Carbonaceous meteorites contain a wide range of extraterrestrial nucleobases

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All terrestrial organisms depend on nucleic acids (RNA and DNA), which use pyrimidine and purine nucleobases to encode genetic information. Carbon-rich meteorites may have been important sources of organic compounds required for the emergence of life on the early Earth; however, the origin and formation of nucleobases in meteorites has been debated for over 50 y. So far, the few nucleobases reported in meteorites are biologically common and lacked the structural diversity typical of other indigenous meteoritic organics. Here, we investigated the abundance and distribution of nucleobases and nucleobase analogs in formic acid extracts of 12 different meteorites by liquid chromatography–mass spectrometry. The Murchison and Lonewolf Nunataks 94102 meteorites contained a diverse suite of nucleobases, which included three unusual and terrestrially rare nucleobase analogs: purine, 2,6-diaminopurine, and 6,8-diaminopurine. In a parallel experiment, we found an identical suite of nucleobases and nucleobase analogs generated in reactions of ammonium cyanide. Additionally, these nucleobase analogs were not detected above our parts-per-billion detection limits in any of the procedural blanks, control samples, a terrestrial soil sample, and an Antarctic ice sample. Our results demonstrate that the purines detected in meteorites are consistent with products of ammonium cyanide chemistry, which provides a plausible mechanism for their synthesis in the asteroid parent bodies, and strongly supports an extraterrestrial origin. The discovery of new nucleobase analogs in meteorites also expands the prebiotic molecular inventory available for constructing the first genetic molecules.

Meteorites provide a record of the chemical processes that occurred in the solar system before life began on Earth. Carbonaceous chondrites are a rare class of meteorite and are composed of various groups (e.g., CI group, CM group, and CR group) according to their composition and petrography. They are known to contain a diverse suite of organic compounds including many that are essential in contemporary biology (1, 2). Amino acids, which are the monomers of proteins, have been extensively studied in meteorites. An extraterrestrial origin for most of the amino acids detected in carbonaceous chondrites has been firmly established based on three factors: the detection of racemic amino acid mixtures (i.e., equal mixtures of D and L amino acids), wide structural diversity (including the presence of many nonprotein amino acids that are rare or nonexistent in the biosphere), and nonterrestrial values for compound-specific deuterium, carbon, and nitrogen isotope measurements (3–13). In contrast to amino acids, nucleobases in meteorites have been far less studied.

Nucleobases are substituted one-ring (pyrimidine) or two-ring (purine) nitrogen heterocyclic compounds that serve as the structural basis of information storage in RNA and DNA and, for a variety of reasons, are believed to have been essential for the origin and early evolution of life (14). The analysis of nucleobases in meteorites has been ongoing since the early 1960s (2). Determining the origin of nucleobases in meteorites has been challenging due to their low abundances relative to many other organics, meteorite heterogeneity, experimental artifacts, and terrestrial contamination. To date, all of the purines (adenine, guanine, hypoxanthine, and xanthine) and the one pyrimidine (uracil) reported in meteorites (15–18) are biologically common and could be explained as the result of terrestrial contamination. Martins et al. performed compound-specific stable carbon isotope measurements for uracil and xanthine in the Murchison meteorite (19) and interpreted the isotopic signatures for these nucleobases as nonterrestrial. However, other meteoritic coeluting molecules (e.g., carboxylic acids known to be extraterrestrial) could have contributed to the $\delta^{13}C$ values for these nucleobases. Furthermore, there have been no observations of stochastic molecular diversity of purines and pyrimidines in meteorites, which has been a criterion for establishing extraterrestrial origin of other organic compound classes. Thus, an extraterrestrial origin for nucleobases detected in carbonaceous chondrites has never been established unequivocally, nor has the detection of nucleobases been demonstrated in more than a handful of meteorites.

We analyzed the formic acid extracts of Orgueil (CI1), Meteorite Hills (MET) 01070 (CM1), Scott Glacier (SCO) 06043 (CM1), Allan Hills (ALH) 83100 (CM1/2), Lewis Cliff (LEW) 90500 (CM2), Lonewolf Nunataks (LON) 94102 (CM2), Murchison (CM2), Grosvenor Mountains (GRO) 95577 (CR1), Elephant Moraine (EET) 92042 (CR2), Graves Nunataks (GRA) 95229 (CR2), Queen Alexandra Range (QUE) 99177 (CR3), and the Almahata Sitta meteorite fragment #4 (ureilite) by liquid chromatography–mass spectrometry using both triple quadrupole detection and high resolution, accurate mass orbitrap detection. Despite the great potential of high resolution mass spectrometry to investigate highly complex samples, these techniques have rarely been applied to the study of carbonaceous chondrites (1). To our knowledge, with the exception of Murchison and Orgueil, these meteorites have not been examined for nucleobases and nucleobase analogs.

Results and Discussion

We investigated the abundance and distribution of nucleobases and nucleobase analogs in 11 different carbonaceous chondrites from three different groups (CI, CM, and CR) representing the entire range of aqueous alteration (types 1, 2, and 3) and one ureilite meteorite. Eleven out of the 12 meteorites studied contained at least the nucleobase adenine. The three CM2 carbonac-

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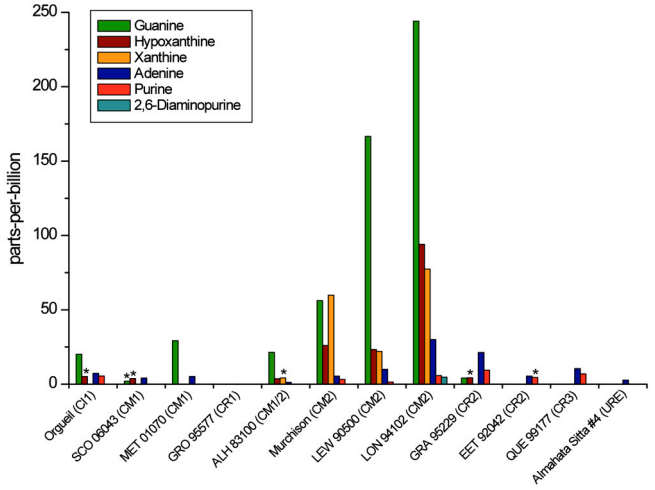

Fig. 1. Distribution of guanine, hypoxanthine, xanthine, adenine, purine, and 2,6-diaminopurine in 11 carbonaceous chondrites and one ureilite. The three CM2 carbonaceous chondrites in this study (Murchison, LEW 90500, and LON 94102) contained significantly higher (approximately 4× to 12×) abundances of purine nucleobases as well as greater structurally diversity. The * represents a tentative assignment. The meteorites are roughly ordered by increasing aqueous alteration (*Right* to *Left*) as determined using mineralogical and isotopic evidence (38–41). The relative degree of aqueous alteration among carbonaceous chondrites within the same group and of the same petrologic type is less certain, although some ordering can be made.

eous chondrites (Murchison, LEW 90500, and LON 94102) particularly stood out because they had the most diverse and abundant set of purines measured (Fig. 1 and *SI Text*). Total purine abundances were 4 to 12 times higher in CM2 carbonaceous chondrites compared to the other meteorites examined. As the degree of aqueous alteration increases in CM carbonaceous chondrites, the overall abundance and diversity of nucleobases decreases as seen in ALH 83100 (CM1/2), SCO 06043 (CM1), and MET 01070 (CM1). Meteorites of other groups (CI and CR) with varying degrees of aqueous alteration (types 1, 2, and 3) also had comparatively less total purine abundance and structurally diversity compared to CM2 carbonaceous chondrites. Furthermore, there is an apparent correlation between purine diversity and the diversity of other small organic species, such as amino acids (5), with the maximum diversity found in CM2 carbonaceous chondrites. Interestingly, this correlation does not hold for the abundances of such compounds; for example, CR2 and CR3 meteorites are rich in amino acids and small amines (5, 20, 21) but poor in purines. Based on our measurements, the CM2 carbonaceous chondrites appear to have provided a more favorable environment for the formation and/or preservation of purines compared to other types of carbonaceous chondrites.

Establishing an unambiguous extraterrestrial origin for any biological nucleobase in carbonaceous chondrites is challenging. Unlike meteoritic amino acids, nucleobases are achiral so enantiomeric ratios (i.e., D/L ratios) cannot be used to help distinguish between abiotic and biotic origins. With sample-limited meteorites, compound-specific stable isotope analysis may be impractical or impossible due to the large amount of meteorite material required. Additionally, other meteoritic organics may prevent an unambiguous stable isotope ratio measurement despite extensive sample cleanup and chromatography (19). Indigenous organic compounds in meteorites are usually present in structurally homologous series (2); therefore, finding nucleobase analogs not typically found in terrestrial biochemistry would strongly support an extraterrestrial origin for these canonical nucleobases because they are often produced concurrently in abiotic syntheses.

Purine, 2,6-diaminopurine, and 6,8-diaminopurine were unambiguously identified in LON 94102 (Fig. 2) and a larger extract of Murchison by their chromatographic retention time, accurate mass spectrum (including accurate mass measurements on multiple fragmentation products), and coinjection with standards (resulting in the detection of a single peak) (22). Additionally, two different formic acid extracts of LON 94102 were analyzed on three different liquid chromatography–mass spectrometry instruments (one triple quadrupole and two Orbitraps) in two separate laboratories [National Aeronautics and Space Administration (NASA) Goddard Space Flight Center and Thermo Scientific], which all produced similar results. Purine and 6,8-diaminopurine were identified (by their chromatographic retention time and an accurate mass measurement for the parent mass) in several other meteorites as well (Fig. 1 and *SI Text*). This demonstrates that both purine and 6,8-diaminopurine are widely distributed in carbonaceous chondrites, particularly in CM2 and CR2 meteorites, and provides additional support that purines found in these meteorites are indigenous and not terrestrial contaminants. Aside from one report of 2,6-diaminopurine occurring in cyanophage S-2L (23), these three purines are rare or absent in terrestrial biology. Studies of 8-aminoadenosine, as a potential cancer therapeutic, have shown that this compound is known to inhibit transcription by multiple mechanisms (24) so that the presence of 6,8-diaminopurine (8-aminoadenine) in meteorites is highly unlikely to be the result of terrestrial biological contamination.

All of the purines observed in Murchison and LON 94102 (i.e., adenine, guanine, hypoxanthine, xanthine, purine, 2,6-diaminopurine, and 6,8-diaminopurine) were also generated from aqueous reactions of NH_4CN (see *SI Text*). Adenine (normalized to 1) was the most abundant nucleobase in the formic acid extracted NH_4CN samples followed by purine (0.79), hypoxanthine (0.23), 6,8-diaminopurine (0.07, assuming the same response factor as 2,6-diaminopurine), 2,6-diaminopurine (0.05), guanine (0.02), and xanthine (0.01). Although the relative abundances of these purines are different than those detected in carbonaceous chondrites, this may be attributable to the extensive aqueous and energetic processing the asteroid parent bodies have undergone during their approximately 4.5 billion-year history (25) compared to the NH_4CN reactions. The presence of hydrogen cyanide and ammonia as synthetic precursor molecules has been deduced in hydrated carbonaceous chondrites based on the presence of α-amino acids, α-hydroxy acids, and iminodicarboxylic acids reported in the Murchison meteorite, which supports a Strecker-type synthesis requiring hydrogen cyanide and ammonia (13, 26–29). Additionally, abundant ammonia has been detected in the CR2 carbonaceous chondrite GRA 95229 after hydrothermal treatment (30), which was one of the meteorites in our study.

Purine, 2,6-diaminopurine, and 6,8-diaminopurine were not detected (above our parts-per-billion detection limits) in the procedural blanks, nucleobase procedural samples, serpentine control samples, Murchison soil sample (see *SI Text*), or Antarctic ice sample (see *SI Text*), which strongly suggests that these compounds are indigenous to the meteorites. Because adenine, guanine, hypoxanthine, and xanthine were observed in both the soil and Antarctic ice samples (though at different ratios and lower abundances than observed in meteorites; see *SI Text*), it could still be argued that these nucleobases are the result of terrestrial contamination. On the other hand, these same nucleobases are also synthesized concurrently with purine, 2,6-diaminopurine, and 6,8-diaminopurine in reactions of NH_4CN. Furthermore, the distributions of purines measured in the nine Antarctic meteorites appear to correlate with meteorite petrology and the extent of parent body alteration rather than with the content of the terrestrial environments from which they were recovered, arguing against terrestrial contamination from the ice. Based on the elevated abundances of these compounds in the meteorites compared with terrestrial sources, we propose that the adenine,

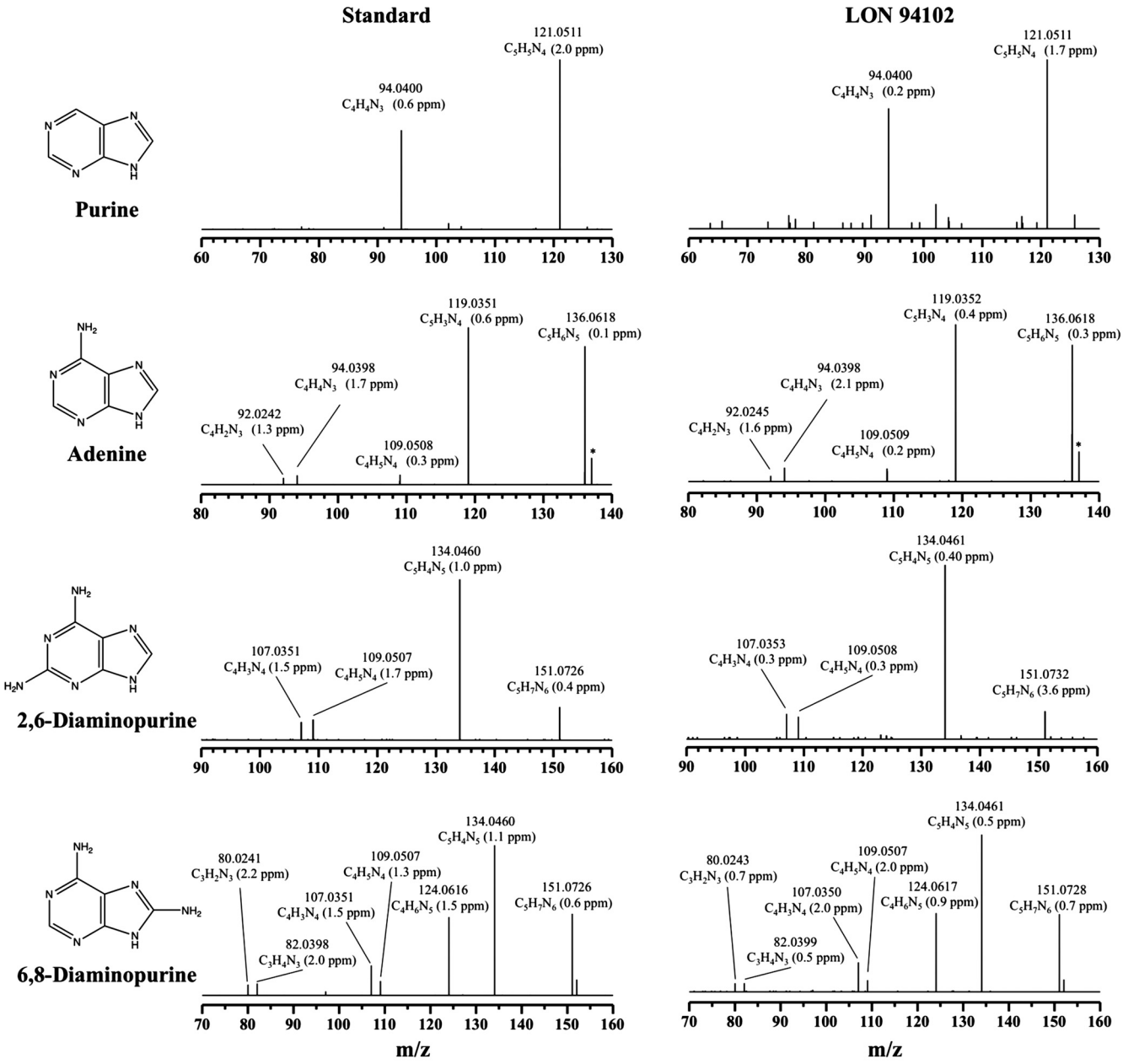

Fig. 2. Mass-selected fragmentation spectra of reference standards (left spectra) and compounds found in the meteorite LON 94102 (right spectra) measured on an LTQ Orbitrap XL hybrid mass spectrometer using an HCD (higher energy collision dissociation) setting of 90 to 100%. Purine, adenine, 2,6-diaminopurine, and 6,8-diaminopurine were identified using accurate mass measurements on the parent mass and multiple fragment masses and chromatographic retention time. Mass accuracy of less than 5 ppm allows for the unambiguous assignment of elemental formulae. The * represents inferences in the fragmentation spectra that are present in both the meteorite and reference standard spectra.

guanine, hypoxanthine, and xanthine observed in CM2 meteorites are largely extraterrestrial, but could potentially also contain traces of terrestrial contamination.

The presence of extraterrestrial purines in meteorites has far-reaching implications. The first cellular systems on the early Earth were presumably assembled from three components: nucleic acids, proteins, and cell membranes (31). Potential molecular subunits for constructing all of these macromolecular species (e.g., amino acids, amphiphilic compounds, and from this study—a variety of purine nucleobases) have been identified in meteorites and appear to be indigenous. Thus, meteorites may have served as a molecular kit providing essential ingredients for the origin of life on Earth and possibly elsewhere.

The identification of purine, 2,6-diaminopurine, and 6,8-diaminopurine in the meteorites Murchison and LON 94102 also expands the inventory of nucleobases that could have been available during the origins of life. The stability of 2,6-diaminopurine is similar to that of adenine, guanine, and xanthine and the accumulation of these compounds on the early Earth may have been possible (32). Furthermore, 2,6-diaminopurine can base pair with uracil (or thymine), and the additional amino group permits the formation of three hydrogen bonds (33). Because meteorites may have provided a significant source of prebiotic organic material including purines, it is plausible that alternative nucleobases such as 2,6-diaminopurine, 6,8-diaminopurine, xanthine, and hypoxanthine were available for constructing the first genetic molecules. It has been proposed that an "expanded genetic alphabet" was present, and perhaps required, in the RNA World (34); conversely an all-purine primitive RNA has also been proposed (35).

Materials and Methods

We employed a targeted approach for analysis that focused on the five canonical RNA/DNA nucleobases (adenine, guanine, cytosine, thymine, and uracil) as well as 17 nucleobase analogs (see *SI Text*), which have been synthesized under plausible prebiotic conditions in the laboratory (with the exception of 3,7-dimethylxanthine; theobromine) (36, 37). Meteorite analysis was carried out using either a Waters 2695 high performance liquid chromatograph (LC) coupled to a Waters 2996 photodiode array detector and Waters Quattro Micro API triple quadrupole mass spectrometer operating in multiple reaction monitoring (MRM) mode or a Thermo Scientific Accela LC coupled to a LTQ Orbitrap XL hybrid mass spectrometer. Typically, initial screening and quantitation of compounds was performed by the LC-triple quadrupole mass spectrometer in MRM mode while unambiguous structural confirmation was obtained using the LC-Orbitrap mass spectrometer, which permits high mass resolution (approximately 60,000 for our target masses) and excellent mass accuracy ($\ll$5 ppm). Experimental details are provided in *SI Text*.

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Supporting Information

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SI Text

Supporting Online Material. ***Reactions of HCN with NH_3.*** Sodium cyanide and stearic acid were heated under vacuum and the evolved HCN gas was collected in a liquid nitrogen cold finger (1–3). The HCN was then distilled twice in vacuum. An appropriate pressure of HCN gas was expanded into an evacuated glass bulb of known volume and then frozen into a known mass of 3X-freezed-pumped-thawed 18.2 MΩ, 3 ppb total organic carbon Millipore water to give a final concentration of 2 M. Gaseous ammonia was likewise frozen into a separate volume of Millipore water to give a concentration of 2 M. Once thawed, aliquots of these two solutions were mixed to give a final solution containing 1 M NH_4CN.

The 1 M NH_4CN was flame sealed in pyrolyzed glass tubes with minimal headspace. Solutions were allowed to react for approximately 6 mo at room temperature (to obtain sufficient HCN polymerization). The tubes were then opened and an aliquot removed and centrifuged briefly using a benchtop centrifuge to separate any insoluble material (HCN polymer) that had formed. A portion of this supernatant was dried, extracted in formic acid (see below), and analyzed using a liquid chromatograph coupled to an LTQ Orbitrap XL hybrid mass spectrometer.

Meteorite workup and analysis. All glassware and ceramics used in sample processing were pyrolyzed at 500 °C in air overnight prior to use. Individual meteorite fragments were powdered and homogenized by using a mortar and pestle in a positive pressure high-efficiency particulate air (HEPA)-filtered laminar flow bench. Powdered meteorite samples (approximately 50 to 500 mg) were then extracted with 95% formic acid at 100 °C for 24 h in glass ampoules. The extracts were purified using solid phase extraction. Meteorite extracts were loaded onto a Waters Oasis Max SPE (solid phase extraction) cartridge and rinsed with 5% ammonia in water followed by methanol. Nucleobases were then eluted using 5% formic acid in methanol. Individual recoveries of nucleobases after the SPE procedure were determined using standards and calculated using an average of three runs.

As a control, serpentine (a hydrated magnesium silicate) that had been previously heated at 500 °C overnight was carried through the identical extraction procedure. Analyses of serpentine samples did not contain any nucleobases above our detection limits (which were typically <1 ppb for purines). Pure standards carried through the same workup conditions were used to verify that no significant degradation of the canonical nucleobases occurred, especially with respect to deamination of guanine to xanthine and adenine to hypoxanthine (which were both less than 0.04%).

In multiple reaction monitoring (MRM) mode, a specific parent-to-daughter ion transition for each nucleobase is acquired in addition to a specific retention time given by the HPLC separation. Typically two MRM transitions were monitored for each nucleobase for identification and the most intense MRM transition was used for quantitation. We also collected the full fragmentation MS/MS spectrum when the individual nucleobase concentration was sufficient for this type of acquisition for further verification. We did not make any molecular assignments based on the UV chromatograms measured for meteorites because they were all very complex and contained a strong UV-absorbing background. We may have identified uracil in the UV chromatograms of Murchison and Orgueil; however, this could not be confirmed with our mass spectrometric analysis due to the well-known poor electrospray ionization efficiency of uracil. 6,8-Diaminopurine was prepared from 8-bromoadenine by the method described in Robins (4). Only the crude product was used; therefore, no quantitation of 6,8-diaminopurine in Murchison and Lonewolf Nunataks (LON) 94102 was attempted.

Additional Discussion of Meteorite and Terrestrial Sample Results. We investigated the abundance and distribution of nucleobases and nucleobase analogs in 11 different carbonaceous chondrites from three different groups (CI, CM, and CR) representing the entire range of aqueous alteration (types 1, 2, and 3) and one ureilite meteorite. We did not detect the other nucleobase analogs we searched for, such as 2-aminopurine, 6-cyanopurine, 3,7-dimethylxanthine, isocytosine, or 2,4-diaminopyrimidine above a 1-ppb detection limit in any of the meteorites examined. We also did not detect pyrimidine, dihydrouracil, 5-aminouracil, 5-hydroxymethyluracil, 5-aminoorotic acid, or isoguanine, although these compounds were searched for only in CM2 meteorites where a larger extracted sample was typically used (with a detection limit of approximately 5 ppb). A range of detection limits was possible and calculated using the different meteorite extraction masses (approximately 50 to 500 mg). A peak in the MRM chromatogram was tentatively identified as 4-hydroxypyrimidine; however, we could not confirm its structure on the Orbitrap mass spectrometer due to its low signal-to-noise ratio.

We detected only trace amounts of the nucleobase adenine (3 ppb) in Almahata Sitta fragment #4 ureilite, which is a meteorite that has experienced no aqueous alteration (Fig. 1). Previous studies of Almahata Sitta fragment #4 revealed the presence of indigenous amino acids (based on near racemic mixtures of amino acids and unusual C5 amino acids) (5) despite evidence of high temperature processing (approximately 1,100 to 1300 °C) on the parent body (6). The origin of adenine detected in Almahata Sitta #4 remains unclear and, despite the meteorite's relatively short residence time in the Nubian Desert (2 mo) (7) and the lack of other biological nucleobases (e.g., guanine and cytosine) and nearly racemic protein amino acids (23), terrestrial adenine contamination for this meteorite cannot be ruled out.

CR carbonaceous chondrites are believed to contain the most primitive organic matter of any carbonaceous chondrite group (8) and the Antarctic CR2 chondrites EET92042 and Graves Nunataks (GRA) 95229 have the highest amino acid abundances of any meteorite analyzed to date (9–11). Surprisingly, we found very low levels of purines in three CR carbonaceous chondrites with adenine abundances ranging from 5 to 21 ppb in Queen Alexandra Range (QUE) 99177, Elephant Moraine (EET) 92042, and GRA 95229 (Fig. 1 and Table S1). GRA 95229 also contained trace levels of guanine (4 ppb) and hypoxanthine (4 ppb), although the low signal-to-noise ratio ($S/N = 2$) permitted only a tentative assignment for hypoxanthine, and this compound was not detected in the other CR meteorites examined. We did not detect any purines in the amino acid-poor Grosvenor Mountains (GRO) 95577, a highly aqueously altered CR1 carbonaceous chondrite. It appears that the concentration of formic acid-extractable purines do not correlate with total amino acid abundances in these Antarctic CR carbonaceous chondrites.

The distribution of purines in our Murchison sample is similar to those previously reported (12), though the abundance is lower. This discrepancy is likely due to some combination of sample heterogeneity, differing extraction and workup conditions, and/or different quantitative methods (i.e., our integration of the highly selective MRM mass peaks versus UV chromatographic peaks, which are more likely to include interfering UV-absorbing compounds).

We measured 7 ppb adenine and 20 ppb guanine in Orgueil, the only CI carbonaceous chondrite examined in this study (Fig. 1). However, although racemic protein amino acids detected in Orgueil suggest a relatively pristine fragment (9), the results from Orgueil should be interpreted with caution because other fragments of this meteorite have been found to contain significant levels of terrestrial contamination (13).

Nine of the 12 meteorites examined in this study were recovered from the blue ice sheets of Antarctica. If these Antarctic meteorites had been extensively contaminated by exposure to the surrounding ice or ice–meltwater, we would expect the nucleobase distribution in these Antarctic meteorites to be similar to the Antarctic ice–meltwater and to each other. To test this, we analyzed the dried residue from an 8-kg Antarctic ice sample collected from the Graves Nunataks region in 2006 using the same workup procedure as the meteorites. Only ultratrace quantities of guanine [4.6 parts-per-trillion (pptr)], hypoxanthine (9.0 pptr), xanthine (4.6 pptr), and adenine (3.6 pptr) were measured in the Antarctic ice, and we did not detect any purine, 2,6-diaminopurine, and 6,8-diaminopurine above the 0.015-pptr limit of detection (the lower detection limit is due to the larger extracted mass). Thus, the distributions of purines found in Antarctic meteorites appear to correlate with meteorite petrology and the extent of parent body alteration rather than with the content of the terrestrial environments from which they were recovered, arguing against terrestrial contamination from the ice.

We also extracted and analyzed a soil sample that was collected in 1999 near the original Murchison meteorite's 1969 fall site in Australia to assess possible sources of terrestrial nucleobase contamination for this meteorite. The soil sample exhibited high levels of cytosine (1,380 ppb) and thymine (600 ppb) in addition to lower levels of guanine (22 ppb), adenine (26 ppb), hypoxanthine (11 ppb), and xanthine (7 ppb); however, purine, 2,6-diaminopurine, and 6,8-diaminopurine (assuming the same response factor as 2,6-diaminopurine) were not detected above 0.02 ppb. In contrast to the Murchison soil sample, we did not detect any cytosine in the Murchison meteorite. The absence of cytosine and the presence of a diverse set of purines including several nonbiological analogs in the Murchison meteorite strongly suggest that the purines found in the Murchison meteorite are extraterrestrial in origin.

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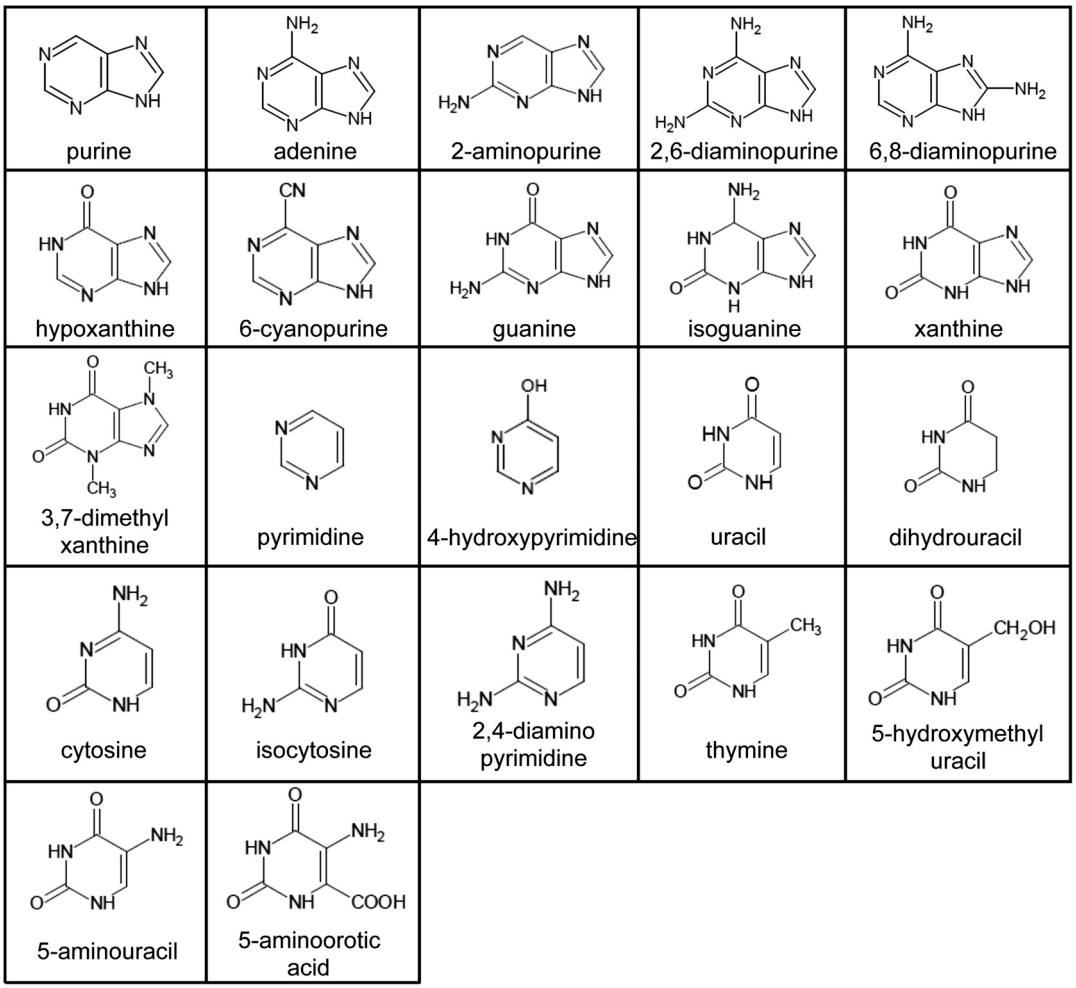

Fig. S1. The structures of nucleobases and nucleobase analogs that were searched for in meteorites.

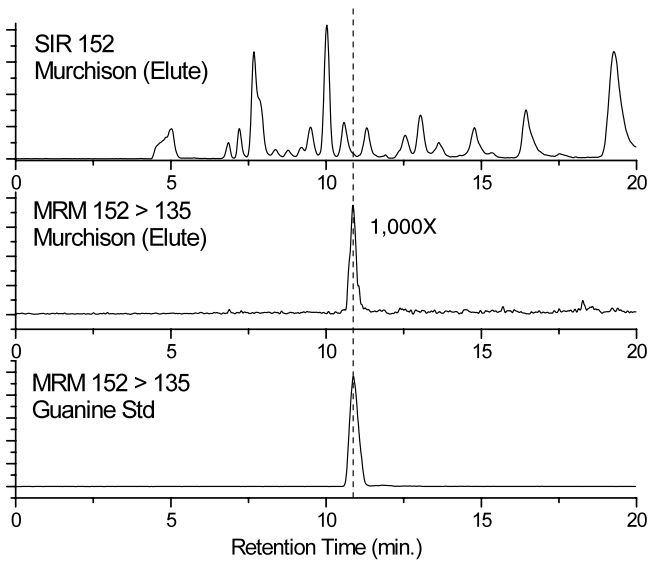

Fig. S2. Single ion chromatogram at m/z 152 (*Top*) and MRM chromatogram monitoring the 152 to 135 transition (*Middle*) for Murchison elution SPE fraction. The MRM peak was used for quantitation. Note that monitoring only the parent ion is not specific enough here. The MRM chromatogram of a guanine standard is also shown (*Bottom*). Nucleobase identification was also confirmed using the liquid chromatograph (LC)-Orbitrap using accurate mass measurements and fragmentation pattern.

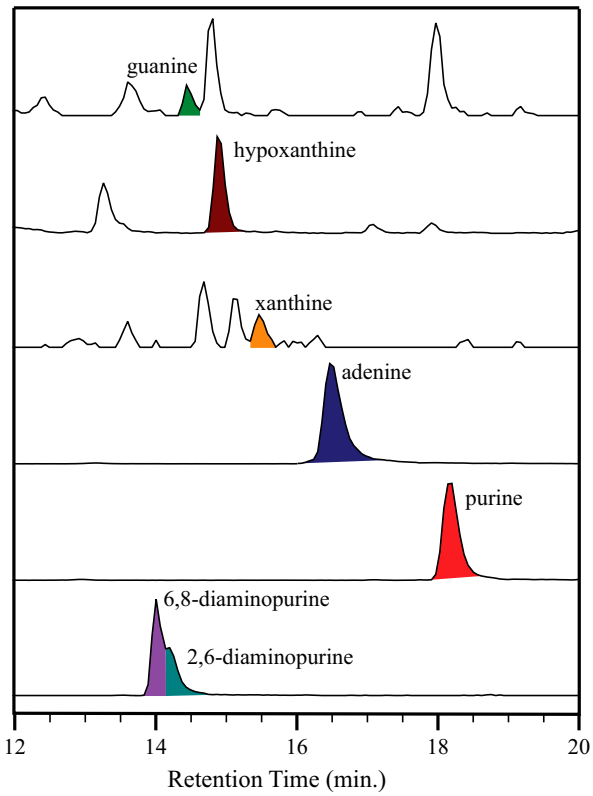

Fig. S3. Single ion accurate mass chromatograms (5-ppm window at each monoisotopic mass) of formic acid extracted 1.0 M NH_4CN measured on the LC-Orbitrap. The shaded peaks correspond to nucleobases and nucleobase analogs identified unambiguously based on their retention time and accurate mass measurements on parent and fragment ions (compared with standards).

Table S1. The concentration of purines (ppb) in meteorites is shown

Meteorite	Type	G	HX	X	A	Pu	2,6-DAPu	6,8-DAPu
Orgueil	CI1	20	(5)	<10	7	5	<2	–
Scott Glacier 06043	CM1	(2)	(4)	<10	4	<1	<2	–
Meteorite Hills 01070	CM1	29	<3	<10	5	<1	<2	–
GRO 95577	CR1	<2	<3	<10	<0.5	<1	<2	–
Allan Hills 83100	CM1/2	21	4	(4)	1	<0.1	<0.2	+
Murchison	CM2	56	26	60	5	3	+	+
Lewis Cliff 90500	CM2	167	23	22	10	1	<0.2	+
LON 94102	CM2	244	94	77	30	6	5	+
GRA 95229	CR2	4	(4)	<10	21	9	<2	+
EET 92042	CR2	<2	<3	<10	5	(4)	<2	+
QUE 99177	CR3	<2	<3	<10	11	7	<2	+
Almahata Sitta #4	URE	<2	<3	<10	3	<1	<2	–

The abbreviations are G (guanine), HX (hypoxanthine), X (xanthine), A (adenine), Pu (purine), 2,6-DAPu (2,6-diaminopurine), 6,8-DAPu (6,8-diaminopurine), and URE (ureilite). Concentrations are calculated from the MRM chromatogram and represent the sum of all the solid phase extraction fractions. Purines that were not detected are reported as upper limits (and are shown in gray). Numbers in parentheses represent concentrations for tentative structural assignments; tentative assignments were usually because of low S/N coupled with a complex MRM chromatogram not allowing for unambiguous assignment. The + sign indicates the positive identification for the compound (without quantitation). No quantitation was performed for 6,8-diaminopurine because an unpurified standard was used in this study. Both 2,6-diaminopurine and 6,8-diaminopurine were unambiguously identified (by their accurate mass fragmentation spectra) in a larger extract of the Murchison meteorite, but no quantitation was performed