

Processing of meteoritic organic materials as a possible analog of early molecular evolution in planetary environments

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The composition of the Sutter's Mill meteorite insoluble organic material was studied both in toto by solid-state NMR spectroscopy of the powders and by gas chromatography–mass spectrometry analyses of compounds released upon their hydrothermal treatment. Results were compared with those obtained for other meteorites of diverse classifications (Murray, GRA 95229, Murchison, Orgueil, and Tagish Lake) and found to be so far unique in regard to the molecular species released. These include, in addition to O-containing aromatic compounds, complex polyether- and ester-containing alkyl molecules of prebiotic appeal and never detected in meteorites before. The Sutter's Mill fragments we analyzed had likely been altered by heat, and the hydrothermal conditions of the experiments realistically mimic early Earth settings, such as near volcanic activity or impact craters. On this basis, the data suggest a far larger availability of meteoritic organic materials for planetary environments than previously assumed and that molecular evolution on the early Earth could have benefited from accretion of carbonaceous meteorites both directly with soluble compounds and, for a more protracted time, through alteration, processing, and release from their insoluble organic materials.

carbonaceous chondrites | extraterrestrial organic materials

The recently fallen Sutter's Mill (SM) meteorite has been described by a first comprehensive report of its mineralogical and organic analyses as "... a regolith breccia composed of CM (Mighei)-type carbonaceous chondrite and highly reduced xenolithic materials. It exhibits considerable diversity of mineralogy, petrography, and isotope and organic chemistry, resulting from a complex formation history of the parent body ..." (1).

In fact, SM soluble organic composition appears to vary from stone to stone, according to its composite nature, but all fragments were found unquestionably depleted in abundance, number, and diversity of molecular species compared with known CMs such as Murchison, Murray, Mighei, and others (2, 3). For example, not only few and low-abundance amino acids and hydrocarbons were measured in the water, and solvent extracts of three SM fragments (SM2, SM12, SM41), with some being likely contaminants, but also no hydroxy-, and carboxylic acids, amines, or ammonia were detected (1). Also, the SM bulk carbon and nitrogen content were determined to be lower than in Murchison, with an N/C ratio being the lowest compared with three other chondrites [Murchison (MN), Tagish Lake (TL), and Maribo]; SM bulk $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ were found lower in that comparison as well (1). The isolation of SM insoluble organic material (IOM) was not attempted during the meteorite's initial analyses. However, determining its possible structure and composition could offer novel insights on the cosmic as well as solar and planetary evolution of complex organic materials.

As the name indicates, all carbonaceous chondrites (CCs) contain carbon and their carbon consists mostly of organic materials that display structures as diverse as kerogen-like macromolecules and simpler soluble compounds. The latter range from polar species, such as amino acids and polyols, to nonpolar

hydrocarbons; several of these have identical counterparts in the terrestrial biosphere and have been extensively studied and reviewed (2). The IOM represents the larger portion of CC organic carbon, up to 99%, and is not known in molecular detail. It is often referred to as kerogen-like because, like kerogen, it is insoluble and isolated after dissolution of free compounds and minerals by repeated washes with strong acids (4). The IOM bulk composition can be only inferred from spectroscopy, e.g., NMR and infrared, or decomposition studies, which have suggested a complex macromolecular structure with both aromatic and aliphatic components also containing S, N, and O (5). These materials are compositionally as well as isotopically heterogeneous upon oxidative and pyrolytic decomposition (6–10) or detailed NMR analysis (11), contain presolar grains, and show isotopic anomalies (2, 12). These traits all point to a likely long cosmic history as well as a possible variety of presolar environments involved in the formation of IOMs. Astrophysical observations of organic compounds in protoplanetary and planetary nebulae, which are descendants of carbon stars (13), support this notion.

Even within many analytical limitations and resulting uncertainties, CC IOMs were also found to clearly differ between meteorite subtypes, both in overall composition, such as relative abundance of their aromatic and alkyl moieties (14), as well as in the type and abundance of molecular species released by hydrothermal treatment (HT). For example, extraction at elevated temperature and pressure (300 °C, 100 MPa, for a week) may free, and/or produce, water- and solvent-soluble compounds from the IOMs, and all nominally insoluble IOMs tested so far released ammonia; however, the ammonia varied from +50‰ to +250‰ in $\delta^{15}\text{N}$ isotopic composition among meteorite types (15).

So far, comprehensive molecular studies between IOM types have not reached any satisfying assessment of their synthetic locales, and, as a consequence, little is known of the extent to which this diversity may result from presolar, solar, and/or asteroidal processes and whether it may relate, at least in part, to

Significance

The data reported here suggest a far larger availability of meteoritic organic materials for planetary environments than previously assumed and that molecular evolution on the early Earth could have benefited from accretion of carbonaceous meteorites both directly with soluble compounds and, for a more protracted time, through alteration, processing, and release from their insoluble organic materials.

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interactions with their host mineral phases. Also entirely unknown is the extent to which this most abundant contingent of extraterrestrial organic material, having had an opportunity to reach the early Earth, might have intervened in prebiotic molecular evolution.

We report here on the composition of SM IOM as determined for two fragments, SM12 and SM41, by NMR spectroscopy and by analysis of the compounds released upon its hydrothermal decomposition. The fragments weighed 1.200 and 0.350 g, respectively, and their demineralization allowed recovery of 28 mg of IOM, i.e., gave an approximate yield of 1.8%. We found that IOM from these fragments did not match in its hydrothermal behavior any of the materials from other meteorites studied so far, and released previously undetected compounds of prebiotic appeal.

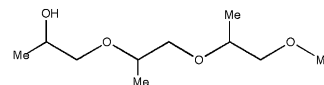
Results and Discussion

Comparative ^{13}C solid-state NMR spectra for SM and MN IOMs are shown in Fig. 1A. The analyses were conducted with equivalent low amounts (8–9 mg) of IOM powders for the two meteorites, which account for the poor signal-to-noise ratios but still show MN two main broad features characteristic of IOM sp^2 and sp^3 hybridized carbon atoms, i.e., olefinic/aromatic and aliphatic, respectively (4).

Although ^{13}C cross-polarization–magic-angle spinning (CP-MAS) NMR spectra are not typically quantitative, the comparison between spectra from IOMs of the two meteorites allowed the general estimate of an SM composition having higher aromatic/aliphatic components ratio with respect to MN and as seen for some of TL stones (16). Quantitative ^1H NMR spectra (Fig. 1B) confirm this composition and also show a complete loss of the aliphatic component of SM IOM after HT, as was observed previously for two meteorites of different type, the CM2 Murray and the CR2 GRA 95229 (17, 18) (the number accompanying the meteorites' group refers to the extent of water alteration revealed by their mineralogy, with the sequence 1, 2, 3, indicating the most to the least altered). The carbon elemental concentration and isotopic values obtained from SM aliquots of IOM powders before and after HT treatment were as follows: $\text{C}\% = 39$ and 35 ; $\delta^{13}\text{C}\text{‰} = -26$ and -24 .

Contrary to the expectations raised from the NMR analyses, the solvent extracts of hydrothermally treated SM IOM did not contain significant amounts of hydrocarbons, aliphatic or aromatic. Sulfur was the dominant component, as cyclo-octaatomic element, the largest component by far, plus di-, tri-, and tetramethylsulfides and benzothiazole, whereas no polycyclic aromatics besides traces of naphthalene were detected. However,

small aliphatic chains were found in diverse oxidized molecules, for example, 2-ethoxyethanol and longer propanol-derived molecules such as the 2-Propanol, 1-[2-(2-methoxy-1-methylethoxy)-1-methylethoxy]- (SI Text) shown in the following scheme, and a mix of several other ether-, as well as ester-linked compounds with longer alkyl substituents, which were recognized by library matching and are shown in part in Table 1. Alkyl carboxylic acids from C_5 to C_9 were detected together with several carboxylic acid methyl esters up to C_{16} .



O-containing aromatic compounds were also relatively abundant in these extracts and include phenol, two methyl-phenols, benzophenone, benzoic acid, and its methyl ester (Table S1). Examples of mass spectra for compounds detected and their matching with standards are shown in Fig. 2 and Fig. S1. The only N-containing aromatic compound detected was benzothiazole.

The N-content of SM IOM powders changed with HT from 1.1% to 0.9%; their water extracts showed predominantly ammonia in the amount of $0.2 \mu\text{g}\cdot\text{mg}^{-1}$ IOM, i.e., lower than for the IOMs of CR2 (Renazzo-type) and CM2 chondrites analyzed previously (15) but still substantial. In contrast to ammonia released by other IOMs, SM IOM ammonia was found to have the isotopic values of $\delta^{15}\text{N}\text{‰} = +2.5$ to $+3.6$ (before and after HT, respectively), i.e., near the terrestrial standard, lower than for the components released at low T from the whole SM rock and similar to the ones shown by its high T released components (attributed in part to SiC) (1). Contamination as a cause of the findings, e.g., from HCl or HF washes of the IOM, can be excluded because the powders were extracted in water at 100°C before HT and the extract was found free of ammonia. The SM IOM water extract contained other less abundant compounds that were difficult to recognize but seemed to be N-, and O-containing; ethanediol was the only one positively identified, and amines were searched for but not found.

Comparison between results from similar treatment of other meteorites' IOMs (Table S2) may be useful for interpreting the results. IOMs of CM2 meteorites like Murchison and Murray, which underwent asteroidal aqueous alteration at about 0°C , have a water content of $\sim 12\%$ and contain abundant soluble organic compounds, are known to yield upon HT of their IOMs a large variety of aliphatic and aromatic, hydroaromatic, and O-, N-, and S-containing molecular species (15, 17).

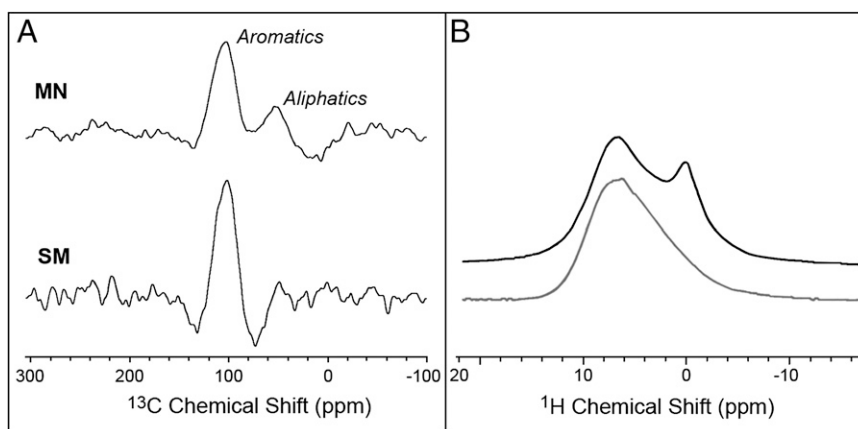


Fig. 1. (A) Comparative ^{13}C CP-MAS solid-state NMR spectra obtained for Sutter's Mill and Murchison IOMs. (B) H-1 MAS solid-state NMR spectra of Sutter's Mill IOM before (black) and after (gray) HT.

Table 1. Aliphatic compounds detected in the hydrothermal extracts of Sutter's Mill IOM

Compound	Formula	Abun.*
Dimethyl trisulfide		++
Dimethyl tetrasulfide		++
Ethanol, 2-ethoxy		++
2-propanol, 1-(2-ethoxypropoxy)		++
Ethanol, 2-(2-ethoxyethoxy)		+++
1-Propene, 3-[2-(2-methoxyethoxy)ethoxy]-		++
2-propanol, 1-[2-(2-methoxy- -1-methylethoxy)-1-methyl ethoxy]		+++
Propanoic acid, 2-methyl-, 1-(2-hydroxy-1-methylethyl) 2,2-dimethylpropyl ester		++
Propanoic acid, 2-methyl-, ethyl-3-hydroxyhexyl ester		+++
C5-C11 linear acids	$\text{CH}_3-(\text{CH}_2)_{3-9}-\text{COOH}$	+
C9-C16 linear acid methylesters	$\text{CH}_3-(\text{CH}_2)_{6-14}-\text{COOMe}$	+

*Approximate abundances in nanograms per milligram of extracted IOM. +++++, >500; +++, 100-500; ++, 10-100; +, <10; (+), <1 ng.

CI1 (Ivuna-type) meteorites such as Orgueil and Ivuna, which display a mineral matrix of exclusively hydrous silicates, are estimated to have undergone extensive water alteration in their parent body at about 120 °C, contain 18–20% water but a less abundant suite of soluble compounds, show in the hydrothermal extracts of their IOMs the same compounds as CM2s but with an overall depletion of smaller aromatic molecules such as naphthalene (Table S1). Because of their alteration histories, the matching molecular species released by CI1 and CM2 IOMs allows the hypothesis that both materials accreted with similar compositions, but their more labile components were later released as soluble compounds in the more water-altered CIs.

However, the IOM hydrothermal extracts of the TL meteorite, which is classified as ungrouped based on differences with known meteorites, differ more from those described above, showing just traces of smaller aromatics and containing only four-ring and above compounds (15). The fact that this TL fragment had shown a considerable abundance of oxidized soluble compounds (16) would suggest that the IOM we examined might have also been altered during the oxidative processes; however, its unusual hydrothermal release of noncondensed aromatics (e.g., terphenyls) and N-containing compounds would also point to initial compositional differences for TL IOM.

Therefore, the results obtained for SM IOM contrast with those from similar treatment of any other CC analyzed to date not only in the lack of release of significant amounts of aliphatic or aromatic hydrocarbons but also in the finding in the extracts of a complex suite of varied O-rich compounds never detected

before. In consideration of these findings, the gas-chromatographic traces obtained from prior analyses of other IOMs extracts were carefully reexamined for similar compounds, on the hypothesis that their detection could have been masked by coelutions with the more numerous hydrocarbons. However, no longer ether or ester-containing moieties as seen in SM were found in these IOMs upon searches of their characteristic fragmentation ions within expected chromatographic elution times.

These searches confirmed that the composition of the organics released by hydrothermally treated SM is so far unique. They also lessened the concern for a contribution to the data by terrestrial contamination. Bulk meteorites are exposed early to terrestrial environments upon reaching the Earth, through the atmosphere, rains, and the milieu of the ground on which they fall; biological contamination in particular can become invasive during their terrestrial or curatorial residence (19). For the IOMs, the possibilities of terrestrial contamination are more limited, i.e., restricted to molecular species that are not easily solubilized during the meteorites' bulk extracts and the demineralization procedure.

Therefore, the fact that SM had short terrestrial residence before analysis and that no compounds containing ether group(s) were detected in IOM extracts of other meteorites with longer terrestrial exposure, or following comparable procedures with other materials, i.e., blanks, lends confidence that these compounds found in SM IOM are not contaminants. Long-chain carboxylic acids, however, could be present because they are common in terrestrial sediments (kerogen) and appear to resist

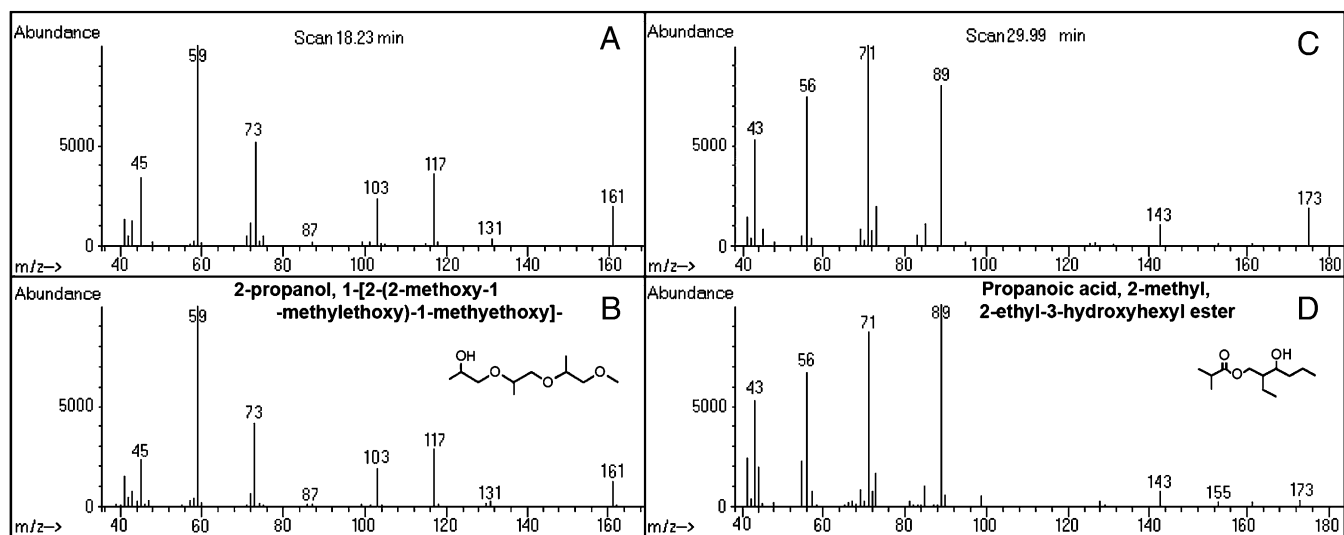


Fig. 2. (A and B) Mass spectra of 2-propanol, 1-[2-(2-methoxy-1-methylethoxy)-1-methylethoxy]- from the SM IOM hydrothermal extracts and library standard, respectively. (C and D) Mass spectra for propanoic acid, 2-methyl, 2-ethyl-3-hydroxyhexyl ester, and corresponding standard.

solubilization enough to be observed in meteoritic IOMs (20). However, the contaminants are easily recognized because biological fatty acids are strictly of even-carbon number (20). The carboxylic acids detected in SM IOM extracts are composed of both odd-, and even-carbon species, but, although the odd-carbon acids decline in abundance with chain length as expected for abiotic syntheses, the even-numbered remain more abundant at higher chain lengths and should be considered at least in part as terrestrial contaminants (1).

Several processes might have led to the results we obtained upon SM IOM HT, making their interpretation difficult. In view of the compositional differences seen for the IOMs of altered meteorites such as TL, the uniqueness of SM extracts' composition might be explained, at least to a certain degree, on the basis of the alteration history of the meteorite fragments we analyzed. In fact, recent X-ray diffraction analyses of several SM fragments by Garvie (21) revealed them to be of two distinct mineralogical types: olivine rich, i.e., anhydrous stones and possibly heated above 700 °C, or clay (smectite) rich (21).

Based on the direct analysis of SM41 and the equivalent solvent- and water-soluble suites of compounds extracted from several pieces of the SM12 fragments, the SM21 and SM41 fragments employed for the IOM analyses reported here were found to be of the second type. In spite of containing abundant clays, however, they also differ from other CMs in their low content of water (just 2.4 wt%), i.e., were also likely heated (21). This mineralogy, therefore, would indicate that SM stones were exposed to higher temperatures than those experienced by CM, CI, and CR chondrites and that their IOM might have undergone alteration as a consequence. This interpretation is supported by earlier studies of several CC IOMs (22, 23) that, using stepwise pyrolysis, showed a correlation between the composition of pyrolytic fragments from the IOMs and the degree of metamorphism of the bulk stones.

The O-containing compounds we observed in SM hydrothermal extracts could also be accounted for based on the finding by Cody et al. (11), who described NMR spectral features in MN IOM that are also shown by a synthetic formaldehyde polymer and proposed that O-containing aryl moieties would be significant components of CC macromolecular materials. However, were these moieties or their fragmentation products easily released from the IOM by HT, molecules similar to the ones observed in SM IOM extracts should have been detected in other IOMs as well. Because they were not detected, we tested the

assumption that they might be more resistant to hydrothermal conditions and were released only following alteration of the meteorite and/or asteroidal parent body at higher temperatures.

We synthesized a polymer from formaldehyde and glycolaldehyde following literature methods (11) and subjected the dry and powdered residue to the same HT used for the IOMs. The extracts showed the release of several O-containing compounds together with aromatic compounds, such as methylated benzenes, naphthalene, and several methyl naphthalenes with up to 4-C branching (Fig. S2). Interestingly, the O-containing molecular species included benzoic acid methyl ester and varied from cyclic compounds containing a single alkene bond, such as several methyl cyclopentenones, to mix aromatic and cyclic compounds, such as indanol, to fully aromatic such as phenols, with up to 4-C branching, benzophenone or naphthalenols (Scheme S1). These results, including the production of aromatic compounds, were not surprising because a related study on the production of hydrocarbons from sugars during biomass alteration into terrestrial kerogens would have predicted them as well (24).

Although a polymer synthesized in the laboratory under controlled and limited settings of materials, temperature, pressure, and time may offer only a simplistic comparison for a natural sample of long cosmic ancestry, its hydrothermal release of several O-containing compounds such as benzophenone and the naphthalenes seen in meteoritic IOMs extracts would seem to corroborate the finding by Cody et al. of an IOM formose polymer component. However, and within the above limitations, there was no evidence of this polymer being particularly resistant to the hydrothermal conditions we used and the experimental results seem to better agree with the hydrothermal extracts of CM, CI, and CR IOMs than of SM in particular. For example, only a trace of naphthalene and no methyl naphthalenes or benzenes were found in SM IOM hydrothermal extracts nor, conversely, were the longer ether compounds seen in SM IOM released hydrothermally by the laboratory polymer; methylbenzoate was the lone ester detected.

The uniqueness of the SM data also leads to the questions of whether the compounds detected in the extracts were released hydrothermally by SM IOM or, at least in part, formed during the treatment by the release of even simpler indigenous components. The formation of esters in water at high temperatures has been observed experimentally (25), but most experiments described in the literature used different overall conditions. As

an approximation of the conditions used in this study, we performed a hydrothermal experiment using methanol, octanoic and benzoic acids in water, in nanomole amounts, at the temperature and pressure used to treat all meteoritic IOMs. Results were somewhat unexpected in that they did show several products from decarboxylation of the starting acids such as benzene but also toluene, alkylated benzenes (up to hexamethyl), phenol, and alkylated phenols plus traces of ethers and octanoic and benzoic acid methyl esters.

Therefore, on the assumption that carbonaceous asteroids accreted with refractory organic materials of diverse but common presolar provenance, the above analytical and experimental data suggest that the composition of SM IOM represents an end product of oxidative alteration processes incurred in the meteorite's asteroidal parent body and that its organic content comprises both survival compounds and, possibly, molecules formed during such processes. The same hypothesis also allows the inference that these organic materials might have undergone an analogous alteration upon reaching the early Earth and encountering hydrothermal environments, e.g., as found near volcanic activity or impact craters (26). The assumptions cannot be definite, because our collection of meteoritic materials is still too small to reject an alternative origin for SM IOM, but seems a reasonable proposal on several bases.

One, as mentioned above, is the altered mineralogy observed for the SM stone fragments we analyzed. Another is the deep history of meteoritic IOM, which is suggestive of many possible alteration events. Complex organic materials are observed in our and other galaxies as unidentified emission bands in the infrared wavelengths and appear to form early (27) and fast (28) upon dust condensation in circumstellar environments of carbon stars; at the same time, the finding that meteoritic IOMs are isotopically inhomogeneous indicate that these materials must contain diverse components, although their formation and the cosmochemical events producing them are not well constrained.

The latter case might help justify the finding that SM IOM released ammonia with minor ^{15}N -enrichment. Stepwise combustion of IOMs of this and other meteorites have shown the release of components with varying ^{15}N -composition at different temperatures, with definite dips in several cases to near terrestrial $\delta^{15}\text{N}\text{‰}$ values along the N-release profiles (1, 9). We could speculate, therefore, that the ammonia released from SM IOM upon HT came from one such component.

The unquestionable conclusion that can be drawn from the experimental data are that soluble organic compounds can be released in considerable amount from meteoritic IOMs even if their parent meteorite is largely depleted of free organics (1) and was altered by heat (21). That is, molecular evolution on the early Earth could have benefited from accretion of a variety of carbonaceous meteorites, both directly with soluble compounds and, likely for a more protracted time, through the alteration of and release from their IOMs.

The experimental conditions of elevated temperature and pressure we used were selected to be in a range where diagenesis of clays is known to ensue, to plausibly mimic within laboratory timescales the hydrothermal activity of both asteroidal parent bodies (29) and the early Earth. On the Earth, the finding of detrital zircons dating as far as 4.4 Gy ago (30) also indicates that a hydrosphere came early in its history and, with that, there would have been extended opportunities for alteration of carbonaceous material accumulating during the asteroidal late heavy bombardment (estimated between 4.1–3.8 Gy) (31).

Could the type of compounds released from SM IOM have been significant for prebiotic evolution? The question is obviously hard to answer, given the utterly unknown nature of the chemical beginnings of life; however, it would seem that the long-chain acids found in CC and their esters formed upon hydrothermal conditions could have been valuable in the development

of membranous enclosures (32). Polyethers, such as the compound shown in Scheme 1, have properties suggesting their possible usefulness as hydrophobic backbones as well. These compounds, industrially used as solvents and soaps, are stable and have amphiphilic properties, i.e., are insoluble in water due to their lipophilic backbone and could have provided repeat opportunities for water-soluble polar compounds, such as protonated amines and amino acids (33), to hydrogen bond to their electron-rich O-pockets.

The study of polyethers has focused mainly on their interaction and complexation with inorganic cations; such properties suggest that mineral environments of the early Earth might have aided in stabilizing the ethers and further allowed their bonding with organic cations (34). Although we searched and did not detect any cyclic (crown) ethers in SM extracts, it seems reasonable to expect that the type of compounds we detected could also have cyclized following protracted exposure to hydrothermal conditions on the early Earth via either mineral binding (34) or intramolecular ester linkages, so adding further opportunities to develop reactive cavities and enclosures for water-soluble organic compounds.

Conclusions

The IOM isolated from two fragments of Sutter's Mill meteorite (SM12 and SM41) released several nanograms per milligram of water-, and solvent-soluble organic compounds upon their HT, despite having shown few and low-abundance molecular species upon extraction of their bulk powders.

The composition of these hydrothermally released compounds is so far unique and comprises mainly O-containing species, such as polyethers and polyether esters, which had not been extracted from other meteorites' IOMs upon comparable treatment.

Based on the data and the meteorite's mineralogy, it appears reasonable to assume that the organic compounds released hydrothermally from Sutter's Mill insoluble material were formed upon heating of the parental asteroid and could equally have been produced on the early Earth by carbonaceous meteorites upon encountering analogous conditions and environments.

The addition of polyethers to the inventory of meteorite organics delivered to the early Earth is particularly intriguing due to the chemical stability and amphiphilic properties of the compounds.

Materials and Methods

Sutter's Mill powders from the SM12 and SM41 fragments were separately extracted with water and dichloromethane (DCM)/methanol (MeOH) (9:1, vol:vol) for analyses of their soluble compounds (1), dried, combined, and demineralized as previously described (4).

HT. The chosen aliquots of IOM powders (10 mg) were extracted before the HT experiment with 2 mL of water at 100 °C for 24 h. The extracts were then decanted and dried. HT experiments were conducted in pure gold tubes, 5-mm i.d. (0.125-mm wall) by ~300 mm, which were annealed at 500 °C in air overnight before use. Before loading the powders, one end of the tube was sealed by an Auto Arc TIG 50A Precision Welder. The IOM powders were loaded into the Au-tubes and degassed water was added in equal proportion by weight (10 μL) with a syringe. The tubes were frozen in liquid nitrogen, purged with Ar gas, and then sealed by arc welding under argon atmosphere. The sealed Au-tubes were then placed in a stainless-steel cold-seal pressure vessel capped with a Teflon Bridgman seal (35) and pressurized with distilled deionized water. The experiments were conducted at 300 °C and 100 MPa for 6 d. The temperature was measured by two internal thermocouples placed in the center of the long axis of the vessel at each end of the Au-tubes, with a measured gradient of ≤ 5 °C. Pressure was monitored using a Bourdon-tube gauge with an accuracy of ± 5 MPa.

After the HT, the hydrothermal vessel was quenched in ice and Au-tubes were removed, weighed to certify no weight loss or gain, rinsed with water and solvents, and then opened by slicing their midsection with a sterile razor blade. The IOM powders' suspension was transferred with distilled water to a vial and centrifuged. The extract was decanted, dried by rotary evaporation, and derivatized for molecular analyses as described below. The

powders were then dried and extracted with 1 mL of DCM/MeOH. The solvent extracts were also centrifuged, decanted, and dried under He.

Molecular Analyses by Mass Chromatography–Mass Spectrometry. The HT IOM dry solvent extracts were redissolved in DCM; their GC-MS analyses were performed using a DB-17 capillary column (J&W Scientific; 25 m × 0.25 mm, 0.25- μ m film thickness). The GC oven temperature program was 70 °C initial, 1-min hold, 70–100 °C at 2 °C·min⁻¹, from 100 to 300 °C at 4 °C·min⁻¹, and 60-min hold. Aliquots from all of the sample solutions were injected into the GC by liquid injection, with a pulse program for 1 min. Identification of compounds were made by comparison of their peak retention times and mass spectra with those of standard compounds by comparison of the mass spectra with library data (NIST98) and individual examination of the suggested match reliability.

The dried water extracts were reacted with trifluoroacetic anhydride at room temperature for 30 min and, after evaporation of the reagent under He, dissolved in DCM for analysis (36). GC-MS analyses were performed with an Agilent 6890N GC-5973N Mass Selective Detector Network System equipped with a CP Chirasil-dex CB (CHROMPACK) column, 25 m × 0.25 mm, 0.25- μ m df. The GC oven temperature program was as follows: 30 °C initial, 5-min hold, 85 °C at 1 °C·min⁻¹, 85–200 °C at 5 °C·min⁻¹.

Elemental Analysis–Isotope Ratio Mass Spectrometry. The C and N concentration and ¹³C and ¹⁵N isotopic composition of IOM residue were measured on a Costech Elemental Analyzer coupled to a Finnigan Thermo Delta Plus Advantage mass spectrometer. As described in the text, the values obtained from the SM aliquots of powders before and after HT treatment were as follows: C% = 39 and 35, $\delta^{13}\text{C}\text{‰}$ = -26 and -24; N% = 1.1 and 0.9, $\delta^{15}\text{N}\text{‰}$ = +2.5 and 3.6.

Solid-State NMR. Carbon-13 CP-MAS and proton MAS solid-state NMR spectra were collected on a Varian VNMRS 800-MHz spectrometer equipped with a 1.6-mm triple-resonance MAS probe. The experimental parameters for obtaining ¹³C CP-MAS spectra were a 2- μ s ¹H $\pi/2$ pulse, a 1-ms ramped (~20%) ¹H spin-lock pulse, and a ¹³C square contact pulse with a radio-frequency (rf) field strength of 80 kHz. The MAS frequency (ν_R) was 35 kHz and the ¹H→¹³C CP condition was matched to the -1 spinning side band in the Hartmann–Hahn profile on the ¹H channel. Two-pulse phase-modulated ¹H decoupling with 125-kHz rf field strength was applied during acquisition with an 12° phase shift. Typical acquisition parameters for ¹³C CP-MAS spectra were 100-kHz sweep width, 1,024 complex points, 8,192 scan averages, and a 5-s recycle delay. Proton MAS NMR spectra were obtained with a DEPTH (37) pulse sequence with ¹H $\pi/2$ pulse lengths of 2 μ s and 40-kHz MAS. Typical acquisition parameters for ¹H MAS spectra were 100-kHz sweep width, 320 complex points, 32 scan averages, and a 5-s recycle delay. The ¹H and ¹³C chemical shift were indirectly referenced to tetramethylsilane by setting the chemical shift of adamantane to 1.63 and 38.56 ppm, respectively.

Materials. The water used was triply distilled; 6 M HCl, 48% HF solution, DCM, and MeOH were twice distilled.

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- Jenniskens P, et al. (2012) Radar-enabled recovery of the Sutter's Mill meteorite, a carbonaceous chondrite regolith breccia. *Science* 338(6114):1583–1587.
- Pizzarello S, Cooper GW, Flynn GJ (2006) The nature and distribution of the organic material in carbonaceous chondrites and interplanetary dust particles. *Meteorites and the Early Solar System II*, eds Lauretta D, McSween HY, Jr. (Univ of Arizona Press, Tucson, AZ), pp 625–651.
- Schmitt-Kopplin P, et al. (2010) High molecular diversity of extraterrestrial organic matter in Murchison meteorite revealed 40 years after its fall. *Proc Natl Acad Sci USA* 107(7):2763–2768.
- Cronin JR, Pizzarello S, Frye JS (1987) ¹³C NMR spectroscopy of the insoluble carbon of carbonaceous chondrites. *Geochim Cosmochim Acta* 51:299–303.
- Cody G, Alexander CMO, Tera F (2002) Solid state (¹H and ¹³C) NMR spectroscopy of the insoluble organic residue in the Murchison meteorite: A self-consistent quantitative analysis. *Geochim Cosmochim Acta* 66:1851–1865.
- Hayatsu R, Matsuoka S, Scott RG, Studier MH, Anders E (1977) Origin of organic matter in the early solar system—VII. The organic polymer in carbonaceous chondrites. *Geochim Cosmochim Acta* 41:1325–1339.
- Hayatsu R, et al. (1980) Phenolic ethers in the organic polymer of the murchison meteorite. *Science* 207(4436):1202–1204.
- Alexander CM, et al. (1998) The origin of chondritic macromolecular organic matter: A carbon and nitrogen isotope study. *Meteorit Planet Sci* 33(4):603–622.
- Sephton MA, Pillinger CT, Gilmour I (1998) ¹³C of free and macromolecular aromatic structures in the Murchison meteorite. *Geochim Cosmochim Acta* 62:1821–1828.
- Sephton MA, et al. (2003) Investigating the variations in carbon and nitrogen isotopes in carbonaceous chondrites. *Geochim Cosmochim Acta* 67:2093–2108.
- Cody GD, et al. (2011) Establishing a molecular relationship between chondritic and cometary organic solids. *Proc Natl Acad Sci USA* 108(48):19171–19176.
- Alexander CMO, Fogel M, Yabuta H, Cody GD (2007) The origin and evolution of chondrites recorded in the elemental and isotopic composition of their macromolecular organic matter. *Geochim Cosmochim Acta* 71:4380–4403.
- Kwok S, Zhang Y (2011) Mixed aromatic-aliphatic organic nanoparticles as carriers of unidentified infrared emission features. *Nature* 479(7371):80–83.
- Cody GD, Alexander CMO (2005) NMR studies of chemical structural variation of insoluble organic matter from different carbonaceous chondrite groups. *Geochim Cosmochim Acta* 69:1085–1097.
- Pizzarello S, Williams LB (2012) Ammonia in the early solar system: An account from carbonaceous meteorites. *Ap J* 749:161–166, 10.1088/0004-637X/749/2/161.
- Pizzarello S, et al. (2001) The organic content of the Tagish Lake meteorite. *Science* 293(5538):2236–2239.
- Yabuta H, Williams LB, Cody GD, Alexander CMO, Pizzarello S (2007) The insoluble carbonaceous material of CM chondrites: A possible source of discrete organic compounds under hydrothermal conditions. *Meteorit Planet Sci* 42:37–48.
- Pizzarello S, Williams LB, Lehman J, Holland GP, Yarger JL (2011) Abundant ammonia in primitive asteroids and the case for a possible exobiology. *Proc Natl Acad Sci USA* 108(11):4303–4306.
- Oró J, Tornabene T (1965) Bacterial contamination of some carbonaceous meteorites. *Science* 150(3699):1046–1048.
- Huang Y, Alexandre MR, Wang Y (2007) Structure and isotopic ratios of the aliphatic side chains in the insoluble organic material of the Murchison carbonaceous chondrite. *Earth Planet Sci Lett* 259:517–525.
- Garvie LAJ (2013) Mineralogy of the Sutter's Mill carbonaceous chondrites. *44th Lunar and Planetary Conference* (Lunar and Planetary Institute, Houston, TX), Abstract 2148. Available at www.lpi.usra.edu. Accessed August 15, 2013.
- Muray T, Kitajima F, Masuda A (1991) Pyrolytic nature of carbonaceous matter in carbonaceous chondrites and secondary metamorphism. *Proc NIPR Symp Antarct Meteorites* 4:384–389.
- Kitajima F, Nakamura T, Takaoka N, Muray T (2002) Evaluating the thermal metamorphism of CM chondrites by using the pyrolytic behaviour of carbonaceous macromolecular matter. *Geochim Cosmochim Acta* 66:163–172.
- Popoff T, Theander O (1972) Formation of aromatic compounds from carbohydrates. *Carbohydr Res* 22:135–149.
- Rushdi AI, Simoneit BRT (2006) Abiotic condensation synthesis of glyceride lipids and wax esters under simulated hydrothermal conditions. *Orig Life Evol Biosph* 36(2):93–108.
- Kelley DS, Baross JA, Delaney JR (2002) Volcanoes, fluids, and life at mid-ocean ridge spreading centers. *Annu Rev Earth Planet Sci* 30:385–491.
- Kwok S (2004) The synthesis of organic and inorganic compounds in evolved stars. *Nature* 430(7003):985–991.
- Ney EP, Hatfield BF (1978) The isothermal dust condensation of Nova Vulpeculae (1976). *Astrophys J* 219:L111–L115.
- Zolensky ME, et al. (1997) CM chondrites exhibit the complete petrologic range from type 2 to 1. *Geochim Cosmochim Acta* 61:5099–5115.
- Wilde SA, Valley JW, Peck WH, Graham CM (2001) Evidence from detrital zircons for the existence of continental crust and oceans on the Earth 4.4 Gyr ago. *Nature* 409(6817):175–178.
- Strom RG, Malhotra R, Ito T, Yoshida F, Kring DA (2005) The origin of planetary impactors in the inner solar system. *Science* 309(5742):1847–1850.
- Deamer DW (2008) Origins of life: How leaky were primitive cells? *Nature* 454(7200):37–38.
- Williamson BL, Creaser CS (1999) Noncovalent inclusion complexes of protonated amines with crown ethers. *Int J Mass Spectrom* 188(Spec):53–61.
- Christensen JJ, Hill JO, Izatt RM (1971) Ion binding by synthetic macrocyclic compounds. *Science* 174(4008):459–467.
- Williams LB, Hervig RL, Holloway JR, Hutcheon I (2001) Boron isotope geochemistry during diagenesis: Part 1. Experimental determination of fractionation during illitization of smectite. *Geochim Cosmochim Acta* 65:1769–1782.
- Pizzarello S, Cronin JR (2000) Non-racemic amino acids in the Murray and Murchison meteorites. *Geochim Cosmochim Acta* 64(2):329–338.
- Cory DG, Ritchey WM (1988) Suppression of signals from the probe in Bloch decay spectra. *J Magn Reson* 80:128–132.