RESEARCH ARTICLE SUMMARY

COSMOCHEMISTRY

# Soluble organic molecules in samples of the carbonaceous asteroid (162173) Ryugu

**Hiroshi Naraoka *et al.***

**INTRODUCTION:** Surface material from the near-Earth carbonaceous (C-type) asteroid (162173) Ryugu was collected and brought to Earth by the Hayabusa2 spacecraft. Ryugu is a dark, primitive asteroid containing hydrous minerals that are similar to the most hydrated carbonaceous meteorites. C-type asteroids are common in the asteroid belt and have been proposed as the parent bodies of carbonaceous meteorites. The samples of Ryugu provide an opportunity to investigate organic compounds for comparison with those from carbonaceous meteorites. Unlike meteorites, the Ryugu samples were collected and delivered for study under controlled conditions, reducing terrestrial contamination and the effects of atmospheric entry.

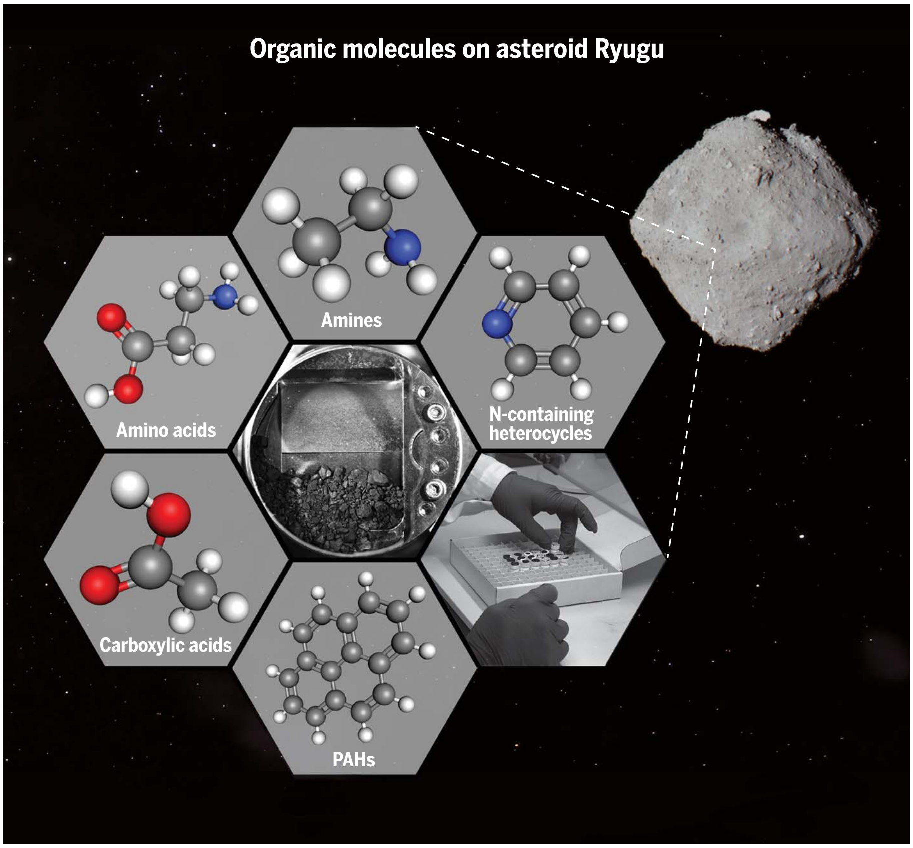
**RATIONALE:** Primitive carbonaceous chondrite meteorites are known to contain a variety of soluble organic molecules (SOMs), including prebiotic molecules such as amino acids. Meteorites might have delivered amino acids and other prebiotic organic molecules to the early Earth and other rocky planets. Organic matter in the Ryugu samples is the product of physical and chemical processes that occurred in the interstellar medium, the protosolar nebula, and/or on the planetesimal that became Ryugu's parent body. We investigated SOMs in Ryugu samples principally using mass spectrometry coupled with liquid or gas chromatography.

**RESULTS:** We identified numerous organic molecules in the Ryugu samples. Mass spectroscopy detected hundreds of thousands of ion signals, which we assigned to ~20,000 elementary compositions consisting of carbon, hydrogen, nitrogen, oxygen, and/or sulfur. Fifteen amino acids, including glycine, alanine, and α-aminobutyric acid, were identified. These were present as racemic mixtures (equal right- and left-handed abundances), consistent with an abiotic origin. Aliphatic amines (such as methylamine) and carboxylic acids (such as acetic acid) were also detected, likely retained on Ryugu as organic salts.

The presence of aromatic hydrocarbons, including alkylbenzenes, fluoranthene, and pyrene, implies hydrothermal processing on Ryugu's parent body and/or presolar synthesis in the interstellar medium. Nitrogen-containing heterocyclic compounds were identified as their alkylated homologs, which could have been synthesized from simple aldehydes and ammonia. In situ analysis of a grain surface showed heterogeneous spatial distribution of alkylated homologs of nitrogen- and/or oxygen-containing compounds.

**CONCLUSION:** The wide variety of molecules identified indicates that prolonged chemical processes contributed to the synthesis of soluble organics on Ryugu or its parent body. The highly diverse mixture of SOMs in the samples resembles that seen in some carbonaceous chondrites. However, the SOM concentration in Ryugu is less than that in moderately aqueously altered CM (Mighei-type) chondrites, being more similar to that seen in warm aqueously altered CI (Ivuna-type) chondrites. The chemical diversity with low SOM concentration in Ryugu is consistent with aqueous organic chemistry at modest temperatures on Ryugu's parent asteroid.

The samples collected from the surface of Ryugu were exposed to the hard vacuum of space, energetic particle irradiation, heating by sunlight, and micrometeoroid impacts, but the SOM is still preserved, likely by being associated with minerals. The presence of prebiotic molecules on the asteroid surface suggests that these molecules can be transported throughout the Solar System. ■



**SOMs detected in surface samples of asteroid Ryugu.** Chemical structural models are shown for example molecules from several classes identified in the Ryugu samples. Gray balls are carbon, white are hydrogen, red are oxygen, and blue are nitrogen. Clockwise from top: amines (represented by ethylamine), nitrogen-containing heterocycles (pyridine), a photograph of the sample vials for analysis, polycyclic aromatic hydrocarbons (PAHs) (pyrene), carboxylic acids (acetic acid), and amino acids (β-alanine). The central hexagon shows a photograph of the Ryugu sample in the sample collector of the Hayabusa2 spacecraft. The background image shows Ryugu in a photograph taken by Hayabusa2.

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RESEARCH ARTICLE

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# Soluble organic molecules in samples of the carbonaceous asteroid (162173) Ryugu

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The Hayabusa2 spacecraft collected samples from the surface of the carbonaceous near-Earth asteroid (162173) Ryugu and brought them to Earth. The samples were expected to contain organic molecules, which record processes that occurred in the early Solar System. We analyzed organic molecules extracted from the Ryugu surface samples. We identified a variety of molecules containing the atoms CHNOS, formed by methylation, hydration, hydroxylation, and sulfurization reactions. Amino acids, aliphatic amines, carboxylic acids, polycyclic aromatic hydrocarbons, and nitrogen-heterocyclic compounds were detected, which had properties consistent with an abiotic origin. These compounds likely arose from an aqueous reaction on Ryugu's parent body and are similar to the organics in Ivuna-type meteorites. These molecules can survive on the surfaces of asteroids and be transported throughout the Solar System.

A variety of organic molecules have been identified in carbonaceous chondrite meteorites, especially the meteorite types that experienced aqueous alteration (reactions with liquid water). Prebiotic molecules, such as amino acids, have been found in meteorite soluble organic matter (SOM) (*1*), suggesting that they could have been delivered to the early Earth (*2*, *3*). It is unclear which Solar System objects are the parent bodies of carbonaceous chondrites (*4*). Carbonaceous (C-type) asteroids, common in the asteroid belt, have been hypothesized as possible parent bodies of carbonaceous chondrites on the basis of spectroscopic similarities (*5*).

The Hayabusa2 spacecraft investigated the near-Earth C-type asteroid (162173) Ryugu. Ryugu has a low-albedo surface consisting of hydrous minerals and carbonaceous materials (*6*). Hayabusa2 collected ~5 g of samples from Ryugu's surface and delivered them to Earth on 6 December 2020 (*7*). Unlike meteorites, these samples were collected from a specific spot on the surface of a well-characterized asteroid and were retrieved without contamination from the biosphere. We analyzed Ryugu samples to characterize their SOM contents with the goal of determining the evolutionary history of these organic compounds. Organics could have formed and/or been modified by chemical processes in the molecular cloud from which the Solar System formed, in the protosolar nebula during the process of planet formation or on the planetesimal that became the parent body of Ryugu. Because the surface of Ryugu is exposed to the vacuum of space, irradiation by energetic particles (cosmic rays), heating by sunlight, and micrometeoroid impacts all could have altered the SOM.

### Ryugu samples investigated for SOM

All Ryugu samples are dominated by hydrous silicate minerals and contain organic matter similar to Ivuna-type carbonaceous (CI) chondrites (*8*). We investigated two samples, both collected during the first Hayabusa2 touchdown operation on 21 February 2019 (*7*, *9*).

Our main analysis was performed on an aggregate sample designated A0106 (fig. S1), consisting of grains <1 mm diameter with a total weight of 38.4 mg, which has elsewhere been investigated spectroscopically (*10*) and had its elemental and isotopic compositions analyzed (*11*). The A0106 sample has typical mineralogy for Ryugu consisting mainly of hydrous silicate minerals, including serpentine and saponite, with other associated minerals such as dolomite, pyrrhotite, and magnetite, indicating extensive aqueous alteration (*10*). We used solvent extracts to investigate the organic molecule content of A0106 following the analysis scheme shown in fig. S2. We also analyzed a single ~1-mm-sized grain (A0080) to determine the spatial distribution of organic compounds on its surface using in situ analysis methods (fig. S2).

### Elemental and isotopic composition

Elemental and isotopic analyses were performed using mass spectrometry (*11*). The A0106 sample contained 3.76 ± 0.14 wt % of total carbon (C), 1.14 ± 0.09 wt % of total hydrogen (H), 0.16 ± 0.01 wt % of total nitrogen (N), and 3.3 ± 0.7 wt % of total sulfur (S). The concentration of pyrolyzed oxygen (O), liberated at 1400°C under a helium gas flow, was 12.9 ± 0.42 wt %. The total CHNOS content (~21.3 wt %) is likely to comprise hydrous minerals, carbonates, sulfides, and organics, including macromolecular insoluble organic matter and SOM, because these are detected in other Ryugu samples (*10*, *12*). The stable isotopic compositions were determined and are expressed in δ notations as offsets from international standards (*11*): $\delta^{13}\mathrm{C} = -0.58 \pm 2.0‰$ relative to the Vienna Peedee Belemnite (VPDB) isotope reference, $\delta\mathrm{D} = +252 \pm 13‰$ relative to the Vienna Standard Mean Ocean Water (VSMOW) isotope reference, $\delta^{15}\mathrm{N} = +43.0 \pm 9.0‰$ relative to Earth atmospheric nitrogen, $\delta^{34}\mathrm{S} = -3.0 \pm 2.3‰$ relative to the Vienna Canyon Diablo Troilite (VCDT) isotope reference, and $\delta^{18}\mathrm{O} = +12.6 \pm 2.0‰$ relative to VSMOW [all analyses were done in triplicate (*11*)]. Because we analyzed small aggregate grains from the first touchdown site, we consider these values representative of the average bulk composition of Ryugu. The corresponding elemental ratios (by weight) were: C/N ratio = 23.5 ± 0.4, O/H ratio = 11.4 ± 0.6, and C/S ratio = 1.15 for A0106 (table S1).

The C, N, and H abundances are at the top of the ranges previously measured for carbonaceous chondrites (Fig. 1, A to D, and table S2). Our measured abundances of C, H, and S are consistent with an independent bulk chemical analysis using ~25 mg of the Ryugu samples, which suggests that Ryugu has a composition more similar to CI chondrites than to other types of meteorite (*12*). The heavy isotope enrichments of H (δD ~+250‰) and N (δ$^{15}$N ~ +40‰) that we found in Ryugu are similar to previous analyses of the Ivuna and Orgueil CI chondrites (*13*) (Fig. 1, E and F). However, elemental and isotopic heterogeneities on small scales have been found in other Ryugu samples (*14*, *15*).

## Diversity of organic molecules

We performed mass spectrometry on a methanol extract of the A0106 sample using electrospray ionization (ESI) and atmospheric pressure photoionization (APPI), coupled with Fourier transform–ion cyclotron resonance mass spectrometry (FT-ICR/MS) (*11*). These produced hundreds of thousands of ion signals with a mass to charge ratio ($m/z$) between 150 and 700 (Fig. 2, A, B, and F). The $m/z$ signals obtained by negative charge ESI [ESI(–)], positive charge ESI [ESI(+)], and positive charge APPI [APPI(+)] were assigned to almost 20,000 elementary compositions consisting of C, H, N, O, and/or S (Fig. 2, C to F, and fig. S3). This diversity of compounds is consistent with previous results for carbonaceous chondrites (*16*). The chemical diversity of ionizable species (small molecules detectable with mass spectrometry) is much higher than terrestrial biological samples.

We identified a continuum of small molecules to macromolecules, with a range of carbon oxidation states from nonpolar or minimally polar (CH-containing, polycyclic aromatic hydrocarbons, and branched aliphatic molecules) to polar small molecules (CHO-containing) with various functional groups (CHN, CHS, CHNO, CHOS, or CHNOS) with different solubility. The most intense signals in the mass spectra were assigned to polythionates (Fig. 2A), indicating formation through a complex sulfur polymer chemistry governed by redox processes involving water-mineral interactions with metal sulfides. A homologous series of known molecular targets (CHN$^+$ or CHNO$^+$) has previously been observed in a solvent extract of the Murchison meteorite, a different type of carbonaceous chondrite (*17*). The Ryugu data contain an abundant series of signals with repetitive mass differences, which we interpret as evidence for a systematic reaction network including methylation, hydration, hydroxylation, and sulfurization. We did not detect magnesium-containing organic compounds such as CHOMg or CHOSMg, which have been observed in other chondritic meteorites including Murchison (*18*). The compound distribution indicates low-temperature (≲150°C) hydrothermal processing on Ryugu's parent body (*19*). The high diversity of N- and S-bearing molecules in Ryugu indicates that chemical processes occurred involving N and S chemistry (*20*, *21*).

## Amino acids

We searched for amino acids in an acid-hydrolyzed hot water extract of the A0106 sample using a combination of three-dimensional high performance liquid chromatography with a high-sensitivity fluorescence detector (3D-HPLC/FD) at Kyushu University and ultrahigh performance liquid chromatography with fluorescence detection and high-resolution mass spectrometry (LC-FD/HRMS) at Goddard Space Flight Center (Fig. 3 and table S3). A total of 15 amino acids were both detected and quantified, and an additional five amino acids were tentatively identified but not quantified. These included proteinogenic (used by biology to form proteins) amino acids such as glycine ($C_2H_5NO_2$), D,L-alanine ($C_3H_7NO_2$), and D,L-valine ($C_5H_{11}NO_2$), as well as nonproteinogenic amino acids including β-alanine ($C_3H_7NO_2$); D,L-α-amino-*n*-butyric acid ($C_4H_9NO_2$); D,L-β-amino-*n*-butyric acid ($C_4H_9NO_2$); and several isomers of valine: D,L-norvaline, D,L-isovaline, and δ-amino-*n*-valeric acid (Fig. 3). The concentrations of each amino acid ranged from ~0.01 to 5.6 nmol g$^{-1}$ (table S3).

Many of the nonproteinogenic amino acids identified in the Ryugu extract are rare or nonexistent in terrestrial biology. The chiral amino acids detected in Ryugu are in approximately racemic mixtures [the abundance of the D- and L-enantiomers are approximately equal (D/L ~ 1)], indicating nonbiological origins. The detection of approximately equal amounts of D- and L-alanine, a common proteinogenic amino acid, indicates that this Ryugu sample is pristine, with negligible biological L-amino acid contamination. However, there were excesses of L-serine and L-valine. There was a trace (picomole levels) of L-valine content in procedural solvent blanks, so contamination is likely the cause of the nonracemic valine in the A0106 extract.

There are differences in the amino acid concentrations measured using LC-FD/HRMS and 3D-HPLC/FD, which we attribute to different acid hydrolysis conditions and analytical techniques. Different sample preparation and analysis approaches are known to yield distinct results when investigating meteorite amino acids (*22*). The much lower glycine abundances measured by LC-FD/HRMS (~0.6 nmol g$^{-1}$) than by 3D-HPLC/FD (5.6 nmol g$^{-1}$) could have been the result of multiple evaporation steps implemented during sample preparation before LC-FD/HRMS analysis. These evaporation steps could have resulted in the additional loss of volatile species such as hydrogen cyanide (HCN) and formaldehyde. HCN, formaldehyde, and ammonia can synthesize glycine under

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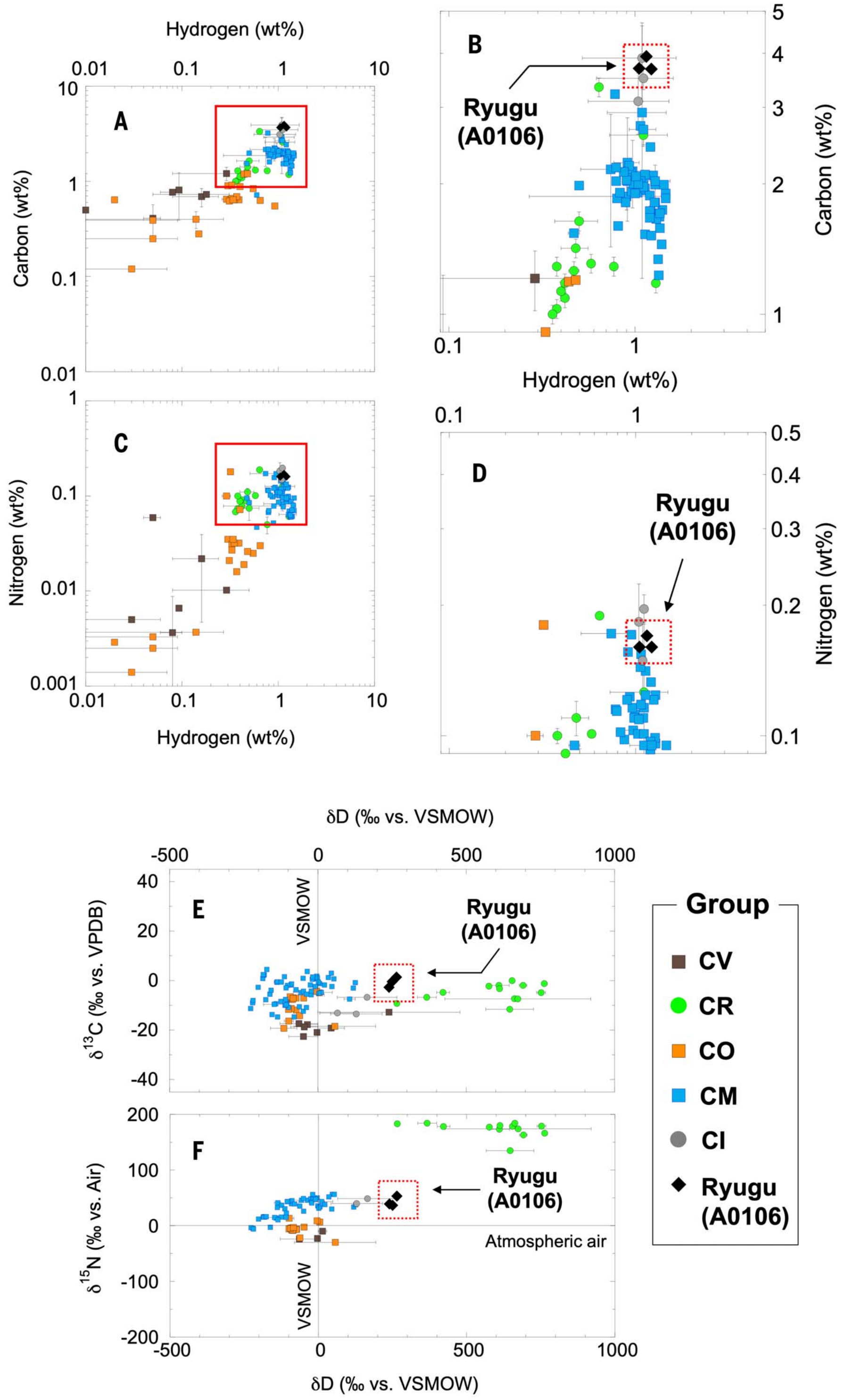


**Fig. 1. Carbon, nitrogen, and hydrogen contents and stable isotopic compositions for the Ryugu sample A0106 compared with carbonaceous chondrites.** Shown are: H-C (wt %) (**A**), enlarged H-C (wt %) (**B**), H-N (wt %) (**C**), enlarged H-N (wt %) (**D**), δD-$\delta^{13}$C (‰) (**E**), and δD-$\delta^{15}$N (‰) (**F**). Symbols shown in the legend indicate different groups of carbonaceous chondrite: Vigarano-type (CV), Renazzo-type (CR), Ornans-type (CO), Mighei-type (CM), and Ivuna-type (CI). Ryugu is most similar to the CI chondrites. Data sources for the carbonaceous chondrites are listed in table S2. Error bars are 1 SD for C, H and δD, and 2 SDs for N, $\delta^{13}$C, and $\delta^{15}$N.

alkaline conditions (Strecker synthesis) such as during sample preparation (*11*).

The overall amino acid distribution in the Ryugu extract is distinct from that in the CI meteorite Orgueil, with Ryugu also having lower amino acid abundances than Orgueil (*23*) (table S3). This could reflect different chemical formation environments or subsequent alteration conditions on their parent bodies. It is possible that Strecker synthesis could have been active during parent body aqueous alteration, producing glycine and other α-amino acids (those with an amino group one bond away from a carbonyl carbon) identified in the Ryugu extract. However, other amino acid formation and fractionation mechanisms must also have occurred on the Ryugu parent body, because β-, γ-, and δ-amino acids were also found (table S3). The straight-chain *n*-ω-amino acids, β-alanine, γ-amino-*n*-butyric acid, and δ-amino-*n*-valeric acid have higher abundances than other amino acids measured by LC-FD/HRMS in the Ryugu extract (table S3). This trend was similarly observed in previous measurements of thermally altered CO (Ornans-type) and CV (Vigarano-type) carbonaceous chondrites (*24*). These non–α-amino acids have been shown to be more resistant to thermal decomposition, surviving at temperatures up to ~300°C (*25*, *26*), which could explain their higher abundances (relative to α-amino acids) in the Ryugu sample.

### Aliphatic amines and carboxylic acids

Hot water extracts of A0106 were measured using liquid chromatography with fluorescence detection and time-of-flight mass spectrometry (LC-FD/TOFMS) (*11*). Aliphatic amines were detected (Fig. 4); methylamine ($CH_3NH_2$) was the most abundant, followed by ethylamine ($C_2H_5NH_2$) and isopropylamine [$(CH_3)_2CHNH_2$], then *n*-propylamine ($C_3H_7NH_2$). These amines are likely present as salts in the grains, because the free amines are highly volatile and reactive (boiling point; ~267 K for free $CH_3NH_2$ at 1013 hPa compared with ~503 K for $CH_3NH_2$ hydrochloride at ~20 hPa). We applied the same technique to hexane and dichloromethane (DCM) extracts of A0106, but did not find other volatile compounds that have previously been detected in carbonaceous chondrites, such as methanol ($CH_3OH$), ethanol ($C_2H_5OH$), methyl formate ($HCOOCH_3$), acetone ($CH_3COCH_3$), diethyl ether ($C_2H_5OC_2H_5$), or acetonitrile ($CH_3CN$), which were all below the detection limits (fig. S4). This is consistent with our interpretation that the amines were retained as salts, not trapped volatiles in inclusions, insoluble organic material, or minerals. Ammonium salts (and amine salts) are known to be the major reservoir of nitrogen on the dwarf planet Ceres and in comets (*27*, *28*). A previous hyperspectral microscope study of Ryugu grains found evidence of amine or ammonium bonds (NH; ~3.1 μm) (*29*).

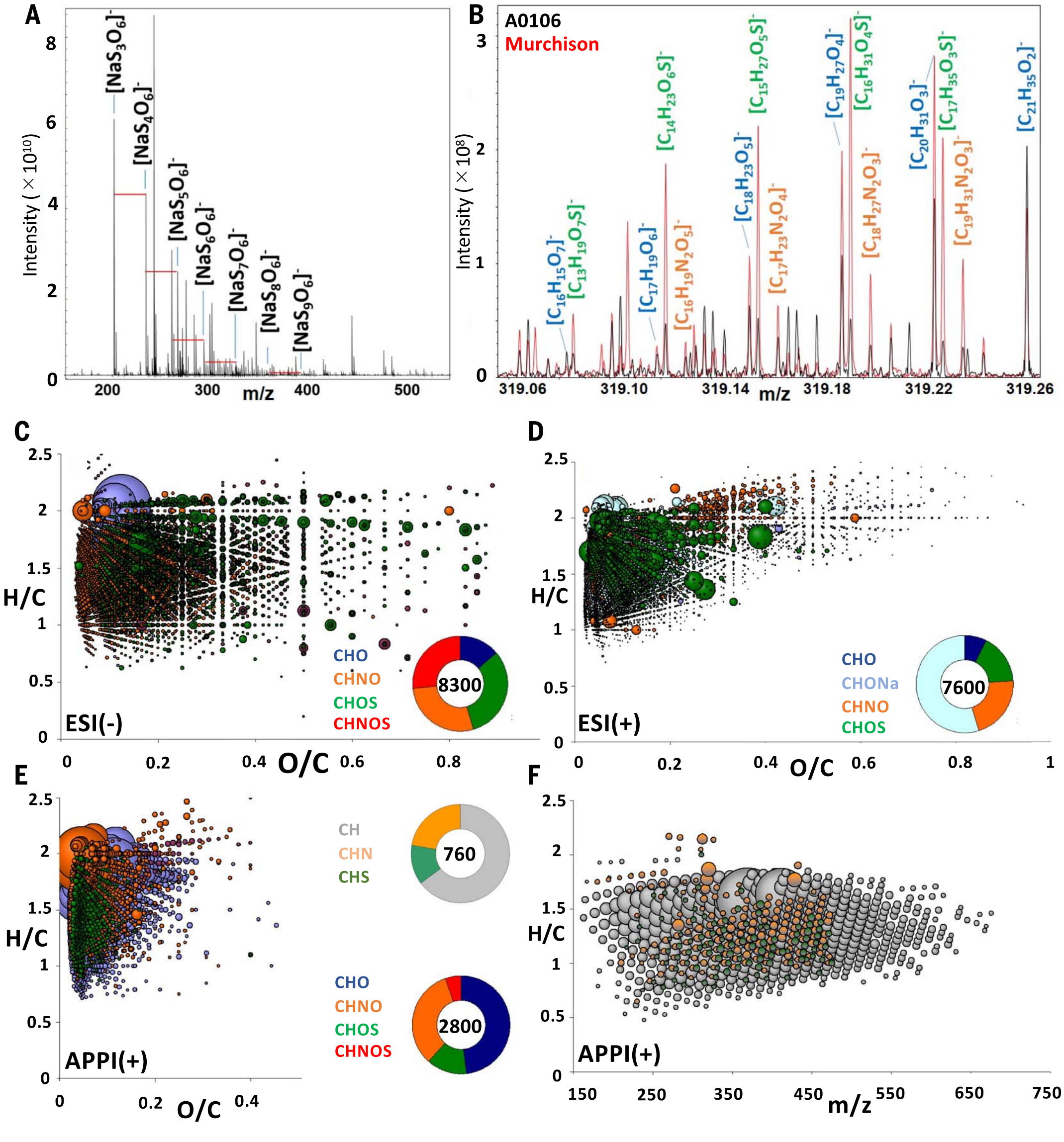


**Fig. 2. Mass spectra of the Ryugu extract and derived elemental compositions.** (**A**) Mass spectrum of negative ESI FT-ICR/MS with peaks assigned polythionates with three to nine sulfur atoms. (**B**) Detail around *m/z* = 319 with annotated elementary compositions, with Ryugu (black) compared with the Murchison meteorite (red) (*16*). (**C** to **E**) O/C-H/C atomic ratios of the compositional data as obtained with ESI(−) (C), ESI(+) (D), and APPI(+) (E). Colored annuli enclose the number of molecules assigned, with colors indicating the relative ratios of the chemical families (indicated in each legend). Data points use the same colors to indicate the family, and the size of each bubble indicates the intensity of the signal in the mass spectrum. (**F**) H/C atomic ratio as a function of *m/z*, measured using APPI(+), for nonoxygenated CH, CHN, and CHS compositions; colors are the same as used in (E). Figure S3 shows separate plots of each chemical family identified in (C) to (E).

Isopropyl amine, which has a branched chain, was more abundant than straight-chain propylamine. This is consistent with previous results for several carbonaceous chondrites (*30*, *31*). The predominance of branched chains could indicate that synthesis of these molecules occurred by a radical reaction. Alternatively, it might indicate a period of heating during aqueous alteration, because branched-chain carbon compounds are more thermodynamically stable than their straight-chain counterparts. The presence of methyl-, ethyl-, and propylamines in Ryugu is distinct from Orgueil, which contains butylamines ($C_4H_9NH_2$) at about half the abundance of *n*-propylamine (*32*). If this same ratio occurred in the Ryugu sample, butylamines would have been above the detection limits. The amines in Ryugu are also unlike the dust grains collected from the comet Wild 2 by the Stardust mission, for which only methyl- and ethylamine were detected (*33*).

Monocarboxylic acids (MCAs) were searched for using gas chromatography quadrupole mass spectrometry of the hot water extract of A0106. Formic acid (5.7 μmol $g^{-1}$) and acetic acid (9.5 μmol $g^{-1}$) were detected, and were the only MCAs above the detection limits (fig. S5 and table S4). MCAs are typically among the most abundant organic compounds in organic rich carbonaceous chondrites such as the CM (Mighei-type) meteorites Murchison and Murray and the CR (Renazzo-type) chondrites (*34*–*36*). We detected MCAs in A0106 with high concentrations and low molecular diversity, both consistent with low-temperature hydrothermal processing, as is thought to have occurred on Ryugu's parent body (*10*). The concentration of MCAs is known to decrease with increasing aqueous and/or thermal alteration experienced by meteorite samples (*36*, *37*). Although MCAs in A0106 have low molecular diversity, the concentrations of formic and acetic acids are high, similar to those observed in highly aqueously altered carbonaceous chondrites including ALH 83100 (a CM) and Orgueil and Ivuna (both CIs) (*38*, *39*). Aliphatic MCAs are substantially more abundant in the Ryugu sample than other structurally related organics such as aliphatic amino acids and amines. This is consistent with carbonaceous chondrites, for which the concentrations of MCAs (and most other meteoritic organic compounds) are known to decrease with increasing molecular weight (*1*, *36*). We found the same relationship between formic acid and acetic acid in A0106 (table S4).

## Polycyclic aromatic hydrocarbons

We applied 2D gas chromatography with time-of-flight mass spectrometry (GC×GC-TOFMS) to the organic solvent extracts of the A0106 sample. We detected aromatic hydrocarbons at below parts per million abundances, including from alkylbenzenes

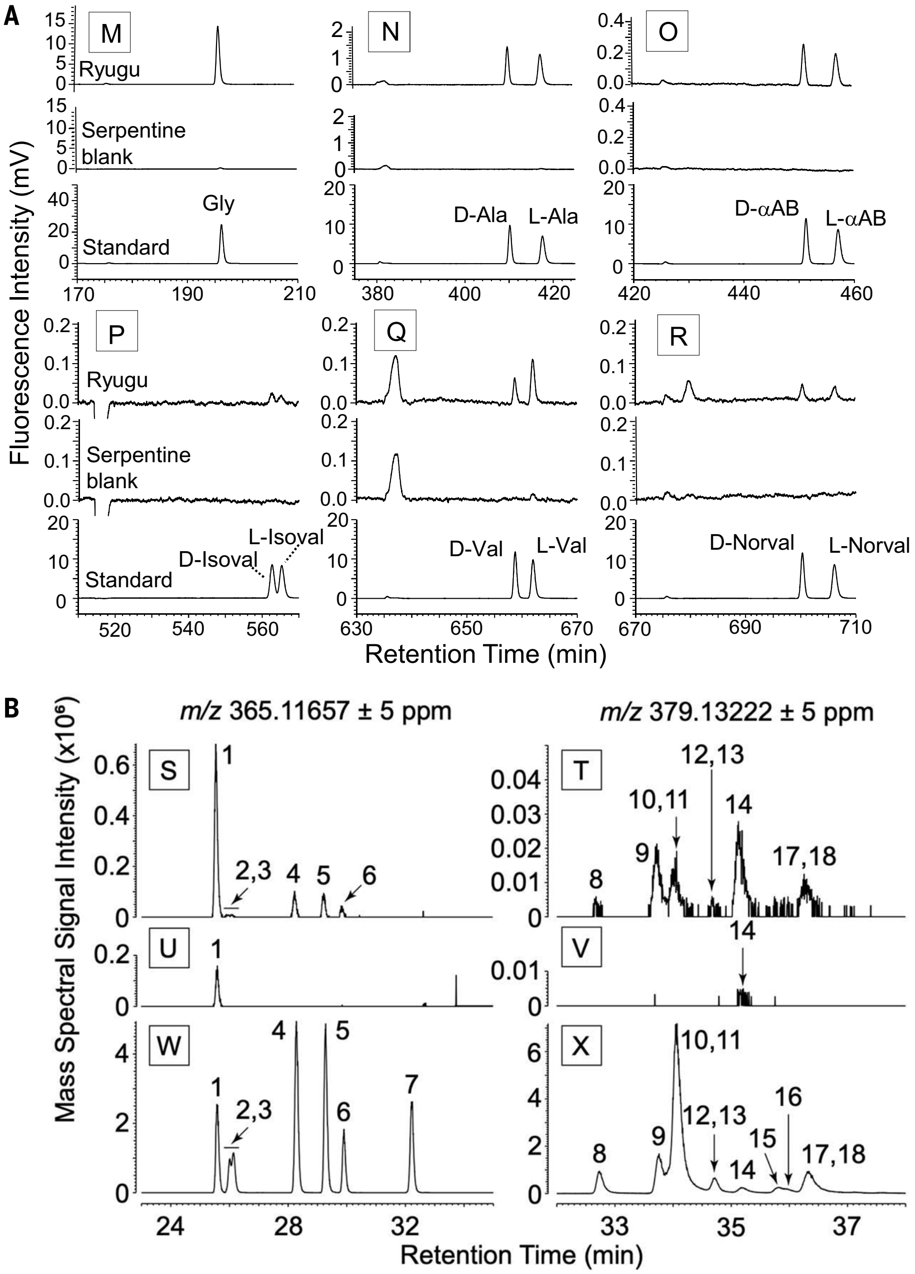


**Fig. 3. Amino acids detected in the hydrolyzed hot water extract of the Ryugu sample.** (**A**) Partial chromatograms obtained by 3D-HPLC/FD for glycine (Gly) (M), alanine (Ala) (N), α-amino-*n*-butyric acid (αAB) (O), isovaline (Isoval) (P), valine (Val) (Q), and norvaline (Norval) (R). In each panel, the Ryugu extract (top traces) is compared with baked serpentine blanks (middle traces) and terrestrial standards (lower traces). (**B**) Ion-extracted chromatograms from LC-FD/HRMS analysis of Ryugu sample (S and T), a serpentine blank (U and V), and mixed amino acid standards (W and X). Amino acids composed of four and five carbon atoms were detected in the Ryugu sample. Peak identifications are: (1) γ-amino-*n*-butyric acid, (2) D-β-amino-isobutyric acid, (3) L-β-amino-isobutyric acid, (4) D-β-amino-*n*-butyric acid, (5) L-β-amino-*n*-butyric acid, (6) α-amino-isobutyric acid, (7) D,L-α-amino-*n*-butyric acid, (8) 3-amino-2,2-dimethylbutyric acid, (9) γ-amino-*n*-valeric acid, (10) 3-amino-2-methylbutyric acid, (11) 4-amino-3-methylbutyric acid, (12) 3-amino-2-methylbutyric acid, (13) R-3-amino-2-ethylpropanoic acid, (14) δ-amino-*n*-valeric acid, (15) L-4-amino-2-methylbutyric acid, (16) D-4-amino-2-methylbutyric acid, (17) γ-amino-*n*-valeric acid, and (18) 3-amino-3-methylbutyric acid.

and polycyclic aromatic hydrocarbons (PAHs) (Fig. 5). Homologous series of large alkylated PAHs were identified using APPI FT-ICR/MS and assigned to methylation and hydration (Fig. 2C). The presence of alkylated PAHs (including alkylbenzenes) in the organic solvent extracts was confirmed using Fourier-transform infrared (FTIR) spectroscopy (11), which showed bands due to $CH_2$ or $CH_3$ bonds at 2850 to 2950 $cm^{-1}$ (3.51 to 3.39 μm) (fig. S6A). The highest abundance PAHs were fluoranthene and pyrene (which contain four benzene rings) followed by chrysene/triphenylene (also four rings) and methylated fluoranthene and pyrene. Smaller PAHs containing two rings (naphthalene) and three rings (phenanthrene and anthracene) were detected at lower abundances.

Fluoranthene and pyrene are structural isomers (both have the formula $C_{16}H_{10}$) that are present in roughly equal amounts in CM chondrites (40–42). In the Ryugu sample, however, fluoranthene is substantially less abundant than pyrene (Fig. 5C). In the CI meteorite Ivuna, both fluoranthene and pyrene are below the detection limits, although phenanthrene and anthracene are abundant (43). Because selective synthesis is not expected to favor three- or four-ring PAHs, their variable relative abundances in meteorites could be due to aqueous fluid flow in their parent body. It has been proposed that three-ring and four-ring PAHs could be spatially separated during aqueous alteration of the Ivuna parent body because of their different aqueous solubilities (an effect known as asteroidal chromatography) (44). On Earth, hydrothermal petroleum often contains alkylbenzene and lower abundances of fluoranthene than of pyrene (45). Therefore, the difference in proportions of PAHs between Ryugu and carbonaceous chondrites could be due to different aqueous alteration effects on different parent bodies. However, we cannot rule out the possibility that the different proportions could be inherited from presolar syntheses in the interstellar medium, where PAHs are ubiquitous (46). PAHs with higher stability and lower volatility might have preferentially survived accretionary and hydrothermal processes on the parent body. For example, the higher thermal stability and lower volatility of pyrene over fluoranthene could have contributed to the unequal abundances of the two species in the Ryugu sample. Vaporization fractionation could be responsible for the lower abundance (compared with pyrene) of smaller PAHs such as naphthalene.

The FTIR spectrum of the fine suspended material in the water extract of the A0106 grain (fig. S6C) has its strongest absorption band at ~1000 $cm^{-1}$ (~10 μm) due to silicates (Si-O bonds). Other bands are present at 750 to 1650 $cm^{-1}$ (13.3 to 6.1 μm). Peaks at these wavelengths have often been observed in the interstellar medium (47) and have been assigned to large PAHs (47–50). The broad peaks at ~1400 $cm^{-1}$ (7.14 μm) could also have a contribution from carbonates (51). The lack of the aromatic C–H stretching bands at ~3030 $cm^{-1}$ (3.30 μm) suggests that the PAHs present in the Ryugu water extract are highly depleted in hydrogen, indicating large, unsaturated structures. Because small- to moderate-sized PAHs can be extracted with organic solvents such as DCM and methanol (MeOH), which we applied

**Fig. 4. Aliphatic amines in the hot water extract of Ryugu.** Chromatograms were measured using LC-FD/TOFMS for methylamine (**A**), ethylamine (**B**), and n-propylamine and iso-propylamine (**C**). In each panel, the Ryugu sample (top trace) is compared with a baked serpentine blank (middle trace) and terrestrial standards (bottom trace). Asterisks indicate peaks introduced by the reagent used for derivatization.

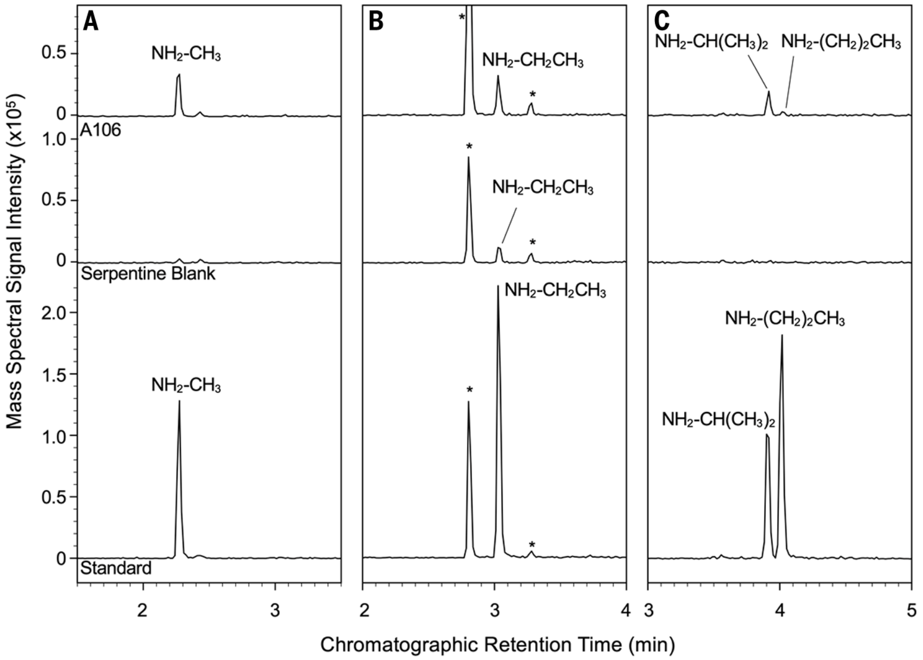
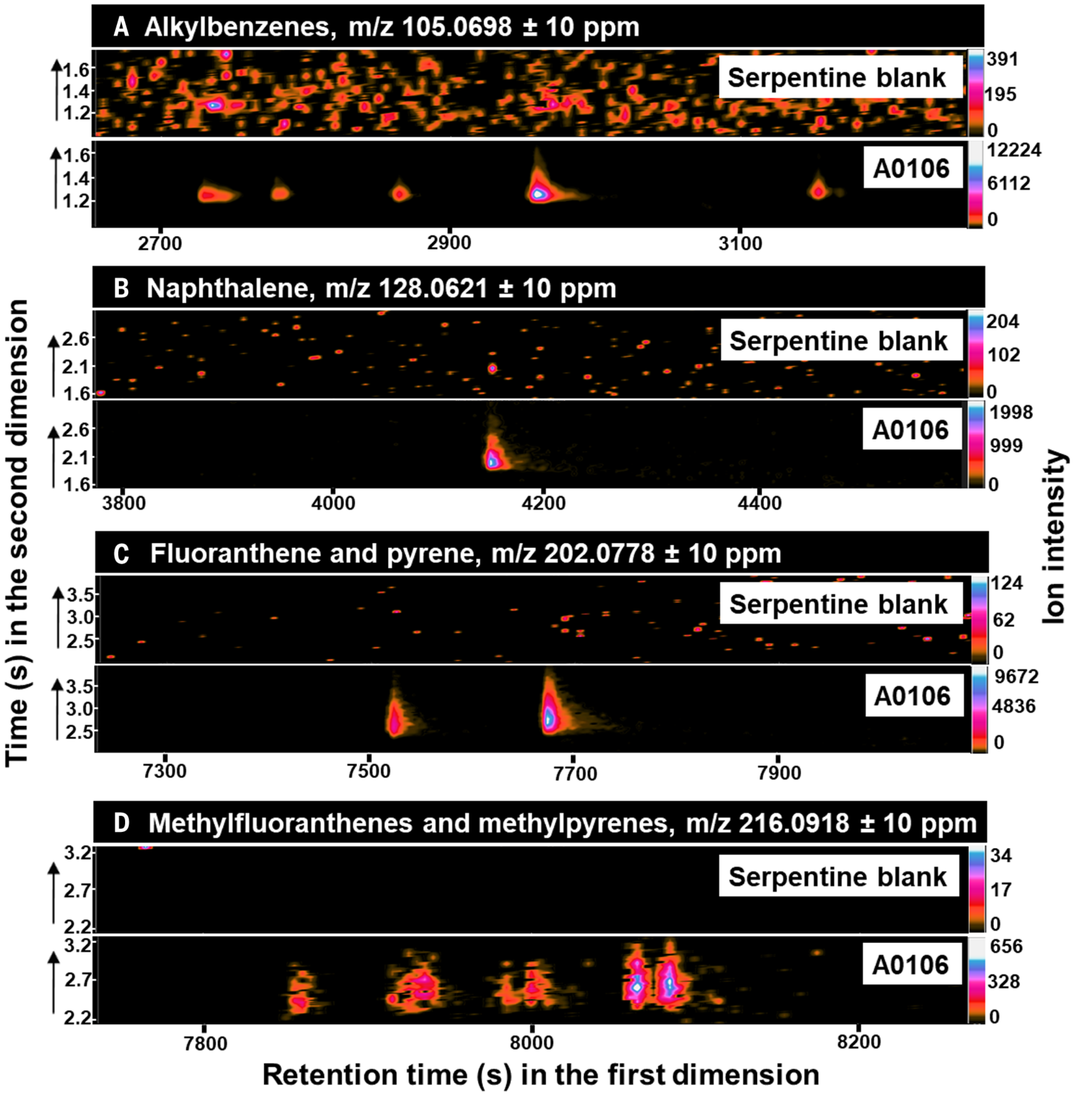


**Fig. 5. Aromatic hydrocarbons in the Ryugu extract.** Data were measured using GC×GC-TOFMS. (**A**) Alkylbenzenes in the hexane extract ($m/z$ = 105.0698). (**B**) Naphthalene ($m/z$ = 128.0621) in the DCM extract. (**C**) Fluoranthene (~7520 s) and pyrene (~7680 s) ($m/z$ = 202.0778) in the DCM extract. (**D**) Methylfluoranthenes and methylpyrenes ($m/z$ = 216.0918) in the DCM extract. In each panel, the Ryugu sample (lower) is compared with a fbaked serpentine blank (upper). Colors indicate concentration, as indicated on the color bar.



before extraction with water (fig. S2), we expect that the PAHs suspended in the water extract were dominated by very large and less soluble molecules that were not removed by the earlier analysis steps. The FTIR spectrum of the Ryugu sample is unlike those of other extraterrestrial materials, including carbonaceous chondrites. It is most similar to astronomical observations of interstellar PAHs (*50*), so it is possible that presolar PAHs (formed in the interstellar medium) were incorporated into Ryugu's parent body during its accretion, and then survived the subsequent aqueous alteration.

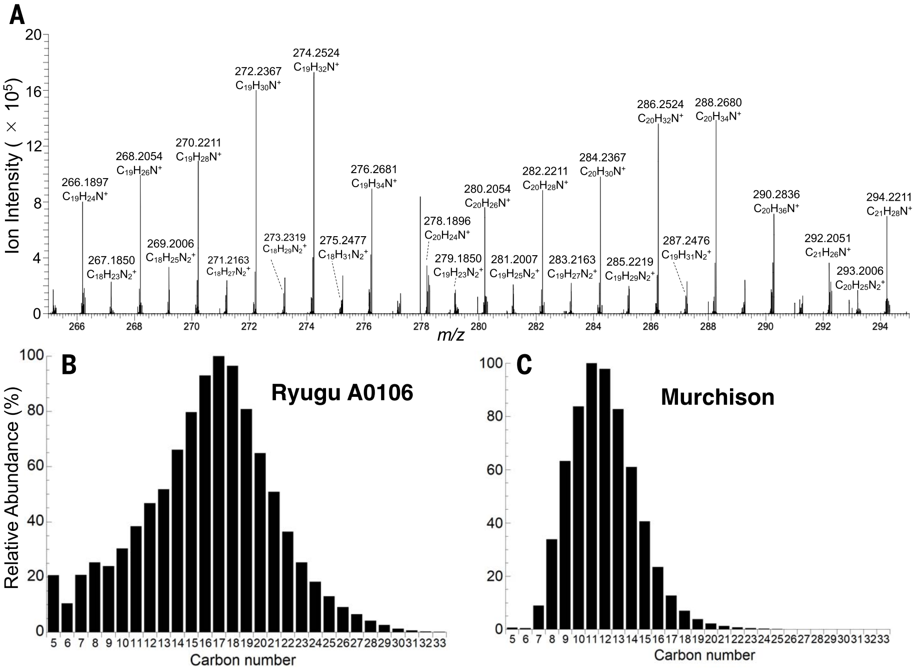


**Fig. 6. CHN compounds in the methanol extract determined using nanoLC/high resolution mass spectrometry.** (**A**) Example region of the mass spectrum of the A0106 sample (*73*), with peaks assigned to $C_nH_{2n-16}N^+$, $C_nH_{2n-14}N^+$, $C_nH_{2n-12}N^+$, $C_nH_{2n-10}N^+$, $C_nH_{2n-8}N^+$, $C_nH_{2n-6}N^+$, $C_nH_{2n-4}N^+$, $C_nH_{2n-15}N_2^+$, $C_nH_{2n-13}N_2^+$, $C_nH_{2n-11}N_2^+$, $C_nH_{2n-9}N_2^+$, and $C_nH_{2n-7}N_2^+$ (where $C_n$ is the carbon number). (**B** and **C**) Histograms showing the relative abundances of $C_nH_{2n-4}N^+$ (alkylpyridines) as a function of carbon number, for Ryugu (B) and Murchison (*11*) (C). Abundances are normalized to a peak value of 100. The Ryugu distribution peaks at a higher carbon number than Murchison.

### N-containing heterocyclic compounds

The methanol extract of A0106 was examined using nano-liquid chromatography/high-resolution mass spectrometry (nanoLC/HRMS) (*11*). Several classes of alkylated N-containing heterocyclic molecules were identified, and their presence was confirmed using ESI FT-ICR/MS (Fig. 2E). These alkylated N-heterocycles included pyridine, piperidine, pyrimidine, imidazole, or pyrrole rings with various amounts of alkylation (Fig. 6A). Alkylpyridines and alkylimidazoles (aromatic N-heterocycles) have previously been found in CM chondrites, whereas alkylpiperidines (aliphatic N-heterocycles) are more abundant in CR chondrites (*52*); the difference in relative abundances might reflect differing redox conditions on the meteorite parent bodies.

The alkylpyridine ($C_nH_{2n-4}N^+$) homologs that we identified in the Ryugu sample (Fig. 6B) have a different distribution pattern from those in CM chondrites (Fig. 6C). The number of C atoms in the Ryugu compounds was mostly between 11 and 22, with a maximum at 17, whereas the C number distribution for Murchison had a lower range, mostly from 8 to 16 with its maximum at 11. This difference could be caused by differences in the histories of hydrothermal activity (such as the water/rock ratio), solar radiation, and/or cosmic ray irradiation (*53*, *54*). Gas phase reactions at high temperature can produce polymeric series of N-containing heterocyclic compounds such as those found in meteorites (*55*). If the bell-shaped distributions

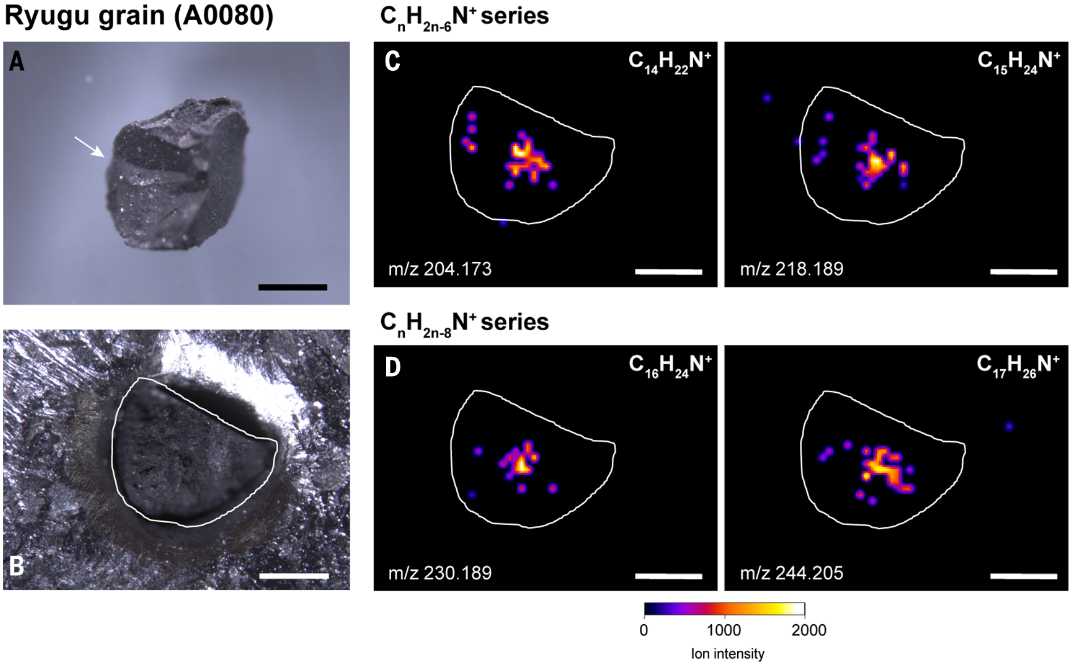


**Fig. 7. Spatial distribution of CHN compounds on the surface of Ryugu grain A0080.** (**A** and **B**) Optical images before sample preparation (A) and after embedding in an alloy (B). White arrow in (A) indicates the grain surface embedded in (B). Maps of organic molecule distribution were measured by DESI coupled with HRMS, for the $C_nH_{2n-6}N^+$ series ($n$ =14, 15) (**C**) and $C_nH_{2n-8}N^+$ series ($n$ =16, 17) (**D**) molecules. White outlines indicate the boundary between the A0080 grain and the surrounding metal. Scale bars, 500 μm.

for Ryugu and Murchison were caused by gas-phase synthesis, then the two bodies could have inherited their SOM from different regions of the solar nebula.

Alternatively, N-heterocyclic compounds can be synthesized through a reaction pathway using ammonia and simple aldehydes such as formaldehyde (*56*), which would require high abundances of aldehyde and ammonia in the Ryugu body in the past. Because formaldehyde and ammonia were abundant in the interstellar medium and the protosolar nebula (*57*, *58*), the Ryugu organic material might have inherited these characteristics from a molecular cloud environment. In interstellar-ice analog experiments at very low temperature, hexamethylenetetramine (HMT: $C_6H_{12}N_4$) is produced as a major compound from single-carbon compounds and ammonia (*59*). However, we did not detect HMT in any extracted fraction of our sample using FT-ICR/MS and nanoLC/HRMS. HMT has previously been detected in aqueous extracts of carbonaceous meteorites including Murchison (*60*). Under hydrothermal conditions, HMT is degraded to formaldehyde and ammonia at ~150°C, especially at alkaline pH, producing N-containing compounds such as amino acids and N-heterocycles (*61*, *62*). Because the aqueous fluid on Ryugu's parent body was probably alkaline ($pH > 9$) (*10*), we attribute the lack of HMT to the aqueous alteration history.

### Sample surface distribution of organic molecules

We performed in situ analysis of the surface of the A0080 grain using electrically charged MeOH spraying by desorption electrospray ionization (DESI) coupled with HRMS (*11*). We detected >200 positive ion peaks ranging from $m/z = 80$ to 400, which we assigned to molecules containing the elements CHN, CHO, or CHNO and their alkylated homologs (Fig. 7 and fig. S7). These compounds were located on the uppermost layer of the intact grain surface; no treatment (e.g., cutting or polishing) was performed on A0080. Methanol spraying detached the molecules from the surface, implying weak interactions between the CHN compounds and the major minerals of the grain. The CHN compounds that we observed were mostly consistent with those detected in the methanol extract of the aggregate sample (A0106); however, the molecular distribution was not identical (Fig. 6A and fig. S7, B and C). We attribute the different molecular distributions to heterogeneous distribution of the SOM compounds between the Ryugu grains and/or differences in sensitivity between the two analytical methods.

Our molecular imaging shows spatial heterogeneity of the compounds across the surface of A0080 (Fig. 7). We expect the ion intensity to depend on the topography of the sample surface, which was not flattened. Although the region with highest SOM concentration is also the highest topographical area, the molecular imaging shows micrometer-scale differences in the spatial distribution of the CHN compounds depending on their molecular sizes and families (Fig. 7). Varying spatial distribution among different molecular sizes and compound classes were also observed among CHO and CHNO compounds. Previous studies have identified different spatial distributions of CHN compounds on CM chondrites, including Murray (*63*). The distinct distributions could be caused by interactions between organic molecules and minerals during aqueous alteration (*64*). Other synthesis routes could also explain these results, for example through SOM reactions with minerals and fluids in the Ryugu parent body (*65*).

### Implications for asteroid organic chemistry

The molecular diversity of SOM in the Ryugu sample A0106 is as high as previously found for carbonaceous chondrites, and includes poly-sulfur-bearing species. By contrast, the molecular diversity of low-molecular-weight compounds, including aliphatic amines and carboxylic acids, was lower in the Ryugu sample than previously measured in the Murchison meteorite. The total SOM concentration in the A0106 sample was less than that of Murchison, closer to those of the unheated CI chondrites Ivuna and Orgueil.

The Ryugu organic matter seems to have been affected by aqueous alteration, which produced aromatic hydrocarbons similar to hydrothermal petroleum on Earth (*45*). However, the Ryugu samples have never experienced high temperatures (*12*). This is unlike the heated CI chondrites Yamato 980115 and Belgica 7904 [parent body temperatures ≲150°C (*66*, *67*)], which contain very low (or undetectable) abundances of amino acids and PAHs (*23*, *68*, *69*). Remote-sensing observations of Ryugu collected by the Hayabusa2 spacecraft showed evidence for thermal metamorphism at 300 to 400°C on Ryugu's parent body (*70*). However, we estimate that the effective heating temperature was ≲150°C for the Ryugu SOM (*11*). We ascribe this difference to protection of the organics by incorporation into hydrous minerals.

The SOM detected in the A0106 and A0080 samples indicates that Ryugu's surface materials host organic molecules despite the harsh environment caused by solar heating, ultraviolet irradiation, cosmic-ray irradiation, and high vacuum. The uppermost surface grains on Ryugu protect organic molecules, unlike meteorites, for which atmospheric ablation during Earth entry removes or modifies analogous near-surface material. Organic compounds on asteroids can be ejected from the surface by impacts or other causes (*71*, *72*), dispersing them through the Solar System (or beyond) as meteoroids or interplanetary dust particles. Therefore, SOM on C-type asteroids could be a source of organics delivered to other bodies.

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**availability:** The mass spectra and chromatographic data used in this study are available at the JAXA Data Archives and Transmission System (DARTS) at https://data.darts.isas.jaxa.jp/pub/hayabusa2/paper/sample/Naraoka_2022/ (*73*). Other data from the mission are available at the DARTS archive https://www.darts.isas.jaxa.jp/planet/project/hayabusa2/ and on the Small Bodies Node of the NASA Planetary Data System https://pds-smallbodies.astro.umd.edu/data_sb/missions/hayabusa2/. Material was allocated by the JAXA Astromaterials Science Research Group; the sample catalog is available at https://darts.isas.jaxa.jp/curation/hayabusa2/, and distribution for analysis is through an Announcement of Opportunity available at https://jaxa-ryugu-sample-ao.net. The samples of Ryugu used in this study were mostly consumed during the analysis, with the remaining materials returned to JAXA.

## SUPPLEMENTARY MATERIALS

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Materials and Methods
Supplementary Text
Figs. S1 to S8
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