Exogenous copper sulfide in returned asteroid Itokawa regolith grains are likely relicts of prior impacting body

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Samples from asteroid 25143 Itokawa returned by the Hayabusa mission have been identified as LL4-6 ordinary chondrite materials and have shown it to be a rubble pile that aggregated after break-up of a parent body. Here we investigate particle RB-CV-0038 from the Itokawa regolith using scanning and transmission electron microscopy and energy dispersive spectroscopy. We identify a cubanite-chalcopyrite-troilite-pyrrhotite assemblage, the phases and structure of which are indicative of low-temperature, aqueous alteration. Cubanite is stable only at temperatures below around 250 °C and has thus far only been identified in CI carbonaceous chondrites and the comet 81P/Wild2 sample suite. Chalcopyrite is also very rare in the meteorite record and is found mostly in R chondrites and some CK chondrites. Because the Itokawa parent body experienced significant thermal alteration with little evidence of low-temperature equilibration or aqueous alteration, we propose that the assemblage we identify is most likely exogenous and represents a component of an impacting body.
he samples returned from asteroid 25143 Itokawa by the Hayabusa spacecraft have provided a significant amount of new information about asteroids in general and S-type asteroids specifically. The mineral and glass phases present and their compositions provide fundamental constraints on how the Itokawa parent body formed and evolved. Observations show that Itokawa is a rubble pile that aggregated after the break-up of the parent body (possibly multiple times). Many of the particles from Itokawa have angular edges, indicating they are fragments of grains from mechanical crushing, while the rounded edges of some particles are likely due to subsequent mechanical abrasion. Evidence of small micrometeorite impacts and some particles are likely due to subsequent mechanical grain crushing. However, small adhered Cu-sulfide grains observed previously on a particle could represent exogenous material. Itokawa is a rubble pile that aggregated after the break-up of the parent body (possibly multiple times). Many of the particles from Itokawa have angular edges, indicating they are fragments of grains from mechanical crushing, while the rounded edges of some particles are likely due to subsequent mechanical abrasion. Evidence of small micrometeorite impacts and some particles are likely due to subsequent mechanical grain crushing. However, small adhered Cu-sulfide grains observed previously on a particle could represent exogenous material.

**Results**

Troilite, pyrrhotite, and olivine (Fo72) are the dominant phases in RB-CV-0038 (hereafter, C0038), with minor plagioclase or glass present either as part of the grain or as adhered particles (Fig. 1; Supplementary Table 1). A ~2 µm Cu-Fe-sulfide grain is present with the Fe-sulfide at the interface with the olivine. The surface of the olivine has many sub-micron adhered grains but no clear impact-related features. Adhered grains captured by the FIB sections are also olivine and of similar composition to the larger grain. There is a large conchoidal fracture on the olivine, as well as some wavy and stepped surfaces, and the scanning transmission electron microscopy (STEM) data show a lack of any distinct space weathering rim. There is also no evidence of a space weathering rim at the grain boundary between the olivine and iron sulfide. The boundary between them is smooth, and there is a distinct step up on the olivine next to the sulfide. The surface of the Fe-sulfide is highly varied, with some portions having a smooth, almost flow-like texture while other regions are fractured (wavy and stepped) or have sharp facets somewhat similar to the concentric stepped surfaces noted on other Itokawa particles.

Within the sulfide portion of the grain, there are several different Fe-sulfide grains in addition to the Cu-Fe-sulfide grain (Fig. 2). The Cu-Fe-sulfide grain contains cubanite (Cb; CuFe2S4) and possibly monoclinic 4C-pyrrhotite (4C-po; FeSb) as evidenced by selected area electron diffraction (SAED) patterns. The pattern in Fig. 2c cannot be matched by the basic unit cell of cubanite (a = 6.463, b = 11.117, c = 6.234;22); some reflections can best be indexed assuming a superstructure with a tripling of c. A better fit to about one-quarter of the collected patterns from the cubanite grain is made by adjusting a slightly to be more similar to b of 4C-pyrrhotite (~6.85023), which could indicate significant strain due to the presence of oxygen in the lattice or incomplete replacement of pyrrhotite by cubanite during the reaction. Most reflections in other SAED patterns from the Cu-Fe-sulfide grain are consistent with the identification of cubanite and pyrrhotite, with remaining reflections not easily matched to any expected phase and likely indicating deformation (Supplementary Fig. 1). Iso-cubanite, which has the same composition as cubanite, is not seen. Rings consistent with magnetite are also seen in some SAED patterns from the cubanite, but this is likely an artifact from FIB preparation. However, magnetite is present elsewhere in the sample, and described in detail below. Electron energy-loss spectroscopy (EELS) Fe and Cu L-edge data are unable to distinguish between cubanite and chalcopyrite (cp) but show clear differences from other Cu-sulfide phases, such as bornite (Cu9FeS8) and covellite (CuS) (Fig. 3).

The Cu content of the Cu-rich sulfide must be estimated due to the Cu system peaks in our STEM energy-dispersive X-ray spectroscopy (EDS) data caused by copper in the microscope pole.

**Fig. 1 Images of RB-CV-0038.** a Secondary electron (SE) image of C0038. Fe-sulfide is in the top left and the rest of the grain is olivine. b SE image showing the Cu-Fe-sulfide grain present with the iron sulfide. c EDS map showing the Cu-rich grain. Dotted lines indicate the olivine-sulfide boundary.
In the Cu-rich phase, Fe/S $\sim 0.65$–$0.73$. If we assume all cation sites are filled (i.e., Fe$^{+}+\text{Cu} = S$), we find Cu/Fe of $0.55$–$0.37$, consistent with cubanite or isocubanite, possibly mixed with pyrrhotite. There is ~8 at% O measured in the bulk of the Cu-Fe-sulfide as well. However, Fe L-edge EELS shows no evidence of oxidation, and oxygen was not included in the calculations to determine Cu/Fe. Both the Cu-Fe-sulfide and Fe-sulfide in CO038 lack Ni.

The iron-sulfide portion of the particle is defect-rich and contains multiple grains in the section near the Cu-Fe-sulfide (Fig. 2). The grain nearest the Cu-Fe-sulfide has a slightly mottled appearance in high-angle annular dark-field (HAADF) imaging (Fig. 2b), and bright regions 50–60 nm across seen in HAADF images correlate with increased Cu in EDS maps (Fig. 4a, b). The average composition for this portion of the Fe-sulfide has ~2 at% more Cu than the Fe-sulfide further from the cubanite. The mottled grain, like the Cu-Fe-sulfide, contains ~6 at% O with no evidence of oxidation in EELS. The Cu-free sulfide contains O ~3 at% showing some of the O is not from sample preparation and could be from the aqueous alteration (Supplementary Fig. 4). The flame-like texture seen in the grain to the right in Fig. 2 is interpreted as the exsolution of two types of pyrrhotite but is too finely intergrown for any compositional differences to be seen in EDS maps. The average measured Fe/S composition for the grain ($x = \sim 0.09$ 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.

Diffraction patterns were collected from several areas within the Fe-sulfide. Closest to the Cu-rich grain, these patterns show the presence of troilite (tr), with spots consistent with both chalcopyrite and cubanite present in some SAED images (Fig. 2d and Supplementary Fig. 2). In the region with the flame texture, the only clearly indexed phase is 4C-pyrrhotite, although streaking and some excess reflections could indicate the presence of NC-pyrrhotite (Fig. 2e and Supplementary Fig. 3). Some diffraction patterns did not index fully to these phases, and there is evidence of deformation and a large number of defects.

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**Fig. 2 FIB section and diffraction patterns from particle CO038.**

(a) Bright field TEM image and (b) HAADF STEM image mosaic of sulfide grains from CO038. Cubanite (cb) is to the left; troilite (tr) with Cu-rich regions is next to the cubanite; pyrrhotite (4C-po) flame texture is to the right. SAED patterns from (c) cubanite, (d) troilite (tr), with faint chalcopyrite (cp) (yellow) and cubanite (red) reflections, and (e) 4C-pyrrhotite with streaking that could indicate the presence of NC-pyrrhotite.

**Fig. 3 EELS data from regions in CO038 and standards.**

(a) O K-edge, (b) Fe L-edge, and (c) Cu L-edge EELS from various regions in and around the crack in the chalcopyrite grain, showing the crack rim (red) is magnetite, Cu-rich nanoparticles are fcc-Cu metal, and Cu in the sulfide matches both chalcopyrite and cubanite$^{47,48}$. Fe-oxide standards shown for comparison$^{49}$. 

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piece cover and in the sample holder (Supplementary Fig. 4 and Supplementary Table 1). In the Cu-rich phase, Fe/S $\sim 0.65$–$0.73$. If we assume all cation sites are filled (i.e., Fe$^{+}+\text{Cu} = S$), we find Cu/Fe of 0.55–0.37, consistent with cubanite or isocubanite, possibly mixed with pyrrhotite. There is ~8 at% O measured in the bulk of the Cu-Fe-sulfide as well. However, Fe L-edge EELS shows no evidence of oxidation, and oxygen was not included in the calculations to determine Cu/Fe. Both the Cu-Fe-sulfide and Fe-sulfide in CO038 lack Ni.

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Several cracks are present in the Cu-Fe-sulfide, one of which is perpendicular to the FIB section. The crack has oxidized Fe-rich edges and is decorated by Cu metal nanoparticles (Fig. 4). No other material (e.g., silica) is present in the crack. The edges of the crack are sulfur-free to 5 nm and have been oxidized to magnetite as indicated by both EELS (Fig. 3) and lattice spacings in high-resolution images. It is unclear if the other O-rich regions in the Cu-Fe-sulfide grain are similar cracks with oxidized edges that were oblique to the section as thinned or if the excess O is an artifact of the FIB preparation.

Discussion

The sulfide grains in Itokawa particle RB-CV-0038 are inconsistent with the primary formation on the Itokawa parent body, and must instead be a microxenolith of carbonaceous chondrite or cometary origin. Cubanite and 4C-pyrrhotite, which has been identified in CI chondrites, indicate temperatures less than 200 °C. By contrast, LL6 particles among the Itokawa sample set equilibrated at temperatures <800 °C with slow cooling to only ~600 °C. The mottled troilite-cubanite-chalcopyrite grain with low amounts of copper present between the cubanite and 4C-pyrrhotite suggests the interaction of the pyrrhotite with a Cu-bearing fluid during low-temperature aqueous alteration to form the cubanite. Structural and petrologic evidence from CI chondrites show the cubanite in those meteorites formed at a later stage than the pyrrhotite as well.

Cubanite, a Cu-Fe-sulfide, is known only in terrestrial ore deposits, comet 81P/Wild2, and CI-chondrite materials. Cubanite goes through an irreversible transformation to isocubanite at 200–250 °C depending on heating rate. Isocubanite is not stable at low temperature (below ~250 °C) and decomposes upon slow cooling to pyrrhotite and chalcopyrite. Experimental work at conditions relevant to the CI-chondrite parent body (150–200 °C; pH 9–10) show the presence of cubanite in runs with both metal and sulfide starting materials, and chalcopyrite was identified by XRD in all of the experimental runs. The experimental grains analyzed for structural details showed doubling or quadrupling of a and c to form superstructures in different grains, while no superstructures were noted in the natural Wild 2 or Orgueil cubanites. This is in contrast to our measured tripling of c and indicates likely differences in formation and/or alteration histories. In addition to the low-temperature formation of the cubanite, monoclinic 4C-pyrrhotite is stable at temperatures <250 °C and has been identified with cubanite in CI chondrites. Exsolution of NCPyrrhotite in 4C-pyrrhotite is common in terrestrial samples.

Low-temperature aqueous alteration did occur on ordinary chondrite parent bodies, as evidenced by bleached chondrules in ordinary chondrites of all metamorphic grades. However, thermal metamorphism occurred after most of the aqueous alteration, and for our grain, would have removed the low-temperature exsolution features. The reported presence of NaCl on at least several different Itokawa grains could indicate later, localized aqueous processing that may also have affected the oxidized crack in the cubanite. However, it is unclear if the NaCl grains are from the asteroid or are due to terrestrial contamination. Magnetite, as seen on the crack rim, forms under high pH (8–11), low-temperature conditions on chalcopyrite. Similar reactions likely would take place for the oxidation of cubanite surfaces and provide constraints on temperature and fluid composition during alteration. Iron sulfates are formed during reactions at low pH while copper oxidation products were also present in non-aqueous (air) experiments.

Copper on LL chondrites is found in Fe-Ni metal and as native Cu, and a localized shock event could lead to the mixing of Cu metal with iron-sulfide to form a Cu-Fe-sulfide. This is the likely formation mechanism of a bornite-like phase reported with troilite and native Cu in the Pultusk meteorite (H4-6). Above 600 °C, sulfide of the composition measured here (~CuFe2S3) is within the range of a cubic intermediate solid solution (iss) that at high temperature falls between the bornite solid solution and the pyrrhotite solid solution. Upon cooling, chalcopyrite can exsolve within the isocubanite matrix, but cubanite does not form. This cubic iss is likely the same phase identified in a number of stony meteorites as chalcopyrrhotite and is structurally the same as isocubanite.

Particle C0038 was likely once part of a larger breccia that fused the exogenous sulfide portion to olivine from the Itokawa parent body, possibly prior to the formation of Itokawa itself. The aqueous alteration event that caused the oxidation of the crack in the cubanite could also have led to its fusing with the olivine. The composition of the olivine in C0038 falls within the expected range for LL chondrite material and is closely related to phases previously measured in Itokawa particles, suggesting that the microxenolith comprises only a portion of the particle. The olivine composition is less magnesian than typical for CI chondrites (Fa9.5–26 in Orgueil compared to Fa25 here), and there is no evidence of any alteration within the olivine itself or along the boundary between the sulfide assemblage and the olivine.

Microxenoliths of carbonaceous chondrite material have been identified in ordinary chondrites, and CI-like material specifically has been found in several meteorites. However, this grain has several clear differences from the cubanite identified in CI chondrites. In Orgueil, veins in two different cubanite grains have Ni-bearing layers, but we observed no Ni in the crack in the cubanite or in the adjacent pyrrhotite. However, it is possible that pentlandite was previously associated with the sulfide grains and was broken off during the impact that brought it to Itokawa or by
located in Room-B, the other particles were from Room-A and than a single micrometeoroid, or that interactions with the same exogenous grains within the sample set suggests the impact event ion beam (FIB) sample preparation were done using an FEI Helios G3 equipped was available for imaging, then coated by 80 nm of evaporated carbon to reduce fi
Lake meteorite20 and a primitive organic-rich clast recently in the meteorite collection. It is also possible the grain is from another parent body that experienced many of the same conditio
considering the relative rarity of Cu-bearing sul
Pyrrhotites in Tagish Lake, as in CIs, are often Ni-rich compared to our grain, although the sulfi
dant sulfi
des in the
comet14, which in turn could mean that cometary material is also a possible source for the cubanite on Itokawa, although such alteration is not thought to be pervasive on comets.
Recently, significant amounts of proposed exogenous materials have been identified spectroscopically on asteroids (101955) Bennu8 and (162172) Ryugu9. Exogenous material was not recognized spectrally on Itokawa, but exogenous material containing significant sulfide phases may not necessarily be apparent. Considering the relative rarity of Cu-bearing sulfides in the meteorite record18, it seems quite possible that the Cu-sulfides noted in a previous Itokawa sample6 are related to the chalco-
pyrite identified here. Identification of multiple, possibly related, exogenous grains within the sample set suggests the impact event that mixed the cubanite with the indigenous material was more than a single micrometeoroid, or that interactions with the same body occurred multiple times. While our particle C0038 was located in Room-B, the other particles were from Room-A and collected during a separate touchdown by Hayabusa46, indicating the exogenous material is more widespread than would be possible from a single micrometeorite or IDP. The presence of exogenous material on Bennu and Ryugu, and now on Itokawa, confirms that asteroids with material on their surface from unrelated parent bodies are the norm rather than an exception.

Methods
Particle RB-CV-0038 (C0038) was provided to NRL as part of the 3rd International Announcement of Opportunity by JAXA. The particle is composed of olivine and sulfide and is ~40 μm across. It was mounted in epoxy such that most of the grain was available for imaging, then coated by 80 nm of evaporated carbon to reduce charging and provide added protection of the surface during the ion beam deposition and milling. Scanning electron microscope (SEM) imaging and focused ion beam (FIB) sample preparation were done using an FEI Helios G3 equipped with an Oxford 150 mm² SDD energy dispersive X-ray spectrometer (EDS). After imaging, protective straps of C or Pt were deposited on regions of interest, and multiple samples suitable for scanning electron microscopy (STEM) analysis were extracted from the particle. Final thicknesses, determined using electron energy-loss spectroscopy (EELS), are ~t < 1 where t is the sample thickness and λ is the scattering cross-section. Samples were prepared using a 50 kV Ga⁺ beam, with final thinning and cleaning of some sections done at a lower voltage (8 or 16 kV). Most samples were mounted on Cu half-grids, but one extracted from a region known to contain Cu (from SEM-EDS) was mounted on a Mo half-grid. STEM analysis was carried out with the Nion UltraSTEM200-X at NRL. The microscope is equipped with a Gatan EELS ER spectrometer for EELS and a windowless, 0.7 sr Bruker SDD-EDS detector. Data were collected at 200 kV, 70–90 pA. Selected area electron diffraction (SAED) patterns and bright-field images were collected on a JEOl2200F. SAED patterns were measured based on calibrated camera constants, and phase identifications were compared to simulated patterns from the software program SingleCrystal by CrystalMaker Software Ltd.

Quantification of STEM-EDS data was performed with the Cliff-Lorimer method and detector-specific k-factors obtained calculated with the Bruker EDS quantitative analysis program SingleCrystal by CrystalMaker Software Ltd. A system Cu peak is present in all data due to Cu being used in the sample holder and pole piece cover. This peak is significantly reduced by the use of a Mo half-grid to support the FIB section and optimization of the sample position relative to the grid posts and EDS detector, but assumptions about phase stoichiometry must be made to determine the Cu content of a material. We calculate Cu in Cu-bearing phases assuming contribution from system peaks is the same as that in Cu-free pyrrhotite or alternatively by assuming (Cu+Fe)/S = 1 and calculating Cu in the sample after measuring Fe and S. We obtain consistent compositions for each calculation method for the cubanite grain, providing validation for our assumptions.

Data availability
The data that support the figures in this article are available at https://doi.org/10.13140/RG.2.2.17633.27689

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