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LETTER

Icosahedrite, $Al_{63}Cu_{24}Fe_{13}$, the first natural quasicrystal

LUCA BINDI,[1,2,*] PAUL J. STEINHARDT,[3,4] NAN YAO,[5] AND PETER J. LU[6]

[1]Museo di Storia Naturale, Sezione di Mineralogia, Università di Firenze, Via La Pira 4, I-50121 Firenze, Italy
[2]CNR-Istituto di Geoscienze e Georisorse, Sezione di Firenze, Via La Pira 4, I-50121 Firenze, Italy
[3]Princeton Center for Theoretical Science, Princeton University, Princeton, New Jersey 08544, U.S.A.
[4]Joseph Henry Laboratories, Department of Physics, Princeton University, Princeton, New Jersey 08544, U.S.A.
[5]Princeton Institute for the Science and Technology of Materials, Princeton University, New Jersey 08544, U.S.A.
[6]Department of Physics and SEAS, Harvard University, Cambridge, Massachusetts 02138, U.S.A.

ABSTRACT

Icosahedrite, ideally $Al_{63}Cu_{24}Fe_{13}$, is a new mineral from the Khatyrka River, southeastern Chukhotka, Russia. It occurs as dark gray-black anhedral to subhedral grains up to 100 μm across, closely associated with spinel, diopside, forsterite, nepheline, sodalite, corundum, stishovite, khatyrkite, cupalite, and an unnamed phase of composition AlCuFe. Icosahedrite is opaque with a metallic luster, possesses a gray streak, and is brittle with an uneven fracture. The density could not be determined. For quasicrystals, by definition, the structure is not reducible to a single three-dimensional unit cell, so neither cell parameters nor *Z* can be given. In plane-polarized incident light, icosahedrite exhibits neither bireflectance nor pleochroism. Between crossed polars, it is isotropic. Reflectance percentages ($R_{min} = R_{max}$) for the four standard COM wavelengths are 62.3 (471.1 nm), 60.6 (548.3 nm), 58.1 (586.6 nm), and 56.0 (652.3 nm), respectively.

The X-ray powder pattern was indexed on the basis of six integer indices, as conventionally used with quasicrystals, where the lattice parameter (in six-dimensional notation) is measured to be a_{6D} = 12.64 Å, with probable space group $Fm\bar{3}\,\bar{5}$. The four strongest X-ray powder-diffraction lines [*d* in Å (I/I_0) (n_1,n_2,n_3,n_4,n_5,n_6)] are: 2.006 (100) ($4\bar{2}0\ 042$), 2.108 (90) ($42\bar{2}\ \bar{2}22$), 1.238 (30) ($60\bar{4}\ 064$), and 3.41 (25) ($31\bar{1}\ \bar{1}11$). Average results of 34 electron-microprobe analyses gave, on the basis of total atoms = 100, the formula $Al_{63.11}Cu_{24.02}Fe_{12.78}Si_{0.03}Co_{0.01}Ca_{0.01}Zn_{0.01}Cr_{0.02}Cl_{0.01}$. The simplified formula is $Al_{63}Cu_{24}Fe_{13}$, which requires the mass fractions Al 43.02, Cu 38.60, Fe 18.38, total 100.00 wt%.

The new mineral is named for the icosahedral symmetry of its internal atomic structure, as observed in its diffraction pattern. Both the new mineral and mineral name have been approved by the Commission on New Minerals, Nomenclature and Classification, IMA (2010-042).

Keywords: Icosahedrite, new mineral, natural quasicrystal, electron-microprobe data, reflectance data, X-ray diffraction data, Khatyrka, Kamchatka, Russia

INTRODUCTION

Historically, all known natural minerals with 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. In this paper, we present the first exception: a natural quasicrystal, icosahedrite (ideally $Al_{63}Cu_{24}Fe_{13}$), with a three-dimensional icosahedral symmetry that is strictly forbidden for crystals. Quasicrystals can violate the conventional rules of crystallography because their structure is "quasiperiodic" rather than periodic (Levine and Steinhardt 1984); that is, their atomic density can be described by a finite sum of periodic functions with periods whose ratio is irrational. Their diffraction pattern consists of true Bragg peaks whose positions can be expressed as integer linear combinations of wavevectors whose magnitudes have irrational ratios. The first synthetic examples were found in the laboratory 25 years ago (Shechtman et al. 1984) and, today, well over 100 quasicrystalline materials have been synthesized, typically by mixing precise ratios of selected elemental components in the liquid and quenching under controlled conditions ranging from rapid to moderately slow (Janot 1994). Many have icosahedral symmetry, which includes 6 fivefold symmetry axes, 10 threefold axes, and 15 twofold symmetry axes, although quasicrystals with other crystallographically forbidden symmetry have also been synthesized (e.g., see Steurer 2004).

The new mineral reported here is the result of a decade-long systematic search for a natural quasicrystal described in Lu et al. (2001). There are numerous motivations for mounting a search. The discovery of natural quasicrystals would fundamentally alter the conventional classification of mineral forms. In condensed matter physics, the fragility and stability of quasicrystals has been a subject of considerable debate; a discovery could push back

* E-mail: luca.bindi@unifi.it

the age of the oldest quasicrystals by orders of magnitude and influence views on how difficult it is for quasicrystals to form. A natural quasicrystal would also enable the study of quasicrystal stability over annealing times and conditions not accessible in the laboratory. Moreover, laboratory searches for new types of quasicrystals have always relied significantly on trial-and-error synthesis; exploring existing geological examples could prove to be an effective complementary approach. Finally, the discovery could reveal exotic new geologic or extra-terrestrial processes.

With these motivations in mind, we developed a novel scheme for identifying likely quasicrystals based on powder diffraction data alone (Lu et al. 2001) and applied it to a large database of over 80 000 powder diffraction patterns compiled by the International Center for Diffraction Data (ICDD-PDF) that includes nearly 9000 mineral patterns and many more synthetic organic and inorganic phases. Although we have not yet found any natural quasicrystals in the ICDD-PDF, applying the same automated identification method to grains found in a natural sample not yet recorded in the ICDD-PDF produced a positive result (Bindi et al. 2009) and led to the discovery of icosahedrite.

Occurrence and physical and optical properties

The sample containing icosahedrite was not found in situ, but originates from a sample from the Mineralogical Collection of the Museo di Storia Naturale, Sezione di Mineralogia e Litologia, Università di Firenze, where it was labeled "khatyrkite, Khatyrka ultramafic zone, Koryak-Kamchata area, Koryak Mountains, Russia." Khatyrkite [$(Cu,Zn)Al_2$] and cupalite [(Cu,Zn)Al] were found by Razin et al. (1985) in heavy mineral concentrates from weathered serpentinite in the Listvenitovyi stream, Chetkinvaiam tectonic mélange, Iomrautvaam Massif, Khatyrka ultrabasic zone, Koryak Upland, Chukhotka Oblast, far eastern Russia. Geological and metallogenetic data concerning this area have been reported by Filatova and Vishnevskaya (1997). We have traced the history of this material and found that the sample containing icosahedrite was originally attached to the holotype material described by Razin et al. (1985); the rock was discovered by V.V. Kryachko in a blue-green clay bed along the Listvenotvyi stream, which flows into the Iomrautvaam tributary of the Khatryka River, in a remote region in southeastern Chukhotka. This locality in the Chetkinvaam tectonic mélange is a Triassic ultramafic zone.

We name the new mineral icosahedrite for the icosahedral symmetry of its atomic structure, which is evident from diffraction data (see below). The new mineral and mineral name have been approved by the Commission on New Minerals, Nomenclature and Classification, IMA (2010-042). Holotype material is deposited in the Mineralogical Collection of the Museo di Storia Naturale, Sezione di Mineralogia e Litologia, Università di Firenze, Firenze (Italy), under catalog number 46407/G.

Icosahedrite occurs associated with khatyrkite and cupalite grains together with minor micrometer-sized grains of an unnamed mineral with nominal stoichiometry AlCuFe (Fig. 1), and occurs intimately associated with forsterite, diopside (Fig. 2), spinel, nepheline, sodalite, corundum, and stishovite. The icosahedrite sample is anhedral and does not show any inclusions of, or intergrowths with, other minerals. The contacts between icosahedrite and the other mineral phases are sharp (Figs. 1 and 2), and the largest grain of icosahedrite is about 100 μm across.

Icosahedrite is opaque with a metallic luster, possesses a gray streak, is brittle with an uneven fracture, and lacks cleavage. We could not measure the density or the micro-hardness of the sample because of the small grain size; furthermore, for quasicrystals, by definition, the structure generally cannot be reduced to a single 3D unit cell, so it is not possible to report unit-cell parameters or *Z* for icosahedrite.

In plane-polarized incident light, icosahedrite exhibits neither bireflectance nor pleochroism, and internal reflections are absent. Between crossed polarizers, the mineral is isotropic. Reflectance measurements were made in air with a MPM-200 Zeiss

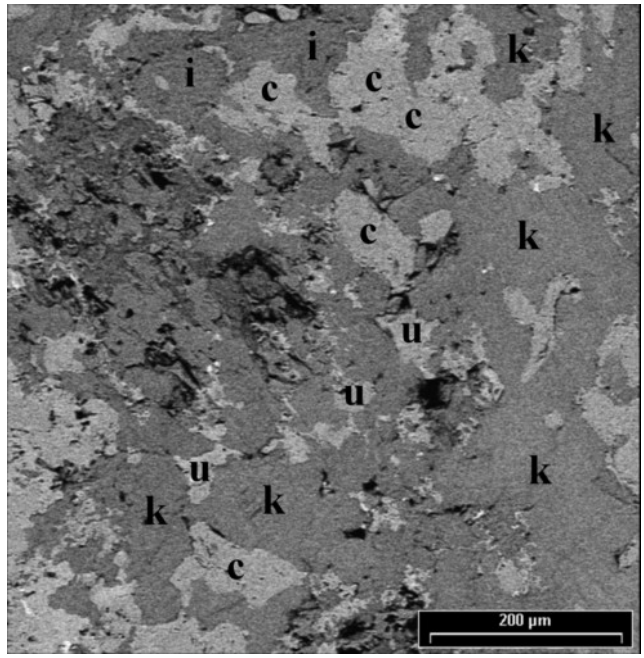

Figure 1. BSE-SEM image of a thin polished slice of the "khatyrkite" sample, with different minerals marked as follows: k = khatyrkite, ($CuAl_2$); c = cupalite (CuAl); u = unknown mineral with composition AlCuFe; i = icosahedrite.

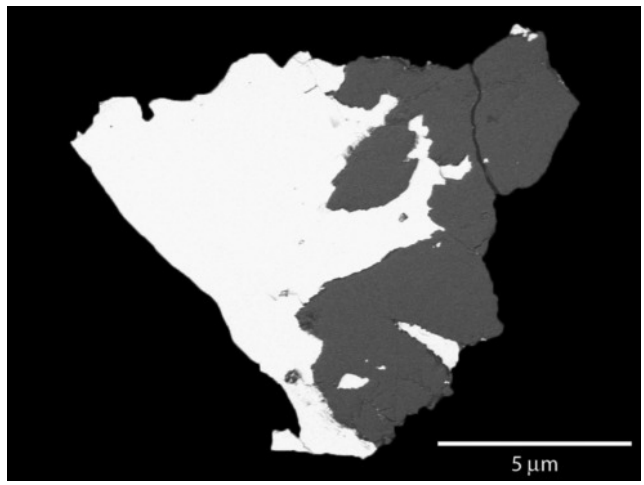

Figure 2. BSE-SEM image of a grain consisting of icosahedrite (white) and diopside (dark gray).

microphotometer equipped with a MSP-20 system processor on a Zeiss Axioplan ore microscope with the filament temperature set to approximately 3350 K. Readings were taken for specimen and standard (SiC) maintained under the same focus conditions. The diameter of the circular measuring area was 0.1 mm. The values ($R_{min} = R_{max}$) for the four standard COM wavelengths are 62.3 (471.1 nm), 60.6 (548.3 nm), 58.1 (586.6 nm), and 56.0 (652.3 nm), respectively. Icosahedrite has a lower reflectance than khatyrkite and cupalite.

X-RAY CRYSTALLOGRAPHY

Two small fragments removed from a polished section were studied with an Oxford Diffraction Excalibur PX Ultra diffractometer fitted with a 165 mm diagonal Onyx CCD detector and using copper radiation (Cu$K\alpha$, $\lambda = 1.54138$ Å). Both fragments had extremely broad X-ray diffraction profiles, indicating that a powder-diffraction study was the only possible means of X-ray investigation, even though their optical characteristics suggested adequate quality. We therefore collected an overexposed (60 h) rotation photograph. The program CrysAlis RED (Oxford Diffraction 2006) was used to convert the observed diffraction rings to a conventional powder diffraction pattern (Table 1), which was then indexed on the basis of six integer indices conventionally used with quasicrystals (Bancel 1991; Janot 1994; Lu et al. 2001). The lattice parameter (in six dimensional notation) can be written as $a_{6D} = 12.64$ Å (Steurer and Deloudi 2009), with probable space group $Fm\bar{3}\,\bar{5}$. The six-dimensional a parameter for the synthetic analog of icosahedrite first synthesized by Tsai et al. (1987) is reported as 4.45 Å (Tsai et al. 1987) and ca. 6.31 Å (Quiquandon et al. 1996; Quiquandon and Gratias 2006). These values are $a_{6D}/\sqrt{(5\tau)}$ and $a_{6D}/2$, respectively, of the value we give for icosahedrite, where τ is the golden ratio $(1+\sqrt{5})/2$; consequently, the values all agree, up to the arbitrary choice of principal axis length for the same 6D reciprocal lattice.

TABLE 1. X-ray powder-diffraction data for icosahedrite

I	d_{meas}	d_{calc}	n_1,n_2,n_3,n_4,n_5,n_6
2	8.94	8.9443	200000
5	5.53	5.5216	$11\bar{1}\bar{1}11$
20	**3.75**	**3.7450**	200022
25	**3.41**	**3.4100**	$31\bar{1}\bar{1}11$
20	**3.24**	**3.2444**	$22\bar{0}022$
5	2.799	2.7962	$31\bar{1}\bar{1}31$
10	**2.451**	**2.4522**	$42\bar{0}022$
5	2.350	2.3505	$31\bar{1}\bar{1}33$
90	**2.108**	**2.1082**	$42\bar{2}\bar{2}22$
100	**2.006**	**2.0048**	$42\bar{0}042$
5	1.728	1.7283	$53\bar{1}\bar{2}33$
15	**1.452**	**1.4528**	$62\bar{2}044$
5	1.418	1.4176	$62\bar{2}\bar{2}44$
30	**1.238**	**1.2390**	$60\bar{4}064$

Notes: The pattern was indexed on the basis of six integer indices as conventionally used with quasicrystals (see text). The strongest reflections are given in bold.

TABLE 2. Electron microprobe data (mean and ranges in wt% of elements), standard deviations (st.dev.), and probe standards for icosahedrite

Constituent	wt%	Ranges	st.dev.	Probe standards
Al	43.07	42.44–43.50	0.22	Al metal
Cu	38.62	37.66–39.67	0.18	Cu metal
Fe	18.07	17.19–18.90	0.11	synthetic FeS
Mg	0.00	0.00–0.02	0.01	Mg metal
Si	0.02	0.00–0.05	0.02	Si metal
Cr	0.02	0.00–0.04	0.01	Cr metal
P	0.00	0.00–0.02	0.01	synthetic Ni_3P
Co	0.01	0.00–0.04	0.01	Co metal
Ni	0.00	0.00–0.02	0.01	synthetic Ni_3P
Ca	0.01	0.00–0.02	0.01	synthetic $CaCl_2$
Zn	0.01	0.00–0.02	0.01	synthetic ZnS
S	0.00	0.00–0.02	0.01	synthetic ZnS
Cl	0.01	0.00–0.02	0.01	synthetic $CaCl_2$
Total	99.84	99.24–100.18		

CHEMICAL COMPOSITION

A preliminary chemical analysis using energy-dispersive spectrometry, performed on the same fragments used for the subsequent studies found no major elements ($Z > 9$) other than Al, Cu, and Fe. The chemical composition (34 analyses on different spots) was then determined using a JEOL JXA-8600 electron microprobe equipped with four wavelength-dispersive spectrometers. Major and minor elements were determined using 15 kV accelerating voltage and 20 nA beam current (1 μm beam diameter), with variable counting times; 30 s for Al, Cu and Fe, and 100 s for the minor elements Mg, Si, Cr, P, Co, Ni, Cl, Ca, Zn, and S. The same analyses were repeated for synthetic $Al_{63}Cu_{24}Fe_{13}$ (Bancel 1991) to check accuracy and precision. The crystal fragment was found to be homogeneous within analytical error. Analytical results, estimated standard deviations, and probe standards are in Table 2.

TEM STUDY

One of the grains studied by X-ray diffraction was carefully removed from the glass fiber for study using TEM. During the detachment process, it became clear that the fragment consisted of many independent granules. One granule, about 1.5 μm across, was found to be sufficiently thin at the edges and near cracks to obtain the TEM diffraction patterns shown in Figure 3. The Philips CM200-FEG TEM used to obtain these patterns was operated at 200 keV with a vacuum pressure of ca. 2×10^{-7} Torr with an electron beam size ranging from 50 nm to 0.3 μm. The regions sampled by TEM were roughly 0.3–0.5 μm across. The angles between the symmetry planes were found to be consistent with icosahedral symmetry. For example, the angle measured between the twofold and fivefold symmetry planes was 31.6(5)°, which agrees with the ideal rotation angle between the twofold and fivefold axes of an icosahedron. A more detailed description is given by Bindi et al. (2009).

ORIGIN

The evidence for the existence of the quasicrystal phase in the rock is therefore overwhelmingly strong. However, the observation of metallic Al in intermetallic compounds with copper and iron, which requires a highly reducing environment, is deeply puzzling. It raises the possibility that the sample originated from slag or another anthropogenic process. However, the sample was found in a remote region very far from any industrial activity. Moreover, we observe forsterite and diopside in direct contact with the metallic aluminum alloys (e.g., Fig. 2); no glass or bubbles (Figs. 1 and 2), unusual zoning of P and Cr in forsterite; concentration of Ni in the forsterite alone and not in the metallic aluminum alloys; no myrmekitic or skeletal textures; and grains of icosahedrite in contact with stishovite, which suggests ultra-high formation pressures greater than 10 GPa. Taken individually, each of these features is

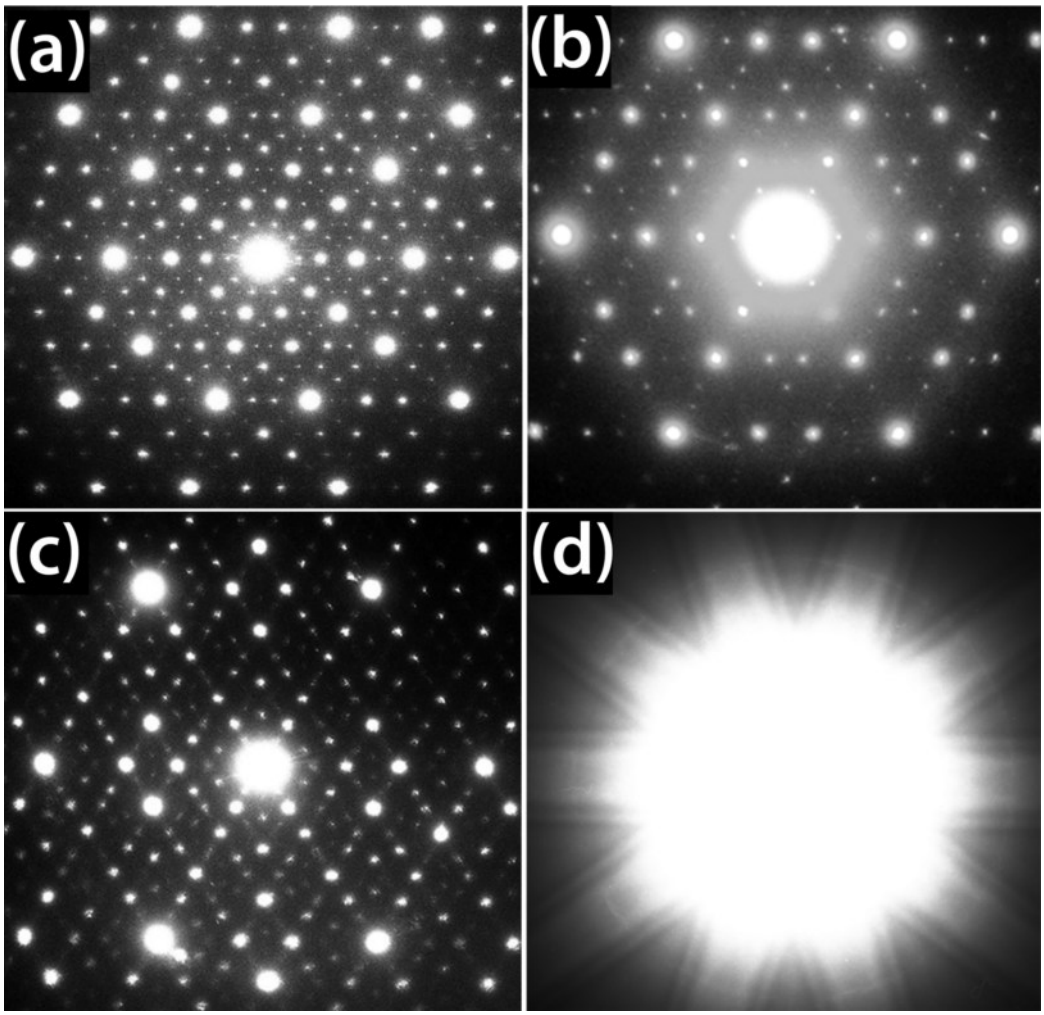

FIGURE 3. The fivefold (**a**), threefold (**b**), and twofold (**c**) electron diffraction patterns for icosahedrite collected in the TEM. The patterns correspond perfectly, up to experimental resolution, with the fivefold, threefold, and twofold patterns predicted for a face-centered icosahedral quasicrystal. Panel (**d**) shows the convergent beam (Kikuchi) diffraction pattern obtained along the fivefold axis, providing further physical evidence of the symmetry and high degree of translational order.

inconsistent with an anthropogenic origin; together, these data provide compelling physical evidence that the rock was formed by some natural process, whose characterization is an important direction for future research.

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