


Uracil in the carbonaceous asteroid (162173) Ryugu

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The pristine sample from the near-Earth carbonaceous asteroid (162173) Ryugu collected by the Hayabusa2 spacecraft enabled us to analyze the pristine extraterrestrial material without uncontrolled exposure to the Earth's atmosphere and biosphere. The initial analysis team for the soluble organic matter reported the detection of wide variety of organic molecules including racemic amino acids in the Ryugu samples. Here we report the detection of uracil, one of the four nucleobases in ribonucleic acid, in aqueous extracts from Ryugu samples. In addition, nicotinic acid (niacin, a B₃ vitamin), its derivatives, and imidazoles were detected in search for nitrogen heterocyclic molecules. The observed difference in the concentration of uracil between A0106 and C0107 may be related to the possible differences in the degree of alteration induced by energetic particles such as ultraviolet photons and cosmic rays. The present study strongly suggests that such molecules of prebiotic interest commonly formed in carbonaceous asteroids including Ryugu and were delivered to the early Earth.

Hayabusa2 spacecraft successfully delivered total 5.4 g of pristine samples, collected during two touchdown operations, from the C-type near-Earth asteroid (162173) Ryugu on 6 December 2020¹. Initial analyses of the samples revealed the similarity with Ivuna-type (CI) carbonaceous chondrites based on spectroscopy, mineralogy, and elemental/isotopic compositions^{2–5}. Surveys of soluble organic matter (SOM) in the Ryugu samples have also been performed in the initial analysis, revealing that a wide range of organic compounds such as racemic non-protein type amino acids, alkylamines, carboxylic acids, polycyclic aromatic hydrocarbons (PAHs), and nitrogen heterocyclic molecules are present in the aqueous or organic extracts^{3,6}. Then, if

Ryugu had a common parent body with CI chondrites, we would expect that other classes of organic compounds, in particular nucleobases, to be present in the Ryugu samples, as has been demonstrated in previous studies on the detection of uracil in the Orgueil CI meteorite^{7–10}.

We have recently developed an analytical method for the small-scale detection and identification of nucleobases at parts per billion (ppb) to parts per trillion (ppt) levels using high-performance liquid chromatography coupled with electrospray ionization high-resolution mass spectrometry (HPLC/ESI-HRMS)^{11,12}. In the aqueous extracts from the Murchison CM meteorite, for which intensive study of organics

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have been made since its fall in 1969, we successfully detected all five canonical nucleobases (adenine, guanine, cytosine, thymine, uracil) at the concentrations ranging from 4 to 72 ppb¹¹. Such highly sensitive methods are well suited for Ryugu analyses where the available sample mass is limited.

Here, we search for nucleobases and other classes of nitrogen (N)-heterocyclic molecules (Supplementary Fig. 1), as well as their alkylated homologs, indigenous to the Ryugu samples A0106 and C0107 (Fig. 1), which were collected from the first and second touchdown sites of the asteroid Ryugu. Such N-heterocyclic molecules including nucleobases would be a good target for better understanding chemical evolution as they are considered to play an important role both as reactants and catalysts for the synthesis of further complex organic molecules such as peptide nucleic acids and nucleotides in prebiotic evolution^{13–15} (Supplementary Fig. 2). The Ryugu samples (~10 mg) are subjected to hot-water extraction at 105 °C for 20 hours, followed by acid hydrolysis (see “Methods” section). As the most suitable reference samples of Ryugu, we also analyze the hot water extract from the Orgueil meteorite and its acid-hydrolysate to compare the nucleobase contents between the Ryugu and Orgueil meteorite.

Results and discussion

Bulk properties of the Ryugu samples

The bulk elemental and isotopic analyses of both samples showed very good similarities between Ryugu and CI chondrites^{5,6} (Fig. 2 and Supplementary Table 1). The infrared reflectance spectral analysis of those Ryugu samples indicated that the signals derived from hydrous silicate minerals (i.e., 2.72 μm for OH absorption) and organic matter (i.e., 3.1 μm and 3.4 μm for CH and NH absorption bands, respectively) were mostly homogeneous between A0106 and C0107 (Fig. 3) and had similar characteristics to a profile of CI chondritic features².

Detection of uracil

Figure 4 shows mass chromatograms at the mass-to-charge ratio (m/z) of 113.0346 Da (atomic mass unit) corresponding to that of protonated uracil ($\text{C}_4\text{H}_4\text{N}_2\text{O}_2 + \text{H}^+$) for the acid hydrolysates of the A0106 and C0107 extracts. Several peaks were observed above the background level in the sample chromatograms. Since there are no peaks in the mass chromatograms for the serpentine blank at the corresponding

m/z , the observed peaks must be indigenous to the samples. Based on the comparison with the retention times using the authentic standard reagents of uracil and its structural isomers (2-imidazole-carboxylic acid and 4-imidazole-carboxylic acid; hereafter 2-ICA and 4-ICA, respectively; Supplementary Fig. 1), the observed peak at -16 min for the Ryugu samples is certainly derived from uracil. This peak was also observed in the extract from the Orgueil meteorite (Fig. 4) and the MS/MS analysis (see Methods) for the peak at -16 min showed a clear match on the mass fragmentation pattern with that for the authentic standard of uracil (Supplementary Fig. 3). The identification of uracil in the Orgueil extracts further strengthens our conclusion that the detected peak at 16 min in the Ryugu extracts is surely derived from uracil. The simultaneous detection of uracil from the A0106 and C0107 extracts by a different separation technique using a capillary electrophoresis-high resolution mass spectrometry (CE-HRMS) instrument is important evidence that reliably supports the analytical detection of uracil with HPLC/ESI-HRMS as discussed above (Fig. 5).

The concentration of uracil was 11 ± 6 and 32 ± 9 ppb in the A0106 and C0107 samples, respectively, which were lower than that detected in the same extract from the Orgueil meteorite analyzed in the present study (140 ppb, Table 1), and lower than that reported previously (73 ppb)⁸, but comparable to that in CM2 chondrites (Table 1). It is likely that acid hydrolysis may have liberated or synthesized uracil from its derivatives or precursor(s) in the hot water extracts, as the case for amino acids in carbonaceous meteorites¹⁶. In fact, in the Orgueil extract, the concentration of uracil increased by a factor 1.5 after acid hydrolysis (Table 1). Applying this factor to the Ryugu samples, the concentration of uracil before acid hydrolysis is estimated to be 7 ± 4 and 21 ± 6 ppb in the A0106 and C0107 samples, respectively. This implies that uracil has been present in the Ryugu samples as a labile form to some extent, which is well consistent with the detection of uracil in the hot water extract from both Ryugu samples before acid hydrolysis (Fig. 5). Other DNA/RNA nucleobases were not positively identified in both the A0106 and C0107 samples. This does not necessarily exclude a possibility that those nucleobases are present in the Ryugu samples, but just they may be below the detection limit under the experimental conditions employed (see Supplementary Information for the non-detection of purine nucleobases). Note that any cytosine which was present may have been deaminated to yield

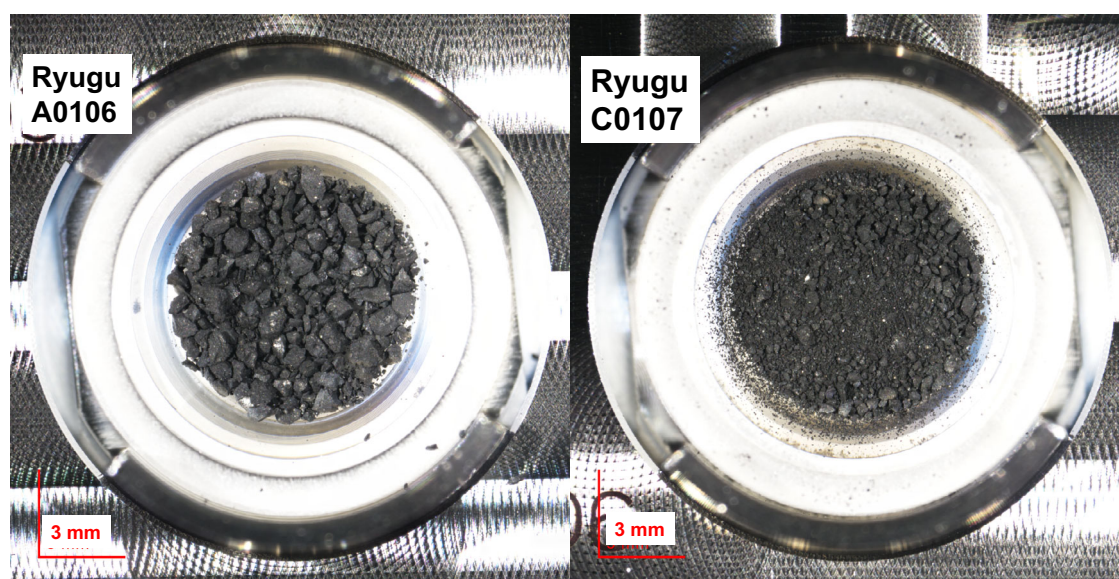


Fig. 1 | Sample returned from asteroid Ryugu (162173). Photographs of initial samples A0106 (total 38.4 mg)⁶ and C0107 (total 37.5 mg) from the asteroid Ryugu (162173) during the 1st touchdown sampling and 2nd touchdown sampling,

respectively^{1,2}. The photos were taken in the clean chamber of the curation facility at Japan Aerospace Exploration Agency before the sample distribution. The scale bar represents 3 mm (red line).

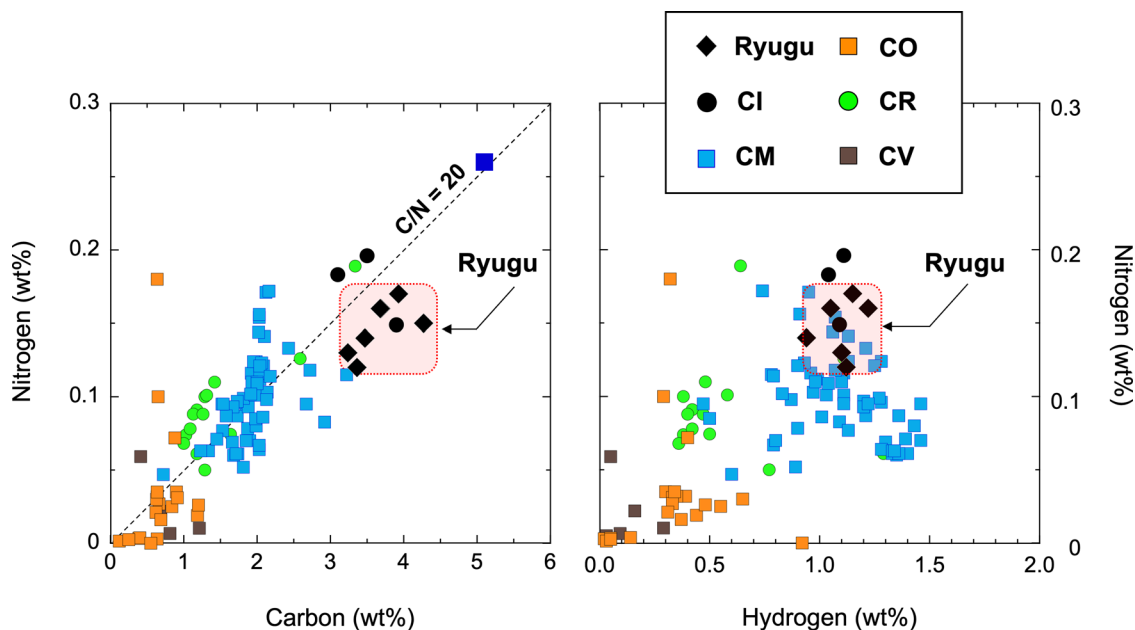


Fig. 2 | Elemental compositions of the Ryugu samples. The elemental profiles of A0106 (i.e., 1st touchdown site) and C0107 (i.e., 2nd touchdown site) for carbon (C, wt%), nitrogen (N, wt%), and hydrogen (H, wt%), with those of reference carbonaceous chondrites (CI, CM, CO, CR, and CV; Naraoka et al.⁶ and the supplementary

information). Based on repeated measurements of very fine-grained samples, both A0106 and C0107 were found to have similar elemental abundances (C, N, H). The blue square stands for bulk C (5.1 ± 0.4 wt%) and N (0.26 ± 0.01 wt%) profiles of the Zag clast⁵³.

uracil upon hot water extraction for 20 h at 105 °C, followed by acid hydrolysis for the same duration at 105 °C, as has been demonstrated in laboratory experiments^{17,18}. Hence, the possibility of cytosine in the Ryugu samples prior to workup cannot be excluded. The upper limit for the concentrations of uracil precursors including cytosine can be estimated from the difference in the concentration of uracil before and after acid hydrolysis, to be 4 and 11 ppb in the A0106 and C0107 samples, respectively. There could be other formation mechanisms of uracil in the Ryugu sample other than hydrolysis of its chemical precursors. Since Ryugu appears to not have heated above 100 °C after aqueous alteration⁵ and above 200 °C by radiative heating at the -1 m depth below the surface after its orbital transition to near-Earth orbit¹⁹, formation mechanisms at relatively low temperatures may play a role for their formation. Photochemical reactions of interstellar ices which are composed of H₂O, NH₃, CH₃OH, and other simple molecules, followed by accretion into the asteroid upon the formation of the Solar system, may be one of the possible pathways for the synthesis of nucleobases^{12,20}. Nucleobases including uracil could also be synthesized through the side-addition to pyrimidine via photochemical reactions in ices²¹ and via energetic processes to formamide on asteroids²².

Detection of other N-heterocycles

In addition to uracil, its structural isomers 2-ICA and 4-ICA were also identified in the chromatogram at the m/z of 113.0346 (Fig. 4). The presence of organics with carboxyl groups is consistent with the finding of low molecular weight organic acids in the previous report⁶. Imidazoles have long been considered to act as a catalyst on the activation of organic monomers like nucleotides and amino acids^{13,14,23}, thus they are expected to play an important role on the chemical evolution on asteroids and also on the early Earth. The concentration of 4-ICA is in the same range of uracil, while that of 2-ICA is clearly lower than other two isomers (Table 1). The relatively low abundance of 2-ICA is well consistent with that observed in the Orgueil meteorite (Table 1) and CM2 carbonaceous meteorites¹¹. Note that imidazoles which substituted at the 4-position of the ring are thought to form from hydrogen cyanide (HCN) via a proposed prebiotic pathway

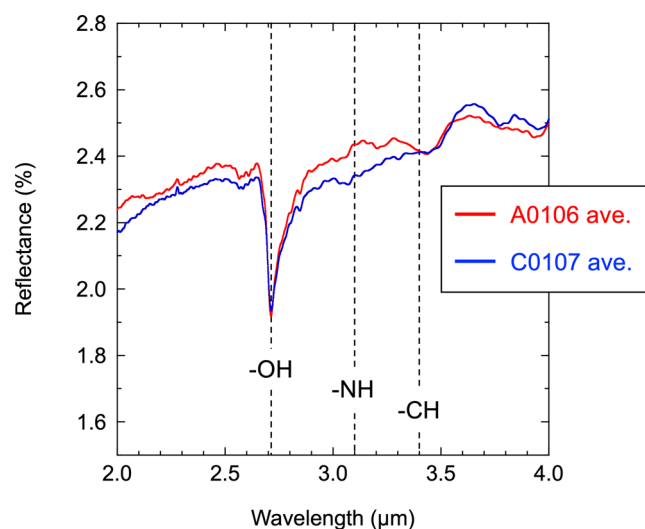


Fig. 3 | Infrared spectra of the Ryugu samples. The raw profiles of infrared reflectance spectra for Ryugu initial bulk samples (A0106 and C0107) within 2.0–4.0 μm. The data acquisition of this non-destructive analysis is described in the literature². Signals for important functional groups (OH, NH, CH) are indicated in each band by dotted lines. The data management policy is declared in the “Data availability” section of this report.

toward the formation of purine nucleobases^{24,25}. If this is the case on carbonaceous asteroids, the preference of 4-ICA over 2-ICA in the Ryugu samples and meteorites may demonstrate such a molecular evolution pathway from HCN to purine nucleobases in a natural environment.

We also detected pyridine-based species in the acid hydrolysate of Ryugu samples. Figure 6 shows mass chromatograms at the m/z of 124.0393, which corresponds to the protonated ion of nicotinic acid (C₆H₅NO₂). Nicotinic acid, known as niacin a B₃ vitamin, and its structural isomer isonicotinic acid were identified in the A0106 and

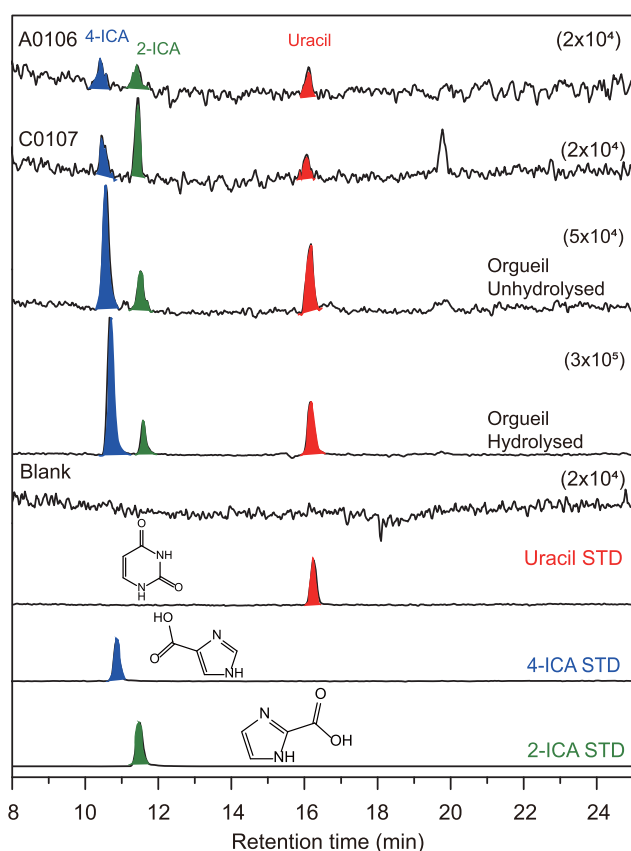


Fig. 4 | Uracil ($C_4H_4N_2O_2$) with their structural isomers detected in Ryugu A0106 and C0107 samples and Orgueil meteorites. Mass chromatograms at the m/z of 113.0346 which corresponds to the protonated ion of exact mass number for uracil in the acid hydrolysate of the hot water extracts from the A0106 and C0107 samples. For Orgueil, mass chromatograms measured before and after acid hydrolysis were also shown. Data for the blank sample and authentic standards are also shown for comparison. Numbers in parenthesis represents the range for the vertical-axis in the sample chromatograms.

C0107 samples (Table 1). These molecules were also identified in the hot water extract and its acid-hydrolysate from the Orgueil meteorite (Fig. 6), although their concentrations are one order of magnitude larger than those in the Ryugu samples. These molecules have also been identified in several carbonaceous chondrites and are more abundant than nucleobases^{11,26}. Their structural isomer, picolinic acid (Supplementary Fig. 1), was identified neither in Ryugu nor in carbonaceous chondrites (Fig. 6). This is well consistent with the distribution of laboratory products which were formed by photochemical reactions of interstellar ice analogs containing H_2O , CO , CH_3OH , and NH_3 at 10 K^{11,12} (Supplementary Fig. 4), also suggesting a contribution from low-temperature photochemical reactions to the origin of N-heterocycles in the Ryugu samples. Nicotinamide ($C_6H_6N_2O$), another B₃ vitamin, was not detected in the acid-hydrolysates from the A0106 and C0107 samples. However, this molecule may have been originally present in the Ryugu samples, but would have decomposed upon acid hydrolysis of the hot water extract. In fact, nicotinamide and its structural isomer isonicotinamide were detected in the hot water extract from the Orgueil meteorite before acid hydrolysis, while they were not after the acid hydrolysis (Supplementary Fig. 5 and Table 1), which supports our assumption above. Since nicotinamide and isonicotinamide are also present in CM2 Murchison meteorites¹¹, they may also be common in CI type carbonaceous asteroids.

Alkylated homologs of uracil, as well as those of other N-heterocyclic molecules such as pyrimidine and nicotinic acid with

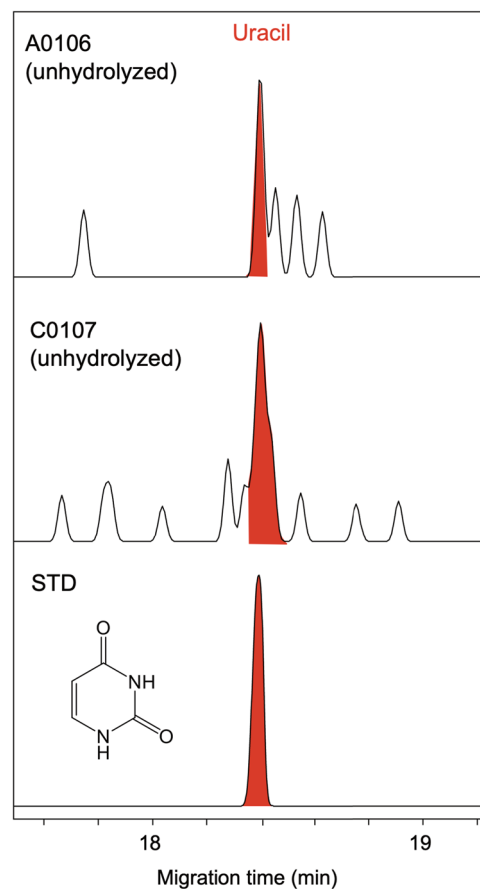


Fig. 5 | Uracil in the hot water extracts from the Ryugu samples. Cross-validation and high-resolution molecular identification of uracil obtained from hot water extracts (unhydrolyzed fraction) for Ryugu A0106 and C0107 by using capillary electrophoresis (CE) coupled with high resolution orbitrap mass spectrometry (CE-HRMS). Data for the authentic standard is also shown for comparison. The signal of red color represents uracil on the migration time (18.4 min).

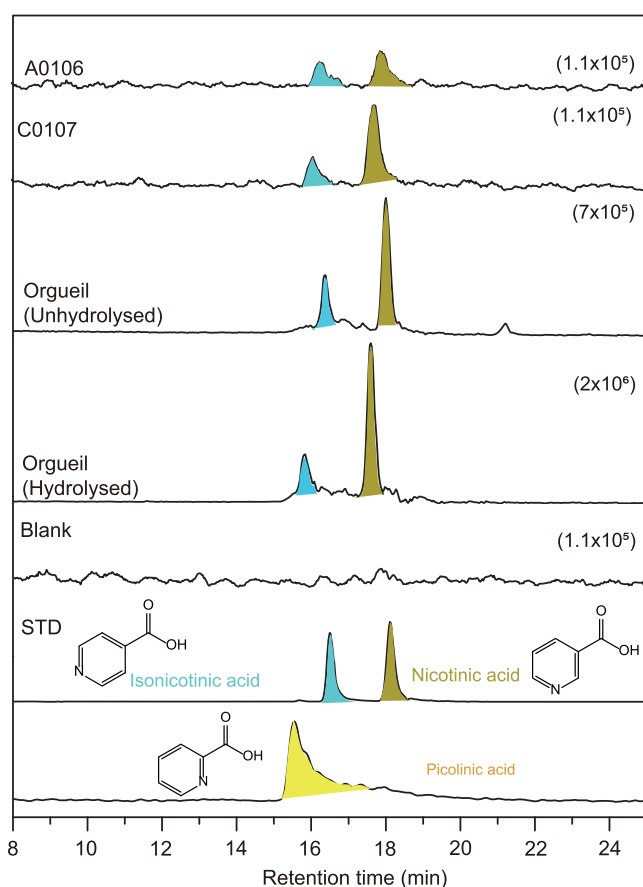
the number of carbon atoms up to 30 were detected in the methanol extracts from both A0106 and C0107 samples (Fig. 7 and Supplementary Figs. 6 and 7). The presence of the alkylated homologs of uracil coupled with the careful contamination control and chain of custody of the Hayabusa2 sample²⁷⁻²⁹ strongly suggests that they are not formed under the control of terrestrial biology but formed through a series of abiotic processes in extraterrestrial environments. Alkylated homologs of N-heterocyclic molecules produced by photochemical reactions of interstellar ice analogs have shorter alkylchains than that observed in the Ryugu samples and meteorites¹¹, which strongly suggests that processes in asteroidal environments contributed to elongate alkylchains in those classes of molecules.

Comparison of N-heterocycles contents between A0106 and C0107

Variations in the concentrations of N-heterocyclic molecules including uracil between A0106 and C0107 samples may be related to the possible differences in the degree of alteration processes induced by energetic particles such as ultraviolet photons and cosmic rays since material in Chamber C may have been ~1 m below the surface of Ryugu for several million years^{3,30}. Organic molecules in the surface materials would have experienced energetic processes more extensively than those in the subsurface materials, which potentially causes preferential degradation of molecules at the surface³¹⁻³³ (Fig. 8). In fact, laboratory experiments have demonstrated that uracil is not strong against energetic processes such as

Table 1 | Qualitative and quantitative summary (in ppb) of uracil and other N-heterocyclic molecules identified in the Ryugu samples (A0106, C0107) and Orgueil meteorite

	A0106	C0107	Orgueil		Orgueil ^c	Murchison ^d	Murray ^d	Tagish Lake ^d
	Hydrolyzed	Hydrolyzed	Unhydrolyzed	Hydrolyzed	H ₂ O and HCOOH extracts	H ₂ O extracts	H ₂ O extracts	H ₂ O extracts
Uracil	11 ± 6 ^a	32 ± 9	92	140	73	15	37	4
Imidazole-2-carboxylic acid	6	9 ± 1	12	12	–	19	14	4
Imidazole-4-carboxylic acid	17 ± 3	19 ± 3	136	218	–	90	99	19
Nicotinic acid	49 ± 1	99 ± 4	602	715	–	91	626	108
Picolinic acid	n.d. ^b	n.d.	n.d.	n.d.	–	–	–	–
Isonicotinic acid	49 ± 20	62 ± 23	237	203	–	53	307	118
Nicotinamide	n.d.	n.d.	214	n.d.	–	10	–	–
Isonicotinamide	n.d.	n.d.	38	n.d.	–	3	–	–
Picolinamide	n.d.	n.d.	n.d.	n.d.	–	1	–	–

^aAveraged value with an error on two measurements.^bNot detected.^cStoks and Schwartz⁸.^dOba et al.¹¹.**Fig. 6 | nicotinic acid (C₆H₅NO₂) with their structural isomers detected in Ryugu A0106 and C0107 samples and Orgueil meteorites.** Mass chromatograms at the *m/z* of 124.0393 which corresponds to the protonated ion of exact mass number for nicotinic acid in the acid hydrolysate of the hot water extracts from the A0106 and C0107 samples. For Orgueil, mass chromatograms measured before and after acid hydrolysis were also shown. Data for the blank sample and authentic standards are also shown for comparison. Numbers in parenthesis represents the range for the vertical-axis in the sample chromatograms.

cosmic ray and ultraviolet photons^{34,35}. While uracil in the subsurface (-5 cm) on planetary bodies can be protected by the surface minerals such as calcium carbonate, calcium sulfate, and kaolinite from radiolysis³⁶. Similar variation has been observed for other

N-heterocycles such as nicotinic acids and other five- and six-membered N-heterocyclic molecules (Table 1). In contrast, the opposite is true for some polycyclic aromatic hydrocarbons (PAHs) such as naphthalene and pyrene where these PAHs in the A0106 are more abundant than those in the C0107³⁷. The observed difference may be indicative of different histories which PAHs and N-heterocycles have experienced on the asteroid Ryugu. For example, PAHs could be produced as a result of surface degradation process of precursor molecules by photolysis and/or radiolysis, while the formation of N-heterocyclic molecules may be less effective compared to their degradation through the same processes. Further studies are necessary to elucidate variations in the concentrations of molecules between surface and subsurface materials of the Ryugu.

Possible formation mechanisms of N-heterocycles and future perspective

Naraoka et al.³⁸ proposed that aldol condensation and formose reaction, both of which requires aldehydes such as formaldehyde, with ammonia are a formation pathway of N-heterocyclic molecules in carbonaceous asteroids. The source of ammonia and formaldehyde in the asteroid Ryugu would be the key factor to constrain the validity of this assumption. In addition, HCN may also be used for the synthesis of nucleobases as explained above^{24,25}. So far, these three molecules have not been identified in the Ryugu samples. However, it is highly likely that they were present in the asteroid Ryugu if it is composed of comet-like materials^{3,39} since HCN, ammonia, and formaldehyde have been identified in cometary ices⁴⁰ and cyanides have been detected in carbonaceous chondrites⁴¹. In fact, the N–H feature has been observed in the Ryugu samples^{4,42}, which supports the assumption above. As for the other candidates for the source of nitrogen, molecular nitrogen (N₂) may also play a role for the synthesis of N-heterocycles regardless of its chemically inert nature⁴³ since it has been detected in cometary environments⁴⁴. Hence, it is likely that availability of N-containing molecules such as ammonia, HCN, and/or their precursors should constrain the synthesis of N-heterocyclic molecules on the asteroid Ryugu. If hexamethylenetetramine was present in Ryugu, as the case for some carbonaceous meteorites including Murchison⁴⁵, it can play a role for the precursor of these molecules upon aqueous and/or thermal activities in Ryugu. Another possible candidate for the synthesis of uracil may be urea (NH₂CONH₂) as has been proposed previously⁴⁶. In fact, urea is abundant in carbonaceous meteorites⁴⁷. In addition, although urea was not detected in the present study, its presence in Ryugu was suggested in another research³. Urea can also

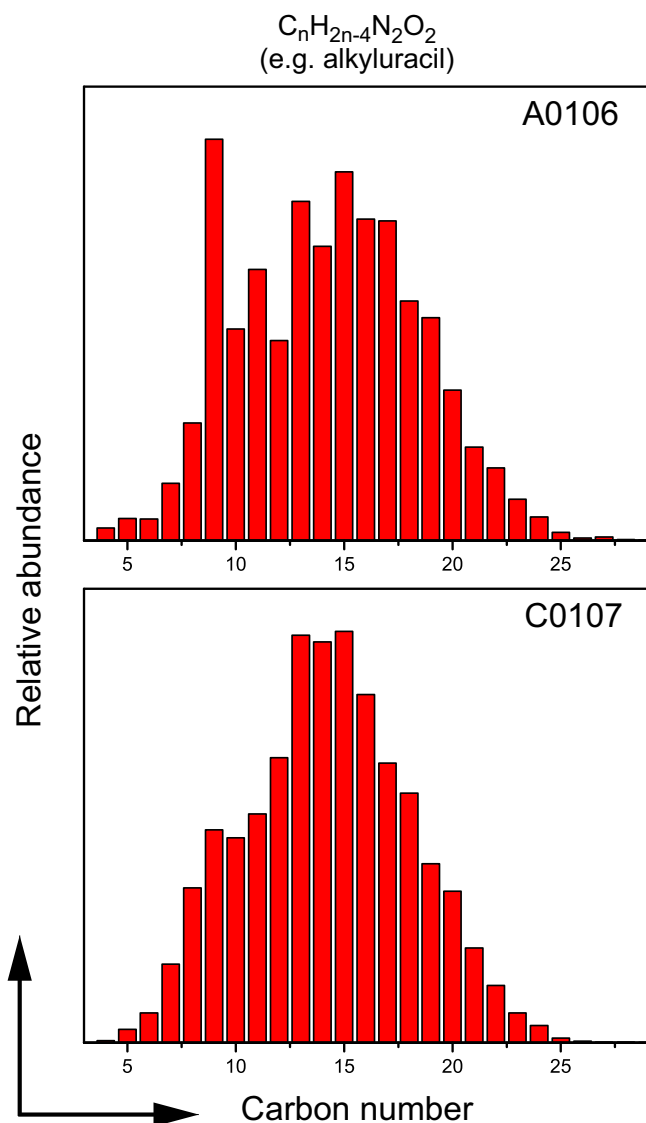


Fig. 7 | Detection of CHNO molecules in the methanol extract from the Ryugu samples. Relative peak area of alkylated analogs of CHNO molecules having a general formula of $C_nH_{2n-4}N_2O_2$ which include uracil and their structural isomers in the methanol extracts from the A0106 (top) and C0107 (bottom) samples with relevance to the number of carbon atoms ($n = 5\text{--}30$) in a molecule. The horizontal axis shows the number of carbon atoms and the vertical axis shows the sum of the peak area at each m/z in arbitrary units.

be synthesized in photochemical reactions of representative components in interstellar ices at low temperatures^{48,49}.

Sample from near-Earth asteroid (101955) Bennu is scheduled in 2023 with subsequent detailed analysis in the NASA's Origins, Spectral Interpretation, Resource Identification and Security-Regolith Explorer (OSIRIS-REx)⁵⁰, further elucidation of the history and prebiotic chemistry inscribed in the CI-type asteroid Ryugu will be definitely important for understanding past and ongoing chemical evolution on both carbonaceous asteroids.

Methods

CNHSO contents and their isotopic compositions

We analyzed the elemental abundance of carbon (C, wt%), nitrogen (N, wt%), hydrogen (H, wt%), pyrolyzable oxygen (O, wt%), and sulfur (S, wt%) and the isotopic compositions of $\delta^{13}C$ (‰ vs. VPDB), $\delta^{15}N$ (‰ vs. Air), δD (‰ vs. VSMOW), $\delta^{18}O$ (‰ vs. VSMOW) and $\delta^{34}S$ (‰ vs. VCDT), respectively⁶. For the total C, N, and S contents with their isotopic

compositions ($\delta^{13}C$, $\delta^{15}N$, $\delta^{34}S$), we used an ultrasensitive nano-EA/IRMS method (Flash EA1112 elemental analyzer/ConFlo III interface/Delta Plus XP isotope-ratio mass spectrometer, Thermo Finnigan Co., Bremen)^{6,51}. For the total H and pyrolyzable O with their isotopic compositions (δD , $\delta^{18}O$), we used a highly sensitive TC/EA/IRMS method (Delta Plus XL isotope-ratio mass spectrometer, Thermo Finnigan Co., Bremen)⁵². Prior to the Hayabusa2 samples, analytical validations using the nano-EA/IRMS system were performed during the rehearsal analyses and application studies of the carbonaceous chondrites^{53,54}.

Extraction of organic molecules from samples

We extracted organic molecules from the A0106 (13.08 mg) and C0107 (10.73 mg) Ryugu samples, as well as 10.86 mg of Orgueil meteorite (CI type, from Denmark National Museum) with hot water at 105 °C for 20 hrs in a N_2 -purged and flame-sealed glass ampoule. The water extract from the Ryugu samples was further hydrolyzed using ultrapure 6 M HCl at 105 °C for 20 hrs of this extract ~20% was made available for this study. Since the majority was allocated acid-hydrolyzed for the detection of amino acids⁶, nucleobases in the hot water extract were not available for analysis with HPLC/ESI-HRMS before acid hydrolysis. The use of the Orgueil extract was not so constrained, so nucleobases in the hot water extract were investigated before and after acid hydrolysis. The same procedure was repeated using baked (500 °C in air for 3 hr) serpentine powder (17.58 mg) as a procedural blank.

Separate aggregates of A0106 (17.15 mg) and C0107 (17.36 mg) were subjected to extractions by a series of organic solvents with an assist of ultrasonication (15 min) in the following order: hexane, dichloromethane, and methanol. After the sonication, the liquid extract was decanted after centrifugation (9677×g, 5 min). About 30% of the methanol extract was allocated for the detection of nucleobases and other N-heterocyclic molecules. For further details, please refer to Naraoka et al.⁶.

Analysis of nucleobases and N-heterocyclic molecules

The acid-hydrolysate of the hot water extracts from the Ryugu samples and the Orgueil meteorite was introduced into an HPLC/ESI-HRMS instrument with a mass resolution of 140,000 at a mass-to-charge ratio (m/z) of 200. The analytical system comprised an Ultimate 3000 and Q-Exactive Plus (Thermo Fischer Scientific) equipped with a reversed-phase separation column (HyperCarbTM, 150 mm length × 1.0 mm i.d., particle size 5 μm , Thermo Fisher Scientific) at 40 °C and operated in positive ion mode. Validations of analytical methods were also performed using a 1290 Infinity II coupled with a 6230 time-of-flight mass spectrometer (Agilent Technologies). The eluent program for the HPLC was as follows: solvent A (water + 0.1% formic acid) and solvent B (acetonitrile + 0.1% formic acid) = 99:1 at $t = 0$ min, followed by a linear gradient of A:B = 70:30 at 20 min, and maintained at this ratio for 25 min. The flow rate was 50 $\mu L/min$ and the column temperature was kept at 40 °C. The injection volume was 5 μL . The mass spectra were recorded in positive ESI mode with an m/z range of 50–600 at the first trial, and the range was narrowed to 111–131 in order to increase the signal to noise ratio of the target species. The voltage was set to 3.5 kV for positive ESI. The capillary temperature was 300 °C.

MS/MS experiments were performed for the Orgueil extract using a hybrid quadrupole-Orbitrap mass spectrometer (Q-Exactive Plus, Thermo Fisher Scientific) with HPLC and ionization conditions identical to those used for the full-scan analyses. The extracted positive ion m/z (for example, for uracil, 113.03 ± 0.2) was reacted with high-energy collision N_2 gas to produce fragmented ions, and the mass range of m/z 50–160 was monitored using an Orbitrap MS with a mass resolution of ~140,000. The MS/MS measurements were not performed for the Ryugu samples due to the unavailability of the sample solution.

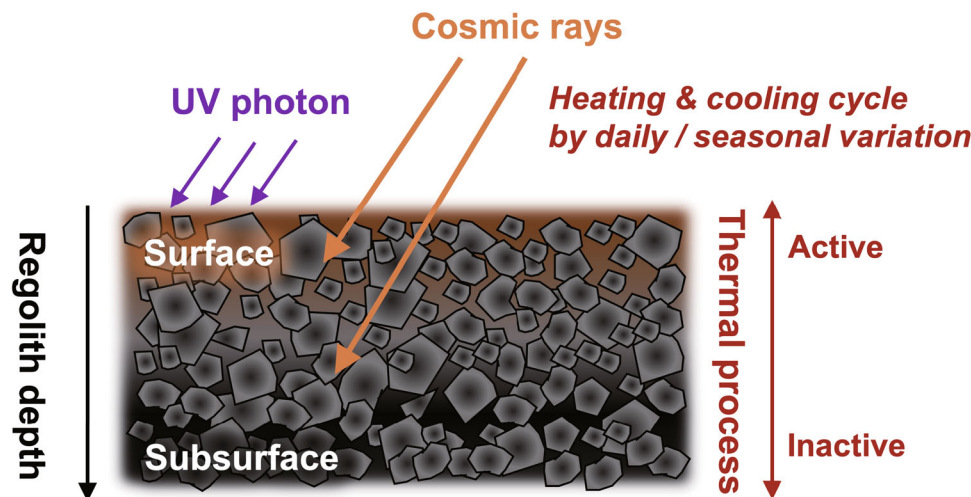


Fig. 8 | Conceptual view of surface and sub-surface physico-chemical features along with regolith depth. Conceptual diagram of the effects of thermal cycling in the diurnal (i.e., variation in daytime and nighttime for max. and min. temperatures; $-100\text{ }^{\circ}\text{C}$)⁴ and seasonal illumination cycles, which are constant exposure processes by photon and cosmic ray irradiation on the surface and subsurface regolith at Ryugu. The purple and orange arrows indicate ultraviolet and cosmic rays,

respectively, and the length of each line is a qualitative model of the penetration depth into the regolith. Kitazato et al.¹⁹ estimated that the current seasonal thermal skin depth of Ryugu is up to ~ 1.1 metre by the model simulation, whereas the total accumulated heat storage within the daily thermal skin depth is estimated to be a few centimeter scale below the surface layer²⁷.

The methanol extract from the Ryugu samples was introduced into a nano liquid chromatograph (UltiMate 3000 RSLCnano, Thermo Fisher Scientific) equipped with a reversed phase C18 column (Aurora, 250 mm length \times 75 mm i.d., particle size 1.6 μm , IonOptics) and a nano electrospray ion source. The eluent program for the nanoLC was as follows: solvent A (water + 0.1% formic acid) and solvent B (acetonitrile + 0.1% formic acid) = 99:1 at $t = 0\text{--}1$ min, followed by a linear gradient of A:B = 75:25 at $t = 25$, and the additional linear gradient of A:B = 15:85 at $t = 30$, maintained at this ratio for 10 min. The flow rate was 400 nL/min. The column temperature was $40\text{ }^{\circ}\text{C}$. The mass spectra were recorded in positive ESI mode with an m/z range of 60.5–600 and a spray voltage of 1.6 kV. The capillary temperature was $250\text{ }^{\circ}\text{C}$.

For cross-validation of the detailed analysis of nucleobases in the Ryugu hot water extracts (unhydrolyzed fraction), we conducted the capillary electrophoresis-high resolution mass spectrometry (CE-HRMS) using an ω Scan package method (Human Metabolome Technologies (HMT), Inc., Japan) described previously⁵⁵. Briefly, CE-HRMS analysis was carried out using an Agilent 7100 CE capillary electrophoresis system (Agilent Technologies, Inc., Santa Clara, CA, USA) equipped with a Q Exactive Plus (Thermo Fisher Scientific Inc., Waltham, MA, USA), Agilent 1260 isocratic HPLC pump, Agilent G1603A CE-MS adapter kit, and Agilent G1607A CE-ESI-MS sprayer kit (Agilent Technologies). The systems were controlled by Agilent MassHunter workstation software LC/MS data acquisition for 6200 series TOF/6500 series Q-TOF version B.08.00 (Agilent Technologies) and Xcalibur (Thermo Fisher Scientific), and connected by a fused silica capillary (80 cm total length \times 50 μm i.d.) with the electrophoresis buffer (H3301-1001, HMT) as the electrolyte. The spectrometer was scanned from m/z 60 to 900 in positive mode⁵⁵. Peaks were extracted using MasterHands, automatic integration software (Keio University, Tsuruoka, Yamagata, Japan) in order to obtain peak information including m/z , peak area, and migration time (MT)⁵⁶.

Data availability

The raw data are available at the following databases in the Hayabusa2 Science Data Archives (DARTS, <https://www.darts.isas.jaxa.jp/planet/project/hayabusa2/>). We declare that all these database publications are compliant with ISAS data policies (www.isas.jaxa.jp/en/researchers/data-policy/).

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Author contributions

Y.O., T.K., Y.Ta, and H.N. outlined the working flow in this study. H.N. and Y.Ta conducted sequential extraction procedure, distributed the SOM samples. Y.O., T.K., and H.N. conducted the analysis of the Orgueil meteorite from the Natural History Museum of Denmark. Y.O., T.K., and H.N. performed the molecular analysis by the LC/Orbitrap system. H.N., N.O.O., N.O., and Y.Ta conducted the analysis of elemental and isotopic compositions. N.O.O. and N.O. provided the series of authentic C, N isotope standards. H.N. provided the series of H, O isotope standards. K.Sas, H.S., and Y.Ta conducted the analysis by the CE/Orbitrap system. D.P.G. and J.P.D. authorized the importance of nitrogen-containing heterocyclic compounds. H.N., Y.Ta, and J.P.D. designed the implementation of the SOM scheme and the initial analysis timelines (~31-May-2022). S.Tac, H.Yu, H.N., T.Na, T.No, R.O., H.Ya, and K.Sak managed the initial analysis processes and wrote the paper. M.A., T.Y., M.N., K.Y., A.N., A.M., T.O., and T.U. curated samples. M.Y., T.S., S.Tan, F.T., S.N., S.W., and Y.Ts contributed to the sample collection at Ryugu. The Hayabusa2-initial-analysis SOM team members are shown in the Supplementary

Information. All authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing interests.

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Supplementary Information for

“Uracil in the carbonaceous asteroid (162173) Ryugu”

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Contents

- List of Hayabusa2-initial-analysis SOM team members
- Supplementary Discussion
 - Bulk analysis of the samples A0106 and C0107
 - Importance of nitrogen (N) for intramolecular electron conjugation
 - Previous assessments for the possible contribution of terrestrial nucleobases
 - Search for purine nucleobases in the Ryugu and Orgueil extracts
 - A rough estimate for the relative abundance of the alkylated N-heterocyclic molecules depending on their carbon numbers
- Supplementary Figures 1–7
- Supplementary Table 1
- Supplementary References 1–30

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Supplementary Discussion

Bulk analysis of the samples A0106 and C0107

Figure 1 shows photographs of initial samples for A0106 and C0107 collected from the 1st touchdown site and 2nd touchdown site, respectively^{1,2}. Following up on the description of surface sample (A0106)³, the subsurface Ryugu sample (C0107) contained 3.58 ± 0.47 wt% ($n = 4$; sample weight of each measurement = 126.3 ± 56.7 μg) of total carbon with the isotopic composition ($\delta^{13}\text{C} = +1.22 \pm 10.0\text{‰}$, $n = 4$), 1.06 ± 0.10 wt% ($n = 3$; average weight = 373.0 ± 137.5 μg) of total hydrogen ($\delta\text{D} = +269 \pm 13\text{‰}$, $n = 3$), 0.14 ± 0.01 wt% ($n = 4$; sample weight = 126.3 ± 56.7 μg) of total nitrogen ($\delta^{15}\text{N} = +36.8 \pm 3.6\text{‰}$, $n = 3$), and 5.5 ± 0.7 wt% ($n = 5$; sample weight = 20.6 ± 5.4 μg) of total sulfur ($\delta^{34}\text{S} = -1.10 \pm 1.62\text{‰}$, $n = 5$). The concentration of pyrolyzed oxygen was 13.4 ± 1.0 wt% ($n = 3$; sample weight = 373.0 ± 137.5 μg) with the isotopic composition for $\delta^{18}\text{O} = +12.1 \pm 1.2\text{‰}$ ($n = 3$). Evaluating the elemental ratios, we find that the weight (wt%)-based elemental ratios converge as follows: C/N ratio = 26.0 ± 2.4 , O/H ratio = 12.7 ± 0.4 , C/S ratios = 0.66 for Ryugu C0107. The isotopic differences between A0106 and C0107 for CHNSO indicated that slight isotopic heterogeneity was found in the samples from the first and second touchdown sites. The assessment of sample heterogeneity must also take into account potential regional differences between two touchdown sites². The data profiles shown in Figure 2 are compiled from the following references³⁻¹⁹.

Importance of nitrogen (N) for intramolecular electron conjugation

Since the valence of atomic nitrogen (N) is three, the remaining electron always form the lone electron pair ($\equiv\text{N}:$) in N-heterocyclic molecules (see Supplementary Fig. 1). The electron conjugation systems in nitrogen-containing compounds have a versatile role in molecular evolution in that they also have a significant impact on secondary molecular formation, molecular diversity, and molecular yield²⁰. The Supplementary Fig. 2 shows the “pyrimidine ($\text{C}_4\text{H}_4\text{N}_2$)” molecule of the uracil skeleton discussed in this report with the electrostatic density as ground state. It is emphasized here that a hexagonal reference of “cyclohexane (C_6H_{12})” consisting only of a carbon backbone, has no electrostatic electronic conjugation system. Therefore, intramolecular electron conjugated systems that encapsulate nitrogen atoms contribute to potential diverse reaction systems and have important molecular evolutionary implications^{21,22}.

Previous assessments for the possible contribution of terrestrial nucleobases

Stoks & Schwartz²³ concluded that the detected uracil was indigenous to meteorites

since the uracil-to-thymine ratio in meteorites was clearly different from that in biogenic products. [Martins et al.](#)²⁴ performed a compound-specific carbon isotopic analysis of nucleobases in the HCOOH extract from the Murchison meteorite. The reported $\delta^{13}\text{C}$ values were +44.5 and +37.7‰ for uracil and xanthine, respectively, implying their extraterrestrial origin. However, due to the possible contribution from other meteoritic organic molecules to the measured $\delta^{13}\text{C}$ values, it remains uncertain whether the reported $\delta^{13}\text{C}$ values are derived from nucleobases or not²⁵. [Callahan et al.](#)²⁵ proposed the indigeneity of the detected nucleobases based on the detection of purine and 6,8-diaminopurine in the same meteorite, both of which are rare in terrestrial samples. In addition, structural diversity typically observed for organic compounds in meteorites might be suggestive of their extraterrestrial origin²⁵. Based on those pioneering findings, [Oba et al.](#)²⁶ detected various nucleobases in meteorites including Murchison. Since the amino acids such as alanine detected in the same specimen of the Murchison were racemic, the indigenous amino acids should be abiotic in origin²⁷, which suggests that the nucleobases in the same specimen are also abiotic in origin. This is a valuable opportunity to make first-hand observations on the molecular evolution of prebiotic amino acids and nucleobases²⁸.

Search for purine nucleobases in the Ryugu and Orgueil extracts

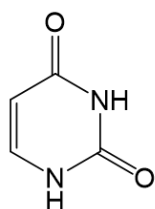
We detected uracil in both the Ryugu and Orgueil samples using a HypercarbTM separation column, which is suitable for the detection of pyrimidine nucleobases²⁶ (Figure 4). However, the detection of purine nucleobases is not the case probably due to the strong interaction between purine nucleobases and the stationary phase of the Hypercarb column²⁶. Hence, any purine nucleobases were not detected in the initial analysis of the Ryugu samples at the m/z range of 50–600. Although purine nucleobases may be detected if we use a different analytical column (InertSustain PFP, GL Science)²⁶, due to the limitation on the sample volume, we could not search for these molecules using this column. On the other hand, purine nucleobases may be present in the Orgueil extract as has been reported in [Callahan et al.](#)²⁵ (20 ppb for guanine and 7 ppb for adenine). However, any purine nucleobases were not detected in the Orgueil extract after acid hydrolysis even when a PFP column was used. A rough estimate for the detection limit of purine nucleobases was 1 ppb under the present analytical conditions where ~10 mg of samples was used. Since the concentrations of purine nucleobases reported in [Callahan et al.](#)²⁵ were higher than the detection limit, they are likely to be detected in the present study. The non-detection in the present study may be attributable to the heterogeneous distribution in Orgueil meteorite and/or different extraction methods (hot water extraction in the present study vs. formic acid extraction in

Callahan et al.²⁵).

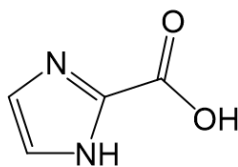
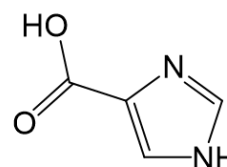
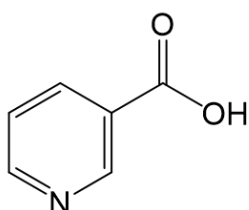
A rough estimate for the relative abundance of the alkylated N-heterocyclic molecules depending on their carbon numbers

Fig. 7 and Supplementary Fig. 7 show variations in the sum of peak area at the m/z corresponding to alkylated homologues of N-heterocyclic molecules (Supplementary Fig. 6). Under the present analytical precision (within 3 ppm), a monoisotopic mass (e.g. 113.0346) is linked to a single molecular formulae ($C_4H_4N_2O_2+H^+$). Assuming that the ionization efficiency is unity among the same classes of molecules, the variations in the sum of peak area are equivalent to those in the concentration of molecules. Note that the peak area of a certain compound (e.g., alkylimidazole) cannot be compared with others (e.g. alkylpyridine) since their ionization efficiencies would not be unity. In addition, some of N-heterocyclic molecules may have their structural isomers (e.g., uracil and imidazole carboxylic acids), which cannot be distinguished on the mass chromatograms due to the low peak resolutions. In that case, the sum of peak area represents the sum of these structural isomers.

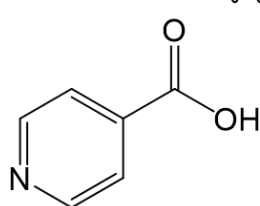
Even under those situations, they can be compared with those in other samples, which may be helpful for discussing the formation/alteration histories on the parent body. In principle, the variations in the peak area for N-heterocyclic molecules are similar between A0106 and C0107 (Fig. 7, Supplementary Fig. 7). However, small but not negligible discrepancy is observed between the two samples. Although both samples are similar in that each N-heterocycle shows unimodal or bimodal distribution with relevance to their carbon numbers, there is a slight difference in the distribution. For example, alkyloxazole shows the highest peak at the carbon number of C_{15} for A0106 but at C_{13} for C0107 (Supplementary Fig. 7). As a general trend, the molecular size seems to be larger for A0106 than C0107. Assuming that A0106, which is surface materials, experiences more extensive alteration processes than C0107 by external energies (Fig. 8), the larger size of N-heterocyclic molecules may be the result of such processes. UV and cosmic ray often cause bond dissociation of molecules to yield smaller reactive radicals. If such radicals are present nearby, they could recombine to form larger species. In contrast, such processes would simply result in the dissociation of N-heterocyclic molecules. In case N atoms are released upon degradation, it is anticipated that PAHs are formed accordingly. This story is consistent with the larger abundances of PAHs in the A0106 than in the C0107²⁹, but further investigation must be necessary to conclude.

Uracil and structural isomersFormula: $C_4H_4N_2O_2$, Monoisotopic Mass: 112.0273

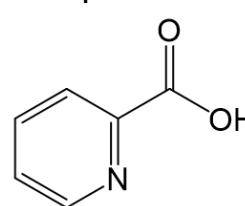
Uracil

2-Imidazole-carboxylic acid
(2-ICA)4-Imidazole-carboxylic acid
(4-ICA)**Nicotinic acid and structural isomers**Formula: $C_6H_5NO_2$, Monoisotopic Mass: 123.0320

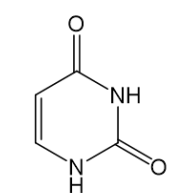
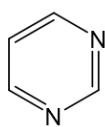
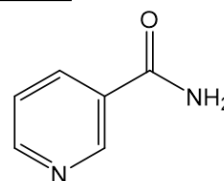
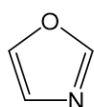
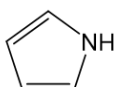
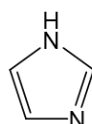
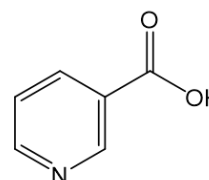
Nicotinic acid



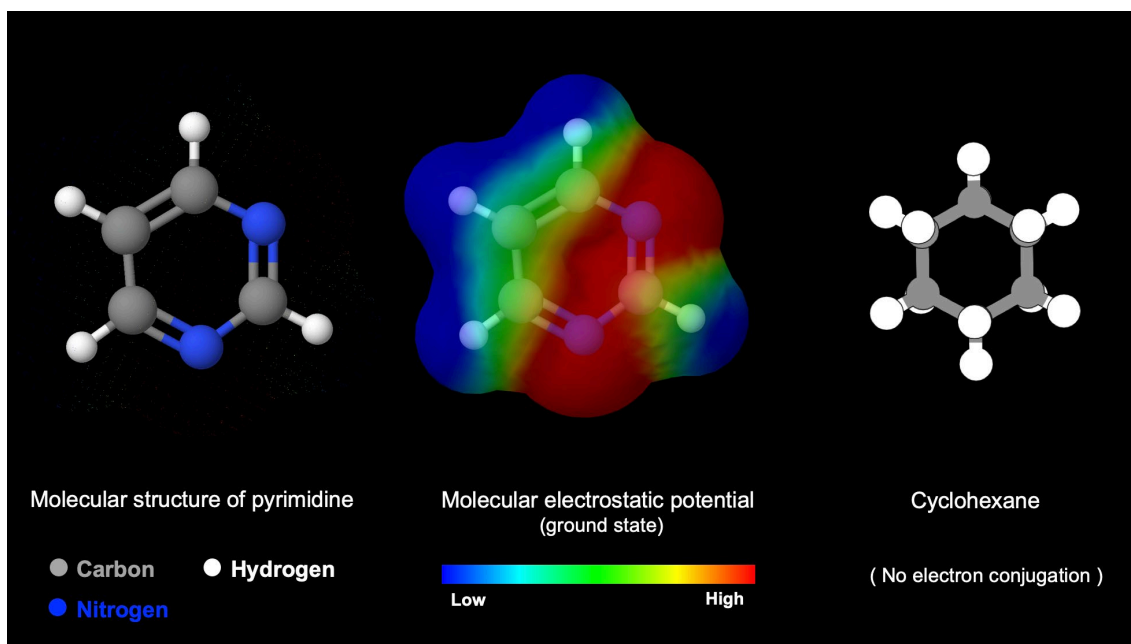
Isonicotinic acid



Picolinic acid

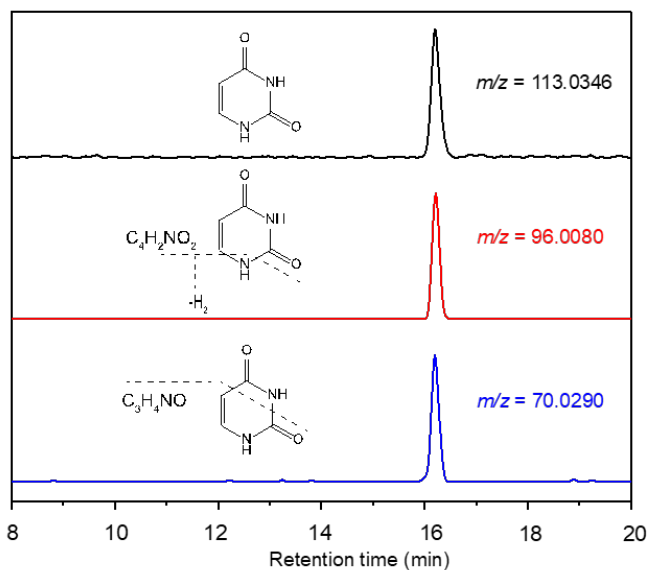
Alkylated homologues of nitrogen heterocyclic moleculesUracil
($C_nH_{2n-4}N_2O_2$)Pyrimidine
($C_nH_{2n-4}N_2$)Nicotinamide
($C_nH_{2n-6}N_2O$)Oxazole
($C_nH_{2n-3}NO$)Pyrrole
($C_nH_{2n-3}N$)Imidazole
($C_nH_{2n-2}N_2$)Nicotinic acid
($C_nH_{2n-7}NO_2$)

Supplementary Figure 1. Molecular structures of N-heterocyclic molecules targeted in the present study. Uracil and its structural isomers, 2-imidazole-carboxylic acid and 4-imidazole-carboxylic acid, nicotinic acid and its structural isomer isonicotinic acid were detected in the acid-hydrolysate of the hot water extracts from the Ryugu samples. In the methanol extract, alkylated homologues of uracil ($C_nH_{2n-4}N_2O_2$), pyrimidine ($C_nH_{2n-4}N_2$), nicotinamide ($C_nH_{2n-6}N_2O$), oxazole ($C_nH_{2n-3}NO$), pyrrole ($C_nH_{2n-3}N$), imidazole ($C_nH_{2n-2}N_2$), and nicotinic acid ($C_nH_{2n-7}NO_2$) were expected to be present where n represents the number of carbon atoms in a molecule.

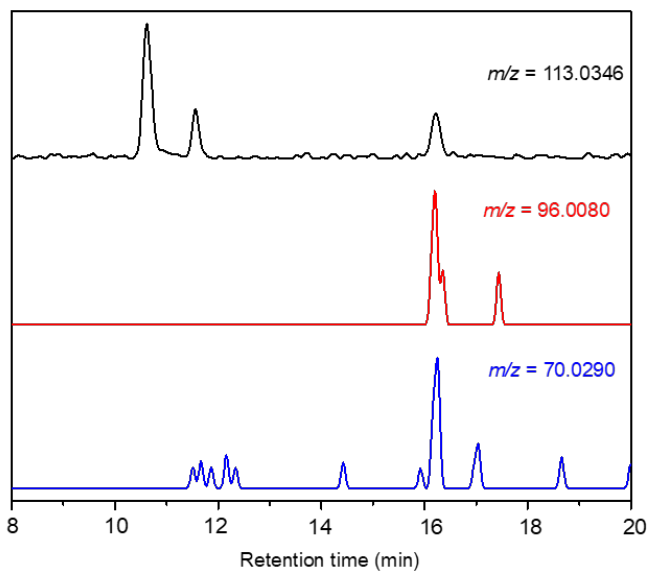


Supplementary Figure 2. Molecular structure and electrostatic potential in the ground state of pyrimidine ($C_4H_4N_2$) and cyclohexane (C_6H_{12}). Due to its variations in the electron densities, N-heterocyclic molecules generally possess higher reactivity than corresponding cyclic hydrocarbons which do not have any electron conjugation in its structure.

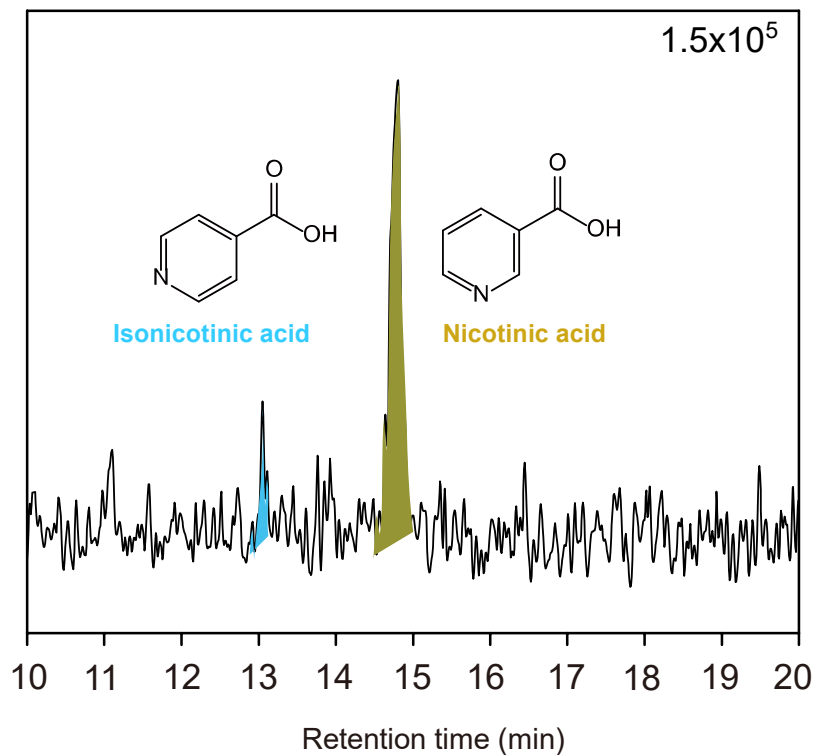
(A) Uracil STD



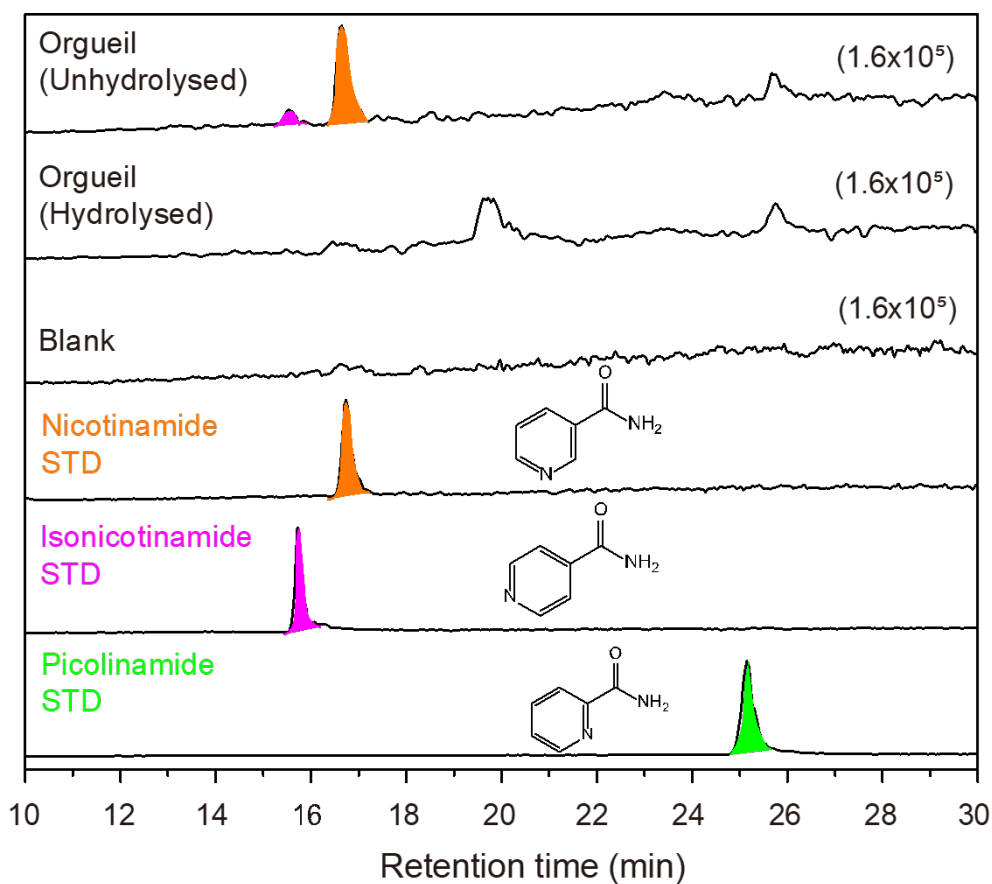
(B) Orgueil Hydrolysed



Supplementary Figure 3. MS/MS measurements of uracil standard reagents and the acid hydrolysate of the Orgueil extract. Extracted mass chromatograms of (A) the uracil standard reagent and (B) the acid hydrolysate of Orgueil extract in the MS/MS measurements. The m/z of 113.0346 represents the parent ion, and that of 96.0080 and 70.0290 represents its fragment ions. The fragmentation patterns are referred to [Oba et al.²⁶](#). The observed mass fragmentation patterns at 16 min in the Orgueil CI meteorite are well consistent with those of the authentic standard of uracil.

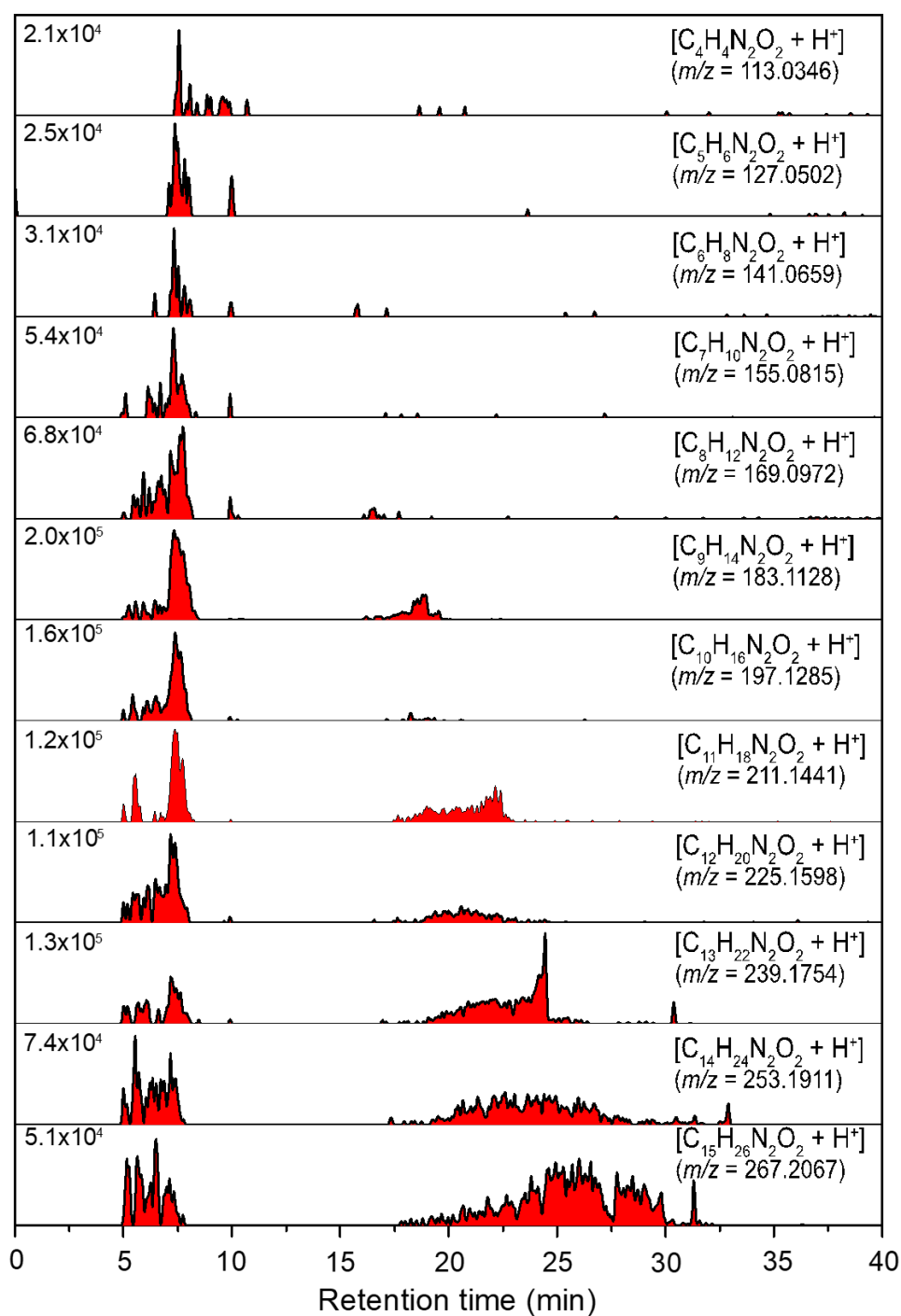


Supplementary Figure 4. Nicotinic acid and isonicotinic acid in organic residues synthesized in laboratory. Both nicotinic and isonicotinic acids were identified in organic residues produced by the photolysis of interstellar ice analogues composed of H₂O, CO, CH₃OH, and NH₃ at 10 K^{26,30}. Analytical conditions were different from those applied in the present study. See [Oba et al³⁰](#). Picolinic acid was not positively identified. The nicotinic acid/isonicotinic acid ratio was ~3.2 in this product. The number on the top right represents the relative intensity at the chromatogram.



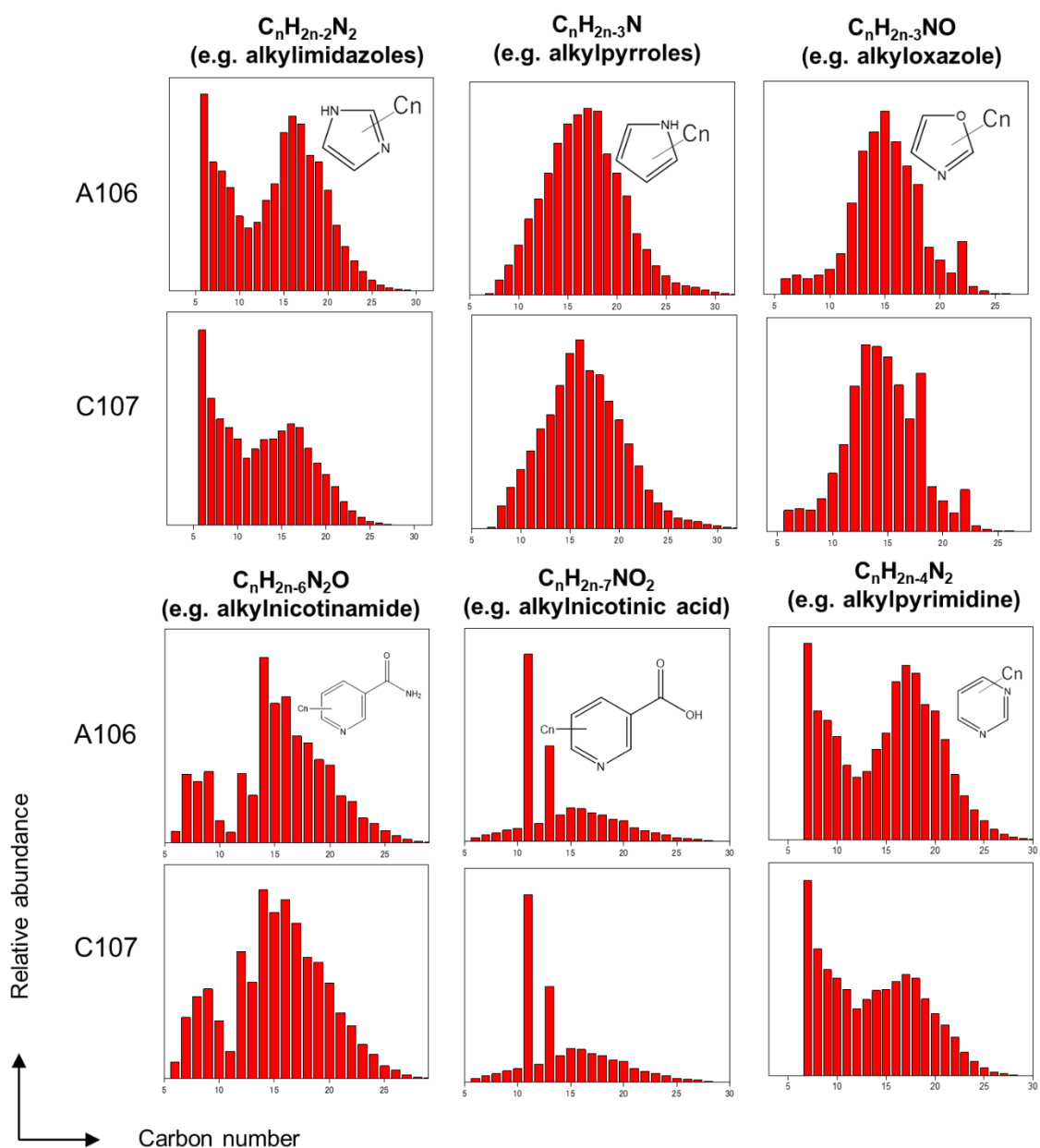
Supplementary Figure 5. Nicotinamide and isonicotinamide detected in the Orgueil extract.

LC/HRMS chromatograms at the m/z of 123.0553 which corresponds to the exact mass number for the protonated ion of nicotinamide and its structural isomers in the hot water extract and its acid hydrolysate from the Orgueil meteorite. Data for the blank sample and authentic standards are also shown for comparison. Numbers in parenthesis represents the relative intensity at each chromatogram. The observed peak at ~26 min on the mass chromatograms for the Orgueil extract was confirmed to be different from picolinamide by MS/MS measurements.



Supplementary Figure 6. Detection of $C_nH_{2n-4}N_2O_2$ molecules from the extract of A0106.

Mass chromatograms at the m/z corresponding to $C_nH_{2n-4}N_2O_2$ molecules with the carbon number (n) of 4 to 15. Alkylated analogues of uracil and imidazole-carboxylic acids are represented by this molecular formula. Numbers on the left indicate the relative intensities for each chromatogram.



Supplementary Figure 7. Relative abundance of alkylated CHNO molecules in the A0106 and C0107 samples. Comparison of the sum of peak area at the m/z ratio corresponding to the alkylated homologues of CHNO molecules having a general formula $C_nH_{2n-2}N_2$, $C_nH_{2n-3}N$, $C_nH_{2n-3}NO$, $C_nH_{2n-6}N_2O$, $C_nH_{2n-7}NO_2$, and $C_nH_{2n-4}N_2$ ($n = 5$ to 30), which include imidazole, pyrrole, oxazole, nicotinamide, nicotinic acid, and pyrimidine, respectively, between A0106 and C0107 samples. The horizontal axis shows the number of carbons (C_n -) and the vertical axis shows the sum of peak area at each m/z .

Supplementary Table 1. Raw data for the elemental and isotopic compositions of Ryugu grains C0107 shown in Figure 2.

Ryugu C0107	Shape	Weight (ug)	1 σ	Carbon (wt%)	1 σ	$\delta^{13}\text{C}$ (‰ vs. VPDB)	1 σ	Nitrogen (wt%)	1 σ	$\delta^{15}\text{N}$ (‰ vs. Air)	1 σ	weight C/N ratio	1 σ
C0107_Initial Bulk_#1	small grains	45.0		3.36		-7.4		0.12				27.0	
C0107_Initial Bulk_#2	small grains	130.5		3.24		-1.3		0.13		39.0		24.0	
C0107_Initial Bulk_#3	small grains	160.0		3.47		-2.1		0.14		32.6		24.1	
C0107_Initial Bulk_#4	small grains	169.6		4.27		15.7		0.15		38.8		28.9	
Average (n = 4)		126.3	±56.7	3.58	±0.47	1.22	±10.0	0.14	±0.01	36.8	±3.6	26.0	±2.4

	Shape	Weight (ug)	1 σ	Hydrogen (wt%)	1 σ	δD (‰ vs. VSMOW)	1 σ	Oxygen (wt%)*	1 σ	$\delta^{18}\text{O}$ (‰ vs. VSMOW)	1 σ	weight O/H ratio	1 σ
C0107_Initial Bulk_#5	small grains	527.6		1.12		255		13.8		11.0		12.3	
C0107_Initial Bulk_#6	small grains	327.2		1.10		281		14.1		12.0		12.8	
C0107_Initial Bulk_#7	small grains	264.2		0.94		270		12.3		13.4		13.0	
Average (n = 3)		373.0	±137.5	1.06	±0.10	269	±13	13.4	±1.0	12.1	±1.2	12.7	±0.4

	Shape	Weight (ug)	1 σ	Sulfur (wt%)	1 σ	$\delta^{34}\text{S}$ (‰ vs. VCDT)	1 σ	weight C/S ratio	1 σ
C0107_Initial Bulk_#8	small grains	29.8		5.77		-2.5		-	
C0107_Initial Bulk_#9	small grains	18.5		5.25		1.7		-	
C0107_Initial Bulk_#10	small grains	16.2		5.07		-1.5		-	
C0107_Initial Bulk_#11	small grains	17.8		4.76		-2.0		-	
C0107_Initial Bulk_#12	small grains	20.6		6.49		-1.2		-	
Average (n = 5)		20.6	±5.4	5.47	±0.7	-1.10	±1.62	Ave./Ave	0.66

*The concentration of pyrolyzed oxygen (i.e., thermally released oxygen, except for anhydrous silicate minerals). The isotope ratios of light elements are shown in each international standard scale.

Note: The raw data for A0106 have been shown in ref. 3.

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