

Carbonaceous meteorites as a source of sugar-related organic compounds for the early Earth

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The much-studied Murchison meteorite is generally used as the standard reference for organic compounds in extraterrestrial material. Amino acids and other organic compounds¹ important in contemporary biochemistry are thought to have been delivered to the early Earth by asteroids and comets, where they may have played a role in the origin of life^{2–4}. Polyhydroxylated compounds (polyols) such as sugars, sugar alcohols and sugar acids are vital to all known lifeforms—they are components of nucleic acids (RNA, DNA), cell membranes and also act as energy sources. But there

has hitherto been no conclusive evidence for the existence of polyols in meteorites, leaving a gap in our understanding of the origins of biologically important organic compounds on Earth. Here we report that a variety of polyols are present in, and indigenous to, the Murchison and Murray meteorites in amounts comparable to amino acids. Analyses of water extracts indicate that extraterrestrial processes including photolysis and formaldehyde chemistry could account for the observed compounds. We conclude from this that polyols were present on the early Earth and therefore at least available for incorporation into the first forms of life.

Our study of Murchison and Murray polyols uses a relatively definitive means of detection, gas chromatography–mass spectrometry (GC–MS). We identified all compounds as their trimethylsilyl (TMS) and/or tertiary butyl-dimethylsilyl (*t*-BDMS) derivatives (see Methods). Earlier studies^{5,6} on the possible presence of sugars in (pre-Murchison) meteorites had reported the six-carbon (6C) sugars glucose and/or mannose, and much smaller amounts of the five-carbon (5C) sugars arabinose and xylose. These earlier studies had been done on a variety of carbonaceous and non-carbonaceous meteorites, using thin-layer chromatography and ultraviolet–visible, infrared, and nuclear magnetic resonance spectroscopy. Most of the examined meteorites had fallen several

	Sugars	Sugar Alcohols	Sugar Acids	Dicarboxylic Sugar Acids	Deoxy Sugar Acids			
3C	$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{C}=\text{O} \\ \\ \text{CH}_2\text{OH} \end{array}$ Dihydroxyacetone	$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$ Glycerol 160 nmol/g (100%)	$\begin{array}{c} \text{CO}_2\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$ Glyceric acid 80 nmol/g	—				
4C	—	$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$ Erythritol & Threitol (1%)	$\begin{array}{c} \text{CO}_2\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$ Erythronic & Threonic acid (4nmol/g)	$\begin{array}{c} \text{CO}_2\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{CO}_2\text{H} \end{array}$ Tartaric & Mesotartaric acid	$\begin{array}{c} \text{CO}_2\text{H} \\ \\ \text{H}_3\text{C}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$ 2-Methyl glyceric acid	$\begin{array}{c} \text{CO}_2\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{CH}_2\text{OH} \end{array}$ 2, 4 Dihydroxy butyric acid	$\begin{array}{c} \text{CO}_2\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_3 \end{array}$ 2, 3 Dihydroxy butyric acid (& diastereomer)	$\begin{array}{c} \text{CO}_2\text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$ 3, 4 Dihydroxy butyric acid
5C	—	$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$ Ribitol & Isomers	$\begin{array}{c} \text{CO}_2\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$ Ribonic acid & Isomers	$\begin{array}{c} \text{CO}_2\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CO}_2\text{H} \end{array}$ 2, 3, 4-Trihydroxy Pentanedioic acid	$\begin{array}{c} \text{CO}_2\text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$ 2-Deoxypentonic acids			
6C	*	$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$ Glucitol & Isomers	$\begin{array}{c} \text{CO}_2\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$ Gluconic acid & Isomers	$\begin{array}{c} \text{CO}_2\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CO}_2\text{H} \end{array}$ Glucaric acid & Isomers	$\begin{array}{c} \text{CO}_2\text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$ 2-Deoxyhexonic acids	$\begin{array}{c} \text{CO}_2\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$ 3-Deoxyhexonic acid		

Figure 1 Polyols identified in the Murchison and Murray carbonaceous meteorites. Some of the acids were also identified in their cyclic (lactone) form. When commercial standards were not available for mass spectral comparison, 'isomers' were identified by comparison of their mass spectrum and GC retention time to that of the listed member of the group. Indicated concentrations are per gram of meteorite. 1% for erythritol and threitol refers to their detector response versus that of glycerol. The detector response (DR) of 2-methyl glyceric acid (TMS derivative) was approximately one-sixth that of glyceric acid. The DR of ribonic acid (TMS) was roughly one-third that of threonic acid. In

the largest Murchison sample, the DRs of the 4C deoxy sugars were roughly 4–5 times larger than those of the 4C mono-acids (erythronic and threonic). The DRs of the 2-deoxypentonic acids were roughly 20 times less than that of ribonic acid. The DR of the 3-deoxyhexonic acid was approximately equal to that of the 2-deoxypentonic acids. The DR of the 3-deoxypentonic acid(s) was clearly less than that of the 3-deoxyhexonic acid. Asterisk indicates that 6C sugar monomers were not seen, but may be present in bound forms. Identifications of 2-deoxyhexonic acids and deoxydicarboxylic acids are tentative (see text).

decades before these studies (Murray was among the exceptions), thus increasing the chances of microbial contamination. A later reviewer concluded that a portion of the identified compounds could have been contaminants⁷. However, if contamination in the above studies had been severe, other sugars, including ribose, should have also been prominent. The authors stated that no other sugars were seen⁶. Although not part of the analyses, the simultaneous identification of sugar derivatives (decomposition products, and so on) would have been supporting evidence for—at least—aqueous sugar chemistry on a meteorite parent body (see below).

Our analyses of several Murchison extracts, and a Murray extract, show a variety of water-soluble polyols (Fig. 1). The compounds

that we identified include a sugar, dihydroxyacetone (sugars by definition are polyhydroxy aldehydes or ketones); sugar alcohols; sugar mono-acids; sugar di-acids; and deoxysugar acids (or 'saccharinic' acids). In general, the compounds follow the abiotic synthesis pattern of other meteorite classes of organic compounds¹: a general decrease in abundance with increasing carbon number within a class of compounds, and many, if not all, possible isomers present at a given carbon number. We positively identified many of the compounds shown (Fig. 2) by comparison of their mass spectra to commercially available standards (standards of deoxysugar acids were synthesized; see below). Murchison and Murray are similar with respect to the presence of individual polyols.

We found dihydroxyacetone in all Murchison extracts and the

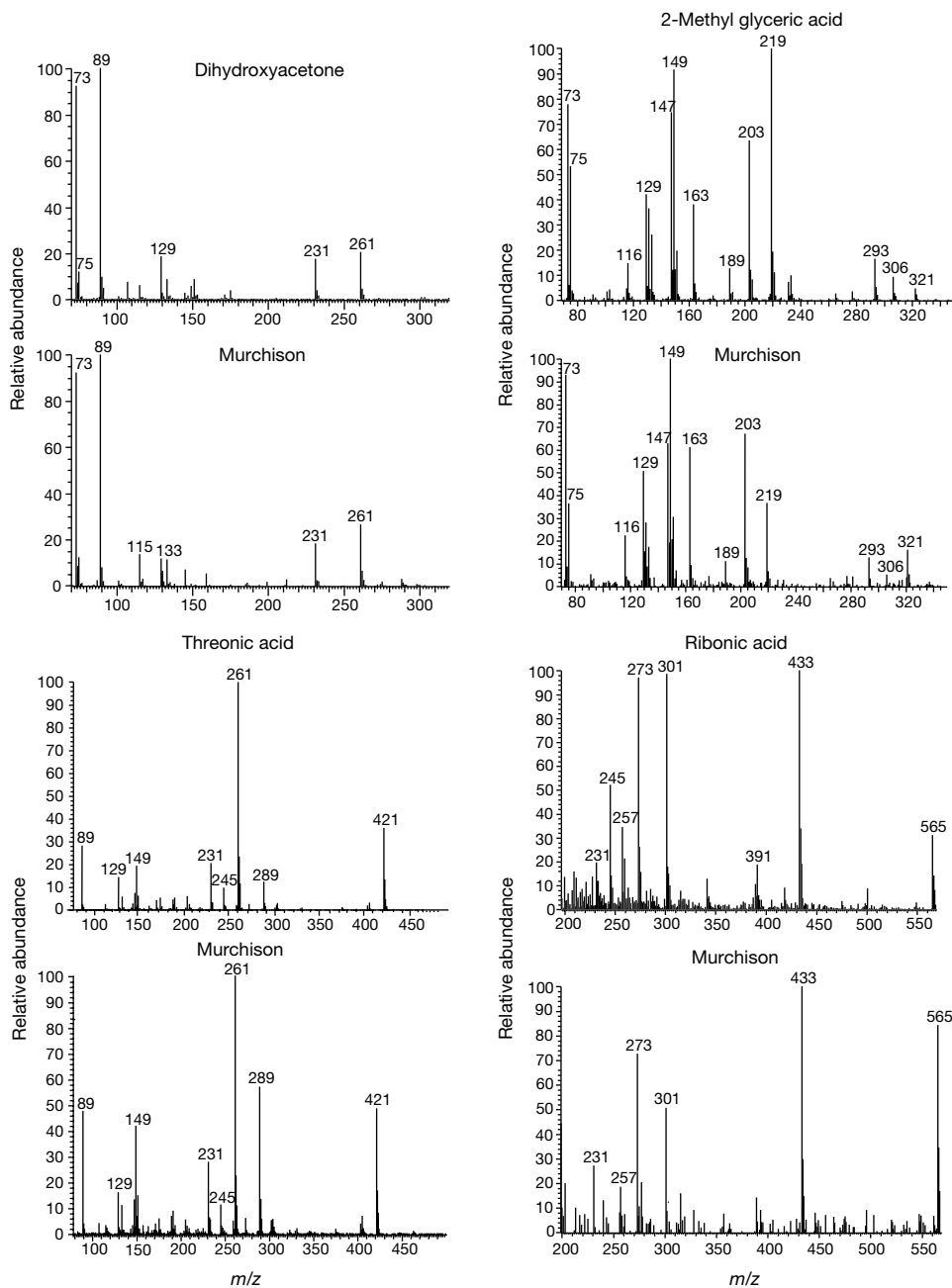


Figure 2 Selected mass spectra of *t*-BDMS and TMS derivatives of standards and corresponding compounds from Murchison and Murray. Dihydroxyacetone was characterized as the di-*t*-BDMS derivative; 2-methyl glyceric acid as the tri-TMS derivative; and threonic acid and ribonic acid as the tri-*t*-BDMS derivatives. *t*-BDMS

derivatives give a characteristic molecular ion minus 57 a.m.u. peak ($M^+ - 57$): for example, dihydroxyacetone(*t*-BDMS)₂ = 318 a.m.u., therefore $M^+ - 57 = 261$. Mass spectra of TMS-sugar derivatives have been described in detail¹³.

Murray extract. It was relatively abundant in one Murchison sample (Fig. 3). In two of the Murchison extracts and in the Murray extract the mass spectrum was weak (due to lower abundance), although it could be identified by ion searches for characteristic mass fragments (Fig. 2). If dihydroxyacetone was present because of contamination by microbes, a wider array of sugars should also have been seen^{8,9}. Results of analysis for the two-carbon (2C) analogue of dihydroxyacetone, glycolaldehyde, were inconclusive, and further analyses are in progress. Although we did not see 6C monomer sugars, we cannot rule out the presence of compounds containing them as there was suggestive evidence (mass spectra) of their presence in di-compounds in the largest Murchison sample.

The sugar alcohol series begins with glycerol; however, the 2C homologue, ethylene glycol, is also present and was seen in both meteorites. The series extends to at least 6C members. We initially identified these compounds as their *t*-BDMS derivatives, based on comparison of their mass spectra and retention times to standards. Ethylene glycol and glycerol are the most abundant of all identified polyols. The detector response of ethylene glycol (*t*-BDMS)₂ was roughly twice that of glycerol in the Murray sample and some of the Murchison samples. Glycerol is present in Murchison at approximately double the highest concentration found for an individual meteoritic amino acid¹ (Fig. 1). There is a significant drop in abundance from glycerol to higher alcohols. Excluding glycerol and ethylene glycol, the sugar alcohols are the lowest in abundance of all polyols. Concentrations of indicated polyols were determined by GC-MS and should be considered approximate, as there is significant variation with sample.

Glycerol, as well as some of the other sugar alcohols, is widespread in nature, and therefore a portion of the compound could be a contaminant either from analytical procedures (although none was seen in blanks) or from microbial action within the meteorite sample. However, given the relatively large amounts seen in all samples and the fact that the sugar alcohols are present in an abiotic distribution pattern, it is likely that a significant amount of the identified glycerol is indigenous to the meteorites. In this regard, the four-carbon (4C) alcohol, erythritol, which is found in nature, and its rare isomer¹⁰, threitol, are nearly equal in abundance in both Murchison and Murray. We did not see the three-carbon (3C) deoxysugar alcohols, 2,3-propanediol and 1,3-propanediol, in any sample. This may be important from a synthetic point of view (below). Also identified in Murchison, as their TMS derivatives, were inositols (6C cyclic alcohols). However, they need to be fully characterized in future work as some of the nine possible stereoisomers are widely distributed in nature¹⁰. Our isotopic analysis of combined neutral polyols found values of $\delta^{13}\text{C} = -5.89\text{‰}$ and $\delta\text{D} = +119\text{‰}$ (see Methods), suggesting that most are indigenous to the meteorite.

Our analyses show that the sugar mono-acids (aldonic acids) begin with the 3C member, glyceric acid, and extend to at least the 6C isomers (Fig. 1). (The 2C analogue of glyceric acid, glycolic acid, and other mono-hydroxy acids, are well known constituents of carbonaceous meteorites¹.) We find that the abundance of glyceric acid ($\sim 80\text{ nmol g}^{-1}$) is similar to that of the more abundant meteoritic amino acids. The pattern of sugar acids that we find is also abiotic: for example, 2-methyl glyceric acid (2-MGA), a relatively uncommon compound in nature, is also abundant (Fig. 1 legend). Erythronic and threonic acids were nearly equal in abundance in one Murchison extract (Fig. 3)—but the ratio of erythronic to threonic acid varied from approximately two to three in other samples. Tartaric acid is the first member of the sugar dicarboxylic acid series. As with erythritol/threitol, tartaric acid (racemic) and its rare terrestrial isomer, mesotartaric acid, are nearly equal in abundance.

Deoxysugar acids (Fig. 1) are polyhydroxylated organic acids in which one or more hydroxyl groups (bonded to C) are replaced by hydrogen. The deoxyacids in Fig. 1 are less common in nature than sugars, and laboratory standards were not available commercially; however, they are well known products of alkaline reactions of sugars^{11,12}. We synthesized deoxysugar acids by known methods of alkaline degradation of 6C sugars; we also synthesized 2-deoxy 5C and 6C acids (Fig. 1) by acid oxidation of the corresponding 2-deoxysugars (see Methods). Their TMS and *t*-BDMS mass spectra were then compared to compounds in both meteorites and (TMS derivatives) to literature spectra¹³. The 4C members are relatively abundant (Fig. 1).

There are two (excluding enantiomers) possible straight-chain 5C 2-deoxymono acids (2-deoxypentonic acids), and both are apparently present in small amounts in Murchison. 2-deoxyhexonic

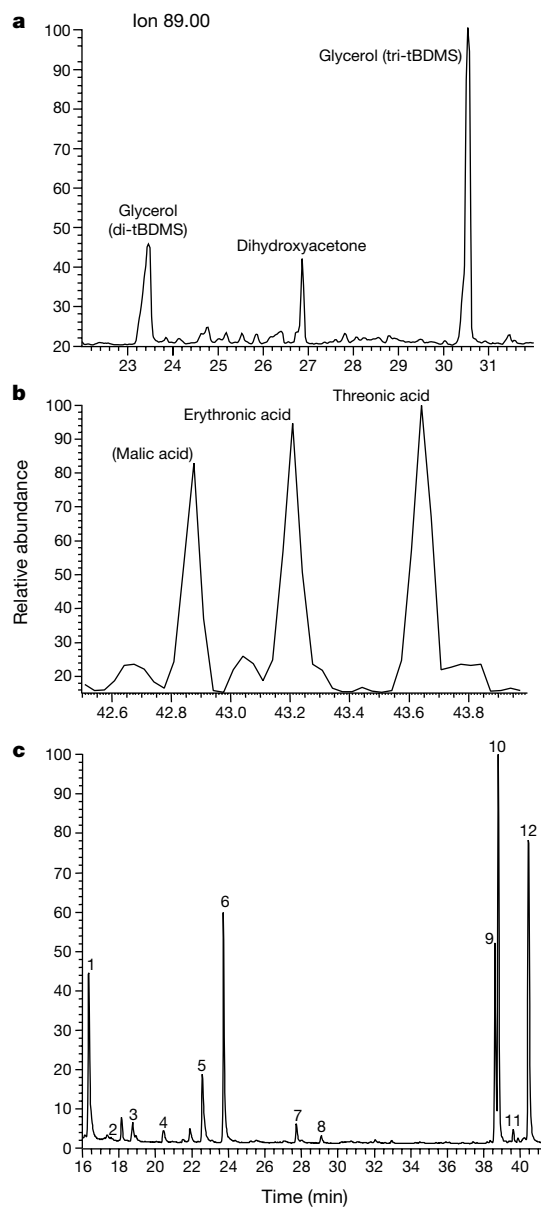


Figure 3 Polyols from meteorites and laboratory synthesis. **a**, Dihydroxyacetone and glycerol from a segment of a GC-MS total ion chromatogram of neutral compounds (water soluble) from Murchison. **b**, A portion of the total ion chromatogram of acidic compounds (*t*-BDMS derivatives) from Murchison. Malic acid and other mono-hydroxy acids are known constituents of Murchison¹. **c**, Reaction products (TMS derivatives) from alkaline reactions of glucose. Peak 1, glycerol; 2, ethylene glycol; 3, 2-methyl glyceric acid; 4, glyceric acid; 5, succinic acid; 6, 2,4-dihydroxybutyric acid; 7, threonic acid; 8, erythronic acid; 9, 10, 3-deoxyhexonic acids (6C); 11, 12, lactones of 3-deoxyhexonic acids.

acids as well as 5C and 6C deoxydicarboxylic acids may also be present, but because of low abundances and resulting lower-quality mass spectra we cannot yet confirm their presence. Compounds of matching GC retention times and apparently of the same molecular masses (*t*-BDMS derivatives) are seen. In Murchison, we identified a 3-deoxyhexonic acid (a 'metasaccharinic' acid) (Fig. 1). At least one 3-deoxypentonic acid is tentatively identified. Other, unidentified, compounds with TMS mass spectra similar to those of deoxysugar acids¹³ are also present. These could include branched deoxysugar acids.

There may have been multiple mechanisms in interstellar space and on the Murchison and Murray parent bodies that synthesized either individual members or groups of the present compounds. Photolysis of small molecules—such as CO, NH₃, H₂O and so on—under simulated interstellar conditions has been shown to form the low-molecular-mass polyols ethylene glycol, glycerol and glyceric acid^{14,15}. If most of the present compounds were derived from sugars, a mechanism capable of producing such a variety of polyols might involve the 'formose reaction'¹⁶. In laboratory formose reactions, formaldehyde (CH₂O), in aqueous solution at neutral to basic pH, condenses to produce a variety of hydroxylated compounds (predominantly sugars but also sugar alcohols) of carbon number up to at least seven. Even in the case of production of only the smallest sugars, dihydroxyacetone and its isomer, glyceraldehyde, a variety of other sugars could then be produced by condensation in the presence of minerals in aqueous solution¹⁷. This may also have implications for the pre-biotic Earth in the case of a limited number of sugars (Fig. 1).

Several lines of evidence suggest that the formose reaction would have been possible on the parent bodies of carbonaceous meteorites: aqueous alteration occurred on the parent bodies and/or precursor interstellar ices^{18,19}; water extracts of carbonaceous meteorites are commonly slightly basic (pH ≈ 7–9); formaldehyde is a relatively abundant and ubiquitous molecule in interstellar space and comets²⁰; several small volatile carbonyl compounds are constituents of Murchison²¹; and glycolaldehyde, a possible formaldehyde reaction product necessary for the formation of higher sugars in the formose reaction, has recently been identified in interstellar space²². In addition, recent research employing ¹³C NMR to study the 'macromolecular carbon' of Murchison has shown that as much as 5% of this carbon has hydroxy and/or ether bonds²³. If formaldehyde condensation was a source of meteoritic polyol monomers, then it may have also contributed to this solid phase.

Sugars readily undergo reactions in alkaline solution^{12,24}, including the formation of multiple sugar acids from an individual sugar: for example, lactic, glyceric and ribonic acid from ribose. The presence of deoxysugar acids in our extracts (Fig. 1) is also consistent with alkaline sugars chemistry. Such acids have been reported to constitute as much as 10–30% of the alkaline degradation products of sugars¹¹. Consistent with previous studies, we found 2,4-dihydroxybutyric and other acids to be major products of the alkaline degradation of glucose (Fig. 3). 3-deoxyhexonic acids have been reported to be relatively abundant in alkaline sugar experiments²⁵, but we find them to be relatively minor products in Murchison. The extent and conditions of laboratory reactions compared to alteration on the meteorite parent body, as well as the presence of formation mechanisms other than the above, could account for differences between our laboratory experiments and observations. □

Methods

Extraction and detection of compounds

In some cases, sample extraction, preparation procedures and GC conditions were similar to those used previously²⁶. Results of sugar analysis include samples extracted under helium (99.999%). Cation exchange procedures were as previously described²⁶. Anion exchange resins were either Biorad AG4-X4 (OH⁻ form) or Biorad AG1-X8 (acetate form). Derivatization reagents were *N*-methyl-*N*-(*t*-butyldimethylsilyl)trifluoroacetamide with

1% *t*-butyldimethylsilyl chloride, Regis Chemical Co. (to obtain *t*-BDMS derivatives), and bis(trimethylsilyl) trifluoroacetamide (BSTFA) with 1% trimethylchlorosilane, Alltech Assoc. (TMS derivatives). Pyridine was used as the solvent in a ratio of 4/1 (pyridine/reagent) in most cases. In most GC–MS analyses, a Finnigan ion trap GCQ GC–MS was used. A DB-17 (30 or 60 m × 0.25 mm) fused-silica capillary column (J & W Scientific) was most often used for separations.

Synthesis of sugar derivatives

In alkaline degradation of sugars, individual sugars were heated (80–100 °C) in 1–8 M NaOH for between 5 min and 2 h. 2-Deoxyribonic acid and 2-deoxygluconic acid standards were obtained by HNO₃ oxidation of 2-deoxyribose and 2-deoxyglucose, respectively. Most acids were identified in their straight-chain form by bringing samples to slightly basic pH before derivatization procedures.

Isotope measurements of neutral compounds

Neutral compounds, including polyols and amides, were obtained by ion exchange chromatography of a Murchison extract as described previously²⁶. Polyols were isolated by acid hydrolysis (HCl) and re-subjecting the fraction to cation and anion exchange chromatography. The isolated polyols were then placed in a quartz tube and dried by rotary evaporation. Copper oxide was then placed in the tube and higher vacuum was used for more complete drying. The samples were then sealed and combusted to carbon dioxide and water at 800 °C. The carbon dioxide and water were collected with a procedure similar to that of ref. 27. The water was converted to hydrogen by the method of ref. 28 using a zinc catalyst (J. M. Hayes, Indiana University). The carbon dioxide and hydrogen were then analysed with 6-60-Nuclide and 3-60-HD Nuclide mass spectrometers. The heavy to light isotope ratio, H/L, for each element (X), reported as per mil (‰), is defined as $\delta X = \{[(H/L)_{\text{sample}} / (H/L)_{\text{standard}}] - 1\} \times 1,000$. The reported values (see text) are uncorrected for terrestrial carbon and hydrogen contributed during analytical procedures and thus should be considered lower limits. Even so, they lie outside the range of typical terrestrial organic compounds²⁹, and are consistent with values obtained for other classes of meteoritic organic compounds¹.

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- Cronin, J. R. & Chang, S. in *Chemistry of Life's Origins* (eds Greenberg, J. M., Pirronello, V. & Mendoza-Gomez, C.) 209–258 (Kluwer, Dordrecht, 1993).
- Oro, J. Comets and the formation of biochemical compounds on the primitive earth. *Nature* **190**, 389–390 (1961).
- Anders, E. Pre-biotic organic matter from comets and asteroids. *Nature* **342**, 255–257 (1989).
- Chyba, C. F. & Sagan, C. Endogenous production, exogenous delivery and impact-shock synthesis of organic molecules: an inventory for the origins of life. *Nature* **355**, 125–132 (1992).
- Degens, E. T. & Bajor, M. Amino acids and sugars in the Bruderheim and Murray meteorite. *Naturwissenschaften* **49**, 605–606 (1962).
- Kaplan, I. R., Degens, E. T. & Reuter, J. H. Organic compounds in stony meteorites. *Geochim. Cosmochim. Acta* **27**, 805–834 (1963).
- Hayes, J. M. Organic constituents of meteorites—a review. *Geochim. Cosmochim. Acta* **31**, 1395–1440 (1967).
- Amelung, W., Cheshire, M. V. & Guggenberger, G. Determination of neutral and acidic sugars in soil by capillary gas-liquid chromatography after trifluoroacetic acid hydrolysis. *Soil Biol. Biochem.* **28**, 1631–1639 (1997).
- Gilbart, J., Fox, A. & Morgan, S. L. Carbohydrate profiling of bacteria by gas chromatography-mass spectrometry: Chemical derivatization and analytical pyrolysis. *Eur. J. Clin. Microbiol.* **6**, 715–723 (1987).
- Brimacombe, J. S. & Webber, J. M. in *The Carbohydrates, Chemistry and Biochemistry* (eds Pigman, W. & Horton, D.) 479–518 (Academic, New York, 1972).
- Pigman, W. & Anet, E. F. L. J. in *The Carbohydrates, Chemistry and Biochemistry* (eds Pigman, W. & Horton, D.) 165–194 (Academic, New York, 1972).
- De Bruijn, J. M., Kieboom, A. P. G. & Van Bekkum, H. Reactions of monosaccharides in aqueous alkaline solutions. *Sugar Tech. Rev.* **13**, 21–52 (1986).
- Petersson, G. Mass spectrometry of aldonic and deoxyaldonic acids as trimethylsilyl derivatives. *Tetrahedron* **26**, 3413–3428 (1970).
- Agarwal, V. K. et al. Photochemical reactions in interstellar grain photolysis of CO, NH₃, and H₂O. *Origins Life* **16**, 21–40 (1986).
- McDonald, G. D. et al. Production and chemical analysis of cometary ice tholins. *Icarus* **122**, 107–117 (1996).
- Langenbeck, W. Die formaldehydkondensation als organische autokatalyse. *Naturwissenschaften* **30**, 30–34 (1942).
- Weber, A. L. Prebiotic sugars: hexose and hydroxy acid synthesis from glyceraldehyde catalyzed by iron (III) hydroxide oxide. *J. Mol. Evol.* **35**, 1–6 (1992).
- Bunch, T. E. & Chang, S. Carbonaceous chondrites—II. Carbonaceous chondrites phyllosilicates and light element geochemistry as indicators of parent body processes and surface conditions. *Geochim. Cosmochim. Acta* **44**, 1543–1577 (1980).
- Zolensky, M. & Mccween, J. Y. in *Meteorites and the Early Solar System* (eds Kerridge, J. F. & Matthews, M. S.) 114–143 (Univ. Arizona Press, Tucson, 1988).
- Irvine, W. M. The composition of interstellar molecular clouds. *Space Sci. Rev.* **90**, 203–218 (1999).
- Jungclaus, G. A., Yuen, G. U., Moore, C. B. & Lawless, J. G. Evidence for the presence of low molecular weight alcohols and carbonyl compounds in the Murchison meteorite. *Meteoritics* **11**, 231–237 (1976).
- Hollis, J. M., Lovas, F. J. & Jewell, P. R. Interstellar glycolaldehyde: the first sugar. *Astrophys. J.* **540**, L107–L110 (2000).
- Cody, G. D., Alexander, C. M. O'D. & Tera, F. New insights into the chemistry of Murchison organic macromolecule using high field ¹³C solid state NMR. *Lunar Planet. Sci. Conf.* **XXX**, 1582–1583 (1999).
- Larralde, R., Robertson, M. P. & Miller, S. L. Rates of decomposition of ribose and other sugars: Implications for chemical evolution. *Proc. Natl Acad. Sci. USA* **92**, 8158–8160 (1995).

25. Lowendahl, L., Petersson, G. & Samuelson, O. Formation of carboxylic acids by degradation of carbohydrates during kraft cooking of pine. *Technic. Assoc. Pulp Paper Ind.* **59**, 118–120 (1976).
26. Cooper, G. W. & Cronin, J. R. Linear and cyclic aliphatic carboxamides of the Murchison meteorite: Hydrolyzable derivatives of amino acids and other carboxylic acids. *Geochim. Cosmochim. Acta* **59**, 1003–1015 (1995).
27. Epstein, S., Krishnamurthy, R. V., Cronin, J. R., Pizzarello, S. & Yuen, G. U. Unusual stable isotope ratios in amino acid and carboxylic acid extracts from the Murchison meteorite. *Nature* **326**, 477–479 (1987).
28. Coleman, M. L. & Moore, M. P. Direct reduction of sulfates to sulfur dioxide for isotopic analysis. *Anal. Chem.* **50**, 1594–1595 (1978).
29. Des Marais, D. J. Isotopic evolution of the biogeochemical carbon cycle during the Proterozoic eon. *Org. Geochem.* **27**, 185–193 (1997).

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Experimental realization of Shor’s quantum factoring algorithm using nuclear magnetic resonance

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The number of steps any classical computer requires in order to find the prime factors of an *l*-digit integer *N* increases exponentially with *l*, at least using algorithms known at present¹. Factoring large integers is therefore conjectured to be intractable classically, an observation underlying the security of widely used cryptographic codes^{1,2}. Quantum computers³, however, could factor integers in only polynomial time, using Shor’s quantum factoring algorithm^{4–6}. Although important for the study of quantum computers⁷, experimental demonstration of this algorithm has proved elusive^{8–10}. Here we report an implementation of the simplest instance of Shor’s algorithm: factorization of *N* = 15 (whose prime factors are 3 and 5). We use seven spin-1/2 nuclei in a molecule as quantum bits^{11,12}, which can be manipulated with room temperature liquid-state nuclear magnetic resonance techniques. This method of using nuclei to store quantum information is in principle scalable to systems containing many quantum bits¹³, but such scalability is not implied by the present work. The significance of our work lies in the demonstration of experimental and theoretical techniques for precise control and modelling of complex quantum computers. In particular, we present a simple, parameter-free but predictive model of decoherence effects¹⁴ in our system.

Shor’s factoring algorithm works by using a quantum computer to quickly determine the period of the function $f(x) = a^x \bmod N$ (the remainder of a^x divided by *N*), where *a* is a randomly chosen small number with no factors in common with *N*; from this period, number-theoretic techniques can be used to factor *N* with high probability^{4–6}. The two main components of the algorithm, modular exponentiation (computation of $a^x \bmod N$) and the inverse quantum Fourier transform (QFT) take only $O(l^3)$ operations^{4–6}. Classically, in contrast, prime factorization takes $O(2^{l/3})$ operations¹, which quickly becomes intractable as *l* increases.

The simplest meaningful instance of Shor’s algorithm is factorization of *N* = 15 (ref. 7)—the algorithm fails for *N* even or a prime power. Even for such a small *N*, quantum factorization poses at present a significant experimental challenge: it requires coherent control over seven quantum bits (qubits) in the course of a long sequence of controlled interactions, even after maximal reduction of the quantum circuit; including the state initialization, interactions between almost all pairs of qubits are needed. In comparison with earlier work^{8–10}, this experiment thus puts extremely high demands on the spin–spin coupling network, the degree of control over the hamiltonian and the spin coherence times. Furthermore, numerically predicting the outcome of these experiments has been considered impractical owing to the enormous size of the state space transformations, which are described by $\sim 4^7 \times 4^7$ real parameters if decoherence effects are included.

Implementation of the algorithm can be broken into four distinct steps (Fig. 1a), with the most complex being the computation of $f(x) = a^x \bmod N$ for 2^n values of *x* in parallel. Following standard classical circuit techniques, this is performed by utilizing the identity $a^x = a^{2^{n-1}x_{n-1} \dots 2^{x_1} a^{x_0}}$, where x_k are the binary digits of *x*. Modular exponentiation thus consists of serial multiplication by $a^{2^k} \bmod N$ for all *k* ($0 \leq k \leq n - 1$) for which $|x_k\rangle = |1\rangle$. The powers a^{2^k} can be efficiently pre-computed on a classical machine by repeated squaring of *a*. For *N* = 15, *a* may be 2, 4, 7, 8, 11, 13 or 14. If we happen to pick *a* = 2, 7, 8 or 13, we find that $a^4 \bmod 15 = 1$, and therefore all $a^{2^k} \bmod N = 1$ for $k \geq 2$. In this case, $f(x)$ simplifies to multiplications controlled by just two bits, x_0 and x_1 . If *a* = 4, 11 or 14, then $a^2 \bmod 15 = 1$, so only x_0 is relevant. Thus, the first register can be as small as two qubits ($n = 2$); however, three qubits ($n = 3$) allow for the possibility of detecting more periods, and thus constitutes a more stringent test of the modular exponentiation and QFT (M.S. et al., manuscript in preparation). Together with the $m = \lceil \log_2 15 \rceil = 4$ qubits to hold $f(x)$, we need seven qubits in total (Fig. 1b). We implemented this algorithm and tested it on two representative parameter choices: *a* = 11 (an ‘easy’ case) and *a* = 7 (a ‘difficult’ case).

The custom-synthesized molecule used as the quantum computer for this experiment contains five ¹⁹F and two ¹³C spin-1/2 nuclei as qubits (Fig. 2). In a static magnetic field, each spin *i* has two discrete energy eigenstates, |0⟩ (spin-up) and |1⟩ (spin-down), described by the hamiltonian $H_0 = -\sum_i \hbar \omega_i I_{zi}$, where $\omega_i/2\pi$ is the transition frequency between |0⟩ and |1⟩ and I_z is the \hat{z} component of the spin angular momentum operator. All seven spins in this molecule are remarkably well separated in frequency $\omega_i/2\pi$, and interact pairwise via the *J*-coupling, described by $H_J = \sum_{i < j} 2\pi \hbar J_{ij} I_{zi} I_{zj}$ (ref. 15).

The desired initial state of the seven qubits is $|\psi_0\rangle = |0000001\rangle$ (Fig. 1). However, experimentally we start from thermal equilibrium. The density matrix is then given by $\rho_{th} = e^{-H_0/k_B T}/2^7$, with $k_B T \gg \hbar \omega_i$ at room temperature so each spin is in a statistical mixture of |0⟩ and |1⟩ (Fig. 3a). We converted ρ_{th} into a 7-spin effective pure state^{11,12} ρ_1 via temporal averaging⁹ (step 0); ρ_1 constitutes a suitable initial state for Shor’s factoring algorithm because it generates the same signal as $|\psi_1\rangle$ (Fig. 3b), up to a proportionality constant^{11,12}. Although ρ_1 is highly mixed and in fact remains separable under unitary transforms, the observed dynamics under multiple qubit operations such as in Shor’s algorithm apparently remain hard to simulate classically^{16–18}.

The quantum circuit of Fig. 1 was realized with a sequence of ~ 300 (*a* = 7) spin-selective radio-frequency (r.f.) pulses separated by time intervals of free evolution under the hamiltonian (Fig. 4). The pulse sequence is designed such that the resulting transformations of the spin states correspond to the computational steps in the algorithm. Upon completion of this sequence, we estimate the state of the first three qubits, $\rho \sim \sum_i w_i |c2^3/r\rangle\langle c2^3/r|$, via nuclear magnetic resonance (NMR) spectroscopy. In the experiment, an ensemble of independent quantum computers rather than a single quantum