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

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Abstract: The Hayabusa2 spacecraft collected samples from the surface of Ryugu, a characterized carbonaceous near-Earth asteroid and returned them isolated from the biosphere. The Ryugu samples have traces of origin of the Solar System and provide a window to the organics available at the origin of life. We analyzed organic molecules extracted from the surface samples of Ryugu. They contain a variety of molecules containing the atoms CHNOS, formed by methylation, hydration, hydroxylation, and sulfurization reactions. The amino acids, aliphatic amines, carboxylic acids, polycyclic aromatic hydrocarbons, and nitrogen-heterocyclic compounds detected are consistent with an abiotic origin. These compounds likely arose from aqueous reaction on proto-Ryugu and show similarities with extant Ivuna-type meteorites. The prebiotic molecules on the asteroid surface can be transported throughout the Solar System. (125/100-125 words)

Main Text: 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 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, a major component in the asteroid belt, have been hypothesized as possible parent bodies of carbonaceous chondrites, based on spectroscopic similarities (5).

The Hayabusa2 spacecraft investigated the near-Earth carbonaceous (C-type) asteroid (162173) Ryugu. Ryugu has a low-albedo, consisting of hydrous minerals and carbonaceous materials (6). Hayabusa2 collected ~5 grams of samples from Ryugu's surface and delivered them to Earth on 2020 December 6 (7). Unlike meteorites, these samples were collected from a specific spot on the surface of a well-characterized asteroid and returned without being obscured by the contamination from the biosphere. We analyzed Ryugu samples to characterize their SOM contents, with the goal of determining the evolutionary history of these organic compound. Organics could have formed and/or been modified by chemical processes in the molecular cloud from which the Solar System form, in the protosolar nebula during the process of planet formation, or the planetesimal which 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, could have altered the SOM.

Ryugu samples investigated for SOM

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

Our main analysis was performed on an aggregate sample (A0106) (fig. S1), consisting of grains less than 1 mm diameter with a total weight of 38.4 mg, which has elsewhere been investigated spectroscopically (10), and analyzed for elemental and isotopic compositions of elements (11). The A0106 sample has typical mineralogy for Ryugu's grain, 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 molecular content of A0106, following the analysis scheme 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 elemental analysis/isotope ratio mass spectrometry (EA/IRMS) (11). The A0106 sample contains 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), which is liberated at 1400°C under a helium gas flow, was 12.9 ± 0.42 wt.%. The total CHNOS content (~21.3 wt.%) would be comprised of hydrous minerals, carbonates, sulfides and organics including macromolecular insoluble organic matter and SOM as these elements are detectable from other Ryugu samples (10, 12). The stable isotopic compositions were determined by the δ notations using international standards (11): $\delta^{13}\text{C} = -0.58 \pm 2.0$ ‰ relative to Vienna Pee Dee Belemnite (VPDB) (11), $\delta\text{D} = +252 \pm 13$ ‰ relative to Vienna Standard Mean Ocean Water (VSMOW) (11), $\delta^{15}\text{N} = +43.0 \pm 9.0$ ‰ relative to Earth atmospheric nitrogen (11), and $\delta^{34}\text{S} = -3.0 \pm 2.3$ ‰ relative to Vienna Canyon Diablo Troilite (VCDT) (11), $\delta^{18}\text{O} = +12.6 \pm 2.0$ ‰ relative to VSMOW (11) (all $n = 3$). Because we analyzed small aggregate grains from the first touchdown

site, we consider these values representative values of the average bulk composition of Ryugu. The corresponding elemental ratios (by weight) are: C/N ratio = 23.5 ± 0.4 , O/H ratio = 11.4 ± 0.6 , C/S ratio = 0.35 for A0106 (table S1).

The C, N and H abundances are at the top of the ranges of carbonaceous chondrites (Fig. 1A-D). Our measured abundances of C, H and S are consistent with a bulk chemical analysis using ~25 mg of the Ryugu samples, which concluded that Ryugu is more similar to CI chondrites than other meteorites (12). The heavy isotope enrichments of H ($\delta D \sim +250$ ‰) and N ($\delta^{15}N \sim +40$ ‰) we find in Ryugu are similar to previous analyses of the Ivuna and Orgueil CI chondrites (13) (Fig. 1E-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 100 and 700 (11) (Fig. 2A). The signals were assigned into almost 20,000 elementary compositions, consisting of C, H, N, O and/or S (Fig. 2A-C). 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 identify 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), having different solubility. The most intense signals in the mass spectra were assigned to polythionates (Fig. 2A), suggesting 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^+ , $CHNO^+$) have previously been observed in a solvent extract of the Murchison meteorite, a different type of carbonaceous chondrite (17). There are 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).

These compounds were produced in low temperature ($\lesssim 150$ °C) hydrothermal processing on Ryugu's parent body (19). The high diversity of N- and S-bearing molecules in Ryugu indicates chemical processes occurred involving nitrogen and sulfur 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 3-dimensional high performance liquid chromatography with a high-sensitivity fluorescence detector (3D-HPLC/FD) at Kyushu University and ultrahigh performance liquid chromatography with tandem UV fluorescence detection and Orbitrap 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, while an additional 5 amino acids were tentatively identified, but not quantified. These included the proteinogenic (in the

genetic code) amino acids such as glycine ($\text{C}_2\text{H}_5\text{NO}_2$), D,L-alanine ($\text{C}_3\text{H}_7\text{NO}_2$) and D,L-valine ($\text{C}_5\text{H}_{11}\text{NO}_2$), as well as the non-proteinogenic amino acids β -alanine ($\text{C}_3\text{H}_7\text{NO}_2$), D,L- α -amino-*n*-butyric acid ($\text{C}_4\text{H}_9\text{NO}_2$), D,L- β -amino-*n*-butyric acid ($\text{C}_4\text{H}_9\text{NO}_2$), 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 non-proteinogenic amino acids identified in the Ryugu extract are rare or non-existent in terrestrial biology. The chiral amino acids are present in Ryugu as approximately racemic mixtures, meaning the abundance of the D- and L-enantiomers of the amino acid are approximately equal ($\text{D/L} \sim 1$), indicating non-biological 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 trace (pico-mole levels) L-valine content in procedural solvent blanks, contamination is likely the non-racemic 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 ($\sim 0.6 \text{ nmol g}^{-1}$) than by 3D-HPLC/FD (5.6 nmol g^{-1}) could have been the result of multiple evaporation steps implemented during sample preparation prior to 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 alkaline conditions (Strecker synthesis) such as during sample preparation (11).

The overall amino acid distribution in the Ryugu extract is distinct from that in CI Orgueil meteorite, 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 the asteroid parent bodies. It is possible that the Strecker synthesis could have been active during parent body aqueous alteration to produce glycine, as well as the other α -amino acids (where an amino group exists one bond away from a carbonyl carbon) identified in the Ryugu extract. However, other amino acid formation and fractionation mechanisms must additionally 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 and CV carbonaceous chondrites (24). These non- α -amino acids have been shown to be more resistant to thermal decomposition, surviving at temperatures up to $\sim 300^\circ\text{C}$ (25, 26), which could explain their higher relative abundances than to α -amino acids in the Ryugu sample.

Aliphatic amines and carboxylic acids

Hot water extracts of A0106 were studied using liquid chromatography with fluorescence detection and electrospray time-of-flight mass detection (LC-FD/ToFMS) (11). Aliphatic amines were detected (Fig. 4); methylamine (CH_3NH_2) was the most abundant followed by ethylamine ($\text{C}_2\text{H}_5\text{NH}_2$) and isopropylamine ($(\text{CH}_3)_2\text{CHNH}_2$), then *n*-propylamine ($\text{C}_3\text{H}_7\text{NH}_2$). These amines are likely present as salts in the grains, because the free amines are highly volatile and reactive

(boiling point; -6.3°C for free CH_3NH_2 at 1013 hPa, compared to $\sim 230^{\circ}\text{C}$ for CH_3NH_2 hydrochloride at ~ 0.11 Pa). 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 ($\text{C}_2\text{H}_5\text{OH}$), methyl formate (HCOOCH_3), acetone (CH_3COCH_3), diethyl ether ($\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$), or acetonitrile (CH_3CN), which were all below the detection limits (fig. S3). This supports our interpretation that the amines were retained as salts, not trapped volatiles in inclusions or 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). Furthermore, Ryugu grains that were examined using the MicrOmega hyperspectral microscope, showed evidence of amine or ammonium bond (NH ; ~ 3.1 μm) (29).

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 synthesis of these molecules occurred by radical addition. Alternatively, it might indicate a period of heating process during aqueous alteration, because branched-chain carbon compounds are more thermodynamically stable than their straight-chain counterparts. The presence of methyl, ethyl, and propyl amines in Ryugu is distinct from Orgueil, which contains butylamines ($\text{C}_4\text{H}_9\text{NH}_2$) 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 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 (GC-QMS) of the hot water extract of A0106. Formic acid (5.7 $\mu\text{mol g}^{-1}$) and acetic acid (9.5 $\mu\text{mol g}^{-1}$) were detected, the only MCAs above the detection limits (fig. S4, table S4). MCAs are typically among the most abundant organic compounds especially in organic rich carbonaceous chondrites, such as Mighei-types (CM) Murchison and Murray, and Renazzo-type (CR) chondrites (34-36). We detected MCAs in A0106 with high concentrations and low molecular diversity, both consistent with low-temperature hydrothermal processing thought to have been experienced by Ryugu. The concentration of MCAs decreases with increasing aqueous and/or thermal alteration experienced by meteorite samples (36-37). Although MCAs in A0106 have little molecular diversity, the concentrations of formic and acetic acids are high, similar to those observed in the highly aqueously altered carbonaceous chondrites including ALH 83100 (CM) and Orgueil and Ivuna (CI) (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 find the same relationship between formic acid and acetic acid in A0106 (table S4).

Polycyclic aromatic hydrocarbons

We applied two-dimensional gas chromatography with time-of-flight mass spectrometry (GC \times GC-TOFMS) to the organic solvent extracts of the A0106 sample. We detected aromatic hydrocarbons at sub-ppm abundances, including from alkylbenzenes 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-transformed infrared (FTIR) spectroscopy (11), which showed bands due to CH_2/CH_3

bonds at 2850-2950 cm^{-1} (3.51-3.39 μm) (fig. S5A). The highest abundance PAHs were fluoranthene and pyrene (four rings) followed by chrysene/triphenylene (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 ($\text{C}_{16}\text{H}_{10}$) that are present in roughly equal amounts in CM-type chondrites (40-42). In the Ryugu sample, however, fluoranthene is substantially less abundance than pyrene (Fig. 5C). In the CI-type Ivuna meteorite, both fluoranthene and pyrene are below the detection limits, though 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 due to their different aqueous solubilities (an effect known as asteroidal chromatography) (44). On Earth, hydrothermal petroleum often contains alkylbenzene concurrent with 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 pre-solar syntheses in the interstellar medium, where PAHs are ubiquitous (46). PAHs with higher stability and lower volatility might have better 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. Vaporization fractionation could be responsible for the lower abundance (compared to pyrene) of smaller PAHs, such as naphthalene.

The FTIR spectrum of the fine suspended material in the water extract of the A0106 grain (fig. S5C) has its strongest absorption band at $\sim 1000 \text{ cm}^{-1}$ ($\sim 10 \mu\text{m}$), which arise from a silicate structure (Si-O bonds). Other bands are present at 750-1650 cm^{-1} (13.3-6.1 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 $\sim 1400 \text{ cm}^{-1}$ (7.14 μm) could also have a contribution from carbonates (51). The lack of the aromatic C-H stretching bands at $\sim 3030 \text{ cm}^{-1}$ (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-size PAHs can be extracted with organic solvents such as DCM and methanol before extraction with water (fig. S2), it is reasonable that these PAHs suspended in the water extract would dominate by very large and less soluble. 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, so it is possible that pre-solar PAHs (formed in the interstellar medium) were incorporated into Ryugu's parent body during its accretion and survived the subsequent aqueous alteration.

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-type chondrites, while

alkylpiperidines (aliphatic N-heterocycles) are more abundant in CR-type chondrites (52); the differing relative abundances might reflect the redox conditions on the meteorite parent bodies.

The alkylpyridine ($C_nH_{2n-4}N^+$) homologues we identify in the Ryugu sample (Fig. 6B) have a different distribution pattern from those in CM-type chondrites (Fig. 6C). The number of carbon atoms in the Ryugu compounds is mostly between 11 and 22 with its maximum at 17, while the carbon number distribution for the Murchison meteorite has a lower range, mostly from 8 to 16 with its maximum at 11. This difference could be caused by differences in the hydrothermal activity, water/rock ratio, and/or histories of solar radiation and cosmic ray irradiation (53, 54). Gas phase reactions at high temperature can produce polymeric series of N-containing heterocyclic compounds, like those found in meteorites (55). If the bell-shaped distributions for Ryugu and Murchison are due to gas-phase synthesis, 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 are abundant in the interstellar medium and the protosolar nebulae (57, 58), the Ryugu organic material might have inherited 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 $\sim 150^\circ\text{C}$, 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 ($\text{pH} > 9$) (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 methanol spraying by desorption electrospray ionization (DESI) coupled with HRMS (11). We detected over 200 positive ion peaks, ranging from m/z 80 to 400, which we assign to molecules containing the elements CHN, CHO or CHNO and their alkylated homologues (Fig. 7, fig. S6). These compounds were located on the uppermost layer of the intact grain surface, because no treatment (such as 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 observed were mostly consistent with those detected in the methanol extract of the aggregate sample (A0106); however, the molecular distribution was not identical (Fig. 7). The different molecular distributions could be attributable to i) heterogeneous distribution of the SOM compounds between the Ryugu grains and/or ii) 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 μm -scale differences in 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 identified the different spatial distributions of the CHN compounds on CM-type chondrites including Murray (63). The distinct distributions could be due to interactions of organic molecules with minerals, during aqueous alteration (64). Other synthesis routes could also explain these results, for example via SOM reactions with minerals and fluids in the Ryugu parent body (65).

Implications for asteroid organic chemistry

The molecular diversity of the SOM in the Ryugu sample A0106 is as high as previously found for carbonaceous chondrites, and includes polysulfur-bearing species. In contrast, the molecular diversity of low-molecular-weight compounds, including aliphatic amines and carboxylic acids, was smaller 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 the high temperatures (12), unlike the heated CI-type chondrites, such as Yamato 980115 and Belgica 7904 (parent body temperature $\lesssim 150^{\circ}\text{C}$ (66, 67)), contain very little (or undetectable) amino acids and PAHs (23, 68, 69). Remote-sensing observations of Ryugu, collected by the Hayabusa2 spacecraft, showed evidence for thermal metamorphism at $300\text{--}400^{\circ}\text{C}$ on the Ryugu parent body (70). However, we estimated the effective heating temperature was $\lesssim 150^{\circ}\text{C}$ for the SOM. 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, UV 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 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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Competing interests: The authors declare no competing interests.

Data and materials availability: All data used in this study are available at the JAXA Data Archives and Transmission System (DARTS) at https://www.darts.isas.jaxa.jp/pub/hayabusa2/paper/sample/Naraoka_2022/. 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/. The samples of Ryugu for this study were mostly consumed with the remaining materials are kept in JAXA. 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>.

Supplementary Materials

Materials and Methods

Supplementary Text

Figs. S1 to S7

Tables S1 to S5

References (73–100)

Data S1 to S12

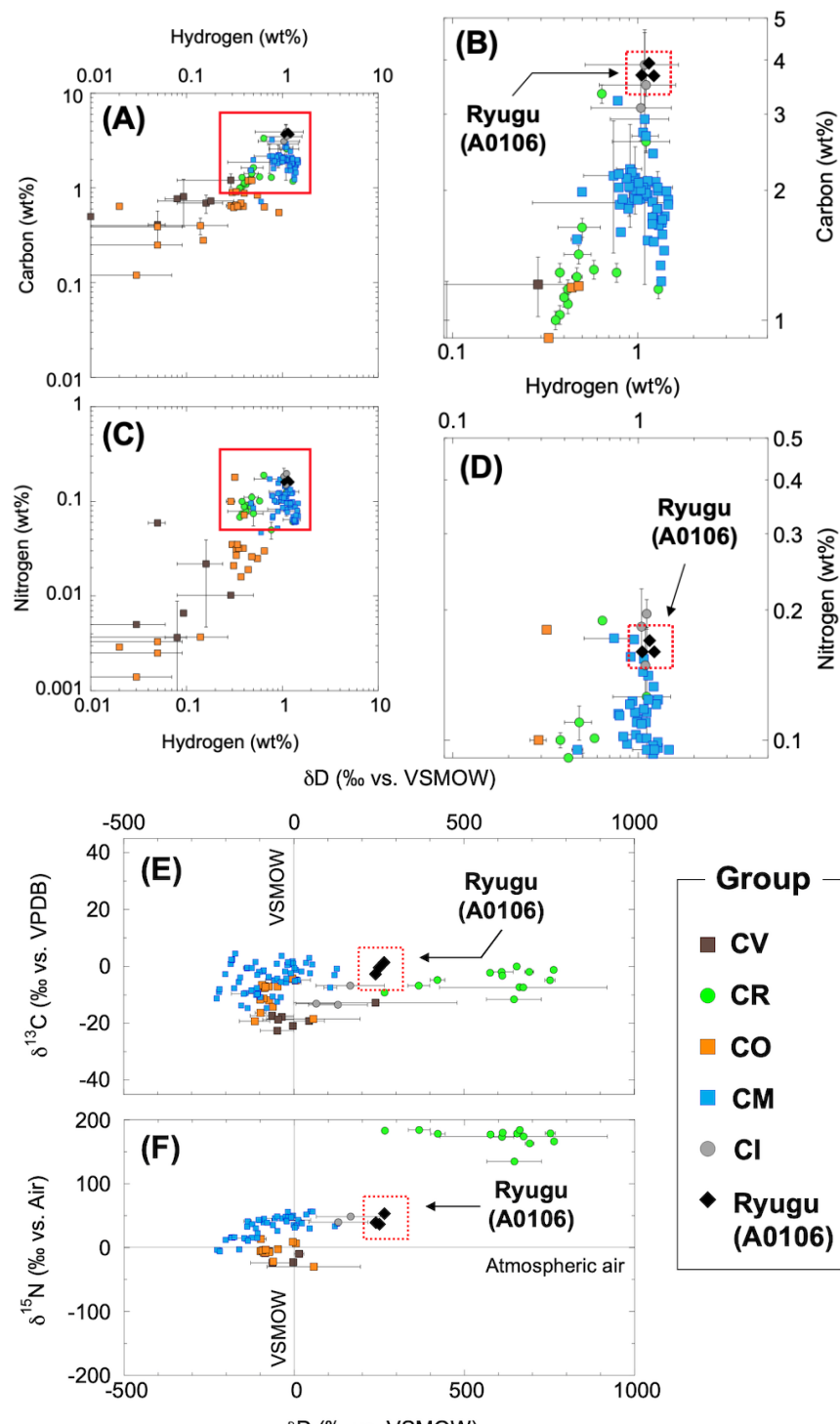


Fig. 1. Carbon, nitrogen, and hydrogen contents and stable isotopic compositions for Ryugu grains in the Ryugu sample A0106 compared with carbonaceous chondrites. (A) H-C (wt%), (B) enlarged H-C (wt%), (C) H-N (wt%), (D) enlarged H-N (wt%), (E) $\delta D - \delta^{13}C$ (‰), and (F) $\delta D - \delta^{15}N$ (‰). Isotope values for carbonaceous chondrite meteorites (CV, Vigarano-type; CR, Renazzo-type; CO, Ornans-type; CM, Mighei-type; and CI, Ivuna-type) are shown for comparison. Ryugu is most similar to the CI chondrites. Data sources for the carbonaceous chondrites are listed in [table S2](#).

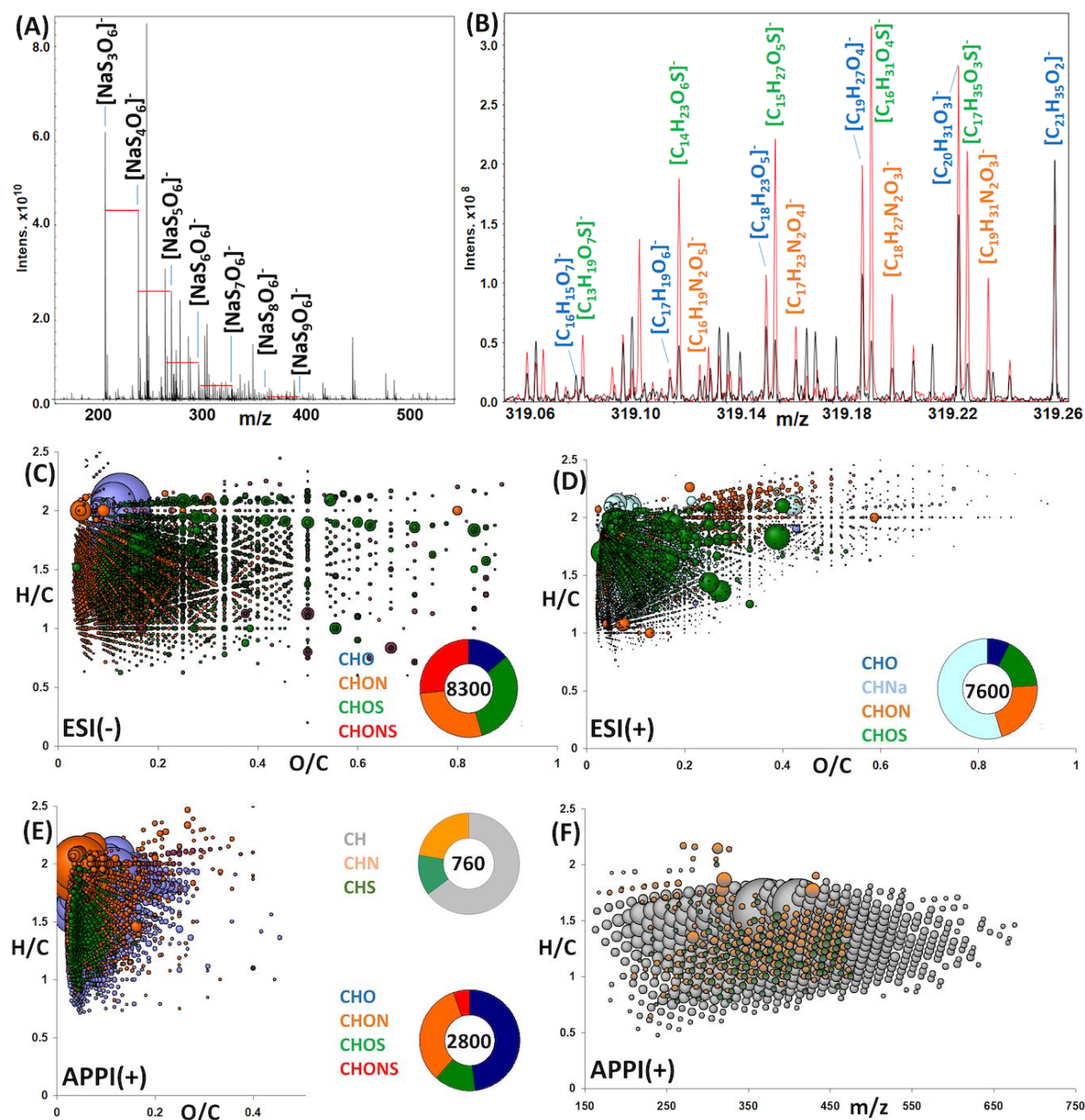


Fig. 2. Mass spectra of the Ryugu extract and derived elemental compositions. (A) Mass spectrum of negative ESI FTICR/MS with peaks assigned to S_3 - S_9 polythionates. (B) Detail around $m/z = 319$ with annotated elementary compositions, with Ryugu (black) compared to the Murchison meteorite (red); (C) O/C-H/C atomic ratios of the compositional data as obtained with electrospray ionization in negative and (D) positive ESI as well as (E) positive APPI. Colors indicate chemical family (indicated in each legend) and the size of the bubble indicates the intensity of the original signals in the mass spectra. (F) m/z -H/C atomic ratio diagram determined by positive APPI for non-oxygenated CH, CHN and CHS compositions include soluble hydrocarbons, and N- and S-containing compounds, respectively. The color legends are the same as used in (E).

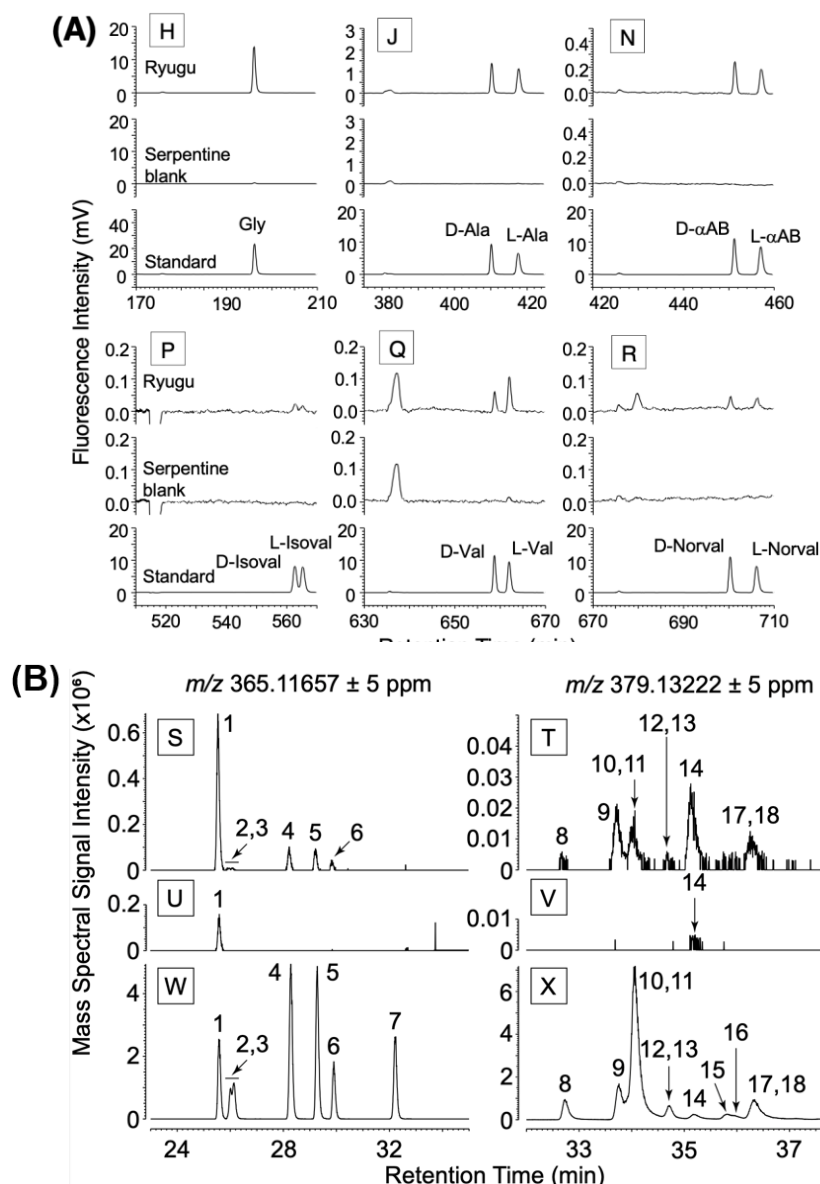


Fig. 3. Amino acids detected in the hydrolyzed hot water extract of the Ryugu sample. (A) Partial chromatograms obtained by 3D-HPLC/FD demonstrating that glycine (Gly) (H), alanine (Ala) (J), α-amino-*n*-butyric acid (αAB) (N), isovaline (Isoval) (P), valine (Val) (Q), and norvaline (Norval) (R) are identified. 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 generated by 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 4 and 5 carbon atoms were detected in the Ryugu sample. Peak identifications for such compounds include: 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, 18) 3-amino-3-methylbutyric acid.

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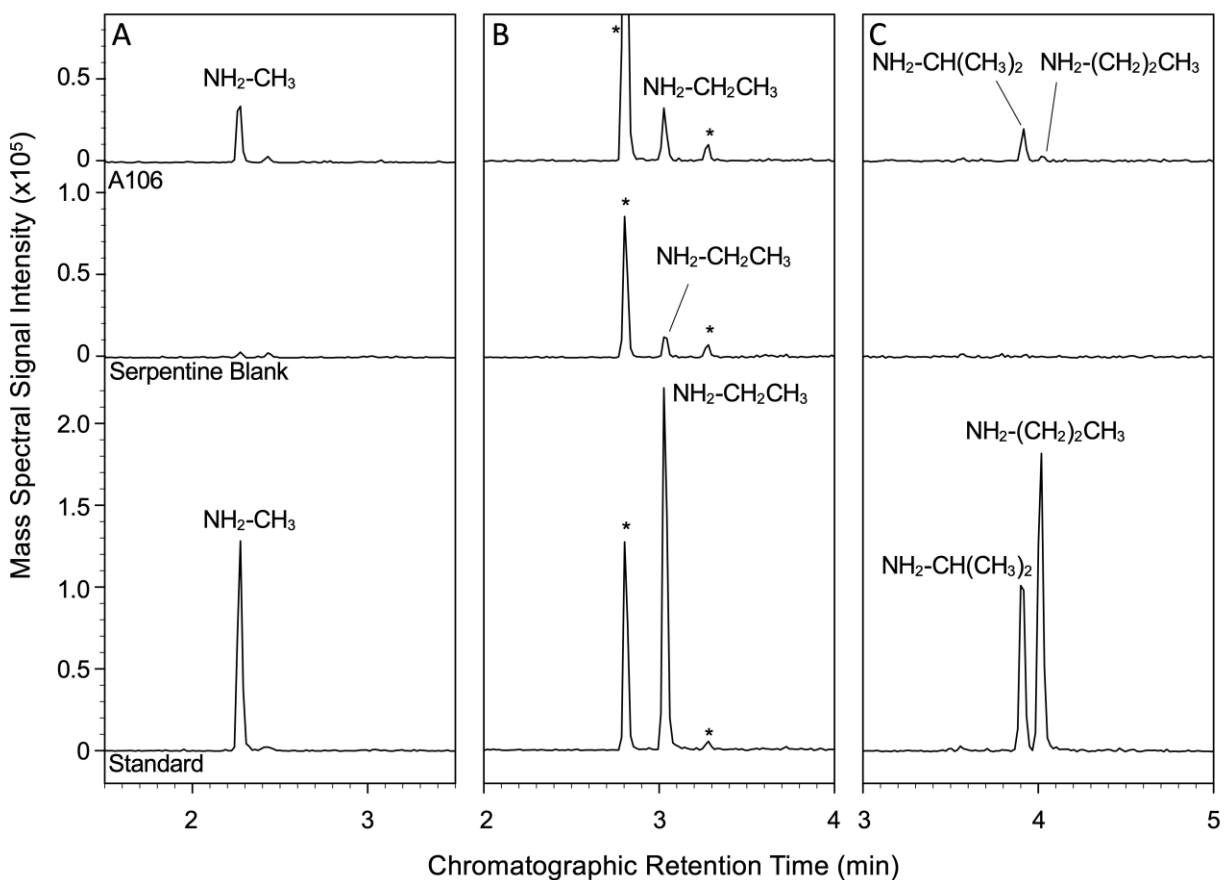


Fig. 4. Aliphatic amines in the hot water extract of Ryugu. Chromatograms measured using liquid chromatography equipped with a fluorescence detector and a time of flight mass spectrometer. (A) methylamine (B) ethylamine, (C) n-propylamine and iso-propylamine. In each panel, the Ryugu sample (upper trace) is compared with a baked serpentine blank (middle trace) and terrestrial standards (lower trace). Asterisks indicate peaks introduced by the reagent used for derivatization.

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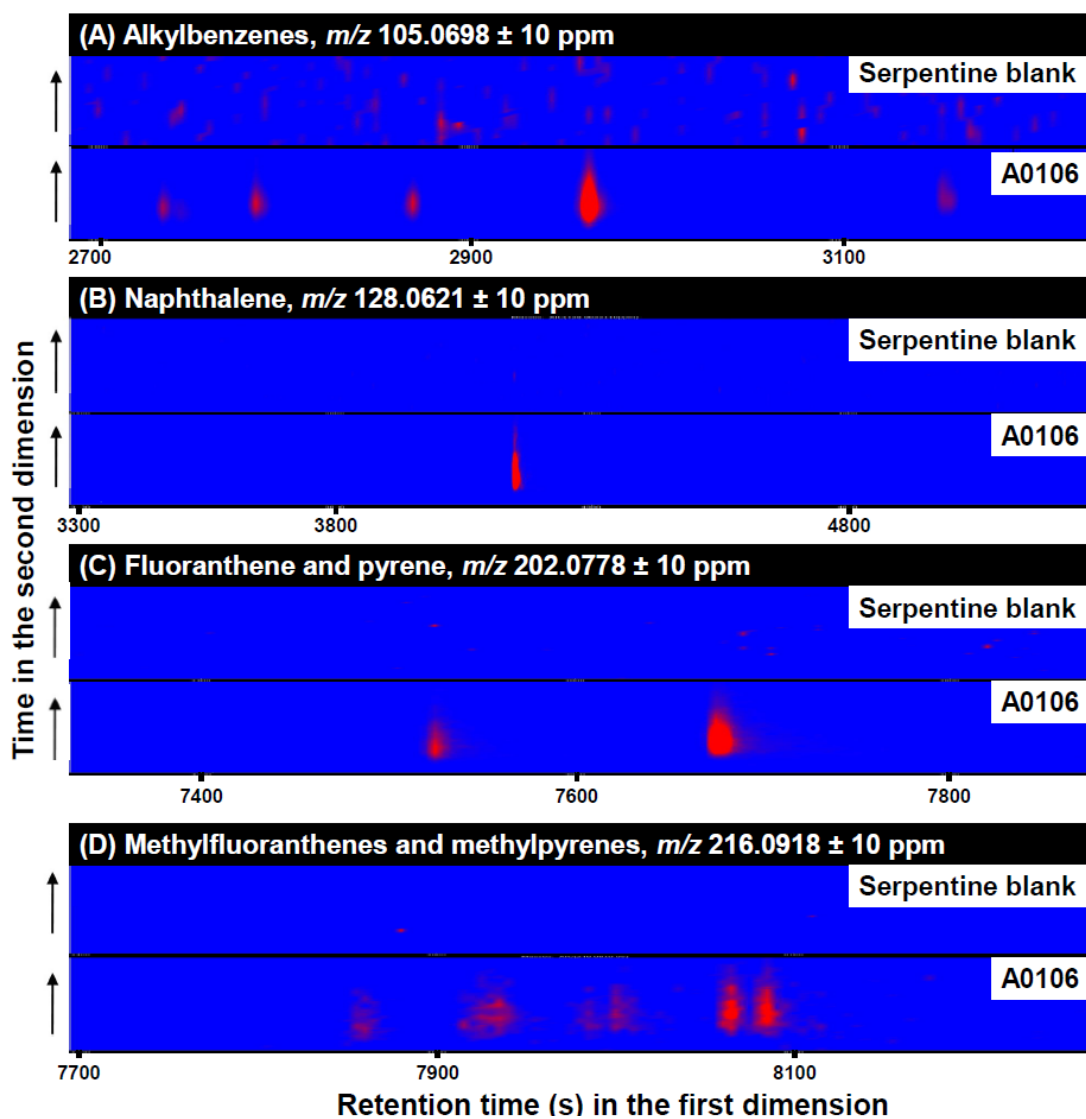


Fig. 5. Aromatic hydrocarbons in the Ryugu extract. Data were measured using GC×GC-TOFMS. Each panel includes equivalent data for a baked serpentine blank for comparison. (A) alkylbenzenes in the hexane extract characterized by m/z 105.0698, (B) naphthalene (m/z 128.0621) in the DCM extract, (C) fluoranthene and pyrene (m/z 202.0778) in the DCM extract, (D) methylfluoranthenes and methylpyrenes (m/z 216.0918) in the DCM extract. The redder color indicates the higher concentration.

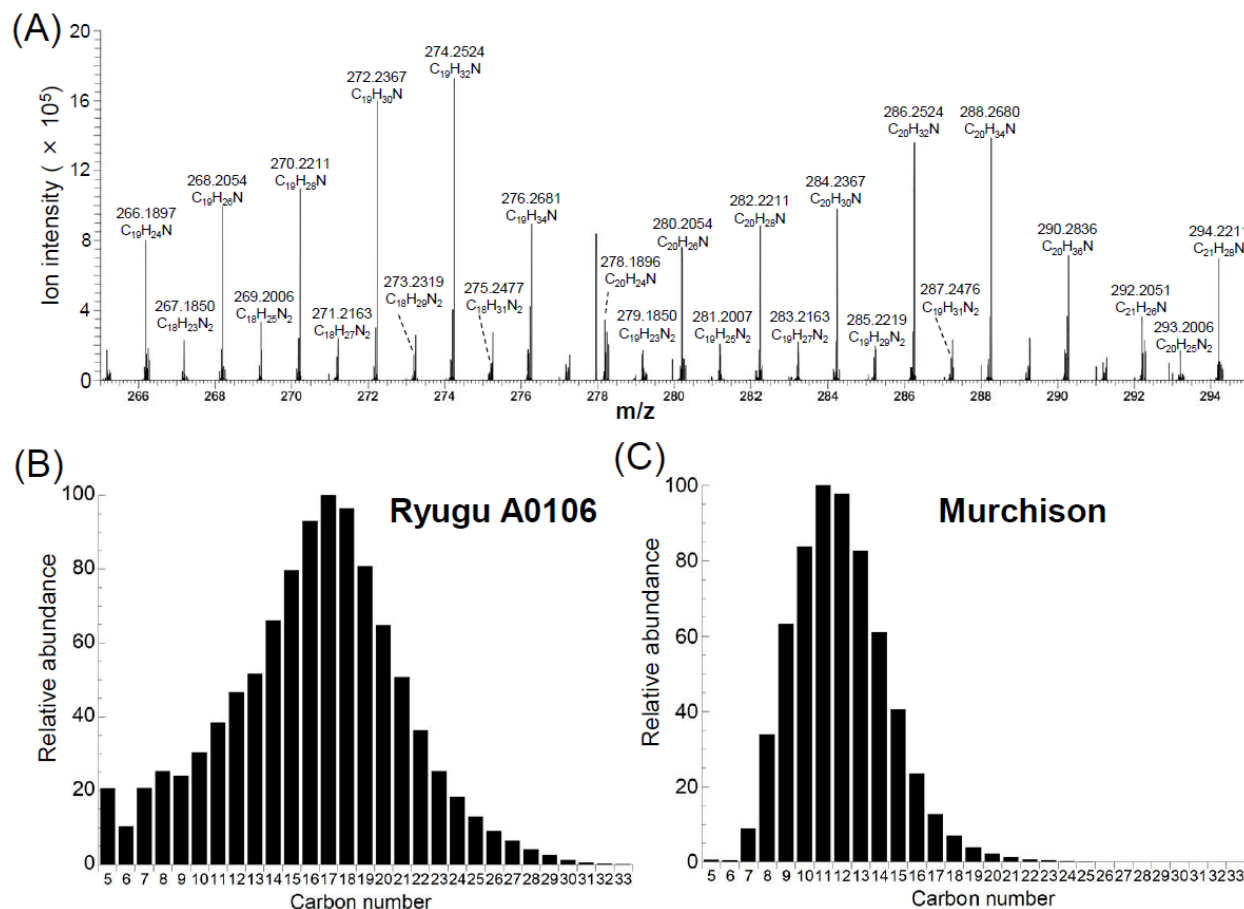


Fig. 6. CHN compounds in the methanol extract determined using nanoLC/high resolution mass spectrometry. (A) A partial mass spectrum of the A0106 sample, with peaks assigned to $C_nH_{2n-16}N^+$, $C_nH_{2n-14}N^+$, $C_nH_{2n-12}N^+$, $C_nH_{2n-10}N^+$, $C_nH_{2n-8}N^+$, $C_nH_{2n-6}N^+$, $C_nH_{2n-4}N^+$,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

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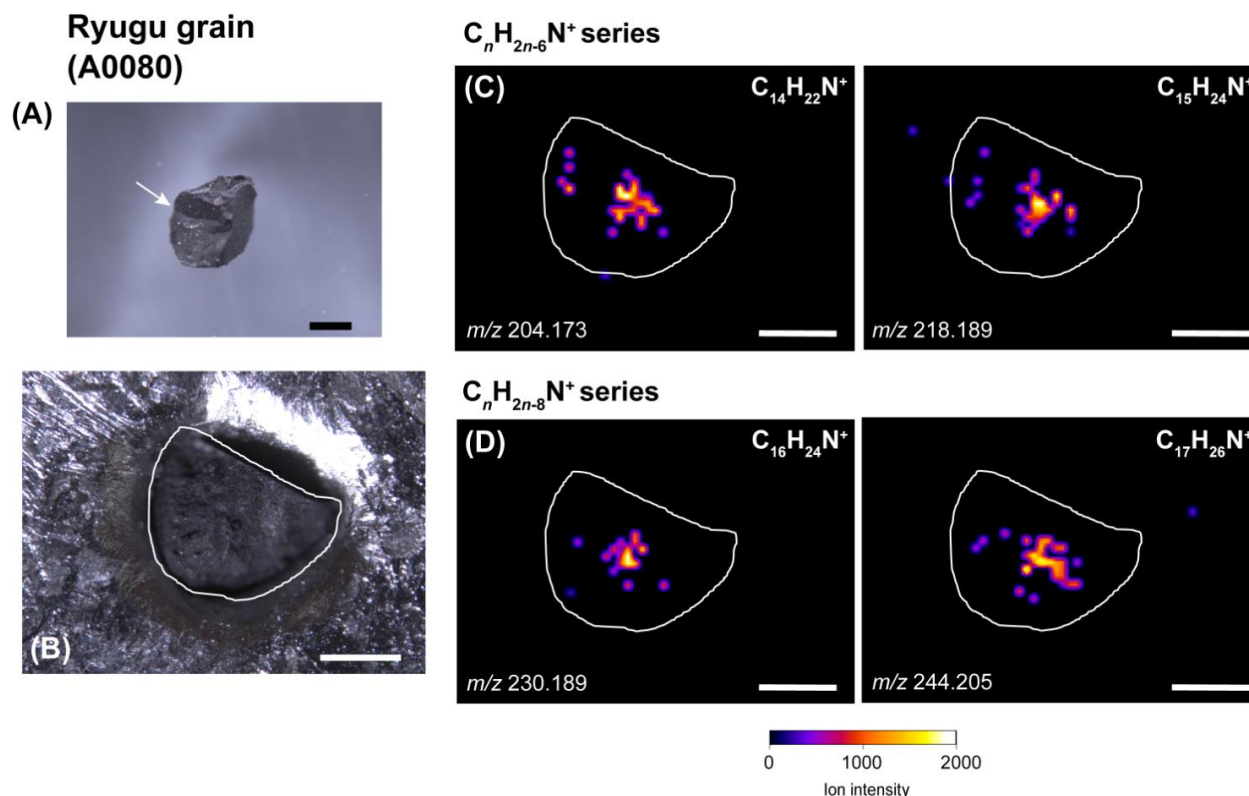


Fig. 7. Spatial distribution of CHN compounds on the surface of Ryugu grain A0080.

Optical images (A) before sample preparation and (B) after embedding in an alloy. A white arrow in (A) shows grain surface of embedded grain in (B). Maps of organic molecule distribution, measured by DESI coupled with HRMS, for (C) $C_nH_{2n-6}N^+$ series ($n=14, 15$) and (D) $C_nH_{2n-8}N^+$ series ($n=16, 17$) molecules. White outlines show boundary between A0080 grain and surrounding metal. All scales in the images correspond to 500 μm .

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