Hayabusa2 returned samples: A unique and pristine record of outer Solar System materials from asteroid Ryugu

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Abstract

C-type asteroids likely formed in the outer Solar System and were then scattered inwards during giant planet migration (Walsh et al., 2011). They may have transported volatiles to the inner Solar System and created the conditions suitable for life on Earth (Alexander, 2017). Carbonaceous chondrites are fragments from C-type asteroids and provide evidence that these generally organic-rich (Garvie and Buseck, 2007) bodies experienced extensive aqueous alteration early in Solar System history (Alexander et al., 2014). On 6th December 2020, ~5.4g of material was delivered to Earth from the C-type asteroid 162173 Ryugu by the Hayabusa2 spacecraft (Yada et al., 2021). Here we present the results of an integrated bulk and micro-analytical study of Ryugu particles, which provides a unique insight into the interrelationship between aliphatic-rich organics and surrounding hydrous minerals at a sub-micrometer scale. This dataset has clear implications for better understanding the origin and early evolution of Solar System organic matter and demonstrates that Ryugu particles are among the most uncontaminated extraterrestrial materials so far studied.

Full Text

Between June 2018 and November 2019, the Japan Aerospace Exploration Agency (JAXA) Hayabusa2 spacecraft undertook extensive remote sensing investigations of asteroid Ryugu. Data from the Near-IR Spectrometer (NIRS3) onboard Hayabusa2 indicated that Ryugu might be composed of material “similar to thermally and/or shock-metamorphosed carbonaceous chondrite meteorites”⁶; the closest match being the CY (Yamato-type) chondrites⁹. The low albedo of Ryugu can be explained by the presence of abundant carbon-rich components, in combination with grains size, porosity and space-weathering effects⁷. The Hayabusa2 spacecraft conducted two touchdowns and sample collections at Ryugu. One on 21st of February obtained surface material that was stored in Chamber A of the return capsule and a second, on 11th of July of 2019, collected material close to an artificial crater formed by a small carry-on impactor. These samples were stored in Chamber C. Initial, non-destructive characterization of the particles in a dedicated, contamination-free and pure nitrogen-filled chamber at the JAXA curation facility revealed that Ryugu particles were “most similar to CI (Ivuna-type) chondrites”⁵ and displayed “a variety of alteration levels”⁸. The seemingly contradictory classifications of Ryugu, as similar to either CY or CI chondrites, can only be resolved by a detailed isotopic, elemental and mineralogical characterization of Ryugu particles. The results presented here provide a firm basis for deciding between these two preliminary interpretations of asteroid Ryugu’s bulk composition.

Eight Ryugu particles (~60 mg in total), four from Chamber A and four from Chamber C, were allocated to the Phase2 curation Kochi team. The principal goals of the research were to elucidate the nature, origin and evolutionary history of asteroid Ryugu, and to document the similarities and differences to other known extraterrestrial samples, such as chondritic meteorites, interplanetary dust particles (IDPs) and returned cometary samples collected by the NASA Stardust mission.

Detailed mineralogical analysis of five Ryugu particles (A0029, A0037, C0009, C0014 and C0068), shows that they consist principally of fine- and coarse-grained phyllosilicates (~64–88 vol%, Figs. 1A,B and S1, Table S1). Anhydrous silicates (olivines, pyroxenes) that could be derived from chondrules and refractory inclusions are rare in the Ryugu particles examined in this study. Such anhydrous silicates have only been positively identified in particle C0009. Coarse-grained phyllosilicates (up to several tens μm in size) with feathery textures are embedded in the fine-grained phyllosilicate-rich matrix. The phyllosilicate grains are a serpentine-saponite intergrowth (Fig. 1C). A (Si+Al)–Mg–Fe plot further shows that bulk phyllosilicate matrices have intermediate compositions between serpentine and saponite (Figs. 2A,B). Carbonate minerals (~2–21 vol%), sulfide minerals (~2.4–5.6 vol%), and magnetite (~3.6–6.8 vol%) occur in the phyllosilicate matrix. Carbonates, as fragments in the matrix (< several hundred μm), are mainly dolomites, with minor Ca-carbonate and breunnerite. Magnetites occur as isolated grains, framboids, plaquettes or spherical aggregates. Sulfides are mostly pyrrhotite showing irregular, hexagonal prism/plate or lath morphologies. Abundant submicron-sized pentlandites occur in the matrix or in association with pyrrhotite. Carbon-rich phases (<several to 10 μm in size) occur ubiquitously in the phyllosilicate-rich matrix. Other accessory minerals are summarized in Extended Data Table 1. Mineral inventories identified by X-ray diffraction patterns of a mixture of A0029 and A0037, and C0087 are in good agreement with those identified in CIs (Orgueil meteorite), but completely different from the CY and CM (Mighei-type) chondrites (Extended Data Fig. 1 and Fig. S2). The bulk elemental abundances of Ryugu particles (A0098, C0068) are also consistent with those of CI chondrites⁹ (Extended Data Fig. 2 and Table S1). In contrast, CM chondrites are characterized by a depletion in moderate- to highly-volatile elements, particularly Mn and Zn, and higher abundances of refractory elements¹⁰. Some elements show highly variable concentrations, which may be a reflection of inherent sample heterogeneity due to the small size of the individual particles and consequential sampling biases. All petrological, mineralogical, and elemental characteristics indicate that the Ryugu particles are very similar to CI chondrites^{11,12,13}. The remarkable exception is the absence of ferrihydrite and sulfate in the Ryugu particles, which indicates that these minerals in CI chondrites formed due to terrestrial weathering¹⁴.

The bulk oxygen isotopic composition of Ryugu particles A0098,2 and C0068,2 and a weighted average for the Hayabusa2 Chamber C particles (n=6) are shown in relation to Orgueil, Y-82162 (CY), CM, C2-ungrouped meteorites^{15,16} in Figs. 2C,D. As is clear from this diagram the average composition of Chamber C particles plots close to that of Orgueil, but away from that of Y-82162 (Table S2). Compared to the average Chamber C point, individual analyses for A0098,2 and C0068,2 have a lighter isotopic composition, which most likely reflects isotopic heterogeneity at the sampling scale involved. Both A0098,2 and C0068,2 were comparatively small particles. Compared to Orgueil, the $\Delta^{17}\text{O}$ compositions of the individual Ryugu particles and the weighted Chamber C average analysis are somewhat higher, but there is overlap at the 2SD (standard deviation) level. In contrast, there is no overlap between the $\Delta^{17}\text{O}$ value of Y-82162 and the Ryugu particles. These results further validate the potential link between Hayabusa2 samples and CI chondrites, while appearing to exclude the possibility of a connection with the CYs. The systematically higher $\Delta^{17}\text{O}$ values of the Ryugu particles compared to Orgueil most likely reflects terrestrial contamination since the meteorites fall in 1864. Weathering in the terrestrial

environment^{11,14} would necessarily result in the incorporation of atmospheric oxygen and so pull the bulk analysis closer to the terrestrial fractionation line (TFL). This conclusion is in keeping with the mineralogical evidence discussed above that Ryugu particles do not contain ferrihydrite or sulfate, whereas Orgueil does.

Using coordinated microanalysis techniques (Fig. S3), we studied the spatial distribution of organic carbon throughout the entire surface area of the C0068-25 focused ion beam (FIB) section (Fig. 3A). Carbon-NEXAFS (near-edge X-ray absorption fine structure) spectra in the C0068-25 section show a variety of functional groups; aromatic or C=C (285.2 eV), C=O (286.5 eV), aliphatic (287.5 eV), and C(=O)O (288.8 eV), without 1s-r* exciton at 291.7 eV of graphene structures (Fig. 3B), implying low degrees of thermal alteration. The aliphatic peak (287.5 eV) of the organics in the C0068-25 is distinct from the previously studied insoluble organic matter (IOM) of carbonaceous chondrites¹⁷ and shows more similarities to IDPs¹⁸ and cometary particles obtained by the Stardust mission¹⁹. The aliphatic-rich organics areas are present locally within coarse-grained phyllosilicates, as well as areas with a poorly aromatic (or C=C) carbon structure (Figs. 3C,D). In contrast, A0002-23 and A0037-22, -23 sections display a lower abundance of aliphatic carbon-rich areas. The bulk mineralogy of these particles shows carbonate-rich lithologies similar to Cls²⁰, indicative of more extensive parent body aqueous alteration (Extended Data Table 1). Oxidizing conditions would promote higher concentrations of carbonyl and carboxylic functional groups in the organic matter association with carbonates⁴. The sub-micrometer-scale distribution of organics with an aliphatic carbon structure may vary significantly depending on the distribution of coarse-grained phyllosilicates. A hint of aliphatic bearing organics in association with phyllosilicate-OH has been reported in the Tagish Lake meteorite²¹. The coordinated microanalysis data suggest that aliphatic-rich organics may be widely distributed in C-type asteroids and exist in close association with phyllosilicates. This inference is consistent with the previous report of aliphatic/aromatic CH in the Ryugu particles demonstrated by the MicrOmega, a hyperspectral microscope operating in the near-infrared range⁸.

A kinetic study of organic matter degradation in the Murchison meteorite²² may provide an important insight into the heterogeneous distribution of organics seen in the Ryugu particles. This study suggests that aliphatic CH bonds decrease with burial depth (maximum temperature of ~30°C) on the parent body. If the parent body did not reach 30°C, then the initial distribution of aliphatic carbon-rich organics in phyllosilicates could be preserved. However, aqueous alteration on the parent body might complicate this scenario because carbonate-rich A0037 does not show any aliphatic carbon-rich regions associated with phyllosilicates. The 30°C temperature is broadly consistent with approximately 25°C value estimated from a comparison between chemical compositions of Fe-sulfides and phase equilibria in the Fe-Ni-S system²³.

A large nanoglobule was found in the C0068-25 section (n.g-1, Figs. 3A,B,C,E) showing highly aromatic (or C=C), moderately aliphatic, and weakly C(=O)O and C=O spectra. The aliphatic carbon feature does not match that of the bulk IOM and associated organic nanoglobules in chondritic meteorites (Fig.

3B)^{4,24}. Raman and infrared spectroscopies of nanoglobules in Tagish Lake show that they are composed of aliphatic and oxidized organic matter, and disordered polycyclic aromatic organic matter, as well more complex organic structures^{3,25}. The aliphatic carbon feature indicated by the nanoglobule “n.g-1” may be an analytical artifact due to the surrounding matrix containing aliphatic-rich organics. An important and as yet unresolved question is whether the unique nature of the aliphatic carbon-rich organics associated with coarse-grained phyllosilicates observed in this study is a feature found only in the Ryugu asteroid.

Nano-scale secondary ion mass spectrometry (NanoSIMS) ion images (Fig. 3F) of the C0068-25 section display relatively homogeneous variation in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, with the exception of a presolar graphite grain (P.G-1 in Fig. 3F- $\delta^{13}\text{C}$ image) with extreme ^{13}C enrichment (Table S3). It is noteworthy that δD (841‰) and $\delta^{15}\text{N}$ (169‰) values of aliphatic-rich organics associated with coarse-grained phyllosilicates are slightly higher than the average for the entire C regions ($\delta\text{D}=528\text{‰}$, $\delta^{15}\text{N}=67\text{‰}$) in C0068-25 (Table S3). This observation indicates that aliphatic-rich organics in coarse-grained phyllosilicates could be more primitive than the surrounding organics because of isotopic exchange with surrounding water in the parent body²⁶. Aliphatic-rich organics might have formed from precursor molecules either in the protoplanetary disc or interstellar medium prior to Solar System formation via Fischer-Tropsch synthesis²⁶, and were then slightly modified during aqueous alteration in the Ryugu (grand)parent body. Aliphatic-rich organics may have maintained their original isotopic ratios due to their association with coarse-grained phyllosilicates. However, the exact nature of the isotopically heavy carrier is still uncertain due to the close proximity of the various components. It could be either the aliphatic-rich organics or the surrounding coarse-grained phyllosilicates.

The hydrogen and nitrogen stable isotopic compositions of solar system objects demonstrate the existence of distinct cosmochemical reservoirs that were likely inherited from the solar nebula. These reservoirs correspond to the Sun, the inner Solar System, and the outer Solar System^{2,27}. One possibility is that they were generated during the formation and subsequent migration of the giant planets, as envisaged in the Grand Tack hypothesis¹. The potential role of giant planet migration within the early Solar System can be examined by determining whether asteroid Ryugu originated from outer Solar System materials, or whether it shares similarities with primitive meteorites and planets from the inner Solar System.

A bulk δD and $\delta^{15}\text{N}$ plot of the A0002, A0037 and C0068 sections obtained by NanoSIMS is shown in Fig. 4 (Table S3) in comparison with other Solar System objects^{2,28,29}. The Ryugu sections show no obvious correlation between $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ (Table S3). Variations of bulk δD and $\delta^{15}\text{N}$ in the A0002, A0037 and C0068 sections are compatible with those seen in CR, C2-ung, IDPs and Wild2 cometary samples, but are higher than CMs and CIs (Fig. 4). The lower δD values for CIs compared to Ryugu particles may reflect the influence of terrestrial contaminations in the former³⁰. The bulk δD and $\delta^{15}\text{N}$ of the Ryugu sections tend to be lighter than the average values of Jupiter family and Oort cloud comets (Fig. 4), but with some exceptions due to aqueous alteration. Although the causes of the hydrogen and nitrogen isotopic

heterogeneities observed in the Ryugu particles are not yet fully understood, due in part to the limited numbers of analyses so far available, the results from these isotopic systems still raise the possibility that Ryugu contains a significant portion of outer Solar System materials and shows some similarities to comets.

The delivery of volatiles (i.e., organics and water) to the Earth is still a subject of significant debate². The aliphatic carbon-rich organics associated with coarse-grained phyllosilicates in Ryugu particles identified in this study likely represent one important source of volatiles. Organics incorporated into coarse-grained phyllosilicates seem to be more protected from degradation^{21,31} and breakdown³² than those in fine-grained matrix during intensive heating events, such as meteoroid impacts on asteroid surfaces and terrestrial atmospheric entry. Because of the heavier hydrogen isotopic composition of the particles, they are unlikely to be the only source of volatiles to the early Earth. They may have been mixed with components having lighter hydrogen isotopic compositions, as recently proposed by the hypothesis of “solar-wind-derived water in silicates”³³.

In this study we clearly demonstrate that (1): CI meteorites, despite their geochemical importance as proxies of the bulk Solar System composition^{9,13}, are biased and terrestrially-contaminated samples, and (2) we provide the first direct evidence of an interaction between aliphatic-rich organics and adjacent hydrous minerals. The findings of this study clearly demonstrate the importance of direct sampling of primitive asteroids and the need to transport returned samples in totally inert and sterile conditions. The evidence presented here shows that Ryugu particles are undoubtedly the most uncontaminated Solar System materials available for laboratory study and ongoing investigations of these precious samples will certainly expand our understanding of the early Solar System processes.

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Methods

Abbreviations

EDS: energy dispersive X-ray spectroscopy

EPMA: electron probe micro analysis

FFTC: facility-to-facility transfer container

FIB: focused ion beam processing

INAA: instrumental neutron activation analysis

NanoSIMS: nano-scale secondary ion mass spectrometry

SEM: scanning electron microscopy

SR-XCT: synchrotron radiation-based computed tomography

SR-XRD-CT: synchrotron radiation-based X-ray diffractometry - computed tomography analysis

STXM-NEXAFS: scanning transmission X-ray microscope - near-edge X-ray absorption fine structure

TEM: transmission electron microscopy

XRD: X-ray diffraction

Designs of analysis for Ryugu particles

To obtain acquire complex micro-texture and chemical characteristics of the sample in sub-micrometer scale, we conducted coordinated micro analysis utilizing an SR-XCT & XRD – FIB-XCT & XRD – FIB – STXM-NEXAFS – NanoSIMS – TEM analysis without degradation, contamination due to the terrestrial atmosphere and small particles, or mechanical sample damage. In parallel, we carried out systematic bulk analysis with SEM-EDS, EPMA, XRD, INAA, and a laser fluorination oxygen isotope facility. The analytical procedure is shown in Fig. S3, and each analysis was described in the following sections.

Sample transportation and handling processes

The Ryugu asteroid particles were recovered from the Hayabusa2 reentry capsule and transported to the JAXA Curation Facility at Sagami-hara Japan without terrestrial atmospheric contamination (Yada *et al.*, 2021). After initial and non-destructive characterizations at the JAXA Curation Facility, an airtight sample transport vessel (FFTC) and a sample capsule pack (made of sapphire glass and stainless steel with 10 mm ϕ or 15 mm ϕ depending on sample size) were used to avoid chemical reactions with the surrounding environment and/or terrestrial contaminants (e.g., water vapor, hydrocarbon, atmospheric gases, and small particles) and cross-contamination between samples during sample preparation and transportation among institutes and universities (Ito *et al.*, 2020). To avoid degradation and contamination due to interaction with the terrestrial atmosphere (water vapor and oxygen gas), all the sample preparations including chipping by a tantalum chisel, cutting by a counter balanced diamond wire saw (Meiwa Fosis Corp. DWS 3400), and epoxy mount preparation) were conducted in a glove box in an atmosphere of pure, dry N₂ (Dew point: -80 to -60°C, O₂ ~50 to 100 ppm). All items used here were cleaned by a combination of an ultra-pure water and ethanol under ultrasonication with different frequencies.

We studied meteorite collections (Orgueil, Yamato (Y)-791198, Y-82162, and Y 980115) of Antarctic meteorite center at the NIPR in this study.

For a transfer between instruments of SR-XCT, NanoSIMS, STXM-NEXAFS, and TEM, we used the universal holders for ultrathin film samples that described in previous studies (Ito *et al.*, 2020; Uesugi *et*

al., 2020; Shirai *et al.*, 2020).

A synchrotron radiation-based computed tomography analysis

SR-CT analyses for Ryugu samples were performed with integrated computed tomography (CT) system at BL20XU/Spring-8. The integrated CT system consists of different measurement modes: wide-field and low-resolution (WL) mode to capture the entire structure of the sample, narrow-field and high-resolution (NH) mode for precise measurement of the region of interest, and X-ray diffraction (XRD) mode to acquire the diffraction pattern of bulk volume of the sample and perform XRD-CT to perform 2D mineral phase mapping of a horizontal plane in the sample. The X-ray detector for the WL mode (BM AA40P; Hamamatsu Photonics) is equipped with a complementary metal oxide semiconductor (CMOS) camera, which has 4608×4608 pixels (C14120-20P; Hamamatsu Photonics), a scintillator consisting of a 10- μm -thick Lutetium Aluminum Garnet ($\text{Lu}_3\text{Al}_5\text{O}_{12}$: Ce) foil, and relay lenses. The pixel size of the WL mode is approximately 0.848 μm . Thus, the field-of-view (FOV) of the WL mode is ~ 6 mm. The X-ray detector for the NH mode (BM AA50; Hamamatsu Photonics) is equipped with a scintillator consisting of Gadolinium Aluminum Gallium Garnet ($\text{Gd}_3\text{Al}_2\text{Ga}_3\text{O}_{12}$) that is 200 μm thick, the CMOS camera which has 2048×2048 pixels (C11440-22CU; Hamamatsu Photonics), and a 20x lens. The pixel size of the NH mode is ~ 0.25 μm and the FOV is ~ 0.5 mm. The detector for XRD mode (BM AA60; Hamamatsu Photonics) is equipped with a scintillator consisting of a P43 ($\text{Gd}_2\text{O}_2\text{S}$: Tb) powder screen that was 50 μm thick, the CMOS camera which has 2304×2304 pixels (C15440-20UP; Hamamatsu Photonics), and relay lenses. Pixel size of the detector is 19.05 μm and the FOV was 39 mm^2 . In order to increase the FOV, we applied the offset CT procedure in the WL mode. Transmitted light image for CT reconstruction was composed by combining images of 180 to 360 degrees which horizontally reflected around the rotation axis, with the images from 0 to 180 degrees.

For the XRD mode, an X-ray beam was focused by a Fresnel Zone Plate. The detector for the XRD mode was placed 110 mm behind the sample, with a 3 mm beam stop just in front of the detector. Diffraction images from $2\theta = 1.43^\circ$ to 18.00° were obtained by the detector. Samples were vertically translated with a certain interval, and a half-rotated for each vertical scan step. Diffraction of mineral grains in a horizontal plane can be obtained if the mineral grains meet the Bragg condition in the half rotation. Diffraction images were then integrated into one image for each vertical scan step (Uesugi *et al.*, 2020). The SR-XRD-CT procedure is almost the same as for SR-XRD, except for the direction of scanning. The sample was scanned horizontally with half rotating of the sample. The SR-XRD-CT image was reconstructed using peak intensity of minerals as pixel value. Typically, samples were scanned with 500 to 1,000 steps for a horizontal scan.

The X-ray energy was fixed to 30 keV for all experiments because it is the lower limit for X-ray penetration of meteorites that are ~ 6 mm in diameter (Uesugi *et al.*, 2010; Uesugi *et al.*, 2013). The number of images acquired for all CT measurements during the half rotation was 1800 (3600 for offset CT

procedure), and the exposure time for an image was 100 ms for the WL mode, 300 ms for the NH mode, 500 ms for XRD, and 50 ms for XRD-CT. The typical scanning time for one sample in WL mode was ~10 min, in NH mode was ~15 min, ~ 3 hours for XRD, and 8 hours for SR-XRD-CT.

CT images were reconstructed by convolution-backprojection (CBP) method and normalized for 0 to 80 cm⁻¹ of linear attenuation coefficient. Slice software was applied for the analysis of 3D data, and muXRD software was used for the analysis of XRD data.

Optical, SEM–EDS and EPMA analyses

The epoxy mount Ryugu particles (A0029, A0037, C0009, C0014, and C0068) were polished on a surface in a stepwise manner down to the level of a 0.5 µm diamond lapping film (3M company) under dry condition avoiding elution of any materials from a surface during polishing. A polished surface of each sample was examined first by an optical microscope, and then by a JEOL JSM-7100F scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS) (AZtec energy) to obtain an overview of the mineralogy and textures of the samples by high-resolution imaging and qualitative chemical mapping at NIPR. Major and minor elemental abundance analysis of each sample were conducted with an electron probe microanalyzer (EPMA, JEOL JXA-8200). A series of natural and synthetic mineral standards were used for external calibration of EPMA performed at typical operating conditions of accelerating voltage of 15 kV and beam current of 5 nA (carbonates, phosphates, olivine, pyroxene, magnetite, and sulfide) or 30 nA (natural and synthetic standards).

High precision oxygen isotopic analysis

Oxygen isotopic analysis was undertaken at the Open University (Milton Keynes, UK) using an infrared laser-assisted fluorination system (Miller *et al.*, 1999; Greenwood *et al.*, 2017). Four distinct Hayabusa2 samples were transported to the Open University in two sealed, nitrogen-filled “FTTC: facility-to-facility transport container” (Ito *et al.*, 2020). One of the two FTTC contained grains from the initial Hayabusa2 touchdown collection (particle A0098,2: 5 grains), the other FTTC contained three sets of particles from the second, post impactor collection: C0014,2 1 particle 5.5 mg; C0068,2 1 particle 0.5 mg; C0087,2 approximately 10 grains, 0.8 mg. Both holders were stored at the Open University in a dedicated cabinet with a continuously purged nitrogen atmosphere. The cabinet was housed within a secure class 100 cleanroom.

Sample loading was undertaken in a nitrogen “glove box” with monitored oxygen levels below 0.1 %. A new Ni sample holder was fabricated for the Hayabusa2 analysis work that consisted of just two sample wells (2.5 mm diameter, 5 mm depth), one for the Hayabusa2 particle and the other for the internal obsidian standard. During analysis, the sample well containing the Hayabusa2 material was overlain by a

~1 mm thick, 3 mm diameter internal BaF₂ window to retain the sample during laser reaction. The flow of BrF₅ to the sample was maintained by gas mixing channels scribed into the Ni sample holder. The sample chamber configuration was also modified so that it could be removed from the fluorination line under vacuum and then opened within the nitrogen-filled glove box. The two-part chamber is made vacuum tight using a compression seal with a copper gasket and quick-release KFX clamp (Miller *et al.*, 1999; Greenwood *et al.*, 2017). A 3 mm thick BaF₂ window at the top of the chamber allows simultaneous viewing and laser heating of samples. Following sample loading the chamber was then resealed and reattached to the fluorination line. Prior to analysis the sample chamber was heated overnight under vacuum to a temperature of about 95°C to remove any adsorbed moisture. Following overnight heating, the chamber was allowed to cool to room temperature and then the section that had been brought up to atmosphere during the sample transfer process was purged using three aliquots of BrF₅ to remove any moisture. These procedures ensured that the Hayabusa2 samples were never opened to the atmosphere or contaminated with moisture from those parts of the fluorination line that had been brought up to atmosphere during the sample loading procedure.

All Hayabusa2 samples were run in modified “single shot” mode (Schrader *et al.*, 2014). Sample heating in the presence of BrF₅ was carried out using a Photon Machines Inc. 50 W infrared CO₂ laser (10.6 μm) mounted on an X-Y-Z gantry. Reaction progress was monitored by means of an integrated video system. After fluorination, the released O₂ was purified by passing it through two cryogenic nitrogen traps and over a bed of heated KBr to remove any excess fluorine. The isotopic composition of the purified oxygen gas was analyzed using a Thermo Fisher MAT 253 dual inlet mass spectrometer with a mass resolving power of approximately 200.

In most cases the amount of O₂ gas liberated during sample reaction was less than 140 μg, the approximate limit for using the bellows facility on the MAT 253 mass spectrometer. In these cases, analysis was undertaken using the microvolume. Following analysis of the Hayabusa2 particle, the internal obsidian standard was fluorinated, and its oxygen isotope composition determined.

The NF⁺ fragment ion of NF₃⁺ can cause interference with the mass 33 beam (¹⁶O¹⁷O). In order to eliminate this potential problem all samples were treated using a cryogenic separation procedure. This was either done in the forward sense prior to analysis on the MAT 253 or as a second analysis with the already analyzed gas pulled back onto a dedicated molecular sieve and then rerun after cryogenic separation. Cryogenic separation involved taking the gas onto the molecular sieve at liquid nitrogen temperature and then releasing it to the main molecular sieve at a temperature of -130°C. Extensive tests have shown that NF⁺ is retained on the first molecular sieve and that no significant fractionation results from the use of this technique.

Overall system precision in bellows mode, as defined by replicate analyses of our internal obsidian standard, is: ± 0.053 ‰ for δ¹⁷O; ± 0.095 ‰ for δ¹⁸O; ± 0.018 ‰ for Δ¹⁷O (2σ) (Starkey *et al.*, 2016). Oxygen isotopic analyses are reported in standard δ notation, where δ¹⁸O has been calculated as:

$$\delta^{18}\text{O} = [({}^{18}\text{O} / {}^{16}\text{O})_{\text{sample}} / ({}^{18}\text{O} / {}^{16}\text{O})_{\text{VSMOW}} - 1] 1000 (\text{‰})$$

and similarly for $\delta^{17}\text{O}$ using the ${}^{17}\text{O}/{}^{16}\text{O}$ ratio. VSMOW is the international standard Vienna Standard Mean Ocean Water. $\Delta^{17}\text{O}$, which represents the deviation from the terrestrial fractionation line, has been calculated as: $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52\delta^{18}\text{O}$

Sample preparation using a focused ion beam (FIB)

Approximately 150 to 200 nm-thick sections were extracted from Ryugu particles using a Hitachi High Tech SMI4050 focused ion beam (FIB) instrument at the Kochi Institute for Core Sample Research (Kochi), JAMSTEC. After deposition of tungsten protection layers, regions-of-interest (up to $25 \times 25 \mu\text{m}^2$) were cut out and thinned using a Ga^+ ion beam at an accelerating voltage of 30 kV and then finalized at 5 kV and probe current of 40 pA to minimize surface damage layers. Subsequently, the ultrathin sections were mounted on scaled-up Cu grids (Kochi grid, Ito *et al.*, 2020) using a micromanipulator equipped with the FIB.

Elemental abundance by Instrumental Neutron Activation Analysis (INAA)

Ryugu particles A0098 (1.6303 mg) and C0068 (0.6483 mg) were doubly sealed in cleaned and high purity polyethylene sheets in a pure N_2 -filled glove box at SPring-8 without any interaction with terrestrial atmosphere. Sample preparation of JB-1 (a geological standard rock sample issued by the Geological Survey of Japan) was carried out at Tokyo Metropolitan University.

INAA was done at Institute for Integrated Radiation and Nuclear Science, Kyoto University. Samples were irradiated two times with different irradiation periods in consideration of half-lives of the nuclides used for elemental quantification. First, samples were irradiated for 30 s at the pn-3 with thermal and first neutron fluxes of 4.6×10^{12} and $9.6 \times 10^{11} \text{ cm}^{-2}\text{s}^{-1}$, respectively, for the determination of Mg, Al, Ca, Ti, V and Mn. Chemical reagents such as MgO (99.99% purity; Soekawa Chemical, Tokyo, Japan), Al (99.9% purity; Soekawa Chemical) and Si metals (99.999% purity; FUJIFILM Wako Pure Chemical, Osaka, Japan) were also irradiated to correct for interfering nuclear reactions such as (n,p). Sodium chloride (99.99% purity; MANAC, Tokyo, Japan) was also irradiated with the samples to correct for neutron flux variations.

After neutron irradiation, the outer polyethylene sheet was replaced with a new sheet and gamma rays emitted from the samples and reference standards were immediately measured using Ge detectors. The same samples were reirradiated for 4 hours at a pn-2 with thermal and first neutron fluxes of 5.6×10^{12} and $1.2 \times 10^{12} \text{ cm}^{-2}\text{s}^{-1}$, respectively, for the determination of Na, K, Ca, Sc, Cr, Fe, Co, Ni, Zn, Ga, As, Se, Sb, Os, Ir and Au. Reference samples for Ga, As, Se, Sb, Os, Ir and Au were prepared by dropping a proper amount of concentration-known standard solutions of these elements onto the two sheets of filter papers

which were then irradiated with the samples. Gamma-ray counting was carried out at Institute for Integrated Radiation and Nuclear Science, Kyoto University and RI Research Center, Tokyo Metropolitan University. For elemental quantification, a reference value of Cr for JB-1 was taken from Kong and Ebihara (1997), while literature values of Jochum *et al.* (2016) were used for the remaining elements. The analytical procedure of INAA is the same as that described by Shirai *et al.* (2020).

Bulk mineralogy by XRD

X-ray diffractometer (Rigaku SmartLab) was used to collect diffraction patterns of Ryugu samples A0029 (1<mg), A0037 (<<1 mg) and C0087 (<1 mg) at the National Institute of Polar Research. All the samples were ground to be fine powders using a sapphire glass plate on a silicon non-reflection plate, and then homogeneously placed onto the silicon non-reflection plate. The measurement conditions are as follows: Cu K α X-ray was produced at 40 kV tube voltage and 40 mA tube current, the length of length limiting slit was 10 mm, the divergence angle was (1/6) $^\circ$, in-plane rotation speed was 20 rpm, two theta range (two-fold Bragg angle) was 3–100 $^\circ$, and it took ~28 hours for single analysis. BraggBrentano optics was used. The detector was one-dimensional SSD (D/teX Ultra 250). Cu K β X-ray was removed using a Ni filter. The peaks were identified from the comparison with the measured data using the available samples, synthesized Mg-saponite (JCSS-3501, Kunimine Industries CO., LTD.), serpentine (antigorite, Miyazu, Nichika #14-4-12-1), and pyrrhotite (monoclinic 4C, Chihuahua, Mexico), and using the PDF data from ICDD, dolomite (PDF 01-071-1662) and magnetite (PDF 00-019-0629). The diffraction data of Ryugu was also compared with those of hydrously altered carbonaceous chondrites, Orgueil CI, Y-791198 CM2.4, and Y 980115 CY (heating stage III). The comparison showed the similarity with Orgueil but not with Y-791198 and Y-980115.

Carbon functional groups by STXM–NEXAFS

The carbon K-edge NEXAFS spectra of ultra-thin section samples made by FIB were measured using the STXM beam line, BL4U, at the UVSOR Synchrotron Facility, Institute for Molecular Science (Okazaki, Japan). The beam spot size focused with Fresnel zone-plate optics was about 50 nm. The energy step size was 0.1 eV in the fine-structure portions of the near-edge region (283.6–292.0 eV), and 0.5 eV in the pre-edge and post-edge regions (280.0–283.5 and 292.5–300.0 eV). The acquisition time per image pixel for each energy step was set to be 2 ms. Helium gas of ~20 mbar was backfilled with the STXM analysis chamber after evacuation. This helps to minimize thermal drift of X-ray optics-related apparatus in the chamber and the sample holder, and to reduce sample damage and/or oxidation (Wang *et al.*, 2009). The carbon K-edge NEXAFS spectra were obtained from stack data using the aXis2000 software and the in-house customized software for STXM data reduction. Note that an in-house sample transfer vessel and a glove box were used to avoid oxidization and contamination on the sample.

Hydrogen, carbon, and nitrogen isotopic imaging analysis using NanoSIMS

The hydrogen, carbon, and nitrogen isotopic compositions of the Ryugu FIB sections were analyzed using isotopic imaging with the JAMSTEC NanoSIMS 50L after STXM-NEXAFS analysis. A focused primary Cs^+ beam of approximately ~ 2 pA was used for carbon, and nitrogen isotopic analyses, and approximately ~ 13 pA was used for hydrogen isotopic analyses, rastered over approximately 24×24 to $30 \times 30 \mu\text{m}^2$ areas on the samples. Each analysis was initiated after stabilization of the secondary-ion beam intensity following three minutes of pre-sputtering with a relatively strong primary-ion beam current. For carbon and nitrogen isotopic analysis, images of $^{12}\text{C}^-$, $^{13}\text{C}^-$, $^{16}\text{O}^-$, $^{12}\text{C}^{14}\text{N}^-$ and $^{12}\text{C}^{15}\text{N}^-$ were acquired simultaneously in multidetection with seven electron multipliers (EMs) at a mass resolving power of approximately 9000, sufficient to separate all relevant isobaric interferences (that is, $^{12}\text{C}^{14}\text{N}$ on ^{13}C and $^{13}\text{C}^{14}\text{N}$ on $^{12}\text{C}^{15}\text{N}$). For hydrogen isotopic analysis, images of $^1\text{H}^-$, $^2\text{D}^-$, and $^{12}\text{C}^-$ were acquired using three EMs in multidetection at a mass resolving power of approximately 3000. Each analysis consisted of 30 scanned images of the same area, with individual images consisting of 256×256 pixels for the carbon and nitrogen isotopic analyses and 128×128 pixels for the hydrogen isotopic analysis. The dwell times were $3,000 \mu\text{s}/\text{pixel}$ for the carbon and nitrogen isotopic analyses and $5000 \mu\text{s}/\text{pixel}$ for the hydrogen isotopic analysis. We used 1-hydroxybenzotriazole hydrate as the hydrogen, carbon, and nitrogen isotopic standards to correct for instrumental mass fractionations (Ito *et al.*, 2014).

For silicon isotopic compositions of the presolar graphite in the C0068-25 FIB section, we acquired secondary ion images of $^{12}\text{C}^-$, $^{13}\text{C}^-$, $^{16}\text{O}^-$, $^{28}\text{Si}^-$, $^{29}\text{Si}^-$ and $^{30}\text{Si}^-$ simultaneously in multidetection with six electron EMs at a mass resolving power of approximately 9000. These images consist of 256×256 pixels with a dwell time of $3,000 \mu\text{s}/\text{pixel}$. We used a silicon wafer as the hydrogen, carbon, and silicon isotopic standard to correct for instrumental mass fractionation.

The isotopic images were processed using the custom written software 'NASA JSC imaging software for NanoSIMS' (Ito and Messenger, 2008). Data were corrected for EM dead time (44 ns), and the QSA effect (Slodzian *et al.*, 2004). Different scans of each image were aligned to correct image drift during acquisition. Final isotopic images were generated by adding the secondary ions of each image from each pixel over the scans.

Micron to submicron scale mineralogical observations by TEM

After STXM-NEXAFS and NanoSIMS analysis, the same FIB sections were studied using a transmission electron microscope (JEOL JEM-ARM200F) operated at an accelerating voltage of 200 kV at Kochi, JAMSTEC. Microtextural observations were performed by bright-field TEM (BF-TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging. Mineral phases were identified using selected-area electron diffraction and lattice-fringe imaging, and chemical analyses

using energy-dispersive X-ray spectrometry (EDS) with a 100 mm² silicon drift detector and JEOL Analysis Station 4.30 software. For quantitative analyses, the intensities of the characteristic X-rays of each element were measured using a fixed acquisition time of 30 s, beam scan area of ~100 × 100 nm², and beam current of 50 pA in scanning TEM mode. The (Si+Al)-Mg-Fe ratios of phyllosilicates were determined using experimental thickness-corrected k-factors obtained from a natural pyrope-almandine garnet standard.

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Declarations

Data availability

Correspondence and requests for materials should be addressed to M.I. All analytical data related to this manuscript will be put on the JAXA Data ARchives and Transmission System (DARTS) after a one-year proprietary period.

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Author contributions

M.I. leads the project and wrote a paper with input from all coauthors. M.I., N.T., M.U., A.Y., N.I., N.S., M-C.L., R.C.G., Y.K., A.N., K.M., N.M., and K.Y. conducted sample handling, preparation, and mounting processes of Ryugu grains. M.I., N.T., M.U., O.T., K.U., K.H., I.S., and I.O. developed universal sample holders for multiple instruments. M.U., M.Y., A. Tsuchiyama, A. Takeuchi and U.K. arranged and performed SR-CT analysis at SPring-8. SEM-EDS analysis was conducted by A.Y., M.K., N.I., and M.I. EPMA analysis and data reduction was conducted by A.Y. XRD analysis was conducted by N.I. FIB sample processing was conducted by Y.K. and N.T. STXM-NEXAFS analysis conducted by T.O., H.Y., M.I., M.U and A.N. NanoSIMS analysis conducted by M.I. TEM work was done by N.T. Oxygen isotopes were measured by R.C.G., R.F., I.A.F., and J.A.M at the Open University. N.S. and S.S. conducted INAA analysis at Kyoto University. S. Tanaka, T.O., S.Sugita, N.N., K.Kitazato, H. Y.I., Naru Hirata, Naoyuki Hirata, K.M., T. Michikami, H.Noda, R.N., Y.S., K. Shirai, K.O., K.W., H. Senshu, Y. Yamamoto, T. Morota, R.H., Y. Yokota, C. Honda, M.M., N.S., E.T., A. Miura, M. Yamada, M.A., T.I., H. Yano, A.F., C. Hirose, S.H., H.I., S.K., Y.M., O.M., M.O., N.O., G.O., H. Sawada, T. Shimada, T.T., Y. Takei, H.T., R.T., K. Yoshikawa, F.T., T. Saiki, S.N., M.Y., S.W. and Y. Tsuda contributed to the spacecraft operations and selected sampling sites. T.Y., A.N., K.Y., M.N., A.N., A.M., K.K, K.H., Y.H., M.S., M. Yoshitake, T.O., M.A., and T.U lead the JAXA curation activities for initial characterization of allocated Ryugu particles. M. Yoshikawa, T. Saiki, S. Tanaka, F.T., S.N., S. Sugita, N.N., K. Kitazato, T.O., Naru Hirata, S.W., and Y.T. administered the project and acted as principal investigators. All authors contributed to the data interpretation, commented, and finalized to the paper.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information is available for this paper: Supplementary Figures S1 – S3, and Supplementary Tables S1 – S3.

Figures

Fig. 1. The Ryugu C0068 thin section images. (A) a combined X-ray map composed of Mg Ka (red), Ca Ka (green), and Fe Ka (blue) of a dry-polished section of the Ryugu C0068 particle. The section consists of phyllosilicate (red: ~88 vol%), carbonate (dolomite; light green: ~1.6 vol%), magnetite (blue: ~5.3 vol%), and sulfide (blue: sulfide= ~2.5 vol%). (B) backscattered electron image of regions of outlined in (A). Bru: brunnerite, Dol: dolomite, Mag: magnetite, Sap: saponite, Srp: serpentine. (C) High-resolution TEM image of typical saponite-serpentine intergrowth area showing 0.7 nm and 1.1 nm lattice fringes of serpentine and saponite, respectively.

Figure 1

See figure for legend.

Fig. 2. Major mineral components and bulk oxygen isotopic compositions of the Ryugu particles. (C) Three Oxygen isotope diagram of Ryugu A0098, C0068 and range of multiple analyses of Chamber C particles (shaded blue region) in comparison with CI (Orgueil), CY (Y-82162), CM, and C2-ung (Tagish Lake & Bells) (Clayton, 1993; Greenwood et al., 2017). Data of Orgueil and Y-82162 meteorites obtained in this study. TFL: terrestrial fractionation line, CCAM: carbonaceous chondrite anhydrous mineral line.

Fig. 2. Major mineral components and bulk oxygen isotopic compositions of the Ryugu particles. (D) $\Delta^{17}\text{O}$ vs $\delta^{18}\text{O}$ plot for a range of Ryugu A0098, C0068 and average value of multiple analyses of Chamber C particles (Average CI, CI (Orgueil) and CY chondrite (Y-82162)). Data of Orgueil and Y-82162 meteorites obtained in this study. TFL: terrestrial fractionation line, CCAM: carbonaceous chondrite anhydrous mineral line.

Figure 2

See figure for legend.

Fig. 3. Scanning transmission X-ray microscopy (STXM) and NanoSIMS ion imaging analyses of a focused ion beam (FIB) section of the Ryugu C0068-25. (A) STXM carbon K-edge spectral image indicates the section is dominated by carbon. (B) Carbon-NEXAFS spectra normalized at 292 eV of aromatic (C=C)-rich regions (red), aliphatic-rich regions (green), and matrix (blue). The grey line is spectrum of Murchison IOM (Cody et al., 2008) in comparison. (C) Combined RGB map in R: Aromatic-rich (C=C) area, G: Aliphatic-rich area, B: Matrix. (D) Aliphatic-rich organics concentrated in coarse-grained phyllosilicates in area enlarged from the white box in (A,C). (E) Large nanoglobule (n.g-1) in area enlarged from the white box in (A,C).

Fig. 3. Scanning transmission X-ray microscopy (STXM) and NanoSIMS ion imaging analyses of a focused ion beam (FIB) section of the Ryugu C0068-25. (F) Elemental images of hydrogen, carbon and nitrogen, elemental ratio image of $^{12}\text{C}/^1\text{H}$, and isotope images of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of the section. P.G-1: presolar graphite with extreme ^{13}C enrichment. n.g-1: nanoglobule of the white box in (D).

Figure 3

See figure for legend.

Fig. 4. Light element isotopic compositions of the Ryugu particles A0002, A0037 and C0068. Comparison of the bulk H and N isotopic compositions of the Ryugu particles (red circles: A0002, A0037; blue circles: C0068) with those of the IDPs, Wild2 cometary samples, and carbonaceous chondrites (CI, CM, CR, C2-ung). The isotopic compositions are given in Table S3, and IDPs from Floss et al. (2006), Wild2 cometary samples from McKeegan et al. (2006) and carbonaceous chondrites from Alexander et al. (2017 and reference there in). Dotted lines are terrestrial isotopic values of H and N.

Figure 4

See figure for legend.

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