METEORITIC ORGANIC MATTER SYNTHESIS INFERRED FROM ALDEHYDES AND AMMONIA WITH OLIVINE. H. Naraoka[1], Y. Yamashita[1], T. Koga[1], Y. Ishibashi[1] and H. Mita[2], [1]Department of Earth and Planetary Sciences, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581 Japan (naraoka@geo.kyushu-u.ac.jp), [2]Department of Life, Environment and Material Science, Fukuoka Institute of Technology, 3-30-1 Wajiro-higashi, Higashi-ku, Fukuoka 811-0295 Japan.

Introduction: Various types of organic matter have been found in carbonaceous meteorites, in which soluble organic matter (SOM) show a variety of polarity, ranging from non-polar hydrocarbons to polar short-chain acids. The significant chemical diversity with tens of thousands of mass peaks having CHO, CHOS, CHNO and CHNOS elemental compositions was reported in SOM of the Murchison meteorite by Fourier transform-ion cyclotron resonance/mass spectrometry (FT-ICR/MS) [1]. However, the detailed chemical structures of individual compounds cannot be determined without any chromatographic separation. Although biologically-interesting organic compounds such as amino acids have been studied, the origins and formation mechanisms of meteoritic organic matter have been little understood. In the previous studies [2, 3], we identified a wide range of N-containing cyclic compounds including alkylpyridines, alkylimidazoles and alkylpiperizines in the methanol extract of Murchison by high-performance liquid chromatography (HPLC)/Orbitrap MS with electrospray ionization (ESI). The extensive alkylhomologues (up to C_{20}) of N-containing cyclic compounds could be produced from aldehydes and ammonia with olivine. In this study, the simulation experiments were performed to explore reaction mechanisms for the occurrence of meteoritic organic matter.

Experimental: Aqueous solution containing aldehydes (HCHO and CH_3CHO) and ammonia were prepared with or without olivine powder in a glass ampoule. A typical ratio of the reaction substrates was approximately 100/1/0.1/0.01 (H_2O/NH_3/HCHO/CH_3CHO) by mol with the olivine/water ratio of 9/1 (w/v). The ampoule were sealed after N_2-purging and heated at 50-100 °C for 3-20 days. The reaction mixtures were analyzed by HPLC/MS with ESI using an amide column in a hydrophilic interaction liquid chromatography (HILIC) mode. Aliquot of some reaction mixtures were also analyzed for amino acids by GC/MS after acid hydrolysis followed by derivatization to N-trifluoroacetyl- and isopropyl esters.

Results and Discussion: Many positive ion peaks having CHN, CHO and CHNO compositions were identified in the reaction mixtures up to m/z ~900 maximizing at m/z ~350. The range of positive ion distribution was similar to that of the Murchison extract [1, 2]. The predominant ion peaks were assigned as CHN compounds including alkylpyridines, alkylimidazoles and alkylpiperazines with their alkylhomologues. The distribution of alkyl-homologues in the products was different depending on the presence or absence of olivine. In the case of alkylpyridines, longer alkylated (up to C_{20}) pyridines were produced using olivine, while only shorter alkylated (up to C_7) ones were identified in the absence of olivine. Thus the olivine surface can serve reaction sites to support elongation of alkyl-chains during aldol condensation for alkylpyridine synthesis. However, the distribution of the alkyl-isomers in the products was different from that of alkylpyridines observed in the methanol extract of Murchison [2], probably because the distribution of alkylpyridine isomers is influenced by many factors (aldehydes composition, substrate concentration and reaction temperature as well as ratios of aldehydes/ammonia and water/olivine).

The occurrence of pyridine carboxylic acids were reported from carbonaceous chondrites [4]. In this study, pyridine carboxylic acids including nicotinic acid were also synthesized using an olivine catalyst. However, no pyridine carboxylic acids were detected in the absence of olivine. The chemical oxidation of unsaturated-alkylated pyridines could be promoted by olivine during heating, which is a similar process during serpetinization on the meteorite parent body [3].

Furthermore, it is interesting to note that N-containing cyclic ketones (lactams) with their carboxylic acids such as pyroglutamic acid were identified in the presence of olivine, while such compounds were not detected during heating without olivine. Because pyroglutamic acid give glutamic acid after hydrolysis, glutamic acid was identified as recemic mixtures by GC/MS in the presence of olivine, while no glutamic acid was detected from the product in the absence of olivine. Thus, this study revealed that the effects of olivine were remarkable as catalysis to control syntheses of biologically-interesting organic compounds including amino acids and pyridine carboxylic acids in carbonaceous chondrites.

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