

NITROGEN SYSTEMATICS DURING HYDROTHERMAL SYNTHESIS OF INSOLUBLE ORGANIC MATTER: SPECIATION AND PH EFFECTS. D. I. Foustoukos, G. D. Cody and C. M. O'D. Alexander, Earth & Planets Laboratory, Carnegie Institution of Washington, Washington DC 20015, USA. (dfoustoukos@ciw.edu).

Introduction: Despite the abundant presence of N in the insoluble organic matter (IOM) isolated from carbonaceous chondrites [1], very little is known about the change in N isotope systematics and speciation during IOM hydrothermal alteration [2, 3]. Previous experimental studies that there is loss of labile N-functional groups during hydrothermal alteration, and a minimal degree of chemical and isotope exchange of N between IOM and the aqueous solutions [4-6]. All the previous studies have been conducted at near-neutral fluid pH conditions. However, alkaline pH conditions have been suggested to promote the synthesis of N-functional groups during aldehyde condensation in N-bearing solutions [7] and to enhance the stability of C-O functional groups during glucose carbonization [8]. Here, we present experimental data to address the effect of pH on the N systematics during hydrothermal synthesis of IOM-analog (syn-IOM) material.

Experimental methods: Hydrothermal experiments of syn-IOM synthesis were performed (150 - 200 °C) to determine the degree of N incorporation in the structure of the organic residue as a function of the fluid pH. The syn-IOM was synthesized by dextrose carbonization under vapor saturation pressures [4]. Reaction times varied from 0.5 to 260 hours. The reactant H₂O solutions were enriched with: (i) NH₄Cl (0.21-2.8 M) at neutral pH, (ii) NH₄Cl (0.5 M) at acidic conditions (0.08 M HCl); (iii) NH₄Cl (0.17-1.93 M) at alkaline conditions (1N NaOH), and (iv) NaCN (0.1 - 0.5 M) solutions that rendered alkaline pH conditions. The starting H/C ratio was ~ 2.07 (dextrose), while the N/C₀ atomic ratios varied from 0.02 to 0.577.

The H-C-N elemental and isotopic analyses were performed with Thermo Scientific Delta V^{Plus} and XL⁺ mass spectrometers by following procedures of [4].

Results and Discussion: Results show that the H/C atomic ratios ranged from ~ 0.85 to 1.4 with a median value of 1.06 (±0.15). At 200 °C, the median H/C ratio was attained within 3 h. However, for a similar H/C evolution at 150 °C longer reaction times were required (Fig. 1). Overall, the extent of H/C variability between the residues was much smaller than the variability of the N/C atomic ratios.

The extent of N incorporation into the syn-IOM depends on the concentration and speciation of N dissolved in the coexisting aqueous solutions (Fig. 2). The attained N/C atomic ratios of the syn-IOM were strongly dependent on the N/C atomic ratios of the starting aqueous solution (N/C)₀. Approximately 15-

30% of the initial N composition was incorporated in the IOM structure. Surprisingly, temperature did not affect the extent of N update, which, appears to be governed by the speciation of N in the aqueous solutions.

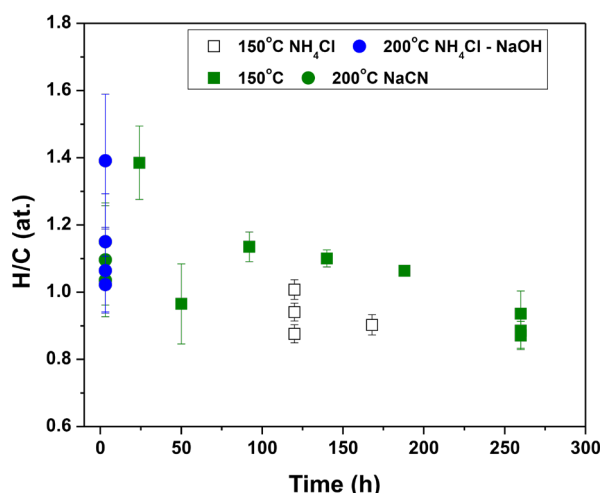


Figure 1. H/C atomic ratios as function of the reaction time.

N systematics: The experiments revealed that incorporation of N into the syn-IOM structure appears to be strongly dependent on the abundance of N-H-bearing aqueous species in solution, but with minimal influence from temperature (Fig. 2). This process likely involves retro-aldol or aldehyde condensation reactions during sugar decarbonylation or formaldehyde condensation [7, 9, 10]. Ammonia has been shown to enhance the yields and the kinetics of synthesis of syn-IOM formed by formaldehyde condensation [11, 12]. Similar results are reported for hydrothermal decarbonylation of sugars [13].

In our study, higher yields of N incorporation were obtained at the elevated pH conditions attained in the NaCN and NaOH-bearing experiments. Under alkaline conditions, the attained N/C atomic ratios were nearly an order of magnitude higher than those measured during synthesis at near-neutral pH conditions. Strong acid conditions inhibited N incorporation, suggesting that pH conditions affect IOM synthesis either by promoting the stability of NH_{3(aq)} relative to NH₄⁺ or by enhancing the formation of N-enriched compounds such as pyrazines and pyridines during sugar decarbonylation [9].

Thus, we hypothesize that the observed pH effect may be associated with either the molecular structure

of the residues (Fig. 3) or the relative abundance of $\text{NH}_{3(\text{aq})}$ and NH_4^+ in solution. Alkaline pH has also been inferred as the optimum condition for alkylpyridines synthesis by aldehyde condensation in the presence of $\text{NH}_{3(\text{aq})}$ at 60 °C [7]. Redox conditions have also been hypothesized to play a key role in the distribution of alkylpyridines (oxidizing) and alkylpiperidines (reducing) in organic matter synthesized by aldehyde condensation in the presence of $\text{NH}_{3(\text{aq})}$ [14]. In our study, redox conditions were not buffered, but aqueous speciation modeling precludes the presence of oxidized N species (e.g., NO_3^-) in solution.

Experiments with ^{15}N -bearing KCN and NH_4Cl aqueous alkaline solutions are in progress to determine the N speciation in the structure of syn-IOM.

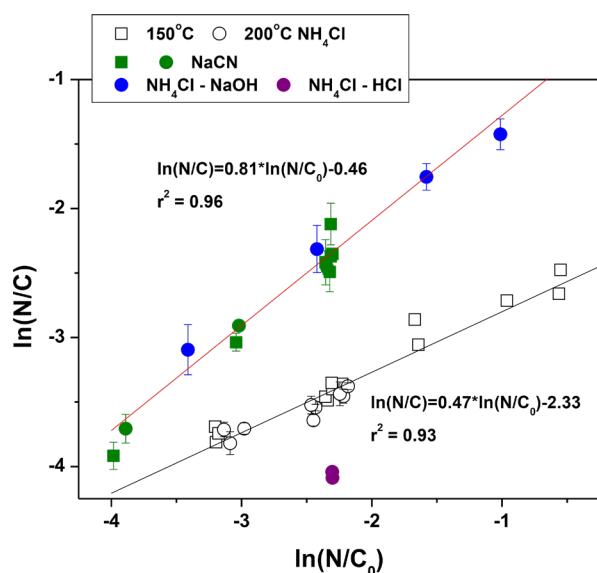


Figure 2. N systematics during synthesis of syn-IOM. N/C_0 corresponds to the composition of the starting mixture of aqueous solution and dextrose.

Molecular Structure: The molecular structure of the C-functional groups depicted by ^{13}C SSNMR analysis also differs between the residues synthesized under near-neutral and alkaline conditions (Fig. 3). Under alkaline pH (i.e., NaCN-bearing experiments) residues are significantly enriched in $\text{CH}_2\text{-O}$ relative to the residues developed at more acidic conditions (i.e., NH_4Cl -bearing experiments). The carboxylic (R-COOH) and the methyl (R-CH_3) functional groups also attained higher abundances. By contrast, the furan fraction of the aromatic C is strongly depleted under alkaline pH. A similar pattern is observed for the carboxyl C (C=O). It appears, therefore, that the stability of the O-bearing aliphatic C has been enhanced at the expense of the O-bearing aromatic functional groups. These

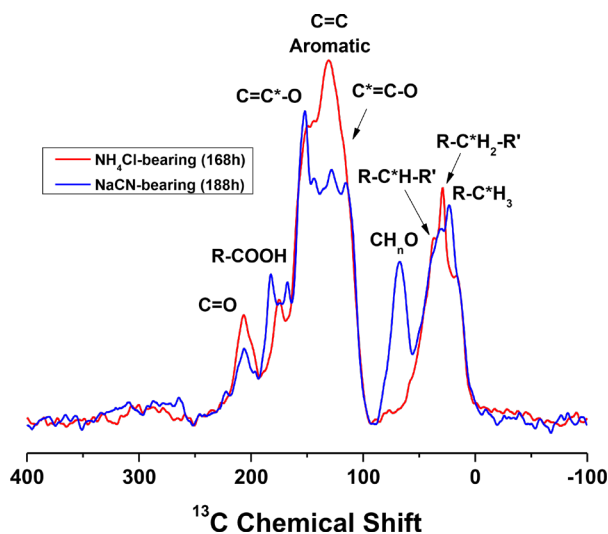


Figure 3. ^{13}C SSNMR spectra of residues synthesized at 150 °C. The NH_4Cl -bearing and NaCN-bearing experiments were conducted at near-neutral and alkaline pH, respectively.

results are in agreement with hydrothermal glucose carbonization experiments performed at 180 °C in the presence of urotropine-bearing alkaline aqueous solutions [8].

The apparent stability of the C-O functional groups in the syn-IOM structures developed under hydrothermal alkaline conditions is expected to have important implications for understanding the extent and kinetics of H and O isotope exchange mechanisms during hydrothermal synthesis and alteration of chondritic IOM.

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