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 biologically important sugars remains unclear. We analyzed sugars in 3 carbonaceous meteorites and show evidence of extraterrestrial ribose and other biologically important sugars in primitive meteorites. The 13C-enriched stable carbon isotope compositions 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.

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 (e.g., 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 biologically important 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.

Author contributions: Y.F. designed research; Y.F., Y.C., N.O.O., C.A., and T.N. performed the experiment; Y.F., Y.C., N.O.O., D.P.G., and J.P.D. contributed new reagents/analytic tools; Y.F., Y.C., and N.O.O. analyzed data; and Y.F. wrote the paper.

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from biologically synthesized sugars (17, 18). For example, pentoses and hexoses in algae, higher plants, and secondary producers all have negative δ13C 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 δ13C values of likely contaminants. The δ13C 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 δ13C 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 13C (δ13C > 0‰) is usually an indicator of extraterrestrial origin, slightly depleted (δ13C ≤ 0) does not always indicate terrestrial contamination. For example, many extraterrestrial carboxylic acids have negative δ13C values (19). Xylose in the Murchison meteorite has a distinct δ13C value from xylose in Murchison soil, although that is insufficiently distinct from biological sugars reported previously (17). Although no δ13C 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

![Diagram of sugar structures](https://example.com/sugar_structures.png)

**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.

![Graphs showing GC/MS identification](https://example.com/gc_ms_graphs.png)

**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.
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.

### Table 1. Results of coordinated analysis of 3 meteorites

|                  | NWA 801 | NWA 7020 | Murchison meteorite | Murchison soil |
|------------------|---------|----------|---------------------|---------------|
| **Sugars**       |         |          |                     |               |
| Ribose           | 4.5     | <0.5     | 25                  | +38           |
| Arabinose        | 11      | NA       | 120                 | +43           |
| Xylose           | 6       | <0.5     | 180                 | -1            |
| Lyxose           | 2.3     | NA       | 6.7                 | NA            |
| **Petrologic type** | CR 3.0 to 2.8 | CR 2.8 to 2.5 | CM 2.5         |               |
| **Carbon chemistry** | $l_{\text{alipha}} > l_{\text{aroma}}$ | $l_{\text{alipha}}/l_{\text{aroma}} \sim$ 1 | $l_{\text{alipha}} < l_{\text{aroma}}$* |               |
| **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)†  |               |

*Ref. 23.
†Ref. 25.

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

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**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.
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 I 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
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 (c–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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Fig. 6. The concentrations of aldopentoses in a formose-like reaction product.

[Graph showing the concentration of aldopentoses in a formose-like reaction product over time.]

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