



# 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 <sup>13</sup>C-enriched stable carbon isotope compositions ( $\delta^{13}\text{C}_{\text{vs. VPDB}}$ ) 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  $\delta^{13}\text{C}$  values of ribose and xylose in NWA 801 and ribose and arabinose in Murchison showed significant <sup>13</sup>C enrichment (+8 to +43‰), whereas xylose in Murchison was lower (–1‰) (Figs. 3 and 4 and see also *SI Appendix*, *SI Text*). The  $\delta^{13}\text{C}$  values of other sugars were not calculated because of low intensity or poor peak separation. The positive  $\delta^{13}\text{C}$  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.**

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The authors declare no competing interest.

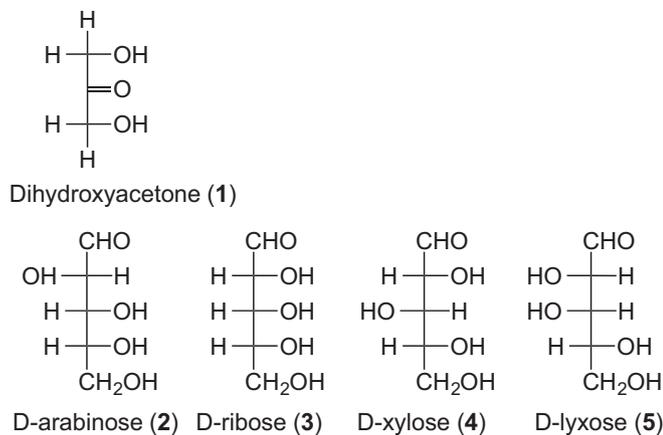
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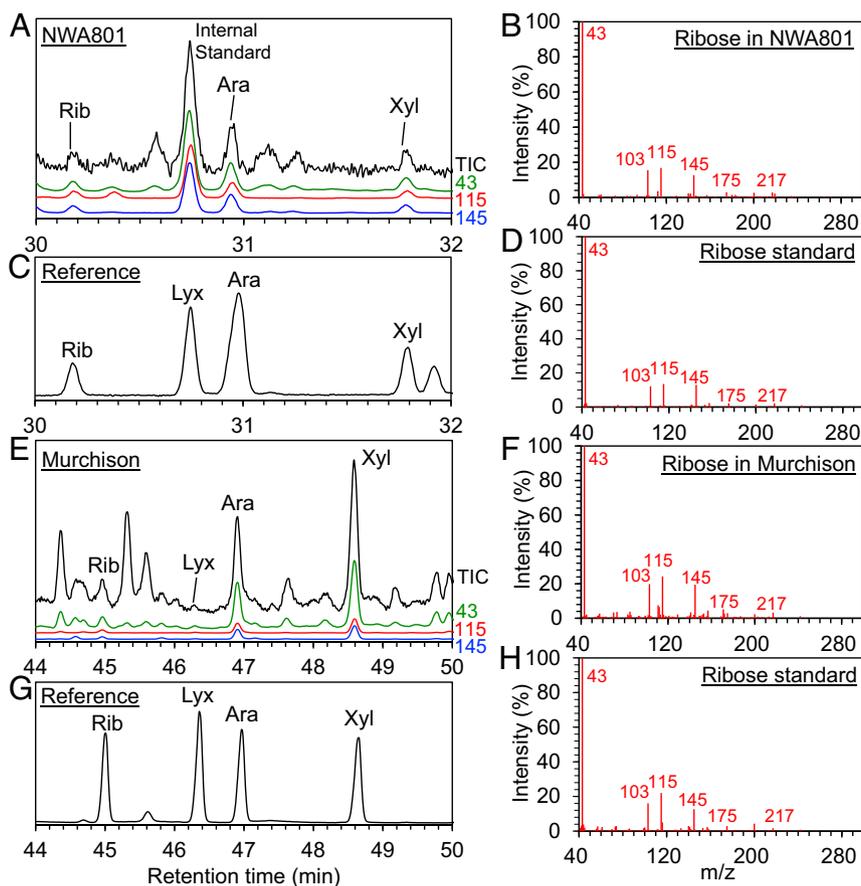
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**Fig. 1.** Structures of sugars detected in this study (structures 2 to 5) and a previous study (structure 1) (shown in Fischer projection) from meteorites. All sugars are shown as D-form for simplicity; however, chirality was not investigated in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

from biologically synthesized sugars (17, 18). For example, pentoses and hexoses in algae, higher plants, and secondary producers all have negative  $\delta^{13}\text{C}$  values ranging between  $-32$  and  $-1\text{‰}$  (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  $\delta^{13}\text{C}$  values of likely contaminants. The  $\delta^{13}\text{C}$  values of ribose ( $-46\text{‰}$ ), arabinose ( $-52\text{‰}$ ), and xylose ( $-44\text{‰}$ ) are even lower and all well outside the range of sugars we detected in meteorites. The  $\delta^{13}\text{C}$  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  $+82\text{‰}$  in GRA 95229 and Murchison meteorites) (15) and those of  $\alpha$ -amino acids in many carbonaceous chondrites, which typically range from  $+3$  to  $+44\text{‰}$  (10). This is very strong evidence that NWA 801 and Murchison contain extraterrestrial pentoses. While enriched  $^{13}\text{C}$  ( $\delta^{13}\text{C} > 0\text{‰}$ ) is usually an indicator of extraterrestrial origin, slightly depleted ( $\delta^{13}\text{C} \leq 0$ ) does not always indicate terrestrial contamination. For example, many extraterrestrial carboxylic acids have negative  $\delta^{13}\text{C}$  values (19). Xylose in the Murchison meteorite has a distinct  $\delta^{13}\text{C}$  value from xylose in Murchison soil, although that is insufficiently distinct from biological sugars reported previously (17). Although no  $\delta^{13}\text{C}$  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)	$\delta^{13}\text{C}$ (‰)	Content (ppb)	$\delta^{13}\text{C}$ (‰)	Content (ppb)	$\delta^{13}\text{C}$ (‰)	$\delta^{13}\text{C}$ (‰)
<b>Sugars</b>							
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	$I_{\text{aliph}} > I_{\text{aroma}}$		$I_{\text{aliph}}/I_{\text{aroma}} \sim 1$		$I_{\text{aliph}} < I_{\text{aroma}}^*$		-
IOM $\delta^{13}\text{C}$ (‰)	-20.7 ( $\pm 1.2$ )		-22.4 ( $\pm 0.61$ )		-18.91 ( $\pm 0.01$ ) <sup>†</sup>		-
IOM $\delta^{15}\text{N}$ (‰)	+66.0 ( $\pm 0.18$ )		+93.4 ( $\pm 6.4$ )		-1.0 ( $\pm 0.4$ ) <sup>†</sup>		-
N/C	0.029		0.030		0.0327 ( $\pm 0.0003$ ) <sup>†</sup>		-

The  $\delta^{13}\text{C}$  values show the isotope ratios of aldopentoses. NA, not analyzed or detected.

\*Ref. 23.

<sup>†</sup>Ref. 25.

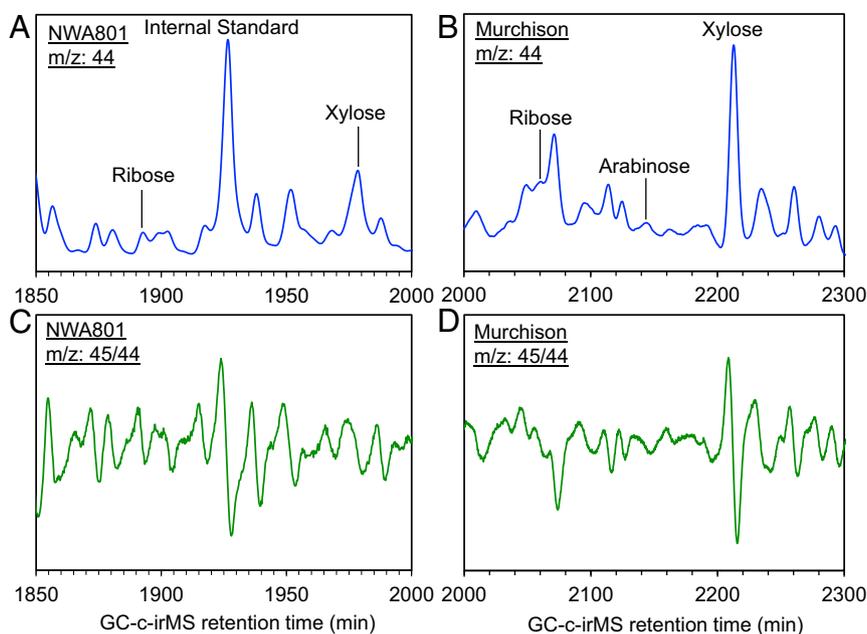
evaluate the extent of biological contamination in abiotic synthesis products. However, this may not be useful for the evaluation of biological sugar contamination in meteorites, since chiral sugar-related compounds in Murchison and other meteorites have been observed to have large D-enantiomeric excesses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

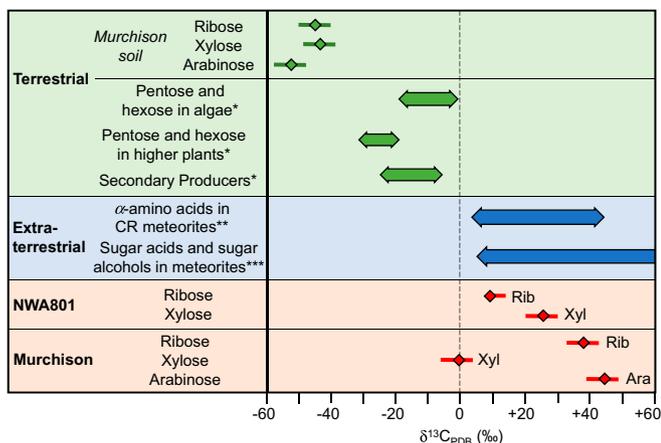
The molecular structures of insoluble organic matter (IOM) were analyzed with solid-state  $^{13}\text{C}$ -NMR (SS-NMR). A chemical shift attributed to aliphatic carbon is clearly more abundant than that from aromatic carbon in NWA 801, whereas the aliphatic carbon signal was comparable to the aromatic 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  $\delta^{13}\text{C}$  values of IOM in these 3 meteorites are comparable to those of typical carbonaceous meteorites (25) (Table 1). The nitrogen isotope composition ( $\delta^{15}\text{N}_{\text{vs. Air}}$ ) of the IOM in the 2 NWA meteorites showed significantly positive values (i.e.,  $\delta^{15}\text{N} = +66.0$  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 NWA801 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.

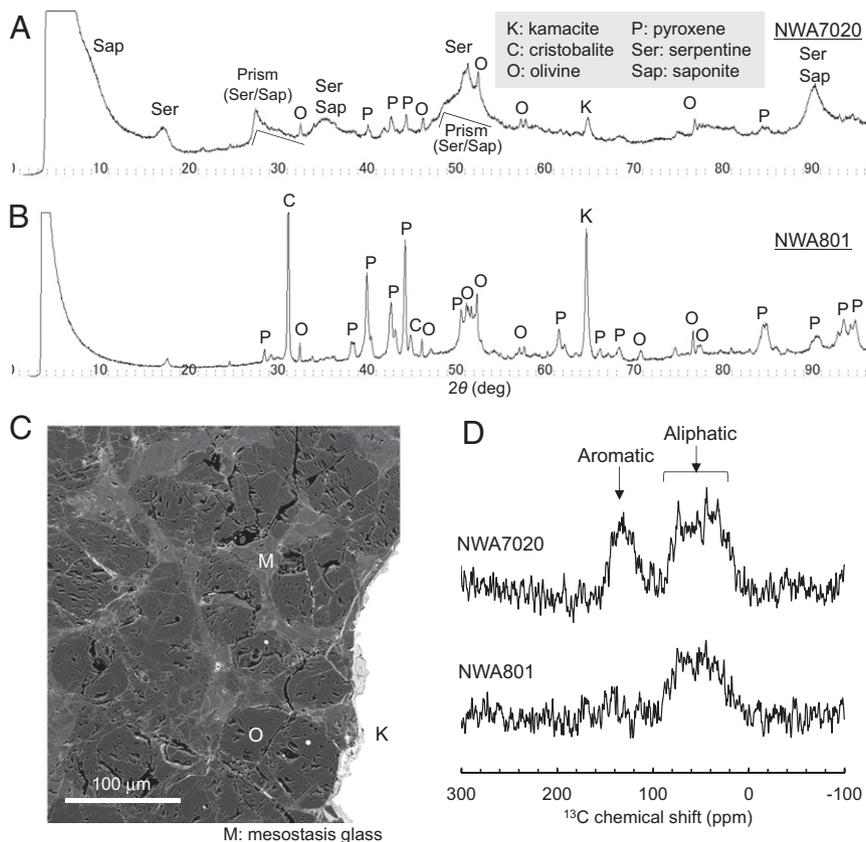


**Fig. 4.** Stable carbon isotopic composition of sugars detected in this study, with representative terrestrial and extraterrestrial organic compounds. \*, ref. 17; \*\*, ref. 10; and \*\*\*, ref. 15.

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 801, 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 1 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.

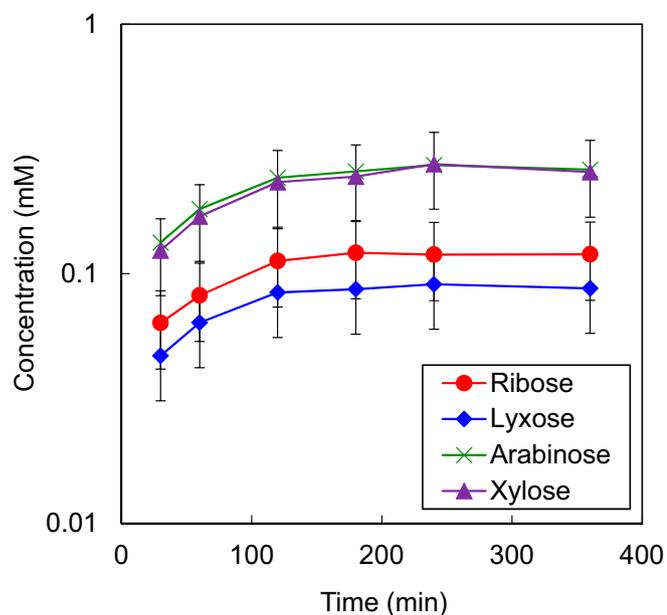


Fig. 6. The concentrations of aldopentoses in a formose-like reaction product.

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  $\text{NH}_3$  content relative to other carbonaceous chondrites (32), and  $\text{NH}_3$  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 ( $D \sim L$ ) 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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