

Formation of diverse water-soluble molecules through experimental hydrothermal alteration of insoluble organic matter from carbonaceous chondrites

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Carbonaceous chondrites preserve the early history of the Solar System. They contain 2–5 wt% total organic carbon, which is divided into insoluble organic matter (IOM) and soluble organic molecules (SOM) (Glavin et al., 2018). Hydrothermal treatments (HT) on IOM have been used to evaluate how aqueous alteration on meteorite parent bodies can impact the chemical and isotopic composition of the macromolecule, with specific SOM being released from the insoluble organic fraction (Yabuta et al., 2007).

While prior studies have extensively characterized solvent-soluble compounds, water-soluble organic molecules (some of the most well-documented compounds in the SOM records of CM chondrites (Pizzarello, 2006)) during HT have not been fully explored. To address this issue, this study investigated the uncharacterized water-soluble molecules released from IOM through experimental parent body aqueous alteration. The main objective of this study is to determine whether a larger variety of known water-soluble compounds of Murchison could have formed through the aqueous alteration of its IOM within the parent body and to further investigate the relationship between soluble organic molecules and insoluble organic matter.

Pulverized samples of Murchison CM2 carbonaceous chondrite were repeatedly subjected to HF/HCl treatment, CsF/HF density separation, and desulfurization. The IOM residue was rinsed and dried at 50°C. The HT experiments were performed with ~5–6 mg of IOM and 0.5 mL of ultrapure water at 200°C for 72 hours. Afterward, the water supernatant was extracted with ethyl acetate, concentrated, and dried with N₂ gas before being analyzed using electrospray ionization (ESI)-Orbitrap high-resolution mass spectrometry (HRMS).

Three hydrothermal experiments (two analyzed by ESI (-) and one by ESI (+)) were conducted. In the ESI (+) mass spectra of the HT-IOM water extract, 15 ion peaks were identified. Based on the composition formula estimated from the exact masses, the peaks mainly included monocarboxylic and dicarboxylic acids, benzene carboxylic acids, and N-heterocycles (i.e., pyridine carboxylic acids). From the two ESI (-) mass spectra, 23 and 19 ion peaks were identified, also representing the aforementioned compound groups. The most intense benzene carboxylic acid was usually benzene tricarboxylic acid (C₉H₆O₆), and from the N-heterocycles, the highest intensity peak was nicotinic acid (C₆H₅NO₂). Benzene carboxylic acids with two to four carboxyl groups and pyridine carboxylic acids were detected for the first time in this study as products of the hydrothermal treatment of IOM, along with the previously reported mono- and dicarboxylic acids (Oba & Naraoka, 2006; Yabuta et al., 2007). Some S-containing molecules such as thiophene carboxylic acids and benzenethiols were also observed.

These results underscore the diversity of molecules resulting from the hydrothermal treatment of the insoluble organic matter. The cleavage of C-O bonds and oxidation of aliphatic linkages possibly led to the formation of mono- and dicarboxylic acids (Oba & Naraoka, 2006; Yabuta et al., 2007), while the

oxidation of aromatic moieties linked by ether bonds possibly produced the wide range of identified benzene carboxylic acids (Watson et al., 2010). In addition, these findings point toward a wider diversity in the labile fraction of the IOM from the Murchison meteorite, where more non-condensed aromatic species such as benzenes, pyridines and thiophenes, could be present.

Most of the products of the hydrothermal treatment are also found as part of the soluble organic molecules in Murchison (Martins et al., 2006; Smith et al., 2014; Glavin et al., 2018), suggesting that multiple free water-soluble molecules could have been formed from IOM during the aqueous alteration within the parent body. Consequently, this process may have generated molecules relevant to the eventual emergence of life, such as nicotinic acid, precursor of NAAD, which plays a leading role in protometabolic processes and influences RNA synthesis (McMurtry et al., 2016). A substantial number of the compounds identified in this experiment have also been reported in the SOM of Ryugu (Naraoka et al., 2023), opening the possibility that the origin of these molecules could be rooted in their insoluble fraction during extensive aqueous alteration.

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