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The universal sample holders of microanalytical instruments of FIB, TEM, NanoSIMS, and STXM-NEXAFS for the coordinated analysis of extraterrestrial materials

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Abstract

We developed universal sample holders [the Kochi grid, Kochi clamp, and Okazaki cell) and a transfer vessel (facility-to-facility transfer container (FFTC)] to analyze sensitive and fragile samples, such as extremely small extraterrestrial materials. The holders and container prevent degradation, contamination due to the terrestrial atmosphere (water vapor and oxygen gas) and small particles, as well as mechanical sample damage. The FFTC can isolate the samples from the effects of the atmosphere for more than a week. The Kochi grid and clamp were made for a coordinated micro/nano-analysis that utilizes a focused-ion beam apparatus, transmission electron microscope, and nanoscale secondary ion mass spectrometry. The Okazaki cell was developed as an additional attachment for a scanning transmission X-ray microscope that uses near-edge X-ray absorption fine structure (NEXAFS). These new apparatuses help to minimize possible alterations from the exposure of the samples to air. The coordinated analysis involving these holders was successfully carried out without any sample damage or loss, thereby enabling us to obtain sufficient analytical datasets of textures, crystallography, elemental/isotopic abundances, and molecular functional groups for µm-sized minerals and organics in both the Antarctic micrometeorite and a carbonaceous chondrite. We will apply the coordinated analysis to acquire the complex characteristics in samples obtained by the future spacecraft sample return mission.

Keywords: Universal sample holder, Coordinated analysis, Hayabusa2 returned sample, Asteroid ryugu

Introduction

Spacecraft sample return missions focus on collecting materials from extraterrestrial bodies, including planets, satellites, asteroids, and comets. Recently, cometary and asteroidal particles were obtained by the NASA Stardust mission (Brownlee et al. 2006) and the JAXA Hayabusa mission (Nakamura et al. 2011), respectively. The extraterrestrial materials obtained from the comet Wild2 by the Stardust mission, and from the asteroid Itokawa (S-type) by the Hayabusa mission, are very small (tens to hundreds of micrometers in size) and composed of complex mixtures of ultrafine minerals and/or organic components (Brownlee et al. 2006; Nakamura-Messenger et al. 2006; Yada et al. 2014). The JAXA Hayabusa2 and NASA OSIRIS-REx are both ongoing sample return

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missions from the primitive asteroids Ryugu (C-type) and Bennu (B-type), respectively (Tachibana et al. 2014; Lauretta et al. 2015). These missions have complementary scientific goals for understanding solar system evolution with regard to organics, water, and associated minerals.

Sample preparation, transfer between instruments, and transportation among institutes with minimal chemical reactions with the surrounding environment and/or terrestrial contaminants (e.g., water vapor, hydrocarbon, atmospheric gases, and small particles) is essential for the analysis of extraterrestrial samples directly collected from the airless planetary bodies, such as asteroids and comets (Yada et al. 2014; Okazaki et al. 2017). Okazaki et al. (2017) pointed out that the small amorphous silicates and ultrathin layered space-weathering rims found in the Itokawa asteroidal samples were decomposed as a result of interaction with atmospheric air during a 200-h analysis. Wirick et al. (2009) reported that the functional groups of carbon in the Stardust cometary samples changed over a time due to chemical reactions with atmospheric oxygen and H_2O based on scanning transmission X-ray microscopy near edge X-ray absorption of fine structure (STXM-NEXAFS) experiments. The Itokawa particles consist of only anhydrous minerals similar to those in ordinary chondrites (Nakamura et al. 2011), while the Ryugu samples (expected amount of returned sample: approximately 100 mg) are expected to be carbonaceous chondrite materials that contain organics and hydrous minerals (e.g., Tachibana et al. 2014). Considering the components of carbonaceous chondrites, the expected composition of the Ryugu sample contains 2–18 wt% extraterrestrial water and 500 µg/g organic matter (Okazaki et al. 2017 and reference therein). Therefore, concerning the in situ analysis of organics and volatiles and sample size, these samples require even more careful handling and proper analytical sequencing without terrestrial contamination and sample damage in texture, morphology, isotopic fractionation, major and trace element abundances (e.g., Ito et al. 2014; Uesugi et al. 2014a; Yabuta et al. 2014) than samples obtained by previous missions, especially the asteroid Itokawa samples by the Hayabusa mission.

Uesugi et al. (2014a) pointed out problems related to sample handling/preparation processes (lost and/or broken) and sample damage (crystal/molecule structural changes, disturbance of elements and isotopic fractionation) of the Itokawa carbonaceous particles (also known as Category 3 organic materials) in electron and ion beam analyses (i.e., TEM and SIMS). They proposed an optimized sample handling system that limited terrestrial contaminations during transportation between laboratory facilities and had the proper analytical sequence of examinations (Uesugi et al. 2014a, 2019). The drawbacks of their research, however, were that these systems were only suitable for µm-sized samples, and the original textures/structures of larger samples were readily lost when the sample was pressed onto an Au thin film (Uesugi et al. 2014a).

A coordinated analysis that utilized focused ion beam (FIB) sample preparation and subsequent STXM-NEXAFS, nanoscale secondary ion mass spectrometry (NanoSIMS), and transmission electron microscopy (TEM) analyses is essential for acquiring information regarding molecular and crystal structures, abundance of major/trace elements and isotopes, and petrographic textures in nanometer- to micrometer-scale samples. These techniques were applied to the carbonaceous materials provided by the Stardust cometary dust and Hayabusa sample return missions (Sandford et al. 2006; Matrajt et al. 2008; Ito et al. 2014; Uesugi et al. 2014a; Yabuta et al. 2014).

Previous research was mostly performed through acid extraction from a large amount (> several grams) of chondrite for the analysis of organic matter (e.g., Sephton and Botta 2005). Therefore, it is difficult to retrieve the original chemical and structural characteristics of the organic matters and its surrounding mineral phases. Since the mid-2000, there have been pioneering works on the in situ analysis of organics and their associated minerals using a coordinated microanalysis (e.g., Nakamura et al. 2005; Zega et al. 2006; Matrajt et al. 2008). More recently, Le Guillou et al. (2014) conducted in situ investigations of FIB sections from carbonaceous chondrites (Orgueil, Murchison, and Renazzo) utilizing STXM and TEM analyses on the FIB sections with known H isotopic distributions by NanoSIMS. Floss et al. (2014) reported on NanoSIMS and FIB-TEM analyses of individual organic matter, including nanoglobules and their associated minerals. Problems here are (1) being time consuming due to the site selected sample preparation by FIB, (2) technical difficulties including accidents, damages, and contamination, in sample mount, and (3) sample transfer between instruments. Therefore, the number of analysis utilizing coordinated analysis is limited due to the above problem. The analytical data set is not sufficient to make robust conclusions.

We need to solve two major problems when we perform a coordinated analysis of samples obtained by future missions. The first problem is in the handling procedure for small samples during preparations and a coordinated analysis. The second one is how we perform a coordinated analysis of small samples under a non-air exposing environment. For example, in previous studies, samples attached to a TEM grid were analyzed in an STXM-NEXAFS by fixing the grid to the sample holder using adhesive tape (e.g., Leontowich and Hitchcock 2012).

After the analysis, the grid was removed from the tape for subsequent TEM and/or NanoSIMS measurements. The commercial TEM grid was easily deformed during the removal process and was therefore difficult to set in the TEM and NanoSIMS sample holders, even under the atmosphere environment. For samples obtained by future missions, we should perform these procedures in a glove box, where there are severe electrostatic forces. However, these procedures could cause unexpected accidents, including damage and/or loss of he samples.

To overcome these problems, we are developing a coordinated analysis procedure that utilizes a series of microanalytical instruments, including FIB, TEM, NanoSIMS, and STXM-NEXAFS, to minimize and avoid terrestrial contamination, mechanical damage, and sample loss. A sample transport container and various universal sample holders were also developed for the coordinated analysis. Note that it is necessary for these devices to fulfill the following requirements: (1) provide secure and safe transportation of the sample, (2) adapt to different analytical instruments, including synchrotron-based analyses, (3) allow for easy handling under a non-air exposing sample system (i.e., in a glove box and sample in/out instrument under a vacuum or an inert gas), and (4) be easy to clean using ultrapure water or organic solvents (acetone or ethanol). The motivation for the development of these devices is to adequately complete the pertinent analyses of extraterrestrial materials obtained by sample return missions (i.e., the JAXA Hayabusa2 and the NASA OSIRIS-REx).

In this study, the performance of the analytical procedure and sample handling that utilized our developed devices was evaluated through coordinated analyses for a well-characterized Antarctic micrometeorite (AMM) and meteorite. We will report the evaluation of the atmospheric shielding performance in subsequent papers.

Developments

Facility to facility transfer container (FFTC)

We developed a sample transport vessel (FFTC) that keeps samples under low pressure or inert gas conditions to allow for secure transportation by avoiding terrestrial contaminations, chemical reactions, and/or other alterations, with minimum contact (Fig. 1). The FFTC is composed of materials permitted in the clean chambers of the Hayabusa2 returned samples at JAXA, such as

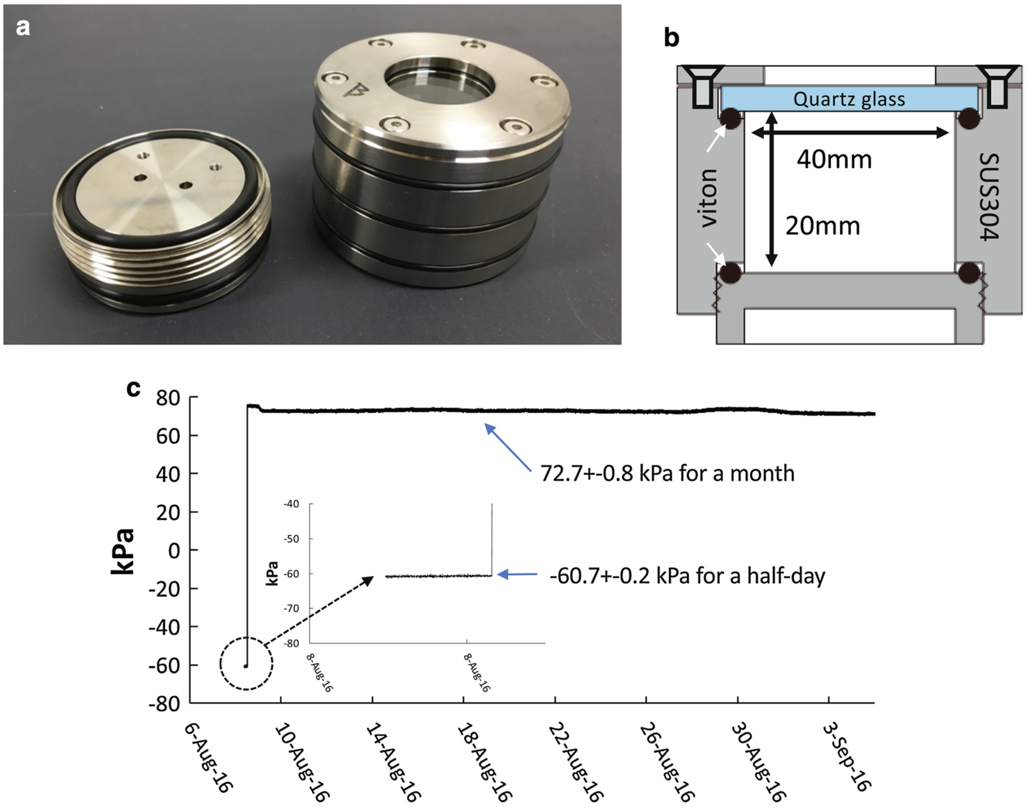


Fig. 1 **a** Picture of the facility-to-facility transfer container (FFTC), **b** schematic diagram of the FFTC and **c** result of the performance test of the FFTC under negative and positive pressures (approximately -61 kPa for a half-d and approximately 73 kPa for a month)

SUS304 and SUS316L stainless steel, and Viton rubber. A synthetic fused silica glass plate was used as the view port window. The FFTC is designed to be able to hold various kinds of sample holders, including universal sample holders (Sato Seiki Corp. 2019). It is 60 mm in height and 50 mm in diameter, while its interior is 20 mm in height and 40 mm in diameter (Fig. 1b). The seal performance of the FFTC under positive and negative pressures showed stable conditions (72.7 ± 0.8 kPa for a month and 60.7 ± 0.2 kPa for a half-day) as a result of an experiment performed from August 8 to September 4 in 2016 (Fig. 1c).

Kochi grid and clamp for FIB, TEM, and NanoSIMS measurements

Two types of universal sample holders, the Kochi grid and Kochi clamp (Fig. 2), were developed to reduce contamination during sample handling (attachments and removals) without adhesive tapes and materials when the samples are transferred among instruments (FIB, TEM, and NanoSIMS) and to improve the handling procedure in the glove box. The Kochi grid is a TEM grid that has handles on both sides, and the Kochi clamp is a holder for easy handling of the commercial TEM grid.

The Kochi grid is composed of copper metal and processed by the synchrotron-based LIGA (Lithographie, Galvanoformung, Abformung) system at the BL8S2 of Aichi Synchrotron Radiation Center (Aichi Science & Technology Foundation, Aichi, Japan). It is 6.57 mm wide, 1.0 mm (left height), 1.47 mm (right height), and 0.2 mm thick with three posts (0.1 mm in width, 0.2 mm in height, and 0.03 mm or 0.02 mm in thickness) and was shaped with left–right asymmetry (Fig. 2a). The posts are used for attaching ultrathin section samples that often have a slight roughness on their surface (Fig. 2b), which means the posts must be sharpened and flattened by an FIB treatment before the grid can be used for reliable fixation of the samples. Copper was selected as the grid material to avoid analytical artifacts in the spectra obtained by TEM equipped with an energy-dispersive X-ray spectrometer (EDS) for elemental analysis. The characteristic X-ray peaks of copper do not overlap with those of extraterrestrial samples. The asymmetric shape provides clearance for access of a micromanipulator to the post in FIB processing and is easy to handle in a glove box. A stainless steel Kochi clamp (12 mm in width, 4 mm in height, and 0.6 mm in thickness) was developed to hold a commercial TEM grid for STXM and NanoSIMS sample processing/analyses (Fig. 2c).

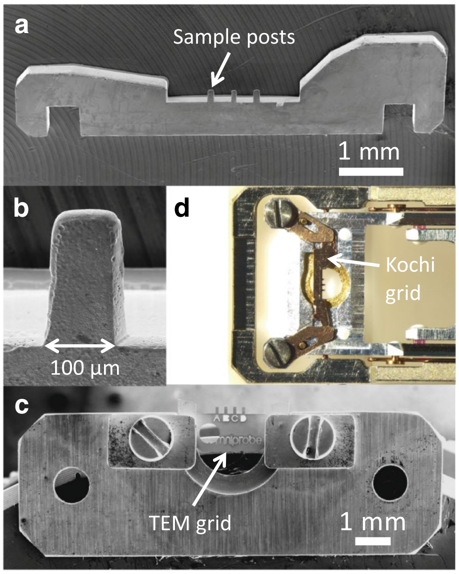


Fig. 2 Pictures of **a** the Kochi grid, **b** a sample post of the Kochi grid, **c** the Kochi grid in a JEOL-type transmission electron microscopy (TEM) sample holder, and **d** the Kochi clamp with a commercial TEM grid

The Kochi grid fits the sample holder for the TEM series manufactured by JEOL Ltd. (Fig. 2d). The Kochi clamp can be used for a commercial 3 mm-diameter TEM grid for TEM series manufactured by the FEI Thermo Fisher Scientific and Hitachi High-Tech Corp. The advantages of the Kochi clamp include its ability to be used repeatedly and its low cost compared to the Kochi grid, while its disadvantage is that the commercial TEM grid has to be removed from the clamp before TEM analysis (Fig. 2c).

For a NanoSIMS imaging analysis, we had to design an attachment that can fix both the grid and clamp onto a NanoSIMS subsample holder, specifically the Kochi subsample holder. The Kochi subsample holder is 12.8 mm in diameter and 4 mm in thickness and is made of stainless steel. The Kochi grid or clamp can be held in the central shallow hole (Fig. 3a, b). The CAMECA NanoSIMS commercial sample holder has six slots for the Kochi subsample holders (Fig. 3c). We used carbon nanotube tape

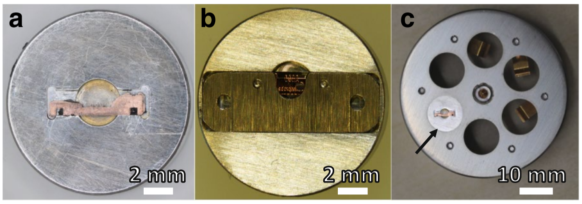


Fig. 3 Pictures of the Kochi subsample holder for the nanoscale secondary ion mass spectrometer (NanoSIMS): **a** a NanoSIMS subsample holder for the Kochi grid, **b** a NanoSIMS subsample holder for the Kochi clamp, and **c** a commercial NanoSIMS holder with a subsample holder for Kochi grid

(Gecko Tape provided by Nitto Denko Corp.) (Maeno and Nakayama 2008), carbon/copper adhesive tapes, or carbon plaster to ensure it held to avoid a sample shift during analysis.

We have designed a separable sample attachment (hereafter the Okazaki cell) for a STXM-NEXAFS measurement at the beamline BL4U of the UVSOR Synchrotron, Institute for Molecular Science, National Institutes of Natural Sciences (Okazaki, Japan) (Fig. 4a). The Okazaki cell is made of stainless steel (a body and a claw) and a phosphor bronze or stainless steel (as springs) and can hold two sets of Kochi grids or clamps without adhesive tapes. The cell is convertible with that of the advanced light source-based STXM systems (Berkeley, United States). The lower part of the Okazaki cell can be separated and placed into the FFTC (Fig. 4b).

Assessment of the in situ analytical sequence for organic matter

Previous research on organics in extraterrestrial materials reported that isotopic compositions, C K-edge spectra, elemental distributions, and textures were affected by extensive electron and ion beam irradiation (De Gregorio et al. 2010; Le Guillou et al. 2013; Ito et al. 2014; Uesugi et al. 2014a; Laurent et al. 2015). Therefore, the analytical sequence must be optimized by the measured target materials, especially organics, to avoid any artifacts on the measured data. De Gregorio et al. (2010) pointed out that extensive electron beam damage during the analysis introduces isotopic disturbances of the D/H ratio in organics. Similar research on hydrogen isotopic fractionation in organics was reported by Guillou et al. (2013) and Laurent et al. (2015). Therefore, the hydrogen isotopic measurement with NanoSIMS in organics should be conducted before the TEM analysis. To mitigate electrostatic charging by ion beam irradiation during NanoSIMS, we used a thin film layer (approximately 20 nm) of Au on the surface of the ultrathin section sample.

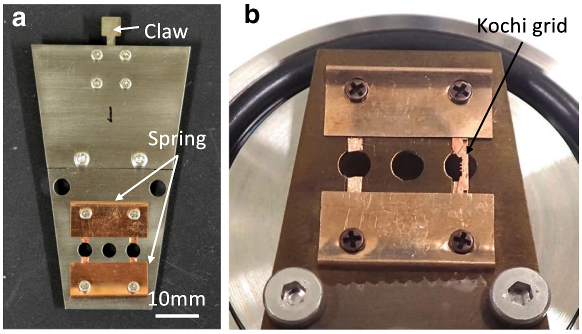


Fig. 4 Pictures of **a** the combined Okazaki cell, **b** the lower part of the Okazaki cell with the Kochi grid set inside an FFTC

Results and discussion

We evaluated the Kochi grid for FIB, TEM, and NanoSIMS, and the Okazaki cell for STXM-NEXAFS through the coordinated analysis of primitive extraterrestrial materials containing minerals and organics. The detailed discussions for minerals are located in "In-situ analysis of mineral phases" while organics are discussed in "In-situ analysis of organic matter".

In situ analysis of mineral phases

The AMM, TT006b101, has a spherical shape of approximately 200 μm in size (approximately 13 μg in weight) (Fig. 5a) and is pressed onto a Gecko tape. An ultrathin section of the sample ($10 \times 8 \times 0.1$ μm^3) was prepared and attached to the Kochi grid by FIB (SMI-4050, Hitachi High-Tech Corp., Minato-ku, Japan) at the Kochi Institute of Core Sample Research, JAMSTEC (Fig. 5b).

We examined the detailed major elemental abundances, mineralogy, and microstructure to gain insight into its petrogenesis by TEM (JEM-ARM200F equipped with EDS, JEOL Ltd., Tokyo) in an ultrathin section that was prepared by the FIB (SMI-4050). Based on the elemental and electron diffraction analyses of the individual grains, the AMM was confirmed to consist of olivine [$(Mg,Fe)_2SiO_4$], Mg,Al-bearing magnetite (Fe_3O_4), and interstitial Ca–Mg–Fe–Al-bearing amorphous silicate (Fig. 5c), where olivine and Mg,Al-bearing magnetite occur as euhedral to subhedral grains of several micrometers in size. Petrography suggests that the precursor material of the AMM was extensively heated to be completely melted and then partially crystallized by rapid cooling. When hydrated carbonaceous chondrites containing abundant phyllosilicates experienced extensive heating, a mineral assemblage of olivine, magnetite, and SiO_2-rich amorphous material was formed (Toppani et al. 2001). Note that the phyllosilicates in the precursor chondritic material would have also been affected by heating and dehydration processes during its atmospheric entry.

Next, we applied rastered ion imaging by the Japan Agency for Marine-Earth Science Technology (JAMSTEC) NanoSIMS 50L ion microprobe (Ametek CAMECA, Inc., Gennevilliers Cedex, France) to acquire an isotope map of oxygen ($^{18}O/^{16}O$ ratio) and elemental maps of Si and Mg as $^{24}Mg^{16}O$, Al as $^{27}Al^{16}O$, Ca as $^{40}Ca^{16}O$, and Fe as $^{56}Fe^{16}O$ for the sample (Fig. 5d). The detailed measured conditions and calculation of $\delta^{18}O_{SMOW}$ were published in a previous study (Ito and Messenger 2008). The elemental ratio maps (Fig. 5d) show the constituent mineralogical features of olivine,

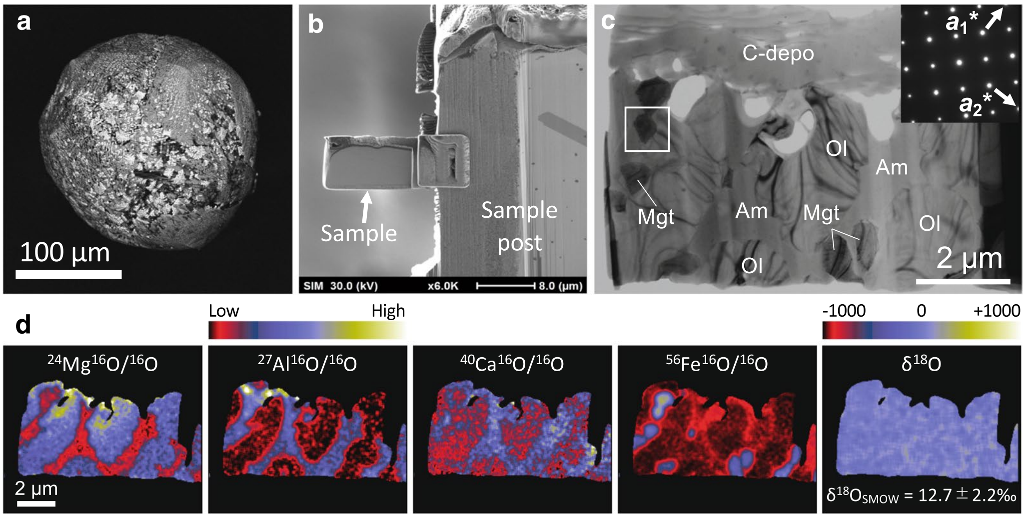


Fig. 5 A thin section of an Antarctic micrometeorite (AMM), **a** back-scattered electron image of the AMM, TT006b101, before focused-ion beam apparatus (FIB) processing, **b** the FIB-thin section attached to a post of the Kochi grid, **c** bright-field TEM image with a selected area electron diffraction pattern of Mg,Al-bearing magnetite as an inset, **d** NanoSIMS elemental ratio and O isotope maps

Mg,Al-bearing magnetite, and a Ca–Mg–Fe–Al-bearing amorphous silicate in the section analyzed by the TEM-EDS elemental and crystallographic analyses (Fig. 5c). The $\delta^{18}O_{SMOW}$ isotopic composition of the sample's mineral phases shows a homogeneous distribution of 12.7 ± 2.2 per mil (Fig. 5d). We did not find a clear difference in the $\delta^{18}O$ value of each phase within the analytical uncertainties. This $\delta^{18}O$ value is broadly consistent with previous O isotopic compositions for various AMMs, which suggests that heavy O isotopic enrichment was caused by atmospheric entry heating or thermal metamorphism in the parent body (Matrajt et al. 2006; Engrand and Dobrica 2012).

In situ analysis of organic matter

A systematic investigation of the carbonaceous grains in Yamato, (Y)-791198, which is an unheated CM2.4 chondrite (Nakamura 2005; Rubin et al. 2007), was carried out using FIB, STXM-NEXAFS, NanoSIMS, and TEM analyses. The universal sample holders of the Kochi grid for FIB, TEM, NanoSIMS, and the Okazaki cell for STXM-NEXAFS were used.

We prepared an ultrathin section (30 × 30 × 0.1 μm^3) of the Y-791198 matrix using the FIB at the Kochi Institute for Core Sample Research, JAMSTEC. The NEXAFS spectra of the C K-edge of the section and the nanometer-scale carbon distribution were measured by an STXM at the UVSOR BL4U (Fig. 6a, f). C and N as $^{12}C^{14}N$ elemental images of the same section were obtained by the JAMSTEC NanoSIMS (Fig. 6b, c) and the H, C, and N isotope maps [details of the analytical conditions are located in Ito et al. (2014)]. Subsequently, a TEM-EDS analysis was performed to obtain carbon X-ray maps and ultrahigh magnification images of each carbon-enriched region (Fig. 6d).

Four carbonaceous grains, G1–G4, were found in the ultrathin section by combining the STXM C K-edge spectral image (Fig. 6a) and NanoSIMS ^{12}C and $^{12}C^{14}N$ elemental images (Fig. 6b, c). The STXM C K-edge spectral image was generated by an accumulation of all the spectral peak intensities in each pixel after a baseline collection at 280 eV. The C-rich regions defined by the STXM C K-edge spectral image are broadly consistent with those of the NanoSIMS ^{12}C and $^{12}C^{14}N$ elemental images (Fig. 6a–c). Table 1 summarizes the results obtained by the TEM-EDS (size) and NanoSIMS (H, C, and N isotopic compositions) analyses.

Representative atomic number contrast images (high-angle annular dark field in scanning TEM mode (HAADF-STEM)) and carbon X-ray images of carbonaceous grains G1 and G3 are shown in Fig. 6d. The size of the grains ranged from 650 to 1000 nm in diameter (Table 1). The HAADF-STEM images in Fig. 6d are similar to the previously reported images of carbonaceous grains found in carbonaceous chondrites (e.g., Floss et al. 2014). However, these grains show different morphologies of nanoglobules (i.e., hollow shape) (e.g., Nakamura-Messenger et al. 2006; De Gregorio et al. 2013).

The STXM C K-edge spectra of G1 to G4 show peak intensities at 285 eV (aromatic or olefinic carbon), 286.5 eV (oxygen substituted double-bonded carbon, e.g., enolic carbon), 288.4 eV (carbonyl carbon in amide

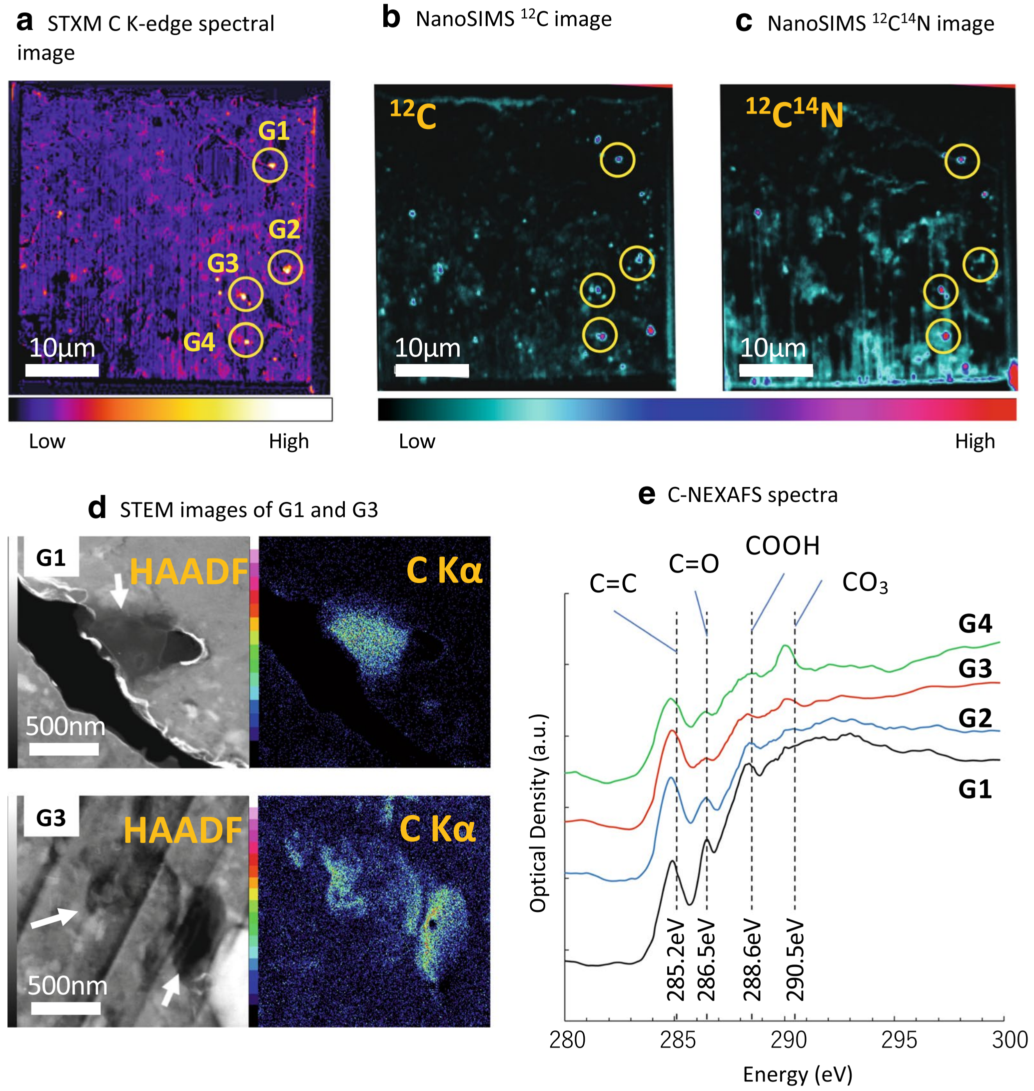


Fig. 6 Images of carbonaceous grains in the FIB section of Y-791198. **a** Scanning transmission X-ray microscopy (STXM) C K-edge spectral image, **b** NanoSIMS ^{12}C image, **c** NanoSIMS ^{12}C^{14}N image, **d** high-angle annular dark field (HAADF) and carbon Kα X-ray images of the G1 and G3 carbonaceous grains in **a** by scanning transmission electron microscopy (STEM-EDS). **e** C K-edge spectra of G1 to G4

Table 1 Summary of analyzed carbonaceous grains in Y-791198

Carbonaceous grain	TEM observation diameter (nm)	NanoSIMS analysis		
		δ13C (PDB) ‰	δ15N (Air) ‰	δ15D (SMOW) ‰
G1	650	289 ± 33	− 307 ± 30	1457 ± 187
G2	1000	− 117 ± 25	33 ± 55	2335 ± 154
G3	800	− 178 ± 27	302 ± 37	219 ± 112
G4	650	42 ± 21	348 ± 27	1128 ± 174

Errors are 1 sigma

PDB Pee Dee Belemnite, *SMOW* standard mean ocean water moieties), and 290.2 eV (carbonate CO_3) (Fig. 6e). These peaks exist at a slightly lower energy, approximately 0.3 eV, in comparison with the peaks found by Vinogradoff et al. (2018) due to the surrounding organics that have a wide variety of molecular configurations (e.g., De Gregorio et al. 2013).

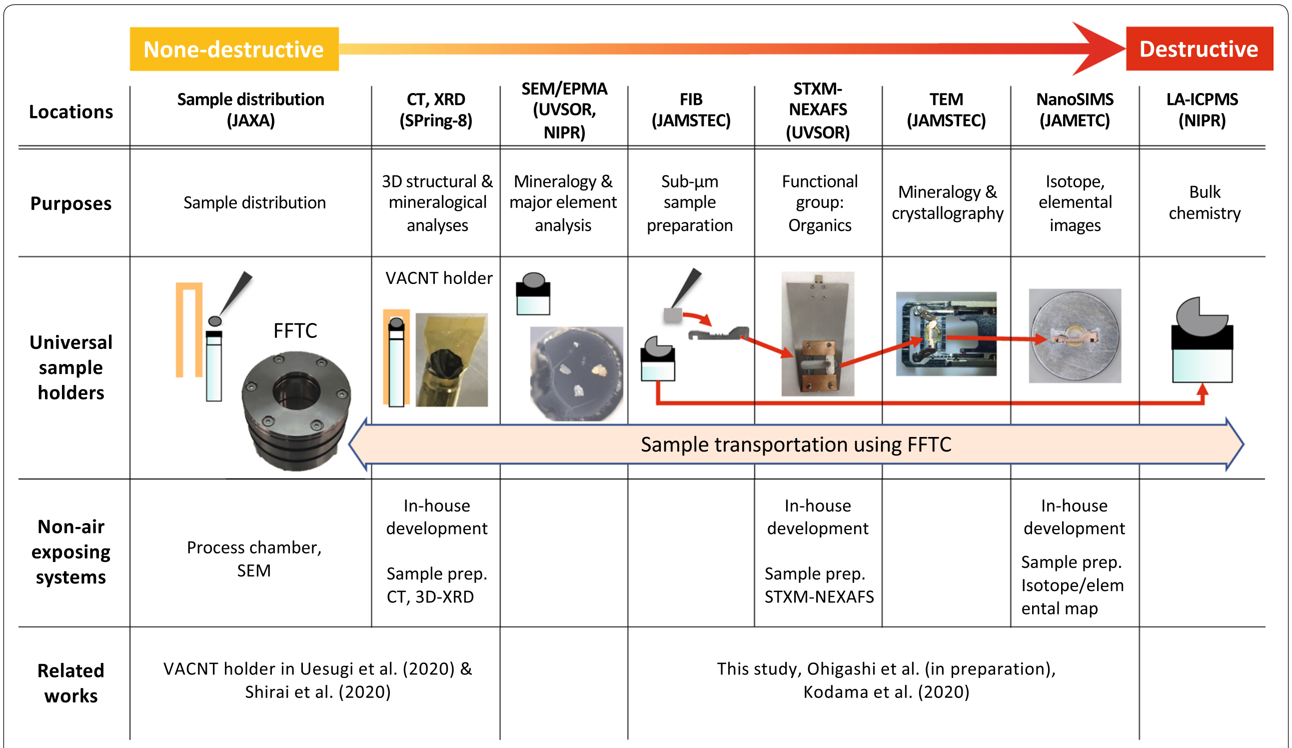
We found two types of carbonaceous grains as a result of the C K-edge spectra that suggest G1 is a ketone-rich, and G2 to G4 are aromatic carbonaceous grains even though they showed no clear size and morphology difference from each other. Aromatic and ketone-rich nanoglobules from IOM residue extracted through acid dissolution treatment were reported by De Gregorio et al. (2013). In situ STXM-NEXAFS analyses for multiple FIB sections in this study have shown aromatic and ketone-rich carbonaceous grains, and that it is not due to IOM chemical extraction (De Gregorio et al. (2013).

The C ($\delta^{13}C_{PDB}$) and N ($\delta^{15}N_{Air}$) isotopic compositions in the carbonaceous grains (G1 to G4) in Y-791198 showed a large variation (Table 1) that is consistent with nanoglobules in the Bells (CM2) and Murchison (CM2) chondrites (De Gregorio et al. 2013). No isotopic “hotspots” with highly enriched ^{15} N ($\delta^{15}N_{Air}$) were observed in the globules. G1 shows a negative $\delta^{15}N_{Air}$ of approximately − 300 per mil and low degree and negative $\delta^{15}N$ were observed in the organic matter of the QUE99117 (CR3) and MET 00,426 (CR3) chondrites (Floss et al. 2014). These N isotopic characteristics are expected to occur in ion–molecule reactions (Wirström et al. 2012). The H isotopic compositions of G1, G2, and G4 showed high D-enrichment, implying that they have interstellar origins, while G3 had only a moderate D-enrichment (δD_{SMOW} = approximately + 200 per mil). The H isotopic variation found in the carbonaceous grains was not caused by analytical artifacts, as we carefully chose an analytical sequence (NanoSIMS isotope map followed by TEM observation) to avoid H isotopic fractionation by electron beam irradiation.

We confirmed that the developed coordinated analytical system of TEM, NanoSIMS, and STXM-NEXAFS provided the same quality analytical dataset as that of previous works by each instrument.

Coordinated analysis of the Ryugu asteroidal sample

As shown in Fig. 7, we established a coordinated analytical sequence for the future analysis of the Ryugu asteroidal samples from nondestructive analyses at synchrotron radiation facilities, such as 3D-CT (computed tomography), XRD (X-ray diffraction), and STXM-NEXAFS, and for destructive analyses, such as TEM, SIMS, and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). This coordinated sequence has the



Locations	Sample distribution (JAXA)	CT, XRD (SPring-8)	SEM/EPMA (UVSOR, NIPR)	FIB (JAMSTEC)	STXM-NEXAFS (UVSOR)	TEM (JAMSTEC)	NanoSIMS (JAMETC)	LA-ICPMS (NIPR)
Purposes	Sample distribution	3D structural & mineralogical analyses	Mineralogy & major element analysis	Sub-µm sample preparation	Functional group: Organics	Mineralogy & crystallography	Isotope, elemental images	Bulk chemistry
Universal sample holders	FFTC	VACNT holder						
Non-air exposing systems	Process chamber, SEM	In-house development Sample prep. CT, 3D-XRD			In-house development Sample prep. STXM-NEXAFS		In-house development Sample prep. Isotope/elemental map	
Related works	VACNT holder in Uesugi et al. (2020) & Shirai et al. (2020)			This study, Ohigashi et al. (in preparation), Kodama et al. (2020)				

Fig. 7 Coordinated analysis of the Ryugu samples

potential to obtain the complex characteristics inside a sample. Regions of interest (ROIs) inside the sample can be found through synchrotron-based 3D-CT and XRD analyses. Prior to conducting a series of microanalyses, we used an FIB to extract the ROIs based on a 3D characterization of the sample (Uesugi et al. 2014b).

The coordinate analysis proposed in this study has been further developed by related studies (Kodama et al. 2020; Shirai et al. 2020; Uesugi et al. 2020). Kodama et al. (2020) described the development of a surface treatment technique using FIB to obtain high-quality electron back-scattered diffraction (EBSD) patterns from minerals in AMMs. Uesugi et al. (2020) developed a vertically aligned carbon nanotube (VACNT) holder for synchrotron-based CT and XRD analyses. Shirai et al. (2020) stated that the elemental abundances of VACNT, polyimide film, and synthetic quartz glass will be used for the analysis of the Ryugu samples to evaluate possible contaminations during the sample handling process. They concluded that these materials showed low levels of contaminants and are therefore adequate for use as sample holders for the Ryugu samples.

An in-house non-air exposing sample loading system that utilized the Okazaki cell for sample transfer between an STXM and a glove box under N_2 or Ar conditions was used for analyzing anaerobic materials at the UVSOR BL4U. A non-air exposing system that includes a glove box is also available for synchrotron-based CT and XRD at SPring-8 (Fig. 8). Note that an *in-house* non-air exposing sample holder for NanoSIMS is currently under development and will be ready for the analysis of the Hayabusa2 returned samples. Commercial non-air exposing sample holder systems are available for TEM and FIB. We have not yet installed these systems, though they will be installed before the analysis. We plan to use the developed holders (the Kochi grid and clamp), FFTC, Okazaki cell, and coordinate analysis under non-air exposing systems between laboratory facilities for extraterrestrial samples (i.e., the asteroid Ryugu) (Fig. 8). These developments of devices and containers under non-air exposure systems will be a potential standard for analyzing extraterrestrial materials obtained by future sample return missions.

Summary

The FFTC was made for the secure transportation of samples avoiding terrestrial contaminations under low-pressure or inert gas (e.g., N_2 or Ar). We developed universal sample holders (the Kochi grid by the LIGA process and the Kochi clamp) for FIB sample preparation and TEM analysis. For the NanoSIMS and STXM-NEXAFS analyses, we made additional attachments, including the Kochi subsample holder for NanoSIMS and the Okazaki cell for STXM, to hold the Kochi grid and the Kochi clamp.

We confirmed that the coordinated analytical system with the Kochi grid and the Okazaki cell was successful in acquiring chemical characteristics (light element isotopes, crystal structures, and molecular functional groups) in AMM samples and carbonaceous chondrite

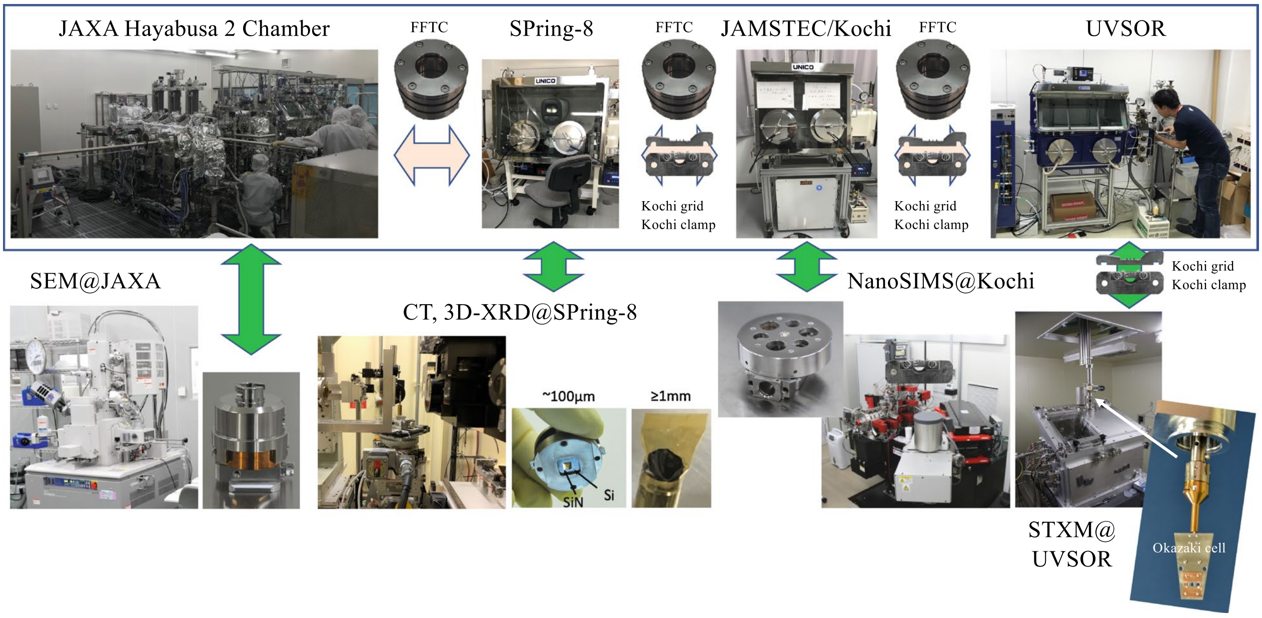


Fig. 8 Research platforms with non-air exposing systems for extraterrestrial materials

at the sub-micrometer scale. The acquired data from the coordinated analysis for both minerals and organics were consistent with previous studies for each instrument. Note that the Kochi grid and Okazaki cell improved the handling procedures of sample transfer between instruments, glove boxes, and the FFTC. Our devices (the Kochi grid/clamp and the Okazaki cell) and the use of the air-free transfer container make the whole coordinated analysis more reliable and minimize possible alteration from terrestrial air exposure of the samples obtained by Hayabusa2 and future sample return missions.

Abbreviations

AMM: Antarctic micrometeorite; CT: computed tomography; EDS: energy-dispersive X-ray spectrometer; FIB: focused-ion beam apparatus; FFTC: facility-to-facility transfer container; HAADF-STEM: high-angle annular dark field in scanning TEM mode; IOM: insoluble organic matter; LA-ICP MS: laser ablation inductively coupled plasma mass spectrometry; LIGA: lithographie, galvanoformung, and abformung; NanoSIMS: nanoscale secondary ion mass spectrometry; PDB: Pee dee Belemnite; ROIs: regions of interest; SMOW: standard mean ocean water; STXM-NEXAFS: scanning transmission X-ray microscope using near-edge X-ray absorption fine structure; TEM: transmission electron microscopy; VACNT: vertically aligned CNTs; XRD: X-ray diffraction.

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Authors' contributions

MI and NT contributed equally to the complete design of the technical developments of this research. MI conducted the NanoSIMS data analyses, image data reduction, interpretation, and preparation of the manuscript. NT performed the TEM analyses, image data reduction, interpretation, and preparation of the manuscript. KU and MU designed the FFTC and its performance test, helped with interpretation, and prepared the manuscript. YK contributed sample preparations by FIB. IS and IO established the LIGA process for preparing the Kochi grid. MU, TO, and HY performed the STXM-NEXAFS experiments at the BL4U, UVSOR synchrotron. AY, NI, NS, YK, TY, and MA participated in the design of the research and interpretation. All authors read and approved the final manuscript.

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Availability of data and materials

The Kochi grid, Kochi clamp, and Okazaki cell can be distributed for scientific purposes upon request through the JAXA curation or authors. The FFTC is available for purchase from the Sato Seki Corporation (Sato Seki Corp. 2019).

Competing interests

The authors declare that they have no competing interests.

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