EXOGENOUS COPPER SULFIDE IN A RETURNED GRAIN FROM ASTEROID ITOKAWA. K. D. Burgess, R. M. Stroud; U.S. Naval Research Laboratory, Washington, DC 20375 (kate.burgess@nrl.navy.mil).

Introduction: Recent identification of potentially significant amounts of exogenous material on both asteroids Ryugu and Bennu [1,2] suggests that mixing between parent bodies was widespread at times during the evolution of the Solar System. However, no clear evidence of exogenous material on asteroid Itokawa has yet been reported, either in the samples returned by the Hayabusa spacecraft or during surveying of the asteroid itself.

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 [3,4]. The materials equilibrated at temperatures near 800°C, with slow cooling to ~600°C [4,5]. We present evidence of the presence of chalcopyrite formed via low-temperature aqueous alteration in a particle from Itokawa. Chalcopyrite is rare in the meteorite record outside of CK and R chondrites [6-9], and the hypothesized conditions of its formation in this grain are inconsistent with conditions on the Itokawa parent body.

Methods: 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.

Results and Discussion: 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. 1). A Cu-Fe-sulfide identified as chalcopyrite was present in contact with the Fe-sulfide. The olivine portion has a number of much smaller adhered particles and possibly some blisters but no obvious impact-related features. The composition of the olivine (Fa_{29}) is consistent with other equilibrated grains measured from the Itokawa regolith [3]. There is very little evidence of a space weathering rim on the olivine. Both the chalcopyrite and Fe-sulfide lack Ni.

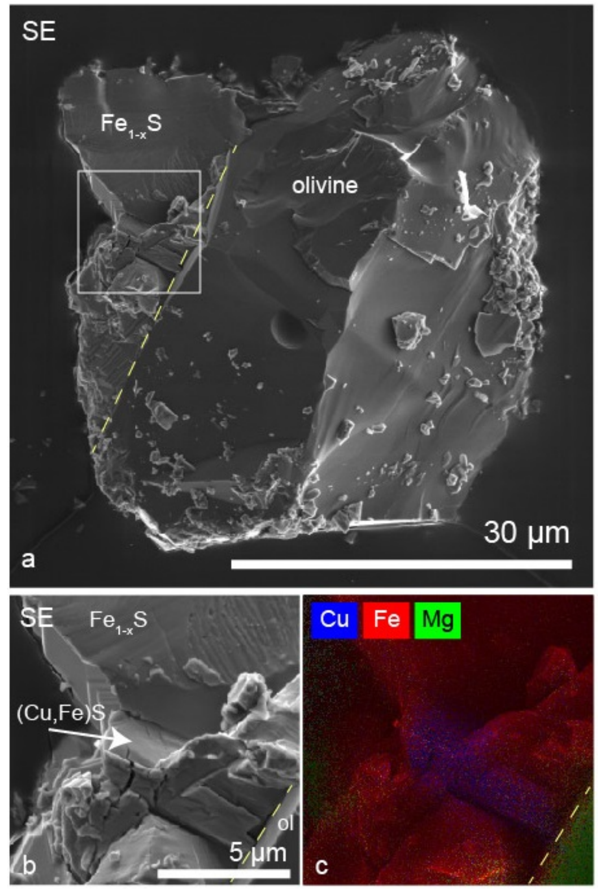

Figure 1. Itokawa particle RB-CV-0038 is mostly olivine with Fe-sulfide and a small Cu-Fe-sulfide grain.

The ~2×5 µm chalcopyrite grain is present with the Fe-sulfide at the interface with the olivine (Fig. 1b,c). Selected area electron diffraction (SAED) patterns from the Cu-grain are indexed to chalcopyrite with faint spots indicating the presence of pyrrhotite (Fig. 3b). Several other Cu-Fe-sulfides have similar diffraction patterns, but EELS data are clearly consistent with chalcopyrite (Fig. 3d). The composition of the Cu-Fe-sulfide is close to $CuFe_2S_3$, which indicates the chalcopyrite and pyrrhotite formed from an intermediate solid solution (*iss*) upon cooling to temperatures below ~300°C [10]. Above this temperature, chalcopyrite can exsolve from the cubic *iss* but pyrrhotite does not.

The chalcopyrite has an open crack with oxidized magnetite edges that is decorated by Cu metal nanoparticles (Fig. 3a). The crack has a ~5 nm rim of Fe-oxide (Fig. 3c), indicating oxidizing conditions during alteration of the grain, similar to features seen in chalcopyrite in R chondrites [8].

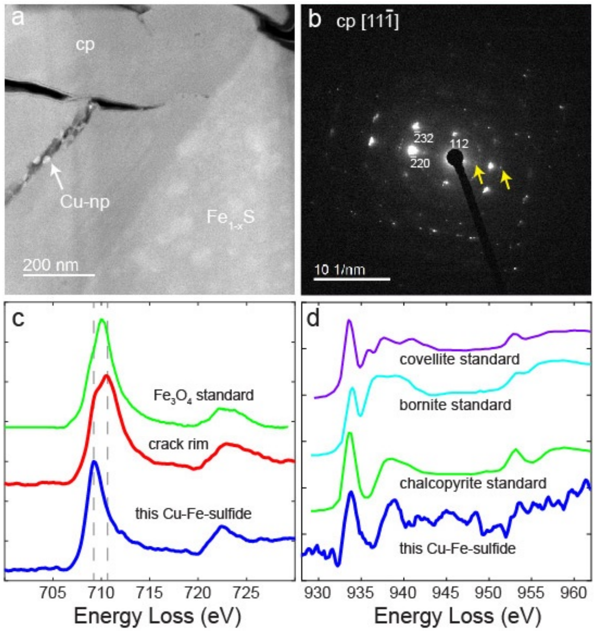

Figure 3. (a) HAADF images of Cu-Fe-sulfide with Cu-np-filled crack adjacent to mottled Cu-rich Fe-sulfide (~2 at% Cu). (b) SAED pattern from chalcopyrite (cp) with faint spots from pyrrhotite (yellow arrows). (c) EELS Fe L-edge showing the rim of the crack in chalcopyrite is oxidized, similar to magnetite. (d) EELS Cu L-edge confirming grain contains chalcopyrite.

Several different grains are present within the Fe-sulfide in the FIB section. Adjacent to the chalcopyrite, the sulfide has a mottled texture (Fig. 3a and 4a), 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. 4b). Further from the chalcopyrite, there is no Cu, and the Fe-sulfide has a "flame" exsolution texture of troilite and pyrrhotite (Fig. 4). This texture indicates equilibration at temperatures below ~180°C [11,12].

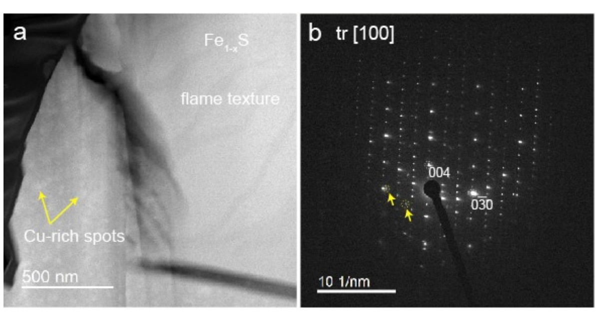

Figure 4. (a) HAADF images of exsolution "flame" texture in Cu-free pyrrhotite-troilite grain adjacent to mottled Fe-sulfide. (b) SAED pattern of troilite from mottled region with faint chalcopyrite spots (yellow arrows).

Cu metal is relatively common in ordinary chondrites [13], and it is possible that a small impact could cause localized mixing between Cu metal and Fe-sulfide. However, the exsolution features of the pyrrhotite-troilite and pyrrhotite within chalcopyrite are present only with equilibration to low temperatures, which is not likely with local shock heating.

Several research groups have found small NaCl grains on the surfaces of Itokawa particles [14,15, our own unpublished work], which could indicate some hydrothermal processing. However, all of the identified NaCl has been on the surfaces of the particles, and it is possible that the NaCl is due to terrestrial contamination. Harries and Langenhorst [5] found the carbide phase haxonite with Fe,Ni metal in an Itokawa particle. They suggest the assemblage formed in a methane-rich fluid at temperatures higher than 600°C, very different from conditions of chalcopyrite formation [10]. No other evidence of low-temperature aqueous alteration has been observed in the Itokawa samples.

Conclusion: We hypothesize that the chalcopyrite grain identified in this Itokawa particle is exogenous. The conditions of its formation and the adjacent Fe-sulfide textures are inconsistent with being on the Itokawa parent body during equilibration of the LL5 and LL6 material. The chalcopyrite formed or was altered during low temperature, aqueous processing, while the flame texture in the pyrrhotite-troilite intergrowth formed at temperatures below 180°C. The presence of exogenous material on Itokawa provides additional constraints on and confirmation of significant mixing of asteroidal material.

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References:

[1] DellaGiustina, D.N., et al. (2020) *Nat Astron*, [2] Tatsumi, E., et al. (2020) *Nat Astron*, [3] Mikouchi, T., et al. (2014) *Earth Planet Space*, *66*, 82. [4] Noguchi, T., et al. (2011) *Science*, *333*, 1121. [5] Harries, D., and F. Langenhorst (2018) *GCA*, *222*, 53. [6] Kallemeyn, G.W., et al. (1991) *GCA*, *55*, 881. [7] Kallemeyn, G.W., et al. (1996) *GCA*, *60*, 2243. [8] Miller, K.E. (2016) Thesis. Ph.D. The University of Arizona. [9] Ramdohr, P. (1963) *JGR*, *68*, 2011. [10] Vaughan, D.J., and J.R. Craig (1997) In: *Geochemistry of Hydrothermal Ore Deposites*. 367-434. [11] Brearley, A.J., and C. Martinez (2010), 1689. [12] Harries, D., and M.E. Zolensky (2016) *M&PS*, *51*, 1096. [13] Rubin, A.E. (1994) *Meteoritics*, *29*, 93. [14] Keller, L.P., and E.L. Berger (2017), 2353. [15] Noguchi, T., et al. (2014) *M&PS*, *49*, 1305.