzzling aspect is the presence of metallic aluminum, which requires a highly reducing environment. The fact that the aluminum occurs in intermetallic compounds with copper and iron decreases the oxygen fugacity requirements. Nevertheless, we have had to give serious consideration to whether the sample could be slag or the result of some anthropogenic process. There is significant evidence against this possibility that will be discussed elsewhere, including: the remote region where the sample was found being very far from any industries; the presence of forsterite and diopside in direct contact with metal alloys; the absence of glass or bubbles; unusual zoning of phosphorus and chromium in forsterite; concentration of nickel in the forsterite but not in the metal alloys; absence of myrmekitic or skeletal texture; and grains of quasicrystal in contact with stishovite (a form of silicon dioxide that only forms at 10000 atm). Each of these features is individually inconsistent with anthropogenic origin for different reasons; collectively, they make a compelling case that the rock was formed by some natural process.

The current evidence does not point strongly to any single formation mechanism. The key challenge is to explain the combination of (*i*) forsterite and diopside; (*ii*) highly reduced metallic aluminum; and (*iii*) stishovite. At present, the three features appear to be most consistent with formation process in a high pressure environment, as might occur in a meteoritic impact or in the deep mantle or perhaps in a subduction zone combined with rapid tectonic uplift.

A nearly structurally perfect, natural quasicrystal that formed under geologic conditions has a number of implications in geology and condensed-matter physics. The spectrum of known minerals, which previously included periodic crystals, incommensurate crystals and amorphous phases, must henceforth include quasicrystals. Their occurrence expands the catalog of structures formed by nature and raises an interesting challenge to explain how they formed naturally. Resolving this issue may provide insights about the formation and stability of quasicrystals at temperatures and pressures not studied in the laboratory previously and perhaps an avenue for discovering new quasicrystals with compositions not yet synthesized.

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FIGURE CAPTIONS

Figure 1. Panel A shows the original khatyrkite-bearing sample used in the study. The lighter-colored material on the exterior contains a mixture of spinel, augite and olivine. The dark material consists predominantly of khatyrkite ($CuAl_2$) and cupalite (CuAl), but also includes granules, like those in (B), with composition $Al_{63}Cu_{24}Fe_{13}$. Panel B shows a BSE image from a thin polished slice of the khatyrkite sample shown in Panel A. At least one microprobe analysis was made at each location marked with a symbol, corresponding to the following phases: khatyrkite, ($CuAl_2$) – yellow squares; cupalite (CuAl) – blue circles; unknown mineral (AlCuFe), corresponding to β phase [5,12] – purple triangles; and QC: natural quasicrystal with approximate composition $Al_{63}Cu_{24}Fe_{13}$ – red pentagons. Panel C shows the diffraction pattern along the five-fold symmetry axis of the natural quasicrystal, which exhibits no significant phason strain.

Figure 2. Panel A shows a 100 μm grain extracted from a slice of the khatyrkite sample. Extensive scans using wavelength dispersive x-ray (WDX) analysis show that the grain consists substantially of quasicrystal (darker shade, below dotted line) with composition $Al_{63}Cu_{24}Fe_{13}$ with standard deviation less than 1%. The lighter shade (lighter shade, above dashed line) corresponds to cupalite and Fe-bearing cupalite, composition $(Cu_{1-x}Fe_x)Al$, with varying $0 < x < 0.05$. Between the two, there is thin layer of Fe-bearing khatyrkite, $(Cu_{1-x}Fe_x)Al_2$ with $0.07 < x < 0.11$. The cupalite also includes a small finger of corundum (dark intrusion, arrow), Al_2O_3. Panel B shows the single crystal x-ray diffraction pattern, the first obtained from a natural quasicrystal. Evidence that the quasicrystal fraction is single crystal is that x-ray pattern consists of spots; and,

also, electron backscatter diffraction (EBSD) pattern, as exemplified in Panel C, showing a uniform alignment of the symmetry axes across the sample.