Extraterrestrial organic compound distribution revealed by ultra-high resolution HPLC-MS

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Many soluble organic compounds have been reported from carbonaceous meteorites in various solvent extracts ranging from non-polar hexane to polar water, in which amino acids and carboxylic acids have been targeted in the water-soluble fraction. The compostional and structural diversities of amino acids and carboxylic acids are well documented up to C8 observed with most structural isomers at each carbon number. The non-polar hexane extract contains non-polar components including aromatic hydrocarbons. To date, about a few thousands of soluble organic compounds have been identified in meteorites by GC and/or LC/MS. However, a high-resolution mass spectral study revealed ~160,000 ion peaks in various solvent extracts of the Murchison meteorite by electrosplay ionization using Fourier transform-ion cyclotron resonance/mass spectrometry (FT-ICR/MS) to assign ~50,000 elemental compositions consisting of CHO, CHNO, CHOS and CHNOS (Schmitt-Kopplin et al., 2010). The methanol extracts of carbonaceous meteorites are enriched in organic content with more enriched in D and 15N relative to other fractions, implying more primitive organic compounds. The FT-ICR/MS study did not clarified the detailed chemical structures due to no chromatographic separation. In particular, the organic compounds with their elemental compositions of CH and CHN were not discussed. In the previous study (Yamashita and Naraoka, 2014), homologous series of alkylated pyridines ($C_nH_{2n-4}N^+$ and $C_nH_{2n-6}N^+$) were predominant peaks in the MeOH extract.
In this study, we further examine the distribution of soluble organic compound using ultrahigh-resolution HPLC/MS in order to investigate reaction mechanisms for extraterrestrial molecular evolution. The exact mass between the observed mass and calculated values matched within 1 ppm. Using a hydrophilic interaction liquid chromatography (HILIC) mode, complex compound mixtures were observed with mass peaks between m/z 80 and 1400, where strong ion peaks are distinguished between m/z 90 and 400 with the maximum at m/z ~300. Most peaks have CHN in composition with minor CHO and CHNO compositions. More than ~600 peaks match with the calculated masses for $C_nH_mN^+$ and $C_nH_mN_2^+$ with the range of $5 < n < 33$. Extensive alkylated N-containing cyclic compounds are distinguished by every 14.0156 (-CH_2-) difference, which consisted of $C_nH_{2n-4}N^+$, $C_nH_{2n-6}N^+$, $C_nH_{2n-8}N^+$, $C_nH_{2n-10}N^+$ and $C_nH_{2n-12}N^+$ in the earlier retention time, and the $C_nH_{2n+4}N^+$, $C_nH_{2n+2}N^+$, $C_nH_{2n}N^+$, $C_nH_{2n-2}N^+$, $C_nH_{2n+3}N_2^+$, $C_nH_{2n+1}N_2^+$, $C_nH_{2n-1}N_2^+$ and $C_nH_{2n-3}N_2^+$ in the later retention time. In addition to the predominant $C_nH_{2n-4}N^+$ (saturate-alkylated pyridines, $C_nH_{2n-5}N$) and $C_nH_{2n-6}N^+$ (unsaturate-alkylated pyridines, $C_nH_{2n-7}N$), alkylated imidazole homologues were identified by MS/MS analysis. Both alkylpyridines and alkylimidazoles could be produced from aldehydes and ammonia through aldol condensation and imine formation under an alkaline environment. Further redox reactions could have proceeded during water-rock interaction to give alkylpiperidines and pyridine carboxylic acids. Aldehyde polymerization with ammonia is an important pathway to produce the relatively high-molecular alkylated N-containing cyclic compounds on the meteorite parent body.

Keywords: extraterrestrial organic compounds, chemical evolution, carbonaceous meteorite, ultra-high resolution liquid chromatography, ultra-high resolution mass spectrometry