Rep. Prog. Phys. **75** (2012) 092601 (11pp) doi:10.1088/0034-4885/75/9/092601

In search of natural quasicrystals

Paul J Steinhardt[1,4] **and Luca Bindi**[2,3]

[1] Department of Physics and Princeton Center for Theoretical Science, Princeton University, Princeton, NJ 08540, USA
[2] Dipartimento di Scienze della Terra, Università di Firenze, via La Pira 4, I-50121 Firenze, Italy
[3] C.N.R., Istituto di Geoscienze e Georisorse, Sezione di Firenze, Via La Pira 4, I-50121 Firenze, Italy

Received 14 May 2012, in final form 9 July 2012
Published 10 August 2012
Online at stacks.iop.org/RoPP/75/092601

Abstract
The concept of quasicrystals was first introduced twenty-eight years ago and, since then, over a hundred types have been discovered in the laboratory under precisely controlled physical conditions designed to avoid crystallization. Yet the original theory suggested that quasicrystals can potentially be as robust and stable as crystals, perhaps even forming naturally. These considerations motivated a decade-long search for a natural quasicrystal culminating in the discovery of *icosahedrite* ($Al_{63}Cu_{24}Fe_{13}$), an icosahedral quasicrystal found in a rock sample composed mainly of khatyrkite (crystalline $(Cu,Zn)Al_2$) labeled as coming from the Koryak Mountains of far eastern Russia. In this paper, we review the search and discovery, the analysis showing the sample to be of extraterrestrial origin and the initial results of an extraordinary geological expedition to the Koryak Mountains to seek further evidence.

(Some figures may appear in colour only in the online journal)

This article was invited by P Chaikin.

Contents

1. Prelude 1
2. Why search for natural quasicrystals? 3
3. Search and discovery 4
4. Too perfect? 5
5. Inner space or outer space? 6
6. Expedition to Chukotka 8
7. Implications 9
Acknowledgments 10
References 10

1. Prelude

For centuries, the long-established view was that pure substances, whether made in the laboratory or found naturally, form crystals. Crystals are solids with long-range periodic translational order and rotational symmetry constrained by rigorous mathematical theorems to one of 32 point symmetries. Most rotational symmetries, including five-, seven- and higher fold symmetries in two dimensions, and icosahedral symmetry in three dimensions, are incompatible with periodicity and absolutely forbidden for crystals. Hence, the announcement in 1984 by Dan Shechtman, Ilan Blech, Denis Gratias and John Cahn (Shechtman *et al* 1984) of an aluminum–manganese alloy that diffracts electrons like a crystal, but with forbidden icosahedral symmetry, was greeted with skepticism. The debate that followed played an important role in motivating the search for natural quasicrystals that followed decades later and that is the subject of this paper.

By sheer coincidence, the theoretical explanation for Shechtman's alloy had already been formulated independently. Beginning in 1981, Dov Levine and one of us (PJS) began exploring the possibility of a new ordered phase of matter with symmetries forbidden to crystals. Their original motivation was a computer simulation of monoatomic Lennard-Jones liquids showing that *finite-range* icosahedral orientational fluctuations appear upon supercooling about 10% below the equilibrium melting temperature (Steinhardt *et al* 1981). The result led to the conjecture that it may be possible to have solids with *infinite*-range icosahedral orientational order by sacrificing periodicity. The two-dimensional Penrose tiling appeared to provide some hope (Penrose 1974). Penrose had identified a pair of tile shapes that can only fit together

[4] Author to whom any correspondence should be addressed.

 © 2012 IOP Publishing Ltd Printed in the UK & the USA

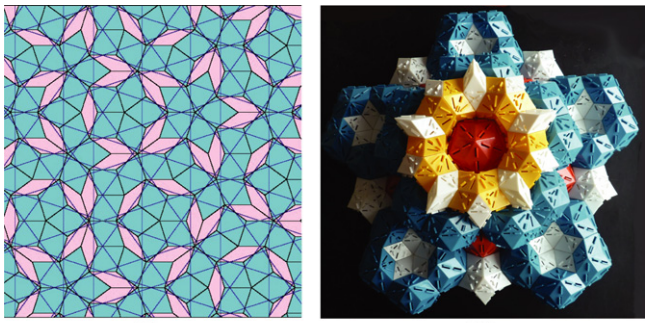

Figure 1. (*a*) Fragment of a two-dimensional Penrose tiling composed of two types of tiles arranged with crystallographically forbidden five-fold symmetry; each type of tile is labeled with the same segments which join across the interfaces to form a five set of parallel lines arranged in a quasiperiodic (Fibonacci) sequence of long and short intervals. (*b*) Fragment of a three-dimensional icosahedral quasicrystal composed of four types of polyhedral units with holes and protrusions that constrain the way the units match face-to-face in such a way as to guarantee that all space-filling arrangements are quasicrystalline. For details of the construction, see Socolar and Steinhardt (1986).

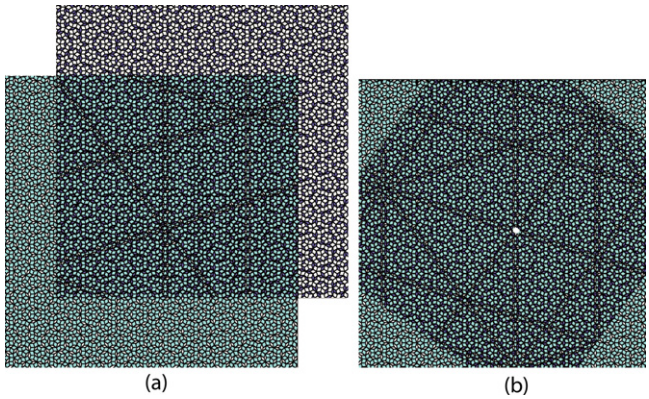

Figure 2. (*a*) There exists a sequence of translations of a Penrose that *almost* overlay the original except for a small density of differences which form the Moiré pattern of dark lines shown in the figure; the density of the Moiré lines can be made arbitrarily small by going to ever larger translations. (*b*) There is sequence of points (such as the point indicated by the white circle) such that a rotation by $2\pi/5$ about the point *almost* overlaps the original and the density of Moiré lines can be made arbitrarily small by choosing different points. These almost symmetries are responsible for the symmetries of the reciprocal lattice.

non-periodically, forming a self-similar pattern full of five-fold symmetric clusters of tiles (figure 1(*a*)). Penrose's tiling had attracted the attention of diverse mathematicians and theorists, several of whom independently had the notion that there might be some analogy for solids (Mackay 1982, Kramer and Neri 1984, Levine and Steinhardt 1984). Levine and Steinhardt's innovation was to identify two features of the tiling, *quasiperiodicity* and *long-range orientational order*, which had not been emphasized previously, but which they envisaged as being symmetry principles for defining a new phase of matter. Quasiperiodicity means the structure can be described by a sum of periodic functions where the ratio of the periods is an irrational number. With quasiperiodicity, they showed, solids with rotational symmetries forbidden to crystals become possible, in principle. In fact, an infinite number of new possibilities can occur. As an example, a three-dimensional quasicrystal was constructed using polyhedral units and certain 'face-to-face matching' rules that force a quasiperiodic arrangement with perfect long-range icosahedral orientational order (figure 1(*b*)), the most famously forbidden symmetry for crystals tiling (Levine and Steinhardt 1983). The hypothetical new phase of matter was dubbed *quasicrystal*, short for quasiperiodic crystal (Levine and Steinhardt 1984).

In real space, the lack of periodicity means that there is no translation of a quasicrystal pattern that *exactly* overlays the original, so that each atom or cluster of atoms in a quasicrystal has a distinct global arrangement of atoms surrounding it. On the other hand, there is a sequence of translations that *almost* overlay the original except for a small density of differences; that density can be made arbitrarily small by going to ever larger translations (figure 2(*a*)). Similarly, there is an ordered sequence of select points such that a rotation by $2\pi/5$ about any one of them *almost* overlaps the original (figure 2(*b*)) except for a small density of differences that becomes arbitrarily small by going to points later in the sequence.

In reciprocal space, the *almost* translational symmetry guarantees a diffraction pattern consisting only of true Bragg peaks. The peaks are arranged in a reciprocal space lattice of points described by an integer sum of basis vectors set by the rotational symmetry, just as for periodic crystals, but with a symmetry that is forbidden to crystals. However, unlike the case for crystals, the number of integer linearly independent basis vectors D in d-dimensions exceeds d, resulting in a reciprocal lattice with a dense arrangement of Bragg peaks labeled by D quasi-Miller indices. For example, the reciprocal lattice for three-dimensional icosahedral quasicrystals has $D = 6$. (A corollary is that the real space structure can also be viewed as a projection or cut through a subset of points in a six-dimensional hypercubic lattice (Kramer and Neri 1984, Duneau and Katz 1985, Kalugin *et al* 1985, Elser 1986).) Hence, the diffraction pattern of a quasicrystal is distinctive and instantaneously recognizable (figure 3). For example, the diffraction pattern for an icosahedral quasicrystal had already been computed when Shechtman *et al*'s preprint first appeared, so the experimental pattern was instantaneously recognized as matching the theoretical calculation and as indicating that the new phase is quasicrystalline (Levine and Steinhardt 1984).

Despite the qualitative agreement between the predicted and observed diffraction patterns, the quasicrystal explanation for Shechtman's icosahedral aluminum–manganese phase was not readily accepted. First, as shown by x-ray studies (Bancel *et al* 1985), the diffraction peaks are not Bragg: they have experimentally resolved finite widths. Because the phase is unstable, annealing leads to crystallization rather than sharper peaks. The instability and finite peak widths opened the door to alternative theoretical interpretations. One proposal, that the phase is a multiply twinned crystal (which tends to be overemphasized in some histories because of the prominence of its author (Pauling 1985)), was quickly dispelled because test after test failed to find evidence of individual crystallites. The serious contender was the *icosahedral glass model*, first described by Shechtman and Blech (1985), and then fully

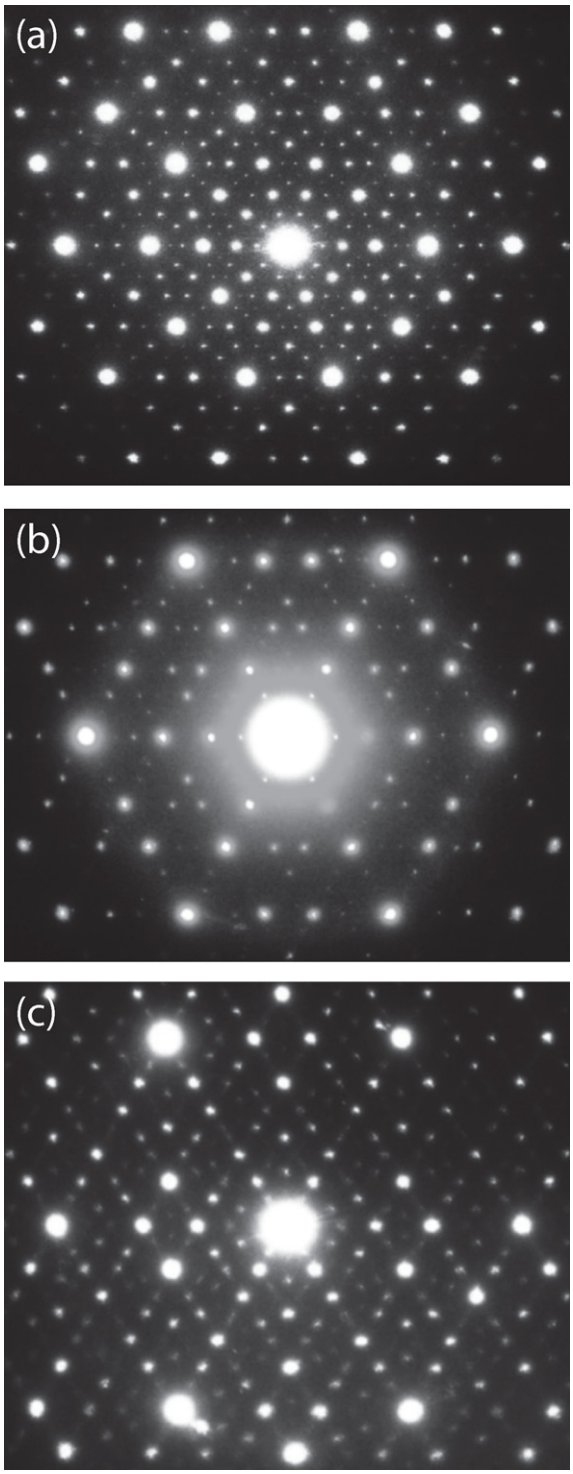

Figure 3. The unmistakable signature of an icosahedral quasicrystal consists of patterns of sharp peaks arranged in straight lines in an incommensurate lattice with five-fold (*a*), three-fold (*b*) and two-fold (*c*) symmetry. The patterns shown here, taken from a grain of icosahedrite, match those predicted for a face-centered icosahedral quasicrystal, as do the angles that separate the symmetry axes. Reproduced with permission from Bindi *et al* (2009). Copyright 2009 American Association for the Advancement of Science.

developed by Stephens and Goldman (1986). An icosahedral glass consists of a random, densely packed arrangement of icosahedral clusters arranged with common orientation. Despite the lack of translational order, the icosahedral glass model produces surprisingly sharp finite-width peaks whose positions and widths fit the measured results well. Even today, the data are not good enough to distinguish clearly whether Shechtman *et al*'s phase is an icosahedral glass or a quasicrystal with quenched defects formed through rapid solidification.

Adding to the debate was a seemingly compelling heuristic argument suggesting that the quasicrystal phase is physically impossible to achieve in realistic atomic systems. In a quasiperiodic structure, it was argued, no two atoms or clusters occupy identical positions in the overall structure, so they cannot self-organize into a perfect quasicrystalline arrangement (unless the atoms have long-range interactions, which is physically implausible). Tessellating with Penrose tiles appears to reinforce this conclusion: randomly adding tiles sequentially to a cluster of Penrose tiles leads to frequent mismatches and defects.

Two developments totally undid this line of reasoning. On the theoretical front, Onoda *et al* (1988) found alternative local rules for adjoining Penrose tiles that allow perfect growth of a quasicrystal tiling. The heuristic argument above was wrong—there was no theoretical barrier after all. On the experimental front, Tsai *et al* (1987) discovered a quasicrystal phase ($Al_{63}Cu_{24}Fe_{13}$) that can be very slowly quenched and exhibits resolution-limited Bragg peaks, decisively ruling out the icosahedral glass picture. This alloy, which plays an important role later in this story, should perhaps be viewed as the first *bona fide* quasicrystal to be synthesized in the laboratory. Since then, well over one hundred high-quality quasicrystalline materials have been identified, many with icosahedral symmetry, but also with other forbidden symmetries predicted by the quasicrystal theory (Janot 1997, Steurer and Deloudi 2008).

2. Why search for natural quasicrystals?

Despite the successes of the quasicrystal picture, there has been no consensus about the status of quasicrystals as a fundamental state of matter. A common view is that quasicrystals are too complicated to be stable states of matter. Quasicrystals are regarded as inherently delicate, metastable oddities that may only be entropically stabilized and must be synthesized under highly controlled artificial conditions. Yet the original theory, supported by the construction of tilings with matching rules and growth that can force quasicrystallinity, argued that quasicrystals can be as energetically stable and robust as crystals. On the atomic level, the stability could be due to local interactions between atoms (or atom clusters) or as a result of the pseudogaps in the electronic density of states, as in the Hume–Rothery mechanism (Steurer and Deloudi 2008). Which view is correct? Settling the debate is important for determining the impact of quasicrystals in condensed matter physics and other fields.

An interesting test is to see if Nature beat us to the punch. If quasicrystals are on the same footing as crystals, as the latter view suggests, then it is conceivable that quasicrystals formed under natural conditions and simply have not been noticed until now. The oldest quasicrystal on Earth would not be a synthetic sample made in the last century, but perhaps a mineral

formed millions of years ago. If so, the discovery would not only have an impact on our understanding of quasicrystals and solid states of matter, but also open a new chapter in the study of mineralogy, forever altering the conventional classification of mineral forms. Finding a natural quasicrystal would also be a novel way of studying quasicrystal stability over annealing times and conditions of pressure and temperature not accessible in the laboratory. Identifying materials that form quasicrystals has always relied significantly on serendipity, and searching through Nature could prove to be an effective complement to laboratory methods. Finally, the discovery could point to exotic geologic or extraterrestrial processes not noted previously. These were the optimistic considerations that motivated the search for natural quasicrystals.

3. Search and discovery

The search for natural quasicrystals began in 1984 as an informal hunt by one of us (PJS) through major museum collections soon after quasicrystals were found in the laboratory; but these modest efforts yielded no results. Then, a dozen years ago, a systematic search was initiated using a scheme for identifying quasicrystals based on powder diffraction data (Lu *et al* 2001). The advantage of using powder diffraction data is that there exists a collection of over eighty thousand patterns in the International Center for Diffraction Data Powder Diffraction File (ICDD-PDF) that includes nearly nine thousand mineral patterns in addition to a majority of diffraction patterns of synthetic phases. The disadvantage of powder patterns is that only the magnitude (and not the direction) of the peak wavevectors are preserved, so the distinctive non-crystallographic 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 known quasicrystals and promising quasicrystal candidates from the vast majority of powder patterns in the ICDD-PDF. A combination of two figures of merit proved optimal, one that measures how closely the powder peak wavevectors match those for an ideal icosahedral pattern and one that measures how closely the relative intensities match. Using these two figures of merit, the search by Lu *et al* (2001) ranked all the patterns in the catalog and identified six minerals among the one hundred most promising candidates (figure 4). Each of the minerals was acquired and studied by TEM and x-ray diffraction, but, in the end, no new quasicrystals, synthetic or natural, were discovered in the original study.

The paper included an offer to share the names of additional candidates on the list with any collaborators willing to test minerals from their collection. Six years later, the call was answered by one of us (LB) who began by testing samples on the list that were also in the collections of the Museo di Storia Naturale of the Università degli Studi di Firenze (Italy). A year later, when no successes were found among candidates on the list, the decision was made to test minerals that were not listed in the ICDD-PDF catalog altogether but whose compositions were similar to known quasicrystals synthesized in the laboratory. The search soon focused on a sample labeled

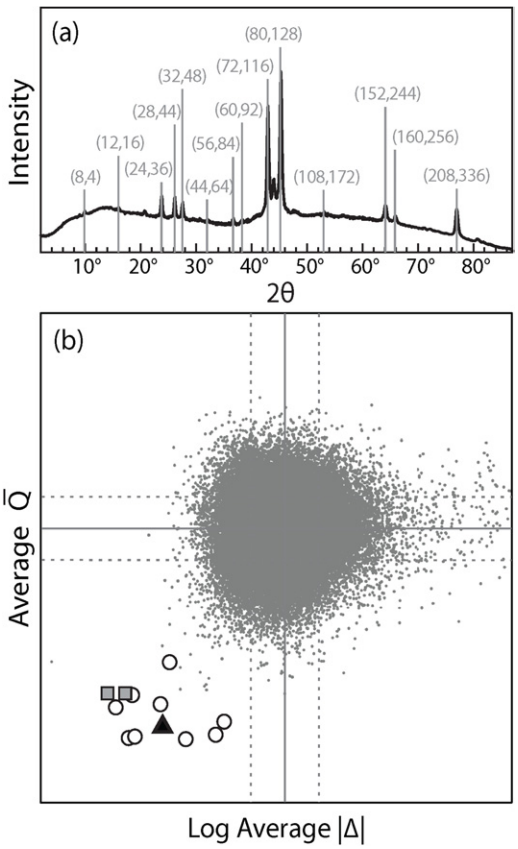

Figure 4. Powder XRD pattern for icosahedrite is shown in (*a*) with major peaks indexed by the automated scheme given in Lu *et al* (2001). The narrow, sharp peaks indicate a high degree of translational order. Plot (*b*) shows the distribution of two figures of merit introduced by Lu *et al* (2001) to separate quasicrystals from among a large collection of powder patterns in the ICDD-PDF: the logarithm of the intensity-weighted average $|\Delta|$, where Δ is the absolute deviation of each wavenumber $\boldsymbol{Q}$ from the closest-matching face centered icosahedral (FCI) peak; and the intensity-weighted average of the complementary (perp) wavevector $\bar{\boldsymbol{Q}}$ (for definition, see Levine *et al* (1985)). Known synthetic FCI quasicrystals are indicated with gray squares (AlCuFe) and white circles (other examples). They cluster far from ordinary crystalline minerals (gray dots), whose average and standard deviation are indicated by solid and dashed lines, respectively. Icosahedrite, marked with the black triangle, is several standard deviations away from the average and well within the cluster of known FCI quasicrystals. Reproduced with permission from Bindi *et al* (2009). Copyright 2009 American Association for the Advancement of Science.

'khatyrkite' (catalog number 46407/G; figure 5), acquired by the Florence museum in 1990 and catalogued as coming from the Khatyrka region of the Koryak Mountains in the Chukotka autonomous okrug, on the northeastern part of the Kamchatka peninsula (Bindi *et al* 2009, 2011). As first reported by Razin *et al* (1985), khatyrkite, nominally $(Cu,Zn)Al_2$, is a tetragonal crystal found in association with cupalite, nominally (Cu,Zn)Al, which is orthorhombic. Although the museum label indicated the Florence sample as coming from the same location as the khatyrkite–cupalite holotype sample placed by Razin *et al* at the St Petersburg Mining Institute, there was no direct evidence to substantiate the claim.

Through a forensic investigation lasting more than a year and with more twists and turns than can be recounted here,

Figure 5. A picture of the original khatyrkite-bearing sample belonging to the collections of the Museo di Storia Naturale of the Università degli Studi di Firenze (catalog number 46407/G). The lighter-colored material on the exterior contains a mixture of spinel, clinopyroxene and olivine. The dark material consists predominantly of khatyrkite ($CuAl_2$) and cupalite (CuAl), but also includes granules of icosahedrite with composition $Al_{63}Cu_{24}Fe_{13}$.

the history of the sample was traced back through a series of trades, smuggling and platinum prospecting back to its original discoverer, V V Kryachko, who unearthed both the Florence sample and the holotype in 1979. Kryachko had been sent by Razin to the Koryak Mountains to search for platinum. He collected and panned several hundred kilograms of blue-green clay bed along the Listvenitovyi stream off a tributary of the Khatyrka River and found no platinum; however, he did find a few rocks with metallic phases that he submitted to Razin upon his return. The holotype, roughly 1 mm across, is superficially an aggregate of metallic crystals reported to consist of khatyrkite and cupalite (Razin *et al* 1985); the interior has not been examined to date. A second rock made its way eventually to the Florence collection. In the Florence sample, khatyrkite was found to be intergrown with important rock-forming minerals (e.g., forsterite, $(Mg,Fe)_2SiO_4$, and diopside, $CaMgSi_2O_6$), other metallic crystal phases (cupalite 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 the diffraction patterns of the new phase were obtained using transmission electron microscopy (TEM), the unmistakable signature of an icosahedral quasicrystal was found (figure 3): patterns of sharp peaks arranged in straight lines in an incommensurate lattice with five-, three- and two-fold symmetry (Levine and Steinhardt 1984). In an incommensurate lattice, between every pair of peaks are yet more peaks, though the intensity progressively becomes too small to detect, so only a finite number of peaks is visible in figure 3. In addition, the angles between the symmetry axes are consistent with icosahedral symmetry. For example, the angle between the two- and five-fold symmetry planes was measured to be $31.6 \pm 0.5°$, which agrees with the ideal rotation angle between the two-fold and five-fold axes of an icosahedron ($\arctan 1/\tau \approx 31.7°$). Twenty-five years after the concept of quasicrystals was first introduced and a decade into the systematic search, the first natural quasicrystal had been discovered (although, as explained below, definitive confirmation would require several more years).

Historically, all known natural minerals exhibiting translational order have been crystals or incommensurate crystals with rotational symmetries restricted to the finite set of crystallographic possibilities established mathematically in the 19th century. The natural quasicrystal represents the first exception: a three-dimensional icosahedral symmetry strictly forbidden for crystals. Moreover, it exhibits a new composition, $Al_{63}Cu_{24}Fe_{13}$, never observed for other natural substances. According to the rules of the International Mineralogical Association, when a mineral with a new chemistry and a new structure is found in Nature, it merits a new name to be included in the catalog of substances formed by Nature. The first natural quasicrystal has been officially accepted by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association and named *icosahedrite* for the icosahedral symmetry of its atomic structure (Bindi *et al* 2011). The mineral is classified as icosahedral (with a face-centered icosahedral symmetry abbreviated as $Fm\bar{3}\bar{5}$) with peaks labeled by six indices (corresponding to the six basis vectors that define the reciprocal lattice).

4. Too perfect?

The diffraction patterns and lattice images of icosahedrite have a significantly higher degree of structural perfection than the aluminum–manganese phase found by Shechtman *et al* or typical quasicrystals produced in the laboratory. Quasicrystals made by rapid quenching and/or embedded in a matrix of another phase generically exhibit easily detectable phason strains (Levine *et al* 1985, Lubensky *et al* 1986).

Phasons are hydrodynamic (gapless) modes that occur in incommensurate crystals and quasicrystals in addition to the usual phonon modes. If the atomic density $\rho(x)$ is decomposed into a sum of incommensurate density waves, a phason *shift* corresponds to uniform phase shifts between density waves whose periods have an irrational ratio. A phason strain corresponds to a spatial gradient in the phase shift. At the atomic level, phason strains produce rearrangements of atoms relative to the ideal, ground state configuration, that require diffusive motion to relax away, so the phason strains remain after solidification unless the sample is grown under a very carefully controlled protocol. In reciprocal space, the signature of phason strain is a systematic shift in the Bragg peak positions from the ideal by an amount that increases as the peak intensity decreases. The effect is easily observed by holding the diffraction pattern at a grazing angle and viewing down rows of peaks. The phason strain can be observed as deviations of the dimmer peaks from straight lines (Lubensky *et al* 1986).

The electron diffraction patterns in figure 3 display no discernible evidence of phason strain. Similarly, the second figure-of-merit test (Lu *et al* 2001) that compares the observed intensities with those of an ideal quasicrystal is a sensitive

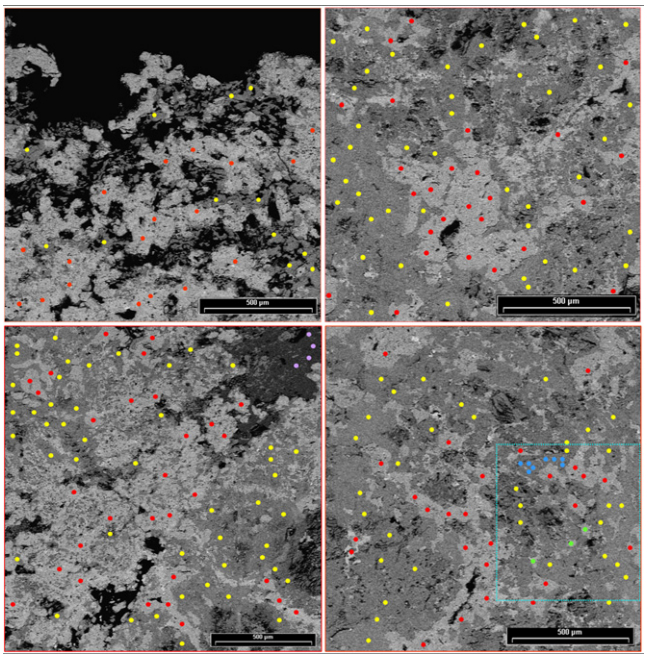

Figure 6. Scanning electron microscope-backscattered electron (SEM-BSE) images of polished slices of the khatyrkite sample shown in figure 4. At least one microprobe analysis was made at each location marked with a colored circle, corresponding to the following phases: khatyrkite, ($CuAl_2$)—yellow; cupalite (CuAl)—red; unknown mineral (AlCuFe), corresponding to β-phase (Bancel 1991) in the synthetic alloy—green; forsteritic olivine ($(Mg_{0.95}Fe_{0.05})_2SiO_4$), intimately associated with khatyrkite—purple; and icosahedrite: natural quasicrystal with approximate composition $Al_{63}Cu_{24}Fe_{13}$—blue.

quantitative test of phason strain. According to Bindi *et al* (2009), icosahedrite scored as well on the figure-of-merit tests as the best laboratory specimens (figure 4).

Yet, the icosahedrite was not formed under pristine laboratory conditions but, rather, intergrown in a complex aggregation with the other metallic phases (khatyrkite and cupalite), forsteritic olivine and diopsidic clinopyroxene within the core of the Florence sample (figure 6). The olivine grains co-existing with icosahedrite are near end-member forsterite (for most grains, the atomic Mg/(Fe + Mg) is in the range 94–99%) and the pyroxene grains are near end-member diopside ($CaMgSi_2O_6$, with atomic Mg/(Fe+Mg) generally 97–99%). Evidence of zoning in Fe and Cr was found in some of the forsterite grains (figure 7). Particularly notable are some icosahedrite grains found in direct contact with clinopyroxene (figure 8) with no sign of reactions at the interface.

Based on past laboratory experience, forming quasicrystals with such a high degree of perfection under these complex conditions seems nearly impossible. Either the mineral samples formed without phason strain in the first place, or subsequent annealing was sufficient for phason strains to relax away, either of which implies unusual geological conditions.

Equally puzzling is the fact that the quasicrystal contains metallic aluminum. Metallic aluminum has such a strong affinity for oxygen that it only forms under highly reducing conditions that cannot be found naturally on the surface of the Earth. The combination of a structurally perfect quasicrystal and metallic aluminum indicates that

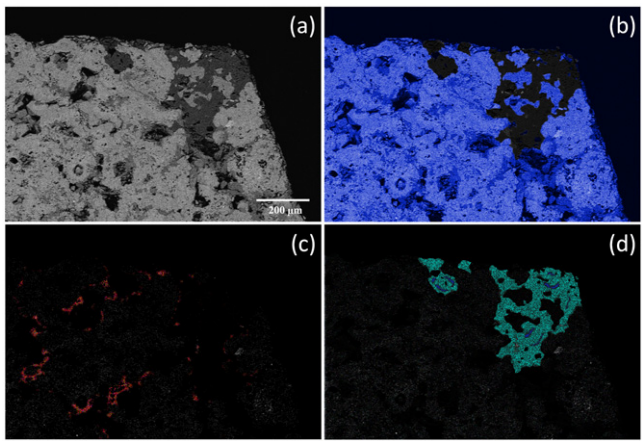

Figure 7. Polished slice of the original rock sample. (*a*) BSE image of the slice (Bindi *et al* (2012)), the darker regions (upper right) correspond to silicates (olivine and clinopyroxene) and the lighter region corresponds to Cu–Al alloys (khatyrkite and cupalite); (*b*) x-ray elemental map of Cu + Al (cameo); (*c*) x-ray elemental map of Fe; (*d*) x-ray elemental map of Cr+Mg (cameo).

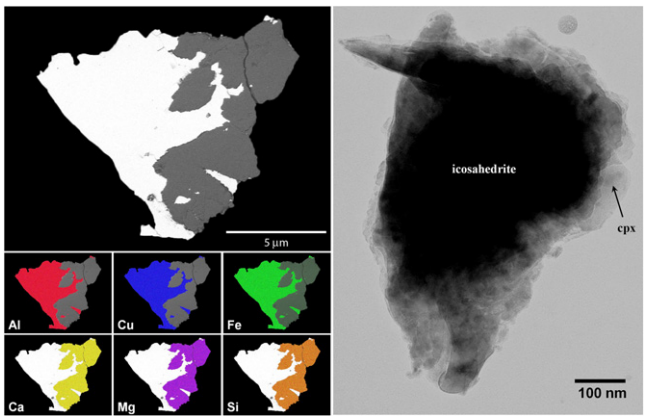

Figure 8. On the left, SEM-BSE image of a micrograin showing an interface between icosahedrite (left, white) and clinopyroxene (right, gray). X-ray element (below the BSE—lower left) and WDS scans show that the icosahedrite composition is $Al_{63}Cu_{24}Fe_{13}$ and clinopyroxene is close to pure diopside, $CaMgSi_2O_6$. Reproduced with permission from Bindi *et al* (2012). Copyright 2012 National Academy of Sciences. On the right, TEM image showing the contact between icosahedrite and clinopyroxene. Both images show no indication of reaction at the interface.

the formation of icosahedrite occurred under highly unusual conditions. Numerous proposals were floated, including formation deep under the Earth, in outer space, as the result of a lightning strike, or by hydrothermal processes near the collisions between tectonic plates. In addition, the possibility had to be considered that the sample is anthropogenic, e.g. slag formed in an aluminum foundry. The next two years following the discovery were spent confirming that icosahedrite is natural and trying to explain how it formed.

5. Inner space or outer space?

A critical clue to the origin of the Florence sample was the discovery of a 50 nm grain of stishovite (figure 9), a tetragonal polymorph of silica with unit-cell parameters $a \approx 4.2$ Å and

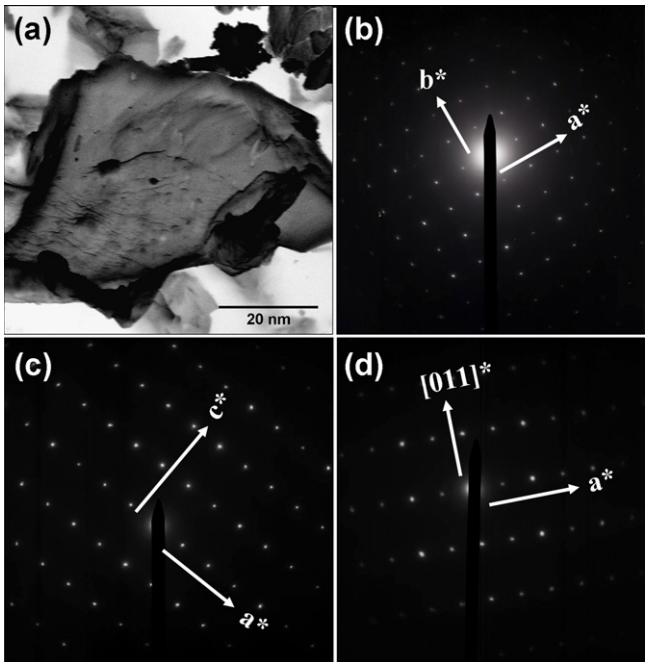

Figure 9. (*a*) TEM image of a 50 nm stishovite grain, a tetragonal polymorph of SiO_2; (*b*) selected area diffraction pattern taken down the [0 0 1] axis; (*c*) selected area diffraction pattern taken down the [0 1 0] axis; (*d*) selected area diffraction pattern taken down the [0 1 1] axis. All the collected diffraction patterns establish the tetragonal symmetry and lattice parameters $a = 4.2$ Å and $c = 2.7$ Å, typical for the mineral stishovite. Reproduced with permission from Bindi *et al* (2012). Copyright 2012 National Academy of Sciences.

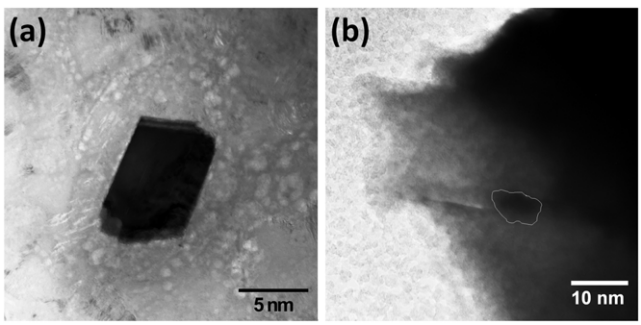

Figure 10. Panel (*a*) shows an inclusion of icosahedrite in the stishovite grain shown in figure 9(*a*). (*b*) Rotated TEM image showing enclosed icosahedrite which, when combined with (*a*), establishes that icosahedrite is totally encased in stishovite (the boundary of inclusion has been depicted with a dashed line for clarity).

$c \approx 2.7$ Å (identified through TEM). Stishovite forms at high pressures ($\geqslant$10 GPa) and temperatures ($\geqslant$1500 K). Its presence in our sample points strongly to formation in an extreme environment, as might occur in a hypervelocity impact or in the deep mantle. The stishovite contains inclusions of quasicrystal (figure 10), an indication that the quasicrystal formed before or during an extremely high-pressure event (Bindi *et al* 2012). The image encapsulates everything that seems puzzling about natural icosahedrite—a quasicrystal grain with metallic aluminum surrounded by silicon dioxide with no reaction rim in between—combined with clear evidence that it formed

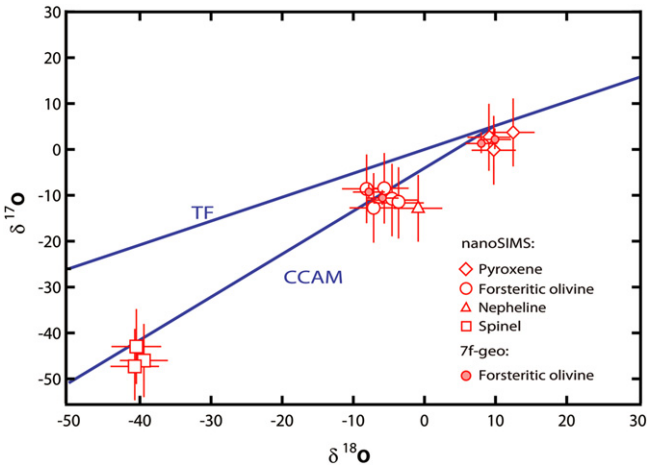

Figure 11. A plot of oxygen three-isotope composition as suggested by Clayton *et al* (1976) to discriminate terrestrial and extraterrestrial minerals, containing data for four minerals (pyroxene, nepheline, olivine and spinel) in the sample studied. All data are ion probe measurements made with either the Cameca nanoSIMS (large error bars) or the Cameca 7f geo (small error bars). The error bars are 2σ. The plotted compositional indices, $\delta^{18}O_{VSMOW}$ and $\delta^{17}O_{VSMOW}$, are, respectively, the difference between the ratios $^{18}O/^{16}O$ and $^{17}O/^{16}O$ and the same ratios in Vienna Standard Mean Ocean Water (VSMOW), expressed in parts per mil. Terrestrial minerals fall along the upper gently sloping line (TF); the oxygen isotope compositions measured for our sample lie along the line corresponding to anhydrous minerals in the CO or CV carbonaceous chondrites (the 'CCAM'). Reproduced with permission from Bindi *et al* (2012). Copyright 2012 National Academy of Sciences.

under high-pressure conditions that could not be the accidental byproduct of human activity.

Furthermore, the image reduces the possible origin to two high-pressure possibilities: inner space, deep under the Earth near the core-mantle boundary, or outer space, in meteorite collisions. (Various lines of evidence point against the quasicrystal/stishovite grain forming on impact with the Earth.) The two possibilities were discriminated by an ion probe investigation of the rare oxygen isotope ($^{18}O/^{16}O$ and $^{17}O/^{16}O$) compositions (Clayton *et al* 1976). Anhydrous carbonaceous chondrites commonly contain minerals that differ markedly in oxygen isotope composition from terrestrial materials because they condensed from or underwent isotopic exchange with nebular gas near the formation of the solar system that had a different radiogenic history. Figure 11 is the standard Clayton–Mayeda 3-isotope plot showing the measured ratios in various silicate and oxide minerals found in the Florence sample. The plot contrasts terrestrial minerals, which fall on the terrestrial fractionation (TF) line, and extraterrestrial anhydrous minerals found in carbonaceous chondrites (CCAMs). The indices, $\delta^{18}O_{VSMOW}$ and $\delta^{17}O_{VSMOW}$, are, respectively, the difference between the ratios $^{18}O/^{16}O$ and $^{17}O/^{16}O$ and the same ratios in Vienna Standard Mean Ocean Water (VSMOW), expressed in parts per mil.

The oxygen isotope measurements for the spectrum of minerals in the Florence sample are spread along the CCAM line and clearly inconsistent with the TF line. Spinel, which was only found in grains extracted from the exterior rind of

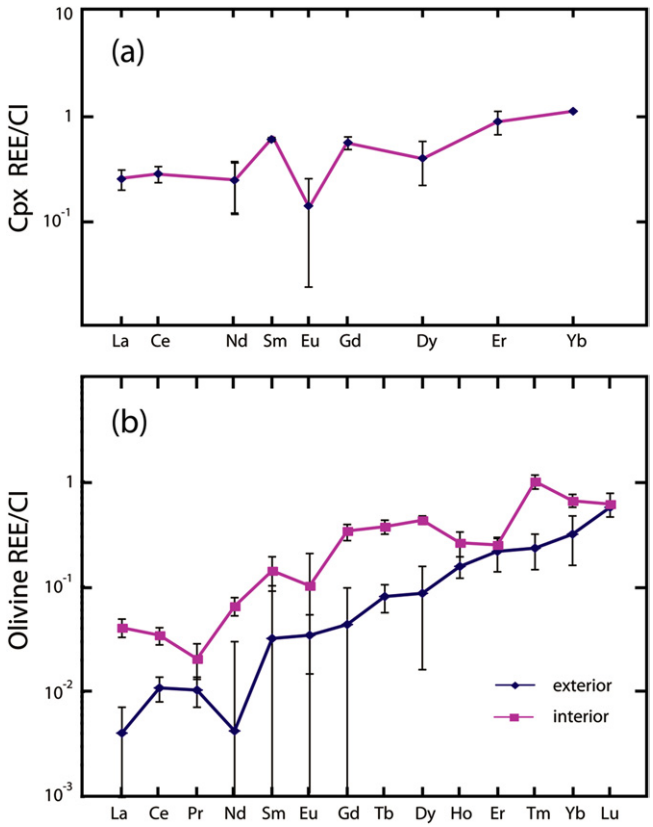

Figure 12. Rare-earth-element (REE) distribution in (*a*) a clinopyroxene grain from the exterior of the Florence rock sample and (*b*) olivine grains both from the interior and exterior of the rock sample. The values have been normalized to the CI chondrite abundances (Anders and Grevesse 1989). Reproduced with permission from Bindi *et al* (2012). Copyright 2012 National Academy of Sciences.

the sample, plots down in the range of CAI spinel. Hence, the silicates and oxides in the rock sample clearly identify our sample as an extraterrestrial. The presence of ^{16}O-rich spinel, dominant olivine composition near $\delta^{17}O_{VSMOW} = -10$ and $\delta^{18}O_{VSMOW} \sim -5\%$, and somewhat higher values for nepheline ($NaAlSiO_4$) all resemble constituents of calcium aluminum rich inclusions (CAIs) from CV3 and CO3 carbonaceous chondrites, among the oldest meteorites to have formed in our solar system.

Secondary-ion mass spectrometry (SIMS) was used to measure the abundances of rare-earth elements (REEs) in clinopyroxene and olivine (figure 12). The clinopyroxenes exhibit chondritic abundances, light REE depleted patterns and a pronounced negative depletion of europium, Eu. The olivines are characterized by lower overall REE abundances, more extreme light REE depletions, weak Eu depletion, and, for one grain, a peculiar depletion in Ho and Er compared with adjacent heavy REEs. Although the REE profiles for olivine and clinopyroxene from the sample have certain features in common, these minerals cannot be in equilibrium with one another at high temperatures.

In order to search for the former presence of the short-lived extinct radionuclide ^{26}Al at the time of quasicrystal formation, the concentration of the decay product ^{26}Mg in the natural quasicrystal was analyzed with SIMS. Despite extremely high Al/Mg ratios, no detectable radiogenic ^{26}Mg excesses were found in the quasicrystal. This implies either that the quasicrystal never contained live ^{26}Al, or that it formed more than 3 million years later than most CAIs, or that its Mg isotopic composition re-equilibrated with co-existing Mg-rich phases after the decay of ^{26}Al (Bindi *et al* 2012).

The conclusion based on the analyses of the Florence sample is that it is a CV3 carbonaceous chondrite that formed more than 4.5 Gya in the solar nebula. The copper–aluminum metallic grains, including icosahedrite, appear in many cases to be closely intergrown with the silicates and oxides, suggesting they formed together. However, aluminum–copper grains have not been observed in CV3 carbonaceous chondrites previously, and their formation could not be understood by examining the few micrograins of the Florence sample that remained after all the previous tests. The only hope for pushing the exploration further was to find new samples; but the only real chance of finding more samples with the same remarkable properties was to return to the place where the original samples were found: the Listvenitovyi stream in the Koryak Mountains in far eastern Russia. Yet the prospects for such an expedition were dim. Funding, guides, transportation and equipment were not sufficient. Only one person in the world knew the precise spot where there original sample was discovered in 1979, and travel to the autonomous okrug of Chukotka is restricted. Nonetheless, thanks to the extraordinary efforts of Valery Kryachko and Drs Vadim Distler and Marina Yudovskaya of the Institute of Ore Mineralogy (IGEM) of the Russian Academy of Sciences . . .

6. Expedition to Chukotka

On 22 July 2011, a team of ten scientists from the US, Russia and Italy, two drivers and a cook gathered at the edge of the town of Anadyr, the capital of Chukotka, ready to board the odd-looking double-track vehicles that would take them across the tundra and into the Koryak Mountains to the stream 230 km to the southwest (figures 13 and 14). The US contingent consisted of: Chris Andronicos (Cornell University), an expert on structural geology; Glenn MacPherson (Smithsonian Institution, Washington), former Chairman of the Division of Mineral Sciences at the Natural History Museum; graduate students in geoscience, Will Steinhardt (Harvard University) and Michael Eddy (MIT); translator and general assistant with a background in oil exploration, Alexander Kostin (BH Billiton) and the expedition organizer, Paul Steinhardt (Princeton University). Italian Luca Bindi (University of Florence), co-discoverer with Steinhardt of the first natural quasicrystal, brought his expertise in mineralogy. Yudovskaya, Distler and Kryachko, the Russian contingent, contributed their expertise in ore minerals and the region. Dr Yudovskaya worked tirelessly to arrange the multitude of permissions and special visas. Kryachko brought together an experienced support team consisting of Victor Komelkov and Bogdan Makovskii, who were the drivers and maintenance crew for the two tractor vehicles (figure 13), and responsible for netting fish for the team; and Victor's wife Olga Komelkova was the

Figure 13. Members of the Koryak 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). Photo by W M Steinhardt.

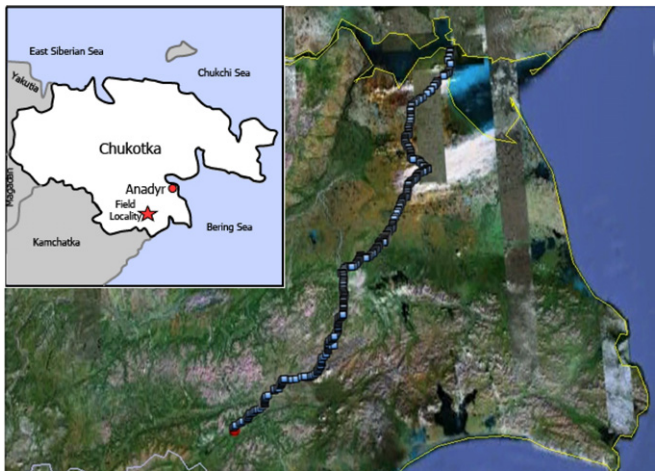

Figure 14. The expedition path (as recorded by GPS) from Anadyr to the north to the Listvenitovyi stream, with inset showing the entire Chukotka autonomous okrug.

cook. The support team had additional expertise: Victor and Olga were trained as geologists; Victor had worked in the Listvenitovyi area exploring for gold, Olga is a lawyer who helped clear legal hurdles for the expedition and Bogdan had extensive railroad and mining experience.

The trip to the Listvenitovyi stream took four full days of difficult travel by snow-cat over the tundra and mountains moving at a top speed of 15 km h^{-1}. After reaching the site and surveying the setting, the scientific team was divided into three components: an excavation and panning team that removed more than 1.5 tons of sediment (mostly clay) from sites spanning over a kilometer along the stream—the panning process separated the mineral and rock fragments from the host clay; an analysis team, which examined the separates; and a field team, which surveyed the tectonic mélange that feeds the stream and the local mountains that surround the area,

Figure 15. Field operations at the Listvenitovyi stream (clockwise): mapping the structural geology, examining mineral samples, extracting clay from areas along the stream, and panning the clay down to mineral separates.

measuring and gathering samples from representative outcrops (figure 15).

The results of the analyses of the samples collected by the expedition are not yet submitted for publication, but the following can be reported. First, the structural geological studies found no evidence for a terrestrial environment with the extreme reducing conditions needed for formation of the metallic aluminum alloys, thus strengthening the case for meteoritic origin. Second, our observations indicate that the sediment in which the meteoritic samples were found was brought to the area during or following the last glacial period; this suggests that the meteorite most likely fell around that time (<15 000 ya). Third, the new meteoritic grains contain icosahedrite and the other Cu–Al metallic phases. The study of the associated minerals affirms the conclusion that the meteorite is a carbonaceous chondrite. The other minerals include novel metallic and silicate phases.

7. Implications

Natural icosahedrite has the same structure and stoichiometry as the first sample of icosahedral $Al_{63}Cu_{24}Fe_{13}$ synthesized and characterized in the laboratory in 1987 (Tsai *et al* 1987). The laboratory samples were prepared under controlled conditions: casting from the melt in an argon atmosphere; solidifying under vacuum at a cooling rate of 1 °C min^{-1} until room temperature; then annealing for 10 days at 825 °C, for example (Audier *et al* 1990, Bancel 1991). The stability of the phase was examined in a series of studies (Bancel 1991). The range of stable compositions of the quasicrystal phase as a function of temperature narrows as the temperature decreases down to 550 °C, below which isothermal sections are difficult to obtain because of prohibitively long equilibration times (Bancel 1991). At 550 °C (in vacuum), there remains a small stability zone centered around the stoichiometry measured in the natural icosahedrite sample (to within measurement uncertainties).

The discovery of icosahedrite pushes the age of the oldest known example of this phase and of quasicrystals generally

back to ca. 4.5 Gya, the age of all known unequilibrated chondrites. The occurrence inside the meteorite demonstrates that a quasicrystal phase can form naturally within a complex, inhomogeneous medium. This sample formed under astrophysical conditions; whether a quasicrystal of some type can form in the course of planetary evolution or under terrestrial conditions remains an open question, but the likely answer is yes, now that a first example has been found. Hopefully, the discovery will now trigger the re-examination of other terrestrial and extraterrestrial minerals in search of different quasicrystals.

From the perspective of condensed matter physics, the observations constitute significant new support for the original proposal that icosahedral quasicrystals can be energetically stable states of matter, on the same footing as crystals (Levine and Steinhardt 1984). This proposal was based on the notion that short-range atomic interactions can impose energetic constraints analogous to the face-to-face matching rules shown in figure 1(*b*), and thereby ensure that the icosahedral quasicrystal is energetically preferred. The alternative view rejects the matching rule idea as being too complicated and proposes instead that icosahedral quasicrystals can only form because of entropic effects. An analogy is having units with no matching rules (random tilings (Henley 1991)), in which case on-average icosahedral symmetry has the maximum entropy. The entropic picture, which assumes that the atoms have enough time to explore many different random configurations, is hard to reconcile with the extreme conditions under which icosahedrite formed and annealed. The finding of natural quasicrystal enclosed within stishovite and other evidence not presented here indicates that formation likely occurred under shock conditions and rapid cooling, where entropic effects were unimportant compared with energetics and kinetics in forming the phase. Furthermore, all the icosahedrite grains that have been studied thus far have the same composition, to within better than one per cent, even though the phases surrounding them are different. This observation is expected if the composition corresponds to an energetically preferred structure, whereas the entropic model generally allows a continuous range of composition (corresponding to crystal approximant structures). Further laboratory studies could shed light on this issue. For example, investigations of $Al_{63.5}Cu_{23}Fe_{12.5}$ in diamond-anvil cells (Gupta *et al* 2004, Sadoc *et al* 1994) at high pressures up to 35 GPa have not shown evidence of a phase transformation, but there have not yet been systematic studies of the phase diagram of quasicrystals at high pressure.

In terms of geoscience, one of the puzzles presented by our sample is the presence of metallic aluminum, which requires highly reducing conditions to form even in alloys. Metallic aluminum has never been detected even as a trace component in metal within enstatite chondrites and achondrites (aubrites). Furthermore, the association of aluminum, a lithophile that condenses at very high temperatures, with copper, a chalcophile that condenses at much lower temperatures, is not yet understood. Resolving these and other mysteries posed by this sample will not only further clarify the origin of the quasicrystal phase but also provide insights on previously unobserved early solar-system processes.

Last but not least, the opportunity remains for mineralogy to play another important role: namely, through further searches, the discovery of quasicrystalline phases not yet observed in the laboratory.

Acknowledgments

This paper reviews work that has benefitted greatly from our valued collaborators K Deffeyes, J Eiler, Y Guan, L Hollister, P Lu, N Yao and the expeditionary team shown in figure 13. Many who have given valuable advice and support including C Ballhaus, J Beckett, P Bonazzi, A El Goresy, A Ishiwatari, H-C Jeong, J Jones, S Menchetti, M Morozov, G Poirier, P Robinson, V Rudashevkij, P Spry and E Stolper. We give special thanks to the Institute for Ore Mineralogy (IGEM) for their support in organizing the expedition and collaboration. Thanks are also due to Centro di Microscopia Elettronica e Microanalisi, Florence, Italy and Centro Interdipartimentale di Cristallografia Strutturale, Sesto Fiorentino, Florence, Italy (LB). This work is supported in part by the Ministero dell'Istruzione, dell'Università e della Ricerca, Progetti di Ricerca di Interesse Nazionale 2007, project 'Complexity in minerals: Modulation, phase transition, structural disorder' issued to Silvio Menchetti; and by the National Science Foundation Materials Research Science and Engineering Center program through New York University Grant DMR-0820341.

References

Anders E and Grevesse N 1989 Abundances of the elements: meteoritic and solar *Geochim. Cosmochim. Acta* **53** 197–214

Audier M, Guyot P and Brechet Y 1990 High-temperature stability and faceting of theicosahedral Al–Fe–Cu phase *Phil. Mag.* **61** 55–62

Bancel P A 1991 *Quasicrystals: The State of the Art* ed D DiVincenzo and P J Steinhardt (Singapore: World Scientific) pp 17–56

Bancel P A, Heiney P A, Stephens P W, Goldman A I and Horn P M 1985 Structure of rapidly quenched Al–Mn *Phys. Rev. Lett.* **54** 2422–5

Bindi L, Eiler J, GuanY, Hollister L S, MacPherson G J, Steinhardt P J and Yao N 2012 Evidence for the extra-terrestrial origin of a natural quasicrystal *Proc. Natl Acad. Sci.* **109** 1396–401

Bindi L, Steinhardt P J, Yao N and Lu P J 2009 Natural quasicrystals *Science* **324** 1306–9

Bindi L, Steinhardt P J, Yao N and Lu P J 2011 Icosahedrite, $Al_{63}Cu_{24}Fe_{13}$, the first natural quasicrystal *Am. Min.* **96** 928–31

Clayton R N, Onuma N and Mayeda T K 1976 A classification of meteorites based on oxygen isotopes *Earth Planet. Sci. Lett.* **30** 10–18

Duneau M and Katz A 1985 Quasiperiodic patterns *Phys. Rev. Lett.* **54** 2688

Elser V 1986 The diffraction pattern of projected structures *Acta Crystallogr.* A **42** 36–43

Gupta A J, Neelima P, Vijaykumar V and Godwal B K 2004 High pressure Mössbauer studies of stable quasicrystal $Al_{63.5}Cu_{24}Fe_{12.5}$ *J. Non-Cryst. Solids* **334–335** 243–6

Henley C 1991 *Quasicrystals: The State of the Art* ed D DiVincenzo and P J Steinhardt (Singapore: World Scientific) pp 429–524

Janot C 1997 *Quasicrystals: A Primer* ed D DiVincenzo and P J Steinhardt (Oxford: Oxford University Press)

Kalugin P A, Kitaev A Yu and Levitov L S 1985 6-dimensional properties of Al(86)Mn(14) alloy *J. Physique Lett.* **46** L601–7

Kramer P and Neri R 1984 On periodic and non-periodic space fillings of E^m obtained by projection *Acta Crystallogr.* A **40** 580–7

Levine D and Steinhardt P J 1983 Crystalloids *Patent disclosure* UPENN-9-23-83

Levine D and Steinhardt P J 1984 Quasicrystals: a new class of ordered structures *Phys. Rev. Lett.* **53** 2477–80

Levine D, Lubensky T C, Ostlund S, Ramaswamy A and Steinhardt P J 1985 Elasticity and defects in pentagonal and icosahedral quasicrystals *Phys. Rev. Lett.* **54** 1520–3

Lu P J, Deffeyes K, Steinhardt P J and Yao N 2001 Identifying and indexing icosahedral quasicrystals from powder diffraction patterns *Phys. Rev. Lett.* **87** 275507

Lubensky T C, Socolar J E S, Steinhardt P J, Bancel P A and Heiney P A 1986 Distortion and peak broadening in quasicrystal diffraction patterns *Phys. Rev. Lett.* **57** 1440–3

Mackay A 1982 Crystallography and the Penrose pattern *Physica* **114A** 517

Onoda G Y, Steinhardt P J, DiVincenzo D P and Socolar J E S 1988 Growing perfect quasicrystals *Phys. Rev. Lett.* **60** 2653–6

Pauling L 1985 Apparent icosahedral symmetry is due to directed, multiple twinning of cubic crystals *Nature* **317** 512–4

Penrose R 1974 The role of aesthetics in pure and applied mathematical research *Bull. Inst. Math. Appl.* **10** 266–71

Razin L V, Rudashevskij N S and Vyalsov L N 1985 New natural intermetallic compounds of aluminum, copper and zinc—khatyrkite $CuAl_2$, cupalite CuAl and zinc aluminides from hypui erbasites of dunite-harzburgite formation *Zapiski Vses. Mineralog. Obshch.* **114** 90–100

Sadoc A, Itié J P, Polian A, Lefebvre S, Bessière A and Calvayrac Y 1994 X-ray absorption and diffraction spectroscopy of icosahedral Al–Cu–Fe quasicrystals under high pressure *Phil. Mag.* **70** 855–66

Shechtman D and Blech I 1985 The microstructure of rapidly solidified Al_6Mn *Metall. Trans.* A **16** 1005–12

Shechtman D, Blech I, Gratias D and Cahn J 1984 Metallic phase with long-range orientational order and no translational symmetry *Phys. Rev. Lett.* **53** 1951–4

Socolar J and Steinhardt P J 1986 Quasicrystals: II. Unit cell configurations *Phys. Rev.* B **34** 617–47

Steinhardt P J, Nelson D R and Ronchetti M 1981 Icosahedral bond orientational order in supercooled liquids *Phys. Rev. Lett.* **47** 1297–300

Stephens P W and Goldman A I 1986 Sharp diffraction from an icosahedral glass *Phys. Rev.* B **33** 655–8

Steurer W and Deloudi S 2008 Fascinating quasicrystals *Acta Crystallogr.* A **64** 1–11

Tsai A P, Inoue A and Masumoto T 1987 A stable quasicrystal in Al–Cu–Fe system *Japan. J. Appl. Phys.* **26** L1505

View publication stats

ResearchGate

See discussions, stats, and author profiles for this publication at: https://www.researchgate.net/publication/230643198

In search of natural quasicrystals

Article *in* Reports on Progress in Physics · August 2012

DOI: 10.1088/0034-4885/75/9/092601 · Source: PubMed

CITATIONS
14

READS
1,013

2 authors, including:

Luca Bindi
University of Florence

436 PUBLICATIONS **3,255** CITATIONS

SEE PROFILE

Some of the authors of this publication are also working on these related projects:

Project Molecular crystals View project

Project Extraterrestrial materials View project

All content following this page was uploaded by Luca Bindi on 26 March 2015.

The user has requested enhancement of the downloaded file.

IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

In search of natural quasicrystals

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2012 Rep. Prog. Phys. 75 092601

(http://iopscience.iop.org/0034-4885/75/9/092601)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 150.217.74.78
The article was downloaded on 10/08/2012 at 10:09

Please note that terms and conditions apply.