FIRST SHOCK SYNTHESIS OF KHATYRKITE, STOLPERITE AND A NEWLY-FOUND NATURAL QUASICRYSTAL: IMPLICATIONS FOR THE IMPACT ORIGIN OF QUASICRYSTALS FROM THE KHATYRKA METEORITE.

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Introduction: Quasiperiodic crystals (quasicrystals, QCs) synthesized by shock recovery experiments shine light on the impact origin of natural QCs in the Khatyrka meteorite [1,2]. The first natural QC, icosahedrite, has icosahedral symmetry with 5-fold rotation axes and an average composition of $Al_{63}Cu_{24}Fe_{13}$, which is also optimal composition for synthesizing Al-Cu-Fe QC at ambient pressure. Another newly found natural icosahedral QC (i-phase II, $Al_{62}Cu_{31}Fe_7$), in association with stolperite (AlCu) and khatyrkite (Al_2Cu), falls out of the stability field of QC in Al-Cu-Fe system at low pressure and was not produced in laboratories before this study [3]. Previous shock experiments so far synthesized icosahedrite with an average composition of $Al_{72}Cu_{12}Fe_{12}Cr_3Ni_1$ [1,2], similar but not identical to the natural occurrence. The variability in starting materials and/or shock conditions potentially account for those distinct compositions of shock-induced QCs [1].

In this study, we performed shock recovery experiment on a mixture of Al + Cu and reproduced the near-exact i-phase II QC + stolperite + khatyrkite assemblage as natural observation for the first time. A second experiment on $Al_{63}Cu_{24}Fe_{13}$ icosahedrite powder is employed to explore its stability under shock.

Methods: Two shock recovery experiments were performed at Caltech. An Al-Cu graded density impactor (GDI) was used as the starting material for experiment S1253. The GDI is made of bonded granular mixture with a gradient in composition from Al to Cu and thus provides a full range of Al/Cu ratios in the starting material. The second experiment S1250 used Sigma-Aldrich $Al_{63}Cu_{24}Fe_{13}$ icosahedrite powder. The peak shock pressure is ~ 24 GPa for both experiments by wave reverberation between the sample and 304 stainless steel (SS304) sample. Textures, compositions and structures of the run products were analyzed by SEM, EDS and EBSD at Caltech.

Results: The following sections describe the results from two shock experiments, respectively.

Icosahedral QC (i-phase II) + stolperite + khatyrkite in the GDI shot. In most part of the sample, the coherently fitted boundary between the GDI and SS304 chamber indicates limited shear and the reaction is not pervasive. Nevertheless, the side walls of the GDI is heavily squeezed along the direction of impact and interact extensively with the chamber (Figs. 1-2). Figure 1 shows that reaction zones occur on both sides of the deformed wall. In these regions, the Cu and Al grains are strongly deformed and elongated in the direction of impact shear. One side starts with the Al-rich base (Al+Cu in Fig. 1) of the GDI and contains a variety of intermetallic Al-Fe alloys, including hollisterite (Al_3Fe), which was first identified in Khatyrka [4].

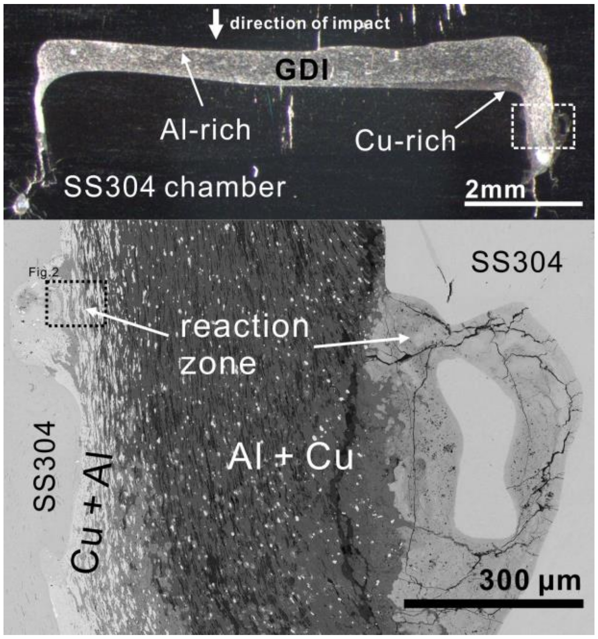

Figure 1. Top: shock-deformed GDI in SS304 recovery chamber from S1253. White-box area is enlarged at the bottom: BSE image of the reaction zones along the deformed wall. Details in the black box is shown in Figure 2.

In contrast, the reaction zone that starts with the Cu-rich base of the GDI (Cu+Al in Fig. 1) produces icosahedral QC plus Al-Cu intermetallic phases. Al grains in this zone are completely reacted, resulting in that the space between Cu grains is full of icosahedral QC (i-phase II) + stolperite + khatyrkite (Fig. 2). Compositions of the observed phases, summarized in Table 1, well resemble the corresponding natural occurrences in Khatyrka [3]. Al/Cu ratio of khatyrkite and stolperite are close to the typical number of 2:1 and 3:2, respectively. The Cr content results from stainless steel chamber as the Fe source. For the micro-texture of the assemblage, khatyrkite is predominant and stolperite fills in the interstitial spaces. I-phase II QC has a similar composition and BSE contrast as khatyrkite (Fig. 2). Nevertheless, I-phase II shows a petal-like shape, likely resulting from its icosahedral symmetry.

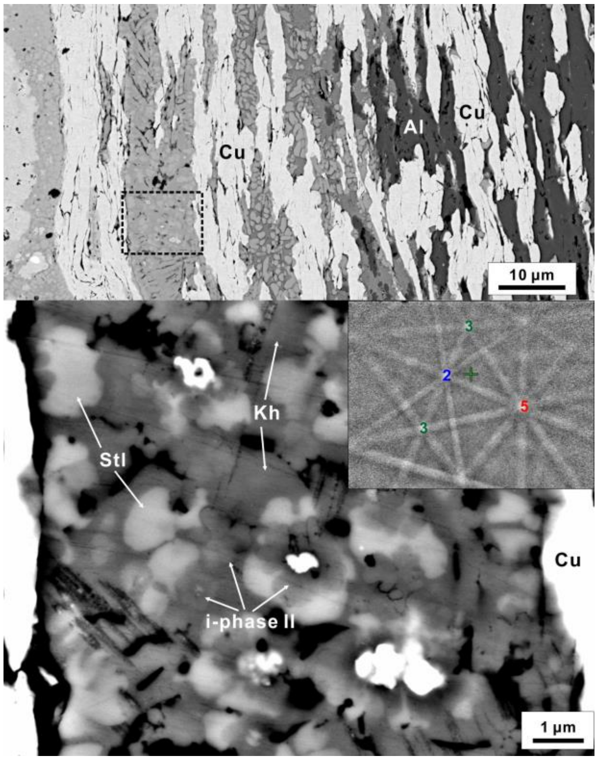

Figure 2. Top: BSE image of reaction zone with deformed Al/Cu grains and new product phases. The black box is enlarged at the bottom: Assemblage of i-phase II QC plus khatyrkite (Kh) and stolperite (Stl). The inset shows an EBSP of i-phase II labeled by the order of rotation axes.

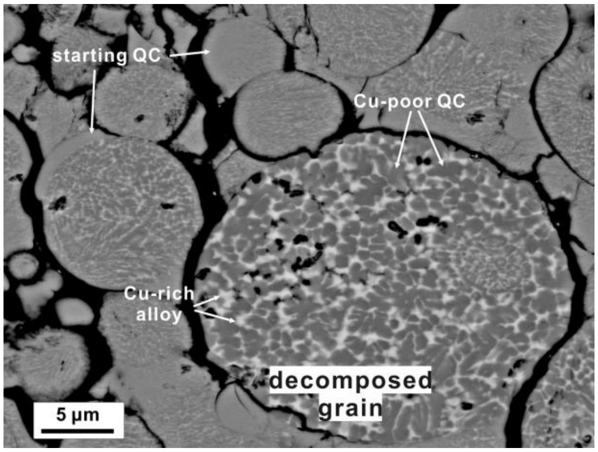

Figure 3. BSE image of shock-induced QC grain breakdown in shot S1250. Local areas contain unreacted starting QC.

Shock-induced decomposition of $Al_{63}Cu_{24}Fe_{13}$ icosahedrite powder. The shocked QC powder shows consistent decomposition features through the whole sample. Most individual grains preserve their original grain boundary but break down to two phases with distinct BSE contrast (Fig. 3). EDS and EBSD indicate the bright phase has a bcc cell and Cu-enriched composition of $Al_{45-62}Cu_{23-52}Fe_{3-13}$. The dark-grey phase inherits the icosahedral symmetry with a AlFe-rich composition of $Al_{62-66}Cu_{17-24}Fe_{13-17}$. The compositional variation of the breakdown phases is also revealed by BSE contrasts. There are grains with weak contrast, indicating the breakdown phases are compositionally similar to the starting material (Fig. 3). In addition, not all grains are completely reacted. The starting material survived in a small amount of grains, with the exact starting composition and homogeneous texture (Fig. 3). Nevertheless, the EBSD patterns of these regions are poor in quality, indicating shock deformation.

Table 1. Mineral compositions in the QC assemblage

atom	khatyrkite		stolperite		i-phase II QC	
	syn	nat	syn	nat	syn	nat
Al	65.24	66.53	57.42	57.39	62.13	62.32
Cu	34.76	33.46	40.61	40.45	30.11	30.87
Fe	-	0.01	1.58	2.15	6.41	6.81
Cr	-	-	0.4	-	1.36	-

Compositions in at% are normalized to 100% total. Syn and nat stand for synthetic (this study) and natural [3,4].

Discussions: In our shock experiment, reactions among Cu, Al and steel, in the Cu-rich region of the GDI, produce the near-exact assemblage of icosahedral $Al_{62}Cu_{31}Fe_7$ QC (i-phase II) + khatyrkite + stolperite as the natural occurrence in Khatyrka. Starting material with high Al/Cu ratio under the same shock condition only produce Al-Fe-Cu intermetallic phases. Although the observed QC and associated minerals all have Al/Cu ratios great than 1, apparently a Cu "saturated" condition is optimal to create this assemblage under high pressure. In contrast, previous experiments with Al_5Cu alloys make QCs that are always 10 at% higher Al content than the natural occurrence [1,2]. This result is favored because thermodynamically it is easier to stabilize Cu than Al to start with in Khatyrka under nebula or parent body conditions.

Despite that this study reproduced the natural QC i-phase II, the optimal composition (in nature and synthesis) $Al_{63}Cu_{24}Fe_{13}$ of icosahedrite has yet been made in shock experiments. In fact, shock-induced breakdown of this composition, combined with static high-pressure experiment results [5], suggest that pressure moderately affects the stability field of icosahedrite in Al-Cu-Fe system. This is supportive of Khatyrka experiencing multiple impacts of different conditions to contain both icosahedrite and i-phase II [6].

References: [1] Asimow, P.D. *et al.* (2016) *PNAS*, 113, 7077. [2] Oppenheim, J. *et al.* (2017) *Sci. Rep.*, 7, 15629. [3] Bindi, L. *et al.* (2016) *Sci. Rep.*, 6, 38117. [4] Ma, C. *et al.* (2017) *Am. Min.*, 102, 690. [5] Stagno, V. *et al.* (2017) *PEPI*, 271, 47. [6] Meier, M. *et al.* (2018) *EPSL*, 490, 122.