Effects of Pressure on Model Compounds of Meteorite Organic Matter

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ABSTRACT: Extraterrestrial organic matter has been widely studied; however, its response to pressure has not. Primitive organic matter bearing meteorites, such as CI and CM carbonaceous chondrites, have experienced variable pressures, up to 10 GPa. To appreciate the effects of these pressures on the organic content of these bodies, the model compounds isophthalic acid, vanillin, and vanillic acid were subjected to pressures of up to 11.5 GPa and subsequently decompressed. High-resolution synchrotron source Fourier transform infrared spectroscopy was used to determine the effects of different benzene substituents at high pressure on both the vibrational assignments of the benzene core of the molecules and the ability of the aromatic compounds to form intermolecular hydrogen bonds. The presence of additional peaks at high pressure was found to coincide with molecules that contain carboxyl groups; these features are interpreted as C–H···O intermolecular hydrogen bonds. The formation of these hydrogen bonds has implications for the origination of macromolecular organic matter (MOM), owing to the importance of such attractive forces during episodes of cross-linking, such as esterification. Pressure-induced hydrogen-bond formation is a process by which aromatic MOM precursors could have cross-linked to generate the organic polymers found within extraterrestrial bodies today.

KEYWORDS: intermolecular hydrogen bonding, high pressure, Fourier transform infrared spectroscopy, meteorite organic matter, carbonaceous chondrite, aromatic, extraterrestrial

INTRODUCTION

Carbonaceous chondrites are a primordial class of meteorites, which formed shortly after the formation of the solar system, <4567.30 ± 0.16 My. These meteorites possess abiotic organic material (>3 wt % in some cases), which was incorporated in their asteroid parent bodies. Approximately 30% of this is free organic matter (FOM), while ~70% is macromolecular organic matter (MOM). The use of the terms solvent soluble and insoluble to describe meteorite organic matter have been avoided as a result of the ambiguity of solvent choice.

Carbonaceous chondrite parent bodies have experienced a range of pressures. The Murchison meteorite (CM2) is an aggregate of grains that has experienced both lower (<5 GPa) and higher (up to ~10 GPa) pressures, while Murray and Mighei contain at least one grain indicative of these higher pressures. It is also important to remember that, during the first 100 Ma of the solar system, collisions were commonplace and it is unlikely that the parent bodies of carbonaceous chondrites escaped these phenomena; thus, the effect of pressure on their organic cargo represents a new study area with great potential.

Previous work on methyl-substituted polycyclic aromatic hydrocarbons has led to the establishment of the first cosmobarometer. Very few pressure studies have been undertaken on cosmologically relevant organic molecules. Meteorite organic matter is host to a diverse collection of aromatic molecules. Aromatic acids are among the most common FOM compounds and have been found previously within carbonaceous chondrites, such as Orgueil (CI1), Murchison (CM2), and Tagish Lake (C2 ungrouped). The MOM fraction of Murchison has also yielded aromatic acids as methyl derivatives after treatment with tetramethylammonium hydroxide (TMAH) and pyrolysis.

Meteorite organic matter is complex, and its origin is widely debated; however, it is largely accepted that a portion of the organic matter is presolar in origin (see ref 10 for a detailed review). Studies exposing polar ices to ultraviolet (UV) radiation have shown that it is possible to create both aromatic and aliphatic compounds resembling those found in meteorite organic matter, although only small quantities of aromatic compounds were recorded by Nuevo et al. Other experiments using polycyclic aromatic hydrocarbons mixed with polar ices have yielded aromatic structures with functional groups, such as those found previously in meteorites, including carboxyl, methoxy, and aldehyde moieties.

As a result of the complexity of meteorite organic matter, the current study will focus on model compounds that could represent the aromatic components of the initial precursor compounds but also the aromatic acids or ketones found within the insoluble portion and aromatic cores found within the insoluble portion of present day meteorite organic matter.
molecules isophthalic acid, vanillin, and vanillic acid (Figure 1) are all benzene derivatives but with different substituent groups. Isophthalic acid ($C_8H_6O_4$), a benzene dicarboxylic acid, has been found within the FOM extracts and among MOM degradation products of Murchison. Vanillin ($C_9H_8O_3$) supports alcohol, methoxy, and aldehyde functionalities, and vanillic acid ($C_9H_8O_4$) differs from vanillin only in that it possesses a carboxyl group in place of aldehyde. Both the latter two compounds have been selected because they are representative of side groups that are thought to be present on aromatic units within MOM.

All three compounds are monoclinic and have a crystal unit cell composed of four molecules, which form dimers connected by a pair of intermolecular hydrogen bonds in the case of isophthalic and vanillic acids and a single intermolecular hydrogen bond in the case of vanillin. Further details concerning the structural parameters of these benzene derivatives can be found in Table 1.

Table 1. Structural Parameters and Numbers of Potential Hydrogen Bonds and Repulsions between Atoms in the Crystals of Isophthalic Acid, Vanillin, and Vanillic Acid

|                      | Isophthalic Acid | Vanillin | Vanillic Acid |
|----------------------|------------------|----------|---------------|
| space group          | $P2_1/c$         | $P2_1$   | $P2_1/c$      |
| $a$ (Å)              | 3.76             | 14.05    | 3.91          |
| $b$ (Å)              | 16.36            | 7.87     | 17.39         |
| $c$ (Å)              | 11.70            | 15.02    | 11.33         |
| $β$ (deg)            | 90               | 115      | 95            |
| $Z$ (molecules/unit cell) | 4       | 4        | 4             |
| C–H–O (per molecule) | 4                | 4        | 4             |
| O–H–O (per molecule) | 4                | 2        | 2             |
| H–H (per molecule)   | 2                | 2        | 2             |
| O–O (per molecule)   | 4                | 0        | 3             |

No previous studies have attempted to study the effects of high pressure on our selected benzene derivatives; however, there have been multiple studies concerning benzoic acid, which consists of a benzene ring and carboxyl group, such as vanillic acid, but without the additional alcohol and methoxy functionalities. Horsewill et al. undertook the first study of benzoic acid under pressure using nuclear magnetic resonance (NMR) and concluded that two phase transitions were present, one at 0.1 GPa and the other at 0.4 GPa. Wang et al. used a combination of Raman and photoluminescence spectroscopies to determine three phase transitions (at 0.55, 3.67, and 11.10 GPa), with the third phase transition relating to the amorphization of benzoic acid to its anhydride form. A further Raman study suggested a phase transition between 6 and 8 GPa, resulting from changes to the symmetry of the hydrogen bonding. However, phase transitions up to 18 GPa were disputed by Kang et al. Similarly, Cai and Katrusiak did not record phase transitions in their X-ray diffraction studies of benzoic acid. Instead they described the shortening of hydrogen bonds and the decrease in distance between oxygen atoms in carboxyl groups at pressures above 0.5 GPa.

Previously, Fourier transform infrared (FTIR) spectroscopy has been used to monitor the influence of pressure on organic molecules. FTIR spectroscopy was used to recognize the point at which laser-induced pressure reduction converted benzene to an amorphous solid. Similarly FTIR spectroscopy was used to determine the melting curve of formic acid and assess the stabilities of polycyclic aromatic hydrocarbons under pressure. More recently, FTIR spectroscopy aided the determination of hydrogen-bond symmetrization in a study of glycinium oxalate under pressure.

In this paper, the effects of different substituent groups on the molecular response of molecular crystals to high pressure and associated hydrogen-bond formation have been determined. The data have implications for the effect of the pressure on the organic matter found within meteorites.

**EXPERIMENTAL SECTION**

Isophthalic acid, vanillin, and vanillic acid were loaded separately into a membrane-driven diamond anvil cell (DAC) (Figure 2) and subjected to pressures up to 11.5 GPa. In situ high-pressure synchrotron source FTIR spectroscopy was used to observe changes to the bonding of the compounds. A 0.15 mm thick pre-induced Inconel gasket, containing a sample chamber hole of 0.25 mm in diameter, was placed between two type-II diamonds with 0.5 mm cutlets. Within the sample chamber, a cesium iodide (CsI) window was created.
The pressure was observed throughout the duration of the experiment using the ruby fluorescence technique. The error in the pressure calculation relating to the precision of the spectrometer unit was less than 0.01 GPa, and the uncertainty of the pressure in the DAC resulting from non-hydrostatic conditions was estimated to be ±0.1 GPa. The pressure was increased incrementally by 0.5 to 3 GPa and then by 1 GPa to above 10 GPa, where the pressure was decreased by 2.5 GPa until the minimum pressure was reached. The samples were held for between 15 and 60 min at each pressure. Further details regarding the apparatus and methodology can be accessed elsewhere.

Transmission FTIR microspectrometry was undertaken using synchrotron source light at the SMIS beamline, SOLEIL Synchrotron, France. The beamline is host to a custom-made horizontal infrared (IR) microscope, with two Schwarzschild objectives (47 mm working distance, NA 0.5) yielding a 22 μm (full width at half maximum) IR spot and 4 cm⁻¹ resolution. Each spectra recorded consisted of 128 scans. The system spectrometer was a Nexus 6700, operated concurrently with the liquid N₂-cooled MCT/A detector.

Background spectra were taken at every measured pressure in a blank area of the sample chamber before the acquisition of sample spectra. The corresponding background signal for a given pressure was removed from the sample spectra. The resulting spectra were truncated to yield two files using Fityk, a low-wavenumber region (650–1800 cm⁻¹) and a high-wavenumber region (2600–3700 cm⁻¹), omitting the region of interference generated by the diamond. The high-wavenumber region experiences fringing, resulting from reflections between internal and external diamond faces, which were removed by a custom program. The peaks were fitted as Gaussian peaks using Fityk, to demonstrate peak center shifts.

**RESULTS**

The vibrational assignments of key functionalities are reported at ambient pressure and summarized in Table 2. Observed peaks are referred to by their ambient wavelength center at the lowest pressure and highest amplitude. Spectra are displayed for each pressure for a given molecule where data are simple. Pressure versus peak center plots are provided where the data are complex.

**Vibrational Assignments.** Vibrations can refer to a variety of motions; stretching vibrations are the major focus of this study. However, the bending modes of OH and 18b in isophthalic acid are discussed. The character “ν” is used to denote internal stretching vibrations of a substituent, while “β” is used to represent the bending vibrations where the atoms retain a well-defined plane and “γ” where they do not. The numbers and letters “8a”, “8b”, “19a”, and “19b” describe different tangential C–C stretching vibrations found within the benzene ring. The other stretching vibration of importance in this study is “13”, which describes one of the radial C–X stretching vibrations of the benzene ring. The vibration 18b is unlike the other normal vibrations of benzene mentioned thus far and represents an in-plane bending vibration. More specifically, the 18b vibration is a translational mode resulting from the displacement of a carbon atom as a result of the angular momentum of its bonded hydrogen. The assignments of 8a, 8b, 19a, 19b, and 13 were taken from Varsányi.

**Isophthalic Acid (C₈H₆O₄).** Peak assignments have not been made previously for isophthalic acid. Here, we assign peaks to isophthalic acid, guided by those published for phthalic acid: βOH (1417 cm⁻¹), νC=O (1685 cm⁻¹), νOH (3081 cm⁻¹), 8a (1608 cm⁻¹), 8b (1581 cm⁻¹), 13 (1078 cm⁻¹), 18b (1102 cm⁻¹), 19a (1457 cm⁻¹), 19b (1487 cm⁻¹), and 13 (1078 cm⁻¹).

**Vanillin (C₈H₈O₃).** Peak assignments have been made formerly, and those of interest to the current work are νCH (aldehyde) (811 cm⁻¹), νOH (alcohol) (827 cm⁻¹), βC–CHO/νC=O (857 cm⁻¹), νCO–CH₃ (1025 cm⁻¹), νCO (1192 cm⁻¹), νC=O (1685 cm⁻¹), νOH (3081 cm⁻¹), 18b (1102 cm⁻¹), 8b (1581 cm⁻¹), 19a (1457 cm⁻¹), 19b (1487 cm⁻¹), and 8a (1608 cm⁻¹).
and 1249 cm$^{-1}$), $\nu$C=O (1660 cm$^{-1}$), $\nu_{\text{sym}}$CH$_n$ (2917 cm$^{-1}$), $\nu_{\text{asym}}$CH$_n$ (2933 and 2967 cm$^{-1}$), and $\nu$OH (3212 cm$^{-1}$).

**Vanillic Acid (C$_8$H$_8$O$_4$).** Peak assignments have been made previously$^{38}$ and those of interest to the present study are $\nu$CO (1205 and 1282 cm$^{-1}$), $\nu$C=O (1680 cm$^{-1}$), $\nu_{\text{sym}}$CH$_n$ (2857 cm$^{-1}$), $\nu_{\text{asym}}$CH$_n$ (2954 and 2989 cm$^{-1}$), and $\nu$OH (3485 cm$^{-1}$). Additionally, $\nu$CO$-$CH$_3$ (1028 cm$^{-1}$) has been inferred from comparison to the vanillin spectra.

**DISCUSSION**

At lower wavenumbers, the behavior of isophthalic acid is quite complex (Figure 3); the 18b and 13 peaks converge and finally coalesce by 6 GPa, and the $\nu$C=O response moves toward the 8a peak before diverging and then finally merging after 8 GPa.

The convergence of the 18b and 13 peaks suggests a limitation on their translational bending and radial C$-$X stretching movements, respectively, with increasing pressure. The C$-$C stretching vibrations associated with the 8a, 8b, 19a, and 19b peaks appear to be relatively unaffected by increasing pressure, only showing the typical blue shift during pressurization.$^{30,31}$ The $\nu$C=O response adds an extra layer of complexity; it appears that the stretching vibrations associated with this peak both increase and decrease with pressurization. Although it is not clear why this complex behavior may occur, the formation of a new peak (3139 cm$^{-1}$) coincides with the divergence of the $\nu$C=O response around 4 GPa (Figure 4).

At lower wavenumbers, vanillin shows only minor variation (Figure 5). The major change is the splitting of the $\nu$C=O peak into a doublet at pressures above ambient, followed by the convergence of this doublet by 4.3 GPa, which may result from a change in the symmetry of the C=O bond. Other changes include the decrease in intensity of the peaks in the 800$-$860 cm$^{-1}$ region, relating to vibrational suppression of the $\gamma$CH (aldehyde), $\gamma$OH (alcohol), and $\beta$C$-$CHO/$\nu$CO moieties with increasing pressure.

Vanillic acid varies only slightly with pressure in the lower wavenumber region (Figure 6). The notable changes include the splitting of the lower wavenumber $\nu$CO peak and the trend of decreasing $\nu$C=O peak amplitude with increasing pressure.

The higher wavenumber region of isophthalic acid depicts the $\nu$OH peak (3081 cm$^{-1}$) (Figure 7a), but no red shift is present, suggesting that the O$-$H bond remains stable during the pressures experienced in this study. More significant is the appearance of a separate peak (3139 cm$^{-1}$) at 4 GPa, which persists to 9.5 GPa, the maximum pressure reached during this

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**Figure 3.** Diagram depicting the low-wavenumber FTIR peak centers of isophthalic acid during pressurization up to 9.5 GPa and subsequent decompression to 1.3 GPa. Note the merging of the 18b peak (green) with the 13 peak (orange) and the undulating $\nu$C=O peak center (red) and its final coalescence with the 8a peak (blue).

**Figure 4.** Diagram depicting the low-wavenumber FTIR spectra of the 8b, 8a, and $\nu$C=O peaks of isophthalic acid during pressurization up to 9.5 GPa and subsequent decompression to 1.3 GPa. Note the convergence of the 8a and $\nu$C=O peaks toward 4 GPa and their subsequent divergence to 6 GPa, before they finally merge at around 8 GPa. A similar behavior is also reported in reverse on decompression.

**Figure 5.** Diagram depicting the low-wavenumber FTIR spectra of vanillin during pressurization up to 10 GPa and subsequent decompression to 2.8 GPa.

Vanillic acid varies only slightly with pressure in the lower wavenumber region (Figure 6). The notable changes include the splitting of the lower wavenumber $\nu$CO peak and the trend of decreasing $\nu$C=O peak amplitude with increasing pressure.
experiment. The peak (3127 cm$^{-1}$) then disappears by 5 GPa during decompression. This peak could arise from the formation of further intermolecular hydrogen bonds between the carboxyl functionalities of isophthalic acid or between carboxyl oxygen and aromatic ring or methoxy hydrogen (Figure 1).

The higher wavenumber region of vanillin exhibits the typical red shift of the νOH peak with increasing pressure (Figure 7b). However, unlike isophthalic acid, there is no evidence of a separate peak forming. This indicates a lack of further hydrogen-bond formation within vanillin at higher pressures, likely as a result of the lack of a carboxyl group.

The higher wavenumber region of vanillic acid (Figure 7c) shows a red shift of the νOH peak (3485 cm$^{-1}$), similar to that observed for vanillin. A separate peak is not superposed on the νOH peak, as was observed in the case of isophthalic acid. However, there are three peaks found within the area associated with C–H$_n$ bonding. The peak found at 3098 cm$^{-1}$ is due to the C–H ring stretch, but the other two have not been previously reported. At ambient pressure, only one of these peaks is present (3139 cm$^{-1}$), and this peak increases in amplitude with increasing pressure up to 6.1 GPa, after which it remains constant, before decreasing upon depressurization. The other peak is first seen at 5.1 GPa and has begun to merge with the νOH peak by 10.1 GPa. Tao et al.$^{25}$ reported two peaks in a similar region in their Raman study of benzoic acid (3154 and 3163 cm$^{-1}$), which form between 6 and 8 GPa. It is not clear what modes these relate to and, thus, whether they are IR-active, but there is a possibility that these may relate to the

![Figure 6. Diagram depicting the low-wavenumber FTIR spectra of vanillic acid during pressurization up to 11.5 GPa and subsequent decompression to 1.0 GPa.](image1)

![Figure 7. Diagram depicting the high-wavenumber FTIR spectra of (a) isophthalic acid, (b) vanillin, and (c) vanillic acid during pressurization and subsequent decompression. In the spectra of isophthalic acid, the red dot highlights the appearance of a new peak at around 4 GPa, which persists to the highest pressure used in this experiment. The vanillic acid spectra show three peaks in the high-wavenumber region apart from the νOH peak: C–H ring stretch (3098 cm$^{-1}$) and two peaks that potentially relate to hydrogen bonds. The first peak is present at ambient (3139 cm$^{-1}$), and the second peak (red dot) is first seen at 5.1 GPa. Vanillin does not produce any new peaks at high pressure but does demonstrate a red shift with increasing pressure.](image2)
formation of intermolecular hydrogen bonds between carboxyl oxygen and aromatic ring hydrogen of different vanillic acid molecules (Figure 1). Similarly, Chang et al.\textsuperscript{19} reports the appearance of two peaks (2891 and 2994 cm\textsuperscript{-1}) associated with the formation of C−H···O hydrogen bonds at around 1.9 GPa in solutions of 1,4-dioxane and D\textsubscript{2}O.

The distances between nearest neighbors can be affected by pressure,\textsuperscript{40} and this may help to explain the appearance of new peaks in isophthalic and vanillic acids. Figure 1 demonstrates that there is geometric potential for numerous C−H···O hydrogen bonds in both isophthalic and vanillic acids. With increasing pressure, the distances between C−H on both the aromatic rings and methoxy functionalities and oxygen atoms becomes shorter, and this may result in the formation of C−H···O hydrogen bonds.\textsuperscript{57} It is also the case that the distance between oxygen atoms and hydrogens will decrease, and may result in an increase in the strength of repulsions, although these can be overcome by the increased attraction of C−H···O and O−H···O hydrogen bonds with increasing pressure.\textsuperscript{41,42}

In the case of isophthalic and vanillic acids, the reason for the appearance of peaks in the νC=O and νCH=O regions may be the result of the C−H···O bond forming between either the aromatic or methoxy C−H bond and the C−O−H of their carboxyl groups, respectively. Vanillin does not possess a carboxylic functionality and contains an aldehyde group instead; therefore, peak formation at a high pressure is not expected. Peak formation could also arise from symmetric changes to the crystals of isophthalic or vanillic acid arising from C−H···O bond formation or changes to the lengths of both of these and classic hydrogen bonds (O−H···O). Indeed, the increase in amplitude of the peak at 3139 cm\textsuperscript{-1} (Figure 7c) in vanillic acid at higher pressures may result from the lengthening of a hydrogen bond, caused by reorganization of the molecules in the crystal structure. Symmetric changes in the carboxyl groups have been described as the cause of hydrogen-bond lengthening in benzoic acid.\textsuperscript{57}

An alternative explanation might be a change in the nature of interactions between the dimerized carboxyl groups of isophthalic and vanillic acids. An increase in hydrostatic pressure can reduce the distance between oxygen atoms and hydrogen-bond lengths in carboxyl groups, forcing these functionalities closer together and potentially facilitating the formation of different intramolecular hydrogen bonds, C−H···O and C=O···H, through H hopping.\textsuperscript{27,56} This change in hydrogen-bond dynamics may introduce new peaks as a direct result of these new hydrogen bonds or as a result of crystal-wide symmetry changes resulting from different bond parameters.

The formation of hydrogen bonds with increasing pressure is of potential interest to the formation of MOM from simpler precursors because of the role of pressure in cosmic environments. Hydrogen-bond interactions may have allowed for the assembling of some macromolecular organic matter from individual aromatic units, such as those observed in the interstellar medium and meteorite FOM, via cross-linking of oxygen-containing moieties, such as ether or ester bonds. Indeed, it was demonstrated by Cai and Katrusiak\textsuperscript{27} that esterification can occur between benzoic acid units, in methanol and ethanol, at 1.48 GPa and 483 K.

\section*{CONCLUSION}

Three organic model compounds, with chemical relevance to the organic matter within meteorites, were investigated for their responses to pressure. Synchrotron FTIR data reveal that the lower wavenumber regions of the three benzene derivatives are significantly different. Isophthalic acid demonstrates the highest degree of complexity; translational and radial skeletal stretching movements are reduced with increasing pressure, while C−C stretching vibrations are unaffected. Meanwhile, the νC=O stretching vibrations appear to both increase and decrease during pressurization. Vanillin displays the least complex response to increasing pressure, with only the splitting of the νC=O peak and the vibrational suppression of the peaks relating to γCH (aldehyde), γOH (alcohol), and βC−CHO/νCO above ambient pressure notable. With increasing pressure, vanillic acid displays splitting of the lower wavenumber νCO peak and a decrease in the amplitude of the νC=O peak.

At higher wavenumbers, the spectra of both isophthalic and vanillic acids record peaks that may relate to C−H···O hydrogen-bond formation. However, the peak at 3139 cm\textsuperscript{-1} in vanillic acid, which increases in amplitude with higher pressures, may represent hydrogen-bond lengthening, potentially resulting from changes in the symmetries of the carboxyl groups present.

Oxygen-containing substituent groups facilitate the formation of intermolecular hydrogen bonding during the application of pressure. It appears that in isophthalic and vanillic acids the presence of a carboxyl side chain gives rise to greater hydrogen bridging than in vanillin. The role of the methoxy group may lead to hydrogen-bond formation between methoxy hydrogen and alcohol oxygen as well as between methoxy oxygen and aldehyde hydrogen at increased pressure in vanillin and give rise to bond lengthening and further formation of intermolecular hydrogen bonds in vanillic acid at increased pressure. The migration of the νC=O peak in isophthalic acid is not fully understood, but the formation of C−H···O intermolecular hydrogen bonds between different molecules may be responsible. This may occur through either the interaction of different substituent groups or H hopping between two carboxyl groups.

The presence of certain functional groups seems to promote the formation of hydrogen bonds under pressure. Hydrogen-bond formation may be a precursor to esterification and, thus, the cross-linking of aromatic molecules to form organic polymers. The findings reported here may help to constrain the origin of some meteorite MOM units. MOM is thought to contain numerous ester and ether linkages. The recognition of pressure-induced intermolecular hydrogen-bond formation that promotes the assembly of organic networks from oxygen-containing aromatic precursors will help the identification of records of such processes in meteorite organic matter. Future work, such as the undertaking of high-pressure neutron diffraction studies, will allow for a better understanding of the formation of hydrogen bonds in these molecules under pressure.

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\textbf{Author Contributions}

All authors have contributed to the manuscript, and the developments leading to the manuscript can be divided into four sections: Mark A. Sephton and Wren Montgomery...
designed the experiment; Christian Potiszil and Wren Montgomery acquired data; Christian Potiszil and Wren Montgomery interpreted data; and Christian Potiszil, Mark A. Sephton, and Wren Montgomery wrote the paper. All authors have given their approval to the final version of the manuscript.

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ABBREVIATIONS USED
FTIR, Fourier transform infrared; DAC, diamond anvil cell; MOM, macromolecular organic matter; FOM, free organic matter; NMR, nuclear magnetic resonance

REFERENCES
(1) Connolly, J. N.; Bizzarro, M.; Krot, A. N.; Nordlund, Å.; Wielandt, D.; Ivanova, M. A. The absolute chronology and thermal processing of solids in the solar protoplanetary disk. Science 2012, 338 (6107), 651–655.
(2) Sephton, M. A. Organic compounds in carbonaceous meteorites. Nat. Prod. Rep. 2002, 19 (3), 292–311.
(3) Scott, E. R. D.; Keil, K.; Stöffler, D. Shock metamorphism of carbonaceous chondrites. Geochim. Cosmochim. Acta 1992, 56 (12), 4281–4293.
(4) Vernazza, P.; Beck, P. Composition of Solar System Small Bodies. In Planetismals: Early Differentiation and Consequences for Planets; Elkins-Tanton, L. T., Weiss, B. P., Eds.; Cambridge University Press: Cambridge, U.K., 2017; Vol. 16, pp 269–297, DOI: 10.1017/9781139339794.013.
(5) Youdin, A. N.; Rieke, G. H. Planetismals in Debris Disks. In Planetismals: Early Differentiation and Consequences for Planets; Elkins-Tanton, L. T., Weiss, B. P., Eds.; Cambridge University Press: Cambridge, U.K., 2017; Vol. 16, pp 340–362, DOI: 10.1017/9781139339794.016.
(6) Montgomery, W.; Watson, J. S.; Sephton, M. A. An organic cosmo-barometer: Distinct pressure and temperature effects for methyl substituted polycyclic aromatic hydrocarbons. Astrophys. J. 2014, 784 (2), 98.
(7) Pizzarello, S.; Huang, Y.; Becker, L.; Poreda, R. J.; Nieman, R. A.; Cooper, G.; Williams, M. The organic content of the Tagish Lake meteorite. Science 2001, 293 (5538), 2236–2239.
(8) Martins, Z.; Watson, J. S.; Sephton, M. A.; Botta, O.; Ehrenfreund, P.; Gilmore, I. Free dicarboxylic and aromatic acids in the carbonaceous chondrites Murchison and Orgueil. Meteorit. Planet. Sci. 2006, 41 (7), 1073–1080.
(9) Watson, J. S.; Sephton, M. A.; Gilmore, I. Thermochemicals of the Murchison meteorite: Identification of oxygen bound and occluded units in the organic macromolecule. Int. J. Astrobiol. 2010, 9 (4), 201.
(10) Sephton, M. Organic Geochemistry of Meteorites. In Treatise in Geochemistry, 2nd ed.; Turekian, K., Ed.; Elsevier: Amsterdam, Netherlands, 2014; Vol. 12, pp 1–31, DOI: 10.1016/B978-0-08-095975-7.01002-0.
(11) Greenberg, J. M.; Li, A.; Mendoza-Gómez, C. X.; Schutte, W. A.; Gerakines, P. A.; de Groot, M. Approaching the interstellar grain organic refractory component. Astrophys. J. 1995, 455 (2), L177.
(12) Bernstein, M.; Allamandola, L.; Sandford, S. Complex organics in laboratory simulations of interstellar/cometary ices. Adv. Space Res. 1997, 19 (7), 991–998.
(13) Nuevo, M.; Milam, S. N.; Sandford, S. A.; De Gregorio, B. T.; Cody, G. D.; Kilcoyne, A. L. D. XANES analysis of organic residues produced from the UV irradiation of astrophysical ice analogs. Adv. Space Res. 2011, 48 (6), 1126–1135.
(14) Ciesla, F. J.; Sandford, S. A. Organic synthesis via irradiation and warming of ice grains in the solar nebula. Science 2012, 336 (6080), 452–454.
(15) Danger, G.; Orthous-Daunay, F.-R.; de Marcellus, P.; Modica, P.; Vuitton, V.; Duverney, F.; Flandinet, L.; Le Sergeant d'Hendecourt, L.; Thissen, R.; Chiavassa, T. Characterization of laboratory analogs of interstellar/cometary organic residues using very high resolution mass spectrometry. Geochim. Cosmochim. Acta 2013, 118, 184–201.
(16) Bernstein, M. P.; Sandford, S. A.; Allamandola, L. J.; Gillette, J. S.; Clemett, S. J.; Zare, R. N. UV irradiation of polycyclic aromatic hydrocarbons in ices: Production of alcohols, quinones, and ethers. Science 1999, 283 (5405), 1135–1138.
(17) Bernstein, M. P.; Elsa, J. E.; Dworkin, J. P.; Sandford, S. A.; Allamandola, L. J.; Zare, R. N. Side group addition to the polycyclic aromatic hydrocarbon coronene by ultraviolet photolysis in cosmic ice analogs. Astrophys. J. 2002, 576 (2), 1115.
(18) Cody, G. D.; Alexander, C. M. O. D.; Tera, F. Solid-state (H and 13C) nuclear magnetic resonance spectroscopy of insoluble organic residue in the Murchison meteorite: A self-consistent quantitative analysis. Geochim. Cosmochim. Acta 2002, 66 (10), 1851–1865.
(19) Derissen, J. L. The crystal structure of isophthalic acid. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 1974, 30 (11), 2764–2765.
(20) Košlevčar, B.; Orladžek, D.; Golobić, A.; Pevec, A.; Strauch, P.; Segedin, P. Complexes with lignin model compound vanillic acid. Two different carboxylate ligands in the same dinuclear tetracarboxylate complex [Cu3(C8H7O4)2(O2CCH3)2(CH3OH)2]. Polyhedron 2006, 25 (5), 1161–1166.
(21) Velavan, R.; Sureshkumar, P.; Sivakumar, K.; Natarajan, S. Vanillin-I. Acta Crystallogr., Sect. C: Struct. Crystallogr. Commun. 1995, 61 (6), 1131–1133.
(22) Lee, T.; Chen, H. R.; Lin, H. Y.; Lee, H. L. Continuous co-crystallization as a separation technology: The study of 1:2 co-crystals of phenazine–vanillin. Cryst. Growth Des. 2012, 12 (12), 5897–5907.
(23) Horsewill, A. J.; McDonald, P. J.; Vijayaraghavan, D. Hydrogen bond dynamics in benzoic acid dimers: A photoinduced ring opening of benzene. Phys. Rev. Lett. 2004, 93 (5), 085505.
(24) Wang, Z. P.; Tang, X. D.; Ding, Z. J. Raman and photoluminescence spectroscopy study of benzoic acid at high pressures. J. Phys. Chem. Solids 2005, 66 (5), 895–901.
(25) Tao, Y.; Dreger, Z. A.; Gupta, Y. M. High pressure effects on benzoic acid dimers: Vibrational spectroscopy. Vib. Spectrosc. 2014, 73, 138–143.
(26) Kang, L.; Wang, K.; Li, X.; Zou, B. High Pressure Structural Investigation of Benzoic Acid: Raman Spectroscopy and X-ray Diffraction. J. Phys. Chem. C 2016, 120 (27), 14758–14766.
(27) Cai, W.; Katrusiak, A. Pressure effects on H-ordering in hydrogen bonds and interactions in benzoic acid. CrystEngComm 2012, 14 (13), 4420–4424.
(28) Gibin, L.; Santoro, M.; Bini, R.; Schettino, V. High pressure photinduced ring opening of benzene. Phys. Rev. Lett. 2002, 88 (8), 085505.
(29) Montgomery, W.; Zaug, J. M.; Howard, W. M.; Goncharov, A. F.; Crowhurst, J. C.; Jeanloz, R. Melting curve and high-pressure chemistry of formic acid to 8 GPa and 600 K. J. Phys. Chem. B 2005, 109 (41), 19443–19447.
(30) Jennings, E.; Montgomery, W.; Lerch, P. Stability of coronene at high temperature and pressure. *J. Phys. Chem. B* **2010**, *114* (48), 15753−15758.

(31) O’Bannon, E., III; Williams, Q. Vibrational spectra of four polycyclic aromatic hydrocarbons under high pressure: Implications for stabilities of PAHs during accretion. *Phys. Chem. Miner.* **2016**, *43* (3), 181−208.

(32) Bhatt, H.; Murli, C.; Mishra, A. K.; Verma, A. K.; Garg, N.; Deo, M. N.; Chitra, R.; Sharma, S. M. Hydrogen Bond Symmetrization in Glycinium Oxalate under Pressure. *J. Phys. Chem. B* **2016**, *120* (4), 851−859.

(33) Mao, H. K.; Xu, J.; Bell, P. M. Calibration of the ruby pressure gauge to 800 kbar under quasi-hydrostatic conditions. *J. Geophys. Res.* **1986**, *91* (B5), 4673−4676.

(34) Dumas, P.; Polack, F.; Lagarde, B.; Chubar, O.; Giorgetta, J. L.; Lefrançois, S. Synchrotron infrared microscopy at the French Synchrotron Facility SOLEIL. *Infrared Phys. Technol.* **2006**, *49* (1), 152−160.

(35) Wojdyr, M. Fityk: A general-purpose peak fitting program. *J. Appl. Crystallogr.* **2010**, *43* (5), 1126−1128.

(36) Varsányi, G. *Assignments for Vibrational Spectra of Seven Hundred Benzene Derivatives*; Adam Hilger: London, U.K., 1974; Vol. 1.

(37) Balachandran, V.; Parimala, K. Vanillin and isovanillin: Comparative vibrational spectroscopic studies, conformational stability and NLO properties by density functional theory calculations. *Spectrochim. Acta, Part A* **2012**, *95*, 354−368.

(38) Clavijo, E.; Menéndez, J. R.; Aroca, R. Vibrational and surface-enhanced Raman spectra of vanillic acid. *J. Raman Spectrosc.* **2008**, *39* (9), 1178−1182.

(39) Chang, H.-C.; Jiang, J.-C.; Chuang, C.-W.; Lin, S. H. Evidence for hydrogen bond-like C−H−O interactions in aqueous 1,4-dioxane probed by high pressure. *Chem. Phys. Lett.* **2004**, *397* (1), 205−210.

(40) Cysewski, P. Pressure-imposed changes of benzoic acid crystals. *J. Mol. Model.* **2015**, *21* (4), 83.

(41) Marciniak, J.; Bąkowicz, J.; Dobrowolski, M. A.; Dziubek, K. F.; Kaźmierczak, M.; Paliwoda, D.; Rajewski, K. W.; Sobczak, S.; Stachowicz, M.; Katusiak, A. Most frequent organic interactions compressed in toluene. *Cryst. Growth Des.* **2016**, *16* (3), 1435−1441.

(42) Patyk-Każmierczak, E.; Warren, M. R.; Allan, D. R.; Katusiak, A. Intermolecular contacts in compressed α-α-mannose. *Cryst. Growth Des.* **2016**, *16* (12), 6885−6890.