1 Title

2 **Further characterization of carbonaceous materials in Hayabusa-returned samples to understand their**
3 **origin**

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30 **Abstract**

31 Carbonaceous materials in the sample catcher of the Hayabusa spacecraft were assigned as category 3 particles.
32 We investigated the category 3 particles with a suite of *in situ* microanalytical methods. Possible contaminants
33 collected from the cleanrooms of the spacecraft assembly and extraterrestrial sample curation center (ESCuC)
34 were also analyzed in the same manner as category 3 particles for comparison. Our data were integrated with
35 those of the preliminary examination team for category 3 particles. Possible origins for the category 3 particles
36 include contamination before and after the operation of the Hayabusa spacecraft.

37

38 **Glossary**

39 HASPET = Hayabusa Sample Preliminary Examination Team; ESCuC = Extraterrestrial Sample Curation
40 Center; FE–SEM–EDS = field emission–scanning electron microscopy–energy dispersive X-ray spectroscopy;
41 NanoSIMS = nano-scale secondary ion mass spectrometry; ToF–SIMS = time-of-flight–secondary ion mass
42 spectrometry; TEM = transmission electron microscopy; XANES = X-ray absorption near-edge structure;
43 STXM = scanning transmission X-ray microscopy; FT–IR = Fourier transform–infrared spectrometry; BSE
44 image = back-scattered electron image; CC = clean chamber; FIB = focused ion beam; SFA = Fairing
45 Assembly Building; IOM = insoluble organic matter.

46

1. Introduction

The sample catcher of the Hayabusa spacecraft contained carbonaceous particles that were classified as “category 3” (Uesugi et al., 2014; Yada et al., 2014). Their size is similar to the silicate particles in the sample catcher, ranging from a few to several hundred microns. During the preliminary examination of silicate particles (Ebihara et al., 2011; Nagao et al., 2011; Nakamura et al., 2011; Noguchi et al., 2011; Tsuchiyama et al., 2011; Yurimoto et al., 2011), organic materials inside and on the surface of the silicate particles were also investigated by Naraoka et al. (2012). However, no evidence for an extraterrestrial origin of the organic materials has yet been found. Thus, the relationship between the silicate particles and category 3 particles in the sample catcher remains uncertain.

The Hayabusa Sample Preliminary Examination Team dedicated to the category 3 particles (HASPET for category 3 particles; HASPET-C3) was organized by the ESCuC in 2012. The ultimate goal of HASPET-C3 is to determine the origins of category 3 particles. Given that the category 3 particles are too small (i.e., in size and amount) to obtain full information related to their organic chemistry using general analytical methods, HASPET-C3 planned a series of *in situ* microanalytical methods to investigate the particles. The team also evaluated the damage and contamination that would affect the isotopic compositions, chemical formulae, and micro-textures caused by the analysis of the category 3 particles and possible contaminants. Some of the analytical results were reported in 2014 and 2015 by members of HASPET-C3 (Ito et al., 2014; Uesugi et al., 2014; Yabuta et al., 2014; Kitajima et al., 2015; Naraoka et al., 2015), including important characteristics of the category 3 particles; however, their origin remains unclear.

In this paper, we present new results from coordinated chemical, isotopic, and micro-textural studies of the category 3 particles, and detailed analyses of possible contaminants considered in our previous studies (Ito et al., 2014; Uesugi et al., 2014; Kitajima et al., 2015; Naraoka et al., 2015; Yabuta et al., 2015). We further discuss the nature and origin of the category 3 particles, considering the results of all analyses undertaken by HASPET-C3. This study includes new NanoSIMS, STXM-XANES, and TEM analyses of particles RA-QD02-0180 and RB-QD04-0037-01 (Figs 1–18).

2. Samples and analytical methods

The subset of category 3 samples allocated for the preliminary examinations and the materials investigated in this study are listed in Table 1.

2-1. Category 3 particles

A total of six category 3 particles were allocated for the preliminary examination. Sequential analysis was applied to five particles (RB-QD04-0047-02, RA-QD02-0120, RB-QD04-0001, RB-QD04-0037-01, and RA-QD02-0180; Fig. 1a–b), with one particle (RA-QD02-0008) being lost during sample handling. The allocated particles were 19 to 55 μm in diameter and exhibit some variation in chemical composition as determined by FE–SEM–EDS. RA-QD02-0120 and RB-QD04-0047-02 did not show clear N peaks in the FE–SEM–EDS analysis, and one particle (RA-QD02-0180) had a clear spectrum of NaCl and KCl in an EDS spot analysis. Uesugi et al. (2014) classified the category 3 particles into blocky, faint, and fibrous types according to their

textures. The allocated samples include five blocky types and one faint type. These morphological characteristics may reflect their original materials. Images of these particles obtained by FE–SEM are shown in fig. 1 of Uesugi et al. (2014).

2-2. Possible contaminants collected in cleanrooms

We have investigated possible contaminants for comparison with the category 3 particles, in order to evaluate their origins. Kitajima et al. (2015) reported FT–IR and Raman spectroscopy results for IOM from the Murchison (CM2) meteorite, a white object found in the sample catcher, Kapton, VITON (i.e., fluorocarbon rubber), and Tufram. They found that some category 3 particles did not have characteristics of organics from extraterrestrial material. In addition, RB-QD04-0047-02 showed some similarities with the white object and was probably a reaction product of Kapton with hydrazine.

We investigated particles collected from a witness plate made of Al in a cleanroom where the Hayabusa2 spacecraft was constructed at ISAS/JAXA. The plate was exposed to the cleanroom for four months during construction of the spacecraft. Given that the cleanroom was also used for the construction of the Hayabusa spacecraft, we can assess the contamination into the sample catcher before the launch of the spacecraft. Figure 2 shows an SE image of the witness plate, which contains >100 particles with sizes of $\leq 100\ \mu\text{m}$. Most of the particles were carbonaceous materials and some have a fibrous structure; these likely originated from human activities in the cleanroom. The particles show C, N, O, Cl, Na, and K peaks in SEM–EDS analyses. We selected two particles from the witness plate (WP2 and WP5; Table 1) for analysis in the same manner as for the category 3 particles.

Materials employed in the cleanrooms used to analyze the Hayabusa-returned samples at the ESCuC were also examined as possible contaminants during the sample curation process after the return of the spacecraft to Earth. We investigated silicon rubber used for sealing the cleanroom and VITON fluoro rubber used for the gloves in the clean chambers for the Hayabusa-returned samples. Figure 3 shows the BSE images and EDS spectra of particles of VITON and silicon rubber. The chemical compositions of VITON and silicon rubber obtained by SEM–EDS are listed in Table 1. Given that we did not use a coating of conductive material, the surface of the particle charged up during SEM observations. The sample was pressed into the center of a Au plate with a diameter of 3 mm and thickness of $300\ \mu\text{m}$. However, because the particles were very soft and not flattened by pressing, they still show an irregular surface shape in the BSE image. In EDS spectra, the particles show distinct chemical compositions, including concentration peaks of F, Mg, Si, Ti, and Zn. Of note, these materials did not show a N peak like that observed for the category 3 particles during their preliminary examination. The EDS spectra show background peaks of Au and Al from the sample holder. Peaks of C, O, F, Zn, and Mg are from the particle, as these were also observed during TEM–EDS analysis (Figs 21 and 22).

2-3. Insoluble organic matter (IOM)

We examined IOM from carbonaceous chondrites in the preliminary examination, as we presumed the category 3 particles might originate from exotic component from other asteroids or comets into Itokawa surface. Carbonaceous chondrite-like clasts are often present in metamorphosed ordinary chondrites (e.g.,

123 Brearley, 1990). Kitajima et al. (2015) examined IOM from Murchison and found significant differences in
124 FT-IR absorption features, the Raman spectroscopy peak position, and Full Width of Half Maximum of the
125 G-band as compared with category 3 particles. In Uesugi et al. (2014), we additionally investigated IOM
126 extracted from a CM2 carbonaceous chondrite (Asuka(A)-881458; IOM01) and showed results of TEM and
127 O-XANES analyses. We present new NanoSIMS, FT-IR, Raman spectroscopy, and N-XANES results of
128 IOM01 in this paper, and compare it with the characteristics of IOM from Murchison and category 3 particles.
129

130 **2-4. Sample preparation**

131 Hayabusa-returned samples in the sample catcher of the Hayabusa spacecraft were picked up in Clean
132 Chamber 2 (CC2) at the ESCuC with an electrostatically controlled micro-manipulator (Yada et al., 2014).
133 Subsequently, their texture, size, and general chemical composition were obtained by FE-SEM-EDS (Hitachi
134 SU6600 and S4300-S/N) with an acceleration voltage of 10 kV. Samples allocated to HASPET-C3 were
135 pressed into Au or In plates to fix the small particles during analysis and transport. Details of the sample
136 pressing process were described by Uesugi et al. (2014). We used an electrostatically controlled quartz
137 manipulator for transferring the samples between the sample holder and Au or In plates in GloveBox3 of
138 ESCuC. We did not use any adhesive materials such as glues, resins, or liquids during sample handling. Ultra-
139 thin sections (UTSs) of category 3 particles were prepared by FIB (Hitachi FB2200) from the pressed samples
140 at ESCuC for TEM and XANES analyses.

141 Possible candidates (i.e., contaminants) for the origins of the category 3 particles were processed in a
142 similar manner to the category 3 particles. At the beginning of sample preparation, particles of VITON (FR01
143 in Table 1) and silicon rubber (SR01) were observed by SEM-EDS on a Au plate. After SEM observations,
144 they were pressed onto In plates. IOM01 was pressed onto a Au plate. After pressing, UTSs of these were
145 prepared by FIB and subjected to XANES and TEM-EDS analyses.

146 All pressed samples and UTSs were transferred between facilities by parcel delivery services. All
147 processes were tested prior to analysis of the category 3 particles using analog samples, IOM01, and particles
148 collected from the spacecraft and the relevant SFA of the Tanegashima Space Center/JAXA (S01) (Uesugi et
149 al., 2014). The particle S01 was measured by NanoSIMS at the beginning of the investigations by HASPET-
150 C3 to determine its H isotopic ratio and to confirm whether it shows terrestrial value. After we confirmed the
151 H isotopic ratio of S01 was terrestrial (Table 2), we analyzed IOM01 with NanoSIMS, FT-IR, Raman
152 spectroscopy, STXM-XANES, and TEM methods, as applied to the category 3 particles. These analyses
153 confirmed that our methods yield robust data, indicating they are suitable for analysis of the category 3
154 particles.
155

156 **2-5. Analytical methods**

157 Although we finally established a sequential analytical flow of organic materials as shown in table 3 of
158 Uesugi et al. (2014), we applied different scheme for each category 3 particle for some reasons. In previous
159 studies, we found that data of some analyses were affected by previous analyses (Ito et al., 2014; Naraoka et
160 al., 2014; Uesugi et al., 2014). In these cases, we modified the procedure of our analysis, such as changing the

metal plate from Au to In and changing the order of FT–IR, Raman, NanoSIMS, and ToF–SIMS analyses for RA-QD02-0180 and R-QD04-0037-01. In addition, Uesugi et al. (2014) skipped the FT–IR analysis of RA-QD02-180 because the particle contains NaCl inclusions on its surface. FT–IR instruments do not have an atmospheric shielding system and, as such, the inclusions might have been destroyed by interaction with water vapor in the terrestrial atmosphere during analysis. In the present study we skipped the Raman spectroscopy analysis of RA-QD02-0180 for the same reason. RB-QD04-0001 was almost destroyed by NanoSIMS analysis and could not be further analyzed. Thus, the category 3 particles were subjected to the various analytical methods in a certain order according to the sample characteristics (Table 1).

169

170 3. Results

171 We report new results for the category 3 particles RA-QD02-0180 and RB-QD04-0037-01, and other
172 materials that might constrain the origins of category 3 particles.

173

174 3-1. NanoSIMS

175 We obtained NanoSIMS isotopic and elemental images of the category 3 particles RB-QD04-0037-01a–b
176 (Figs 4–5) and RA-QD02-0180 (Fig. 6). RB-QD04-0037-01a–b have homogeneous and terrestrial H, C, and
177 N isotopic compositions ($\delta D = -3\text{‰} \pm 5\text{‰}$, $\delta^{13}C = -4\text{‰} \pm 4\text{‰}$, and $\delta^{15}N = 15\text{‰} \pm 10\text{‰}$). RA-QD02-0180 has
178 $\delta D = +7\text{‰} \pm 6\text{‰}$, $\delta^{13}C = -25\text{‰} \pm 4\text{‰}$, and $\delta^{15}N = 13.5\text{‰} \pm 0.5\text{‰}$. RA-QD02-0180 contains numerous O-, S-,
179 and Cl-enriched, micron-sized regions scattered throughout the sample. The locations of the O-, S-, and Cl-
180 enriched areas do not overlap with each other, indicating that the distributions of these element are not related
181 to each other. We readily determined the C and N isotopic ratios of each of the ^{16}O , ^{32}S , and ^{35}Cl areas in the
182 field of view by defining regions of interest. The δD , $\delta^{13}C$, and $\delta^{15}N$ isotopic images show no obvious isotopic
183 anomalies in these areas of the sample.

184

185 3-2. XANES

186 After isotopic imaging by NanoSIMS, we used FIB for sub-sampling of the category 3 particles, which
187 yielded RA-QD02-0180-02, RA-QD02-0180-03 and RB-QD04-0037-01-02.

188 Elemental maps of RA-QD02-0180-02 and RB-QD04-0037-01-02 acquired by STXM are shown in Figs
189 7 and 8, respectively. RA-QD02-0180-02 contains a range of elements. C and N are abundant in almost the
190 entire region of RA-QD02-0180-02, apart from in several micron-sized inclusions (Fig. 7b, d) that show Cl
191 absorption (Fig. 7g). Oxygen is scarce in the sample (Fig. 7e) and Ca is locally concentrated in C-rich regions
192 (Fig. 7c). Linear absorption features observed during Ca mapping along the lines of FIB fabrication may be an
193 artifact of sample preparation. A similar artifact is evident with respect to N depletion in the upper part of the
194 particle (Fig. 7d). Only one grain showed Fe and/or Ti absorptions (Fig. 7f, h). F is absent in this sample (Fig.
195 7i). In contrast, C, N, and O are almost homogeneously distributed in RB-QD04-0037-01-02 (Fig. 8b, d, e),
196 apart from the possible secondary depletion of N. No other elements were recorded in this sample (Fig. 8c, f,
197 g).

198 C-K-edge-XANES spectra of RA-QD02-0180-02 and RB-QD04-0037-01-02 are different to each other
199 (Fig. 9a), and distinct from those of other category 3 particles (RA-QD02-0120-01 and RB-QD04-0047-02-
200 01) reported by Yabuta et al. (2014). The spectrum of RA-QD02-0180-02 shows a peak of amide (R–NH–
201 (C=O)–R') and/or carboxyl/ester (R–(C=O)O–R') (288.1 eV), and a small peak of aromatic carbon (C=C)
202 (285.0 eV). The spectrum of RB-QD04-0037-01-02 is more complex, showing aromatic carbon (284.8 eV),
203 amide and/or carboxyl (287.9 eV), urea (NHx(C=O)NHx) (288.9 eV), and carbamoyl (NHx(C=O)OR) (289.8
204 eV). The peak corresponding to aromatic carbon is slightly shifted as compared with those of the other samples,
205 and it has a shoulder at ca. 285.5 eV, indicating that RB-QD04-0037-01-02 is composed of a variety of
206 aromatic moieties (i.e., in terms of ring numbers and constituent elements).

207 N-K-edge-XANES spectra of RA-QD02-0180-02 and RB-QD04-0037-01-02 are compared in Fig. 9b. The
208 spectrum of RA-QD02-0180-02 shows a major peak of amide (401.0 eV), and shoulder peaks of N-
209 heterocycles (C–N=C) and/or nitrile (C≡N) (399.8 eV) and pyridinic N (398.8 eV). The spectrum of RB-
210 QD04-0037-01-02 shows a clearer amide peak than that of RA-QD02-0180-02, with a small shoulder peak of
211 N-heterocycles and/or nitrile. Both samples are enriched in amide, whereas the sample investigated in a
212 previous study is composed mainly of N-heterocycles (Yabuta et al., 2014).

213 The O-K-edge-XANES spectrum of RA-QD02-0180-02 is similar to that of RB-QD04-0047-02-01
214 (Yabuta et al., 2014), but the peak of C=O is slightly shifted (Fig. 9c), which is reflected by the difference in
215 X-ray absorption energy between ketone (531 eV) and carboxyls (532 eV). In contrast, the O-XANES
216 spectrum of RB-QD04-0037-01-02 exhibits a remarkably large ketone peak (~532 eV), and alcohol and/or
217 ether peaks (534 eV).

218 The coordinated C-K-edge- and Ca-L2,3-edge-XANES spectrum of the Ca-rich region in RA-QD02-0180-
219 02 is shown in Fig. 9c. There is no peak corresponding to carbonate C (290.5 eV) in the C-XANES spectrum,
220 whereas the Ca-XANES spectrum shows four absorption peaks at 347.9, 349.2, 351.2, and 352.5 eV. This
221 indicates that RA-QD02-0180-02 contains Ca compounds, but it is unlikely that these are carbonates.

222

223 3-3. TEM

224 We used a JEM-2800 instrument (JEOL Tokyo, Japan) for TEM and STEM analyses of UTSs of the
225 category 3 particles and possible contaminants. Figures 11 and 12 show TEM-EDS maps of RA-QD02-0180-
226 02 after the XANES analysis and RA-QD02-0180-03 before the XANES analysis, respectively. RA-QD02-
227 0180-02 contains very small NaCl, KCl, and S inclusions, as does RA-QD02-180-03 (Fig. 12). There is a
228 homogeneous distribution of N and Si, and localized concentrations of F and Ca, in both RA-QD02-0180-02
229 and RA-QD02-0180-03. The distribution of Ca in RA-QD02-0180-02 (Fig. 11) is consistent with the XANES
230 results (Fig. 7c). The distribution of Ca in RA-QD02-0180-02 is aligned along the tracks of FIB treatment.
231 The homogeneous F distribution on the sample surface could be contamination acquired during sample storage
232 or transfer after the XANES analysis. The images of RA-QD02-0180-02 (Fig. 11) reveal spotty concentrations
233 of Na and K, which do not correlate with the almost homogeneously distributed Cl. However, in XANES
234 analysis (Fig. 7g) it is clear that the distribution of Cl in this UTS is inclusion-like and correlates with the
235 distributions of Na and K in TEM observations. Thus, these spotty concentrations of Na and K could be NaCl

or KCl that was present at the time of XANES analysis, as found in RA-QD02-0180-03 (Fig. 12), but which were destroyed during or after the XANES analysis, prior to the TEM analysis. Investigation of the sample damage caused by analysis and storage of UTSs observed in this study will be reported in a subsequent paper (Nakato et al., in prep.). Figure 13 shows the TEM–EDS maps of RB-QD04-0037-01-02. In this sample, we only found C, N, and Si. The chemical composition and heterogeneous distribution of N and Si are similar to those in RB-QD04-0047-02-01 (fig. 4 of Uesugi et al., 2014).

3-4. Analysis of witness plate contaminants and laboratory equipment

Figure 14 shows TEM–EDS maps of WP2-01, which is the UTS prepared from a particle on the witness plate from a cleanroom used for construction of the Hayabusa2 spacecraft. Although the chemical composition of WP2 obtained by SEM–EDS shows a chloride signal, similar to that of RA-QD02-0180 during SEM–EDS analysis, no NaCl or KCl inclusions were found in TEM observations. The chloride peaks in the EDS spectrum have a broad distribution and do not correlate with each other. We also found a broad distribution of Si and very small inclusions of S.

TEM images of VITON (FR01-01) and silicon rubber (SR01-01) are shown in Figs 15 and 16. The silicon rubber has a uniform distribution of Si and contains visible Ti inclusions due to the doping used to color the rubber. In the elemental maps of VITON (Fig. 16), we observed a broad distribution of F, localized concentrations of Si, and inclusions of Zn and Mg. These elements are also evident in the SEM–EDS spectrum.

Figure 17 shows the XANES spectra of WP2-01 and WP5-01, together with that of RA-QD02-0180-02. WP2-01 and WP5-01 show absorption peaks of aromatic/olefinic carbon (C=C), nitrile (C≡N), amide (O=C–NH_x), alcohol, and ether (C–O) and/or urea ((NH_x)₂(C=O)). The shapes of the C-, N-, and O-XANES spectra of WP2-01 are similar to those of RA-QD02-0180-02, as discussed in the next section. Figure 18 shows the XANES spectra of VITON (FR01-01) and silicon rubber (SR01-01) materials used in the cleanroom (cf. chemically released aliphatic carbon compounds from the VECTRAN in Supplementary Fig. S1).

4. Discussion

4-1. Summary of new data for category 3 particles

RA-QD02-0180 shows C, O, NaCl, and KCl peaks in FE–SEM–EDS analysis. During ToF–SIMS analysis, F, Si, and Cl were also observed. These elements were also observed in TEM–EDS analysis, in addition to a broad N distribution and very small Ca inclusions. NaCl, KCl, and S inclusions were also observed in this particle. Isotopic compositions were $\delta D = +7\text{‰} \pm 6\text{‰}$, $\delta^{13}C = -25\text{‰} \pm 4\text{‰}$, and $\delta^{15}N = +13.5\text{‰} \pm 0.5\text{‰}$. STXM-XANES analysis shows that this particle contains aromatic/olefinic carbon (C=C), amide (NH_x(C=O)C), CH_x, nitrile (C≡N) and/or nitrogen heterocyclics (C–N=C), carboxyl carbon (C=O(OH)), and TiO₂.

NanoSIMS analysis of RB-QD04-0037-01 identified very small S inclusions. TEM analysis identified Si, which is consistent with the ToF–SIMS analysis, although S and F were not detected by TEM–EDS. Isotopic compositions were $\delta D = -3\text{‰} \pm 5\text{‰}$, $\delta^{13}C = -4\text{‰} \pm 4\text{‰}$, and $\delta^{15}N = +15\text{‰} \pm 10\text{‰}$. According to XANES

analysis, this particle uniquely contains amide ($\text{NHx}(\text{C}=\text{O})\text{C}$), urea ($(\text{NHx})_2(\text{C}=\text{O})$), and carbamoyl ($\text{NHx}(\text{C}^*=\text{O})\text{OR}$), in addition to aromatic/olefinic carbon ($\text{C}=\text{C}$), nitrile ($\text{C}\equiv\text{N}$), and carboxyl carbon ($\text{C}=\text{O}(\text{OH})$). Unlike the other particles, both FT-IR (Uesugi et al., 2014) and XANES analyses revealed that this particle contains a variety of N-bearing functional groups.

After further analysis of TEM-EDS mapping data of RA-QD02-0120-01 reported by Uesugi et al. (2014), we found a needle-like Mg-silicate inclusion and Fe inclusions in RA-QD02-0120-01 (Fig. 19). We also found a weak distribution of Si that positively correlates with O and negatively with C and N. The presence of Si is consistent with the FT-IR absorption peak at 1100 cm^{-1} in fig. 5 of Kitajima et al. (2015).

4-2. Summary of IOM data from A-881458 (CM2)

We obtained H, C, and N isotopic images of IOM01, as representative of extraterrestrial organic matter. Figure 20 shows the elemental and isotopic images of IOM01. The sample shows isotopically anomalous hot spots of D and ^{15}N , which are not observed in category 3 particles. Figure 21 shows a summary of the FT-IR, Raman, and XANES analyses of IOM01 from A-881458 (CM2). The FT-IR spectrum in Fig. 21a shows absorption from aliphatic C-H, C-O stretching, and O-H stretching, which are similar to the results from Murchison (CM2) presented by Kitajima et al. (2015). Figure 21c is modified from Kitajima et al. (2015) and shows the close similarities between the Raman spectra of IOM01 (Fig. 21b) and Murchison, and the difference between the IOM from CM chondrites and all the category 3 particles. N- and O-XANES spectra of the IOM01 in Fig. 21d (modified from Uesugi et al., 2014) and Fig. 21e show absorption peaks of carboxyl ($\text{C}=\text{O}(\text{OH})$), imine ($\text{C}=\text{N}$), nitrile ($\text{C}\equiv\text{N}$), and amide ($\text{NHx}(\text{C}=\text{O})\text{C}$). Uesugi et al. (2014) reported TEM analyses of IOM01, in which they located a hollow organic nano-globule in a TEM image.

4-3. Origin of category 3 particles

In this subsection, we discuss the origin of category 3 particles based on all the obtained data, including those from previous studies. In Table 2, we summarize the data obtained for category 3 particles by HASPET-C3.

Figure 22 shows a summary of C-, N-, and O-XANES spectra of category 3 particles. The data for RA-QD02-0120 and RB-QD04-0047-02 are from Yabuta et al. (2014). Notably, there are several differences in the C-XANES spectra between the category 3 particles, indicating that they have different origins and/or have experienced different chemical processes.

Figure 23 shows a H-C isotopic plot for category 3 particles, including RB-QD04-0047-02, RA-QD02-0120, RB-QD04-0001, RB-D04-0037-01, and RA-QD02-0180, which were analyzed in preliminary examinations (data for RB-QD04-0047-02, RA-QD02-0120, and RB-QD04-0001 are from Ito et al., 2014). None of the category 3 particles show obvious isotopic anomalies like those for IOM from carbonaceous chondrites (Fig. 23). As discussed by Ito et al. (2014), this result does not completely rule out an extraterrestrial origin, because extraterrestrial organic materials do not always contain micron-sized, isotopically anomalous regions.

310 Particles collected from the witness plate of the clean room used to assemble Hayabusa2 (WP2 and WP5)
311 show C, N, O, Na, Mg, Al, Si, S, Cl, and K peaks in SEM–EDS analysis. Magnesium and Al would be derived
312 from the witness plate. TEM–EDS analysis identified C, N, O, Si, S, Na, Cl, and K in WP2-01. The chemical
313 composition and texture of WP2-01 are similar to those of RA-QD02-0180. Furthermore, the XANES spectra
314 of WP2-01 and RA-QD02-0180 are very similar (Fig. 17), which indicates contamination into the sample
315 catcher by particles from the cleanroom used for spacecraft assembly before the launch of the Hayabusa
316 spacecraft. The presence of Ti-oxide in RA-QD02-0180-02 was also identified by XANES analysis. Although
317 Ti was not found in the TEM analysis, it may suggest this particle was derived from artificial material, such as
318 rubber or paint, including Ti used to colorize these materials. Titanium was also evident in the SEM–EDS
319 analysis of WP5 (Table 2). The presence of F and Si in RA-QD02-0180, RB-QD04-0037-01, and RB-QD04-
320 0047-02 is significant. Naraoka et al. (2015) suggested that those elements are rarely found in natural materials
321 and were derived from artificial materials. Finally, the presence of amide and NaCl inclusions in RA-QD02-
322 180 and in particles from the witness plate suggests that human skin is a possible source for these particles.
323 Further investigation is needed to confirm the similarities and differences between the particles collected from
324 the witness plate and category 3 particles.

325 Kitajima et al. (2015) discussed the relationship between RB-QD02-0047-02 and carbonaceous materials
326 found in the sample container (not the sample catcher) of the Hayabusa spacecraft, which was termed the
327 “white object”, based on FT–IR and Raman spectroscopy analysis. The white object is a mixture of polyamide
328 and a small amount of polyimide, and the polyamide would be a reaction product of polyimide and hydrazine,
329 which was used as propellant for the Hayabusa spacecraft and leaked from the spacecraft after touchdown on
330 the asteroid Itokawa (https://curation.isas.jaxa.jp/ao/pdf_files/contaminations.pdf). If the white object and RB-
331 QD04-0047-02 have a common origin, then contamination into the sample catcher would have occurred during
332 the operation of the Hayabusa spacecraft.

333 Silicon rubber and VITON show clear differences from the category 3 particles analyzed in this study.
334 SEM–EDS analysis of silicon rubber and VITON identified C, O, Si, and Ti, and C, F, O, Mg, and Zn,
335 respectively. Nitrogen or its functional groups were not detected by SEM–EDS, TEM–EDS, FT–IR, or
336 XANES analysis, whereas all the category 3 particles contain N. In addition, we found inclusions of Ti, Zn,
337 and Mg in such rubbers by TEM–EDS analysis. Those inclusions were not observed by TEM in any category
338 3 particles. The XANES spectra of the rubbers also differ from those of category 3 particles. These results
339 strongly indicate that the category 3 particles analyzed in this preliminary examination are unlikely to have
340 originated from these materials (i.e., during curation). However, FE–SEM–EDS library data for Hayabusa-
341 returned samples (<https://curation.isas.jaxa.jp/curation/hayabusa/index.html>) reveal a possible relationship
342 between such rubbers and category 3 particles. For example, RA-QD02-0091 shows a strong peak of Si in an
343 EDS spectrum. If Ti inclusions were present inside the particle (Fig. 15), then it is possible to determine its
344 origin as the silicon rubber used in the ESCuC cleanroom. Category 3 particles containing F, such as RA-
345 QD02-0078 and RB-QD04-0052, might have originated from fluoro rubber, such as the VITON gloves used
346 in clean chambers. In this case, the strong peak of the C–F bond in FT–IR spectra and Zn and Mg inclusions

may be important indicators of their origin, and might identify contamination after the operation of the Hayabusa spacecraft.

ToF-SIMS analysis identified F in three category 3 particles (RA-QD02-0180, RB-QD04-0037-01, and RB-QD04-0047-02; Naraoka et al., 2015). Fluorine was also detected by NanoSIMS analysis of RB-QD04-0047-02 and by TEM-EDS analysis of RA-QD02-0180, although the amounts were very small. However, no F-related features in category 3 particles were identified by FT-IR or XANES analysis (Kitajima et al., 2014; Yabuta et al., 2014; this paper), although strong features related to C-F bond stretching were observed in analysis of VITON by FT-IR (Kitajima et al., 2015). In addition, the N content is inconsistent with the rubber compositions. These results might suggest that the F detected by NanoSIMS, ToF-SIMS, and TEM-EDS analyses was not derived from organic-fluoro compounds as polymer constituents (e.g., C-F), but that inorganic F was physically trapped into the polymer structure. Although this hypothesis requires further testing, the F contents of category 3 particles do not presently indicate an origin from fluoro rubbers.

We analyzed IOM from A-881458 and Murchison CM2 chondrites to explore a genetic link between the IOM and category 3 particles. The results of the IOM analysis differ from the results for the category 3 particles. The IOM01 contains micron-sized hotspots of D and ^{15}N enrichments, and heterogeneous distributions of these isotopes (Fig. 20). In addition, inclusions of silicate materials and nano-globules were found in TEM observations of the UTS made from IOM01 (Uesugi et al., 2014). These isotopic and micro-textural characteristics were not observed in any category 3 particles. The FT-IR spectra of IOM show aliphatic C-H absorption, whereas those of most category 3 particles did not reveal aliphatic C (Kitajima et al., 2015). Unusually, aliphatic C-H absorption was detected in RA-QD02-0120 by FT-IR analysis. However, the functional group compositions and nano-scale texture of RA-QD02-0120 observed by STXM-XANES and TEM differ from the IOM. The G-band position and its FWHM in the Raman spectrum shown in Fig. 21c also highlights the difference between the IOM of CM2 chondrites and category 3 particles, as discussed by Kitajima et al. (2015). There is currently no obvious genetic link between category 3 particles and IOM.

Our analyses showed several differences between category 3 particles and extraterrestrial organic matter, and some similarities to terrestrial materials. The result indicates that the category 3 particles have multiple origins due to contamination by terrestrial materials before, during, and after operation of the Hayabusa spacecraft. Further detailed studies of category 3 particles will provide more information on their origins.

4-4. Future work

Future work should examine the effects of cosmic ray exposure on the materials that contaminated the sample catcher before and during the operation of the Hayabusa spacecraft, to assess its effects on their chemical composition and molecular structure. The alteration of the original particles during the reaction with N-containing propellants such as hydrazine also needs to be investigated. Further searches for extraterrestrial organic matter in the Hayabusa-retuned samples should be continued. Although the Itokawa asteroid is an ordinary chondrite parent body, which has experienced moderate heating ($\sim 800^\circ\text{C}$; Nakamura et al., 2011), it may contain a small amount of organic compounds. As such, future research should analyze IOM from ordinary chondrites in the same manner as in the present study.

385 RA-QD02-0180 contains trace amounts of Na, K, and Cl (Uesugi et al., 2014). Bridges and Grady (1999)
386 reported that a halite assemblage was present in the Nakhla Martian meteorite, implying a low-temperature
387 formation process by crystallization from an aqueous fluid. It is important to explore the nature and origin of
388 the NaCl-bearing sample to understand water–mineral interactions and their relationship with organic matter.
389 Result of the investigation for NaCl-bearing samples will provide feedback for the investigations of Hayabusa
390 and future returned samples (e.g., Hayabusa2, OSIRIS-REx, Mars Moon Exploration missions).

391 It is important to continue investigations of possible contaminants in the cleanrooms used for spacecraft
392 construction and sample curation. We have already begun investigations of other materials, such as VECTRAN
393 (a fiber of aromatic polyester used in the sampler horn of the Hayabusa spacecraft), as shown in Fig. S1.

394 A careful analytical strategy (i.e., the order of analyses) will be required for the robust description of
395 extraterrestrial organic matter in future sample return missions (e.g., Hayabusa2; Tachibana et al., 2014;
396 Okazaki et al., 2017; Sawada et al., 2017; Watanabe et al., 2017; cf. OSIRIS-Rex; Dworkin et al., 2018).
397 Carbonaceous materials are affected by electron, ion, and synchrotron radiation beams. Once carbonaceous
398 materials are contaminated by terrestrial materials, they are difficult to distinguish from each other. In future
399 work, we will establish a state-of-the-art analytical scheme including combustion and/or dissolution methods
400 for the analysis of higher molecular structures, including high-precision, compound-specific measurement of
401 amino acids with the corresponding stereoisomers (Naraoka et al., 2012; Hamase et al., 2014; Takano et al.,
402 2015; Sugahara et al., 2018), as well as *in situ* molecular analysis by desorption electrospray ionization coupled
403 with high-resolution mass spectrometry (Naraoka and Hashiguchi, 2018).

404

405 5. Conclusions

- 406 1) In this paper, we investigated RA-QD02-0180 and RB-QD04-0037-01 by NanoSIMS, STXM-XANES,
407 and TEM methods. We also investigated possible contaminants collected from cleanrooms used for the
408 construction of the Hayabusa spacecraft and sample curation, such as particles captured by a witness plate
409 (silicon and fluoro rubber), by FE–SEM–EDS, STXM-XANES, and TEM.
- 410 2) Currently, we have not found any evidence of an extraterrestrial origin, and terrestrial contaminants might
411 represent at least some of the category 3 particles. We will further analyze the category 3 particles showing
412 similarities to the terrestrial materials, to create a framework for the robust identification of the origins of
413 organic matter obtained by sample return missions.
- 414 3) More investigations of the possible contaminants and artificial substances such as VECTRAN (see
415 Supplementary Information) with the same manner of category 3 particles are needed to clarify the
416 contamination pathway of terrestrial organic materials into the sample container and/or catcher.
- 417 4) We are exploring the possibility to combine combustion or dissolution methods with our analytical flow,
418 in order to add the information of higher molecular structures, such as amino acids, in future work.

419

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554

555 **Figure captions**

556

557 Figure 1. Secondary electron images of (a) RB-QD04-0037-01 and (b) RA-QD02-0180 on individual In plates
558 after NanoSIMS measurements. The samples were prepared and transferred within a shielded atmospheric
559 environment. RB-QD04-0037-01 was broken into two pieces during sample preparation.

560

561 Figure 2. Secondary electron image of the witness plate (WP) exposed to the cleanroom used for construction
562 of the Hayabusa2 spacecraft. The diameter of the witness plate is 5 mm. There are many tiny particles and
563 fibers inside and outside of the witness plate, most of which are carbonaceous materials.

564

565 Figure 3. BSE images and EDS spectra of the possible contaminants. (a-1) A piece of VITON from fluoro
566 rubber gloves in the clean chambers in the ESCuC. (a-2) EDS spectrum of VITON showing peaks of C, F, O,
567 Zn, and Mg corresponding to the measured point 003 in a-1. (b-1) A piece of silicon rubber used for sealing
568 the cleanroom used for Hayabusa-returned samples at the ESCuC. (b-2) EDS spectrum showing peaks of C,
569 O, Si, and Ti corresponding to the measured point 009 in b-1.

570

571 Figure 4. NanoSIMS ion images of (a) ^{12}C , (b) $^{12}\text{C}^{14}\text{N}$, (c) ^{16}O , (d) ^{32}S , (e) ^1H , (f) δD , (g) $\delta^{13}\text{C}$, and (h) $\delta^{15}\text{N}$ of
572 RB-QD04-0037-01a.

573

574 Figure 5. NanoSIMS ion images of (a) ^{12}C , (b) $^{12}\text{C}^{14}\text{N}$, (c) ^{16}O , (d) ^{32}S , (e) ^1H , (f) δD , (g) $\delta^{13}\text{C}$, and (h) $\delta^{15}\text{N}$ of
575 RB-QD04-0037-01b.

576

577 Figure 6. NanoSIMS ion images of (a) ^{12}C , (b) $^{12}\text{C}^{14}\text{N}$, (c) ^{16}O , (d) ^{32}S , (e) ^{35}Cl , (f) ^1H , (g) δD , (h) $\delta^{13}\text{C}$, and (i)
578 $\delta^{15}\text{N}$ of RA-QD02-0180. Ion images for the Cl-bearing region are also shown in (j) for $\delta^{13}\text{C}$ and (k) for $\delta^{15}\text{N}$.

579

580 Figure 7. (a) STXM image of RA-QD02-0180-02 acquired at 390 eV and the corresponding elemental maps
581 of (b) C, (c) Ca, (d) N, (e) O, (f) Fe, (g) Cl, (h) Ti (arrow indicates a Ti inclusion), and (i) F. The dashed squares
582 on the samples indicate the areas analyzed to acquire the XANES spectra (Figs 9–12).

583

584 Figure 8. STXM image of RB-QD04-0037-01-02 acquired at 390 eV and the corresponding elemental maps
585 of (b) C, (c) Ca, (d) N, (e) O, (f) Fe, and (g) F. The dashed squares on the samples indicate the areas analyzed
586 to acquire the XANES spectra (in Figs 9–12).

587

588 Figure 9. (a) C-, (b) N-, and (c) O-K-edge-XANES spectra of category 3 particles A (RA-QD02-0180-02) and
589 B (RB-QD04-0037-01-02). The peaks assigned include the following: $1s\text{-}\pi^*$ transition of aromatic/olefinic
590 carbon ($\text{C}=\text{C}$) at 285 eV; $1s\text{-}\pi^*$ transition of vinyl-keto ($\text{C}=\text{C}-\text{C}=\text{O}$), nitrile ($\text{C}\equiv\text{N}$), and/or nitrogen
591 heterocycles ($\text{C}-\text{N}=\text{C}$) at 286.7 eV; $1s\text{-}\pi^*$ transition of amide ($\text{R}-\text{NH}-(\text{C}=\text{O})-\text{R}'$) and/or carboxyl carbon

592 (COOH) at 288 eV; 1s- π^* transition of urea ($\text{NH}_x(\text{C}=\text{O})\text{NH}_x$) at 288.9 eV; 1s- π^* transition of carbamoyl
593 ($\text{NH}_x(\text{C}=\text{O})\text{OR}$) at 289.8 eV; 1s- π^* transition of imine ($\text{C}=\text{N}$) at 398.8 eV; 1s- π^* transition of nitrogen
594 heterocycles ($\text{C}-\text{N}=\text{C}$) and/or nitrile ($\text{C}\equiv\text{N}$) at 399.8 eV; 1s- π^* transition of amide ($\text{R}-(\text{C}=\text{O})\text{NR}'_2$) at 401 eV;
595 1s- π^* transition of ketone/carboxyl group ($\text{C}=\text{O}$) at 532 eV; 1s-3p/s* transition of alcohol ($\text{C}-\text{OH}$)/ether ($\text{C}-$
596 $\text{O}-\text{R}$) at 534 eV.

597

598 Figure 10. (a) The coordinated C-K-edge- and Ca-L2,3-edge-XANES spectra of RA-QD02-0180-02
599 highlighting the absence of a peak (290.5 eV) derived from carbonate, but the presence of other Ca species.
600 (b) Calcium-K-edge-XANES spectrum of RA-QD02-0180-02. Two peaks around 349.2 (B) and 352.5 eV (D)
601 are assigned to the L3 and L2 edges of Ca, respectively. Two other smaller peaks (A and C) at 347.9 and 351.2
602 eV are the coordination peaks of peaks B and D. The spectral pattern is distinct from those of calcium
603 carbonates.

604

605 Figure 11. TEM-EDS maps and EDS spectrum of all areas of the UTS for RA-Q02-0180-02 obtained by JEOL
606 JEM-2800 and NORAN System SIX EDS systems. There is a uniform distribution of C, N, O, Si, and Cl in
607 the sample, and localized concentrations of F, Na, S, K, and Ca. For this UTS, XANES analysis was conducted
608 before the TEM analysis.

609

610 Figure 12. TEM-EDS maps and EDS spectrum of all areas of the UTS of RA-Q02-0180-03 obtained by the
611 same systems as in Fig. 11. In this case, TEM-EDS analysis was conducted prior to the XANES analysis.

612

613 Figure 13. TEM-EDS maps and EDS spectrum of the whole of RB-QD04-0037-01-02 obtained by the same
614 setup as in Fig. 11. This sample shows the C, N, and Si distributions.

615

616 Figure 14. TEM-EDS maps and EDS spectrum of the whole of WP2-01 obtained by the JEOL JEM-2800 and
617 JED EDS systems. This sample was also investigated by TEM after XANES analysis.

618

619 Figure 15. TEM-EDS maps and EDS spectrum of the whole view of the silicon rubber obtained by the same
620 systems as in Fig. 14. Inclusions of Ti used to dope the rubber for color are evident in the maps and spectrum.

621

622 Figure 16. TEM-EDS maps and EDS spectrum of the whole view of the VITON (i.e., the fluoro rubber used
623 for the gloves in the cleanroom in the ESCuC; Fig. 3) obtained by the same systems as in Fig. 14.

624

625 Figure 17. (a) C-, (b) N-, (c) O-, and (d) Ca-K-edge-XANES spectra of the category 3 particles RA-QD02-
626 0180-02, WP2-01, and WP5-01. The peak assignments for RA-QD02-0180-02 are the same as in Fig. 9.
627 Spectra for RA-QD02-0180-02 and WP2-01 have similar shapes for all elements and indicate a common
628 origin. In contrast, WP5-01 shows a weak signal for N- and O-XANES, and slightly shifted peak positions in

629 C-XANES, although its chemical composition obtained by SEM–EDS analysis is similar to those of WP2 and
630 RA-QD02-0180.

631

632 Figure 18. (a) C-, (b) N-, and (c) O-K-edge-XANES spectra of a category 3 particle (RA-QD02-0180-02),
633 VITON (fluoro rubber), and silicon rubber. The peak assignments for RA-QD02-0180-02 are the same as in
634 Fig. 9. The shape of the spectrum is largely different from other two materials. This is consistent with the
635 results of TEM–EDS analysis, indicating VITON and silicon rubber have different characteristics from
636 category 3 particles.

637

638 Figure 19. Elemental maps and EDS spectrum of the whole view of another region of RA-QD02-0120-01
639 obtained by re-analysis of the TEM–EDS data acquired by Uesugi et al. (2014). We found a small Mg-silicate
640 inclusion, Fe inclusions, and Ca inclusions.

641

642 Figure 20. NanoSIMS ion images of (a) δD , (b) $\delta^{13}C$, and (c) $\delta^{15}N$ of IOM01 from A-881458. There are tiny
643 hot spots of D, ^{13}C , and ^{15}N enrichments in the sample.

644

645 Figure 21. Summary of the analyses of IOM01 including data from Kitajima et al. (2015) and Uesugi et al.
646 (2014). (a) FT–IR spectrum, (b) Raman spectroscopy spectrum, (c) plot of the G-band peak and its FWHM
647 (modified from Kitajima et al., 2015), (d) O-K-edge-XANES spectrum modified from fig. 3 of Uesugi et al.
648 (2014), and (e) N-K-edge-XANES spectrum of IOM01. (a), (b), and (e) are new data for IOM01, and (c) and
649 (d) are modified from previous studies. We added a plot for IOM01 in (c) and the plot shows similar values to
650 IOM from the Murchison CM2 meteorite. A peak at 532 eV in the O-XANES spectrum of IOM01 in (d)
651 corresponds to the carboxyl group (C=O). The absorption features at 537 and 541 eV can be assigned as oxygen
652 p–p hybridization with another nearby oxygen peak specific to edge-sharing oxygens. The N-XANES spectra
653 of IOM01 in (e) shows the peaks of $1s-\pi^*$ transition of imine (C=N) (398.9 eV), $1s-\pi^*$ transition of nitrogen
654 heterocycles (C–N=C) and/or nitrile (C $\equiv$ N) (399.9 eV), and $1s-\pi^*$ transition of amide (NHx(C=O)C) (401.8
655 eV).

656

657 Figure 22. Summaries of (a) C-, (b) N-, and (c) O-K-edge-XANES spectra of the category 3 particles, modified
658 from Yabuta et al. (2014) and this paper. The shapes of the spectra differ from each other, indicating that the
659 particles had different origins and/or evolutionary histories.

660

661 Figure 23. Summary of H and C isotope data obtained by NanoSIMS analysis including data from Ito et al.
662 (2014), modified from Sephton and Botta (2005). Data for all the particles plot within the terrestrial region.

663

664 Figure S1. (Upper) FT–IR spectrum (JASCO IRT-5000) of VECTRAN and (Lower) NMR spectra (proton
665 probe of 5 mm; 400 MHz, Bruker Biospin) of chemically released residue from VECTRAN. To determine the
666 potential organic artifacts by NMR analysis we soaked VECTRAN (0.18 g) in 2-propanol (10 mL) overnight

667 and then evaporated it with gentle N₂ flow. We then added 500 µL of CDCl₃ with an internal standard (0.05%
668 trimethylsilane; TMS) for the full-scan measurement by proton NMR.