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Macromolecular organic matter in samples of the asteroid (162173) Ryugu

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5 **Samples of the carbonaceous asteroid (162173) Ryugu were collected and brought to Earth by the Hayabusa2 spacecraft. We investigate the macromolecular organic matter in Ryugu samples, finding they contain aromatic and aliphatic carbon, ketone and carboxyl functional groups. The spectroscopic features of the organic matter are consistent with those in chemically primitive carbonaceous chondrite meteorites that experienced parent body aqueous alteration (reactions with liquid water). The morphology of the organic carbon includes nanoglobules and diffuse carbon associated with phyllosilicate and carbonate minerals. Deuterium and/or nitrogen-15 enrichments indicate the organic matter formed in a cold molecular cloud or the pre-solar nebula. The diversity of the organic matter indicates variable levels of aqueous alteration on Ryugu's parent body.**

15 Organic compounds in asteroids and comets were produced and modified within the pre-solar molecular cloud, the protoplanetary disk, during formation of planetesimals in the early Solar System, and their subsequent evolution. Delivery of extraterrestrial organic compounds might have contributed to the habitability of terrestrial planets, including the Earth. Analysis of pristine samples collected from primitive small bodies (asteroids and comets) could provide information on how organic compounds were formed and modified in space, and which organic compounds were supplied to the early Earth. Macromolecular organic matter, a dark, complex, acid-insoluble organic matter (IOM), accounts for most carbon in primitive carbonaceous chondrite meteorites.

25 The Hayabusa2 asteroid sample return mission visited the carbonaceous (C-type) asteroid (162173) Ryugu. The mission goals included investigating the origin and evolution of organic compounds in the early Solar System (1). Remote sensing and lander observations showed that Ryugu is a dark rubble-pile asteroid that contains hydrated minerals on its surface (2-4) and indicated a relationship between C-type asteroids and carbonaceous chondrites (3, 4). The average albedo of Ryugu is consistent with the thermally metamorphosed subgroups of the CI1 and CM2 meteorites (3, 4). CI1 meteorites are Ivuna-type carbonaceous chondrites of petrologic type 1 (extensively altered by aqueous fluids on the parent asteroid), and CM2 meteorites are Mighei-type carbonaceous chondrites of petrologic type 2 (moderately aqueously altered). Spectral and thermal inertia variations indicated that Ryugu consists of boulders that experienced different degrees of thermal and space weathering processes (5-7), derived from a much larger parent body, and potentially additional materials from different asteroids (8).

35 The Hayabusa2 spacecraft collected the surface material from two touchdown sites on Ryugu and returned them to Earth on 2020 December 6. The Ryugu samples exhibit near-infrared absorption features due to OH and carbonate/organic C-H bonds, at 2.7 and 3.4 μm respectively (9, 10), indicating that the Ryugu samples are similar to CI carbonaceous chondrites (9).

40 We sought to determine the distributions and chemical characteristics of macromolecular organic matter in the Ryugu samples. We therefore measured the elemental, isotopic, and functional group compositions, structures, and textures of organic macromolecules from the Ryugu samples. The analytical procedures included micro-Fourier transform infrared (FTIR) spectroscopy, micro-Raman spectroscopy, synchrotron-based scanning transmission X-ray microscopy (STXM), X-ray absorption near edge structure (XANES), scanning transmission

electron microscopy (STEM) coupled with electron energy loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy (EDS), atomic force microscope based infrared (AFM-IR) spectroscopy, and nanometer-scale secondary ion mass spectrometry (NanoSIMS) (11). The analytical workflow (fig. S1) was designed to optimize the use of these complementary techniques.

The samples we used were selected aggregates stored in collection chamber A (from the first touchdown) and collection chamber C (from the second touchdown) of the spacecraft sample catcher (12) (table S1). We studied i) intact grains (taken from aggregates designated A0108 and C0109), ranging from 200 to 900 μm in size per particle; and ii) insoluble carbonaceous residues (fig. S2) isolated by acid treatment of Ryugu aggregates (designated A0106 and C0107). Each of these samples was split into several sub-samples for analysis with different techniques (table S1).

Structural properties of macromolecular organic matter

To characterize the macromolecular structures of organic matter in Ryugu, we applied micro-Raman spectroscopy. Two peaks, identified as the D- ($\sim 1350\text{ cm}^{-1}$) and G-bands ($\sim 1580\text{ cm}^{-1}$) of polyaromatic molecular structures (13), are present in the Raman spectra of A0108 and C0109 (Fig. 1A and fig. S3A). The spectral features are broad, indicating lattice disorder in the organic macromolecules, and are superimposed on a fluorescence background. The numerical values of the derived spectral parameters of the D- and G-bands, such as their full widths at half maximum (FWHM_{D} and FWHM_{G} , respectively), peak positions (ω_{D} , ω_{G}), and intensity ratio ($I_{\text{D}}/I_{\text{G}}$), are similar for all grains examined from the two aggregates (Figs. 1B-D and figs. S3B-D).

The macromolecular structures of organic matter in meteorites reflect the thermal histories of the meteorite parent bodies (13-16). To evaluate the thermal history of Ryugu, we compared the Raman parameters measured from the Ryugu samples to those measured from meteorites (Figs. 1B-D and figs. S3B-D). The closest matches to Ryugu are the primitive CI1 and CM2 carbonaceous chondrites. The Ryugu samples are distinct from carbonaceous chondrites of petrologic type 3 (thermally metamorphosed) (Fig. 1B) and from the thermally metamorphosed subgroup of CM2, such as the Jbilet Winselwan meteorite (Fig. 1C, D), and other ungrouped carbonaceous chondrites of petrologic type 2 (C2), such as the Wisconsin Range (WIS) 91600 and Pecora Escarpment (PCA) 02012 meteorites (Fig. 1C, D). This indicates that the Ryugu samples A0108 and C0109 did not experience long duration radiogenic thermal metamorphism on their parent bodies, as petrologic type 3 chondrites did (17), or impact-induced short duration heating, as experienced by some petrologic type 2 chondrites (18).

Functional group compositions

We used micro-FTIR spectroscopy to characterize the organic molecules and minerals. The FTIR spectra of the Ryugu grains show bands due to organic aliphatic C-H stretching (3000 to 2800 cm^{-1} , 3.33 to $3.57\text{ }\mu\text{m}$), aromatic C=C stretching ($\sim 1600\text{ cm}^{-1}$, $\sim 6.25\text{ }\mu\text{m}$), and carbonyl C=O stretching modes ($\sim 1700\text{ cm}^{-1}$, $\sim 5.88\text{ }\mu\text{m}$), as well as bands due to mineral Si-O stretching ($\sim 1000\text{ cm}^{-1}$, $\sim 10.00\text{ }\mu\text{m}$), structural OH stretching of phyllosilicates ($\sim 3680\text{ cm}^{-1}$, $\sim 2.72\text{ }\mu\text{m}$), and the ν_3 stretching mode of carbonates ($\sim 1435\text{ cm}^{-1}$, $\sim 6.97\text{ }\mu\text{m}$) (Fig. 2A). The spectra also contain bands from interlayer water, of varying intensities, contributing at $\sim 3300\text{ cm}^{-1}$ ($\sim 3.03\text{ }\mu\text{m}$, stretching) and 1640 cm^{-1} ($6.10\text{ }\mu\text{m}$, bending). Part of this water is intrinsic to the Ryugu grains, and part can be attributed to water adsorbed on the grains under atmospheric conditions.

These absorption bands are commonly observed in unheated, aqueously altered carbonaceous chondrites (19, 20), while organic features are weaker in thermally metamorphosed CM chondrites, such as the Jbilet Winselwan meteorite (Fig. 2A). The spectral shape of the OH band in the Ryugu samples is characteristic of Mg-rich phyllosilicates, which have been observed in CI chondrites as saponite and serpentine (21, 22). There were large spectral heterogeneities among the Ryugu grains, but there is no obvious difference in the spectral variations observed between samples from chambers A and C. Compared to CI chondrites, the sulfate S=O stretching band (~1100 to 1200 cm^{-1} , ~9.09 to 8.33 μm) is absent from the spectra of Ryugu samples. The absence of sulfates is consistent with other elemental and mineralogical measurements of Ryugu samples (23, 24). Sulfate can be produced by oxidation of sulfides during terrestrial weathering of the meteorites (25), so the lack of sulfate indicates that the Ryugu samples are pristine (23).

The shapes of the FTIR spectra of the grains are consistent with the reflectance spectra of Ryugu's surface acquired by the Hayabusa2 spacecraft (4). The OH band and aliphatic C-H band features in our absorption spectra are similar to reflectance spectra of other Ryugu samples (9), but we find lower intensities of aliphatic C-H peaks.

The FTIR spectra of insoluble carbonaceous residues obtained from our Ryugu samples show similar functional groups to those of the intact Ryugu grains (Fig. 2B). The aliphatic C-H stretching band (3000 to 2800 cm^{-1} , 3.33 to 3.57 μm) from the carbonaceous residue from Ryugu is more intense than those of IOM from meteorites (26, 27). The peak intensity ratios of CH_2 to CH_3 ($I_{\text{CH}_2}/I_{\text{CH}_3}$) of the Ryugu residues are 1.9, while those of IOMs in Murchison and Ivuna meteorites are 1.2 and 1.3, respectively. Because $I_{\text{CH}_2}/I_{\text{CH}_3}$ ratios are proportional to the molar ratios of CH_2 to CH_3 (CH_2/CH_3), we infer the CH_2/CH_3 ratios of the residue, which are higher than those of meteoritic IOMs. This could indicate that Ryugu's organic matter contains longer aliphatic chains, or aliphatic chains with a higher degree of cross-linking. The Ryugu carbonaceous residue also exhibits an absorption band of C=O (~1670 cm^{-1} , ~5.99 μm) which is not seen in meteoritic IOMs. We assign this C=O band to unsaturated ketones, aldehydes or amides.

Chemical and morphological variations

Macromolecular diversity

We used synchrotron-based STXM, with spatial resolution of 30 to 50 nm, to produce elemental X-ray maps and XANES spectra. Carbon X-ray maps (Figs. 3A, B) show discrete grains of organic material with sizes of ~200 nm. X-ray absorption by carbon atoms is also present in the phyllosilicate matrix, at low levels but nearly ubiquitously (Fig. 3B). Carbon-XANES spectra of the discrete grains show three major peaks, due to aromatic carbon (C=C, 285 eV), aromatic ketone (C=C-C=O, 286.7 eV), and carboxyl (COOH, 288.5 eV) functional groups (Fig. 3E), which have been observed in primitive extraterrestrial carbonaceous matter, such as carbonaceous chondrites (28, 29) and their extracted IOMs (30), interplanetary dust particles (IDPs) (31), dust particles from Comet Wild 2 (32), and Antarctic micrometeorites (AMMs) (33). Some spectra of fine-grained matrices in the Ryugu samples contain an additional peak at 290.4 eV, which corresponds to a $1s-\pi^*$ transition of carbonate groups, e.g., in calcite and other carbonate minerals. However, our matrix XANES spectra containing this feature lack extended X-ray absorption fine structure (EXAFS) features at higher energies (294-304 eV), indicating that the carbonate is not in a crystalline structure, so is more likely to be molecular carbonate. A similar carbonate feature has previously been reported in clay-bound carbon from extensively

hydrated carbonaceous chondrites, Ivuna (CI1), Orgueil (CI1), and Tagish Lake (C2) (34), and in diffuse carbon (organic matter) in the fine-grained matrices of Renazzo (CR2; a Renazzo-type carbonaceous chondrite of petrologic type 2), Murchison (CM2), and Orgueil (28).

We classify the STXM spectra of Ryugu organic matter based on spectral shape similarities into four representative types: i) Highly aromatic (~25% of individual carbon grains), ii) Aromatic (~35% of individual grains), iii) IOM-like (~40% of individual grains), and iv) Diffuse carbon associated with a molecular carbonate peak (Fig. 3E). Aromatic spectra show higher ratios of aromatic carbon to aromatic ketone than IOM-like spectra, while highly aromatic spectra show a broader peak for aromatic carbon, indicating increased diversity of aromatic structures. The frequency distributions of these classes were similar for both chamber A and C samples. We find a relationship between the morphology of organic matter and XANES spectral shape, with particulate and nanoglobular regions having more frequent aromatic or highly-aromatic XANES spectra, while organic matter dispersed in the matrix more commonly has IOM-like or diffuse carbon spectra. These observations indicate that the molecular functional groups present are influenced by aqueous processing on the asteroid parent body. We did not find any evidence of long-duration thermal metamorphism, such as the $1s\text{-}\sigma^*$ exciton (291.6 eV) peak of graphite or other graphitized carbon materials (35).

Similar characteristics are found for the insoluble carbonaceous residues from Ryugu. Average C-XANES spectra have IOM-like spectral shapes, but with more prominent aromatic C=C, ketone, and carboxyl peaks, compared to IOM from Orgueil and Murchison (Fig. 3E). Several hollow and solid organic nanoglobules are apparent in the X-ray absorption images (Figs. 3C, D), which we confirmed using TEM imaging (Figs. 4A, B). Their XANES spectra were either IOM-like, aromatic, or highly-aromatic (Fig. 3E). The 290.4 eV carbonate feature was not observed in the insoluble carbonaceous residue, perhaps because this organic phase was incorporated into phyllosilicate interlayers, so was removed or destroyed during the acid extraction process.

Nitrogen-XANES spectra (fig. S4A) of the Ryugu intact grains and insoluble residue did not show clear absorption peaks, indicating low abundances of N-rich Ryugu organics. This is consistent with carbonaceous chondrites, where nitrogen-rich particles are only occasionally observed (32). Oxygen-XANES spectra (fig. S4B) of Ryugu organic matter often contain a peak at ~531.3eV, corresponding to carbonyl C=O bonds in the ketone and carboxyl functional groups (36). The peak intensity of the carbonyl absorption, relative to the main oxygen $1s\text{-}\sigma^*$ peak in Ryugu, is similar to that of aqueously altered carbonaceous chondrites. We cannot determine whether these carbonyl functional groups are also present in the phyllosilicate-bound diffuse organic matter, because its oxygen-XANES spectrum is dominated by the surrounding phyllosilicate.

Nanoscale morphologies

We performed TEM and STEM-EELS-EDS analysis (Fig. 4) on ultrathin sections of particles and carbonaceous residues, including from some of the same sections we analyzed previously with STXM. The two most abundant organic microstructures are nanoglobules (Figs. 4A, B), and diffuse carbon mixed with phyllosilicates, i.e, clay-bound carbon (Figs 4C, E). Other microstructures include dense, irregularly shaped particles (Fig. 4B), diffuse organic matter trapped in vesicles in carbonate grains (Figs. 4D, F), and organic matter coatings on sulfide grains. The presence of organic matter associated with Mg-rich phyllosilicates and carbonates, which likely formed through aqueous alteration (24), implies that much of the organic material

was altered by low temperature aqueous processing on Ryugu's parent body. However, we also find nanodiamonds associated with amorphous organic carbon, which probably formed in the interstellar medium or the Solar System's protoplanetary nebula (37, 38). The insoluble carbonaceous residues contain large nanoglobules, and fluffy or porous material, comprising demineralized grain coatings, intergranular material and small nanoglobules. These microstructures are present in samples from both chambers A and C; they are consistent in size and shape with those in CI and CM chondrites (28, 34).

Organic nanoglobules have previously been found in early Solar System materials, such as primitive carbonaceous chondrites (39-42), dust particles from Comet Wild 2 (32), IDPs (43), and AMMs (33, 44). The nanoglobules in Ryugu grains occur in solid and hollow form, typically 50 to 500 nm in diameter, with a few reaching 2000 nm, consistent with nanoglobules in other extraterrestrial materials. The carbon EELS spectra of many of the Ryugu nanoglobules are dominated by an aromatic carbon peak at around 285 eV (Fig. 4G), corresponding to the aromatic-rich carbon-XANES spectra (Fig. 3E). Other prominent peaks are due to aromatic ketone (286.7 eV) and carboxyl (288.5 eV). The fluffy material in the insoluble carbonaceous residues shows these three peaks in varying intensities. The presence of both aromatic- and IOM-like nanoglobules of various sizes indicates that Ryugu experienced heterogeneous aqueous alteration on its parent body. Correlated STEM-NanoSIMS measurements of a 2000-nm nanoglobule (particle A0108-37; figs. S6 and S7) show high abundances of aromatic carbon, and isotopically anomalous H and N, indicating preservation of material from the interstellar medium or protoplanetary nebula.

The widespread diffuse carbon mixed into phyllosilicates could have been formed from soluble molecules intercalated into clays, through oxidation during aqueous alteration (34). Alternatively, the clay-bound diffuse carbon might have been released by hydrolysis of macromolecular organic material, during the flow of aqueous fluids (28). The EELS spectra show peaks of either aromatic ketones or aliphatic carbon (287 eV) and carbonate (CO_3 at 290.4 eV), along with aromatic carbon (285 eV) (Fig. 4G). These EELS data are consistent with the carbon-XANES spectrum of the diffuse carbon (Figs. 3B, E). The relative intensities of the 287 eV and 285 eV peaks vary, compared to the 290.4 eV peak. This is consistent with clay-bound organics in CI chondrites (34), but sometimes is a better match to the ungrouped C2 chondrite Tagish Lake (34). In all cases, Mg is detected in the EDS spectra from the clay-bound organic matter (Fig. 4F), however we cannot determine whether the Mg is associated with the carbonate. We find no evidence for crystalline Mg carbonate in the clay-bound organics, but the CO_3 feature could be associated with either molecular CO_3 , or MgCO_3 , or a combination of these.

Pockets of organic matter occur in vesicles inside carbonates (Fig. 4D). A STEM-EDS image (Fig. 4F) shows this vesicle-bound diffuse organic matter is associated with phyllosilicates and particles of sulfide and Fe-Ni with size of ~10 nm, embedded in a larger grain of calcite. This morphology could indicate carbonate formation from diffuse organic matter. The lack of distinct particle boundaries for the organic matter could indicate it is soluble, and therefore potentially lost during our sample preparation, which used ultra-microtomy with a water bath.

We obtained AFM-IR maps of organic inclusions and nanoglobule-like matter at lateral resolutions of 25 and 50 nm. AFM-IR measurements map specific vibrational modes; we used the C=O and C=C modes. Samples from chambers A and C were analyzed using AFM-IR, both in tapping and contact modes. Figs. 5A and 5H show combined maps of carbonyl C=O (1720 cm^{-1} , $5.81 \mu\text{m}$), aromatic C=C (1600 cm^{-1} , $6.25 \mu\text{m}$) and Si-O (1020 cm^{-1} , $9.80 \mu\text{m}$) modes. The diffuse organic component within the phyllosilicate matrix is evident in both samples. The maps

show small (up to ~100 nm) organic nanoglobule-like inclusions in the chamber A sample (Fig. 5A) and organic inclusions in the chamber C samples (Fig. 5H). The abundances of carbonyl and C=C vary between the organic inclusions. These AFM-IR results are consistent with, and complimentary to, those from STEM-EELS-EDS and STXM-XANES discussed above.

5

Elemental abundances

The elemental abundances of macromolecular organic matter in meteorites are highly heterogeneous, both between meteorite groups and at the micrometer scale, reflecting the complex histories of these materials (45, 46). We used NanoSIMS to map the H, C, N, O and S elemental abundances of the Ryugu samples.

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The ratios of O/C, N/C, and S/C in the acid-insoluble carbonaceous residues from Ryugu were estimated from NanoSIMS elemental maps of the major isotopes (^{16}O , $^{12}\text{C}^{14}\text{N}$, ^{32}S) and were compared between samples taken from chambers A and C. The bulk O/C ratio (0.12 ± 0.03) in chamber A was consistent with those of CI (0.15 to 0.18), CM (0.11 to 0.23), and CR chondrites (0.11 to 0.22) (45). The bulk O/C ratio (0.04 ± 0.01) in chamber C was three times lower than those values. We cannot determine whether this difference is due to intrinsic differences between the two sampling sites, or heterogeneity within the samples. There are smaller differences in the bulk ratios N/C (0.035 ± 0.006 (A0106); 0.021 ± 0.001 (C0107)) and S/C (0.032 ± 0.001 (A0106); 0.025 ± 0.001 (C0107)) between the two chambers, which are within the ranges of those for CI, CM, and CR chondrites ($0.026 < \text{N/C} < 0.039$ and $0.02 < \text{S/C} < 0.06$) (45).

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We also used STEM-EDS to measure N, O, and S abundances, relative to C, at the nano- to micro-meter scale. An EDS spectrum from a $\sim 1 \mu\text{m}^2$ region of an ultrathin section of carbonaceous residue from chamber A is shown in Fig. 4H. The average compositions measured for carbonaceous residues are $\text{C}_{100}\text{N}_1\text{O}_{10}\text{S}_{0.8}$ for chamber A and $\text{C}_{100}\text{N}_2\text{O}_{10}\text{S}_{0.8}$ for chamber C. The insoluble carbonaceous residues contain some nanoparticulate minerals, including chromite, with varying Al, Mg and Fe, and sulfides with variable Fe, Ni, and (more rarely) CuS. These particles were excluded from the STEM-EDS measurements when > 4 nm in size. These nitrogen abundances are slightly lower than the bulk N/C ratio estimated using NanoSIMS, and consistent with the weak N-XANES absorption of the Ryugu grains.

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Isotopic compositions

NanoSIMS was also used to measure the isotopic compositions of hydrogen, carbon, and nitrogen. The resulting maps (Fig. 6A-C) show bulk enrichments of D (^2H) and/or ^{15}N in most analyzed Ryugu particles from aggregates A0108 and C0109, with a high degree of isotopic heterogeneity at the micrometer scale. The NanoSIMS H measurements are dominated by H from the organic matter, but also include H in phyllosilicates and possible contamination by terrestrial water. The isotopic compositions are expressed in delta notation: $\delta R \equiv (R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000$, where R_{sample} is the isotopic ratio of sample and R_{standard} is the ratio of a terrestrial standard. The average measured H isotopic compositions (δD) of particles range from $+254 \pm 52\text{‰}$ to $+490 \pm 100\text{‰}$ (table S3), consistent with the $\delta\text{D} = +252 \pm 13\text{‰}$ measured in an analysis of other Ryugu grains with a different technique (47). There is no obvious difference between grains from chambers A and C. The bulk N isotopic compositions $\delta^{15}\text{N} = +39 \pm 5$ to $+43 \pm 4\text{‰}$ are also within the range reported for other Ryugu grains, measured with different methods [$\delta^{15}\text{N}$

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= $+43.0 \pm 9.0\%$ (47) and $\delta^{15}\text{N} = 0$ to $+20\%$ (48)]. Figure S8 shows that the bulk δD and $\delta^{15}\text{N}$ of the Ryugu grains are between the bulk values of CI chondrites [$\delta\text{D} = +170$ to $+300\%$, $\delta^{15}\text{N} = +39$ to $+52\%$ (49)] and IOM in CI chondrites [$\delta\text{D} = \sim +975\%$, $\delta^{15}\text{N} = +31\%$ (45)].

Isotopic ratios determined for individual sub- μm to μm sized carbonaceous grains within the NanoSIMS maps are similar to those of carbonaceous chondrites and IDPs (43, 46). Most grains are consistent with the bulk average, within the uncertainties, while a small fraction of outliers have D and/or ^{15}N enrichments or depletions (Fig. 6D-F), which we term hot-spots and cold-spots respectively. These have a similar range of compositions to those seen in CI (46) and CM (50) chondrites, but smaller than that seen in CR chondrites (29). There is no correlation between δD and $\delta^{15}\text{N}$ for the hot- or cold-spots and a wide range of compositions occur over small spatial scales (Fig. 6B and C). The origin(s) of the H and N isotopic anomalies in meteorites are debated; current consensus models propose that they reflect isotopic fractionation at low temperatures in interstellar clouds or the outer protoplanetary nebula (51-54).

The NanoSIMS measurements show that the bulk Ryugu particles, and almost all carbon-rich particles within them, have $\delta^{13}\text{C}$ values within the range of organic matter in carbonaceous chondrites [$\delta^{13}\text{C} = -35$ to -5% (45)]. However, $\sim 0.5\%$ of the carbon-rich particles have ^{13}C enrichments or depletions (Fig. 6G), $>2\sigma$ above or below the bulk values. These particles have a range of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values similar to those seen in organic grains with anomalous carbon isotopes in primitive CM chondrites. For the Ryugu samples, ^{13}C -rich particles have a wider range of $\delta^{15}\text{N}$ values than ^{13}C -poor ones, likely reflecting different origins. Two very small (≤ 150 nm) regions have much higher ^{13}C enrichments: $\delta^{13}\text{C} = 700$ and 4800% , indicating they are pre-solar grains that formed in the outflows of previous generations of stars (55).

The acid-insoluble carbonaceous residues from the Ryugu samples showed bulk D-enrichments ($\delta\text{D} = +306 \pm 42\%$ (A0106); $+440 \pm 52\%$ (C0107)) (Fig. 7I), lower than the bulk hydrogen compositions of the IOM in CI chondrites ($\delta\text{D} = +972\%$ for Orgueil, $+978\%$ for Ivuna) and CM chondrites ($+639\% < \delta\text{D} < +893\%$) (45). The distributions of D-rich hotspots (distribution modes $\delta\text{D} = +1030\%$ (A0106) and $+1374\%$ (C0107)) were consistent with CI and CM chondrites, but not CR chondrites (56).

The bulk N isotopic compositions of the insoluble carbonaceous residues from Ryugu samples ($\delta^{15}\text{N} = +17.4 \pm 1.9\%$ (A0106); $+30 \pm 4.3\%$ (C0107)) (Fig. 7J) are consistent with those of IOM in CI chondrites ($\delta^{15}\text{N} = +30.7\%$ for Orgueil; $+31.9\%$ for Ivuna) (45). Delta- ^{15}N was more heterogeneous in the sample from chamber C than chamber A. The ^{15}N -rich hot-spots (distribution modes $\delta^{15}\text{N} = +241\%$ (A0106) and $+348\%$ (C0107)) were within the range of CI and CM carbonaceous chondrites (57). ^{15}N -depleted cold-spots ($\delta^{15}\text{N} = -100$ to -380%) were detected. ^{15}N cold-spots have previously been reported in the matrices of carbonaceous chondrites (57-59) and IDPs (43), and interpreted as indicating organic grains that have been partially equilibrated with proto-solar or interstellar N_2 gas (43).

Comparison with D-type asteroids and Comets

We compare the organic matter of Ryugu (a C-type asteroid) with other primitive small bodies in the early Solar System. Of the carbonaceous chondrites, the Tagish Lake meteorite is thought to be related to dark (D-type) asteroids, which are mainly located in the outer regions of the asteroid belt and among the trojan asteroids of Jupiter (60). Tagish Lake contains organic and mineralogical variations between different specimens that reflect variable degrees of alteration

on the same parent body (61, 62). The ratios D/H, H/C, and aliphatic carbon to aromatic carbon, decrease systematically with increasing alteration of the Tagish Lake meteorite samples (61).

We infer that the organic matter in the Ryugu samples has not been heated to temperatures higher than 200°C, based on the similarity of its chemical features with primitive carbonaceous CI and CM chondrites. Like the IOM from Orgueil (63) and Murchison (64), the organic macromolecules in the Ryugu samples likely contain polyaromatic structures which are composed of small numbers of aromatic rings with short, cross-linked, aliphatic chains and various oxygen- and nitrogen bearing functional groups. This macromolecular structure is distinct from graphitic or glassy carbon produced by heating: we did not find any evidence of highly conjugated sp² carbon. Laboratory experiments have shown that aliphatic carbon in IOM from primitive carbonaceous chondrites is reduced after hydrous heating at 300°C for 6 days (65). Therefore, the higher abundance of aliphatic carbon in organic residue of Ryugu, than in that of primitive carbonaceous chondrites, indicates that the Ryugu grains did not experience short heating equivalent to the experimental conditions.

The distribution of organic functional groups present in the Ryugu samples is unlike aqueously altered carbonaceous chondrites, for which organic particles and nanoglobules show predominantly IOM-like XANES spectra, with only occasional highly aromatic grains (28, 30, 66). Ryugu samples contain abundant aromatic-rich particles and nanoglobules, a high abundance of IOM-like diffuse carbon in matrix, and molecular carbonate associated with phyllosilicates. Progressive aqueous alteration in situ causes i) an increase in the amount of diffuse organic matter associated with matrix phyllosilicates, ii) an increase in the proportion of aromatic and oxygen-bearing functional groups in discrete organic particles and nanoglobules, and iii) an increase in the variety of XANES spectral features. Based on these trends, much of the internal spectral variation in the Ryugu samples, including carbon grains with an aromatic XANES spectral shape (Fig. 3E), likely developed through redistribution of organic matter and formation of additional organic molecules during aqueous alteration on the parent body, rather than pre-accretionary diversity inherited from the proto-solar molecular cloud. Carbonaceous grains and nanoglobules with highly-aromatic XANES spectra (not aromatic spectra; Fig 3E) provide a possible exception to this proposal. These highly-aromatic grains are more likely to represent original accreted materials, because similar XANES spectra have been found in unaltered, petrologic type 3, carbonaceous chondrites (30) and in cometary dust particles (32). This is consistent with our observation of a large highly-aromatic nanoglobule containing D and ¹⁵N isotopic anomalies (figs. S6 and S7).

The δD distributions of the carbon-rich particles in the Ryugu grains are consistent with those in the Tagish Lake meteorite (56), CI and CM chondrites (46, 57). The δD distributions of the Ryugu insoluble carbonaceous residues from chambers A and C are within the ranges of IOMs in the most and least altered fragments of Tagish Lake, respectively (61). The hydrogen isotopic variations among the different lithologies of Tagish Lake has previously been explained by depletion of D via hydrogen isotopic exchange or hydrolysis of D-rich structures of IOM during various degrees of planetesimal hydrothermal alteration (65, 67). In contrast, the δD distributions of our Ryugu samples are lower than those of less altered CR chondrites (56), the most primitive class of IDPs (68), and comet-derived AMMs (33, 69). We therefore propose that Ryugu organic matter is a product of heterogeneous aqueous processing, which occurred on both C- and D-type asteroids, of the common primordial materials formed at an earlier stage of the solar nebula. The δ¹⁵N distributions of the intact grains and insoluble residues from our Ryugu samples were within the ranges of carbon-rich particles (39, 56) and IOM (bulk) (61) in Tagish

Lake and Comet Wild 2 (32) as well as CI and CM chondrites. However, they are lower than the $\delta^{15}\text{N}$ distributions of anhydrous IDPs (43, 68) and the IOM from CR chondrite (56). Nitrogen isotopic compositions are less affected than hydrogen isotopes by modification through parent body processes (45, 57, 61, 66), and their variations indicate mixing of different isotopic components from different precursors (53).

Nitrogen content can be an indicator of chemical evolution in the early Solar System. The measured N abundance ($\text{N/C} = 0.01$ to 0.035) of the insoluble carbonaceous residue in Ryugu samples is similar to primitive carbonaceous chondrites (45), and consistent with the total bulk N abundance ($\sim 0.15\text{wt}\%$) (47). The N/C ratio of IOM from Tagish Lake (~ 0.042) is higher than those of the Ryugu samples. In contrast, some cometary materials, such as dust particles from Comet Wild 2, anhydrous AMMs, and ultra-carbonaceous AMMs (UCAMMs), contain N-rich organics [$\text{N/C} = 0.07$ to 0.24 (32, 44, 70)]. Those are composed of a variety of nitrogen-bearing functional groups, such as imine, nitrile and/or heterocyclic N, or amide (32, 33, 44, 70, 71). The N contents of Comet 67P/Churyumov-Gerasimenko particles were heterogeneous ($\text{N/C} = 0.018$ to 0.06) (72) but lower than the N/C ratio of the Sun (0.3 ± 0.1) (73). The depletion of N in that comet might be due to the presence of ammonium salts (74, 75). These variations in N/C between different Solar System objects could arise from partitioning between gas and solid phases in the cold interstellar cloud or outer solar nebula, or exposure to warmer inner Solar System during perihelion passage (74), rather than processing in the interiors of planetesimals. Experiments simulating parent body aqueous alteration show the N/C ratios in meteoritic IOM are not substantially modified (65, 76). We therefore conclude that the N abundance in Ryugu macromolecular organic matter is intrinsic, not the product of extensive parent body processing.

Conclusions

Our analysis of Ryugu samples indicate a direct link between macromolecular organic matter in C-type asteroids and that in primitive carbonaceous chondrites. The observed similarities and variations in molecular, isotopic, and morphological compositions between the Ryugu samples and other Solar System materials indicate a continuum of source material in the solar nebula, which was incorporated into C-type asteroids, D-type asteroids and comets in the early Solar System. Macromolecular organic matter in the surface grains of asteroid Ryugu reflects various degrees of parent body aqueous alteration and localized preservation of inherited nebular or molecular cloud history. The highly variable nature of the material indicates that the Ryugu organic matter is likely derived from material that was not subjected to long-term space weathering, and was only recently exposed to the asteroid surface. The macromolecular organic matter shows no record of high temperature impact heating of Ryugu, despite the asteroid being a rubble-pile body formed from impact debris, and geomorphological evidence that it experienced subsequent impact cratering (2, 3). This observation is consistent with the homogeneous reflectance spectra of Ryugu's surface (3).

Ryugu materials are much darker than primitive carbonaceous chondrites, despite having similar carbon contents (23, 47), so some other factor (or factors) must determine the albedo. Possibilities include the macromolecular organic matter mixed with phyllosilicates (this study) or nano-phase sulfides (24), both of which have high light absorption efficiency owing to their small grain sizes. Such complex aromatic macromolecules in C- and/or D-type asteroids could have supplied organic material, and possibly prebiotic molecules (47), to Earth.

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25 **Competing interests:** The authors declare that they have no competing interests.

Data and materials availability:

30 All images used in this study and machine-readable data files are available at the JAXA Data Archives and Transmission System (DARTS) at https://data.darts.isas.jaxa.jp/pub/hayabusa2/paper/sample/Yabuta_2022/ . Data for all Hayabusa2 samples and other data from the mission are available at the DARTS archive at <https://www.darts.isas.jaxa.jp/curation/hayabusa2> and <https://www.darts.isas.jaxa.jp/planet/project/hayabusa2/>, respectively. The samples of Ryugu are curated by the JAXA Astromaterials Science Research Group; distribution for analysis is through an Announcement of Opportunity available at <https://jaxa-ryugu-sample-ao.net> . The samples we used are listed in Table S1.

35

Supplementary Materials

Materials and Methods

Supplementary Text

Figs. S1 to S8

5 Tables S1 to S3

References (77–85)

10 **Fig. 1. Raman spectra and spectral parameters: comparison between Ryugu samples and chondrites.** (A): Average Raman spectra of Ryugu grains from Chamber A (samples A0108-6, -10, and -18) (in grey) and Chamber C (samples C0109-5, -9, and -12) (in black), compared to the meteorites Murchison (CM, green) and Orgueil (CI, yellow). All spectra were acquired in the same analytical conditions (11). (B-D): Average spectral parameters (error bars show standard deviations) determined from the Raman spectra: (B) FWHM_G as a function of ω_G ; (C) FWHM_D as a function of I_D/I_G ; (D) ω_G as a function of ω_D . Data are for individual grains from Chamber A (open circles) and Chamber C (black filled circles) compared to petrologic type 1 (Orgueil, orange diamond), unheated petrologic type 2 chondrites (green filled diamonds), heated petrologic type 2 chondrites (open blue diamonds) and petrologic type 3 chondrites (filled grey diamonds) (11). Petrologic type 2 chondrites were classified (16) as unheated (e.g., Murchison, Nogoya, and Tarda) or heated (e.g., Jbilet Winselwan and WIS 91600).

25 **Fig. 2. Micro-FTIR spectra of Ryugu samples compared to chondrites.** (A) Infrared transmission spectra (11) of six Ryugu grains from the aggregates A0108 and C0109 (black), heated CM chondrite (Jbilet Winselwan) (red), unheated CM Murchison (pink), and two CI chondrites Orgueil (light blue) and Ivuna (dark blue). All the spectra were baseline-corrected using spline curves and normalized by the peak height of the band at $\sim 1000\text{ cm}^{-1}$ ($\sim 10.00\text{ }\mu\text{m}$). Dashed lines indicate identified bands: silicate OH and SiO at 3685 to 3675 cm^{-1} (2.71 to $2.72\text{ }\mu\text{m}$) and $\sim 1000\text{ cm}^{-1}$ ($\sim 10.00\text{ }\mu\text{m}$), aliphatic C-H bands at 2960 cm^{-1} ($3.38\text{ }\mu\text{m}$, CH_3 asymmetric stretching), 2930 to 2925 cm^{-1} (3.41 to $3.42\text{ }\mu\text{m}$, CH_2 asymmetric stretching), 2855 to 2850 cm^{-1} (3.50 to $3.51\text{ }\mu\text{m}$, CH_3 and CH_2 symmetric stretching), 1460 cm^{-1} ($6.85\text{ }\mu\text{m}$) and 1380 cm^{-1} ($7.25\text{ }\mu\text{m}$, bending), other organic features at 1705 to 1690 cm^{-1} (5.87 to $5.92\text{ }\mu\text{m}$, C=O), and $\sim 1600\text{ cm}^{-1}$ ($\sim 6.25\text{ }\mu\text{m}$, aromatic with some water bending mode contribution). Some spectra show a peak at $\sim 1430\text{ cm}^{-1}$ ($\sim 6.99\text{ }\mu\text{m}$) due to carbonates. A broad water stretching band at $\sim 3400\text{ cm}^{-1}$ ($\sim 2.94\text{ }\mu\text{m}$) is observed, which is weaker in samples that was measured at 60°C or higher temperatures. The peaks at 2360 cm^{-1} ($4.24\text{ }\mu\text{m}$) are due to atmospheric CO_2 . The A0108-5 and C0109-1 Ryugu grains, and Murchison and Ivuna meteorites were measured at 60°C under N_2 flow. The Jbilet Winselwan meteorite was measured at 80°C under N_2 flow. The A0108-10 and C0109-12 Ryugu grains were measured at 80°C under vacuum. The Orgueil meteorite was measured at 130°C under vacuum. (B) Same as panel A, but for insoluble carbonaceous residues from the Ryugu samples (A0106 and C0107), compared to IOM from the heated CM meteorite Y-793321 (16), the CM Murchison (27), and CI meteorite Ivuna (27). The spectra were the averages of main fractions of A0106 and C0107, respectively, after baseline-correction using

spline curves and normalization by the peak height of the aromatic C=C band at $\sim 1600\text{ cm}^{-1}$ ($\sim 6.25\ \mu\text{m}$).

Fig. 3. STXM elemental maps and carbon-XANES spectra of Ryugu samples. STXM greyscale images of FIB sections extracted from the Ryugu grains (A) A0108-3, observed at 530 eV and (B) A0108-11, observed at 390 eV (11). In both panels, color overlays on both FIB sections are false-color maps of X-ray absorptions due to aromatic C (cyan), carbonate functional groups (magenta), and calcite minerals (yellow). Dashed circles and boxes indicate regions measured for panel E. (C) STXM image at 290 eV of insoluble carbonaceous residue from Ryugu sample C0107-18. The orange box shows the region in panel D. (D) X-ray absorption map of aromatic carbon (cyan), ketones (magenta), and carboxyl (yellow) functional groups. Circled features are solid nanoglobules except for feature 18f, which is a cluster of typical Ryugu IOM. (E) Carbon-XANES spectra for carbonaceous grains and matrix regions identified in panels A, B and D. IOM from the meteorites Orgueil and Murchison (black) are shown for comparison (11).

Fig. 4. STEM-EELS-EDS analysis of Ryugu samples. All scale bars are 500 nm. (A) False color bright field TEM image of the ultrathin section of C0109-11, indicating nanoglobules (magenta), Mg-phyllsilicates (blue), FeS (orange). (B) bright field TEM image of insoluble organic residue from a microtome slice of sample C0107, showing hollow and solid nanoglobules and fluffy materials. (C) High angle annular dark field (HAADF) STEM image of a FIB section of A0108-11 (region 11h in Fig. 3B) showing two magnetite grains (labelled Mag) adjacent to carbon-bearing Mg-rich phyllosilicates (Mg-phy) with Fe, Ni sulfide nanoparticles (Sulf). (D) HAADF STEM image of a vesicle in the large calcite grain from a FIB section of sample A0108-3 (region 3a in Fig. 3A). (E) EDS element map of carbon (magenta), oxygen (cyan) and sulfur (yellow) of the area shown in (C). (F) EDS element map of carbon (magenta), calcium (green), oxygen (yellow) and sulfur (cyan) of the vesicle shown in (D) showing diffuse organic matter, Fe,Ni-sulfides and Ca- sulfate. (G) Carbon EEL spectra from molecular carbonate incorporated into phyllosilicates, i.e., clay-bound carbon (C0109-11), an aromatic nanoglobule (A0108-39), an IOM-like nanoglobule (C0109-11), and nanodiamonds (A0108-8). Spectra were acquired at 0.02 eV per channel, and are smoothed to 0.4 eV resolution, after power law background subtraction and arbitrary scaling. (H) EDS spectra from molecular carbonate clay-bound carbon (C0109-11, green) and an insoluble organic residue (A0106-9, magenta). The asterisk (*) indicates a Cu background peak from the sample support and microscope.

Fig. 5. AFM-IR analysis of intact Ryugu grains A0108 and C0109. Composite AFM-IR images of the intact Ryugu grains (A) A0108-15 in tapping mode, $2 \times 2\ \mu\text{m}$ and (H) C0109-4, in contact mode, $3 \times 3\ \mu\text{m}$. Colors indicate the C=O (1720 cm^{-1} , $5.81\ \mu\text{m}$, red), C=C (1600 cm^{-1} , $6.25\ \mu\text{m}$, blue) and Si-O (1020 cm^{-1} , $9.80\ \mu\text{m}$, green) peaks. Each image has been normalized to its maximum peak value. Organic matter is widespread throughout each sample. In panel A, small organic globules are visible (red-brown) surrounded by a dominant phyllosilicate. The magenta box indicates the inclusion used for panel D. (B) AFM topographic map of the $2 \times 2\ \mu\text{m}$

area in panel A. (C) Visible light image ($75 \times 75 \mu\text{m}$) showing the location of the AFM-IR map (green square). (D) AFM-IR spectrum (red) of the globule indicated in panel A and shown in the inset, and background spectrum (green) taken in a region 100 nm away. The AFM-IR signal is shown in mV, which is proportional to optical depth (I/I_0). The C=C and C=O absorptions spectral region is also shown with a $\times 5$ factor for better visibility. (E-G) Synchrotron FTIR maps of the same $75 \times 75 \mu\text{m}$ area as panel C, of (G) the C=O (1720 cm^{-1} , $5.81 \mu\text{m}$, red), (F) C=C (1600 cm^{-1} , $6.25 \mu\text{m}$, blue) and (E) Si-O (1020 cm^{-1} , $9.80 \mu\text{m}$, green) peaks. Data were acquired with a $6 \times 6 \mu\text{m}$ beam size, sampled with $3 \mu\text{m}$ steps. Color bars show the integrated optical depths calculated for each band. (H) Organic matter in the Ryugu grain C0109-4 appears as red-purple inclusions standing out from the dominant phyllosilicate signal. Arrows indicate the positions used for the spectra in panel K. (I) AFM topographic map of the $3 \times 3 \mu\text{m}$ area. (J) Visible image ($51 \times 51 \mu\text{m}$) showing the location of the AFM-IR map (green square). (K) AFM-IR spectra of a C=O poor region (labelled 1 in panel H) and organic inclusions (labelled 2), compared to the average synchrotron FTIR spectrum. Red, blue and green tick marks indicate spectral positions corresponding to the AFM-IR images combined in panel H. (L-N) Same as panels E-G, but for the $51 \times 51 \mu\text{m}$ region shown in panel J. To aid color-blind readers, another version of this figure with alternatives colors is provided in fig. S5.

Fig. 6. NanoSIMS analysis of the intact Ryugu grains A0108 and C0109. (A-C) NanoSIMS images of a $\sim 3 \times 3 \text{ mm}$ area of a microtome slice from Ryugu grain A0108-11. (A) map of ^{16}O (cyan) and ^{12}C (red). White outlines indicate four carbon-rich particles embedded in the silicate matrix. (B) Hydrogen and (C) nitrogen isotope abundances of the same region. The ratios vary between the carbonaceous inclusions. (D-F) H and N- isotopic ratios for individual carbon-rich particles (regions of interest, ROIs) within Ryugu grains. Most ROIs are consistent (within the uncertainties) with the bulk averages; they are represented by box-and-whisker plots where the box size represents the inner 50% of data around the median (interquartile range, IQR) and the whiskers indicate the ± 1.5 IQR range beyond that. Dots indicate outliers beyond those ranges (hot-spots and cold-spots) from A0108 (blue) and C0109 (orange). In panel D, white dots indicate the grains shown in panels A-C and the error bar is 1σ . The distributions of H and N isotope ratios are consistent between panel D and those in E and F (acquired in different laboratories) and between the two Ryugu samples. The pink shaded region indicates the ranges of H and N hot-spots and cold-spots in primitive CM chondrite meteorites (50) and the green box indicates the ranges seen in CI chondrite Orgueil (46). The Ryugu outliers span a similar range to the CI and CM chondrites. (G) $\delta^{15}\text{N}$ as a function of $\delta^{13}\text{C}$ for the Ryugu grain A0109. The grey points indicate all carbon-rich ROIs, while blue circles are outliers ($>2\sigma$ away from bulk average). The pink region is the same as in panel D. The Ryugu outliers span a similar range to that seen in CM chondrites. The dashed vertical line indicates the bulk $\delta^{13}\text{C}$ of CI chondrite IOM.

Fig. 7. NanoSIMS analysis of insoluble carbonaceous residues from Ryugu grains A0106 and C0107. Hydrogen (A,B) and Carbon (C,D) maps for insoluble carbonaceous residues of A0106 and C0107, respectively, acquired at the same locations. The corresponding H (E, F) and N (G, H) isotope ratio maps show numerous micron-sized D-rich and ^{15}N -rich hot-spots. The carbon and hydrogen images indicate that these hot-spots consist of organic carbon. (I) Hydrogen

and (J) nitrogen box plot diagrams showing the distributions of isotope ratios in the insoluble carbonaceous residues A0106-8 (orange) and C0107-14 (blue). Open grey circles show hot-spots (or cold-spots), micron-sized areas with isotope ratios much higher (or lower) than the average composition. Large orange and blue circles indicate the bulk average value for each residue. Horizontal dashed lines indicate the mode of each distribution of hot-spots. Data for the IOM of CI (light blue), CM (green), CR (red) and the Tagish Lake (yellow) chondrites are shown for comparison. Filled circles are bulk values (45); for Tagish Lake subsamples 5b (less altered) and 11v (altered) (61) are shown separately. Upward pointing arrows (some extend beyond the plot) indicate the range of hot-spots reported for those meteorites (46, 56, 57). For Orgueil, the downward arrow indicates the extent of ¹⁵N-depleted cold-spots.