This is a preprint, the final version is subject to change, of the American Mineralogist (MSA)
Cite as Authors (Year) Title. American Mineralogist, in press.
(DOI will not work until issue is live.) DOI: http://dx.doi.org/10.2138/am-2017-5991

Revision 1

Hollisterite (Al_3Fe), kryachkoite $(Al,Cu)_6(Fe,Cu)$, and stolperite (AlCu): Three new minerals from the Khatyrka CV3 carbonaceous chondrite

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ABSTRACT

Our nanomineralogy investigation of the Khatyrka CV3 carbonaceous chondrite, has revealed three new alloy minerals hollisterite (IMA 2016-034; Al_3Fe), kryachkoite (IMA 2016-062; $(Al,Cu)_6(Fe,Cu)$), and stolperite (IMA 2016-033; AlCu), in section 126A of USNM 7908. Hollisterite occurs only as one crystal with stolperite, icosahedrite and khatyrkite, showing an empirical formula of $Al_{2.89}Fe_{0.77}Cu_{0.32}Si_{0.02}$ and a monoclinic *C*2/*m* structure with a = 15.60 Å, b = 7.94 Å, c = 12.51 Å, β = 108.1°, V = 1472.9 Å^3, Z = 24. Kryachkoite occurs with khatyrkite and aluminum, having an empirical formula of $Al_{5.45}Cu_{0.97}Fe_{0.55}Cr_{0.02}Si_{0.01}$ and an orthorhombic $Cmc2_1$ structure with a = 7.460 Å, b = 6.434 Å, c = 8.777 Å, V = 421.3 Å^3, Z = 4. Stolperite occurs within khatyrkite, or along with icosahedrite and/or hollisterite and khatyrkite, having an empirical formula of $Al_{1.15}Cu_{0.81}Fe_{0.04}$ and a cubic *Pm*-3*m* structure with a = 2.9 Å, V = 24.4 Å^3, Z = 1. Specific features of the three new minerals, and their relationships with the meteorite matrix material, add significant new evidence for the extraterrestrial origin of the Al-Cu-Fe metal phases in the Khatyrka meteorite. Hollisterite is named in honor of Lincoln S. Hollister at Princeton University for his extraordinary contributions to Earth Sciences. Kryachkoite is named in honor of Valery Kryachko who discovered the original samples of the Khatyrka meteorite in 1979. Stolperite is named in honor of Edward M. Stolper at California Institute of Technology for his fundamental contributions to petrology and meteorite research.

Keywords: hollisterite, Al_3Fe, kryachkoite, $(Al,Cu)_6(Fe,Cu)$, stolperite, AlCu, new minerals, Khatyrka, carbonaceous chondrite, meteorite

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INTRODUCTION

During a nanomineralogy investigation of the Khatyrka CV3 carbonaceous chondrite, we have identified three new alloy minerals, hollisterite (Al_3Fe with a *C*2/*m* structure), kryachkoite ($(Al,Cu)_6(Fe,Cu)$ with a $Cmc2_1$ structure), and stolperite (AlCu with a *Pm*-3*m* CsCl structure), in metal assemblages in section 126A of USNM 7908 (Fig. 1). The section belongs to the larger Grain 126 (Bindi et al. 2015a), which is one of the fragments recovered from 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 samples that would provide information on the origin of the quasicrystal mineral icosahedrite (Bindi et al. 2009; 2011; 2012). The recovered fragments have meteoritic (CV3-like) oxygen isotopic compositions and are identified collectively as coming from the Khatyrka meteorite (MacPherson et al. 2013), a recently described CV3 carbonaceous chondrite that experienced shock metamorphism, local melting (with conditions exceeding 5 GPa and 1,200°C in some locations), and rapid cooling, all of which likely resulted from impact-induced shock in space (Hollister et al. 2014). Khatyrka is unique, so far being the only meteorite to host metallic Al.

A field-emission scanning electron microscope (SEM) equipped for energy-dispersive X-ray spectrometry (EDS) and electron backscattered diffraction (EBSD), as well as an electron probe microanalyzer (EPMA) were used to characterize chemical compositions and structures of minerals in section 126A. Synthetic Al_3Fe with a *C*2/*m* structure, $(Al,Cu)_6(Fe,Cu)$ with a $Cmc2_1$ structure, and AlCu with a *Pm*-3*m* structure, are well known as λ, α, and β phase, respectively, in the Al-Fe-Cu system (e.g., Black 1955; Black et al. 1961; Freiburg and Grushko 1994; Zhang et al. 2005). We present here their first natural occurrence as new minerals in close association with the first quasicrystalline mineral icosahedrite in a primitive meteorite. Preliminary results on hollisterite and stolperite are given in Ma et al. (2016b).

MINERAL NAMES AND TYPE MATERIALS

The three new minerals, hollisterite (IMA 2016-034), kryachkoite (IMA 2016-062), and stolperite (IMA 2016-033), have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (Ma et al. 2016a, 2016c; Lin et al. 2016). Hollisterite is named in honor of Lincoln S. Hollister, Emeritus Professor in the Department of Geosciences at Princeton University, for his extraordinary contributions to Earth Sciences in general. Throughout his career, Lincoln Hollister has studied the largest metamorphic complex in the world: the Coast Mountains of British Columbia, Canada and southeast Alaska. Moreover, his enthusiastic support of the quasicrystal project and, more specifically, his contributions to the study of the mineralogy of the Khatyrka meteorite, a unique CV3 carbonaceous chondrite represent added reasons for the dedication. Kryachkoite is named in honor of Valery Kryachko who found the first samples of the Khatyrka meteorite in the Koryak Mountains in 1979 and later played a leading role in the expedition to recover more fragments in 2011. Stolperite is named in honor of Edward M. Stolper, petrologist and geochemist at California Institute of Technology, for his many fundamental contributions to petrology and meteorite research. His advice and support at critical stages of the search for natural quasicrystals and the studies of the Khatyrka meteorite make this dedication especially fitting.

The polished section 126A, prepared from a larger Grain 126, contains the holotype materials of the three new minerals. The section 126A was deposited in the Smithsonian Institution's National Museum of Natural History, Washington DC, USA, under the catalog number USNM 7908. Section 126A also contains micro-sized icosahedrite (quasicrystal with an icosahedral symmetry) in association with stolperite and hollisterite.

APPEARANCE, PHYSICAL, AND OPTICAL PROPERTIES

The three new alloy minerals appear as fine-grained crystals in certain metal assemblages, surrounded by a layer of fine-grained spinel and hercynite, sitting in forsterite-bearing silicate glass. Hollisterite occurs only as one subhedral single crystal, 2×7 μm in size on the section surface (Fig. 2a), which is the holotype material with a calculated density of 3.84 g·cm^{-3}. Kryachkoite occurs as subhedral crystals, 0.5 to 1.2 μm in size (Figs. 2b & 2c), which are the holotype material, with a calculated density of 3.79 g·cm^{-3}. Stolperite occurs as irregular grains, 0.5 to 3 μm in size (Figs. 2a, 2c & 2d), which are the holotype material, with a calculated density of 5.76 g·cm^{-3}. The three minerals are opaque and non-cathodoluminescent under the electron beam in an SEM. Their color, luster, streak, hardness, tenacity, cleavage, fracture, density, and optical properties could not be determined because of the small grain sizes.

CHEMICAL COMPOSITION

Backscattered electron (BSE) images were obtained using a ZEISS 1550VP field emission SEM and a JEOL 8200 electron microprobe with solid-state BSE detectors. Quantitative elemental microanalyses were conducted with the JEOL 8200 electron microprobe operated at 12 kV and 5 nA in focused beam mode. Standards for the analysis of all metal phases were Al (Al*K*α), Fe (Fe*K*α), Cu (Cu*K*α), Cr (Cr*K*α), and Si (Si*K*α). Analyses were processed using the CITZAF correction procedure (Armstrong 1995).

Compositions of the three new minerals and associated metal phases by EPMA are given in Table 1. The empirical formula of hollisterite (based on 4 atoms *pfu*) is $Al_{2.89}Fe_{0.77}Cu_{0.32}Si_{0.02}$. The simplified formula is $Al_3(Fe,Cu)$. The end-member formula is Al_3Fe, which requires Al 59.17, Fe 40.83, total 100.00 wt%. The empirical formula of kryachkoite (based on 7 atoms *pfu*) is $Al_{5.45}Cu_{0.97}Fe_{0.55}Cr_{0.02}Si_{0.01}$. The general formula is $(Al,Cu)_6(Fe,Cu)$. There is no end-member formula. All three elements must be present to form this phase. The empirical formula of stolperite (based on 2 atoms *pfu*) is $Al_{1.15}Cu_{0.81}Fe_{0.04}$. The simplified formula is Al(Cu,Fe). The end-member formula, AlCu, requires Al 65.83, Cu 22.18, total 100.00 wt%.

CRYSTALLOGRAPHY

Single-crystal electron backscatter diffraction (EBSD) analyses at a sub-micrometer scale were performed using an HKL EBSD system on the ZEISS 1550VP scanning electron microscope operated at 20 kV and 6 nA in focused beam mode with a 70º tilted stage and in a variable pressure mode (25 Pa), following methods described in Ma and Rossman (2008, 2009). The EBSD system was calibrated using a single-crystal silicon standard. The structures were checked and cell constants were obtained by matching the experimental EBSD patterns with structures of synthetic Al-Cu-Fe, Al-Cu and Al-Fe phases.

The EBSD patterns for hollisterite, obtained at different orientations from the holotype crystal, can be indexed only by the monoclinic *C*2/*m* Al_3Fe structure (Black 1955) and give a best fit by the cell parameters from Freiburg and Grushko (1994) (Fig. 3a), with a mean angular deviation of 0.30º~0.45º, revealing the cell parameters: a = 15.60 Å, b = 7.94 Å, c = 12.51 Å, β = 108.1°, V = 1472.9 Å^3, Z = 24.

The EBSD patterns for kryachkoite can be indexed and give a best fit by the orthorhombic $Cmc2_1$ $(Al,Cu)_6Fe$ structure (Black et al. 1961) (Fig. 3b), with a mean angular deviation of 0.30º~0.45º, showing the cell parameters: a = 7.460 Å, b = 6.434 Å, c = 8.777 Å, V = 421.3 Å^3, Z = 4.

The EBSD patterns for stolperite can be indexed and give a best fit by the cubic *Pm*-3*m* AlCu structure (Zhang et al. 2005) (Fig. 3c), with a mean angular deviation of 0.21º~0.30º, showing the cell parameters: a = 2.9 Å, V = 24.4 Å^3, Z = 1.

Calculated X-ray powder diffraction data for the three new minerals are given in Tables S1, S2 and S3[1].

OCCURRENCE AND ASSOCIATED MINERALS

Hollisterite occurs only as one subhedral crystal with stolperite, icosahedrite and khatyrkite in one metal assemblage (Fig. 2a). Quasicrystal icosahedrite, revealed by EBSD, occurs as micro-crystals, 1 to 2 µm in size, showing an empirical formula of $Al_{63.3}Cu_{25.7}Fe_{10.7}Si_{0.4}Ni_{0.1}Cr_{0.1}$, which is very close to that originally reported for the mineral (Bindi et al. 2009; 2011). Associated khatyrkite has an empirical formula of $Al_{2.04}(Cu_{0.89}Fe_{0.06}Si_{0.01})$. Kryachkoite occurs in contact with khatyrkite and aluminum $(Al_{0.97}Cu_{0.03})$ (Figs. 2b & 2c). Stolperite occurs within khatyrkite, or in contact with icosahedrite and/or hollisterite and khatyrkite (Figs. 2a. 2c & 2d). All the metal assemblages are surrounded mainly by a thin layer of spinel and hercynite, then by forsterite and silicate glass.

Other minerals identified in section 126A are chromite, magnetite, corundum, iron, taenite, suessite (Fe_3Si), naquite (FeSi; empirical formula $Si_{1.05}Fe_{0.86}Al_{0.03}Cu_{0.03}Cr_{0.02}Ni_{0.01}$; its first meteoritic occurrence), xifengite (Fe_5Si_3), nickel $(Ni_{0.91}Fe_{0.05}Cu_{0.04})$, copper $(Cu_{0.96}Fe_{0.04})$, plus glass with various compositions. High-pressure silicate or oxide phases were not observed in this section.

Associated minerals in other fragments of Grain 126 include trevorite, diopside, forsterite, ringwoodite, clinoenstatite, nepheline, coesite, stishovite, pentlandite, Cu-bearing

[1] For a copy of Table S1, S2 and S3, document item ……., contact the Business Office of the Mineralogical Society of America.

troilite, khatyrkite, taenite and Al-bearing taenite, holotype steinhardtite (Bindi et al. 2014) and holotype decagonite (Bindi et al. 2015b).

DISCUSSION

Hollisterite and kryachkoite correspond to the synthetic λ and α phase, respectively, of the Al-Cu-Fe system (Black et al. 1961; Zhang and Lück, 2003). Stolperite is a polymorph of cupalite (Razin et al. 1985), corresponding to the synthetic β phase of the Al-Cu-Fe system (Zhang and Lück 2003), which is usually associated with the icosahedral phase (natural icosahedrite) and the λ phase (natural hollisterite).

Studies of the section (126A) in which these three minerals were found have revealed the clearest evidence to date of reduction-oxidation reactions between Al-Cu-Fe metal phases and meteoritic matrix material in the Khatyrka meteorite that resulted from a high-velocity impact in space 250-300 Ma (Hollister et al. 2014; Meier et al. 2016). The studies further show that there are relic Al-Cu-Fe phases, including quasicrystals, that existed prior to the impact, perhaps forming as early as 4.564 Ga. 126A thereby adds significant new evidence for the extraterrestrial origin of the Al-Cu-Fe metal phases in the Khatyrka meteorite. Further details will be released in an upcoming manuscript.

IMPLICATIONS

The discovery of three other new Al-bearing metal phases in Khatyrka, among which is notably the first natural Al-Fe-alloy (hollisterite), has implications for Earth and planetary sciences. Such phases, together with the two natural quasicrystals icosahedrite and decagonite, present a challenge for meteorite science and our understanding of novel processes in the early solar system. We still are not certain of how these minerals in the Khatyrka meteorite formed but in any scenario, the sequence of events leading to the exchange of metallic Al that formed them can only be plausibly imagined to occur in space under low fO_2 solar nebular conditions. However, it is well known that in the early stages of the solar system, aluminum formed solids when copper was still a gas. Also, aluminum has an affinity for oxygen, whereas copper has an affinity for sulfur. Understanding the formation of the Al-Cu alloys in Khatyrka could provide insights about a spectrum of geochemical processes that were unknown before. The ongoing study of Khatyrka can continue to surprise and have an impact on other disciplines, including geoscience, solar system evolution, planet formation, condensed matter physics, and materials engineering.

ACKNOWLEDGEMENTS

SEM, EBSD and EPMA were carried out at the Caltech GPS Analytical Facility, which is supported, in part, by NSF grants NSF EAR-0318518 and DMR-0080065.

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Table 1. Mean elemental composition by EPMA for hollisterite, kryachkoite, stolperite, and associated khatyrkite and icosahedrite in section 126A.

Constituent	hollisterite		kryachkoite		stolperite		khatyrkite		icosahedrite	
wt%	n=4	sd	n=8	sd	n=15	sd	n=65	sd	n=3	sd
Al	55.0	0.4	61.0	0.4	36	2	48.0	0.3	43.2	0.1
Fe	30.4	0.6	12.6	0.8	2.7	0.9	1.0	0.5	15.0	0.5
Cu	14.2	0.3	25.5	0.7	60	2	50.9	0.8	41.0	0.4
Ni	b.d.		b.d.		b.d.		b.d.		0.17	0.09
Si	0.30	0.01	0.17	0.02	b.d.		b.d.		0.14	0.01
Cr	0.16	0.03	0.40	0.08	b.d.		b.d.		0.14	0.01
Total	100.1		99.7		99		99.9		99.7	

n: number of point analyses
sd: standard deviation
b.d.: below detection limits, 0.09 wt% Ni, 0.05% Si, 0.05% Cr.

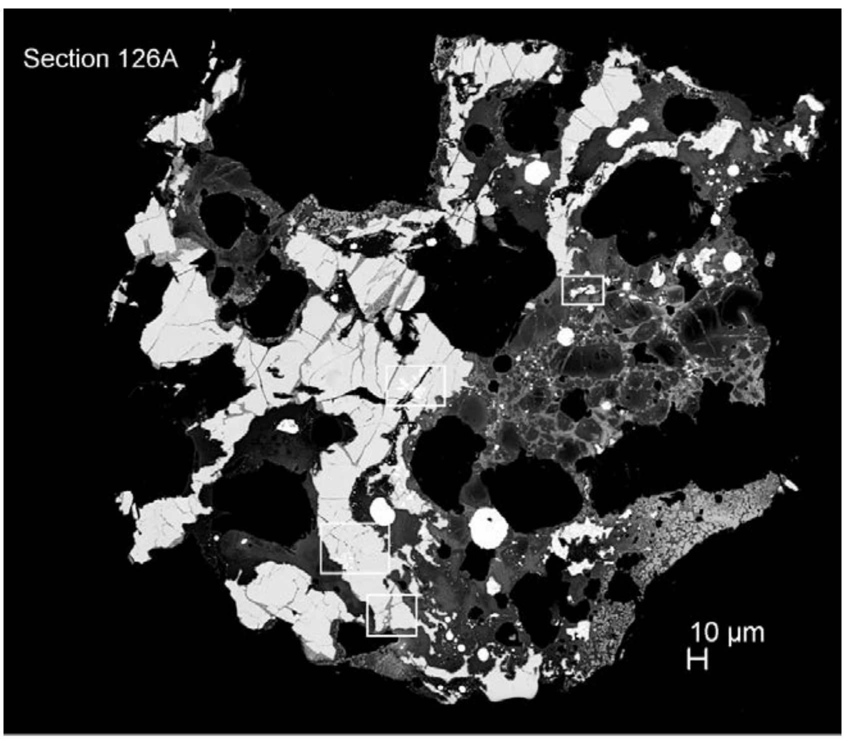


Figure 1. Backscattered electron (BSE) image of Section 126A of the Khatyrka meteorite from USNM 7908. The locations of three new minerals in Fig. 2 are marked by rectangles.

Fig. 2a

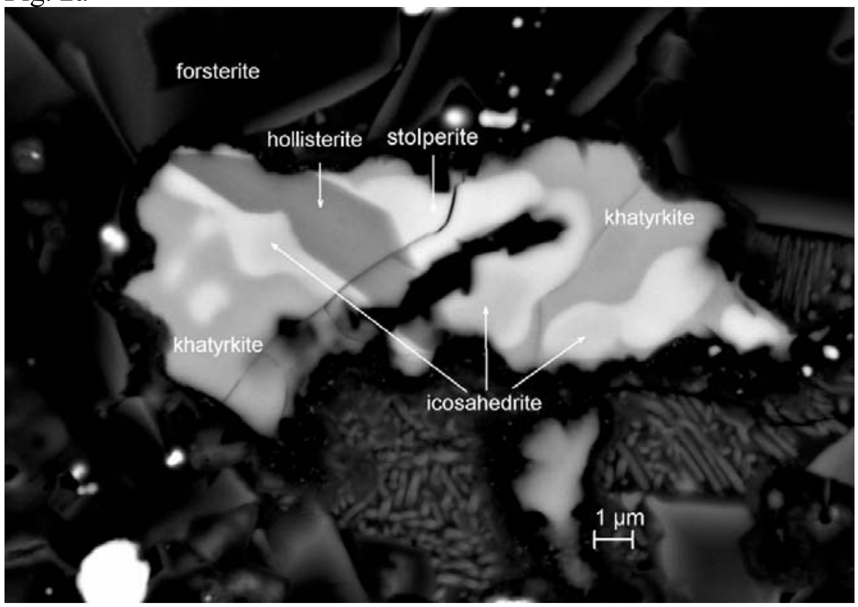

forsterite
hollisterite
stolperite
khatyrkite
khatyrkite
icosahedrite
1 µm

Fig. 2b

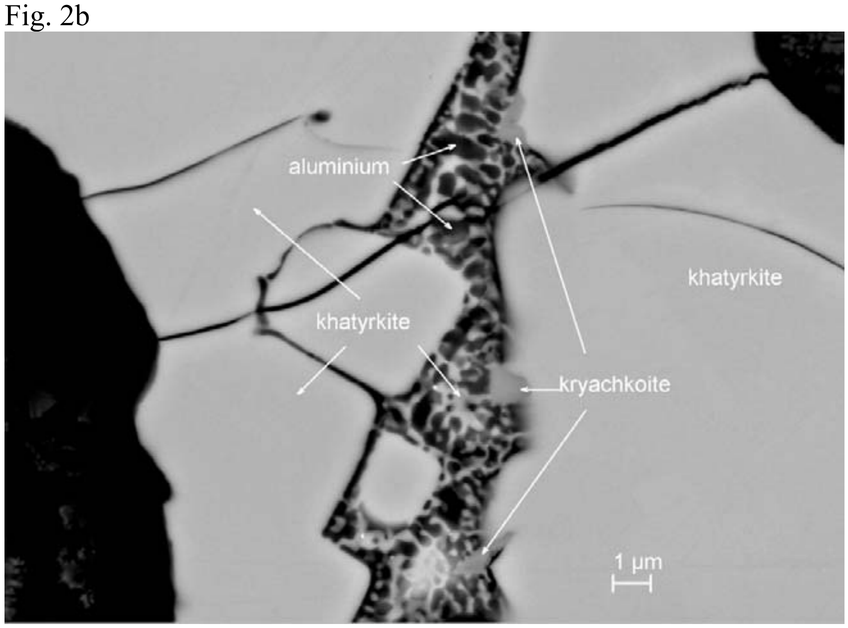

aluminium
khatyrkite
khatyrkite
kryachkoite
1 µm

Fig. 2c

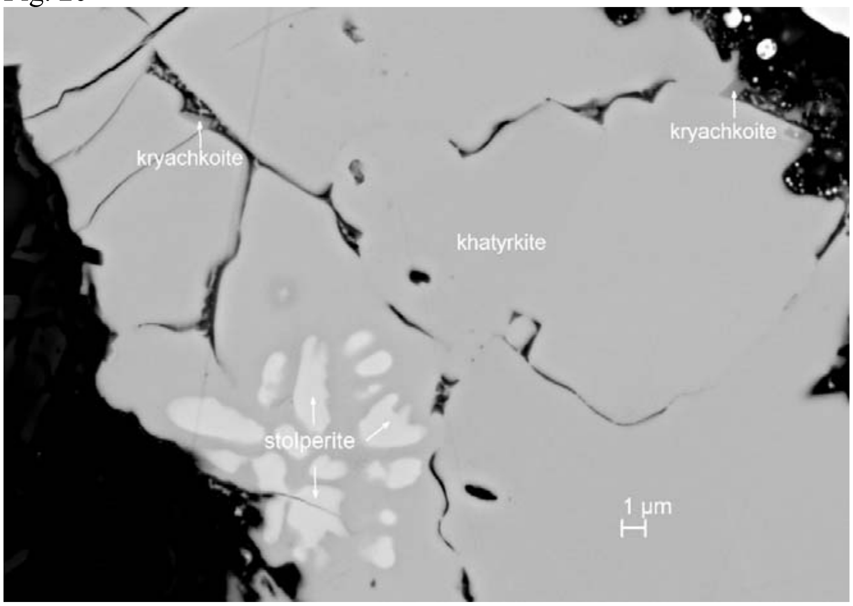


Fig. 2d

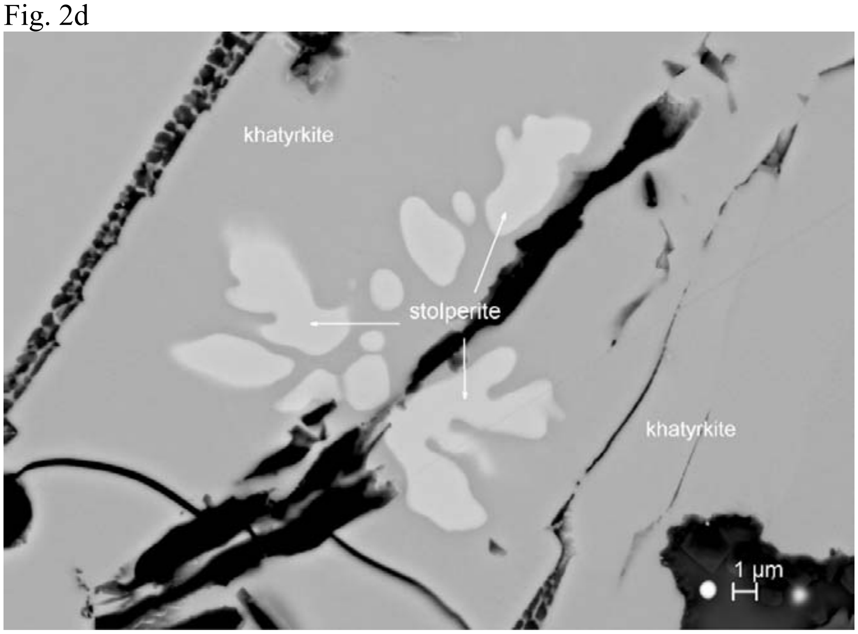
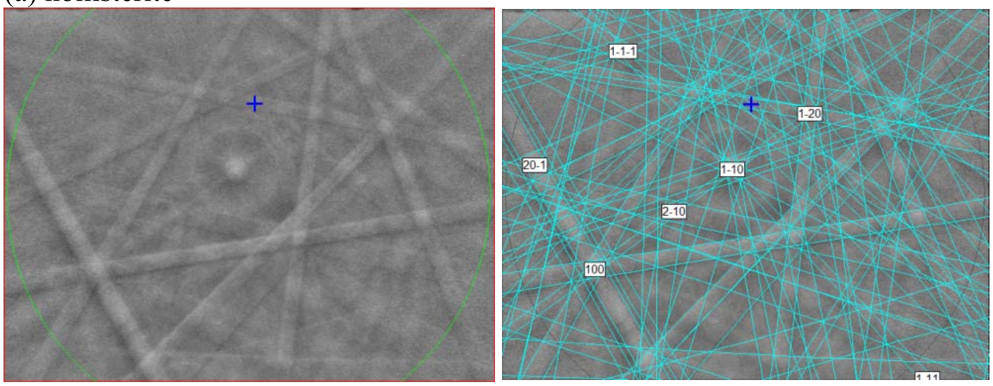
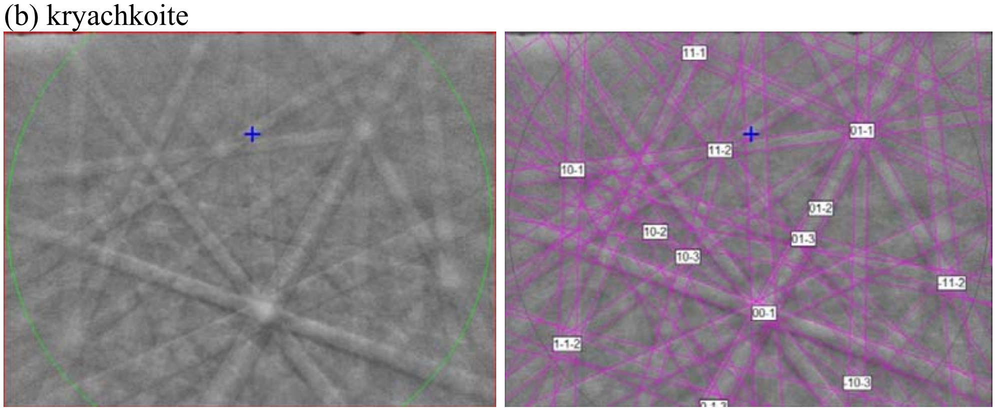


Figure 2. Enlarged BSE images showing (a) hollisterite with stolperite, icosahedrite and khatyrkite; (b) kryachkoite in contact with khatyrkite and aluminum, (c) stolperite and kryachkoite with khatyrkite; (d) stolperite in khatyrkite.

(a) hollisterite



(b) kryachkoite



(c) stolperite

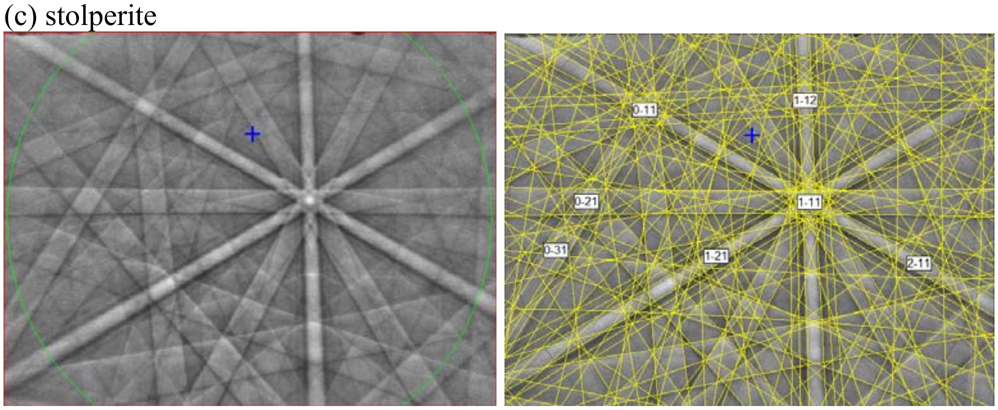


Figure 3. EBSD patterns of (a) the type hollisterite crystal, indexed with the *C*2/*m* Fe_3Al structure; (b) one kryachkoite crystal, indexed with the *Cmc*2_1 $(Al,Cu)_6Fe$ structure; (c) one stolperite crystal, indexed with the *Pm*-3*m* AlCu structure.