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LETTER

# Decagonite, $Al_{71}Ni_{24}Fe_5$, a quasicrystal with decagonal symmetry from the Khatyrka CV3 carbonaceous chondrite

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## ABSTRACT

Decagonite is the second natural quasicrystal, after icosahedrite ($Al_{63}Cu_{24}Fe_{13}$), and the first to exhibit the crystallographically forbidden decagonal symmetry. It was found as rare fragments up to ~60 μm across in one of the grains (labeled number 126) of the Khatyrka meteorite, a CV3 carbonaceous chondrite. The meteoritic grain contains evidence of a heterogeneous distribution of pressures and temperatures that occurred during impact shock, in which some portions of the meteorite reached at least 5 GPa and 1200 °C. Decagonite is associated with Al-bearing trevorite, diopside, forsterite, ahrensite, clinoenstatite, nepheline, coesite, pentlandite, Cu-bearing troilite, icosahedrite, khatyrkite, taenite, Al-bearing taenite, and steinhardtite. Given the exceedingly small size of decagonite, it was not possible to determine most of the physical properties for the mineral. A mean of seven electron microprobe analyses (obtained from three different fragments) gave the formula $Al_{70.2(3)}Ni_{24.5(4)}Fe_{5.3(2)}$, on the basis of 100 atoms. A combined TEM and single-crystal X-ray diffraction study revealed the unmistakable signature of a decagonal quasicrystal: a pattern of sharp peaks arranged in straight lines with 10-fold symmetry together with periodic patterns taken perpendicular to the 10-fold direction. 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. The likely space group is $P10_5/mmc$, as is the case for synthetic $Al_{71}Ni_{24}Fe_5$. The five strongest powder-diffraction lines [$d$ in Å ($I/I_0$)] are: 2.024 (100), 3.765 (50), 2.051 (45), 3.405 (40), 1.9799 (40). The new mineral has been approved by the IMA-NMNC Commission (IMA2015-017) and named decagonite for the 10-fold symmetry of its structure. The finding of a second natural quasicrystal informs the longstanding debate about the stability and robustness of quasicrystals among condensed matter physicists and demonstrates that mineralogy can continue to surprise us and have a strong impact on other disciplines.

**Keywords:** Quasicrystal, aluminum, meteorite, chemical composition, TEM, X-ray diffraction, new mineral, decagonite

## INTRODUCTION

Quasicrystals, solids with quasiperiodic atomic arrangements that violate the mathematical constraints of conventional crystallography, exhibit rotational symmetry forbidden to crystals, such as fivefold, sevenfold, and higher-order symmetry axes (Levine and Steinhardt 1984; Shechtman et al. 1984). The first occurrence of a quasicrystalline phase in nature, icosahedrite $Al_{63}Cu_{24}Fe_{13}$ (Bindi et al. 2009, 2011), displayed a fivefold symmetry in two dimensions and icosahedral symmetry in three dimensions and was found in the Khatyrka meteorite, a CV3 carbonaceous chondrite (Steinhardt and Bindi 2012; MacPherson et al. 2013; Bindi and Steinhardt 2014). The discovery represents a breakthrough in mineralogy and in condensed matter physics. The intriguing discovery in Grain 126 of the Khatyrka meteorite (Bindi et al. 2014, 2015) of steinhardtite grains with composition $Al_{0.38–0.50}Ni_{0.32–0.40}Fe_{0.10–0.30}$, and the fact that decagonal quasicrystals have been reported in the Al–Ni–Fe system (Tsai et al. 1989), stimulated us to continue the search for other quasicrystals.

Here we report the description of the second natural quasicrystal and the first with decagonal symmetry, which is named

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decagonite for the 10-fold symmetry of its structure. The mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA2015-017). The holotype material is deposited in the mineralogical collections of the Museo di Storia Naturale, Università di Firenze (Italy), under catalog number 3146/I.

## OCCURRENCE

Decagonite was found in Grain 126, one of the meteoritic fragments (Fig. 1; see Hollister et al. 2014 for more details) found during an expedition to the Koryak Mountains in far eastern Russia in 2011 (Steinhardt and Bindi 2012; Bindi and Steinhardt 2014) as a result of a search for material that would provide information on the origin of icosahedrite (Bindi et al. 2009, 2011, 2012; MacPherson et al. 2013; Hollister et al. 2014).

In the meteoritic fragments, which present a range of evidence indicating that an impact shock generated a heterogeneous distribution of pressures and temperatures in which some portions of the meteorite reached at least 5 GPa and 1200 °C, decagonite occurs as small grains, one of which is in contact with a $(Fe,Mg)_2SiO_4$ phase (marked "Ol" in the bottom panel of Fig. 1). This is either an intermediate composition olivine similar to the $Fo_{45-50}$ found in Grain 125 or the high-pressure polymorph ahrensite, which was also observed in Grain 125 (Hollister et al. 2014). Other minerals identified in the Khatyrka meteorite fragments include trevorite, diopside, forsterite, ahrensite, clinoenstatite, nepheline, coesite, stishovite, pentlandite, Cu-bearing troilite, icosahedrite, khatyrkite, cupalite, taenite, Al-bearing taenite, Ni-Al-Mg-Fe spinels, magnetite, aluminum, steinhardtite, and an unnamed spinelloid with composition $Fe_{3-x}Si_xO_4$ ($x \approx 0.4$).

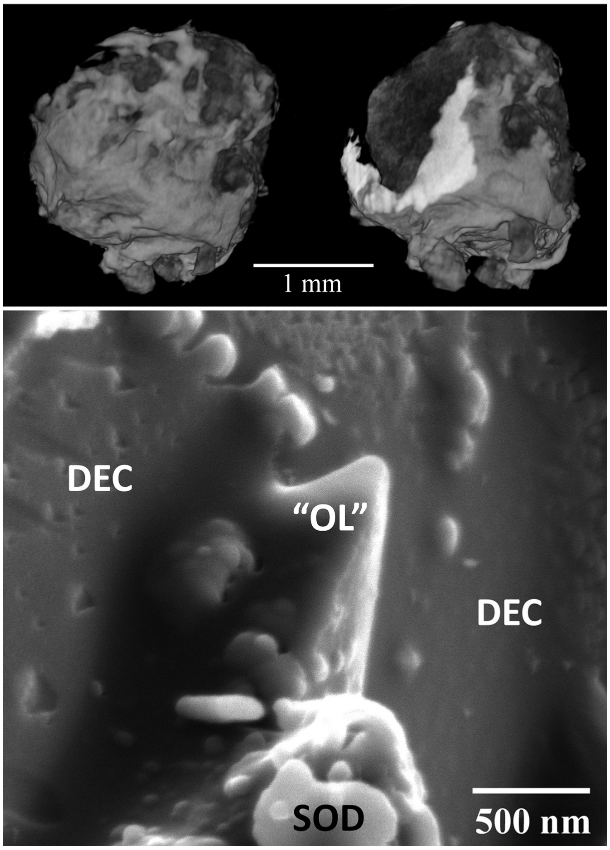

**FIGURE 1.** The **top panel** shows micro-CT-SCAN 3D-images (at different rotations) of the whole of Grain 126. The brighter and the darker regions are Cu-Al metals and meteoritic silicates, respectively. The **bottom panel** shows a SEM-BSE image of decagonite (DEC) in apparent growth contact with "olivine" ("OL"). See text for discussion of the "olivine" composition. The image also contains sodalite (SOD).

The three identified fragments of decagonite are generally anhedral, up to 60 μm across, and do not contain inclusions or intergrowths of other minerals. Decagonite is metallic, gray to black in color. It is not possible to calculate the density because, as noted below, there does not exist a three-dimensional unit cell or a value of *Z* for a quasicrystal. Moreover, the density was not measured owing to the very small size of the fragments.

## EXPERIMENTAL METHODS

### X-ray diffraction

Two decagonite fragments were mounted on two different 0.005 mm diameter carbon fibers (which were, in turn, attached to glass rods) and checked on both a CCD-equipped Oxford Diffraction Xcalibur 3 single-crystal diffractometer, operating with Mo*K*α radiation (λ = 0.71073 Å), and an Oxford Diffraction Xcalibur PX Ultra diffractometer equipped with a 165 mm diagonal Onyx CCD detector at 2.5:1 demagnification operating with Cu*K*α radiation (λ = 1.5406 Å). One of the fragments consisted of many tiny grains and thus a powder diffraction pattern was collected (Table 1). The pattern matched precisely that reported for the synthetic decagonal $Al_{71}Ni_{24}Fe_5$ quasicrystal (Tsai et al. 1989). The diffraction analysis of a second fragment revealed the unmistakable signature of a decagonal quasicrystal: a pattern of sharp peaks arranged in straight lines with 10-fold symmetry together with periodic patterns taken perpendicular to the 10-fold direction (as illustrated in Fig. 2). The likely space group of decagonite is $P10_5/mmc$, as is the case for synthetic $Al_{71}Ni_{24}Fe_5$ (Tsai et al. 1989).

### Chemical analyses

Three decagonite fragments were analyzed via wavelength-dispersive spectrometry WDS) using a JEOL JXA-8600 electron microprobe at 15 kV, 20 nA beam current, and 1 μm beam diameter. Variable counting times were used: 30 s for Al, Ni, and Fe, and 60 s for the minor elements Mg, Si, Cr, P, Co, Cu, Cl, Ca, Zn, and S. Replicate analyses of synthetic $Al_{53}Ni_{42}Fe_5$ were used to check accuracy and precision. The crystal fragments were found to be homogeneous within analytical error. The standards used were: Al metal, synthetic $Ni_3P$ (Ni, P), synthetic FeS (Fe), Mg metal, Si metal, Cr metal, Co metal, Cu metal, synthetic $CaCl_2$ (Ca, Cl), and synthetic ZnS (Zn, S). Mg, Si, Cr, P, Co, Cu, Cl, Ca, Zn, and S were found to be equal to or below the limit of detection (0.01 wt%).

Seven point analyses on different spots were performed on the three samples. Table 2 reports the chemical analyses (in wt% of elements), standard deviations, and atomic ratios calculated on 100 atoms per formula unit.

### Transmission electron microscopy

Because of the small size of the grains, the single-crystal X-ray investigation was combined with a structural study done by transmission electron microscopy. The Philips CM200-FEG TEM was operated at 200 keV with an electron beam size ranging from 30 nm to 0.2 μm. The sample was placed on a Cu mesh TEM grid (300 mesh, 3 mm in diameter) that was previously covered by a thin carbon

**TABLE 1.** Measured X-ray powder-diffraction data for decagonite (Cu*K*α radiation)

| 2θ (°) | *d* (Å) | $I_{rel}$ |
|---|---|---|
| 23.61 | 3.765 | 50 |
| 26.15 | 3.405 | 40 |
| 38.58 | 2.332 | 25 |
| 44.12 | 2.051 | 45 |
| 44.75 | 2.024 | 100 |
| 45.79 | 1.9799 | 40 |
| 50.63 | 1.8014 | 30 |
| 65.60 | 1.4219 | 35 |
| 78.03 | 1.2235 | 25 |

layer (support film). Energy-dispersive (EDS) data were obtained using Evex NanoAnalysis System IV attached to the Philips CM200-FEG TEM. A small probe diameter of 20–100 nm was used, with a count rate of 100–300 cps and an average collection time of 180 s. The quantitative analyses were taken at 200 kV and are based on using pure elements and the NIST 2063a standard sample as a reference under the identical TEM operating conditions.

## RESULTS AND DISCUSSION

The TEM study of one of the three studied fragments of decagonite revealed that, at the sub-micrometer length scale, the particles are homogeneous. Selected-area electron diffraction patterns (Fig. 3) consist of sharp peaks arranged in periodically spaced planes with 10-fold symmetry. This pattern is characteristic of a decagonal quasicrystal. The high-resolution transmission electron microscopy image in Figure 3 shows that the real space structure in the plane normal to the viewing axis consists of a homogeneous, quasiperiodic, 10-fold symmetric pattern. Collectively, TEM (Fig. 3) and single-crystal X-ray data (Fig. 2) provide conclusive evidence of crystallographically forbidden decagonal symmetry in a naturally occurring phase.

As already observed for icosahedrite (Bindi et al. 2009, 2011), decagonite exhibits a high degree of structural perfection, particularly the absence of significant phason strains (Levine et al. 1985; Lubensky et al. 1986). This is unusual because this high degree of perfection occurs in a quasicrystal intergrown with other phases under conditions far from equilibrium, and not under controlled laboratory conditions. We think that either the mineral samples formed without phason strain in the first place, or subsequent annealing was sufficient for phason strains to relax away.

Figure 4 is a ternary diagram showing the compositions (WDS and EDS data) of all the AlNiFe fragments we analyzed from Grain 126, plotted in terms of Al-Ni-Fe atomic percent. The compositions of steinhardtite (red open circles and black open squares) are approximately collinear with decagonite (green open triangles) and taenite (light blue open diamonds). This suggests a reaction relation among these phases. That is, steinhardtite could break down to decagonite and taenite, or taenite plus decagonite could react to produce steinhardtite.

The Al–Ni–Fe of the projected composition of the Al-bearing trevorite spinel plots very close to that of steinhardtite in Figure 4. As documented by Hollister et al. (2015), shock can reduce iron, with the oxygen going into the vapor. Similarly, steinhardtite could form as a result of shock of pre-existing Al-bearing trevorite.

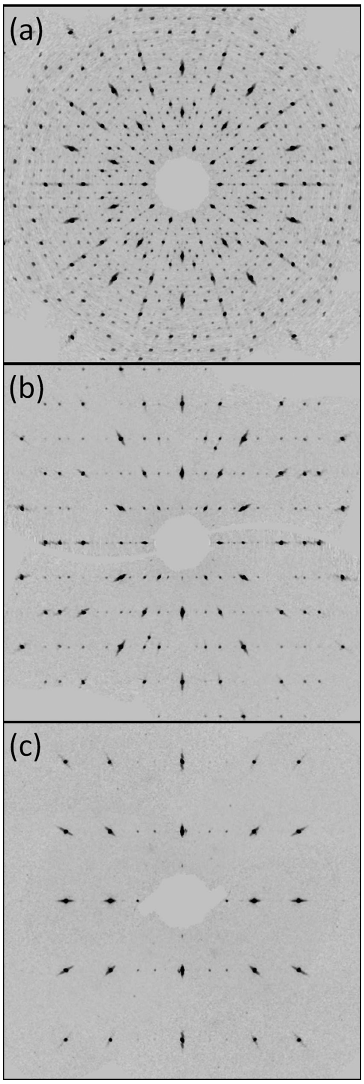

**FIGURE 2.** Reconstructed precession images along the 10-fold symmetry axis (**a**) and perpendicular to the 10-fold direction (**b**,**c**) obtained using the single-crystal X-ray data set (Mo$K\alpha$ radiation) collected from decagonite.

## IMPLICATIONS

The discovery of two different types of quasicrystals in a meteorite has implications for other scientific disciplines. From the perspective of condensed matter physics, the fact that these phases formed under astrophysical conditions constitutes significant new support for the original proposal (Levine and Steinhardt 1984) that quasicrystals can be energetically stable states of matter, on the same footing as crystals. The fact that both icosahedrite and decagonite contain metallic aluminum represents a challenge to geochemistry, given the strong affinity of Al for oxygen.

Conceivably, the Al–Ni–Fe phases might have also formed in the highly reducing conditions near the core-mantle bound-

**TABLE 2.** Electron microprobe analyses (values and standard deviations in wt% of elements) and atomic ratios (on the basis of 100 atoms) for three fragments of decagonite

| | 1 | | 2 | | 3 | | | mean |
|---|---|---|---|---|---|---|---|---|
| | *a* | *b* | *a* | *b* | *a* | *b* | *c* | |
| Al | 52.23(60) | 51.74(64) | 52.01(71) | 51.60(66) | 52.10(44) | 52.64(40) | 53.01(46) | 52.19 |
| Ni | 39.85(51) | 38.92(49) | 40.45(53) | 39.41(55) | 40.01(34) | 39.23(39) | 39.01(37) | 39.55 |
| Fe | 8.02(10) | 8.74(12) | 7.55(14) | 8.23(15) | 8.10(9) | 8.16(12) | 8.47(11) | 8.18 |
| Total | 100.10 | 99.40 | 100.01 | 99.24 | 100.21 | 100.03 | 100.49 | 99.92 |
| | | | | | | | | |
| Al | 70.18 | 70.06 | 70.05 | 70.02 | 70.03 | 70.55 | 70.65 | 70.22 |
| Ni | 24.61 | 24.22 | 25.04 | 24.59 | 24.71 | 24.17 | 23.90 | 24.46 |
| Fe | 5.21 | 5.72 | 4.91 | 5.39 | 5.26 | 5.28 | 5.45 | 5.32 |

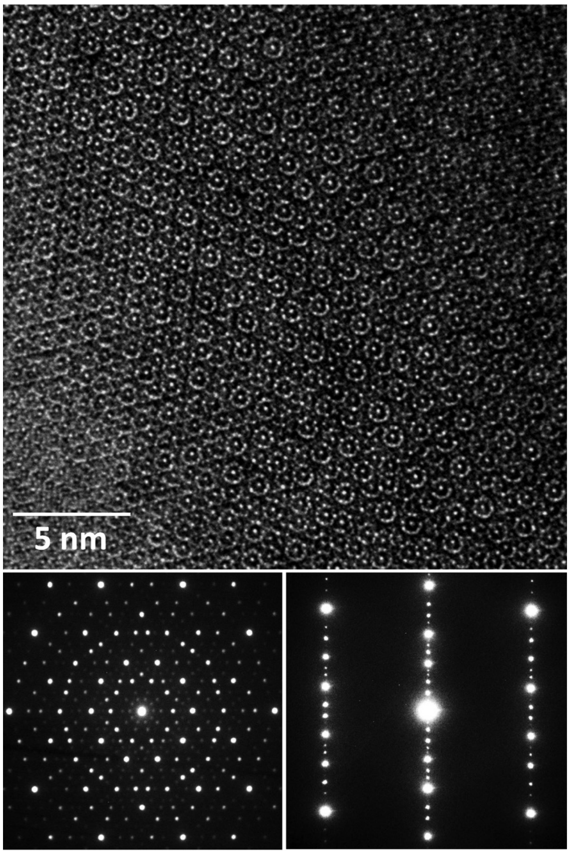

**Figure 3.** The **top panel** is a high-resolution transmission electron microscopy (HRTEM) image showing that the real space structure of decagonite normal to the viewing axis consists of a homogeneous, quasiperiodic, and 10-fold symmetric pattern. The **bottom panel** reports two selected-area electron diffraction patterns collected down the 10-fold axis (**left**) and along an axis out of the 10-fold plane (**right**). The combination of quasiperiodicity (10-fold symmetry) in one plane and periodicity along the third dimension is characteristic of decagonal symmetry.

ary, as we speculated during the early stages of our investigation (Steinhardt and Bindi 2012). This opportunity seems worthy of exploring since it may give us new insights on core composition and properties. However, the origin of the occurrence of Cu with the Al compounds remains elusive.

Finally, our discoveries should motivate the re-examination of other terrestrial and extraterrestrial minerals in search of different quasicrystals. We believe that mineralogy can continue to surprise us and have an impact on other disciplines, including cosmochemistry, condensed matter physics, and materials engineering.

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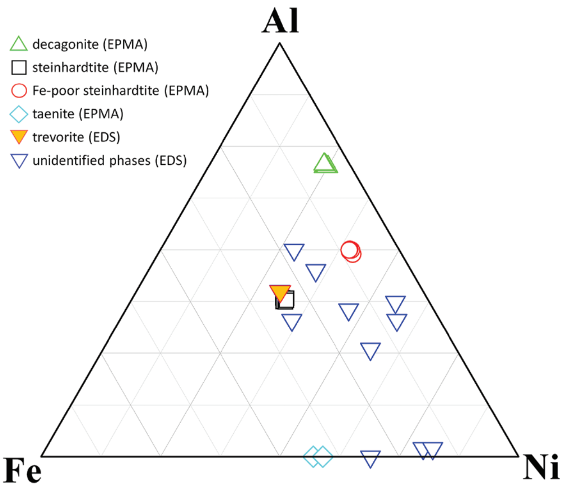

**Figure 4.** Ternary Al-Ni-Fe diagram reporting all the chemical data we obtained on minerals belonging to Grain 126. The cloud of data in the steinhardtite region (blue downward triangles) lies between decagonite and FeNi solid solution. (Color online.)

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