## Coordinated Analyses of Hayabusa particles RB-CV-0234, RB-QD04-0039, and RA-QD02-0310: Constraints on asteroid Itokawa formation from sulfides and silicates

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**Introduction:** Sulfides are important phases in planetary materials because their compositions, textures, and crystal structures can be used to constrain oxygen fugacity of formation, shock stage, and aqueous-, thermal-, and cooling-histories [e.g., 1–8]. The pyrrhotite-group sulfides are largely nonstoichiometric and have a range of compositions (typically  $0 \le x \le 0.125$ , but x can be  $\le 0.2$ ; i.e., FeS [troilite] to Fe<sub>0.8</sub>S) and distinct crystal structures (polytypes). The stoichiometric end members are 2C (troilite; FeS, hexagonal) and typically 4C (Fe<sub>7</sub>S<sub>8</sub>, monoclinic) pyrrhotite. There are also pyrrhotites of intermediate compositions with  $0\le x\le 0.2$  (all hexagonal), including the non-integral NC-pyrrhotites and the integral 5C (Fe<sub>9</sub>S<sub>10</sub>), 6C (Fe<sub>11</sub>S<sub>12</sub>), and 11C (Fe<sub>10</sub>S<sub>11</sub>) pyrrhotites [e.g., 9–11]. Geothermometry of pyrrhotite-pentlandite intergrowths in meteorites shows that most formed via primary cooling from high temperature (i.e., chondrule cooling in the protoplanetary disk) or thermal alteration on the parent body [e.g., 12–14]. Sulfides in the LL4 to LL6 chondrites typically equilibrated  $\le 230^{\circ}$ C, consistent with formation during cooling after thermal metamorphism [2]. Analyses of Hayabusa particles identified asteroid 25143 Itokawa as LL4–6 chondrite material (~10% LL4 and ~90% LL5–6) [e.g., 15–18] that was thermally metamorphosed between ~780 and 840°C [15]. Itokawa particles were found to record shock stages between S2 and S4, with most particles around S2 [19,20]. Sulfides in Hayabusa particles [e.g., 15,21,22] may record additional and/or complementary information on the

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Figure 1. Composite TEM X-ray element map (RGB=FeSNi) of RB-CV-0234 FIB Section; where po = pyrrhotite and pn = pentlandite.

We performed coordinated analyses of the Hayabusa particles RB-CV-0234, RB-QD04-0039, and RA-QD02-0310, allocated in Hayabusa AO5. Preliminary analysis by JAXA's Hayabusa examination team via scanning electron microscopy (SEM) determined that particle RB-CV-0234 (25.9  $\mu$ m in diameter) consists of FeS, Fe, FeNiS, and CuS, making it an ideal target potentially containing both pyrrhotite group sulfides [(Fe,Ni,Co,Cr)<sub>1-x</sub>S] and the rare Ni-rich sulfide, pentlandite [(Fe,Ni,Co,Cr)<sub>9</sub>S<sub>8</sub>]. In addition, JAXA's Hayabusa examination team determined that particle RB-QD04-0039 (52  $\mu$ m in diameter) consists of olivine, low-calcium pyroxene, and troilite, and that particle RA-QD02-0310 (127  $\mu$ m in diameter) consists of olivine, plagioclase, and troilite. These two Hayabusa particles provided excellent opportunities to identify sulfides with petrographic context and to analyze their adjoining silicate minerals, unlike RB-CV-0234 that only contained sulfides. Here, we compared

in situ analyses of these particles to the results from LL3–6 chondrite silicates and sulfides [e.g., 1,2], with the goal of further constraining the formation and alteration conditions of asteroid Itokawa. Preliminary analyses from RB-CV-0234 and RB-QD04-0039 were presented in [23,24,25].

**Samples and Analytical Procedures:** We mounted RB-CV-0234, RB-QD04-0039, and RA-QD02-0310 each on epoxy bullets, using a method modified from [21], and microtomed them in preparation for analysis and sample extraction using the FEI Helios NanoLab 660 focused-ion-beam-SEM (FIB-SEM) at the University of Arizona (UAz). X-ray element maps and high-resolution images of the microtomed RB-CV-0234 and RB-QD04-0039 were obtained with the FIB-SEM prior to extraction of a  $\sim 10 \times 10 \mu m$  sections from each particle, which were then thinned to electron transparency (<100 nm) following the methods of [26]. The FIB sections were then analyzed using the 200 keV aberration-corrected Hitachi HF5000 scanning transmission electron microscope (S/TEM) at UAz. After a FIB section of the sulfide from RB-QD04-0039 was obtained, RB-QD04-0039 was analyzed on the Cameca SX-100 electron microprobe (EPMA) at UAz. Microtome preparation of RA-QD02-0310 did not reveal sulfides for further structural analyses via TEM, but the compositions of its silicates were determined via EPMA at UAz. **Results:** FIB-SEM X-ray element maps showed that the microtomed surface of RB-CV-0234 consisted entirely of pyrrhotite. However, X-ray element maps of the extracted FIB section, determined via TEM analysis, revealed a single large grain of pyrrhotite and a single smaller grain of pentlandite (4.8 × 1.3  $\mu$ m) at the bottom of the section (**Fig. 1**). Selected-area electron-diffraction (SAED) patterns of the pyrrhotite and pentlandite grains index to 2C pyrrhotite (troilite) and pentlandite along the [110] zone axis (i.e., they are crystographically oriented), respectively. The compositions of RB-CV-0234 via quantitative

energy-dispersive X-ray spectroscopy [27] are 35.2 wt.% S and 64.8 wt.% Fe for pyrrhotite, and 32.4 wt.% S, 49.4 wt.% Fe, and 18.2 wt.% Ni for pentlandite. The microtomed surface of RB-QD04-0039 showed a single sulfide grain, as well as olivine (Fa28.1–29.5, Fa28.9±0.5 [1 $\sigma$ ]; n = 7) and low-calcium pyroxene (Fs23.8–24.9, Fs24.3±0.6, Wo1.1±0.1 [1 $\sigma$ ]; n = 3) (**Fig. 2**). A FIB section of the sulfide grain in RB-QD04-0039 revealed it to be troilite. The microtomed surface of RA-QD02-0310 showed a grain of olivine (Fa28.9–31.3, Fa30.2±0.8 [1 $\sigma$ ]; n = 12), with two chrome-spinels.

Discussion: The sulfides in RB-CV-0234 are most consistent with it being a sulfide grain from an LL6 chondrite, similar to the sulfides from Saint-Séverin studied by [1,2]. We infer this because: (1) the Ni content of pentlandite is consistent with the characteristic Ni contents of LL chondrite pentlandite [2,14]; and (2) based on results from the LL3-6 chondrite sulfides we previously studied [1,2,14], sulfide grains in Saint-Séverin (LL6, S2 [2,28]) contain a similar pentlandite/pyrrhotite morphology (i.e., blocky pentlandite in pyrrhotite) and 2C pyrrhotite (troilite) with pentlandite [1]. The other LL chondrites we studied contained either a distinct morphology (e.g., pentlandite lamellae) and/or multiple polytypes of pyrrhotite [1,2]. The compositions of pyrrhotite and pentlandite in RB-CV-0234 are consistent with equilibrating <300°C, perhaps as low as 230°C, similar to that of LL4–6 chondrites [2,25]. The olivine grain in RB-QD04-0039 contains planar fractures, indicating a shock stage of at least S3 and minimum shock pressures of 5-10 GPa [29]. The silicate compositions of both RB-QD04-0039 and RA-QD02-0310 (Fa28.9±0.5 and Fa30.2±0.8, respectively) are consistent with that of equilibrated LL chondrites, consistent with that found by [15] for Hayabusa particles. Relative to the iron-wüstite (IW) buffer, the oxygen fugacity constraints on the formation of troilite [30] and of pentlandite [14] indicates that RB-CV-0234 and RB-QD04-0039 were likely altered between approximately IW-2.2 and IW, consistent with that found for LL5 and LL6 chondrites by [14]. Therefore, the morphology and chemical compositions of sulfides and silicates of RB-CV-0234, RB-QD04-0039, and RA-QD02-0310, as well as inferred sulfide equilibration temperature and oxygen fugacity constraints are consistent with equilibrated LL chondrites.



Figure 2. (a) Back scattered electron (BSE) image and composite EPMA X-ray element map (RGB=FeMgSi) of RB-QD04-0039; LCP = low-calcium pyroxene.

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