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Distribution of extraterrestrial nucleobases, other N-heterocycles, and their precursors in a sample from asteroid Bennu

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The recent discovery of all five canonical nucleobases in samples from Bennu provides compelling evidence that some of life's ingredients were synthesized abiotically in the parent body of this asteroid and/or its precedent components. However, due to the sample availability and the limited method for the analysis, the detailed distribution of nucleobases in the samples remains elusive. Here we report the concentrations of a diverse suite of nitrogen (N)-heterocycles including nucleobases extracted by 2% and 20% hydrochloric acid from a homogenized Bennu sample. The detection of both canonical and non-canonical nucleobase pairs confirms that these biologically important compounds are extraterrestrial. Pyrimidines are more abundant than purines—like the Orgueil meteorite, but unlike the Murchison meteorite and asteroid Ryugu samples—suggesting preferential synthesis in ammonia-rich ices from the outer Solar System. The distribution of other N-heterocycles is consistent with extensive aqueous alteration on the parent body. High concentrations of urea underscore its role in N-heterocycle synthesis. Our findings offer important information on the prebiotic inventory of N-heterocycles in the Solar System.

More than 200 chemical species have been identified in the interstellar medium by radio telescopes[1], and the number of detected species will increase in future astronomical observations using very sensitive telescopes such as the Atacama Large Millimeter/submillimeter Array (ALMA) and the James Webb Space Telescope (JWST). However, it is still far below the tens of thousands of organic molecules with elemental compositions containing carbon (C), hydrogen (H), nitrogen (N), oxygen (O), and sulfur (S) measured in carbonaceous meteorite solvent extracts[2], which are among the most primitive materials in the Solar System. The observed molecular diversity in meteoritic organics is a consequence of the chemical processes that interstellar molecules have undergone during the evolution of molecular clouds toward the formation of stars and planetary systems (Fig. 1). Therefore, the keys to understanding prebiotic chemistry in space should be recorded in such primitive Solar System materials.

Our understanding of organic molecules in carbonaceous meteorites has been substantially improved thanks to the development of analytical techniques over the past few decades. We now know that various classes of organic molecules of biological relevance such as amino acids, carboxylic acids, sugars, nucleobases and their chemical precursors including ammonia and aldehydes are present in carbonaceous meteorites[3–5]. Given that the flux of exogenous material to the early Earth (~10^9 kg carbon yr^{-1})[6] was much higher than it is today (~10^6 kg carbon yr^{-1})[7], carbon-rich asteroids and their fragments could have been a source of the prebiotic organic inventory on Earth[6].

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Direct analysis of organic compounds from pristine samples of the carbonaceous asteroid (101955) Bennu offers a rare opportunity to test long-standing hypotheses about the extraterrestrial origins of life's building blocks. NASA's Origins, Spectral Interpretation, Resource Identification, and Security–Regolith Explorer (OSIRIS-REx) spacecraft delivered 121.6 g of Bennu samples to Earth on September 24, 2023, without any uncontrolled exposure to the terrestrial atmosphere[8]. Early analysis of the organic composition in solvent extracts from aggregate (unsorted) samples indicated that Bennu material is rich in ammonia and includes over 10,000 nitrogen-containing soluble organic molecules such as amino acids, amines, purines and pyrimidines[9] whose concentrations are comparable to or higher than those previously found in carbonaceous meteorites such as Tarda (ungrouped, petrologic type 2 (C2-ung.)) and Orgueil (Ivuna-like, petrologic type 1 (CI1))[10], as well as those in samples from the carbonaceous asteroid Ryugu[11–13].

Bennu material has also been shown to have all five canonical nucleobases[9,14]—adenine (A), guanine (G), cytosine (C), thymine (T), and uracil (U)—as well as sugars, including ribose[15], which serve as essential structural components of deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) in terrestrial biology. The detection of these components is significant from the perspective of prebiotic evolution toward the emergence of functionalized molecules. In addition, various N-heterocycles (nitrogen-containing ring molecules), including their structural isomers and nicotinic acid (vitamin B_3), were detected in a hydrochloric acid (HCl) extract, suggesting rich nitrogen chemistry occurring on the Bennu parent body and/or its precedent environments[9]. Hence, uncovering asteroidal biomolecule inventories teaches one about the potential diverse prebiotic chemistry not only on asteroids but also throughout the Solar System, including the early Earth.

The way molecules are extracted from a sample strongly influences which species are detected and how their origins are interpreted. Glavin & Dworkin et al. [9] used concentrated HCl (20% w/w) to extract N-heterocycles from a Bennu sample. This method efficiently characterizes nucleobases in natural samples and builds on recent technical developments[5,12,16,17]. However, this extraction method could have led to the decomposition of more acid-fragile molecules such as hexamethylenetetramine and nicotinamide[12,18]. This decomposition may have caused a loss of information about the original distribution of some N-heterocycles in the samples prior to extraction. Moreover, extraction using a strong acid could also result in a loss of some information about the spatial distribution of molecules and their interactions with minerals in samples. For example, Oba et al.[5] used diluted (2%) HCl with ultrasonication at room temperature for the extraction of nucleobases from carbonaceous meteorites and detected all five in Murchison (Mighei-like, petrologic type 2 (CM2)), four in Tagish Lake (C2-ung.), and three in Murray (CM2). These findings imply that some N-heterocycles are present in labile form (e.g., isolated or weakly bound to others) in meteorites.

Furthermore, Koga et al.[16] performed a detailed survey of the distribution of nucleobases in the Murchison meteorite using a stepwise extraction (hot water followed by hot 20% HCl). In addition to detecting all canonical nucleobases, they found that pyrimidine bases were primarily detected in the hot water extract, whereas purine bases were primarily detected in the HCl extract. These findings suggest that most pyrimidines were originally present in labile form, while the major fraction of purines was present as acid-labile macromolecules and/or had strong associations with minerals in the Murchison meteorite. Such information might be helpful to understand the evolutionary history of nucleobases and other N-heterocycles in asteroid parent bodies and subsequent environments.

In the present study, we extend the research on the distribution of nucleobases and other N-heterocycles in Bennu by using a larger sample (~0.6 g, sample id OREX-800107-108, vs. ~0.02 g, OREX-800044-101 ref. 9) and an updated analytical protocol (Samples and Methods, Supplementary Fig. 1). OREX-800107-108 was subsampled from a 6.425 g aggregate sample that was physically homogenized by crushing[19]. We detected all canonical nucleobases (cytosine, uracil, thymine, adenine, and guanine), as well as their structural isomers and homologues, which are rare in terrestrial biology, and other N-heterocycles, including some acid-fragile molecules (Fig. 2 and Supplementary Fig. 2). Detection of this diverse suite of N-heterocycles, including canonical nucleobases, constrains the prebiotic organic inventory of the early Solar System, given that Bennu samples have not been compromised by terrestrial contamination and provide a critical abiotic chemical baseline to aid in the search for chemical biosignatures in our Solar System and beyond.

Results and Discussion

Nucleobases in Bennu sample OREX-800107-108

To determine which nitrogen-bearing bases this Bennu sample contains, we analysed both mild (2%) and strong (20%) HCl extracts using high-resolution mass spectrometry.

Detection of pyrimidine and purine bases in 2% HCl extract. Supplementary Fig. 3 shows mass chromatograms at the mass-to-charge ratios (m/z) corresponding to the protonated ions of canonical nucleobases ($[M + H]^+$: M = nucleobase) detected in the 2% HCl extract from the Bennu sample and those in the procedural control (Samples and Methods), as well as those of the corresponding authentic chemical reagents. For the pyrimidine nucleobases (cytosine, thymine, and uracil), several peaks appeared in the sample chromatograms, and one peak in each chromatogram appeared at the same retention time with their standard reagents.

The concentrations of the detected pyrimidine nucleobases were 21 ± 4, 341 ± 44, and 143 ± 14 pmol g^{-1} for cytosine, uracil, and thymine, respectively (Table 1). For the canonical purine nucleobases, peaks corresponding to adenine and guanine were observed above the procedural control levels in the Bennu sample chromatograms. The tandem mass spectrometry (MS/MS) analysis of the Bennu extracts and the corresponding standard reagents (Supplementary Fig. 4) confirmed the presence of both molecules in the 2% HCl extract. Their blank-corrected concentrations were 37 ± 2 and 4 ± 1 pmol g^{-1} for adenine and guanine, respectively (Table 1). In addition to the canonical nucleobases, some non-canonical nucleobases such as 6-methyluracil, 2-hydroxypyrimidine, 4-hydroxypyrimidine, 5-hydroxypyrimidine, and a trace amount of hypoxanthine were also detected in the 2% HCl extract (Supplementary Figs. 3 and 5). The total concentration of the detected pyrimidine and purine nucleobases in the 2% HCl extract was 738 ± 47 and 42 ± 2 pmol g^{-1}, respectively, showing pyrimidine enrichment, with an abundance ratio of purine to pyrimidine nucleobases (Pu/Py) of 0.057.

Isomeric and non-canonical nucleobases in 20% HCl extract. The 20% HCl extract reveals a broader chemical inventory, including isomeric and non-canonical nucleobases that extend beyond the five canonical bases detected in the milder extract. Figure 3 shows mass chromatograms at the m/z corresponding to the protonated ions of canonical nucleobases in the 20% HCl extract from the Bennu sample and the SiO_2 control experiment, as well as those of the authentic chemical reagents of nucleobases and their isomers. Following the same procedure for the peak assignment described above, we have successfully detected all canonical nucleobases in the 20% HCl extract from the sample. The presence of adenine, guanine, and cytosine was also confirmed by additional measurements such as MS/MS analyses and a co-injection with chemical reagents (Supplementary Figs. 6 and 7). The blank-corrected concentration of canonical nucleobases ranged from 36 to 180 pmol g^{-1}, where cytosine was the most abundant (Table 1). In addition to canonical nucleobases, several nucleobase isomers including isocytosine (59 ± 2 pmol g^{-1}), isoguanine (17 ± 11 pmol g^{-1}), 8-aminopurine (21 ± 1 pmol g^{-1}), 1-methyluracil (1 ± 1 pmol g^{-1}), and 6-methyluracil (99 ± 27 pmol g^{-1}), as well as other nucleobases that are rare in biology including 5-methylcytosine (43 ± 4 pmol g^{-1}), hypoxanthine (20 ± 1 pmol g^{-1}), 7(H)-purin-8-ol (60 ± 6 pmol g^{-1}), xanthine

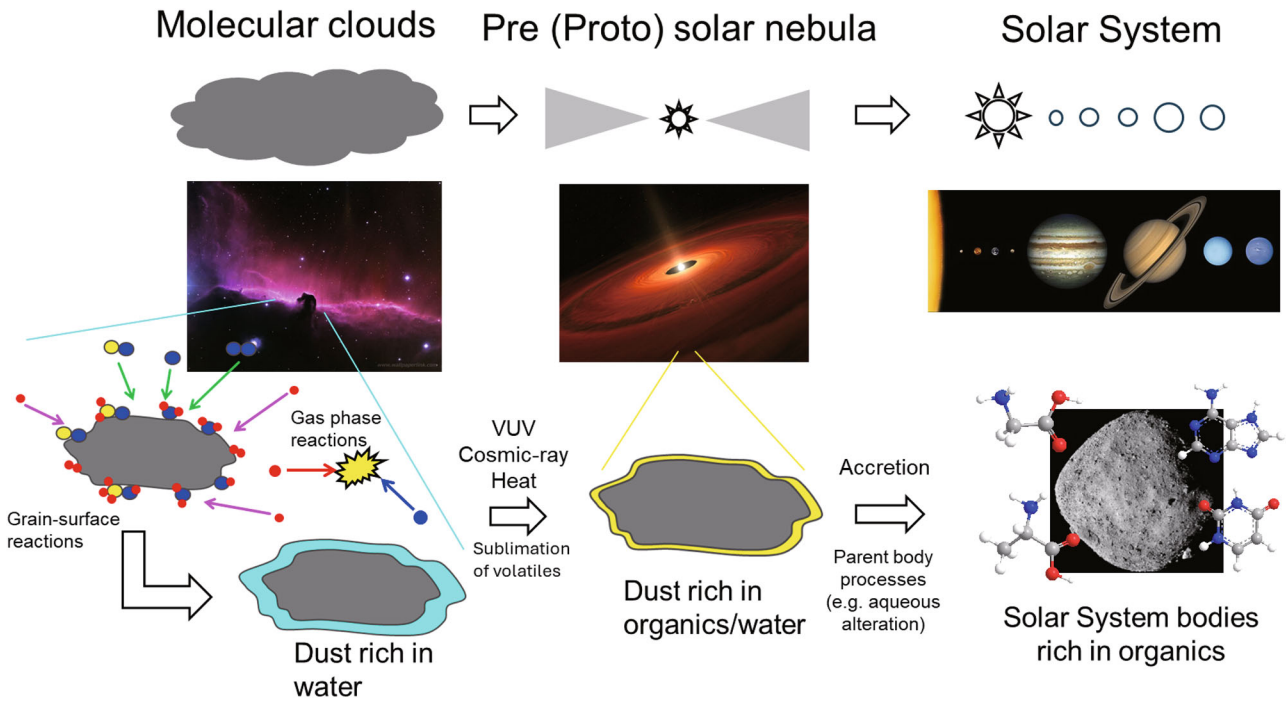

Fig. 1 | A brief overview of planetary and chemical evolution. Chemical processes in molecular clouds, such as grain-surface reactions and reactions in the gas phase, yield fundamental molecules, such as water, methanol, and ammonia. After experiencing further processes induced by energetic particles such as vacuum ultraviolet (VUV) photons and cosmic rays in the pre- or protosolar nebula stage, as well as (hydro)thermal events occurring on Solar System bodies after their formation, further complex organic molecules, such as those found in Bennu, Ryugu, and carbonaceous meteorites, may have been synthesized. (Image credit: NAOJ, NASA).

(66 ± 10 pmol g^{-1}), 2,6-diaminopurine (3 ± 1 pmol g^{-1}), and 6,8-diaminopurine (67 ± 5 pmol g^{-1}) were identified in the same extract (Figs. 3 and 4, Supplementary Fig. 8, Table 1). 2-hydroxypyrimidine was predominant with a concentration of 375 ± 21 pmol g^{-1} (Table 1). 4-hydroxypyrimidine, also known as 4(3H)-pyrimidinone, a structural isomer of 2-hydroxypyrimidine, was also abundant in the 20% HCl extract (351 ± 14 pmol g^{-1}). This molecule was also identified in the 2% HCl extract of Murchison[5], but at a lower concentration (~63 pmol g^{-1}) than we found for Bennu. The presence of 2,8-diaminopurine was inferred from the mass chromatogram (Fig. 4)[16]. However, due to the lack of a 2,8-diaminopurine standard, the precise assignment and quantification of this purine was not possible.

The total concentrations of the detected pyrimidine and purine nucleobases in the 20% HCl extract were 1292 ± 40 and 442 ± 22 pmol g^{-1}, respectively (Pu/Py = 0.34). The sum of the detected nucleobase concentrations in both extracts was 2030 ± 61 pmol g^{-1} for pyrimidines and 484 ± 20 pmol g^{-1} for purines, showing a pyrimidine-enriched nature overall (Pu/Py = 0.24). This is opposite to the distribution of nucleobases in Murchison, where the total purine nucleobases were several times more abundant than pyrimidines[16], due to the possible explanation for which we consider in the "Comparison with nucleobases in Ryugu and carbonaceous meteorites" section.

Comparison of nucleobases between 2% HCl and 20% HCl extracts

By comparing mild and strong acid extractions, we can distinguish between molecules that were freely available in Bennu's matrix (extractable by mild solution) and those that were bound within minerals or macromolecular material (requiring a stronger solution to extract), revealing how organics were stored on the asteroid.

The abundances of purine and pyrimidine nucleobases detected in the 20% HCl extract of Bennu sample OREX-800107-108 were ~11 and ~1.8 times higher, respectively, than those in the 2% HCl extract (Table 1), suggesting that the 20% HCl solution is more efficient at extracting nucleobases from the Bennu matrix. A similar trend was observed for purine nucleobases in the Murchison meteorite. Koga et al.[16] performed a similar stepwise extraction—but with pure water followed by 20% HCl—of nucleobases from Murchison and found that purines were ~12 times more abundant in the 20% HCl extract than in the pure water extract. In the case of Murchison, this could be partly attributed to the lower solubility of purine nucleobases than pyrimidines in neutral water[20]. However, purine and pyrimidine nucleobases are soluble in both 2% and 20% HCl solutions. Hence, the difference in solubility of nucleobases may not be the main reason for the higher concentration of purine that we observed in the 20% HCl extract of Bennu sample OREX-800107-108. We therefore consider other possible explanations.

Nucleobases within carbonate minerals. Interactions between nucleobases and inorganic materials in the sample could have caused the observed differences in extraction efficiencies between 2% and 20% HCl. For example, nucleobases might be trapped within carbonates. Lauretta & Connolly et al. [8] reported several kinds of carbonates (e.g., dolomite and calcite) in Bennu samples. CO_2-bearing fluids have been observed in a nanosized inclusion inside a calcite crystal in the Sutter's Mill carbonaceous meteorite (CM2)[21], as have amino acids in synthetic $CaCO_3$ ref. 22. To evaluate whether carbonate minerals could retain and later release nucleobases, we conducted controlled laboratory experiments using synthesized $CaCO_3$ (Methods). In brief, we synthesized $CaCO_3$ (calcite) from aqueous solutions containing nucleobases (Supplementary Fig. 9) and extracted nucleobases from $CaCO_3$ using the procedure outlined in the Methods, except that we substituted 2% HCl with H_2O. We found that ~90% of the nucleobases were extracted with H_2O, while the remaining ~10% were extracted after the dissolution of $CaCO_3$ by 20% HCl (Supplementary Fig. 10). Although the physicochemical conditions for the synthesis of $CaCO_3$ in a laboratory may not reproduce those on the parent asteroid of Bennu, our preliminary experimental data indicate that nucleobases could be trapped inside or adsorbed on the surface of the carbonates.

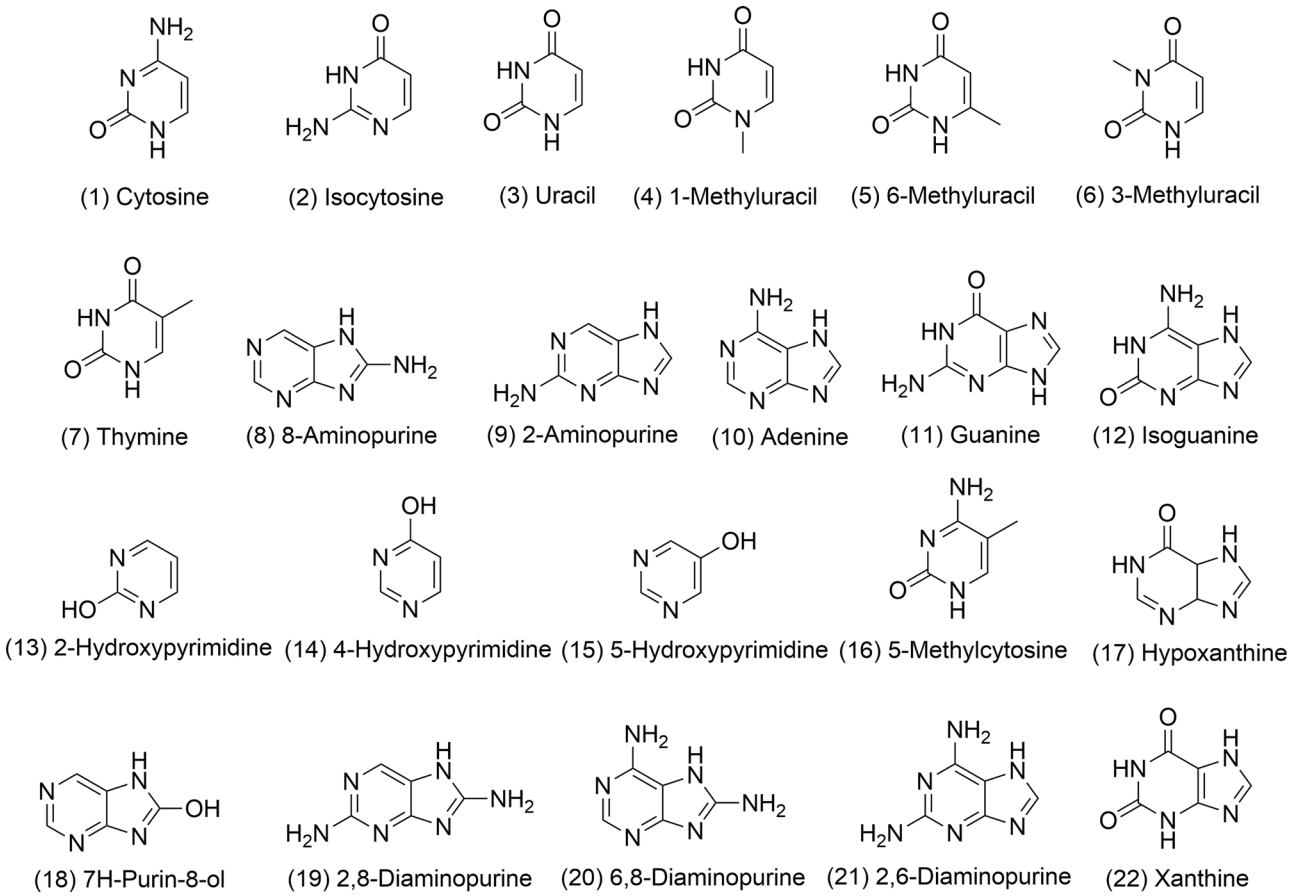

Fig. 2 | Structures of representative pyrimidine and purine nucleobases. Molecular structures of pyrimidine and purine nucleobases detected in Bennu sample OREX-800107-108. The numbers in parentheses correspond to those shown in the chromatograms (e.g., Figs. 3 and 4).

However, when the synthesized carbonates were exposed to 2% HCl with ultrasonication at room temperature, they were also dissolved in the solution. Thus, if nucleobases were trapped in carbonates in the Bennu sample, they should have been extracted by the 2% HCl. In contrast, for stepwise extraction with H_2O followed by 20% HCl, as in Koga et al., [16] some fractions of nucleobases in carbonates might not be extractable until the second step. Hence, the higher concentrations of nucleobases in the 20% HCl extract vs. the water extract of Murchison[16] could be partly attributable to the release of the trapped nucleobases from carbonates, but this does not seem to be the case for the Bennu sample we analyzed.

Effects of adsorption onto clay minerals. Another possible explanation for the higher abundance of purine nucleobases in the 20% vs. the 2% HCl extract of OREX-800107-108 is that the degree of adsorption onto clay minerals varies between purines and pyrimidines. Previous laboratory experiments demonstrated that nucleobases can be adsorbed on clay minerals with differing degrees of interaction[23]. Because clay minerals such as smectite are common in Bennu samples[8], adsorption of nucleobases is likely to occur. As a general trend, with increasing size of molecules, the efficiency of adsorption also increases because van der Waals forces contribute more to adsorption affinity[23]; this trend suggests a more effective adsorption of purine bases than pyrimidine ones. This is in accordance with our finding of a higher Pu/Py in the 20% HCl extract than in the 2% HCl extract. Cytosine was mainly detected in the 20% HCl extract, unlike the other pyrimidine bases; this may be partly because cytosine has higher adsorption energies on clay minerals[24].

Comparison of nucleobases between Bennu samples

Placing our results from sample OREX-800107-108 alongside those of earlier analyses allows us to trace chemical diversity across Bennu samples. In Fig. 5, the concentrations of each canonical nucleobase in the 2% and 20% HCl extracts are compared with those reported by Glavin & Dworkin et al.[9], who extracted nucleobases from Bennu sample OREX-800044-101 with 20% HCl only. The total (sum of 2% and 20% HCl extracts) concentration of each nucleobase we detected in OREX-800107-108 was less than that detected in the 20% HCl extract from OREX-800044-101 (except in the case of guanine). This is likely due to the heterogeneous distribution of nucleobases in Bennu samples, as has often been observed for organic molecules in carbonaceous meteorites (e.g., amino acids in different portions of Tagish Lake)[25]. Indeed, isocytosine and 5-methylcytosine were detected in OREX-800107-108 only, while purine ($C_5H_4N_4$) was in OREX-800044-101 only (Table 1). The Bennu samples likely have a heterogeneous spatial distribution of N-heterocycles on micrometer scales, as observed in a sample returned from the asteroid Ryugu[26].

Chemical precursors and acid hydrolysis effects. One of the other possible reasons for the lower concentrations detected in the sample we analyzed is the presence of nucleobase precursors. These precursors are likely soluble in water and can release nucleobases through acid hydrolysis. Treatment with 20% HCl at 110 °C, as in the case of OREX-800044-101, would promote this conversion more effectively. Extraction from OREX-800107-108 by sonication at room temperature in 2% HCl may not have been sufficient to promote acid hydrolysis; hence, some precursors may have remained intact. Indeed, acid hydrolysis of the water extract from the Murchison and Orgueil meteorites with 20% HCl yielded nucleobases whose concentrations exceeded those in the water extract[12,16].

To test whether acid hydrolysis of precursor molecules could account for the higher nucleobase yields, we conducted laboratory experiments using synthesized guanosine isomers (Supplementary Methods and

Table 1 | Concentrations (in picomoles per gram) of canonical nucleobases and their analogues in Bennu samples OREX-800107-108 and OREX-800044-101[a], Ryugu samples A0480 and C0370[b], and the Murchison meteorite[c]

Sample Name	Bennu (800107-108) pmol g^{-1}			Bennu (800044-101)[a] pmol g^{-1}	Ryugu (A0480)[b] pmol g^{-1}	Ryugu (C0370)[b] pmol g^{-1}	Murchison (CM2)[c] pmol g^{-1}
Fraction	2% HCl	20% HCl	SUM	20% HCl	SUM	SUM	SUM
Canonical Nucleobases							
Uracil	341 ± 44 [d]	148 ± 9	490 ± 45	893 ± 56	86 ± 15	199 ± 11	1080 ± 128
Thymine	143 ± 14	36 ± 8	178 ± 16	571 ± 39	58 ± 5	134 ± 14	532 ± 81
Cytosine	21 ± 4	180 ± 6	201 ± 8	306 ± 73	21 ± 4	307 ± 24	180 ± 6
Adenine	37 ± 2	60 ± 2	97 ± 2	261 ± 118	83 ± 11	49 ± 3	689 ± 17
Guanine	4 ± 2	126 ± 15	131 ± 15	119 ± 70	106 ± 3	558 ± 10	3980 ± 685
Canonical Sum	546 ± 47	550 ± 20	1097 ± 51	2151 ± 170	352 ± 20	1247 ± 32	6461 ± 702
Other Purines and Pyrimidines							
Isocytosine	n.d.[e]	59 ± 2	59 ± 2	n.d.	n.r.	n.r.	n.r.
2-Hydroxypyrimidine	60 ± 3	375 ± 21	435 ± 21	n.r.[g]	n.r.	n.r.	n.r.
4-Hydroxypyrimidine	50 ± 5	351 ± 14	401 ± 15	n.r.	n.r.	n.r.	n.r.
5-Hydroxypyrimidine	18 ± 1	n.d.	18 ± 1	n.r.	n.r.	n.r.	n.r.
5-Methylcytosine	n.d.	43 ± 4	43 ± 4	n.r.	n.r.	n.r.	n.r.
1-Methyluracil	n.d.	1 ± 1	1 ± 1	33 ± 6	n.r.	n.r.	32
3-Methyluracil	n.d.	n.d.	n.d.	n.d.	n.r.	n.r.	n.r.
6-Methyluracil	105 ± 0.4	99 ± 27	204 ± 27	393 ± 44	73 ± 7	88 ± 16	198 ± 8
Hypoxanthine	1 ± 0.2	20 ± 1	21 ± 1	124 ± 51	44 ± 2	123 ± 1	1066 ± 16
7(H)-Purine-8-ol	n.d.	60 ± 6	60 ± 6	n.r.	n.r.	n.r.	n.r.
Xanthine	n.d.	66 ± 10	66 ± 10	402 ± 117	36 ± 2	108 ± 9	1276 ± 94
Purine	n.d.	n.d.	n.d.	4 ± 1	n.r.	n.r.	28 ± 1
2-Aminopurine	n.d.	n.d.	n.d.	n.d.	n.r.	n.r.	4 ± 1
8-Aminopurine	n.d.	21 ± 1	21 ± 1	n.d.	n.r.	n.r.	230 ± 7
2,6-Diaminopurine	n.d.	3 ± 1	3 ± 1	165 ± 31 [h]	n.r.	n.r.	171 ± 7 [h]
6,8-Diaminopurine	n.d.	67 ± 5	67 ± 5		n.r.	n.r.	
2,8-Diaminopurine	n.d.	tentative[f]	n.d.	n.d.	n.r.	n.r.	n.r.
Isoguanine	n.d.	17 ± 11	17 ± 11	129 ± 28	n.r.	n.r.	589 ± 9
Other Purines and Pyrimidines Sum	234 ± 6	1184 ± 41	1418 ± 40	1195 ± 186	153 ± 8	319 ± 18	3594 ± 97
Total Pyrimidines	738 ± 47	1292 ± 40	2030 ± 61	2197 ± 77	238 ± 17	727 ± 32	2022 ± 152
Total Purines	42 ± 2	442 ± 23	484 ± 20	1204 ± 162	269 ± 12	849 ± 14	8033 ± 692
Pu/Py	0.057	0.34	0.24	0.55	1.1	1.2	4.0
Canonical/Others	2.3	0.5	0.8	1.7	2.3	3.9	1.8

[a]ref. 9
[b]Sum of the H_2O and 20% HCl extracts[31]
[c]Sum of the H_2O and 20% HCl extracts[16]
[d]Values are the average of two measurements ($n = 2$) with a standard error, $\delta x = \sigma_x \cdot (n)^{-1/2}$. The error in the total sum was determined by adding the absolute errors of the individual compounds in quadrature.
[e]Not detected
[f]Tentatively detected but not quantified.
[g]Not reported
[h]2,6-Diaminopurine and 6,8-diaminorpurine were not distinguished.

Results). We found that the yield of guanine was 20–30% after the treatment with pure H_2O or 2% HCl, whereas after that with the 20% HCl solution, the guanine yield was 100%; that is, all guanosine was quantitatively hydrolysed to yield guanine (and ribose) (Supplementary Fig. 11). We expect that other possible precursors with acid-labile bonds may also yield nucleobases upon treatment with 20% HCl.

Contributions from insoluble organic matter. Koga et al. [16] suggested another possibility for the origin of purine nucleobases in the 20% HCl extract from Murchison: they are fragments of insoluble organic matter (IOM) present in the meteorite. Previous studies have demonstrated that the hydrous (or hydro-) pyrolysis of IOM can yield various organic molecules such as monocarboxylic acids[27], dicarboxylic acids[28], and polycyclic hydrocarbons[29]. Therefore, we expect that nucleobases are also released by the degradation of IOM. Because IOM is present in Bennu samples[30], the IOM-derived formation pathways may be possible to occur, which could be investigated in future studies.

Comparison with nucleobases in Ryugu and carbonaceous meteorites

Oba et al.[12] reported the detection of uracil in samples returned from the asteroid Ryugu (A0106 and C0107), but other nucleobases were not detected in their study. This is mainly due to the limited abundance of Ryugu samples used for nucleobase analyses. However, very recently, all canonical nucleobases and some of their structural isomers were found in H_2O and 20% HCl extracts from different Ryugu samples (A0480 and C0370)[31].

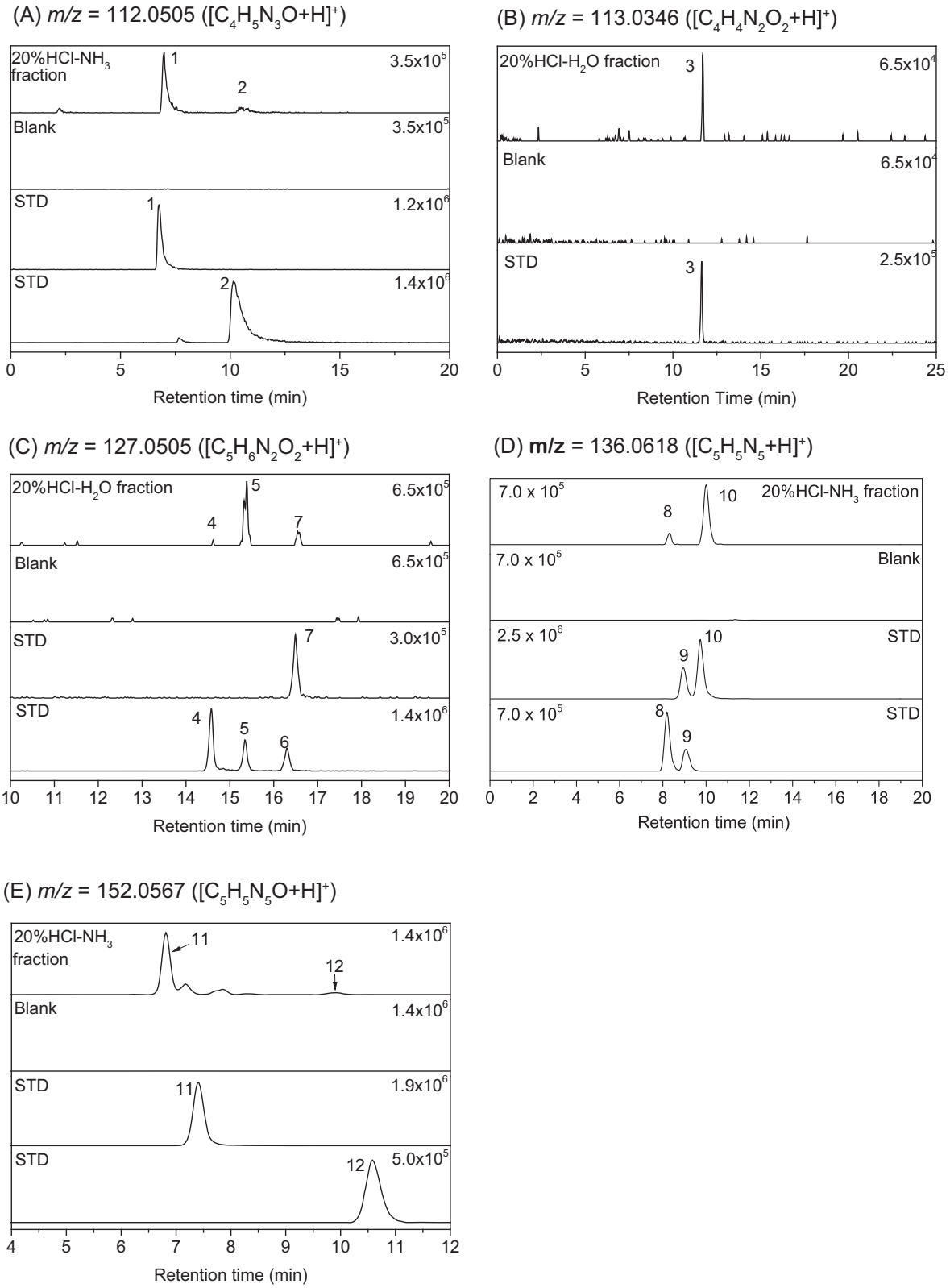

Fig. 3 | Detection of all canonical nucleobases in the 20% HCl extract. Extracted ion chromatograms at *m/z* of (**A**)112.0505, (**B**) 113.0346, (**C**) 127.0502, (**D**) 136.0618, and (**E**) 152.0567, corresponding to the protonated ions of cytosine, uracil, thymine, adenine, and guanine, respectively, in the 20% HCl extract from the Bennu sample OREX-800107-108, and those for the blank samples and their standard reagents are shown for comparison. Peaks were identified by comparison of their retention times, exact monoisotopic masses with those in the standard reagents analyzed on the same day, an MS/MS analysis and/or a co-injection measurement, and are designated by peak number as follows: (1) cytosine, (2) isocytosine, (3) uracil, (4) 1-methyluracil, (5) 6-methyluracil, (6) 3-methyluracil, (7) thymine, (8) 8-aminopurine, (9) 2-aminopurine, (10) adenine, (11) guanine, and (12) isoguanine. The numbers in the upper right corners indicate the y-axis scale for each chromatogram.

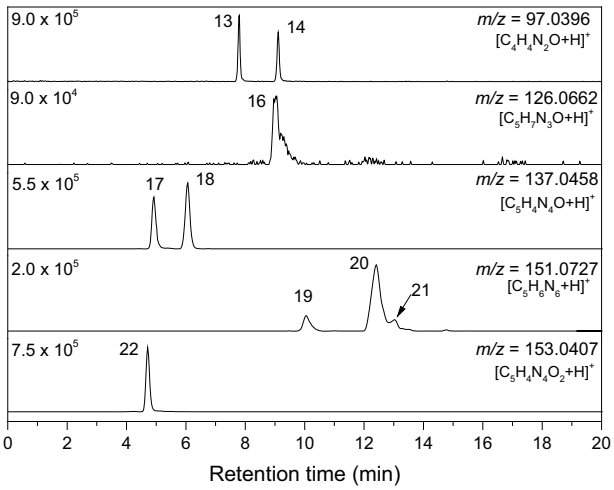

Fig. 4 | Detection of other nucleobases in the 20% HCl extract. Extracted ion chromatograms (EICs) at *m/z* of (from top to bottom) 97.0396, 126.0662, 137.0458, 151.0727, and 153.0407, in the 20% HCl extract from Bennu sample OREX-800107-108. Peaks were identified by comparison of their retention times and exact monoisotopic masses with those in the standard reagents analyzed on the same day, and are designated by peak number as follows: (13) 2-hydroxypyrimidine, (14) 4-hydroxypyrimidine, (16) 5-methylcytosine, (17) hypoxanthine, (18) 7H-purin-8-ol, (19) 2,8-diaminopurine (tentative)[16], (20) 6,8-diaminopurine, (21) 2,6-diaminopurine, and (22) xanthine. The numbers on the left indicate the y-axis scale for each chromatogram. The EICs of the corresponding blank samples and the standard reagents are shown in Supplementary Fig. 8.

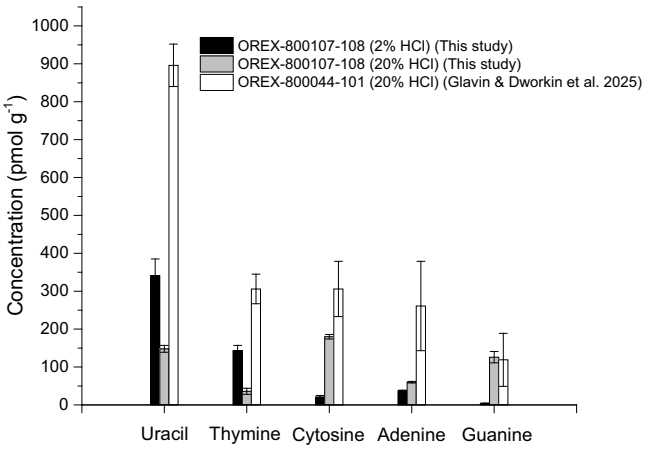

Fig. 5 | Distribution of nucleobases in Bennu samples OREX-800107-108 (this study) and OREX-800044-101. Concentrations with standard errors of canonical nucleobases detected in the 2% and 20% HCl extracts from OREX-800107-108 and those in the 20% HCl extract from OREX-800044-101[9]. Note that the 20% extract from OREX-800107-108 was obtained after the extraction with 2% HCl (Methods).

From the viewpoint of mineral and elemental compositions, both Bennu and Ryugu are similar to the CI carbonaceous meteorites, which are primarily composed of phyllosilicates with minor fractions of other minerals such as magnetite and sulfides[8,32]. These two asteroids also show some similarity in nucleobase distribution. For example, the total concentration of canonical nucleobases in Bennu sample OREX-800107-108 (1097 ± 51 pmol g^{-1}) is close to that in Ryugu sample C0370 (1247 ± 32 pmol g^{-1}). Even at the compound-specific level, some molecules are similar between Bennu and Ryugu (Table 1).

However, the relative abundances of purine and pyrimidine nucleobases are very different. The total concentration of pyrimidine nucleobases exceeded that of purine nucleobases in Bennu samples OREX-800044-101 (ref. 9) and OREX-800107-108 (this study), with Pu/Py being 0.55 and 0.24, respectively. In contrast, the Pu/Py was 1.1 and 1.2 for the Ryugu samples, indicating that the abundances of purines and pyrimidines were comparable (Table 1)[31]. The Pu/Py of the CI1 meteorite Orgueil is highly pyrimidine-dominant (Pu/Py = 0.099)[31], similar to the Bennu samples. On the other hand, nucleobases in Murchison (CM2) are highly purine-enriched (Pu/Py = 4.0 for the sum of hot water and 20% HCl extracts)[16].

Controls on purine-to-pyrimidine ratios (Pu/Py). The ratio of purine to pyrimidine bases (Pu/Py) acts as a chemical fingerprint of the environment in which these molecules formed. We expect that the Pu/Py is constrained by some parameters in samples that are relevant for the formation of nucleobases. For example, Glavin & Dworkin et al.[9] reported that Bennu samples contain abundant ammonia (NH_3; 13.6 μmol g^{-1}), concluding that the parent body of Bennu likely accreted ammonia-rich ices that were from the outer Solar System. Because ammonia might be an important N-source for pyrimidine nucleobases and their precursors, such as urea (NH_2CONH_2) and guanidine ($NHC(NH_2)_2$) in prebiotic chemical reactions[33], the NH_3-enriched environments and the alkaline-biased aqueous alteration (i.e., pH = 8.23 ± 0.02 in the water extract[15]) could lead to the preferential synthesis of pyrimidine nucleobases.

Indeed, we detected urea at a concentration far exceeding the total concentration of N-heterocycles including nucleobases (171 nmol g^{-1}; Table 2, Supplementary Fig. 12), which can also be effectively synthesized in presolar NH_3-enriched environments at low temperatures[34,35]. We also detected alkylated analogues of urea, such as 1-methylurea and 1,3-dimethylurea, whose concentrations significantly decreased with increasing number of carbon atoms (Table 2). Fox and Harada[36] proposed a formation pathway of uracil by the reaction of malic acid ($HOOCCH_2CH(OH)COOH$) with urea. In addition, Robertson & Miller[37] reported an effective prebiotic synthesis of cytosine and uracil in the reaction of urea with the enol form of 2-cyanoacetaldehyde or 3-hydroxyacrylonitrile (HOCH=CHCN) under relevant conditions on the early Earth.

Therefore, both NH_3 and urea are likely involved in the synthesis of N-heterocycles, including nucleobases. Urea and NH_3 have also been detected in Ryugu samples[31,38,39], but their concentrations are much lower than those in the Bennu samples analysed, which could have contributed to the observed difference in the Pu/Py ratio between samples from these two asteroids.

The preferential synthesis of pyrimidine bases in cold (<200 K), ammonia-rich environments such as Bennu's parent body[9] could explain the low Pu/Py ratios observed in Bennu samples and Orgueil. In addition, it has been proposed that the effective radius of the NH_3 snowline is much smaller than that of the H_2O snowline when NH_3 is preserved as an ammonium ion (NH_4^+)[40]. Under such circumstances, a slightly higher-temperature (>200 K) scenario for reproducing pyrimidine-enriched distributions in Bennu and Orgueil could also be possible to promote chemical processes, depending on the types of ammonium salts present in those parent bodies (e.g., ammonium acetate, $NH_4^+CH_3COO^-$, desorbs from dust surfaces at ~200 K[40]). The pyrimidine enrichment is also consistent with the distribution of nucleobases formed by photochemical processes under simulated conditions in molecular clouds[41], suggesting a possible interstellar origin.

The Pu/Py ratio may also be constrained by the abundance of hydrogen cyanide (HCN) in the environments where nucleobases were synthesized, based on earlier prebiotic experiments showing an effective formation of purine nucleobases from HCN and its relevant molecules[42,43]. Indeed, abundant HCN has been detected in Murchison (up to 400 nmol g^{-1})[44,45], which could have resulted in the high abundance of purine nucleobases (Pu/Py ~ 4.0). In addition, even higher concentrations of cyanide have been reported in other CM chondrites (up to ~2500 nmol g^{-1})[45], suggesting preferential purine synthesis in the parent body(ies) of such meteorites.

Table 2 | Concentrations (in picomoles per gram) of non-nucleobase N-bearing molecules in Bennu samples OREX-800107-108 and OREX-800044-101[a], Ryugu A0408[b], and the Murchison meteorite[c]

Sample Name	Bennu (OREX-800107-108) pmol g^{-1}			Bennu (OREX-800044-101)[a] pmol g^{-1}	Ryugu (A0480)[b] pmol g^{-1}			Murchison (CM2)[c] pmol g^{-1}
Fraction	2% HCl	20% HCl	SUM	20% HCl	H_2O	20% HCl	SUM	2% HCl
Melamine	4 ± 1 [d]	n.d[f]	4 ± 1	n.r.[g]	n.r.	n.r.	n.r.	34579[i]
Ammeline	8 ± 1	n.d	8 ± 1	n.r.	n.r.	n.r.	n.r.	496[i]
Ammelide	200 ± 22	n.d	200 ± 22	n.r.	n.r.	n.r.	n.r.	16[i]
Cyanuric acid	2748 ± 262	n.a.	2748 ± 262	n.r.	n.r.	n.r.	n.r.	23[i]
Imidazole	4044 ± 180	2767 ± 336	6811 ± 381	tentative[h]	n.r.	n.r.	n.r.	1412
2-Imidazole carboxylic acid	393 ± 22	226 ± 19	619 ± 29	50 ± 6	n.r.	n.r.	n.r.	170
4-Imidazole carboxylic acid	n.d.	2562 ± 39	2562 ± 39	134 ± 22	n.r.	n.r.	n.r.	804
Nicotinic acid	520 ± 103	2537 ± 120	3057 ± 158	434 ± 73	1201 ± 60	183 ± 18	1385 ± 63	740
Isonicotinic acid	221 ± 31	502 ± 7	714 ± 32	171 ± 36	164 ± 15	29 ± 5	193 ± 16	431
Picolinic acid	n.d.	tentative	tentative	n.d.	n.r.	n.r.	n.r.	n.r.
Nicotinamide	n.d.	n.d.	n.d.	n.r.	n.r.	n.r.	n.r.	82
Isonicotinamide	n.d.	n.d.	n.d.	n.r.	n.r.	n.r.	n.r.	25
Picolinamide	n.d.	n.d.	n.d.	n.r.	n.r.	n.r.	n.r.	8
1-Methyl-1H-imidazole-2-carboxylic acid	<49 ± 3[e]	421 ± 46	<470 ± 46[e]	n.r.	n.r.	n.r.	n.r.	n.r.
1-Methyl-1H-imidazole-5-carboxylic acid	15 ± 6	22 ± 1	38 ± 6	n.r.	n.r.	n.r.	n.r.	167
2-Methyl-1H-imidazole-4-carboxylic acid	143 ± 6	565 ± 42	708 ± 43	411 ± 55	n.r.	n.r.	n.r.	n.r.
4-Methyl-1H-imidazole-5-carboxylic acid	<49 ± 3[e]	178 ± 75	<227 ± 75[e]	n.r.	n.r.	n.r.	n.r.	1190
2-Methylnicotinic acid	n.d.	85 ± 4	85 ± 4	39 ± 12	25 ± 8	12 ± 5	38 ± 9	206
4-Methylnicotinic acid	n.d.	126 ± 0.1	126 ± 0.1	n.r.	131 ± 6	14 ± 5	145 ± 7	n.r.
5-Methylnicotinic acid	n.d.	528 ± 12	528 ± 12	115 ± 30	32 ± 9	29 ± 1	61 ± 9	n.r.
6-Methylnicotinic acid	n.d.	641 ± 14	641 ± 14	138 ± 33	68 ± 6	47 ± 8	115 ± 10	n.r.
Other N-heterocycles Sum	8336 ± 337	11161 ± 362	19546 ± 419	1489 ± 111	1621 ± 64	314 ± 22	1935 ± 67	40348
Total N-heterocycles Sum (incl. nucleobases)	9117 ± 340	12895 ± 375	22012 ± 507	4834 ± 275	7079 ± 162	23577 ± 689	30656 ± 708	41702
Other N-bearing molecules								
Urea	141225 ± 5475	30259 ± 2788	171485 ± 6144	n.r.	10024	40415	50439	n.r.
1-Methylurea	1365 ± 239	1590	2955 ± 239	n.r.	n.r.	n.r.	n.r.	n.r.
1-Ethylurea	150 ± 30	180	330 ± 30	n.r.	n.r.	n.r.	n.r.	n.r.
1,3-Dimethylurea	20 ± 4	38	58 ± 4	n.r.	n.r.	n.r.	n.r.	n.r.
Guanylurea	782 ± 8	107	889 ± 8	n.r.	n.r.	n.r.	n.r.	n.r.

[a]ref. 9
[b]ref. 31
[c]ref. 5
[d]Values are the average of two measurements ($n = 2$) with a standard error, $\delta x = \sigma_x \cdot (n)^{-1/2}$. The error in the total sum was determined by adding the absolute errors of the individual compounds in quadrature.
[e]Upper limit due to the peak overlapping on the chromatogram.
[f]Not detected
[g] Tentatively detected but not quantified.
[h]Not reported
[i]Extracted in our previous study (ref. 5) but quantified in the present study (Supplementary Methods).

Assuming that both NH_3 and HCN were incorporated into planetary bodies as solids upon the formation of the Solar System, their abundances in asteroids would be affected by their initial abundances and the temperatures they experienced. In presolar environments such as cold molecular clouds, HCN is generally depleted compared to NH_3 in the solid state[46]. On the other hand, a typical abundance of HCN in comets is 0.08–0.25% relative to water, similar to that of NH_3 (0.3–0.7%)[47], suggesting fractionation of HCN and NH_3 abundances through the evolution of planetary systems. HCN can be retained in H_2O ice at almost all distances from the Sun where H_2O-rich planetesimals could have formed[48]. Under such HCN-enriched asteroidal environments, purine nucleobases could have been synthesised preferentially, resulting in a high Pu/Py ratio, as in Murchison[16]. Smith et al. [45] reported cyanide enrichment in CM chondrites, but depletion in Vigarano-like (CV) and Renazzo-like (CR) carbonaceous chondrites. If the cyanide concentration is low in Bennu and CI chondrites, as is the case for CV and CR chondrites, the low Pu/Py ratio in Bennu and Orgueil may be explained by the hypothesis described above. Analysis of cyanide in

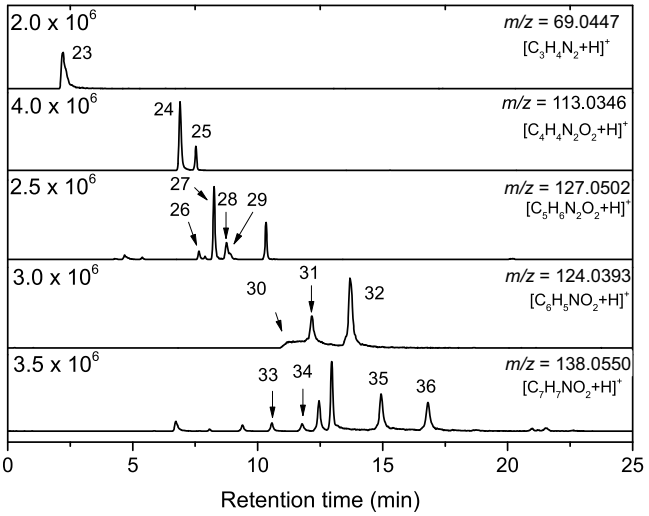

Fig. 6 | Detection of N-heterocycles other than nucleobases in the 20% HCl extract. Extracted ion chromatograms (EICs) at *m/z* of (from top to bottom) 69.0447, 113.0346, 127.0502, 124.0396, and 138.0550, in the 20% HCl extract from Bennu sample OREX-800107-108. Peaks were identified by comparison of their retention times and exact monoisotopic masses with those in the standard reagents analyzed on the same day, and are designated by peak number as follows: (23) imidazole, (24) 4-imidazole carboxylic acid, (25) 2-imidazole carboxylic acid, (26) 1-methyl-1H-imidazole-5-carboxylic acid, (27) 2-methyl-1H-imidazole-4-carboxylic acid, (28) 1-methyl-1H-imidazole-2-carboxylic acid, (29) 4-methyl-1H-imidazole-5-carboxylic acid, (30) picolinic acid (tentative)[12,16], (31) isonicotinic acid, (32) nicotinic acid, (33) 2-methylnicotinic acid, (34) 4-methylnicotinic acid, (35) 6-methylnicotinic acid, and (36) 5-methylnicotinic acid. The numbers on the left (right in the bottom panel) indicate the y-axis scale for each chromatogram. The EICs of the corresponding blank samples and the standard reagents are shown in Supplementary Fig. 13.

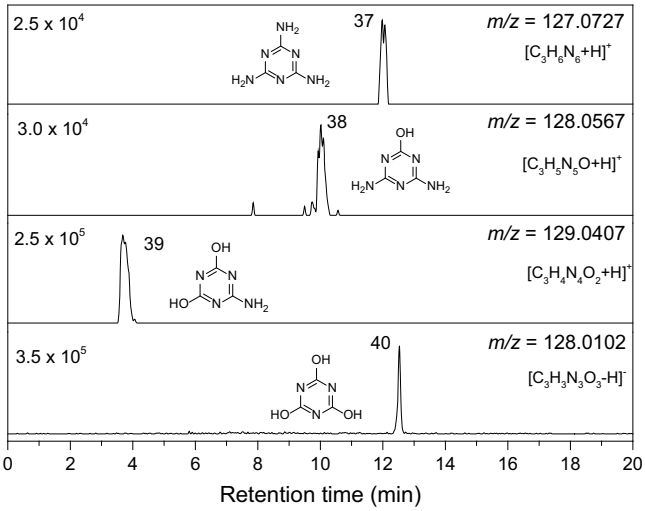

Fig. 7 | Detection of melamine and its homologues in the 2% HCl extract. Extracted ion chromatograms (EICs) at *m/z* of (from top to bottom) 127.0727, 128.0567, 129.0407, and 128.0102, in the 2% HCl extract from Bennu sample OREX-800107-108. The chromatogram at the bottom was measured in the negative ion mode, while others were in the positive ion mode. Peaks were identified by comparison of their retention times and exact monoisotopic masses with those in the standard reagents analyzed on the same day and are designated by peak number as follows: (37) melamine, (38) ammeline, (39) ammelide, and (40) cyanuric acid. The numbers on the left indicate the y-axis scale for each chromatogram. The EICs of the corresponding blank samples and the standard reagents are shown in Supplementary Fig. 14.

Bennu samples and various classes of carbonaceous meteorites including CI chondrites is needed to test this hypothesis.

Other N-heterocycles in OREX-800107-108

Abundance and diversity of non-nucleobase N-heterocycles. In addition to the purine and pyrimidine nucleobases, 11 and 13 other N-heterocycles were identified in the 2% and 20% HCl extracts from OREX-800107-108, respectively (Figs. 6, 7 and Table 2). Among the detected N-heterocycles, imidazole was the most abundant in each extract (4044 ± 180 and 2767 ± 336 pmol g^{-1} in 2% and 20% HCl extracts, respectively). Nicotinic acid, also known as niacin or B_3 vitamer, was also detected in both extracts, and the total concentration (2% HCl + 20% HCl, 3057 ± 158 pmol g^{-1}) exceeds that detected in the water and 20% HCl extracts from Murchison (2382 pmol g^{-1})[16]. In addition, we identified some N-heterocycles such as 4-methylnicotinic acid in OREX-800107-108 that have not been reported in OREX-800044-101. However, several peaks could not be assigned to any specific molecules due to the lack of authentic chemical reagents (Fig. 6). Indeed, a number of peaks, most certainly derived from N-heterocycles, were detected on the mass chromatograms of the Bennu extracts (e.g., Supplementary Fig. 15), indicating a more diverse suite of N-heterocycles than we were able to detect.

Cyanuric acid is the second most abundant N-heterocycle after imidazole in the 2% HCl extract (2748 ± 262 pmol g^{-1}). The detection of cyanuric acid and its structural homologues such as melamine (4 ± 1 pmol g^{-1}), ammeline (8 ± 1 pmol g^{-1}), and ammelide (200 ± 22 pmol g^{-1}), which possess an 1, 3, 5-triazine ring with hydroxy (-OH) and/or amino ($-NH_2$) functional groups (Supplementary Fig. 2), is of special interest from the viewpoint of aqueous processes which the parent asteroid of Bennu would have experienced. As a general trend, their concentrations become higher with increasing number of OH functional groups in the structure (Fig. 8A).

The detection of melamine, ammeline, and cyanuric acid in the Orgueil meteorite was reported by Hayatsu and coworkers more than 50 years ago, whose concentrations were orders of magnitude higher than the Bennu samples[49,50]. One of the possible processes for the synthesis of melamine could be the reaction of urea[51], which is the most abundant N-bearing molecule detected in the present study (141 ± 5 nmol g^{-1} in the 2% HCl fraction; Table 2), via the formation of guanylurea, which is also abundant in the same sample (782 ± 8 pmol g^{-1}, Table 2). Another example of the prebiotic formation pathways of cyanuric acid and ammelide is the reaction of urea with cyanic acid (NCOH), via the formation of biuret and/or triuret[51,52]. However, neither biuret nor triuret was detected in OREX-800107-108, suggesting that this formation pathway was probably not predominant.

Hydrothermal alteration experiments: melamine and cyanuric acid. To test whether the molecular signatures we observed could arise from aqueous alteration, we simulated the geochemical conditions in the laboratory—i.e., reactions in NH_3-enriched fluids. We heated melamine in aqueous ammonia solutions with $MgSiO_3$ powders at 120–160 °C. Although this temperature range may be higher than that Bennu has experienced, we selected these temperatures to promote the chemical processes effectively within a reasonable laboratory timescale. Its concentration decreased as heating time increased (Supplementary Fig. 16A). Accordingly, the concentrations of its hydrolysis products, such as ammeline, ammelide, and cyanuric acid, increased with time, likely resulting from a stepwise hydrolysis of amino groups in a melamine molecule (Supplementary Fig. 16B).

On the other hand, when cyanuric acid was heated in aqueous ammonia solutions at 110–140 °C, it was decomposed accordingly (Supplementary Fig. 16C), while its NH_2-substituted homologues such as ammelide, ammeline, and melamine were not formed after heating, indicating that the conversion from melamine to cyanuric acid is a one-way process under the heating conditions used. Therefore, cyanuric acid should be the final product of melamine homologues during such hydrothermal processes in NH_3-rich fluids. Given that ammonia would have been

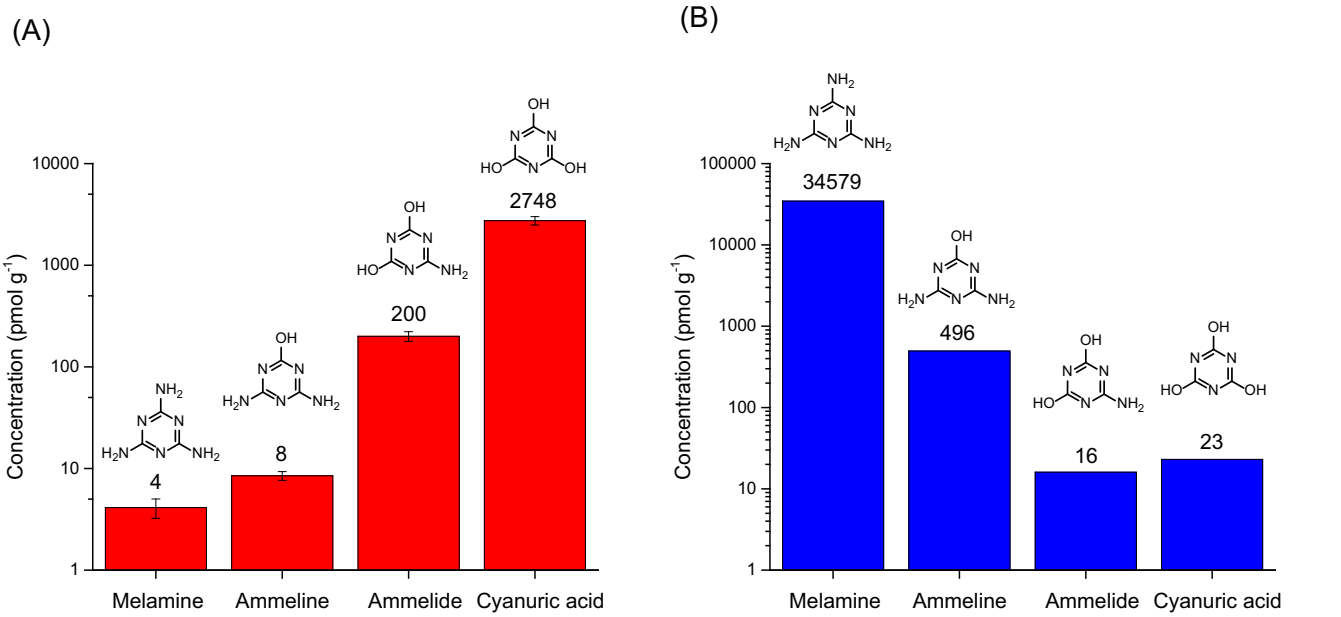

Fig. 8 | Distribution of melamine and its homologues in Bennu sample OREX-800107-108 and Murchison. Concentrations of melamine and its homologues (ammeline, ammelide, and cyanuric acid) in the 2% HCl extract from (**A**) OREX-800107-108 and (**B**) Murchison meteorite. The error bar represents a standard error of two measurements ($n = 2$), $\delta_x = \sigma_x \cdot (n)^{1/2}$. The number above each bar corresponds to their concentrations in picomoles per gram.

abundant in aqueous solutions within Bennu's parent body[9], the hydrolysis of melamine is likely to have occurred. Because the concentration of cyanuric acid dominates those of melamine, ammeline, and ammelide in the Bennu sample (Table 2), the observed distribution may be attributed to extensive hydrothermal processing on the parent asteroid.

For comparison, we reanalyzed our earlier aqueous extracts from the Murchison meteorite, which had been originally analyzed for the detection of nucleobases and hexamethylenetetramine[5,53], and found that the distribution of melamine and its hydrolysis products was different from that in Bennu sample OREX-800107-108; the concentration of melamine was greatest (34,579 pmol g^{-1}), followed by ammeline (496 pmol g^{-1}), cyanuric acid (23 pmol g^{-1}), and ammelide (16 pmol g^{-1}) (Fig. 8B). Because this distribution is distinct from that in soil samples taken at the meteorite's landing site (Supplementary Fig. 17), we can be confident that it is specific to the Murchison meteorite. Assuming that the parent body of Murchison (CM2) experienced aqueous alteration much less significant than that of CI chondrites (all of which are petrologic type 1, the most altered type), the observed difference of melamine and its homologues between Bennu and Murchison might be attributable to the different degrees of aqueous processes experienced on each parent body. If this is the case, their precursor molecule, namely, melamine, should have been present before the onset of the hydrothermal processes.

Additional evidence for aqueous alteration. The overall mineralogy and petrology of Bennu samples demonstrate that the parent body of Bennu went through aqueous alteration on a significant scale and that this alteration was heterogeneous and occurred multiple times[8,54–56]. The non-detection of nicotinamide and its structural isomers in our 2% HCl extract of OREX-800107-108 is consistent with this history. Nicotinamide and its isomers are easily hydrolyzed to yield their acid counterparts, such as nicotinic acid (from nicotinamide) and isonicotinic acid (from isonicotinamide), in hot water[12] and in NH_3-rich fluids (Supplementary Fig. 18). Indeed, the concentrations of nicotinic acid and isonicotinic acid in the 2% HCl extract from OREX-800107-108 are comparable to those in the 2% HCl extract from Murchison, although their amide counterparts are surely present in the latter[5]. Assuming that both nicotinic acid and nicotinamide were formed in the interstellar medium with the ratio of ~1, as has been suggested from laboratory experiments simulating photochemical processes in presolar environments like interstellar molecular clouds[5,41], the observed predominance of nicotinic acid over its amide counterpart, nicotinamide, is a result of significant aqueous processing.

Search for nucleosides: bridging sugars and bases

Nucleosides bridge the gap between simple organics and biological polymers, making their presence (or absence) crucial to understanding prebiotic potential. It is widely accepted that nucleosides, consisting of a nucleobase linked to a 5-carbon sugar such as ribose and 2-deoxyribose, are key chemical precursors for the formation of nucleotides (the building blocks of DNA and RNA) in prebiotic chemistry. Given that ribose and other bioessential sugars have been successfully identified in carbonaceous meteorites[4] and, more recently, in the 2% HCl extract from OREX-800107-108 (ref. 15) that we analyzed here, we expected to find nucleosides, which can be synthesized from both components (i.e., nucleobases and sugars). However, we did not identify any nucleosides in the 2% HCl extract from OREX-800107-108 above analytical detection limits (Supplementary Fig. 19). The upper limits for the concentrations of cytidine (cytosine + ribose), uridine (uracil + ribose), and inosine (hypoxanthine + ribose), were estimated as 1.0, 0.17, and 6.5 pmol g^{-1}, respectively, which are orders of magnitude lower than the concentrations of nucleobases and sugars detected in the same Bennu sample (Table 1 and ref. 15). Guanosine (guanine + ribose) was also not detected in the sample (Supplementary Fig. 19), but its detection limit was not determined due to technical issues. Although nucleosides are easily decomposed in the treatment with 20% HCl at 110 °C, they are not with 2% HCl in the analytical procedure we used (Supplementary Information). Hence, the non-detection of these molecules in the 2% HCl extract is not due to analytical artifacts, but to their intrinsically low concentrations in the sample.

Previous laboratory experiments demonstrated the synthesis of nucleosides by the reaction of nucleobases and sugars in the presence of certain catalysts; however, the yield of products in the reaction of nucleobases and ribose in the dry-down experiment was limited (<4% at 100 °C and <1% at 65 °C)[57]. Hence, under the expected low-temperature evaporative conditions in Bennu's parent body (20–55 °C)[55], the reaction of sugars and nucleobases may have been suppressed, resulting in the absence of nucleosides at detectable concentrations. Other synthetic

pathways for prebiotic nucleosides require compounds that have not been found in meteorites or Bennu samples, including trimetaphosphate, cyanamide, and cyanoacetylene[58,59]. The absence of nucleosides, despite abundant sugars and bases, highlights a critical transition point in prebiotic chemistry, the barrier between molecular assembly and the onset of biological complexity.

What does the detection of nucleobases and other N-heterocycles in Bennu samples tell us about prebiotic chemistry in the early Solar System?

Heterogeneity among samples. The total concentration of N-heterocycles including nucleobases in the 20% HCl extract was ~12.9 nmol g^{-1}, which is ~1.4 times higher than that in the 2% HCl extract (~9.1 nmol g^{-1}). The summed concentration (2% HCl + 20% HCl extracts) of the N-heterocycles was ~22 ± 0.5 nmol g^{-1}, which is less than those of amines (1060 nmol g^{-1}), C_2–C_6 amino acids (70 nmol g^{-1}), and carboxylic acids (7210 nmol g^{-1}) in Bennu sample OREX-803001-0, but higher than that in OREX-800044-101 (4.8 nmol g^{-1})[9], even after excluding the contributions from some molecules such as imidazole and cyanuric acid, which were not quantified for that sample. In particular, the total concentrations of 4-imidazolecarboxylic acid and nicotinic acid were an order of magnitude higher in OREX-800107-108 (Table 2). We expect that this difference is mainly due to the heterogeneous distribution of N-heterocycles in the Bennu samples, as has been suggested for Ryugu samples and carbonaceous meteorites[11,26,60].

Establishing extraterrestrial provenance. Establishing the origin of these kinds of molecules—extraterrestrial or terrestrial—has been a central challenge in cosmochemistry. Since the first report on the detection of extraterrestrial N-heterocycles in carbonaceous meteorites in the early 1960s[49], extensive discussions on the validity of the detection, the origin of N-heterocycles in such extraterrestrial materials, and their possible roles in the origin of life on Earth have been conducted. Although there have been multiple reports of the detection of nucleobases in carbonaceous meteorites, it was not easy to conclude that the detected nucleobases were indigenous to the meteorite because they are ubiquitously distributed in terrestrial environments as a part of DNA and RNA in organisms. Carbon isotopic analyses of nucleobases in Murchison[61] were expected to provide evidence for their extraterrestrial origin. However, due to the lack of appropriate methods for the measurement of isotopic compositions of individual nucleobases[17] and the possible presence of coexisting molecules in the same analysis that would have significant contributions to the measured isotopic compositions[43], it is still challenging to accept the only reported value as an indicator of their extraterrestrial origin. Even in the case of the detection of all canonical nucleobases in Murchison[5], there is no definitive evidence to show their extraterrestrial origin; that study instead used multiple lines of indirect evidence to validate it (e.g., the detection of chiral amino acids in the same meteorite fragment, different distributions of nucleobases between the meteorite and the soil samples where it landed)[5].

In this regard, the detections of all canonical nucleobases in samples returned from Bennu and Ryugu[31], which have the least terrestrial contamination among extraterrestrial materials ever analysed, must be the direct evidence for the presence of these molecules in extraterrestrial environments that we have been eager to obtain for a long time. Thus, we propose that our findings can be considered a benchmark for the distribution of nucleobases in extraterrestrial samples, which may help to constrain their extraterrestrial origin in meteorites.

For example, because purine and pyrimidine bases other than the canonical nucleobases, such as isocytosine, 6-methyluracil, 8-aminopurine, and isoguanine, are uncommon in terrestrial biology[62], their presence in the same sample with concentrations comparable to or far exceeding canonical nucleobases would be a unique property of extraterrestrial materials. Considering that canonical nucleobases themselves do not have a clear parameter indicative of their extraterrestrial or abiotic origin, unlike the case for the racemic nature of amino acids, their relative fractions may constrain the origin of nucleobases in samples.

Table 1 compares the distribution of canonical and other nucleobases between Bennu samples and Murchison meteorites[5,9,16]. We found that the ratio of canonical to other nucleobases (canonical/others) is almost identical in OREX-800107-108 (0.8) and OREX-800044-101 (1.7). These values are upper limits due to the presence of other nucleobases that were not identified and/or quantified in the present study (e.g., 2,8-diaminopurine at the *m/z* 151.0727; Fig. 3)[16].

Based on these distributions in Bennu, we posit that this parameter may be useful for qualitatively evaluating the possible contribution of terrestrial contamination to the distribution of nucleobases in other extraterrestrial samples, particularly carbonaceous meteorites. For example, nucleobases in Murchison possess several features similar to those observed in Bennu: a canonical/others ratio of 1.8 and the predominance of uracil among pyrimidine bases (concentrations ~2 and 6 times those of thymine and cytosine, respectively). These similarities strongly support the conclusion that nucleobases detected in Murchison are mostly indigenous to the meteorite[5,16].

In addition, the predominance of uracil among pyrimidine nucleobases in Bennu samples (Table 1) implies the presence of a favorable environment for uracil synthesis in asteroids. The predominance of uracil has also been observed in meteorites[63]; if uracil-enriched carbonaceous meteorites show moderate canonical/others ratios similar to those of Bennu samples, the detected nucleobases may not have a significant contribution from terrestrial biology.

Implications for prebiotic chemistry on the early Earth. Given that the molecular diversity in Bennu samples can be regarded as a consequence of prebiotic chemical evolution from interstellar molecular clouds to the Solar System (Fig. 1), the detection of canonical base pairs (e.g., adenine-uracil, guanine-cytosine, adenine-thymine) and some non-canonical ones (e.g., isoguanine-isocytosine, xanthine-diaminopurines) indicates that these biologically important molecules can form in the absence of life throughout the Solar System, including on the early Earth. Moreover, the presence of abundant triazine heterocycles such as cyanuric acid in Bennu and melamine in Murchison implies that such molecules could have accumulated on Solar System bodies, helping to form the "proto-RNA" (or proto-nucleobases) proposed in earlier studies[64]. In addition, the presence of abundant urea (~171 nmol g^{-1}; Table 2), whose concentration far exceeds the sum of C_2 to C_6 amino acids and is comparable to ethylamine, the third most abundant N-bearing molecule after ammonia and methylamine in the earlier study of Bennu samples[9], is indicative of its role not only as a precursor to nucleobases[33,65] but also as an organocatalytic reagent[66,67]. Given the historical paucity of information on the distribution of N-bearing molecules in carbonaceous meteorites, their recent detection in Murchison[5,16] and returned asteroid samples[9,12,31] has opened a new era for a more precise understanding of the N-bearing molecules prebiotically synthesized in space and possibly delivered to the early Earth.

The Bennu samples show that prebiotic chemistry can advance remarkably far in the absence of biology. Complex mixtures of nucleobases, sugars, and other N-bearing molecules assembled in space, interacted with fluids and minerals, and endured for billions of years without ever crossing the boundary into life. These results sharpen a fundamental question in astrobiology: what additional conditions or thresholds, energy sources, catalytic environments, or self-organizing feedbacks, were present on the early Earth but missing on Bennu's parent asteroid? By demonstrating how far chemistry can go on its own, the Bennu samples provide a reference point for the transition from geochemistry to biochemistry, guiding future searches for life's universal chemical prelude.

Samples and methods

Bennu samples

A subsample (OREX-800107-108, 603.40 mg) from a homogenized bulk aggregate sample (unsorted material with particles sizes <5 mm; OREX-800107-0) recovered from the OSIRIS-REx Touch-and-Go Sample Acquisition Mechanism (TAGSAM) was distributed to two analytical teams with the respective aims of detecting sugars[15,68] and N-heterocycles (present study) in the same sample. The homogenization of the parent sample into powder is described by Ryan et al.[19] The physical homogeneity of the powdered sample has been verified by X-ray computed tomography, which causes negligible changes in organic molecules present in the processed samples[68]. As a processing control, ~7 g of granular silica chips (Isomass Analytics, 0.85–1.7 mm) heated at 500 °C overnight in air was carried through the same steps as this Bennu sample.

Extraction of N-heterocycles

The sample extraction and purification processes were performed in an ISO Class-5 clean bench. The powdered Bennu sample OREX-800107-108 was soaked in 15 mL of 2% HCl (TAMAPURE-AA10, Tama Chemicals) in a glass tube with sonication to extract sugars and N-heterocycles from the sample. Sonication was performed for 30 min with the temperature of the sonication bath kept below 25 °C. The extract was centrifuged (2000 rpm for 45 min), and the supernatant was recovered into a glass vessel. This process was repeated five times. The extracted residue was further washed with 15 mL of ultrapure water (TAMAPURE-AA, Tama Chemicals), and the supernatant was added to the HCl extract. This process was repeated three times. The combined extract was dried under reduced pressure using a rotary evaporator. After drying, the remaining residue was washed with 10 mL of methanol (Q-Tof grade, Wako Pure Chemicals) five times. The methanol solution was collected in a flask and dried under reduced pressure with the rotary evaporator. The dried extract was dissolved in 0.1 M (~0.4%) HCl solution and subjected to cation-exchange chromatography to remove inorganic salts[69]. In brief, ~40 mL (in wet volume) of AG 50W-X8 cation-exchange resin (Bio-Rad Laboratories, Inc.; biotechnology grade, 200-400 mesh, hydrogen form; stored in 10% aqueous ammonia (NH_4OH)) was placed in a glass tube and rinsed with solvents in the following order: 120 mL of 10% NH_4OH, ultrapure water, 1 M HCl, ultrapure water, 1 M NaOH, ultrapure water, 1 M HCl, and ultrapure water. The extract was loaded onto the cation-exchange resin, which was pre-washed with 100 mL of ultrapure water to recover acidic, neutral, and weakly basic compounds referred to as "2%HCl-H_2O fraction". Subsequently, 200 mL of 10% NH_4OH was loaded onto the H_2O-washed cation-exchange resin to elute basic compounds, including most nucleobases referred to as "2% HCl-NH_3 fraction". The 2%HCl-H_2O fraction includes sugars and some anionic N-heterocycles such as uracil, thymine, and cyanuric acid, and the 2%HCl-NH_3 fraction includes purine nucleobases, cytosine, and other N-heterocycles. The purified fraction was once dried and redissolved in 1 mL of H_2O. Most (90%) of the 2%HCl-H_2O fraction was used for the analysis of sugars[15]. The remaining 10% of the 2%HCl-H_2O and all 2%HCl-NH_3 fractions were used in the present study.

After the extraction with 2% HCl solution, the residue was further soaked in a more concentrated, 20% HCl solution (TAMAPURE-AA10) in a closed glass ampoule whose headspace was replaced with dry N_2. The sample in the HCl was heated at 110 °C for 12 h to extract N-heterocycles that remained in the residue[16]. After the heating, the HCl solution and the residue were moved to a glass tube, and the supernatant was separated from the residue by centrifugation (2000 rpm for 5 min). The residue was washed with 2 mL of ultrapure water three times, and the supernatants were mixed with the HCl solution. The combined solution was dried under reduced pressure with a rotary evaporator. About 1 mL of 1% HCl solution was added to the residue, and the solution was subjected to cation-exchange chromatography. This purification procedure is in principle the same as that applied to the 2% HCl extract as mentioned above. The purified H_2O and NH_4OH fractions (20%HCl-H_2O and 20% HCl-NH_3 fractions, respectively) were once dried and redissolved into 1 mL of H_2O prior to analysis.

All glassware was prebaked at 500 °C in air for 6 h before use. The same procedures shown above were applied to SiO_2 powders (613.84 mg, pre-baked at 500 °C for 6 h before use) as a procedural blank test.

Analysis of N-heterocycles in Bennu samples

All fractions recovered from the Bennu sample and the SiO_2 procedural blank, as well as the authentic standards of the targeted molecules, were analyzed using an online high-performance liquid chromatography coupled with an electrospray ionization high-resolution mass spectrometry (HPLC/ESI-HRMS) system comprising an UltiMate 3000 and Q Exactive™ Plus Hybrid Quadrupole-Orbitrap™ mass spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA) with a mass resolution of 140,000 at m/z 200. The HPLC instrument was outfitted with a reversed-phase separation column maintained at 40 °C. For the detection and quantification of purine nucleobases and some other N-heterocycles, we employed the following two isocratic HPLC eluent programs with an InertSustain PFP column (1.0 mm × 250 mm, particle size = 3 μm, GL Sciences Inc., Tokyo, Japan): solvent A (water) and solvent B (acetonitrile with 0.1% formic acid) = 90 : 10, or solvent A (water with 0.1% formic acid) and solvent B (acetonitrile with 0.1% formic acid) = 99 : 1, held for 20 min with a flow rate of 0.05 mL min^{-1}. For the analyses of pyrimidine nucleobases and other 5- or 6-membered N-heterocycles, we used the following gradient HPLC eluent program with the HyperCarb™ column (2.1 mm × 150 mm, particle size = 3 μm, Thermo Fisher Scientific Inc., Waltham, MA, USA): solvent A (water with 0.1% formic acid) and solvent B (acetonitrile with 0.1% formic acid) = 99 : 1 at t = 0 min, followed by a linear gradient of A:B = 70:30 at 20 min with a flow rate of 0.2 mL min^{-1}.

The ESI voltage and capillary temperature of the ion-transfer system were 3.5 kV and 295 °C, respectively. To detect various organic molecules in the HCl extracts, we recorded the mass spectra of the vaporized compounds in positive or negative ion modes over an m/z range of 50–500, with the mass determined to an accuracy better than 5 ppm, as defined by [(measured m/z) – (calculated m/z)]/(calculated m/z) × 10^6 (ppm). The mass accuracy was occasionally calibrated using the exact masses of protonated tyrosine (m/z 182.0812), *tert*-butylamine (m/z 74.0964), and a fragment ion of *tert*-butylamine (m/z 57.0699). A positive ion with m/z 83.0604, corresponding to an acetonitrile dimer, was used as the lock mass. The signal-to-noise ratio for all assigned peaks was above 10, which was estimated from the peak height and area of the target peak and the background noise. For robust identification and quantification of the nucleobases, we performed the tandem mass spectrometry (MS/MS) experiments using the same ionization conditions as those used for the full-scan analyses. We subjected the targeted positive ions isolated by the quadrupole (using an isolation window of 0.4 m/z) to high-energy collisions with N_2 gas to produce fragment ions and monitored specific mass ranges using an Orbitrap MS with a mass resolution of 140,000 at m/z 200.

Peak areas were measured in the Qual Browser or FreeStyle software (Thermo Fisher Scientific). After measuring the calibration solutions (10–1000 nM), calibration curves were created using Microsoft Excel to perform absolute quantification of the target molecules.

Synthesis of calcium carbonates including nucleobases

Chemical reagents of calcium chloride ($CaCl_2$, 95.0 + %) and sodium carbonate (Na_2CO_3, 99.0%) were purchased from Junsei Chemical Co. Ltd., and used without further purification. Each aqueous solution (0.02 M, 20 mL) was prepared in a separate glass vial. Standard reagents of canonical nucleobases (20–60 μg) were added to the Na_2CO_3 solution. Then, these solutions were mixed in a glass vessel with stirring, resulting in the formation of white precipitates in the vessel. The details of $CaCO_3$ synthesis have been described elsewhere[22,70]. The mixed aqueous solution was frozen at −30 °C and dried under vacuum for 48 h. After that, the formed white precipitates, consisting of $CaCO_3$ and NaCl

($Na_2CO_3 + CaCl_2 \rightarrow CaCO_3 + 2NaCl$), were kept in another glass vessel prior to use.

Extraction of nucleobases from the synthesized $CaCO_3$

About 65 mg of white precipitates were placed into a glass ampoule with 400 μL of pure H_2O. After purging the headspace with dry N_2, the ampoule was flame-sealed and heated at 110 °C for 12 h. After heating, the aqueous solution was separated from the ampoule, and the white residues in the ampoule were rinsed with pure H_2O (400 μL) twice. The H_2O rinses were mixed with the H_2O solution (denoted as H_2O fraction). Then, 400 μL of 20% HCl solution was added to the remaining white solids in the glass ampoule. After purging with dry N_2, the ampoule was flame-sealed and heated at 110 °C for 12 h. After heating, the HCl solution was removed and the glass ampoule was rinsed with pure water as explained above. The HCl extract and the H_2O rinses were mixed into one (denoted as H_2O-HCl fraction). The obtained H_2O and HCl extracts were dried under gentle N_2 flow and redissolved into 1 mL of pure H_2O. Then, the obtained solution was analyzed by liquid chromatography coupled with time-of-flight mass spectrometry (HPLC/TOF-MS) (6230B TOF LC/MS system, Agilent). The LC is equipped with an InertSustain PFP column (1.0 mm × 250 mm, particle size = 3 μm, GL Sciences Inc., Tokyo, Japan). The following isocratic eluent program was used for the identification and quantification of nucleobases: solvent A (water) and solvent B (acetonitrile with 0.1% formic acid) = 90:10, held for 20 min with a flow rate of 0.05 mL min^{-1} at 40 °C. The ionization voltage and capillary temperature were set to 3.5 kV and 325 °C, respectively. The positive ions were measured in full-scan mode over a range of *m/z* 50 to 1000 with a mass resolving power setting of ~12,000 at full-width-half-maximum for *m/z* 100.

Heating of N-heterocycles in aqueous ammonia solutions

A chemical reagent of melamine (99%, Sigma Aldrich), cyanuric acid (>98%, Tokyo Chemical Industry Co., Ltd.), or nicotinamide (>99.0% Tokyo Chemical Industry Co., Ltd) was dissolved in aqueous ammonia solution (0.3%, prepared by diluting 28% NH_4OH solution, Ultrapur™, Kanto Kagaku) to yield a stock solution with a concentration of ~1000 μM. Each stock solution (50 μL) was put into a glass ampoule with ~50 mg of amorphous $MgSiO_3$ powders (~50-100 nm in diameter) synthesized in an induction thermal plasma furnace at Nisshin Flour Milling Inc[71]. as an analog of mineral phases of asteroidal materials. After purging with dry N_2, the ampoule was flame-sealed and heated at 120–160 °C (ammeline), 110-140 °C (cyanuric acid), or 110 °C (nicotinamide) for up to 4 days. After heating, the products were extracted with pure water (500 μL × 2). After filtration through a membrane filter (Millex®-LG, pore size: 0.20 μL, Merck Millipore Ltd., Ireland), the concentrations of target molecules (melamine, ammeline, ammelide, and cyanuric acids for the melamine and cyanuric acid experiments, and nicotinamide and nicotinic acid for the nicotinamide experiment) were determined using the HPLC/TOF-MS by following the method shown above.

Data availability

The instrument data products underlying the findings of this work are listed with their DOIs in Supplementary Table 1. The numerical source data of the graphs in Figures S16 and S18 are shown in Supplementary Data 1.

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Author contributions

Y.O. and T.K. contributed equally. Y.O., T.K., Y.T., Y.F., H.N., D.P.G., J.P.D., H.C.C., and D.S.L. conceptualized the study. T.K., Y.F., Y.H., and S.S. extracted N-heterocycles from the sample. Y.O. and T.K. analysed N-heterocycles. Y.O. and T.T. performed laboratory experiments on the heating of N-heterocycles. Y.O. and T.Y. performed the synthesis of calcium carbonates and their analysis using transmission electron microscopy. The original draft was written by Y.O. All coauthors reviewed and edited the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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