Extraterrestrial ribose and other sugars in primitive meteorites

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Sugars are essential molecules for all terrestrial biota working in many biological processes. Ribose is particularly essential as a building block of RNA, which could have both stored information and catalyzed reactions in primitive life on Earth. Meteorites contain a number of organic compounds including key building blocks of life, i.e., amino acids, nucleobases, and phosphate. An amino acid has also been identified in a cometary sample. However, the presence of extraterrestrial bioimportant sugars remains unclear. We analyzed sugars in 3 carbonaceous chondrites and show evidence of extraterrestrial ribose and other bioessential sugars in primitive meteorites. The ^{13}C-enriched stable carbon isotope compositions ($\delta^{13}C$ vs. VPDB) of the detected sugars show that the sugars are of extraterrestrial origin. We also conducted a laboratory simulation experiment of a potential sugar formation reaction in space. The compositions of pentoses in meteorites and the composition of the products of the laboratory simulation suggest that meteoritic sugars were formed by formose-like processes. The mineral compositions of these meteorites further suggest the formation of these sugars both before and after the accretion of their parent asteroids. Meteorites were carriers of prebiotic organic molecules to the early Earth; thus, the detection of extraterrestrial sugars in meteorites establishes the existence of natural geological routes to make and preserve them as well as raising the possibility that extraterrestrial sugars contributed to forming functional biopolymers like RNA on the early Earth or other primitive worlds.

meteorite | carbohydrate | exogenous delivery | ribose | RNA

S ugars are indispensable molecules for life, working along essential metabolic pathways and as constituents of sugar phosphate backbone of genetic molecules (DNA and RNA). Ribose is particularly essential as a building block of RNA, which could have both stored information and catalyzed reactions in primitive life on Earth (1, 2). Thus, the availability of abiotic sugars and their precursors on the prebiotic Earth has been investigated for many years (3–5).

Numerous studies have been conducted on meteoritic organic compounds, particularly amino acids and nucleobases (6–10). However, unlike these organic compounds, an extraterrestrial origin for biological sugars in meteorites has not yet been proven. In the 1960s, researchers reported the detection of common biological sugars, including arabinose **2**, xylose **4**, glucose, and mannose (Fig. 1), in both carbonaceous and ordinary chondrites in comparable concentrations (11, 12). As noted by the authors and the authors of a subsequent review, a major problem was the possibility of terrestrial contamination of the detected aldoses (13). Since the 2000s, Cooper and coworkers carefully analyzed carbonaceous meteorites by gas chromatography/mass spectrometry (GC/MS) and detected the simplest ketose, dihydroxyacetone **1**, in the Murchison and Murray meteorites with several sugar alcohols and sugar acids; however, dihydroxyacetone has a lesser role in biology, the phosphate is used in central metabolism, but it has no known structural or informational roles (14). Cooper and Rios (15) verified that several sugar acids and sugar alcohols are

extraterrestrial in origin, having stable carbon isotope ratios that differ substantially from terrestrial sugar alcohols and sugar acids. Therefore, to date, no previous research has verified the presence of extraterrestrial aldoses or other sugar compounds related to biological macromolecules in any astronomical sample (16).

We detected all 4 types of aldopentoses (i.e., ribose **3**, arabinose, xylose, and lyxose **5**) in concentrations of 2.3 to 11 ppb from NWA 801 and 6.7 to 180 ppb from the Murchison meteorite (Fig. 2; Table 1; and *SI Appendix*, Figs. S2 and S3). Several hexoses are also found in the NWA 801 and the Murchison meteorites. Conversely, in NWA 7020, these sugars were below our detection limit for the amount of sample analyzed (<0.5 ppb). Tetroses, sugar acids and sugar alcohols containing 5 carbon atoms (e.g., ribitol and ribonic acid), as well as 2-deoxyribose and branched isomers of aldopentoses, were below our detection limit in both meteorites (<0.5 ppb). We also analyzed serpentine which had been baked in air at 500 °C overnight as an analytical blank, and no pentoses were detected.

The $\delta^{13}C$ values of ribose and xylose in NWA 801 and ribose and arabinose in Murchison showed significant ^{13}C enrichment (+8 to +43‰), whereas xylose in Murchison was lower (−1‰) (Figs. 3 and 4 and see also *SI Appendix*, SI Text). The $\delta^{13}C$ values of other sugars were not calculated because of low intensity or poor peak separation. The positive $\delta^{13}C$ values are clearly distinct

Significance

Ribose is an essential sugar for present life as a building block of RNA, which could have both stored information and catalyzed reactions in primitive life on Earth. Meteorites contain a number of organic compounds including components of proteins and nucleic acids. Among the constituent molecular classes of proteins and nucleic acids (i.e., amino acids, nucleobases, phosphate, and ribose/deoxyribose), the presence of ribose and deoxyribose in space remains unclear. Here we provide evidence of extraterrestrial ribose and other bioessential sugars in primitive meteorites. Meteorites were carriers of prebiotic organic molecules to the early Earth; thus, the detection of extraterrestrial sugars in meteorites implies the possibility that extraterrestrial sugars may have contributed to forming functional biopolymers like RNA.

H
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H——OH
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H

Dihydroxyacetone (**1**)

CHO	CHO	CHO	CHO
OH—H	H—OH	H—OH	HO—H
H—OH	H—OH	HO—H	HO—H
H—OH	H—OH	H—OH	H—OH
CH₂OH	CH₂OH	CH₂OH	CH₂OH

D-arabinose (**2**) D-ribose (**3**) D-xylose (**4**) D-lyxose (**5**)

Fig. 1. Structures of sugars detected in this study (structures 2 to 5) and a previous study (structure 1) (shown in Fischer projection) from meteorites. All sugars are shown as D-form for simplicity; however, chirality was not investigated in this study.

from biologically synthesized sugars (17, 18). For example, pentoses and hexoses in algae, higher plants, and secondary producers all have negative $\delta^{13}C$ values ranging between −32 and −1‰ (Fig. 4). We also analyzed the carbon isotope composition of pentoses

extracted from a soil sample that was collected in 1999 from the original Murchison meteorite's 1969 fall site in Australia (9) to indicate the $\delta^{13}C$ values of likely contaminants. The $\delta^{13}C$ values of ribose (−46‰), arabinose (−52‰), and xylose (−44‰) are even lower and all well outside the range of sugars we detected in meteorites. The $\delta^{13}C$ values of ribose and xylose in NWA 801 and ribose and arabinose in Murchison are comparable to those of sugar acids and sugar alcohols detected previously (i.e., +5 to +82‰ in GRA 95229 and Murchison meteorites) (15) and those of α-amino acids in many carbonaceous chondrites, which typically range from +3 to +44‰ (10). This is very strong evidence that NWA 801 and Murchison contain extraterrestrial pentoses. While enriched ^{13}C ($\delta^{13}C > 0‰$) is usually an indicator of extraterrestrial origin, slightly depleted ($\delta^{13}C \leq 0$) does not always indicate terrestrial contamination. For example, many extraterrestrial carboxylic acids have negative $\delta^{13}C$ values (19). Xylose in the Murchison meteorite has a distinct $\delta^{13}C$ value from xylose in Murchison soil, although that is insufficiently distinct from biological sugars reported previously (17). Although no $\delta^{13}C$ value could be determined for lyxose, this sugar may also be extraterrestrial due to its rarity in the biosphere. Furthermore, the composition of sugars in the NWA 801 and Murchison meteorites are distinct from the compositions of sugars in extracellular carbohydrate polymers of desert soil algae, showing the presence of ribose and lyxose in the meteorites and absence of these sugars in desert soil algae also support an extraterrestrial origin for these sugars (20–22). The enantiomeric ratios of chiral molecules are sometimes used to
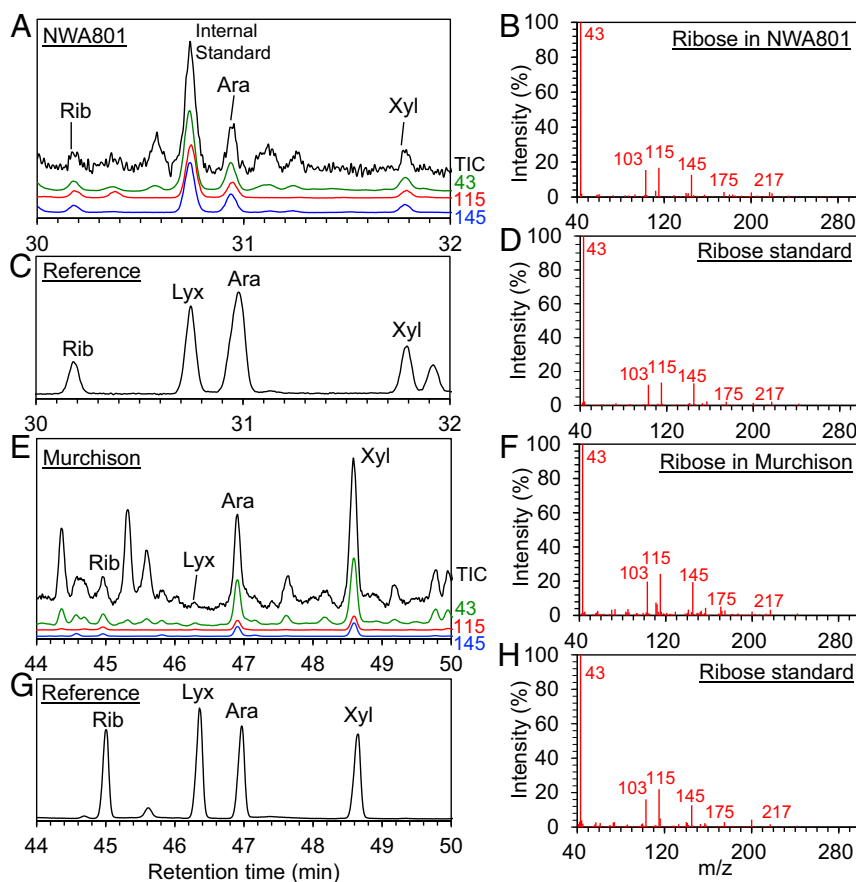
Fig. 2. GC/MS identification of pentoses in meteorites and reference standards. (*A*) Total ion chromatogram and selected ion chromatograms of NWA 801 extract. (*B*) Mass fragment spectrum of ribose in NWA 801. (*C*) Total ion chromatogram and selected ion chromatograms of the reference standard mixture. (*D*) Mass fragment spectrum of ribose in the reference standard. (*E*) Total ion chromatogram and selected ion chromatograms of the Murchison extract. (*F*) Total ion chromatogram and selected ion chromatograms of the reference standard mixture. (*G*) Mass fragment spectrum of ribose in the Murchison. (*H*) Mass fragment spectrum of ribose in the reference standard.

Table 1. Results of coordinated analysis of 3 meteorites

	NWA 801		NWA 7020		Murchison meteorite		Murchison soil
	Content (ppb)	$\delta^{13}C$ (‰)	Content (ppb)	$\delta^{13}C$ (‰)	Content (ppb)	$\delta^{13}C$ (‰)	$\delta^{13}C$ (‰)
Sugars							
Ribose	4.5	+8	<0.5	NA	25	+38	−46
Arabinose	11	NA	<0.5	NA	120	+43	−52
Xylose	6	+25	<0.5	NA	180	−1	−44
Lyxose	2.3	NA	<0.5	NA	6.7	NA	NA
Petrologic type	CR 3.0 to 2.8		CR 2.8 to 2.5		CM 2.5		−
Carbon chemistry	$I_{alipha} > I_{aroma}$		$I_{alipha}/I_{aroma} \sim 1$		$I_{alipha} < I_{aroma}$*		−
IOM $\delta^{13}C$ (‰)	−20.7 (±1.2)		−22.4 (±0.61)		−18.91 (±0.01)[†]		−
IOM $\delta^{15}N$ (‰)	+66.0 (±0.18)		+93.4 (±6.4)		−1.0 (±0.4)[†]		−
N/C	0.029		0.030		0.0327 (±0.0003)[†]		−

The $\delta^{13}C$ values show the isotope ratios of aldopentoses. NA, not analyzed or detected.
*Ref. 23.
[†]Ref. 25.

evaluate the extent of biological contamination in abiotic synthesis products. However, this may not be useful for the evaluation of biological sugar contamination in meteorites, since chiral sugar-related compounds in Murchison and other meteorites have been observed to have large D-enantiomeric excesses (15).

The concentrations of detected extraterrestrial sugars are approximately 3 orders of magnitude lower than those of amino acids (8) and comparable to those of purines found in CR2 meteorites (9) and those of 5-carbon sugar acids and sugar alcohols in the Murchison meteorite (15).

The molecular structures of insoluble organic matter (IOM) were analyzed with solid-state ^{13}C-NMR (SS-NMR). A chemical shift attributed to aliphatic carbon is clearly more abundant than that from aromatic carbon in NWA 801, whereas the aliphatic carbon signal was comparable to the aromatic carbon signal in NWA 7020 (Fig. 5D). The ratio of aliphatic/aromatic chemical shifts is 1 indicator of the extent of low-temperature chemical oxidation of meteorite organics associated with water (23). The carbon and

nitrogen isotope ratios of IOM were analyzed with a sensitivity-modified elemental analyzer/isotope ratio mass spectrometer (EA/IRMS) (24). The $\delta^{13}C$ values of IOM in these 3 meteorites are comparable to those of typical carbonaceous meteorites (25) (Table 1). The nitrogen isotope composition ($\delta^{15}N_{vs.\ Air}$) of the IOM in the 2 NWA meteorites showed significantly positive values (i.e., $\delta^{15}N$ = +66.0 and +93.4‰ for NWA 801 and NWA 7020, respectively), which is characteristic of CR chondrites (Table 1).

We also explored the minerals in both meteorites using synchrotron X-ray diffraction (S-XRD) and field-emission scanning electron microscopy (FE-SEM) to assess the environments these meteorites experienced in their parent body asteroids. FE-SEM observation of the NWA 801 fragment showed that it contains large chondrules and metal grains with a small amount of fine-grained matrix. Chondrules and mineral fragments are not aqueously altered and are predominantly composed of olivine and pyroxene. Grain boundaries of olivine in type 1 porphyritic olivine chondrules are filled with unaltered iron-free mesostasis
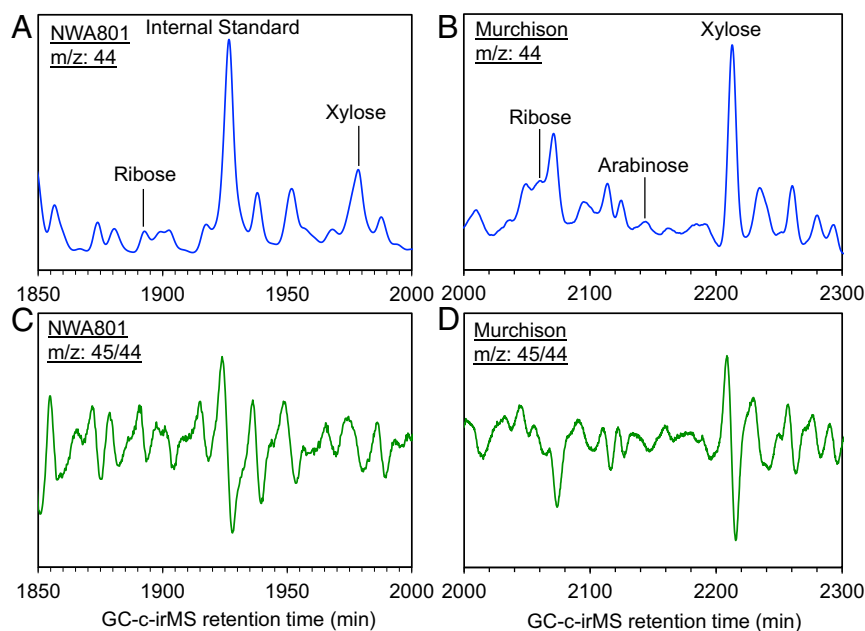
Fig. 3. Gas chromatography/combustion/isotope ratio mass spectrometry (GC/c/irMS) and GC/MS chromatograms of a derivatized NWM801 extract with an internal standard and the Murchison extract. (A) Single ion chromatogram (m/z = 44) of GC/c/irMS of the NWA 801 extract. (B) Single ion chromatogram (m/z = 44) of GC/c/irMS of the Murchison extract. (C) Signal ratio chromatogram of m/z = 45 over m/z = 44 of the NWA 801 extract. (D) Signal ratio chromatogram of m/z = 45 over m/z = 44 of the Murchison extract.

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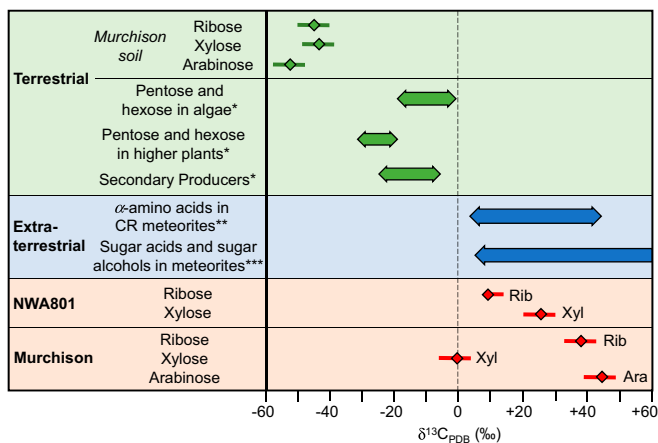
Fig. 4. Stable carbon isotopic composition of sugars detected in this study, with representative terrestrial and extraterrestrial organic compounds. *, ref. 17; **, ref. 10; and ***, ref. 15.

glass (Fig. 5C). X-ray diffraction analysis of the matrix indicates that it is composed mainly of anhydrous silicates and kamacite and does not contain phyllosilicates (Fig. 5B and *SI Appendix,* *Fig. S4*). A small reflection at around 7.2 Å is not serpentine but probably akaganeite (iron hydroxide made by terrestrial weathering of kamacite); if it was serpentine, then prism reflections

should have been detected, as was observed in the NWA 7020 matrix (Fig. 5A). Metals are partially altered to iron hydroxide by terrestrial weathering, but magnetite is absent. Based on the reported classification of CR chondrites, the subtypes of NWA 801 would be 3.0 to 2.8, indicating that this meteorite experienced very limited and low-temperature aqueous processing in its parent body (26). NWA 7020 also contains large chondrules. Grain boundaries of olivine in type 1 porphyritic olivine chondrules are filled with unaltered iron-free mesostasis glass. On the other hand, fine-grained matrix materials are dominated by phyllosilicates, serpentine, and saponite, suggesting that aqueous alteration was pervasive in the matrix of NWA 7020, in contrast to NWA 801. Metals are partially altered to iron hydroxide by terrestrial weathering. The presence of magnetite is not clear. Based on the reported classification of CR chondrites, the subtypes of NWA 7020 would be 2.8 to 2.5 (26). The Murchison meteorite is also phyllosilicate-rich and thus has experienced significant aqueous alteration. The difference in the aqueous alteration history recorded in minerals is consistent with the recorded history of molecular structure of IOM.

The formose reaction is a thermally driven aqueous process producing a number of sugars, including ribose, from aldehydes with alkaline catalysts (3, 5). Formose-like reactions have been hypothesized to be related to IOM formation (27, 28). Formose-like reactions are also capable of forming sugars in natural environments (5). The fluid in the parent bodies of carbonaceous chondrites is thought to be alkaline and contains many cations, including Mg^{2+} (29). Thus, a formose-like reaction would have
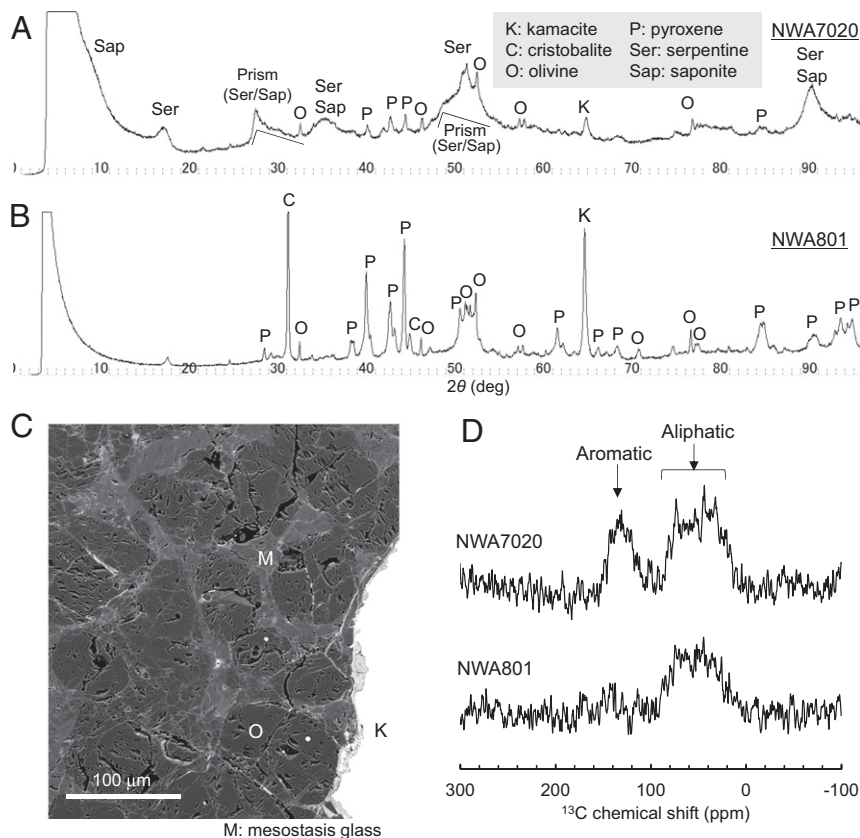
Fig. 5. Alteration of minerals and insoluble organic matter. (A) S-XRD profiles of the matrix in NWA 7020. The matrix is dominated by phyllosilicates (saponite and serpentine) based on the presence of basal and prism reflections of these minerals. (B) S-XRD profiles of the matrix in NWA 801, indicating that anhydrous silicates and FeNi metal kamacite are major phases. (C) Back-scattered electron image of a part of type I porphyritic olivine chondrule in NWA 801. The chondrule mesostasis glass (M) and kamacite (K) are almost free from aqueous alteration products. O represents olivine. (D) RAMP-CP-MAS ^{13}C NMR spectra of IOM from NWA 7020 and NWA 7020. The aliphatic carbon signal of NWA 801 IOM is more abundant than the aromatic signal. The aromatic carbon signal and aliphatic signal of NWA 7020 IOM are comparable.
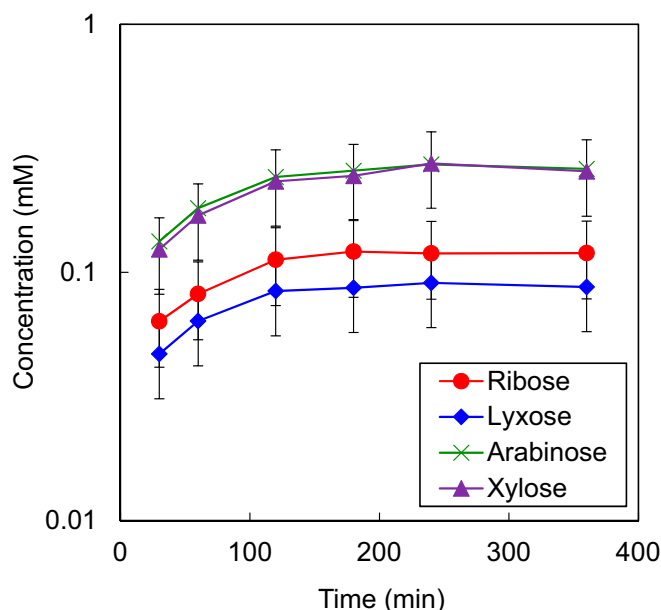
Fig. 6. The concentrations of aldopentoses in a formose-like reaction product.

been possible during aqueous processing in many of the parent asteroids of carbonaceous meteorites. We also conducted a laboratory experiment of the formose-like reaction to compare the product composition with the composition of sugars detected in this study (Fig. 6). The relative composition of aldopentoses in the product of the formose-like reaction is mostly consistent with the relative content of sugars detected in the NWA 801 and Murchison meteorites. This indicates that the sugars in the meteorites detected in this study could be the products of formose-like reactions.

The mineralogy and IOM structure of NWA 801 indicate that aqueous alteration of this meteorite was very limited. Thus, sugars in NWA 801 could have been formed before accretion of the CR2 parent body or during an early parent body aqueous alteration stage. The formation of sugars before the accretion of meteorite parent bodies has been suggested in previous studies (30, 31). The IOM structure and mineral compositions of NWA 7020 show a higher extent of aqueous alteration in its parent body. Thus, sugars in the NWA 7020 meteorite might have degraded in the parent body during aqueous alteration. The CM2 Murchison meteorite experienced a much higher degree of aqueous alteration compared to the CR2 NWA 7020. However, compositional differences in the mineralogy and in the fluid between these parent bodies may have resulted in different formation and preservation conditions for sugars. For example, many CR2 meteorites have a high NH_3 content relative to other carbonaceous chondrites (32), and NH_3 can react with sugars and consume them.

The detection of ribose and other bioessential sugars in NWA 801 and Murchison that are isotopically distinct from terrestrial sugars provides clear evidence of an extraterrestrial origin for these sugars in primitive meteorites. Further, this work provides evidence that prebiotic sugars could have been delivered to ancient environments on the Earth and possibly on Mars. The detection of extraterrestrial sugars in meteorites establishes the existence of natural geological routes, outside of the laboratory, to make and preserve them. The absence of deoxyribose as well as the presence of ribose in the natural geological routes further implies much more availability of ribose than deoxyribose on the prebiotic Earth. This would be geological support of the RNA world hypothesis.

Materials and Methods

We conducted a coordinated analysis of 3 carbonaceous meteorites, which included the identification of sugars, stable carbon isotope analyses of the individual sugars, stable carbon isotope and stable nitrogen isotope analyses of IOM, molecular structure analysis of IOM, and an evaluation of the mineral alteration (*SI Appendix*, Fig. S1). The carbonaceous meteorites investigated in this study were 2 CR2 chondrites (NWA 801 and NWA 7020) and a CM2 chondrite (Murchison meteorite). Typically, CR2 chondrites contain larger amounts of soluble organic compounds, such as amino acids (8, 33), compared with other meteorite types. The fragment of Murchison meteorite investigated in this study was already analyzed for amino acids, and it was established that this Murchison meteorite fragment experienced minimal terrestrial contamination based on a near-racemic (D ~ L) mixture of the common biological amino acid alanine (34). Large fractions of the meteorites were used for sugar extraction (>2 g) because the sugar content was expected to be low.

The Murchison meteorite has been investigated for sugar and sugar-related compounds in previous studies (14, 15). Unlike previous studies, we extracted sugars using hydrochloric acid and water from the meteorites to liberate all sugars from the mineral surfaces. Then, this extract was purified and derivatized into aldonitrile acetates (18, 35). This derivatization has large advantages for the reliable identification and sensitive detection of sugars over traditional methods (*SI Appendix*, SI Text). This derivatization has been used for the analysis of carbon isotope compositions of sugars in biological samples (18).

Data Availability. All data discussed in the paper have been made available to readers.

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Supplementary Information Text

Materials and Methods

Materials. The Murchison meteorite was from the Field Museum of Natural History, Chicago via Clifford N. Matthews's research group that had been stored in a desiccator. NWA 801 and NWA 7020 were both sourced from commercial meteorite trading companies. Hydrochloric acid solutions for extraction and analyses were prepared by diluting a commercial HCl (for proteomics; Wako) with water purified by the Millipore Simplicity UV system (18.2 MΩ cm). This water was also used for other steps. This HCl contains extremely low-level glycine and is free from other amino acids. For derivatization, pyridine (Infinity Pure grade > 99.5%; Wako), hydroxylammonium chloride (98%; Wako), and acetic anhydride (97%; δ^{13}C = −22‰; Wako) were used. Reference sugar standards, except those for lyxose, were also from Wako. Lyxose was sourced from Alfa Aesar. For extraction of polyol fraction and IOM, HF solution (Wako), boric acid (Wako), methanol (for pesticide residue-PCB analysis; Wako), dichloromethane (for pesticide residue-PCB analysis; Wako), ethyl acetate (Infinity Pure grade > 99.8%; Wako), and hexane (for pesticide residue-PCB analysis; Wako) were used.

Extraction and derivatization of sugars. We crushed a single 10 g fragment of the Murchison meteorite to powder using a clean ceramic mortar and pestle and homogenized the powder in a glass vial by mixing with a vortexer for 5 min. A 2 g aliquot of the powder was transferred into a separate glass vial for this study. Approximately 80% and 100% of the outer surfaces of NWA 801 and NWA 7020 were covered with a glassy fusion crust, respectively. The surfaces of these large meteorite samples (16.1 g of NWA 801 and 10.2 g of NWA 7020) were trimmed completely with a cutting machine and a dental drill and then crushed into fragments using a carefully washed stainless steel mortar and agate. Then, the fragments were crushed into powders using thermally-treated glass-made mortar and agate. All mortars and glassware was heated at 500°C in air for 6 h before use.

Sugars were extracted from ~2 g of the powder using 10 mL of 2% HCl three times then further extracted with 10 mL of pure water three times. The pure water was prepared with MilliQ system (18.2 MΩ cm, TOC <5 ppb). During extraction, the sample was occasionally sonicated under ambient temperature. This extraction solution was dried at < 35°C with a rotary evaporator and sugars were extracted using methanol to remove inorganic salts. The methanol was dried under ambient temperature and cations were removed with a cation exchange resin (AG50W-X8; Bio-Rad). The water elute from the resin was dried and subjected to derivatization.

The derivatization of sugars was conducted by a similar procedure to that reported in previous research (S1). Dried samples (i.e., polyol fraction and standard mixture) of sugars were dissolved with 1.5 mL pyridine containing 20 mg hydroxylammonium chloride. Then, this pyridine solution was heated at 90°C for 60 min, followed by heating at 90°C for 60 min with 0.5 mL acetic anhydride. In the first incubation an aldose is treated with hydroxylamine to form the oxime, followed by treatment with acetic anhydride, followed by elimination to give the nitrile. This reaction is also known as the first step of Wohl reaction. The derivatives were dried under N$_2$ flow and re-dissolved with dichloromethane (DCM). The extra pyridine and by-products of the reaction were removed by repeatedly washing with HCl and water. Then, purified derivatives were dried under N$_2$ flow and re-dissolved in hexane/ethyl acetate for GC/MS.

Extraction of IOM. The residues of the soluble organic compound extract were further treated sequentially with 6 M HCl solution at 60°C for 12 h, with 12 M HCl and 46% HF solution at 70°C for 10 h, and with 0.7 wt.% boric acid solution at 70°C for 6 h by continuous shaking to remove

silicates. Then, the carbonaceous matter was washed with methanol, dichloromethane, and hexane to extract soluble organics and yield IOM.

Identification of sugars and sugar related compounds by GC/MS. The identification of sugars was conducted by a gas chromatograph-mass spectrometer (GCMS-QP2010; Shimadzu) with a DB-17ms column (30 m long, 0.25 µm thick, 0.25 mm ID; Agilent). The carrier gas (He) flow rate was 0.8 mL/min. Inlet, interface, and ion source temperatures were 250°C, 250°C, and 200°C, respectively. The column oven temperature was programed as follows: initial temperature of 50°C for 2 min, then ramp up at 15°C/min to 120°C (hold 5 min), 4°C/min to 160°C, and 3°C/min to 170°C. The sample injection was conducted with 1/50 split or splitless. The sample was also analyzed with a different GC/MS system (Agilent 5977B) equipped with a GESTEL PTV injector under identical column and gas flow conditions to confirm the consistency of the results.

Compound-specific carbon isotope analysis by GC/c/irMS. Compound-specific isotope analysis of sugars was conducted by a 7890A gas chromatograph connected to a Delta plus XP isotope ratio mass spectrometer (ThermoFinnigan) via a GC IsoLink conversion unit and a ConFlo IV interface. Separation of sugars was achieved with a DB-17ms column (30 m long, 0.25 µm thick, 0.25 mm ID; Agilent). Details of the instrumental settings are presented elsewhere.

Carbon and nitrogen isotope analysis of IOM by EA/irMS. The carbon isotope ratios of IOM were analyzed with two different systems. The first system was an EA-irMS (Flash 2000 connected to Delta V via ConFlo III; ThermoFinnigan) at Tohoku University. The isotope ratio was calibrated using the USGS40 reference (L-glutamic acid; −26.389‰) and an inhouse standard (l-histidine; −10.7‰). The second system was a modified EA/IRMS (Flash EA 1112 elemental analyzer connected to a Delta plus XP isotope ratio mass spectrometer via a ConFlo III interface; ThermoFinnigan) at JAMSTEC. The isotope ratio was calibrated using four reference materials covering from −60.02‰ to −0.49‰, including: glycine (−60.02‰), l-tyrosine (−20.83‰), l-alanine (−17.93‰), and l-valine (−0.49‰). The $\delta^{13}C$ values acquired using the two independent systems agreed within error ranges.

The nitrogen isotope ratios of IOM were analyzed with a sensitivity modified EA/IRMS (Flash EA 1112 elemental analyzer connected to a Delta plus XP isotope ratio mass spectrometer via a ConFlo III interface; ThermoFinnigan), which is specifically designed to determine $\delta^{15}N$ of small amount of nitrogen (>80ng) contained within incombustible substances with high precision, at JAMSTEC. The isotope ratio was calibrated using five reference materials covering from −26.63‰ to +61.53‰, including: IAEA-N-2 (ammonium sulfate; +20.3‰), L-tyrosine (+8.74‰), glycine (−26.63‰), L-alanine (+43.25‰), and L-valine (+61.53‰).

Molecular structure analysis of IOM by SS-NMR. Cross-polarization (CP) and magic angle spinning (MAS) ^{13}C-NMR was conducted by an 800 MHz NMR spectrometer (JNM-ECA 800 FT NMR; JEOL) at Tohoku University with a 2.5 mm double resonance NMR probe. The CP was conducted with a ramped-amplitude CP sequence (RAMP-CP). The MAS frequency was 30 kHz. Contact time was 2 ms. The spectra were presented as frequencies in ppm shift relative to that of the methyl group in tetramethylsilane using adamantane as an in-house reference (38.52 ppm). The SS-NMR data of the two meteorites can be compared, but it may not be suitable to compare

the present data directly to the SS-NMR data which was previously published (26), since this data was acquired at a higher field (800 MHz) using faster MAS (30 kHz).

Mineral analysis by S-XRD and FE-SEM. A fragment (~5 mm in size) of the inner part of each meteorite was picked from the mortar during the crushing process. Two to three small pieces (~200 μm in size) of matrix were separated from the fragment and analyzed for X-ray diffraction at the beam line 3A of the KEK synchrotron facility (the Photon Factory, Tsukuba) using a Gandolfi camera. X-ray wavelength is 2.16 Å.

The fragments and the small pieces of matrix from NWA 801 and NWA 7020 were embedded in resin, polished, and further analyzed using a JEOL JSM-7001F field emission scanning electron microscope (FE-SEM) equipped with an energy dispersive spectrometer at Tohoku University. The analysis was conducted with 15 kV acceleration voltage and 1 nA probe current.

Experiments of formose-like reaction. 100 mM formaldehyde and 10 mM glycolaldehyde were dissolved in ammonia buffer (pH 9.6). The solution was incubated at 90°C up to 360 min with continuous stirring. Aliquots of the solution were sampled during the incubation and analyzed for the concentration of pentoses with GC/MS as the same method for meteorite analysis.

Supplementary Text

Advantages of aldonitrile acetate derivatization for meteorite analysis. This derivatization has a significant advantage over traditional methods such as trimethylsilylation and simple acetylation. For example, trimethylsilyl derivatization yields four to five anomeric derivatives from a single aldose (e.g., α-ribopyranose, ß-ribopyranose, α-ribofuranose, and ß-ribofuranose derivatives from ribose). Such derivatives result in considerable difficulty for sugar identification, in that the gas chromatogram is generally filled by a large number of derivative peaks and the peak intensity of the original sugar decreases. Conversely, the aldonitrile acetate derivatization used in this study provides a single derivative from a single aldose (ribonitrile acetate derivative from ribose) and enables reliable identification and sensitive detection of sugars in a mixture of multiple sugars and sugar-related compounds.

The product major fragments of aldonitrile tetra-acetate are m/z: 43 (100%), 103 (12%), 115 (14%), and 145 (13%). The fragmentation pattern has been also discussed in the literature (S2). The 43 fragment is attributed to acetate (CH_3CO^+); others are attributed to fragmentation followed by elimination of acetic acid ($-$ 60) and ketone ($-$ 42). Fragmentation patterns are shown in Fig. S5.

Robustness of the derivatization for identification of meteorite sugars. The reliability of the aldonitrile acetate derivatization for the identification of meteorite sugars was carefully assessed. First, we tested whether our target sugars formed during the process of derivatization from sugar precursors. The most probable reaction that forms pentose from precursors present in the meteorite extracts is that between glycolaldehyde and glyceraldehyde. Thus, we derivatized a mixture of commercially available glycolaldehyde and glyceraldehyde using the same protocols

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employed for the meteorite analysis and confirmed that this derivatization does not form the sugars detected in this study.

Secondly, we tested whether the detected sugars formed from their corresponding sugar acid and sugar alcohol during derivatization. To test this, we derivatized commercial ribitol and ribonic acid with this protocol and confirmed that ribose does not form from the reduced and oxidized forms of ribose. Therefore, aldonitrile acetate derivatization is highly reliable for the identification of sugars in meteorite extracts.

Calculation of the carbon isotope ratios of pentoses. As aldonitrile acetate derivatization introduces acetate to form sugar derivatives, the carbon isotope ratios of the detected sugars were corrected by isotopic mass balance for the contribution of acetate carbon atoms (C_{Ac}). The $\delta^{13}C$ value of acetic anhydride used for derivatization is $-22‰$. The $\delta^{13}C_{Ac}$ value after derivatization was determined using internal and external standard. The degree of isotopic fractionation generally differs depending of the molar balance between hydroxyl groups (OH) in the samples and acetic anhydride (AA) in the acetylation, and apparently shows a linear correlation between the two (S3). We constructed this linear calibration line using an external standard ribose and an internal standard lyxose to estimate the $\delta^{13}C_{Ac}$ associated with acetylation (Fig. S6). The amount of OH in the extract was estimated by weighing the sample before the derivatization. Most of the OH is from methanol used in the extraction process. The correctness of the calibration line was confirmed with lyxose internal standard added to the NWA 801 extract before derivatization.

The $\delta^{13}C$ of pentose derivatives from the NWA 801 extract were measured at $-21.5‰$ for ribose and $-15.2‰$ for xylose. The $\delta^{13}C$ values of pentose derivatives from the Murchison meteorite were $-8.9‰$ for ribose, $-7.1‰$ for arabinose, $-23.9‰$ for xylose. These values for the Murchison soil were $-44.7‰$, $-44.0‰$, and $-41.0‰$ for ribose, arabinose, and xylose, respectively. The $\delta^{13}C$ values of acetyl were determined at $-44.2‰$, $-38.5‰$, and $-39.1‰$ for NWA801, Murchison meteorite, and Murchison soil, respectively with the calibration line and internal standard. The 1σ error of the calibration line is $\pm 2.7‰$ this error become $\pm 4‰$ error for the $\delta^{13}C$ values of pentoses. Another potential calibration error may come from the difference between ribose and other pentoses. We calibrated using a ribose calibration line for all pentoses. However, the KIE during derivatization differs among different sugars and provide difference in $\delta^{13}C_{Ac}$ values. This error was reported at $\pm 0.46‰$ (1σ) in a previous work (S4). Therefore, we applied larger errors for each pentoses (i.e., $\pm 5‰$).

Meteorites contain various organic compounds that appear on chromatograms. The peak of ribose in NWA 801 is not completely separated from another peak (Fig. 3A). Thus, the overlapping peak affects the carbon isotope ratio of ribose. However, the 45/44 ratio of the overlapping peak indicates that the carbon isotope ratio is lower than that of ribose (Fig. 3c). Therefore, if the effects of the overlapping peak are completely removed, the $\delta^{13}C$ value of ribose should be greater than the results shown in this study. Isotope composition of ribose in Murchison meteorite is also affected by a peak after the ribose (Fig. 3b). The 45/44 ratio of the overlapping peak is significantly lower than ribose (Fig. 3d) and thus the $\delta^{13}C$ value of Murchison ribose should be greater than the value reported in the present study. Arabinose in Murchison is not affected significantly by co-eluting peak. Conversely, the $\delta^{13}C$ of arabinose in NWA 801 is clearly affected by the large internal standard peak (Fig. 3c). Thus, we do not report the $\delta^{13}C$ of arabinose in NWA 801.

Additional discussion on possible contamination. Carbonates in primitive chondrites are enriched in ^{13}C relative to IOM. If terrestrial microorganisms used extraterrestrial carbonate as a

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source of carbon then the sugars would be heavy relative to terrestrial - biological values. However, a proteinogenic amino acid, alanine, in this fragment is racemic and further α-aminoisobutyric acid, which is a very rare biological amino acid is present in a greater amount than alanine, clearly showing that no biological contamination is present in the Murchison fragment used in this study. Furthermore, if microbes lived in the meteorites analyzed in this study and used ^{13}C-enriched carbonate, the IOM should be enriched in ^{13}C. However, IOM $\delta^{13}C$ values of NWA 801 analyzed in this study and IOM $\delta^{13}C$ values of Murchison reported in many previous works fall in the typical carbonaceous chondrite values (~–20‰) which is not enriched in $\delta^{13}C$ from terrestrial kerogen (~–20‰). Therefore, the sugars detected in this study are not biological products from contaminated terrestrial microbes.
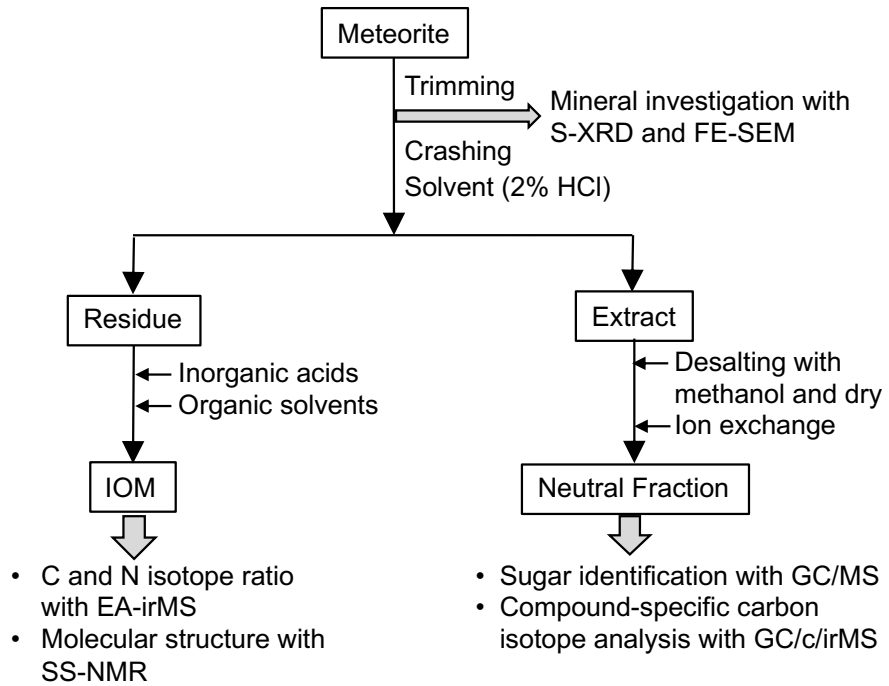
Fig. S1. Sample processing steps in the coordinated analysis of meteorites.
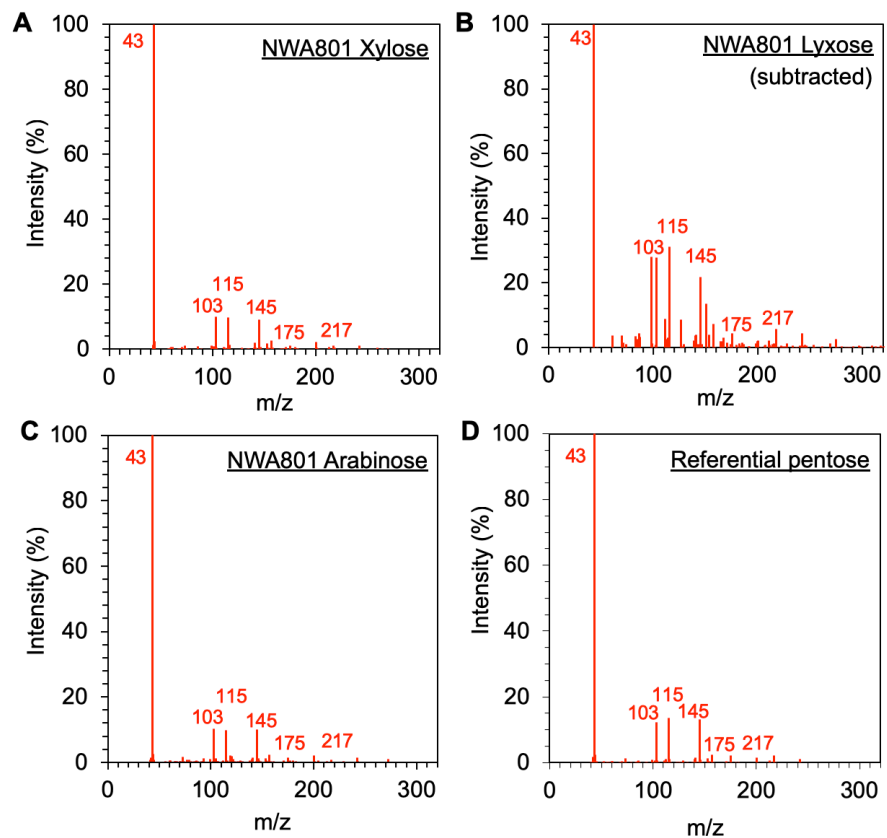
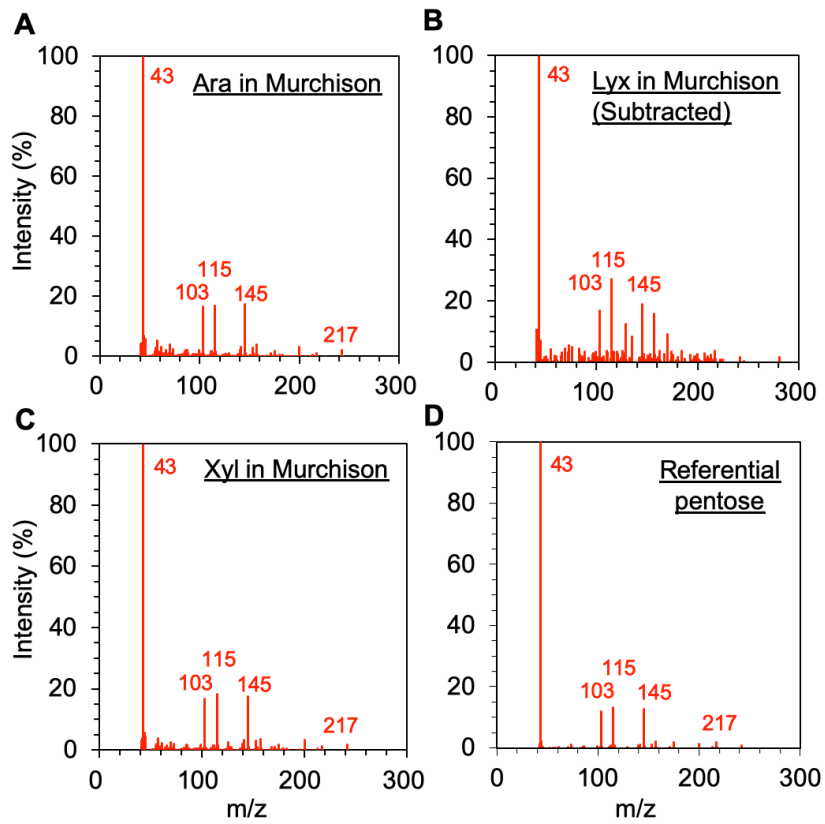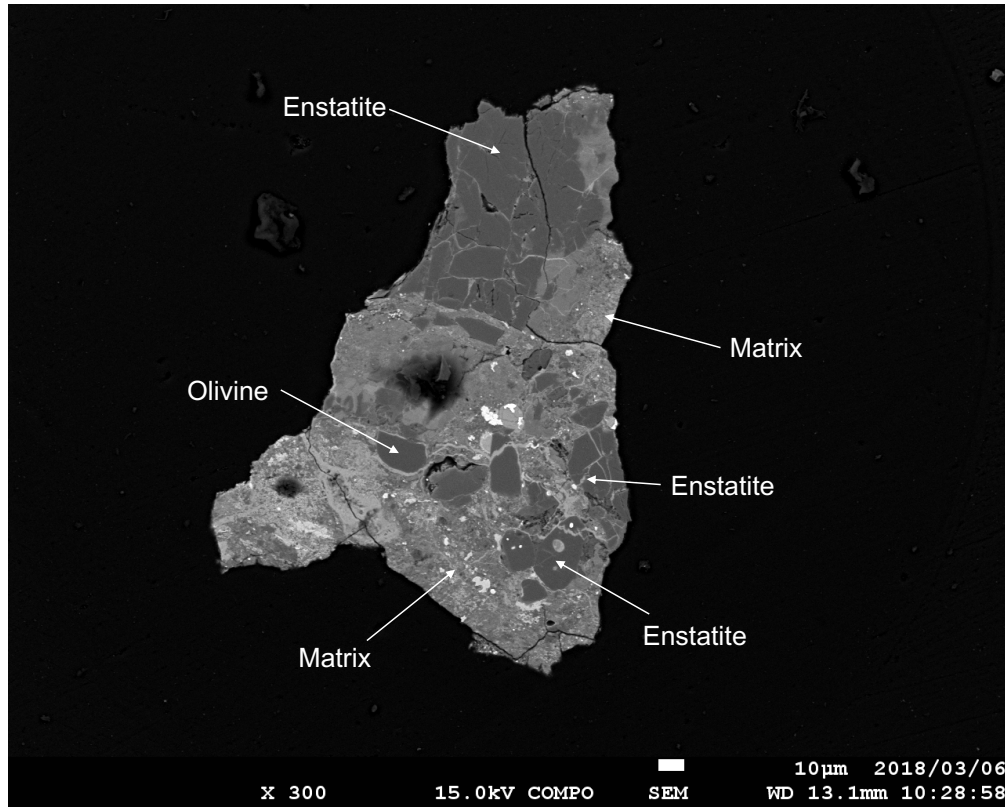**Fig. S2. Mass fragment spectrum of pentoses in NWA 801.**
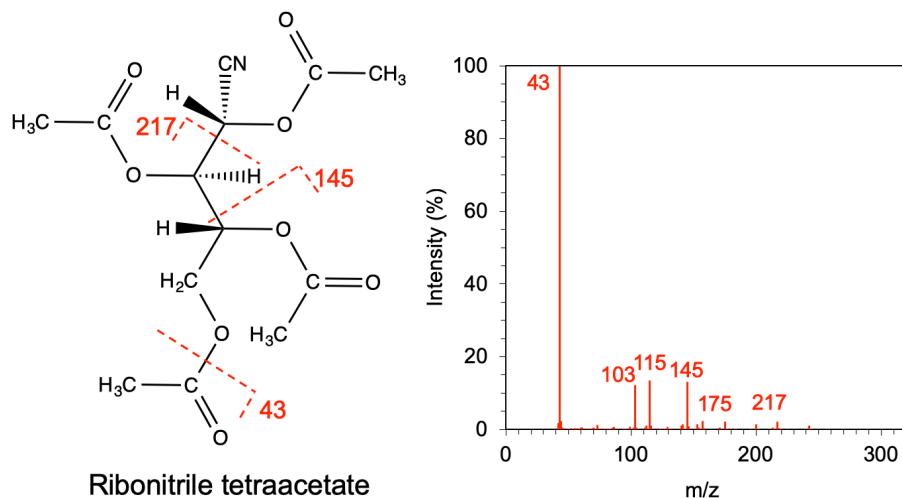
**Fig. S3. Mass fragment spectrum of pentoses in Murchison meteorite.**

Fig. S4. Back-scattered electron image of NWA 801 grain analyzed by S-XRD. This grain contains both matrix and mineral fragments.

Ribonitrile tetraacetate

Fig. S5. Fragmentation pattern of ribonitrile tetraacetate. The molecular ion (m/z = 315) is not yielded. Fragmentation and secondary elimination of acetic acid (–60), -CHOAcCN (–98) and ketone (–42) are observed. The base peak (m/z = 43) is attributed to acetate. The second largest peaks of 103 (145 – 42), 115 (217 – 60 – 42), and 145 are attributed to fragmentation and secondary elimination of acetic acid and ketone. Minor peaks are also attributed from fragmentation and secondary eliminations: 217 (315 – 98) and 175 (217 – 42).
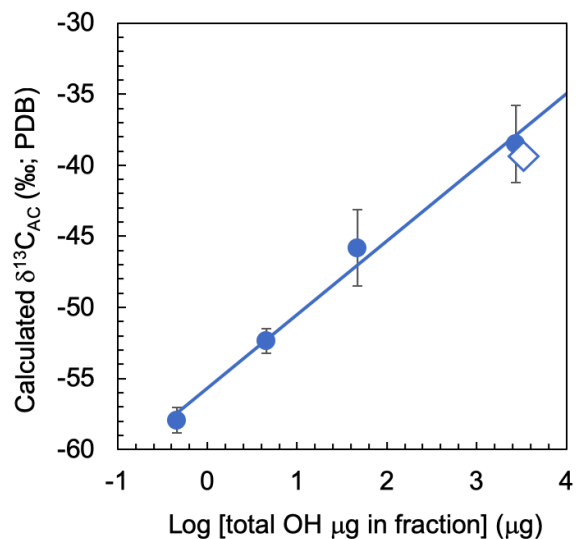
Fig. S6. Calibration line of the carbon isotope ratios of acetyl carbons for pentoses and hexoses. Filled circles s how the carbon isotope ratios of acetyl carbon for the reference aldonitrile acetate derivatives of pentoses in this study (1, 10, 100, and 6000 μg). The open diamond shows $\delta^{13}C_{AC}$ of NWA 801 derivatives calculated using an internal standard. The amount of OH in the sample was estimated by weighing sample before derivatization. The open diamond present almost on the calibration line, indicating the calibration line correctly calibrate the isotope ratio. The filled diamond shows $\delta^{13}C_{AC}$ of Murchison derivatives calculated using this calibration line.

Additional References

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S3.   Chikaraishi Y, Naraoka H, & Poulson SR (2004) Hydrogen and carbon isotopic fractionations of lipid biosynthesis among terrestrial (C3, C4 and CAM) and aquatic plants. *Phytochemistry* 65:1369-1381.

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