Exogenous copper sulfide in a returned grain from asteroid Itokawa

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Asteroid 25143 Itokawa is an S-type asteroid, and the returned samples are dominated by equilibrated, weakly shocked LL5 and LL6 ordinary chondrite material with some weakly equilibrated LL4 material [1,2]. We present evidence of the presence of a cubanite-chalcopyrite-pyrrhotite-troilite assemblage consistent with low-temperature aqueous alteration in a particle from Itokawa [3]. Most of the materials from Itokawa equilibrated at temperatures near 800°C, with slow cooling to ~600°C [2,4], which indicates this sulfide assemblage must have become part of Itokawa after thermal alteration. Cu-bearing sulfides have been reported in only a few meteorite types [5,6], which suggests the conditions necessary to form such phases occur on only a limited number of planetary bodies. Specifically, cubanite has only been reported in CI chondrites and Wild2 material [7]. Thus, we conclude that this grain, and the other Cu-sulfides noted on Itokawa samples [8] likely originated on a primitive, hydrated asteroid source such as CI chondrite-like parent body or D- or P-type asteroids previously linked to unique, aqueously altered meteorites [9,10].

Particle RB-CV-0038 (C0038) was mounted in epoxy such that most of the grain was available for imaging, then coated by 80 nm of evaporated carbon. SEM images and FIB samples were obtained with an FEI Helios G3 equipped with an Oxford 150 mm^2 SDD energy dispersive X-ray spectrometer (EDS). After imaging, protective straps of C were deposited on regions of interest, and multiple sections suitable for STEM analysis were extracted using standard techniques. One section, known from SEM-EDS to contain Cu, was attached to a Mo grid. STEM analysis was performed with the Nion UltraSTEM200-X at NRL. The microscope is equipped with a Gatan Enfinium ER spectrometer for electron energy loss spectroscopy (EELS) and a windowless, 0.7 sr Bruker SDD-EDS detector. Selected area diffraction patterns were collected using a JEOL 2200FS. Data were collected at 200 kV.

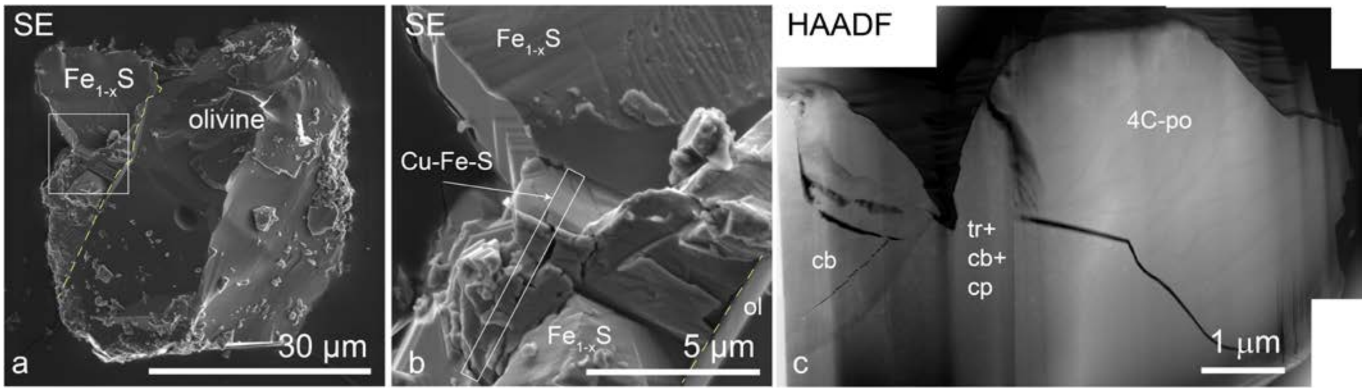

Figure 1. (a,b) Secondary electron (SE) images of particle RB-CV-0038 showing location of cubanite with Fe-sulfide and approximate location of FIB section. (c) HAADF montage of FIB section with cubnaite (cb), troilite-cubanite-chalcopyrite (tr+cb+cp) mottled region, and pyrrhotite (4C-po) with "flame" texture.

C0038 is a multiphase grain, ~40 µm across. The particle is predominantly composed of olivine and iron sulfide with minor (adhered?) plagioclase or glass (Fig. 1a). A ~2×5 µm cubanite grain was present in contact with the Fe-sulfide (Fig. 1b). STEM data show several different grains are present within the Fe-sulfide in the FIB section (Fig. 1c). The Cu-Fe-sulfide contains several cracks are, one of which is perpendicular to the FIB section (Fig. 2a). The crack has oxidized Fe-rich edges and is decorated by Cu metal nanoparticles. The cubanite itself shows a tripling of the *c* axis, apparent in SAED patterns (Fig. 2b). Adjacent to the cubanite, the sulfide has a mottled texture (Fig. 2a), and a small amount of Cu is present (~2 at%), concentrated in the bright spots. SAED patterns from the region index to troilite with faint chalcopyrite spots (Fig. 2d). Further from the chalcopyrite, there is no Cu, and the Fe-sulfide has a "flame" exsolution texture of two types of pyrrhotite (Fig. 2c). The pyrrhotite can be indexed to 4C-pyrrhotite. The average measured Fe/S composition for the grain (x = ~0.09 in $Fe_{1-x}S$) is consistent with a 4C-pyrrhotite or a mixture of 4C and NC-pyrrhotites. In NC-pyrrhotites, NC indicates a variable, non-integral superstructure based on the NiAs-type unit cell where troilite is 2C.

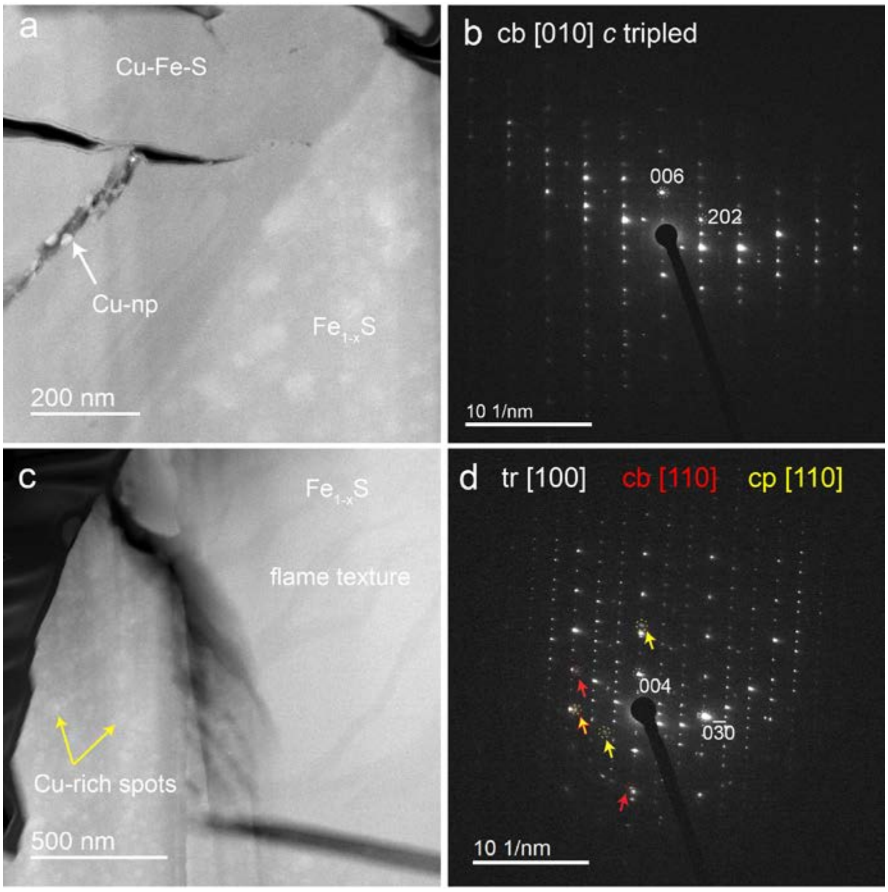

Figure 2. (a,c) HAADF images of cubanite, mottled Fe-sulfide, and pyrrhotite with flame texture. (b) SAED pattern for the cubanite, which shows a tripling of the c axis. (d) SAED pattern for the mottled Fe-sulfide, which has ~2 at% Cu and shows reflections for cubanite and chalcopyrite in addition to troilite.

The presence of cubanite, which forms and is stable only at temperatures below ~250°C [11], together in this grain with 4C-pyrrhotite [7], indicates that this grain must have been brought to Itokawa after thermal alteration and equilibration of the LL-type material. This combination of sulfide phases has previously been identified only in CI chondrite material [7]. However, unlike CI chondrites, no Ni was detected in these sulfides. This could indicate variation in the CI parent body, or that the impactor seen here was from a different parent body, such as the aqueously altered D- or P-type asteroids.

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References
[1] Mikouchi, T., et al. (2014) Earth, Planets and Space, 66, 82. [2] Noguchi, T., et al. (2011) Science, 333, 1121. [3] Burgess, K.D., and Stroud, R.M. (2021) Communications Earth & Environment, 2, 115. [4] Harries, D., and Langenhorst, F. (2018) Geochimica et Cosmochimica Acta, 222, 53. [5] Rubin, A.E. (1997) Meteoritics & Planetary Science, 32, 231. [6] Rubin, A.E., and Ma, C. (2017) Geochemistry, 77, 325. [7] Berger, E.L., et al. (2011) Geochimica et Cosmochimica Acta, 75, 3501. [8] Nakamura, E., et al. (2012) Proceedings of the National Academy of Sciences of the United States of America, 109, E624. [9] Brown, P.G., et al. (2000) Science, 290, 320. [10] Kebukawa, Y., et al. (2019) Scientific Reports, 9, 3169. [11] Dutrizac, J. (1976) The Canadian Mineralogist, 14, 172.