

## OUTLOOKS IN EARTH AND PLANETARY MATERIALS

### Are quasicrystals really so rare in the Universe?

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#### ABSTRACT

Until 2009, the only known quasicrystals were synthetic, formed in the laboratory under highly controlled conditions. Conceivably, the only quasicrystals in the Milky Way, perhaps even in the Universe, were the ones fabricated by humans, or so it seemed. Then came the report that a quasicrystal with icosahedral symmetry had been discovered inside a rock recovered from a remote stream in far eastern Russia, and later that the rock proved to be an extraterrestrial, a piece of a rare CV3 carbonaceous chondrite meteorite (known as Khatyrka) that formed 4.5 billion years ago in the pre-solar nebula. At present, the only known examples of natural quasicrystals are from the Khatyrka meteorite. Does that mean that quasicrystals must be extremely rare in the Universe? In this speculative essay, we present several reasons why the answer might be no. In fact, quasicrystals may prove to be among the most ubiquitous minerals found in the Universe.

**Keywords:** Quasicrystals, meteorite, khatyrka, Universe, Milky Way; Outlooks in Earth and Planetary Materials

#### INTRODUCTION

The discovery of a synthetic alloy of aluminum and manganese with nearly point-like diffraction and axes of fivefold symmetry (Shechtman et al. 1984) and the proposal of the quasicrystal theory to explain it (Levine and Steinhardt 1984) shocked the worlds of crystallography and condensed matter physics. The laws of crystallography had been established since the nineteenth century. They had played a historic role in establishing the atomic theory, had represented the first compelling example of the power of group theory to explain physical phenomena, and were viewed as completely settled science. Only a finite set of symmetries were possible for solids, according to the laws; fivefold, sevenfold, and higher-fold rotational symmetries were completely verboten. The quasicrystal theory not only revealed that these laws were overly restrictive, but that literally an infinite number of symmetry possibilities had been missed (Socolar et al. 1985).

The key realization was that the long-held assumption that any orderly arrangement of atoms or molecules must be periodic—is not true. The quasicrystal theory (Levine and Steinhardt 1984) considered an alternative known as *quasiperiodicity* in which the intervals between atoms are described by a sum of two or more periodic functions for which the ratio of periods is an irrational number. Quasiperiodicity in solids had been considered before 1984 in cases with the usual crystallographic symmetries (two-, three-, four-, and sixfold symmetry axes). Solids of this type, known as *incommensurate crystals*, had been discovered

in the laboratory and in nature (Bindi and Chapuis 2017). But what was missed before 1984 is that, by allowing for quasiperiodicity, it is possible to have symmetries that had been thought to be forbidden. In fact, all constraints on rotational symmetry are lifted, including fivefold symmetry in two dimensions and icosahedral symmetry in three dimensions. (The icosahedron is a three-dimensional Platonic solid with 20 identical faces in a configuration that includes six independent fivefold symmetry axes.)

The hypothetical rule-breaking forms of matter were dubbed *quasicrystals*, short for *quasiperiodic crystals*. The independent discovery by Shechtman et al. (1984) of a real synthetic alloy with apparent icosahedral symmetry and with a diffraction pattern similar to that predicted for icosahedral quasicrystals gave birth to a field that has since synthesized nearly 200 other quasicrystalline forms of matter and identified distinctive physical properties that have led to numerous applications (e.g., Janot and Dubois 1988; Steurer 2018). The first examples were metastable phases formed by rapidly quenching a liquid mix of metals and were composed of grains spanning only a few micrometers. Nearly half the examples known today are stable phases with grain sizes ranging to centimeter scale. All these laboratory examples, though, were grown from specially chosen combinations of ingredients brought together under highly controlled conditions of temperature and pressure. These experiences suggested that quasicrystals only occur through human intervention.

The story changed in 2009 with the discovery of a quasicrystal grain with icosahedral symmetry embedded in a rock sample found in the Museo di Storia Naturale of the Università degli Studi di Firenze (Italy) identified as coming from the Khatyrka ultramafic zone in the Koryak Mountains in the Chukotka

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Autonomous Okrug of Far Eastern Russia (Bindi et al. 2009). The grain's composition,  $\text{Al}_{63}\text{Cu}_{24}\text{Fe}_{13}$ , matched the composition of a synthetic quasicrystal made in the laboratory of An Pang Tsai 22 years earlier that was well known in the field for being the first known near-perfect, stable quasicrystal (Tsai et al. 1987). (Note, here and throughout this essay compositions are expressed as atomic percentages.) However, Tsai's synthetic sample had been made by first isolating the three constituent elements under vacuum conditions, heating and combining them in the liquid state, and then slowly cooling the mixture over a period of days. The quasicrystal grain found in the museum sample was found in a complex assemblage that included diopside, forsterite, stishovite, and additional metallic phases and that appeared to have undergone some kind of violent mixing event.

### THE FIRST NATURAL QUASICRYSTALS

The interpretation of the quasicrystal grain was confounded by the metallic aluminum contained in it and in some of the crystal mineral phases in the rock sample because of metallic aluminum forms under highly reducing conditions not normally found in nature. Another is the geochemically puzzling combination of metallic aluminum, a refractory lithophile, and copper, a moderately volatile siderophile or chalcophile. A plausible explanation was that the rock was slag, a by-product of some laboratory or industrial process.

The investigation to determine whether the sample was anthropogenic or natural reads like a cross between a detective novel and an adventure story. Based on a series of documents and personal encounters, the sample was traced back to a blue-green clay bed along the Listvenitovy stream in the Koryak Mountains, a region far from industrial processing (Bindi and Steinhardt 2018 and references therein). At the same time, an intensive laboratory study revealed 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; Steinhardt and Bindi 2012). Next, a series of ion microprobe measurements of the oxygen isotope abundances in the silicates intergrown with the metal was found to match precisely the known abundances in carbonaceous chondrite meteorites (Bindi et al. 2012), which formed  $>4.5$  billion years ago, coincident with the formation of the solar system.

These results inspired a team of geologists from the U.S., Italy, and Russia to conduct an expedition to Chukotka in 2011 to search the clay bed along the Listvenitovy stream for more samples and to explore the structural geology of the region (Steinhardt and Bindi 2012).

The risky and painstaking efforts yielded eight more grains with similar composition, unambiguously proving the suggestion based on circumstantial evidence that the museum sample traced back to the Listvenitovy and providing important new evidence bearing on the issue of natural vs. anthropogenic origin: (1) carbon-dating of material from the clay layers containing some of the samples showed them to be undisturbed for 6700–8000 yr (MacPherson et al. 2013; Andronicos et al. 2018); (2) the aluminum-copper metal alloys (crystals and quasicrystals) were found to be intimately intermixed with clear evidence of high pressure-induced chemical interactions reaching at least 5 GPa and 1200 °C sufficient to

melt the Al-Cu bearing alloys, which then rapidly solidified into icosahedrite and other phases and consistent with shock heating characteristic of meteoritic collisions (Lin et al. 2017); (3) noble gas measurements verified that the samples experienced strong shocks a few 100 Ma, reaching pressures  $>5$  GPa (Meier et al. 2018); (4) abundant petrographic and chemical evidence established that some metallic alloy grains (including quasicrystals) found in the samples pre-dated the shocks (Hollister et al. 2014; Lin et al. 2017). These exhaustive and diverse investigations provide consistent and independent evidence that the quasicrystal first discovered in the museum sample in 2009 and again in the samples recovered from the Listvenitovy is natural and from a common meteoritic source—the first quasicrystalline mineral to be discovered. The mineral is now officially named *icosahedrite* (referring to its icosahedral symmetry; Bindi et al. 2011).

The studies also led to the discovery of two other distinct natural quasicrystalline minerals. One ( $\text{Al}_{72}\text{Ni}_{24}\text{Fe}_5$ , now officially named *decagonite*; Bindi et al. 2015a, 2015b) is a so-called *decagonal phase* in which atoms form planes with quasiperiodic spacings with 10-fold symmetry, and the planes are periodically spaced along a third direction. The other is another icosahedral phase of aluminum, copper, and iron,  $\text{Al}_{62}\text{Cu}_3\text{Fe}_7$ , but with a significantly different ratio of compositions than icosahedrite; this third example represents the first quasicrystal found in nature and not predicted by laboratory experiments (Bindi et al. 2016).

After years of investigation, the case today is overwhelming that the family of three quasicrystals are extra-terrestrial, having formed in and been brought to Earth in a CV3-carbonaceous chondrite meteorite (now officially named Khatyrka; MacPherson et al. 2013). With that, the status of quasicrystals changed from their all being recent artificial materials made on Earth to their also being among the primal minerals of our solar system. And that raises the question, how rare are quasicrystals in the Universe?

Since only three different quasicrystals with a combined mass of a few nanograms have been discovered in nature to date and there is presently no convincing theory to explain their formation, any attempt to answer the question is necessarily speculative. Nevertheless, with the hope that dreams today can inspire future discoveries tomorrow, we boldly proceed.

### MORE TO BE FOUND?

In considering how common quasicrystals are in the Universe, it makes sense to consider first the three natural quasicrystalline minerals that have already been found.

A common feature is that all three are aluminum alloys. As it has already been noted, they and the crystalline aluminum alloy phases found in the Khatyrka meteorite were the only well-tested examples of natural minerals containing metallic aluminum at the time they were reported. No other meteorites or terrestrial samples containing quasicrystals have been reported since, although there also has not been any sort of systematic search for them. A further hitch in estimating their occurrence is that there is not yet a persuasive explanation for how they formed, particularly how the requisite reducing conditions were reached.

Even so, there is a simple empirical test that can be performed to provide some insight. Namely, if aluminum-containing quasicrystals are not exceedingly rare, a search for metallic aluminum and

aluminum alloys in other meteorites should yield positive results.

In fact, this has already occurred. Although no quasicrystals were found, Suttle et al. (2019) have recently reported a micro-meteorite recovered from the Nubian Desert in Sudan with the same assemblage of aluminum, iron, and copper as icosahedrite and with a morphology that is remarkably similar to Khatyrka. This example includes not only metallic aluminum but also aluminum-copper alloys, a chemical combination that, we noted above, is another cosmochemical puzzle posed by the Khatyrka meteorite. Furthermore, Al-bearing alloys have also been found in the shocked Suizhou L6 chondrite (Xie and Chen 2016), in the Zhamanshin impact structure (Gornostaeva et al. 2018), in the carbonaceous, diamond-bearing stone “Hypatia” (Belyanin et al. 2018), and in the recently reported superconducting material from the Mundrabilla IAB iron meteorite and the GRA 95205 ureilite (Wampler et al. 2020). These are the first indications that the Khatyrka quasicrystals may not be alone in the solar system.

Since metallic aluminum exists in other meteorites, there may exist in our solar system natural quasicrystals with different aluminum-bearing compositions than the three found in Khatyrka. Since 1982, nearly 100 combinations of elements combined with aluminum have been synthesized in the laboratory (Steurer and Deloudi 2009). The reason for so many aluminum-bearing quasicrystals is largely historical. The Shechtman et al. (1984) sample was an alloy of aluminum and manganese, and initial attempts at synthesizing other quasicrystals were made by metallurgists familiar with aluminum who attempted combinations with other elements. For example, icosahedral AlFeSi and AlMnSi phases are known synthetic examples (Steurer and Deloudi 2009).

There is no reason to confine searches to aluminum-bearing meteorites, though. Many have been discovered in the laboratory that do not contain metallic aluminum (Steurer and Deloudi 2009). Furthermore, as exemplified by the third of the Khatyrka quasicrystals, nature may have formed examples that have been missed in the standard materials laboratory. This could occur because there may exist conditions of temperature and pressure in space that are difficult to reproduce in an ordinary laboratory, as exemplified by hypervelocity impact shock (Asimow et al. 2016) or diamond-anvil cell (Stagno et al. 2014, 2015) experiments.

### TERRESTRIAL QUASICRYSTALS?

Although the only natural quasicrystals known today are extraterrestrial, formed in deep space, it is worth noting that there are several terrestrial intermetallic minerals recently described in the literature that suggest the possibility of quasicrystalline minerals forming on the Earth or other terrestrial planets in the Universe. One example is the small metallic inclusions in the enigmatic diamonds from Tolbachik volcano (Galimov et al. 2020). The chemistry of some of these alloys is close to  $Mn_3Ni_2Si$ , a composition range that contains octagonal and/or dodecagonal quasicrystals (e.g., Kuo et al. 1986). Another interesting finding reported by Griffin et al. (2020) is grains of native vanadium with up to 15 wt% of Al trapped as melts in crystals of hibonite ( $CaAl_{12}O_{19}$ ), grossite ( $CaAl_4O_7$ ), and Mg-Al-V spinel in a super-reduced magmatic system near the crust-mantle boundary in northern Israel. The occurrence is significant because V-based quasicrystals are known to exist (Skinner et al. 1988; Chen et al. 2010). Even more fascinating is the case of Mn-silicides. Iwami

and Ishimasa (2015) have described dodecagonal quasicrystalline structures in Mn-rich quaternary alloys containing 5.5 (or 7.5) atom% Cr, 5.0 atom% Ni, and 17.5 atom% Si. Such a composition roughly corresponds to the simplified stoichiometry  $Mn_5Si_2$ , neglecting the minor Cr and Ni that replace Si in the structure. Notably, two minerals with a composition close to this phase have been reported in nature: mavlyanovite,  $Mn_5Si_3$  (found in lamproitic rocks associated with a diamond-bearing diatreme; Yusupov et al. 2009), and unnamed  $Mn_7Si_2$  (found as inclusions of unaltered glass in volcanic breccias; Tatarintsev et al. 1990). Both minerals contain a substantial amount of Fe (in the range 6.5–8.7 wt%) that is absent in the Mn-based quasicrystals. However, the Fe content in the minerals roughly corresponds to the (Ni+Cr) abundances in the synthetic quasicrystals. Thus, given the very similar role of transition elements in the structure of quasicrystals (Steurer and Deloudi 2009; Steurer 2018), the compounds are quite comparable.

It would be important to study in more detail these occurrences since they may incorporate compositions spanning a wide range of Mn/Si ratios. This could be the source of the first terrestrial natural quasicrystal and the first mineral with dodecagonal symmetry.

### IMPLICATIONS: HOW RARE ARE QUASICRYSTALS IN THE UNIVERSE?

Icosahedrite and the other two Khatyrka quasicrystals, the two certain natural quasicrystals known today, formed naturally in CV3 chondrites that comprised the primordial material of our Solar System. Their discovery not only proved that quasicrystals can form outside the laboratory, but also that they can form in space far outside a planetary environment. Especially eye-opening is that they were discovered in complex assemblages that include a mash of oxides and silicates, conditions that were thought to be impossible for quasicrystal formation based on previous laboratory experience. How common might they be in the Universe overall?

Since quasicrystals have only been reported in one CV3 chondrite to date, one cannot reach quantitative conclusions about their mass abundance compared to other minerals throughout the Universe. At the same time, there are some reasonable inferences one can draw. First, even though the process that formed Khatyrka is not known, it definitely did occur, and it is therefore unlikely that Khatyrka is the unique meteorite containing quasicrystals.

No examples were reported previously, but that may have a logical explanation. Few meteorites have been studied with the same exhaustive microscopic detail (down to nanometer scale) as Khatyrka. Even if they had, there is a good chance that, until the Khatyrka case became firmly established—which is only in the last few years—small quasicrystal grains might have been missed or misidentified as crystals.

The history of synthetic quasicrystals provides a pertinent lesson. Synthetic quasicrystals were made in the laboratory and were even incorporated in commercial alloys decades before the notion of quasicrystals was introduced or the first examples were reported. Their presence was not recognized, though, probably because of the overwhelmingly prevalent view that matter with non-crystallographic symmetries is physically impossible. Only

after the first examples of synthetic examples were established were the earlier examples noticed. Similarly, conventional wisdom has been that metallic aluminum and aluminum-copper alloys are impossible as natural crystalline minerals. Perhaps that is why counterexamples were not found earlier. In fact, since the discovery of icosahedrite, two other types of quasicrystals have been discovered in Khatyrka remnants. Also, as described above, there have already been found other examples of meteorites with the essential ingredients, metallic aluminum and aluminum-copper crystal grains. As the scientific community becomes more familiar with these now-proven counterexamples to the conventional wisdom, it may turn out that they are not as uncommon as they seem now.

Even if quasicrystals are rare among minerals today, there are good reasons to believe that, in the distant past, they were much more common than most natural minerals known today. In our solar system's pre-solar phase, only about a dozen different minerals existed according to the analysis of Hazen et al. (2008) of mineral evolution. During the first stage of planetary accretion (>4.56 Ga), characterized by the formation of chondrites like Khatyrka, only sixty different minerals existed. If the quasicrystals formed as a result of impact collision characteristic of the next phase of planetary accretion (between 4.55 and 4.56 Ga), they would still among the first 250 minerals to have formed, and they would be found in other stellar systems. These are, in fact, the leading formation theories based on the compendium of studies of Khatyrka described above. Hence, there are good reasons to believe that quasicrystals might well be in this very rare class of primal minerals. And since our Sun appears to be an average Population II star with an average surrounding Solar System within an average galaxy in the Universe, a plausible extrapolation is that quasicrystals are ubiquitous, among the first minerals to form throughout the Universe, even if they have always been volumetrically rare.

Compare that to most of the minerals in the International Mineralogical Association catalog that first formed on Earth after the complete accretion of the planets and the oxygenation of their atmospheres. These minerals are common on Earth today, but likely much rarer when averaging over the Universe.

Another indicator comes from a series of "collider experiments" that smashed together combinations of crystalline materials (thought to be present in the pristine meteorite) to simulate the possible formation of icosahedrite from high impact collisions of asteroids (Asimow et al. 2016; Oppenheim et al. 2017a, 2017b; Hu et al. 2020). Not only did the experiments succeed in producing icosahedrite and decagonite, but they demonstrated that, even at relatively low impact velocities, it is possible to produce various quasicrystal alloys composed of four or more elements that had not been known before, including reproducing the formation conditions to form icosahedral  $\text{Al}_2\text{Cu}_{31}\text{Fe}_7$ , the third natural quasicrystal found in the Khatyrka meteorite (Hu et al. 2020). These experiments suggest that increasing the number of elemental components favors quasicrystal formation, as explained by Oppenheim et al. (2017a) on the basis of the Hume-Rothery rules and the cluster line approach. Since previous quasicrystal synthesis studies have been confined for the most part to two or three elements, it is a possibility that a wide range of quasicrystals has been missed that could have naturally formed in the countless collisions between

asteroids that have occurred throughout the Universe.

All the studies mentioned so far focus on metallic alloys, but future searches for natural quasicrystals may reveal the existence of non-metallic quasicrystal minerals that are even more common in the Universe (and that may have important applications). It was indeed recently shown (Förster et al. 2013) that oxygen-bearing quasicrystals can exist. On a Pt(111) substrate with threefold symmetry, the perovskite barium titanate  $\text{BaTiO}_3$  was found to form a high-temperature interface-driven structure with dodecagonal symmetry. This example of the interface-driven formation of ultrathin quasicrystals from a typical periodic perovskite oxide potentially extends the quasicrystal quest in nature enormously, given the abundance of natural perovskite-type structures.

A key advance in understanding the abundance of quasicrystals in the Universe will be through the direct investigation of asteroids in situ; that is, in space. The first efforts of this type have already begun, as evidenced by the successful touchdown of Hyabusa2 on the near-Earth asteroid Ryugu in July 2019. Spurred by both a scientific desire to study the composition of asteroids and the prospect of asteroid mining, this technology will certainly improve. In an isotopic study of the noble gas composition of the Khatyrka olivine grains (Meier et al. 2018), a determination of the cosmic ray exposure age of the meteorite combined with reflectance data was used to identify a possible parent body, the large K-type asteroid 89 Julia. Although the prospect of a human-led expedition to explore 89 Julia and search for quasicrystals seems like a fantasy today, so did the notion of quasicrystals before 1984, or the notion of natural quasicrystals before 2009, or a successful expedition to recover natural quasicrystals from the Listvenitovy stream in 2011.

Stepping back from our speculations, we must admit that we really do not know whether quasicrystals are rare in the Universe, but the discovery of natural quasicrystals forces us to set aside the historic arguments that suggested they must be. Scientists will learn more as they conduct further searches for natural quasicrystals and perform the experiments they inspire.

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