

Simulation experiments for meteoritic N-containing cyclic compounds from aldehyde and ammonia with olivine. Y. Yamashita¹, H. Naraoka¹, H. Mita², ¹Dept. Earth and Planetary Sciences, Kyushu University, Fukuoka 812-8581 JAPAN, ²Dept. Life, Environment and Material Science, Fukuoka Institute of Technology, Fukuoka 811-0295 JAPAN.

Introduction:

Carbonaceous chondrites are the primitive meteorites that contain various volatile components including water and organic matter. Although the organic compound variations have been thought to record their environmental conditions, the original chemical structures have not been clarified with respect to the formation mechanism(s). Recently, ultrahigh mass resolution mass spectral analyses of various solvent extracts of the Murchison meteorite (CM2) was performed using Fourier transform-ion cyclotron resonance/mass spectrometry (FT-ICR/MS) with the electrospray ionization [1]. Tens of thousands of mass ions were detected with compositional formulas of CHO, CHOS, CHNO and CHNOS having the extensive homologues series for soluble organic matter (SOM). In our previous work [2], homologous series of saturate- and unsaturate-alkylated pyridines (mainly C_nH_{2n-5}N and C_nH_{2n-7}N series) were identified in MeOH and DCM fractions from Murchison as major compounds. They could be synthesized by the reaction of aldehyde and ammonia in aqueous solution (*Chichibabin pyridine synthesis*). From MeOH extracts of Murchison, other N-containing cyclic compounds, such as alkylated pyridinecarboxylic acids and imidazoles, were also detected with their homologues series. In this study, we will perform simulation experiments in order to reveal the formation environment of the N-containing cyclic compounds and the interaction among water, minerals and organics.

Materials and Methods:

Aqueous solutions of aldehydes (ca. 60mM to 1.6M) and ammonia (ca. 560 to 800mM) were used as starting materials. The aqueous solutions (100 to 600 μl) were mixed with olivine powder (ca. 0.9 to 1.2g) in ampoules. After purging N₂ gas, the ampoules were sealed and heated for 3-20 days. The reaction products were extracted with MeOH and analyzed using HPLC/MS. The analytical methods were identical to those of Murchison meteorite extracts as previously analyzed [2].

Results and Discussion:

Pyridine and other N-containing cyclic compounds (pyridinecarboxylic acid, piperidine, imidazole and pyrrolidine) with their homologous series were detected in experimental products. Mass chromatograms of C₂- and C₃-alkylated pyridines in Murchison and experimental product are shown in Fig. 1 with some standards. The mass range of alkylhomologues was strongly affected by the amount of olivine. Under higher concentrations or

small amounts of olivine, the range of homologues was not much extended. Since larger alkylpyridines and alkylimidazoles have been predominantly present in Murchison, the amount of minerals is a critical factor for the extent of alkylated homologues. The catalysis could offer adsorption sites on the surface and/or alkaline condition via serpentinization to promote the synthesis of N-containing cyclic compounds. However, the experimental products are poorer in structural isomers and unsaturated alkyl chains, probably due to different CH₃CHO/ HCOOH ratio and duration time between experiments and actual environment.

The simulation experiments demonstrated an importance of not only aldehyde and ammonia activity but also olivine as a catalyst on the parent body. In addition, as aldehyde polymers have been discussed for contribution to meteoritic insoluble organic matter (IOM) [3], the result of this study suggests a common reaction pathway between SOM and IOM.

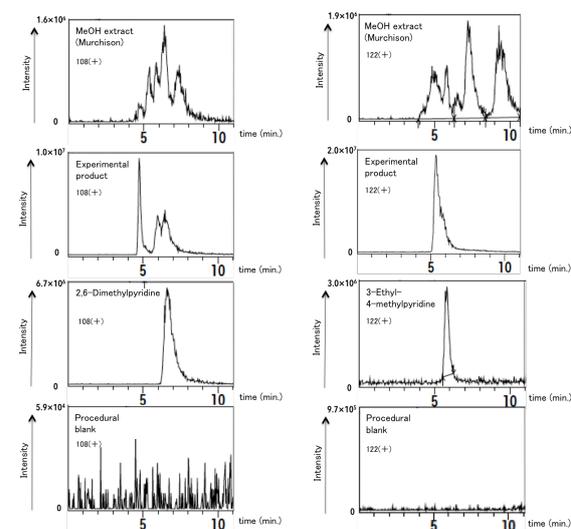


Fig. 1 Mass chromatograms of C₂- (left) and C₃- (right) alkylpyridines in the Murchison MeOH extract (top row), experimental products (2nd row), standards (3rd row) and procedural blank (bottom row).

References:

- [1] Schmitt-Kopplin P. et al. (2010) *Proc. Natl. Acad. Sci.*, **107**, 2763-2768.
- [2] Yamashita Y. and Naraoka H. (2014) *Geochem. J.* in press.
- [3] Kebukawa Y. et al. (2013) *Astrophys. J.*, **771**, 19 (12pp)