THE HOLOTYPE OF Al-Cu-Zn ALLOYS: RELATED TO METEORITE MATERIAL?

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Several grains (up to 1 mm) containing the crystalline Cu-Al alloys khatyrkite and cupalite have been recovered from a single place on Earth: in clay layers along the banks of the Listvenitovy stream in the Khatyrka ultramafic zone in the Koryak Mountains, Chukotka [1,2]. The holotype sample of khatyrkite and cupalite is now at the Mining Museum in St. Petersburg, Russia) [1]. The second sample is at the Florence Museum (Florence, Italy). It contains the quasicrystal ($Al_{63}Cu_{24}Fe_{13}$) [3], Cu-Al alloys and CAIs minerals. The assemblage including the quasicrystal may have meteoritical origin, based on oxygen isotopic compositions of silicates intergrown with the metal [4]. Both samples were found by V.V. Kryachko in 1979. Several other samples were recovered during a 2011 expedition to Khatyrka with the participation of Mr. Kryachko. These samples also contained Cu-Al-Fe alloys with silicates or consisted entirely of the alloys. The silicate material was identified as a CV3 chondrite and named Khatyrka [1]. The Cu-Al-Fe alloys were interpreted to be an accretionary component in the CV3 chondrite [1], but the genesis of Cu-Al-Fe-metal remained enigmatic. Based on the recovery history the origin of all grains should be considered together, although [2] showed different metal compositions than [1,3,4].

Our recent investigations of the first khatyrkite-cupalite holotype polished section included X-ray tomography, BSE imaging, and microprobe analyses. One 1.2 x 0.5 mm particle consists of khatyrkite $(Cu,Zn)Al_2$, cupalite (Cu,Zn)Al and unknown Al-Zn alloy phases (approximately $(Zn,Cu)Al_3$). The Zn-Al phases are rare, represented by thin, elongated 2-12 μm crystals, sometimes rusted, in association with $(Cu,Zn)Al_2$ and (Cu,Zn)Al. All phases contain Zn and lack Fe. Zn contents (wt%) in $(Cu,Zn)Al_2$ is up to 2; in (Cu,Zn)Al up to 8; in Al-Zn alloy ~32 on average. Bulk composition (wt%) is Cu 47.4, Al 46.7, Zn 5.9. Cu/Al and Cu/Zn ratios in the alloy are x100 (CI), x20 (CI).

These results confirm that the holotype sample differs from all other grains recovered in the Khatyrka region and studied in [1,3,4]. The holotype is enriched in Zn and contains no Fe. The Cu-Zn-Al alloy formed intermetallic phases as predicted by the equilibrium Zn-Al-Cu phase diagram, corresponding to phases at 300-500^{o}C [6]. This study raises several questions: (1) Why is the holotype particle substantially different in chemistry compared to other described grains [1,3,4]? (2) How can formation of Cu-Al-Zn alloy be explained from the standpoint of equilibrium nebula condensation, given that Al is lithophile while Cu and Zn are chalcophiles and condense at much lower temperatures than Al? These elements are never associated in chondrites, nor in CAIs. (3) Could the Cu-Zn-Al phases coexist with a quasicrystal form given their different thermal history and stability conditions? This work was supported by *PMHU* (Dedovsk, Russia).

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