

Two homologous series of alkyipyridines in the Murchison meteorite

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Two homologous series of alkyipyridines ($C_nH_{2n-5}N$ and $C_nH_{2n-7}N$) were identified in the methanol extract of the Murchison meteorite by liquid chromatography/high-resolution mass spectrometry. The wide range of saturated- and unsaturated-alkylated (C_1 to C_{21}) pyridines is more diverse than previously found, and could be produced by reactions of aldehyde condensation and aldehydes with NH_3 by imine formation in Solar or pre-solar environments. This finding implies a high aldehyde activity under alkaline conditions in the presence of ammonia during the chemical evolution of soluble organic matters detected in a CM2-type carbonaceous meteorite.

Keywords: Murchison meteorite, alkyipyridines, aldehyde, ammonia, Chichibabin synthesis

INTRODUCTION

Many organic compounds have been detected in carbonaceous chondrites (CCs), in particular water-soluble and biologically-interesting organic compounds such as amino acids and carboxylic acids which have been intensively studied because of their great interests for the origins of life in the universe (e.g., Pizzarello *et al.*, 2006; Burton *et al.*, 2012). Their study has also been aided by the availability of commercial standards. However, the concentrations of these acids often increase significantly after acid hydrolysis of the water extract, and although some studies have attempted to identify the chemical structures of their precursors (e.g., Cooper and Cronin, 1995), the original structures remain largely unclear. Since all CCs had been subjected to some extent of aqueous alteration, the nature and composition of the meteoritic organic matter could have been altered by chemical oxidation associated with the aqueous activity. This oxidation could induce incorporation of oxygen into the original organic matter, resulting in the production of O-rich and H_2O -soluble compounds such as carboxylic acids (Oba and Naraoka, 2006). The large abundance of carboxylic acids in CCs (Naraoka *et al.*, 1999) may be due to such oxidation processes.

In contrast to the compounds extracted by water, less altered (i.e., more primitive) compounds may be extracted by less polar solvents (e.g., methanol). These organic matter are more enriched in D and ^{15}N relative to the H_2O

extract (Krishnamurthy *et al.*, 1992). The heavy isotope enrichments suggest that the more primitive organic compounds may have originated partly from an interstellar environment. However, the less polar solvent extracts of CCs have rarely been studied, despite their relatively high content of organic compounds. Recently, ultrahigh-resolution mass spectral analysis on various solvent extracts of the Murchison meteorite (CM2) was performed by electrospray ionization (ESI) using Fourier transformation cyclotron resonance/mass spectrometry (FT-ICR/MS) to reveal significant chemical diversity with tens of thousands of different mass peaks having CHO, CHOS, CHNO and CHNOS elemental compositions (Schmitt-Kopplin *et al.*, 2010). However, without any chromatographic separation, the detailed chemical structures of the individual compounds present cannot be determined. In particular, the organic compounds with their elemental compositions of CH and CHN were not investigated in spite of their potential importance as primitive organic components because the CH and CHN compounds may have escaped chemical oxidation during parent-body aqueous alteration. In this study, we performed high-performance liquid chromatography/high-resolution mass spectrometry (HPLC/HRMS) analysis of polar solvent extracts of the Murchison meteorite in order to characterize the more primitive organic compounds.

SAMPLE AND ANALYTICAL METHODS

HPLC/MS analysis of the solvent extracts of Murchison

The interior fragments of the Murchison meteorites (835 mg) were powdered on a clean bench and extracted sequentially with hexane (Hex, 1.5 mL \times 4), dichloromethane (DCM, 1.5 mL \times 5), methanol (MeOH,

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Table 1. Bulk CHN concentrations and isotopic compositions of solvent extracts from the Murchison meteorite*

	Hex extract	DCM extract	MeOH extract	H ₂ O extract
Carbon (ppm)	18.2	141	304	169
$\delta^{13}\text{C}$ (PDB)	-10.0	0.0	+5.8	-0.3
Hydrogen (ppm)	6.5	8.5	68	208
δD (SMOW)	+234	+680	+665	+152
Nitrogen (ppm)	—	9.4	29.3	71.5
$\delta^{15}\text{N}$ (Air)	—	+50.5	+98.0	+12.0

—: under detection limit.

*The concentrations and isotope values were determined by a single measurement after the calibration using standards.

1.5 mL \times 4), deionized and distilled water (1 mL \times 3) with sonication (15 min). The procedural blank was also performed using pre-heated (500°C for 3 h) sea sand. Each solution of Hex, DCM and MeOH was reduced in volume to 300 μL under N₂ gas flow. The water extract solution was evaporated under vacuum to 500 μL . A portion of each extract was dried to determine their CHN concentrations and stable isotopic compositions ($\delta^{13}\text{C}$, δD and $\delta^{15}\text{N}$), using an elemental analyzer (NA-1500, Fisons) or a high-temperature pyrolyzer (TC/EA, Thermo Scientific) coupled to a stable isotope ratio mass spectrometer (EA-IRMS; Finnigan DELTAplusXL, Thermo Scientific). The silver cup used for EA-IRMS was heated prior to use at 450°C for 1 hour to remove organic contaminants. Each isotope δ -value was determined by a single measurement after calibration using an isotope standard (acetanilide, C₈H₉NO).

Each residual extract was analyzed by HPLC-MS (LCMS-8030, Shimadzu) with an ESI source using an amide column (2.1 \times 250 mm, 3 μm ; Inertsil Amide, GL Science) at 40°C in hydrophilic interaction liquid chromatography (HILIC) mode. For the ESI source, the nebulizing N₂ gas flow was 3 L/min with an interface voltage of 4.5 kV. The temperature of desolvation line was 250°C and the drying N₂ gas flow was 15 L/min. The block heater of sampling cone was operated at 200°C. Full scan mass spectra were taken over a range of m/z 50 to 1500 using a Q3 scan mode. The mass calibration was performed externally using a standard solution of polyethylene glycol (PEG200, PEG600 and PEG1000; Wako) and polypropylene glycol (PPG2000, Wako). The eluent mixture of A (acetonitrile) and B (10 mM HCOONH₄ plus 0.1% HCOOH; pH = 3.8) was used at 0.3 mL/min, where the ratio (A/B) changed by a linear gradient from 99/1 to 70/30. HPLC/HRMS (full width at half maximum; FWHM = 100,000 at m/z 400) and MS/MS analyses with an ESI source were also performed

using an LTQ Orbitrap XL (Thermo Scientific) to determine the elemental composition and chemical structures of the compounds, in which all mass spectra were acquired in positive ion mode. The ESI source was operated with the N₂ gas for desolvation set to 45 for the sheath gas, 15 for the auxiliary gas, and 0 for the sweep gas in arbitrary units. The capillary voltage and temperature of the ion transfer were 35 V and 250°C, respectively. The tube lens was set to 70 V. Full scan mass spectra were taken over a range of m/z 75 to 1500. MS/MS data were collected using data dependent acquisition with a collision-induced dissociation (CID) energy of 35% (isolation with 1 Da). A lock mass mode was employed to calibrate the accurate mass using dioctyl phthalate ([C₂₄H₃₈O₄+H]⁺ = 391.2843), resulting in a general mass accuracy of <1 ppm. The HPLC conditions were similar to those used for HPLC-MS described above. Commercial standards of 2-methylpyridine (C₆H₇N, Wako), 3-methylpyridine (C₆H₇N, Wako), 2,6-dimethylpyridine (C₇H₉N, Wako) and 3-ethyl-4-methylpyridine (C₈H₁₁N, Wako) were also analyzed by HPLC-MS.

Experiments of alkylpyridine synthesis

Synthesis of alkylpyridines was performed as a reference using aldehydes and ammonia in an aqueous solution, also known as the Chichibabin synthesis (e.g., Frank and Seven, 1949; Krishna Mohan *et al.*, 2009). In this study, 100 μL of 16% HCHO (w/v, Thermo Scientific), 60 μL of 90% CH₃CHO (Wako) and 95 μL of 10% NH₃ (Wako) were mixed with 345 μL of ultrapure water (18.3 M Ω ; Millipore Simplicity UV), added to 1.19 g of olivine powder (San Carlos olivine as a catalyst) in a closed ampoule after N₂ gas purging, and then heated at 60°C for 3 days. The substrate concentrations were 0.85 M HCHO, 0.82 M CH₃CHO and 0.85 M NH₃ in the 600 μL solution. After the centrifugation (3000 rpm \times 10 min) of the reaction mixture, the supernatant solution was analyzed by

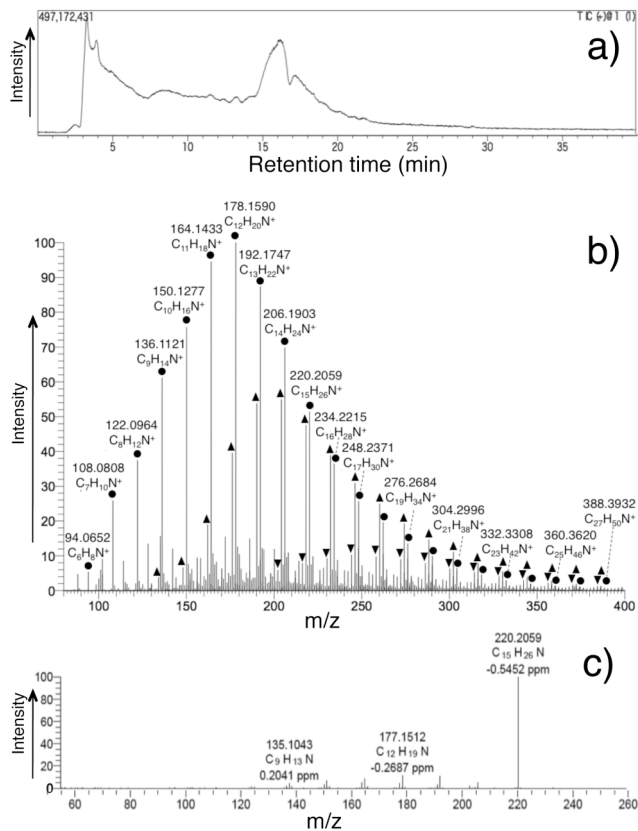


Fig. 1. a) Total ion chromatogram of the MeOH extract from the Murchison meteorite, by HPLC/MS; b) high-resolution mass spectrum ($m/\Delta m = \sim 100,000$ at m/z 400) of the peak in retention time at 3–10 min in a; filled circle: saturated-alkylpyridines, filled triangle (upper): one unsaturated-alkylpyridines, filled triangle (lower): probable two unsaturated-alkylpyridines; c) high-resolution MS/MS spectrum of the precursor ion of m/z 220 in b).

HPLC/MS using an LCMS-8030. The separation column and analytical conditions were similar to those used for analysis of the Murchison extract.

RESULTS AND DISCUSSION

Alkylpyridine occurrence in Murchison

The carbon concentration and $\delta^{13}\text{C}$ value of each fraction are shown in Table 1 and demonstrate that C concentrations in the various extracts show the following order: MeOH extract (304 ppm C, 5.8‰) > H₂O extract (169 ppm C, -0.3‰) > DCM extract (141 ppm C, 0.0‰) > Hex extract (28 ppm C, -10.0‰). The data suggest that most of the carbon is present as polar organic components soluble in water and MeOH, and is relatively ^{13}C -enriched vs. components extracted with DCM and Hex. However, the DCM and MeOH extracts are more enriched in D (+665 and +680‰ vs. +152‰) and $\delta^{15}\text{N}$ (+50 and

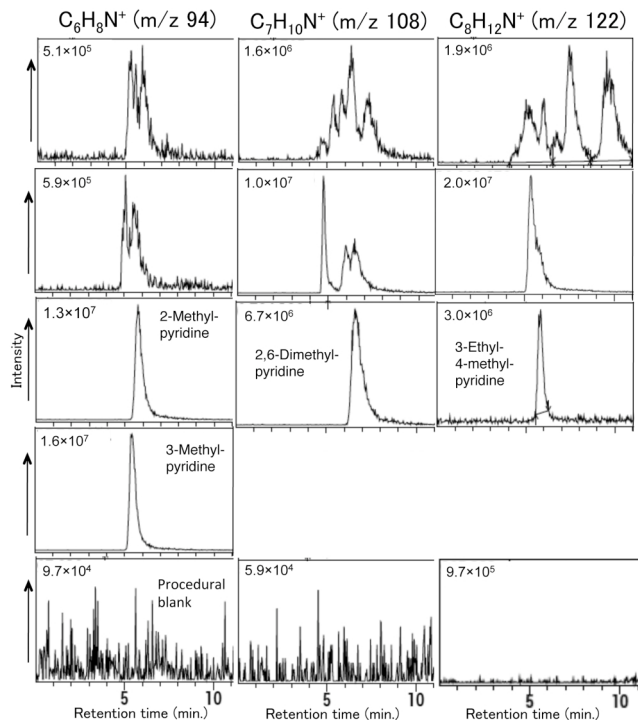


Fig. 2. Partial mass chromatograms of C_1 -, C_2 - and C_3 -alkylpyridines in the MeOH extract of Murchison (top), synthesis experiment (2nd), commercial standards (3rd and 4th) and procedural blank (lowest) by HPLC/MS. Number in each chromatogram denotes the maximum intensity of peak (y-axis).

+98‰ vs. +12‰) relative to the water extract, which is a similar isotope signature to that reported by Becker and Epstein (1982) and Krishnamurthy *et al.* (1992). Considering the high carbon concentration, and the enrichment in ^{13}C , D and ^{15}N , the MeOH extract may be the major repository of exotic organic compounds relative to the other extracts.

The total ion chromatogram for the MeOH extract is shown in Fig. 1a, where two broad peaks with retention times at about 3–10 and 15–20 min. are apparent. These are unresolved and complex mixtures containing mainly mass peaks between m/z 90 and 400. Figure 1b shows a high-resolution mass spectrum of the first peak (retention time 3–10 min.), in which the two series of mass peaks are definitely assigned as $C_nH_{2n-4}N$ ($n = 6$ to 27) and $C_nH_{2n-6}N$ ($n = 9$ to 28) with m/z 14.0156 intervals (i.e., CH_2). Because these masses are protonated during ESI, the original elemental compositions are expressed as $C_nH_{2n-5}N$ and $C_nH_{2n-7}N$, respectively. We further performed MS/MS analysis of m/z 220 ion (Fig. 1c), which mainly produced ions of m/z 220.2059 with minor fragment ions of m/z 220.2059 - 14.0156 $\times n$ ($n = 1$ to 6). The MS/MS analysis indicates that nitrogen is present as cyclic-N, and not in aliphatic chains. In addition, both

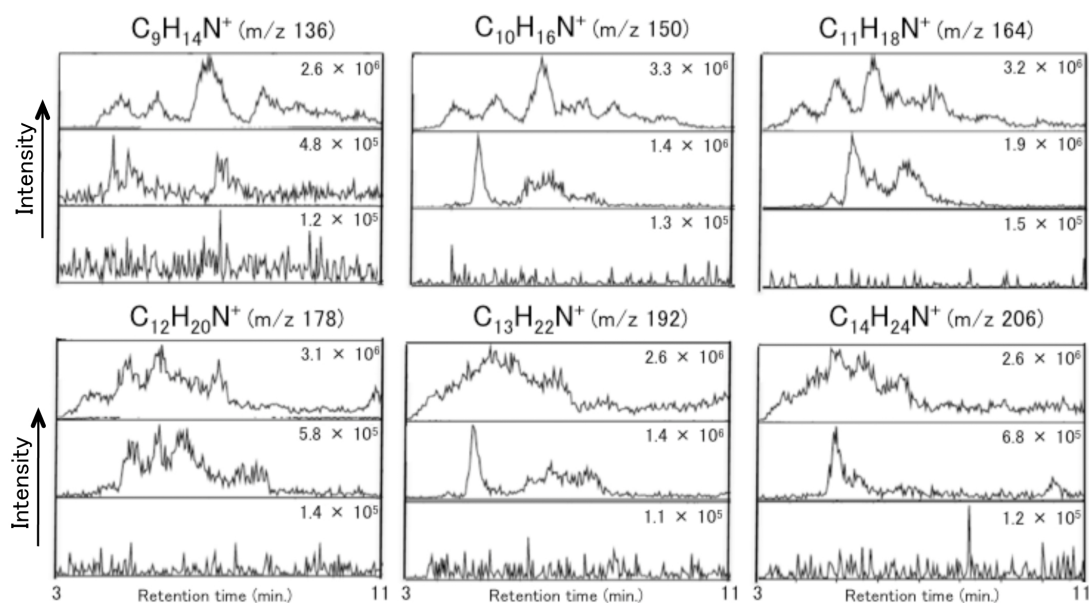


Fig. 3. Partial mass chromatograms of alkylpyridines (C_4 to C_9 alkylated) in the MeOH extract of Murchison (upper), synthesis experiment (middle) and procedural blank (lower) by HPLC/MS. Number in each chromatogram denotes the maximum intensity of peak (y-axis).

series do not show mass peaks $m/z < 80$, suggesting a pyridine ($C_5H_6N^+$, protonated) core for the cyclic-N structure. In addition, Fig. 2 compares chromatograms of C_1 , C_2 and C_3 -pyridines in the MeOH extract and the experimental product (see below) with those of standards and procedural blank. The retention times of meteoritic alkylpyridine peaks match well to those of standards, even though many alkylpyridine standards are not available. Therefore, the two homologues of N-containing compounds are identified as saturated alkylated-pyridines ($C_nH_{2n-5}N$ series) and one-unsaturated alkylated-pyridines ($C_nH_{2n-7}N$ series). Very small amounts of two-unsaturated alkylated-pyridines ($C_nH_{2n-9}N$ series) are also likely to be present between $n = 14$ and $n = 24$ (Fig. 1b). The unsaturated pyridines with $<C_5$ were not observed, while the larger alkylpyridines contain more unsaturated alkylated chains. In particular, for the pyridines with $>C_{14}$, the one-unsaturates were predominant relative to the corresponding saturates.

Alkylpyridines were found in the Murchison extract by gas chromatography analysis (Hayatsu *et al.*, 1975; Stoks and Schwartz, 1982; Pizzarello *et al.*, 2001). However, only alkylated pyridines up to C_5 have previously been reported including trimethyl-, methylethyl-, tetramethyl-, ethyldimethyl-, and diethylmethylpyridines. In contrast, this study revealed the presence of larger (up to C_{23} -alkylated) and more diverse (one- and probably two-unsaturated) alkylpyridines in the Murchison meteorite. The different molecular distribu-

tion between previous studies and this study is probably due to the different analytical methods (GC vs. HPLC) employed as well as the different extraction methods (water and acid extracts vs. DCM and MeOH extracts). Using a 3-ethyl-4-methylpyridine ($C_8H_{11}N$, Wako) standard for calibration, the concentration of C_3 -alkylated pyridines is estimated to be ~ 1.1 ppm. Because no commercial standards were available for most of the alkylpyridines detected in this study, the response factor for all other alkylpyridines was assumed to be similar to that for 3-ethyl-4-methylpyridine, which results in an estimate of 30 ppm for the total concentration of C_1 – C_{23} alkylated pyridines. This estimate is similar or slightly larger to those previously reported for alkylpyridines and alkylpyridine carboxylic acids in the Murchison meteorite (Pizzarello *et al.*, 2001).

Alkylpyridine formation from aldehydes and ammonia

It is known that alkylpyridines can be produced from aldehydes and NH_3 (the Chichibabin synthesis). In the reference experiments, olivine powder was used as a catalyst to promote the reaction, as an example mineral present in the meteorite parent body. However, the relatively high concentrations of substrate (~ 0.8 M), the aldehydes/ NH_3 ratio ($\sim 2/1$ by mol) and the solution/olivine (water/rock) ratio ($\sim 1/2$ by weight) were significantly different than those present in CCs, so the reaction conditions of this study may not have accurately stimulated the reactions that occurred in the meteorite. Nevertheless, various

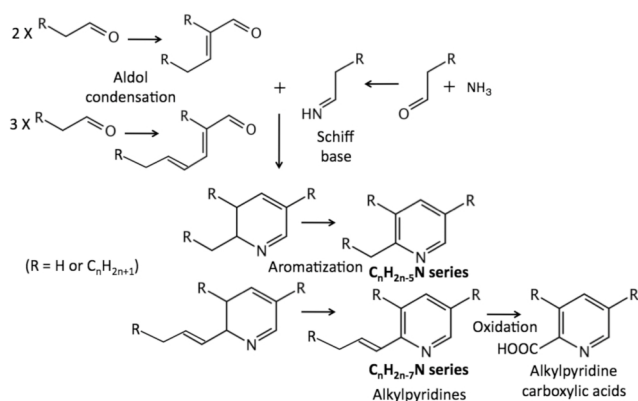


Fig. 4. Probable formation pathway of alkylpyridines and alkylpyridine carboxylic acids observed in carbonaceous meteorites through the Chichibabin synthesis.

alkylpyridines were confirmed in the reaction products (Figs. 2 and 3). In particular, the mass chromatograms of m/z 164 ($C_{12}H_{20}N^+$, C_7 -alkylated pyridines) are similar between the Murchison extract and the reaction product. However, the mass chromatograms for the other alkylated pyridines (e.g., $C_{10}H_{16}N^+$ and $C_{13}H_{22}N^+$) show significant differences between the Murchison extract and the synthesis products, which could be due to different reaction conditions (e.g., materials, concentration, temperature and duration) between the conditions of the synthesis reaction and the actual conditions experienced by the parent body. In the synthesis experiments performed to date, the alkylpyridine distribution has been greatly influenced by many factors including the substrate concentration, reaction temperature and duration as well as the ratios of aldehydes/ammonia and water/rock ratios, and the presence or absence of olivine. However, the overall results from our experiments suggest that alkylpyridines in the Murchison extract were likely formed by the reaction of aldehydes with ammonia in the asteroidal parent body.

A possible reaction mechanism of alkylpyridine formation is shown in Fig. 4. Aldehydes are subjected to aldol condensation under alkaline conditions to form unsaturated- and branched-alkylaldehydes (i.e., aldol condensation), followed by the reaction with alkylimine (Schiff base) formed from aldehyde and ammonia (and alkylamine) to produce di- and tri-alkyl (possibly tetra-alkyl) substituted pyridines. Therefore, the pyridines alkylated up to C_{23} in this study could be di- and tri-alkyl substituted with each alkyl-chain containing up to C_8 , which is consistent with the results that longer ($>C_{10}$) aliphatic hydrocarbons were not detected by pyrolysis of the MeOH extract using a Curie point pyrolyzer-GC and that the more unsaturated alkylpyridines were predominant at higher molecular weights.

Implications of alkylpyridine occurrence to chemical evolution in meteorites

The occurrence of a wide range of alkylated (C_1 to C_{21}) pyridines in the MeOH extract of Murchison suggests a significant activity of aldehydes and ammonia under alkaline conditions. Relatively simple aldehydes such as formaldehyde and acetaldehyde can be found in molecular clouds, and may have been present in protoplanetary disks and primordial solar nebulae (e.g., Charnley, 2004; Tielens, 2005; Snyder, 2006; Dutrey *et al.*, 1997). Formation of a formaldehyde polymer by aldol condensation has been emphasized for a possible origin of insoluble organic matter (IOM) in meteorites (Cody *et al.*, 2011; Kebukawa *et al.*, 2013). This study further indicates a contribution of aldol condensation products to soluble organic matter (SOM). Ammonia is also commonly observed in molecular clouds as well as comets, and is abundant in carbonaceous chondrites (Pizzarello and Williams, 2012). The prominent activity of aldehydes and ammonia in SOM has been also suggested by relatively abundant amino acids, in which aldehydes and ammonia are key components to produce the amino acid precursors through Strecker reactions (Lerner and Cooper, 2005; Burton *et al.*, 2012). These results show an importance of alkaline environments with significant ammonia activity for the chemical evolution of meteoritic organic matter.

It is intriguing to speculate whether the aldehydes are inherited from the interstellar medium or produced by a catalytic reaction of H_2 and CO known as a Fischer-Tropsch type (FTT) reaction in the primordial solar nebulae (Anders *et al.*, 1974). The conditions necessary to promote the reactions are also ambiguous. The reactions between HCHO and NH_3 to produce imines in interstellar ice may be plausible at very cold temperatures (Chen and Woon, 2011), although N-containing heterocycles including pyridine, have not been detected in interstellar environments, which indicates their absence or very low abundance (Charnley *et al.*, 2005). In contrast, the alkylpyridines could be produced from aldehydes and ammonia in liquid water at $\sim 50^\circ C$; a temperature similar to that estimated for the parent bodies of CCs (e.g., Guo and Eiler, 2007). Therefore, the alkylpyridines should be a candidate for more primitive organic compounds in meteorites. In comparison, chemical oxidation process could be effected by OH radicals or aqueous alteration on the parent bodies, in which the progressive oxidation of methylene carbon yields alcohol to ketone followed by carboxylic acid (Cody and Alexander, 2005; Oba and Naraoka, 2006). The carbon double bond in unsaturated alkylpyridines would easily be oxidized to yield alkylpyridine carboxylic acids and dicarboxylic acids, being consistent with the reports that various alkylpyridine carboxylic acids are present in CCs (Stoks and Schwartz,

1982; Pizzarello *et al.*, 2001; Smith *et al.*, 2014).

Hence, further simulation experiments and compound-specific isotope analyses ($\delta^{13}\text{C}$, δD and $\delta^{15}\text{N}$) of alkylpyridines and simulation experiments are promising for the better understanding of their origins and formation environments in molecular clouds and/or primitive solar nebulae.

SUMMARY

A suite of saturated- and unsaturated-alkylated (C_1 to C_{21}) pyridines were found in the dichloromethane and methanol extracts of the Murchison meteorite, which could be produced by the reaction of aldehydes and NH_3 through aldol condensation and Chichibabin-type synthesis on the meteorite parent body. Although the aldehyde polymers have been discussed for contribution to the insoluble organic matter, this result indicates the probable importance of aldehyde activity under alkaline conditions in the presence of ammonia for the chemical evolution of soluble organic matter in carbonaceous meteorites.

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