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The quest for forbidden crystals

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ABSTRACT

The world of crystallography was forced to reassess its rules about thirty years ago with the introduction of the concept of quasicrystals, solids with rotational symmetries forbidden to crystals, by Levine and Steinhardt (1984) and the discovery of the first examples in the laboratory by Shechtman *et al.* (1984). Since then, >100 different types of quasicrystals have been synthesized in the laboratory under carefully controlled conditions. The original theory suggested that quasicrystals can be as robust and stable as crystals, perhaps even forming under natural conditions. This thought 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 museum sample consisting of several typical rock-forming minerals combined with exotic rare metal alloy minerals like khatyrkite and cupalite. Here we briefly recount the extraordinary story of the search and discovery of the first natural quasicrystal.

Keywords: natural quasicrystals, icosahedrite, Al-Cu-alloys, forbidden symmetry, khatyrkite.

Before the beginning

For thousands of years, the only known atomically ordered solids, natural or synthetic, have been crystals in which the atoms are arranged in a regularly repeating periodic pattern that exhibits a discrete rotational symmetry. According to the mathematical theorems discovered in the 19th century, periodicity can occur only for certain rotational symmetries: one-, two-, three-, four- and six-fold symmetry axes are allowed; but five-, seven-, eight- or higher-fold symmetry axes are strictly forbidden (Lima-de-Faria, 1990). Icosahedral symmetry, which includes six independent five-fold symmetry axes, is super-forbidden. Then, in 1984, a new kind of solid was hypothesized that violates the established symmetry rules (Levine and Steinhardt, 1984) and, independently, Dan Shechtman, Ilan Blech, Denis Gratias and John Cahn (Shechtman *et al.*, 1984) announced the discovery of an Al-Mn alloy that diffracts electrons like a crystal, but with forbidden icosahedral symmetry. The hypothetical new class of solids, dubbed ‘quasicrystals’, short for ‘quasiperiodic crystals’, could evade the conventional crystallographic rules because they have an atomic pattern that, instead of being periodic, is described by a sum of two or more incommensurate periodic functions (i.e. whose periods have a ratio that is an irrational number). Quasicrystals exhibit Bragg diffraction-like crystals because they are reducible to a sum of periodic functions, albeit with a symmetry impossible for crystals. The geometric construction that inspired the idea is Penrose tiling [named after its inventor Sir Roger Penrose (1974)], consisting of a pair of tile shapes that can only fit together in a pattern with five-fold symmetry (Fig. 1, left side). Levine and Steinhardt (1984)

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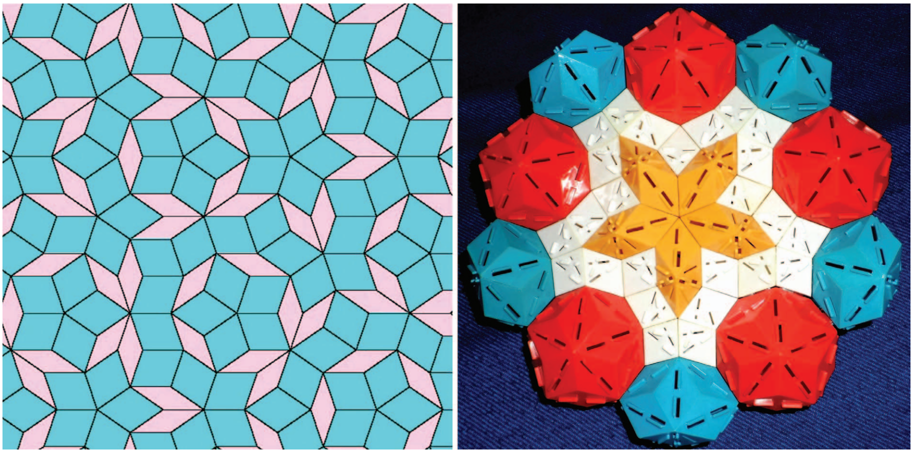

FIG. 1. Left: a fragment of a two-dimensional Penrose tiling consisting of two types of tiles (light blue and pink) arranged with crystallographically forbidden five-fold symmetry. Right: a fragment of a three-dimensional icosahedral quasicrystal composed of four types of polyhedral units with holes 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).

showed that the five-fold symmetry was possible because the Penrose tiles repeat with relatively incommensurate frequencies and that the same quasiperiodic principle could be used to construct polyhedral units with protrusions and holes on their faces that constrain the way they join together such that the units can only fit together in a three-dimensional solid with icosahedral symmetry (Fig. 1, right side). When Shechtman *et al.* (1984) published their surprising diffraction pattern, Levine and Steinhardt (1984) showed further that it agreed well with prediction for an icosahedral quasicrystal.

Despite the agreement, both the theory and the experimental discovery were greeted with scepticism because it was conjectured that atoms could not self-organize into such a subtle pattern without introducing a high density of defects. Indeed, the example presented by Shechtman *et al.* was highly defective, and the intensity distribution in its diffraction pattern did not precisely conform to the quasicrystal prediction. Competing explanations for the Al-Mn phase were proposed that could explain the data just as well without introducing quasiperiodicity. Then, in 1987, An-Pang Tsai and collaborators reported the successful synthesis of the $Al_{63}Cu_{24}Fe_{13}$ quasicrystal (the synthetic analogue of natural icosahedrite) that exhibited resolution-limited Bragg peaks and an extremely high degree of structural perfection (Tsai *et al.*, 1987) clearly fitting the quasicrystal hypothesis and ruling out competing ideas. In this sense, $Al_{63}Cu_{24}Fe_{13}$ might be considered the first *bona fide* quasicrystal. Since then, >100 similarly high-quality quasicrystalline materials have been identified, many with icosahedral symmetry, but also with other forbidden symmetries predicted by the quasicrystal theory (e.g. Janot, 1997; Steurer and Deloudi, 2008). However, despite the laboratory evidence and the mathematical constructions by Levine and Steinhardt (1984) that suggested otherwise, a common view was that quasicrystals may all be inherently delicate, metastable oddities that can only be synthesized under highly controlled artificial conditions.

These considerations were a key motivation for the search for natural quasicrystals. The discovery of a quasicrystal in nature would demonstrate that quasicrystals are robust as crystals and have existed long before they were synthesized in the laboratory. Moreover, the discovery would open a new chapter in the study of mineralogy, forever altering the conventional classification of mineral forms. The search began as an informal hunt by one of us (PJS) through major museum collections soon after quasicrystals were found in the laboratory. Then, at the end of the nineties, the effort transitioned into a systematic search using a scheme for identifying quasicrystals based on powder diffraction data (Lu *et al.*, 2001). Note that Steinhardt was not alone in considering the possibility of natural quasicrystals. John Cahn (pers. comm.) apparently conducted his own informal search through museums and, in 1994, John A. Jaszczack (Michigan Technological University) wrote in *The Mineralogical Record*: "The stability of quasicrystalline materials, their ease of manufacture and their variety of compositions suggest that quasicrystals may be an as yet undiscovered component of the mineral kingdom awaiting the careful inspection of a diligent mineral collector who does not disregard 5-fold symmetry *a priori*" (Jaszczack, 1994).

Lu *et al.* (2001) used powder diffraction data for their systematic search because there exists a collection of >80,000 patterns in the International Centre for Diffraction Data Powder Diffraction File (ICDD-PDF) that includes nearly 9000 mineral patterns in addition to a majority of diffraction patterns of synthetic compounds. 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. Using these figures-of-merit, the search by Lu *et al.* (2001) ranked all the patterns in the catalogue and identified six minerals among the 100 most promising candidates. 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. The call was answered in 2007 by one of us (LB).

First contact: a year of failure

The team began to examine candidates given by Lu *et al.* (2001) from the mineralogical collections of the Museo di Storia Naturale of the Università degli Studi di Firenze (Florence Museum). None of the candidates proved to be an icosahedral quasicrystal or anything remarkable. The problem, as it turned out, was that the data in the ICDD-PDF catalogue contained sufficient errors to give false positives for complex but ordinary periodic crystals.

After a year of failure, Bindi had the intuition to test minerals that were not listed in the ICDD-PDF catalogue but whose compositions were similar to known quasicrystals synthesized in the laboratory. The search soon focused on a sample labelled "khatyrkite" (catalogue number 46407/G; Fig. 2), 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 north-eastern part of the Kamchatka peninsula (Bindi *et al.*, 2009, 2011, 2012). As first reported by Razin *et al.* (1985), khatyrkite, nominally (Cu,Zn)Al_2, is a tetragonal mineral found in association with

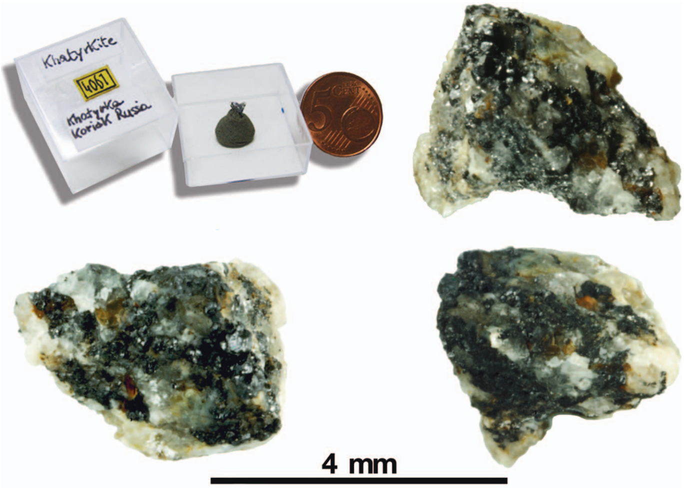

FIG. 2. Different views of the original khatyrkite-bearing sample belonging to the collections of the Museo di Storia Naturale of the Università degli Studi di Firenze (catalogue number 46407/G). The lighter-coloured material on the exterior contains a mixture of spinel, clinopyroxene and olivine. The dark material consists predominantly of khatyrkite ($CuAl_2$) and cupalite (CuAl), but also includes granules of icosahedrite with composition $Al_{63}Cu_{24}Fe_{13}$.

cupalite, nominally (Cu,Zn)Al, which is orthorhombic. In the Florence sample, khatyrkite was found to be intergrown with typical 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 species, with composition $Al_{63}Cu_{24}Fe_{13}$, the X-ray powder diffraction pattern of which did not match that of any known mineral (Bindi *et al.*, 2009, 2011).

Quasi happy new year!

The composition and X-ray powder pattern of the unknown mineral found in the Florence sample (i.e. $Al_{63}Cu_{24}Fe_{13}$) seemed promising because they matched exactly that of the quasicrystal synthesized by Tsai *et al.* (1987), but there had been enough experience with false positives during the search that direct evidence was needed: an image of the reciprocal lattice showing the five-fold symmetry. For this reason, the two extracted grains of the unknown mineral were sent to Princeton in November 2008 for a detailed transmission electron microscopy study by Steinhardt and Nan Yao, an expert in electron and X-ray diffraction and imaging who continues to play an integral role in the ongoing project. The very first day of 2009, when the diffraction patterns of the new mineral were obtained, the unmistakable signature of an icosahedral quasicrystal was found (Fig. 3): patterns of sharp peaks arranged in straight lines in an incommensurate lattice with five-, three- and two-fold symmetry. The angles between the symmetry axes were clearly consistent with icosahedral symmetry. For example, the angle between the two- and five-fold symmetry axes was measured to be 31.6(5)º, which agrees with the ideal rotation angle between the two-fold and five-fold axes of an icosahedron ($\arctan 1/\tau \approx 31.7º$, where $\tau = (1+\sqrt{5})/2$). The email message sent by P.J. Steinhardt to L. Bindi entitled "*Quasi Happy New Year*" reported that the experimental proof we were looking for had been found.

Thirty years after the concept of quasicrystals was first introduced and a decade into the systematic search, the first natural quasicrystal had been discovered – or had it?

Impossible

The electron diffraction patterns showed a significantly higher degree of structural perfection than those found for typical quasicrystals produced in the laboratory. Unless grown under the most carefully controlled conditions, quasicrystals exhibit phason strains (Levine *et al.*, 1985; Lubensky *et al.*, 1986), easily detected as deviations of the dimmer peaks from straight lines when the diffraction pattern is viewed at a glancing angle (Lubensky *et al.*, 1986). The electron diffraction patterns in Fig. 3 for icosahedrite display no discernible evidence of phason strain even though the icosahedrite was not formed under pristine laboratory conditions but, rather, intergrown in a complex aggregation with other metallic phases (khatyrkite and cupalite), forsteritic olivine [Mg/(Fe+Mg) = 94–99%] and diopsidic clinopyroxene [Mg/(Fe+Mg) = 97–99%] (Fig. 2). 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 imply unusual geological conditions.

To help solve the mystery, Steinhardt met with the petrologist Lincoln S. Hollister (Princeton University) who promptly declared the possibility of the sample being natural as "impossible". His concern was not the degree of perfection but, rather, the baffling presence of metallic Al in cupalite, khatyrkite and in the icosahedral quasicrystal phase. Metallic Al has a remarkably strong affinity for O, such that it could not possibly form naturally on the surface of the Earth, he argued. However, upon further discussion, he amended the conclusion to allow for the improbable possibility that it could have formed under the intense heat and pressure that exist near the core mantle boundary or in a high impact collision of meteors in space. This discussion led to a visit to Glenn J. MacPherson at the Natural History Museum of the Smithsonian Institution, an expert on meteorites, who delivered an even more negative verdict, giving several additional reasons why the sample could not be a meteorite and was almost surely anthropogenic. Hollister and Macpherson both offered advice and a series of tests that could be used to settle the issue and ultimately became integral parts of the research team.

International intrigue

Despite the discouraging sceptical response, the two of us continued to pursue hotly our study of the new sample over the next year and a half through a two-pronged attack. Firstly, we tried to

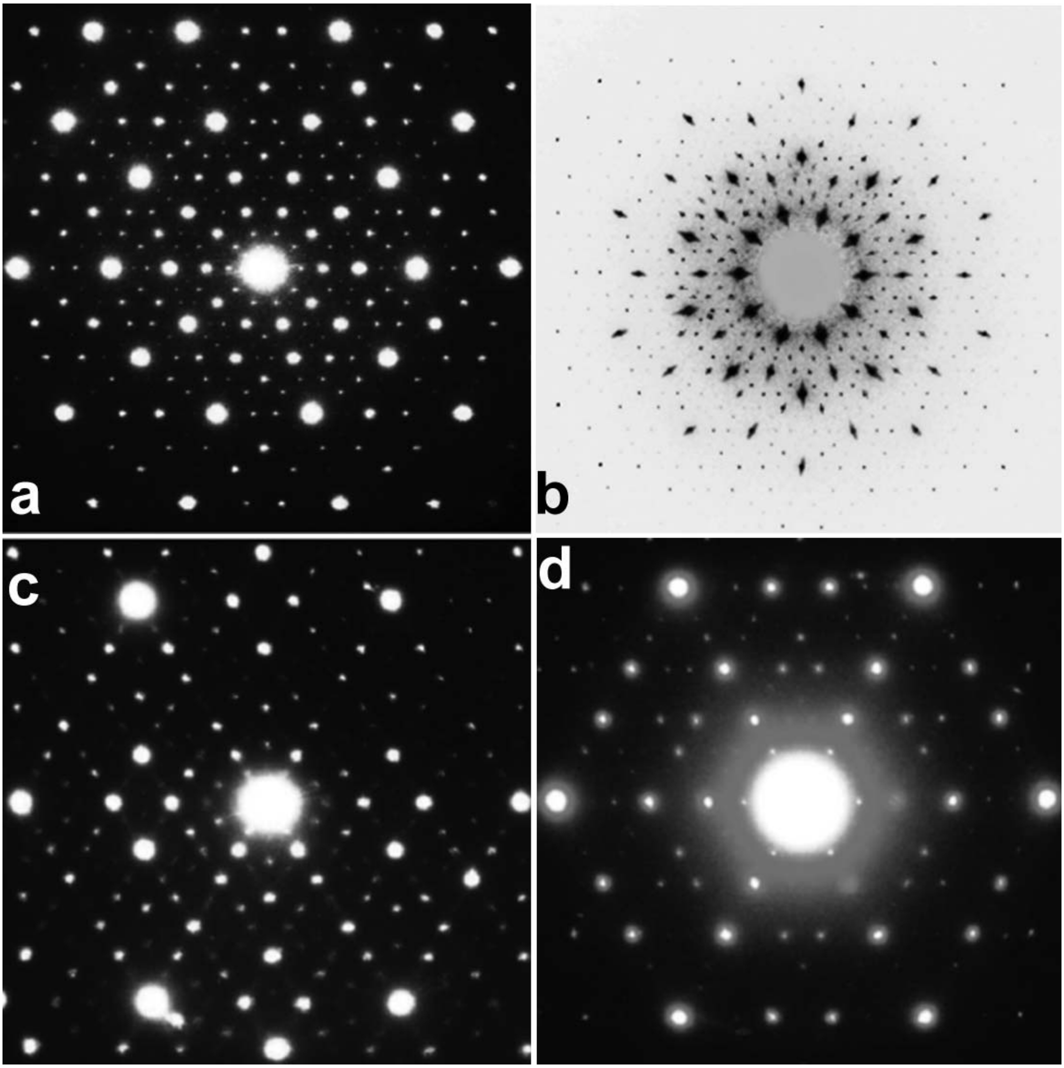

FIG. 3. The unmistakable signature of an icosahedral quasicrystal consists of patterns of sharp peaks arranged in straight lines in an incommensurate lattice with five-fold (*a*), two-fold (*c*) and three-fold (*d*) symmetry. The electron diffraction patterns shown here, taken from a grain of icosahedrite, match those predicted for a face centered icosahedral quasicrystal, as do the angles that separate the symmetry axes. Panel (*b*) is a single-crystal X-ray diffraction precession photograph down one of the five-fold symmetry axes of the icosahedron collected on a small icosahedrite fragment extracted from grain #5 recovered in the Koryak expedition.

trace the provenance of the Florence sample to see if we could legitimate or refute its label claiming it as a natural mineral from the Koryaks. Secondly, we began to examine carefully each grain in the existing powder sample to look for evidence of natural *vs*. anthropogenic origin. The two investigations occurred simultaneously with ebbs and flows that varied from day to day.

The tracing of the provenance was problematic from the start. The only record was a label that described the sample as coming from the same location as the khatyrkite-cupalite holotype described by Razin *et al.* (1985) and placed at the St Petersburg Mining Institute plus a letter stating the sample had been sold in 1990 to the Florence museum by a collector who was then living in Amsterdam. Over the next year and a half, through a forensic investigation with more twists and turns, blind alleys and blind luck than can be recounted here, the provenance of the sample was traced back through a series of trades, smuggling and Pt prospecting back to its original discoverer, V.V. Kryachko, who had unearthed both the Florence sample and the khatyrkite-cupalite holotype sample in St Petersburg. Kryachko had been sent by Razin to the Koryak Mountains to search for Pt. He collected and panned several hundred kg of blue-green clay bed along the Listventovyi stream off a tributary of the Khatyrka River and found no Pt; however, he did find a few rocks with metallic phases that he submitted to Razin upon his return as evidence of his effort. Kryachko did not learn what had happened to his samples after that, until Steinhardt contacted him in 2010. Then, he learned that Razin and collaborators had studied the holotype, which is roughly 1 mm across and 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 through complicated channels to the Florence Museum collection.

Inner space or outer space?

Over the same period that the provenance was being investigated, an intense set of laboratory investigations of the powder sample took place. At the time, a growing number of theoretical explanations for the sample were developed ranging from anthropogenic (including from a rocket or plane exhaust, Al foundry and intentional fakery) to natural (including from lightning, volcanic fumaroles and hydrothermal processes). A major breakthrough was the discovery of a 50 nm grain of stishovite (Bindi *et al.*, 2012) in the powder sample. The discovery of stishovite, a polymorph of SiO_2 that forms only at ultrahigh pressures, eliminated all the anthropogenic theories and almost all of the natural ones, except for the two first raised in the initial discussion with Hollister: a hypervelocity meteor impact in space or material formed in the deep mantle. Most importantly, the stishovite contains inclusions of quasicrystal, an indication that the quasicrystal also formed before or during an extremely high pressure event (Bindi *et al.*, 2012).

Once the provenance was ascertained and clear laboratory evidence for a natural origin was found, we proposed that the quasicrystal be evaluated by the International Mineralogical Association for consideration as a new mineral species. The first natural quasicrystal was officially accepted by the Commission on New Minerals, Nomenclature and Classification and named icosahedrite for the icosahedral symmetry of its atomic structure (Bindi *et al.*, 2011). The mineral is classified as icosahedral (with a face-centred icosahedral symmetry abbreviated as $Fm\bar{3}\bar{5}$) with peaks labelled by six-indices (corresponding to the six basis vectors that define the reciprocal lattice).

However, there remained the issue of resolving the origin of icosahedrite: inner space, deep under the Earth near the core-mantle boundary, or outer space, in meteor collisions. The two possibilities were discriminated by an ion probe investigation of the rare O isotope ($^{18}O/^{16}O$ and $^{17}O/^{16}O$) compositions (Clayton *et al.*, 1976), which was carried out at the California Institute of Technology in collaboration with John Eiler and Yunbin Guan. The O isotope measurements for the spectrum of minerals in the Florence sample were found to be spread along the CCAM (Carbonaceous Chondrite Anhydrous Minerals) line and clearly inconsistent with the TF (Terrestrial Fractionation) line. Hence, the silicates and oxides in the rock sample clearly identify the sample as extraterrestrial with isotope values resembling the constituents of Ca-Al-rich Inclusions (CAIs) from CV3 and CO3 carbonaceous chondrites, among the oldest meteorites to have formed in our solar system. However, Al-Cu 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.

A journey to the ends of the earth

Steinhardt had found V.V. Kryachko by first contacting his Ph.D. thesis advisor, Vadim Distler, at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (IGEM) of the Russian Academy of Sciences in Moscow. Beginning with the first contacts, Distler and Kryachko offered to help organize an expedition to search for new samples. At this point, the stishovite grain had not yet been discovered, and the O isotope results were not in hand, so the possibility seemed remote. However, their gracious offer returned to mind when it became clear how important the quasicrystal and the chondritic matrix might be. Thanks to generous financial support by an anonymous donor, the remote possibility became a plausible reality. However, the trip would not have been possible without the extraordinary preparation, organization and scientific collaboration of Distler, Kryachko and Marina Yudovskaya (IGEM). Consequently, on July 22, 2011, a team of ten scientists from the US, Russia and Italy, two drivers and a cook/lawyer (Fig. 4) 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 Listvenitovyi stream, 230 km to the southwest (Fig. 5). The US contingent consisted of Christopher Andronicos (Purdue University), an

FIG. 4. Members of the Koryak expedition team (left to right): Bogdan Makovskii (driver), Vadim Distler (IGEM, Russia), Marina Yudovskaya (IGEM, Russia), Valery Kryachko (Voronezh, IGEM), Glenn MacPherson (Smithsonian Institution, USA), Luca Bindi (Università di Firenze, Italy), Victor Komelkov (driver), Olga Komelkova (cook), Alexander Kostin (BHP Billiton, USA), Christopher Andronicos (Cornell, USA), Michael Eddy (MIT, USA), Will Steinhardt (Harvard, USA). At the centre Paul Steinhardt (Princeton, USA), leader of the expedition. Photo by W.M. Steinhardt.

FIG. 5. The expedition path (as recorded by GPS) from Anadyr to the north to the Listvenitovyi stream (upper left), with inset showing the entire Chukotka autonomous okrug, together with some scenes from the Koryak expedition.

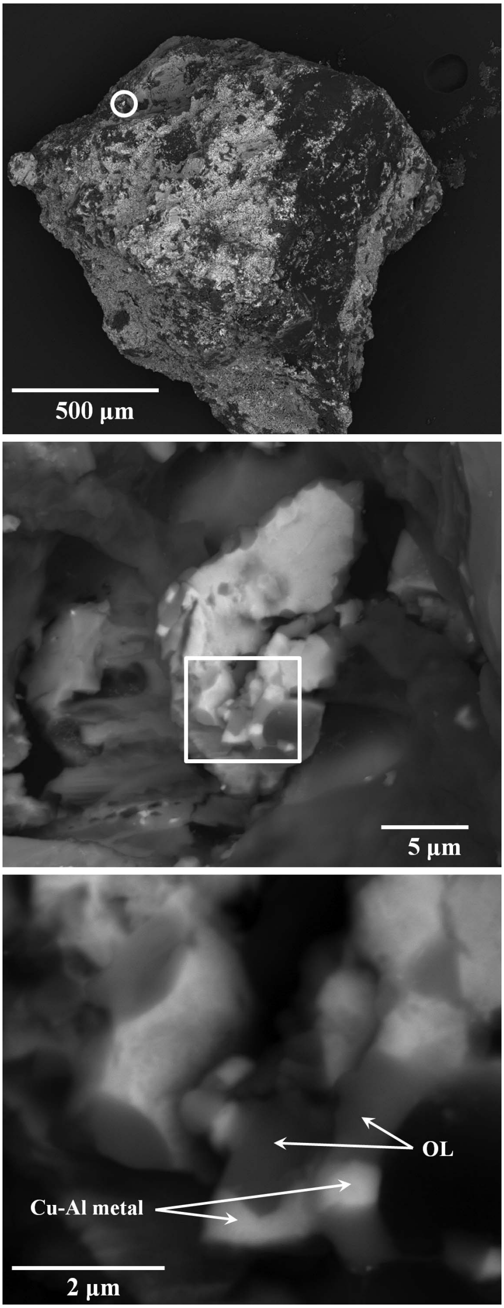

FIG. 6. Scanning electron microscope (SEM) backscatter electron (BSE) image of the whole of grain #5 (top) showing Cu-Al metal grains attached to the surface (white circle). In the other two SEM-BSE images (middle and bottom), successive enlargements are given of the marked region highlighting the metal-silicate contacts.

expert on structural geology, Glenn MacPherson (Smithsonian Institution, Washington), former Chairman of the Division of Meteorites 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), Paul Steinhardt (Princeton University) and Luca Bindi (Università di Firenze). Yudovskaya, Distler and Kryachko, the Russian contingent, contributed expertise in ore minerals and the region. Victor Komelkov and Bogdan Makovskii were the drivers and maintenance crew for the two tractor vehicles and responsible for netting fish for the team; Victor's wife Olga Komelkova was the chef and, normally working as a lawyer, helped to clear legal hurdles with the local government. Victor and Olga were accompanied by Bucks, their indomitable cat.

Is there more?

The extraordinary journey to one of the most remote places on the planet resulted in the extraction and panning of >1.5 tons of clay along

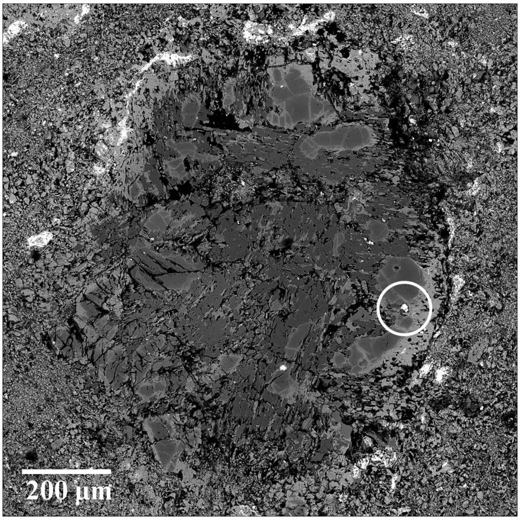

FIG. 7. SEM-BSE image of a porphyritic olivine chondrule in grain #121, showing irregular olivine crystals enclosed within enstatite. Bright rims around and veins within the olivine are Fe-rich and have very sharp boundaries with the surrounding Mg-rich olivine. A small grain of cupalite is enclosed within the olivine crystal (white circle). Fig. after MacPherson *et al.* (2013).

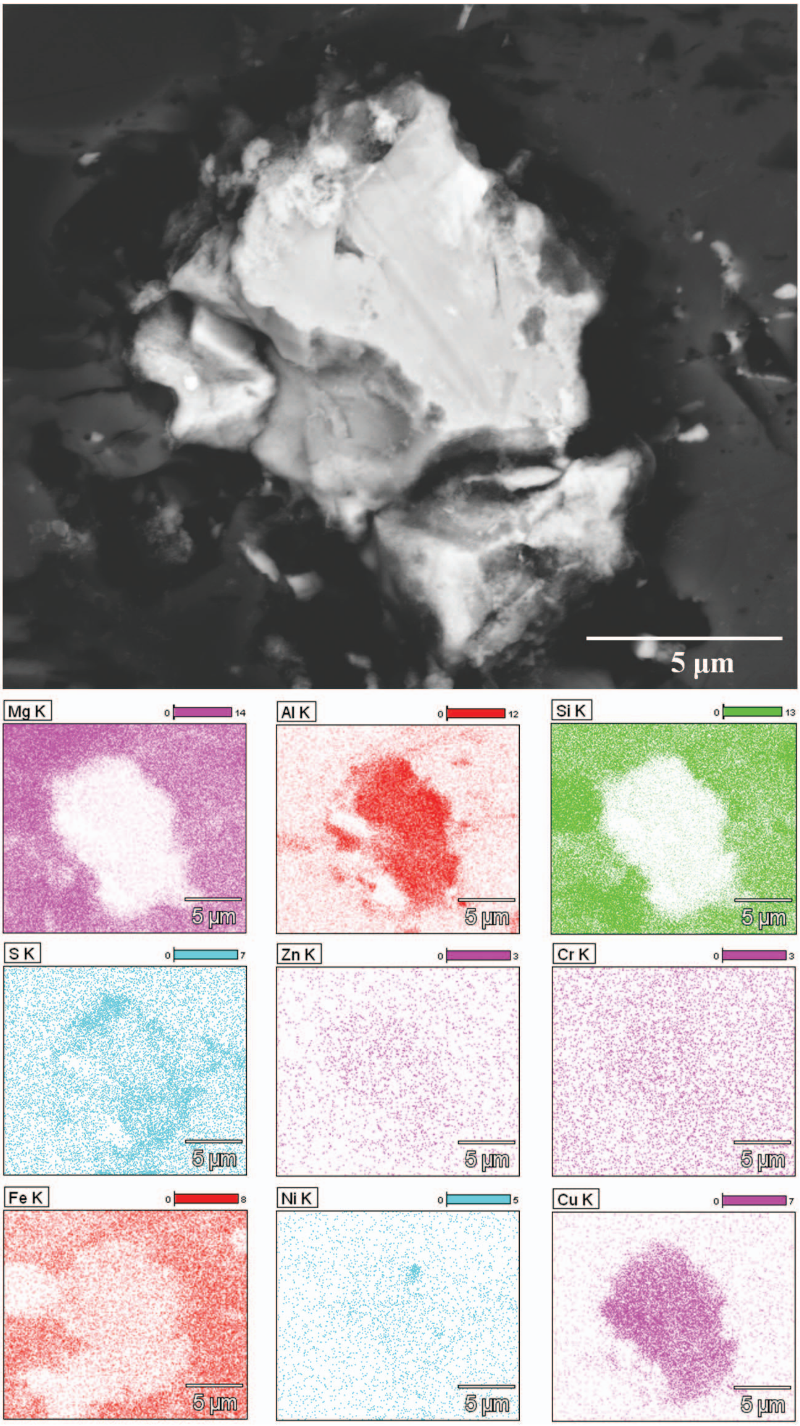

FIG. 8. SEM-BSE image of the cupalite grain inside the chondrule given in Fig. 7 together with X-ray area maps of the grain. The brighter region in the upper part of the cupalite grain corresponds to a Ni-rich metal.

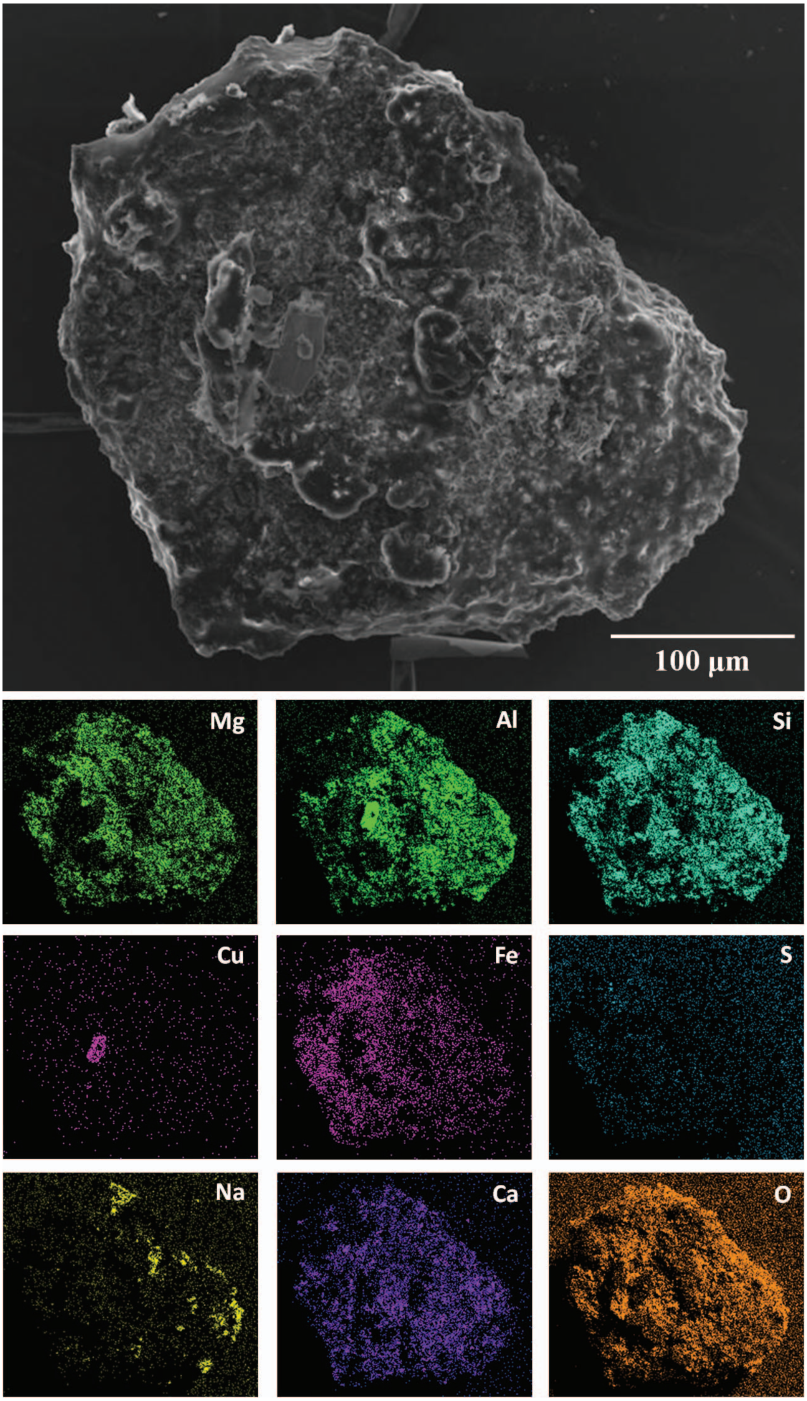

FIG. 9. SEM image of the whole of grain #122 together with X-ray area maps of the grain. Note the well formed Cu-Al fragment on the top of the grain.

the freezing cold waters of the Listvenitovyi stream. Over the next two years, nine new samples were found through a painstaking grain-by-grain search by Bindi and by graduate students Ruth Aronoff and Chaney Lin. These have firmly established that the quasicrystal and the rock containing it are definitely part of a carbonaceous chondritic meteorite with Ca-Al inclusions that date back 4.5 Gy to the formation of the solar system. The new meteorite find has been named Khatyrka (MacPherson *et al.*, 2013). The name derives from the Khatyrka river, which is one of the main rivers draining the Koryak Mountains. That river is also the namesake of the mineral, khatyrkite, which gives an added

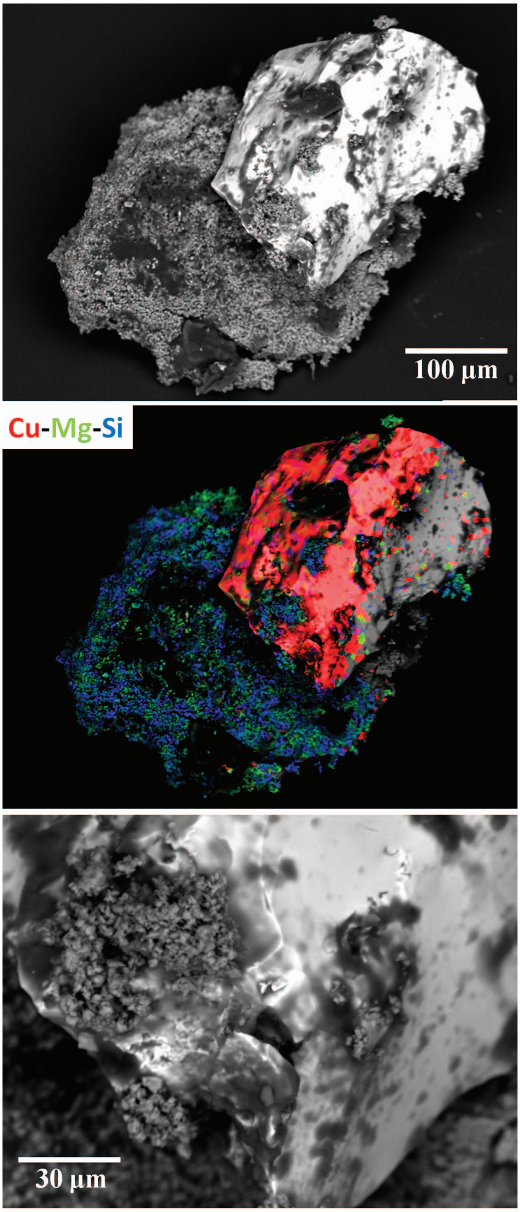

FIG. 10. SEM-BSE image of the whole of grain #123 (top) together with a RGB-cameo (combined X-ray area maps; R = Cu, G = Mg and B = Si) of the grain (middle). An enlargement of the grain is given in the bottom panel.

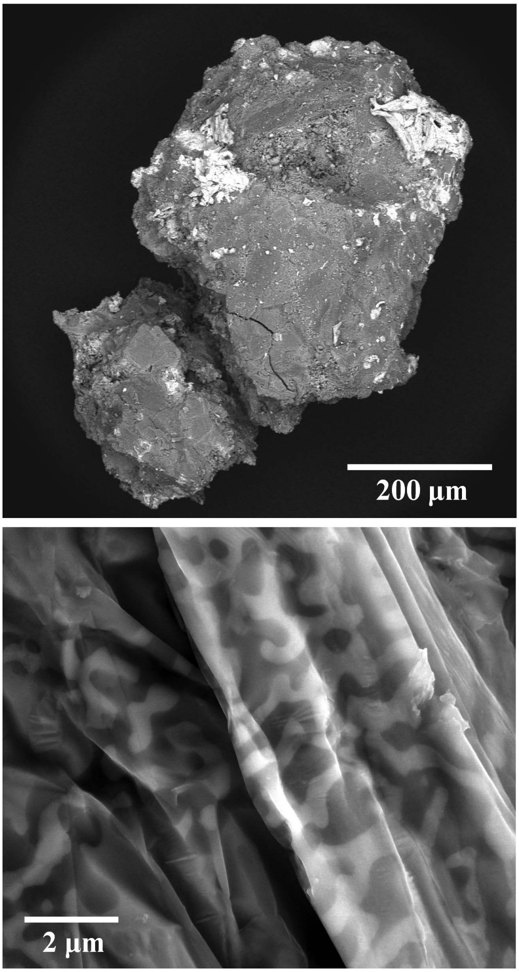

FIG. 11. SEM-BSE image of the whole grain #124 (which broke into two parts) highlighting brighter regions mainly corresponding to khatyrkite, $CuAl_2$ (top). An enlargement of these regions (lower panel) indicates the presence of a worm-like intergrowth of nearly pure Al (darker regions) in khatyrkite (lighter regions).

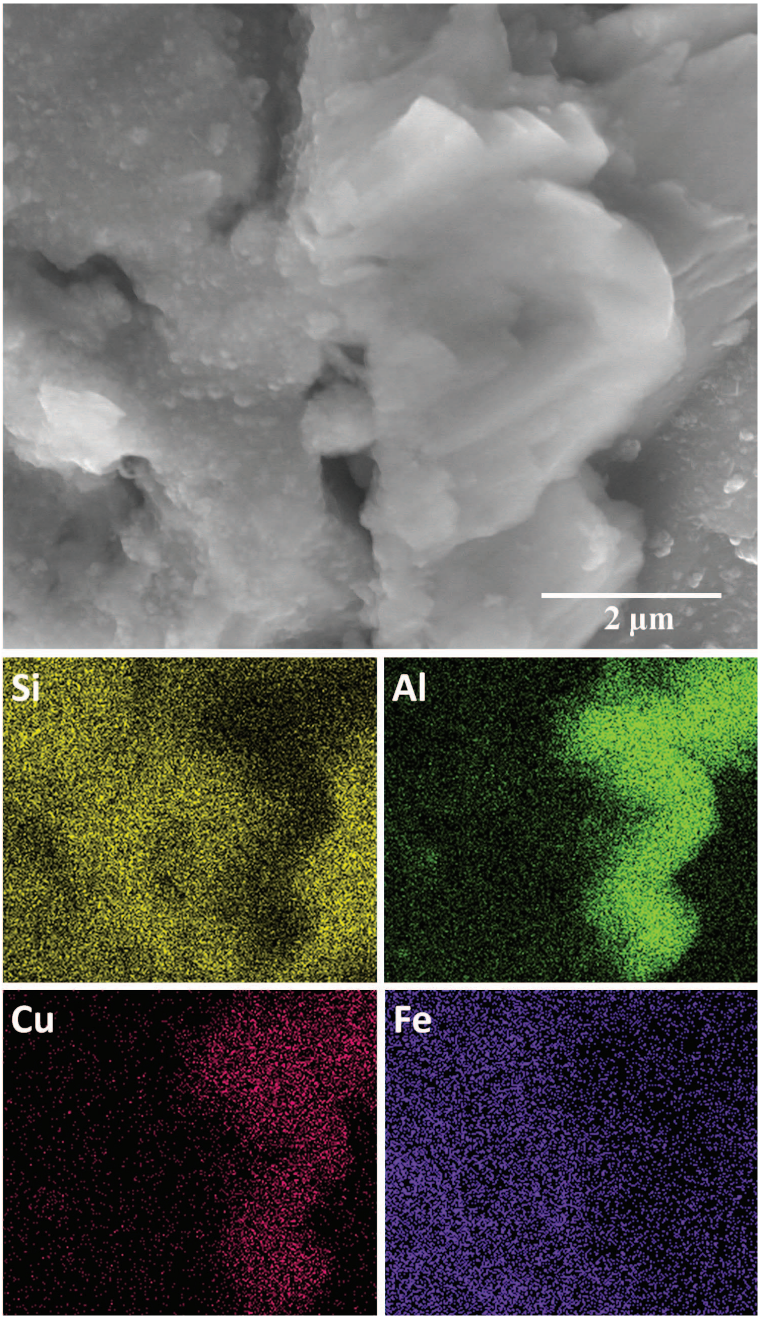

FIG. 12. SEM-SE image of a contact between the Cu-Al-metal and meteoritic silicate in grain #124 together with X-ray area maps of the grain.

symmetry to the meteorite name. Khatyrka has been approved by the Nomenclature Committee of the Meteoritical Society, and representative specimens are on deposit at the USA National Museum of Natural History, Smithsonian Institution, Washington DC.

Although the analyses of the nine samples collected by the expedition are not yet complete, we can report some preliminary results in this paper. Some of the grains are clearly chondritic and contain Type IA porphyritic olivine chondrules enclosed in matrices that have the characteristic platy olivine texture, matrix olivine composition, and mineralogy (olivine, pentlandite, awaruite, nepheline, and calcic pyroxene [diopside-hedenbergite solid solution])

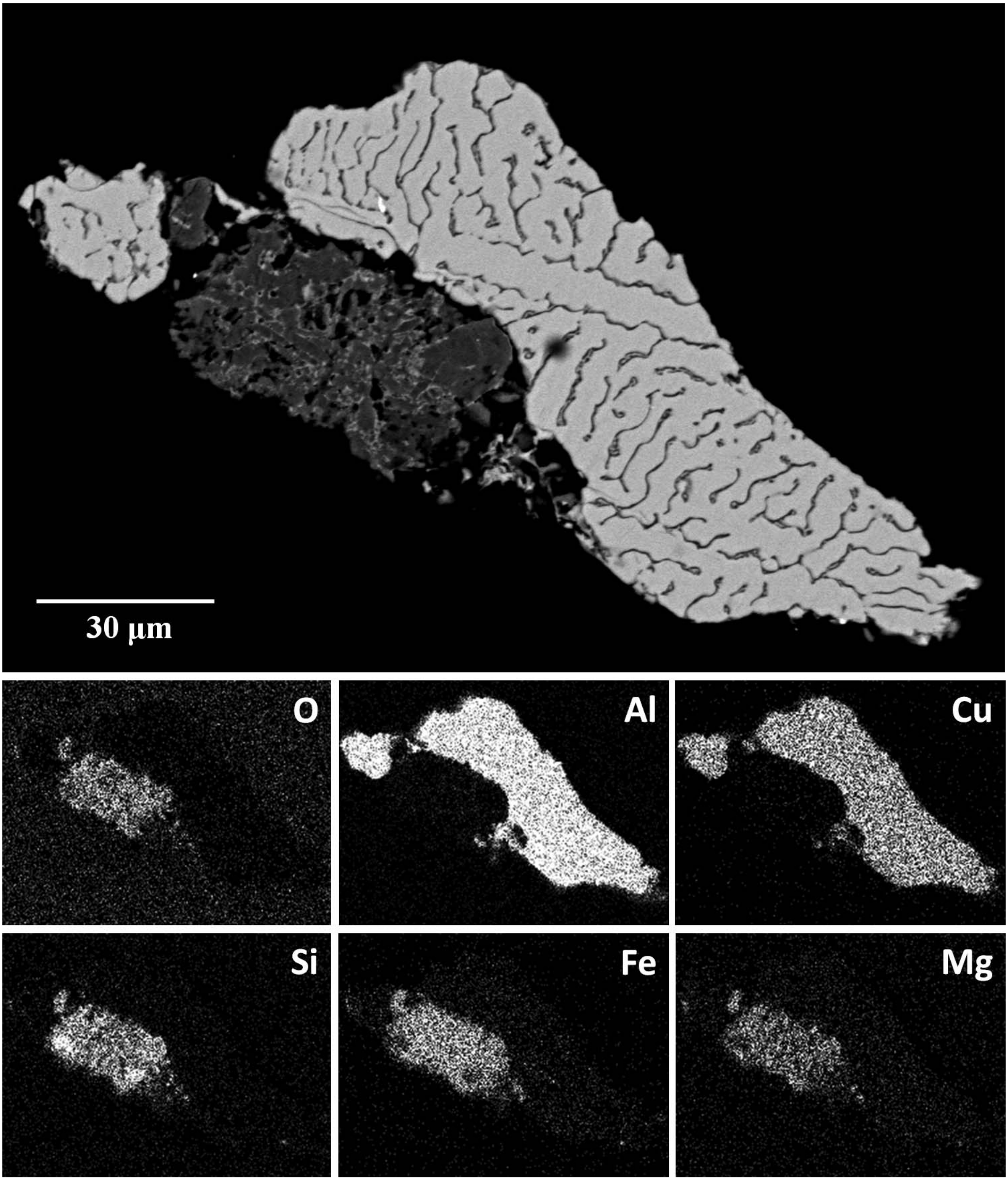

FIG. 13. SEM-BSE image of the whole of grain #125 together with X-ray area maps of the grain. Note the worm-like intergrowth of nearly pure Al (darker regions) in khatyrkite (lighter regions), as already observed in grain #124.

of oxidized-subgroup CV3 chondrites (Figs 6–9). A few grains (Fig. 10) contain fine-grained spinel-rich Ca-Al-rich inclusions (CAIs) with mineral O isotopic compositions again typical of such objects in CV3 chondrites. The chondritic and CAI grains contain small fragments of metallic Cu-Al-Fe alloys that include the quasicrystalline phase icosahedrite (Figs 11–15). Finally, some grains consist almost entirely of metallic alloys of Al + Cu ± Fe (Fig. 16). The Cu-Al-Fe metal alloys and the alloy-bearing achondrite clast are interpreted to be an accretionary component of what is otherwise a fairly normal CV3 (oxidized) chondrite (MacPherson *et al.*, 2013). Of note, a small icosahedrite fragment extracted from grain #5 (Fig. 6) gave the unmistakably five-fold signature of quasicrystal when analysed by single-crystal X-ray diffraction (Fig. 3*b*). Successive electron microprobe analysis gave the $Al_{63}Cu_{24}Fe_{13}$ stoichiometry, thus confirming the chemical homogeneity of icosahedrite. The assemblages of the grains also include novel metallic and silicate mineral species that are currently under investigation.

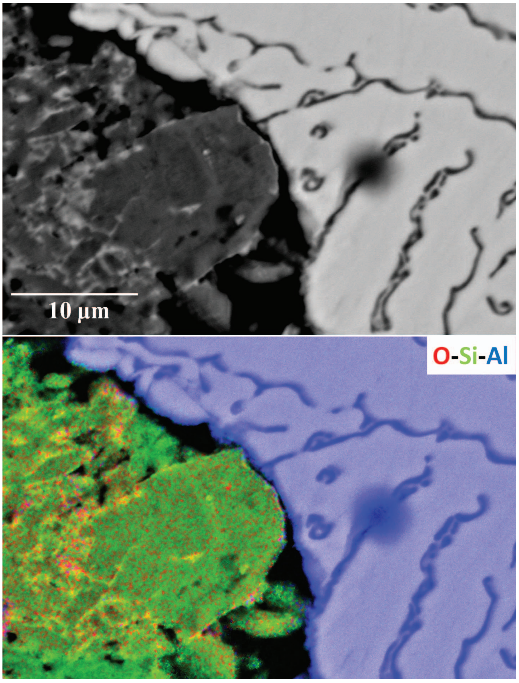

FIG. 14. SEM-BSE image together with a RGB-cameo (combined X-ray area maps; R = O, G = Si and B = Al) of a region of the grain #125.

Concluding remarks

The discovery of icosahedrite pushes the age of the oldest known example of this phase and quasicrystals generally, back to ~4.5 Gy, the age of all known unequilibrated chondrites. The occurrence inside the meteorite demonstrates that quasicrystals can form naturally within a complex, inhomogeneous medium. This sample formed under astrophysical conditions; whether a

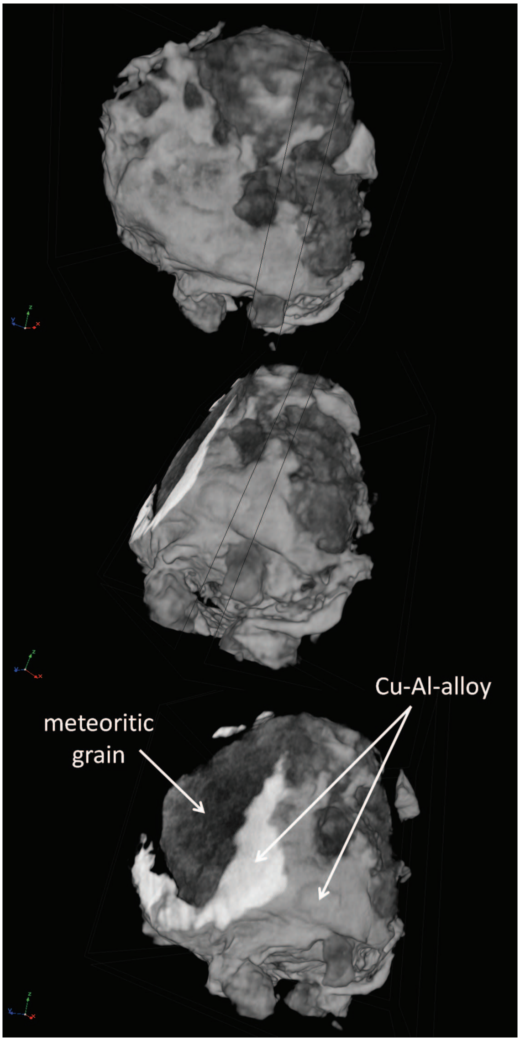

FIG. 15. Micro CT-SCAN 3D-images (at different rotations) of the whole of grain #126 (the grain size is ~1.2 mm). The brighter and the darker regions are Cu-Al metals and meteoritic silicates, respectively.

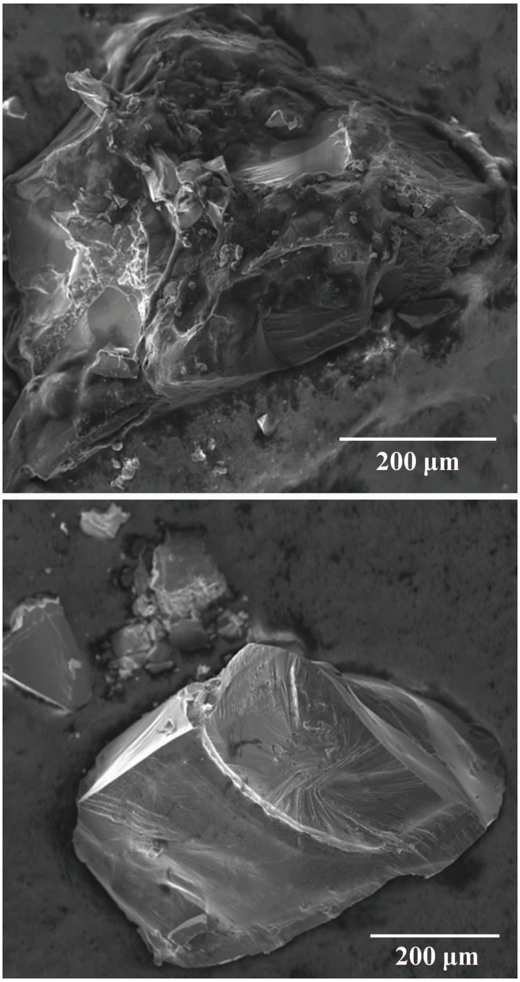

FIG. 16. Two SEM-SE images of grains #127 (top) and #128 (bottom) consisting mainly of pure Cu-Al metals.

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. Our story demonstrates that mineralogy continues to make important contributions to science. Many new minerals have compositions and crystal structures unknown to synthetic chemistry. Perhaps we will discover further quasicrystalline materials with new compositions or new forbidden symmetries not yet observed in the laboratory, or even new phases of matter not yet conceived.

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