

Simulated diagenesis and catagenesis of marine kerogen precursors: Melanoidins as model systems for light hydrocarbon generation

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(Received 16 September 1985; accepted 9 January 1986)

Abstract—Amino acids and sugars are principal constituents of marine organisms. The condensation of amino acids and sugars is one possible non-enzymatic, early diagenetic pathway for the incorporation of these compounds into more complex geopolymers. In this study, aqueous solutions consisting of L-lysine, L-histidine, L-arginine and D-(+)-glucose were heated (100°C) for up to 288 h. Portions of the melanoidin polymer isolated after heating were reheated in the presence of water (hydrous pyrolysis) for 72 h at 325°C. Reaction products were identified by GC and GC/MS. Stable isotopic ($\delta^{13}\text{C}$) and elemental analyses were used to follow thermal evolution.

While the initial melanoidin was synthesized from a simple, four component system, the products generated during hydrous pyrolysis are of considerable complexity, and include straight-chain and branched alkanes, alkadienes, alkynes, indole, dimethyl indane, ethyl phenol, quinoline, and xylenes, in addition to a multitude of as yet, unidentified components. Stable carbon isotopic values for the reactants and products correspond to trends observed for naturally generated geopolymers and light gases. Elemental analyses of the melanoidin prior and subsequent to hydrous pyrolysis indicate a kerogen evolution pathway similar to that observed for natural samples. Considering the intractable nature of kerogen, laboratory simulation studies of simple systems can provide an alternative approach for elucidating the origins of geopolymers and their potential for hydrocarbon generation.

Key words: melanoidin, hydrous pyrolysis, carbon isotopes, diagenesis (simulation), catagenesis (simulation), hydrocarbons, heterocyclics, gas chromatography/mass spectrometry

INTRODUCTION

Proteins and carbohydrates are principal constituents (up to 80% of dry cell material) of marine organisms e.g. algae (Harvey, 1969). Upon an organism's death, these biopolymers are commonly cleaved by microbially mediated enzymatic reactions and non-enzymatic, i.e. hydrolysis reactions, resulting in peptides, free amino acids and sugars. While these compounds provide an important food source for other organisms, it has been proposed for some time that a portion of these biomonomers may condense via non-enzymatic reactions into more complex, polymer-like materials, e.g. melanoidins. The Maillard reaction, i.e. melanoidin synthesis (Maillard, 1912; Hodge, 1953), is an early diagenetic pathway that may contribute to the initial formation of humic material in sea water and recent marine sediments via the condensation of amino acids and sugars (Abelson, 1959; Nissenbaum and Kaplan, 1972; Hoering, 1973; Hedges, 1978). Humic materials that are structurally and chemically very similar to laboratory synthesized melanoidins have been isolated from recent sediments and sea waters (e.g. Nissenbaum and Kaplan, 1972; Ertel and Hedges, 1983).

The intractable nature of geopolymers such as humic material and kerogen, and synthetic melanoidin polymers has resulted in pyrolytic procedures as the methods of choice for the characterization of these materials. In addition to the elucidation of

structure (e.g. Boon *et al.*, 1984), pyrolytic techniques have also been employed to evaluate hydrocarbon (oil and gas) generation potential of ancient kerogens (e.g. Evans and Felbeck, 1983a), Recent sediments (Ishiwatari *et al.*, 1977; Rohrbach *et al.*, 1984) and possible kerogen precursors (Jurg and Eisma, 1964; Thompson and Creath, 1966; Philippi, 1977; Larter and Douglas, 1980; Ioselis *et al.*, 1983b; Evans and Felbeck, 1983b; Wilson *et al.*, 1983).

While the majority of these pyrolysis experiments have been conducted under anhydrous conditions, it has recently been suggested that, in some cases, pyrolysis in the presence of water, may, with respect to the generation of aliphatic hydrocarbons, simulate natural conditions more closely than conventional, anhydrous pyrolytic methods (Lewan *et al.*, 1979; Lewan, 1983; Hoering, 1984).

Ioselis *et al.* (1983a) reported the generation of light hydrocarbons ($\text{C}_1\text{--C}_4$) from synthetic melanoidins using an anhydrous pyrolytic technique. The light hydrocarbons released from the synthetic melanoidins appeared comparable to those evolved by the pyrolysis of immature, humic materials. In the present study, results are presented with respect to the generation of light hydrocarbons from a synthetic melanoidin that was pyrolyzed in the presence of water (hydrous pyrolysis). The elemental and stable carbon isotopic compositions of the reactants and products are discussed, as well as the generation of non-hydrocarbon components.

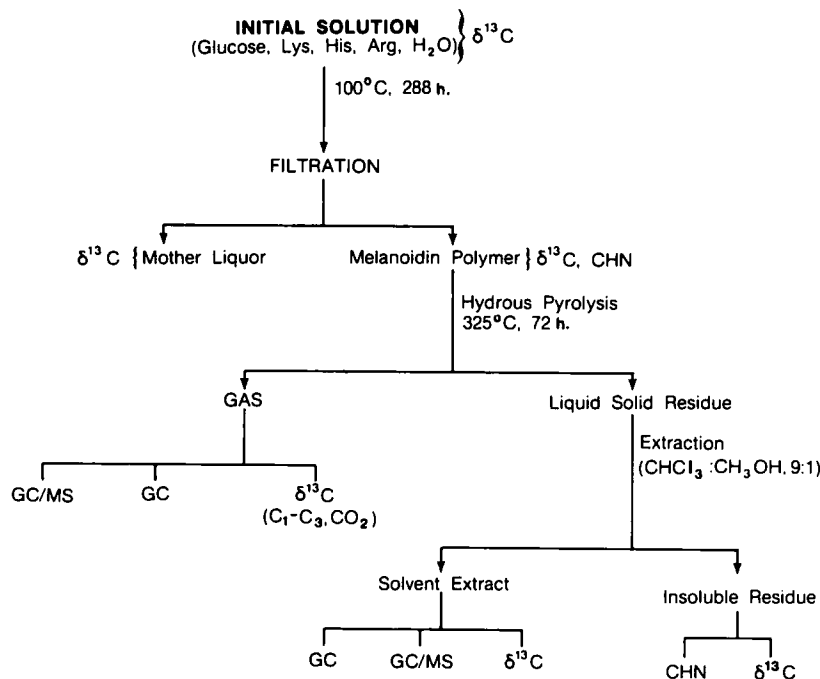


Fig. 1. Summary of the experimental methods.

EXPERIMENTAL METHODS*

A. Melanoidin synthesis

The melanoidin polymer was prepared from an aqueous solution consisting of L-lysine · HCl (0.05 M), L-histidine (0.05 M), L-arginine · HCl (0.05 M) and D-glucose (0.5 M), pH = 7.5. Two-milliliter aliquots of the solution were sealed in Pyrex tubes and heated at 100°C for 288 h. The resultant melanoidin polymer was isolated from the mother liquor by centrifugation followed by filtration with 0.45 µm Gelman Metrical, type VF-6 filters. The melanoidin polymer was rinsed extensively with distilled water.

The individual reactants, the starting aqueous solution, the melanoidin polymer and the mother liquor remaining after isolation of the polymer were analyzed for their respective stable carbon isotopic compositions using the procedure of Sofer (1980). A portion of the melanoidin polymer previously cleaned by Soxhlet extraction with chloroform:methanol (9:1) was analyzed for its elemental composition using a Perkin Elmer # 240 CHN elemental analyzer.

B. Hydrous pyrolysis

One-gram, 0.5 and 0.25 g portions of the remaining dry, water-washed melanoidin polymer were placed in separate 71 ml volume capacity stainless steel high pressure Parr Bombs (bombs A, B and C, respectively) equipped with glass liners and SNO-TRIK high pressure valves. Thirty-milliliters of distilled, deionized water was added to each bomb. The bombs were purged with helium and sealed under an initial helium pressure of 50 lb/in². An additional bomb (bomb D), containing only 30 ml of water and helium, served as a blank. The bombs were heated for 72 h at 325°C and subsequently allowed to cool to room temperature (~2 h).

C. Analysis of pyrolysis products

Portions of the headspace gases of each bomb were sampled and analyzed for their respective light hydrocarbon

compositions. The GC analyses were performed with a Hewlett-Packard 5840 gas chromatograph equipped with gas sampling valves, a 1.8 m × 3.2 mm o.d. stainless steel column packed with *n*-octane on Poracil C (100–120 mesh) and an FID detector. Analytical conditions were: oven temperature, 50–90°C at 10°C/min; carrier gas (He), 25 ml/min. The gas samples were allowed to equilibrate in an open ended 1 ml injection loop prior to injection. Higher molecular weight components (C₅₊) were eluted from the column by backflushing 3.1 min after injection.

One-milliliter of the headspace gas of bomb A was analyzed for higher molecular weight hydrocarbons (C₅₊) by injection onto a Hewlett-Packard 5880A GC equipped with an FID detector and a 50.0 m × 0.25 mm i.d. fused silica column coated with OV-101 (oven temperature, 25°C for 5 min, then 35–60°C at 0.5°C/min; carrier gas (He), 2.5 ml/min).

A portion of the headspace gas of bomb B was sampled to determine the stable carbon isotopic compositions of individual gases that evolved during hydrous pyrolysis, i.e. CO₂, CH₄, C₂H₆ and C₃H₈. These gases were separated with an Antek gas chromatograph equipped with a thermal conductivity detector (Gow-Mac, 10-077) and a 4.5 m × 6.0 mm o.d. stainless steel column packed with Porapak Q (50/80 mesh). The individual gases (except CO₂) were combusted at 950 ± 50°C in a directly attached 20 × 1.3 cm o.d. quartz combustion tube packed with ground cupric oxide wire. The combusted gases were collected with a six-port cold trap (liquid N₂) fixed with vacuum tight solenoid valves. One of the traps was configured so that CO₂ initially present in the gas would bypass the combustion furnace and be collected directly. Details of the separation and combustion procedures are reported in Schiefelbein (1983). Stable carbon isotopic analyses of the individual gases were performed with a Micromass 602D mass spectrometer (Sofer, 1980).

A portion of the headspace gas of bomb A was analyzed for its organic composition by combined gas chromatography/mass spectrometry (GC/MS). In order to remove CO₂ from the sample prior to GC/MS analysis, 80 ml of the headspace gas (94 lb/in²) was introduced into an evacuated

*The experimental methods are summarized in Fig. 1.

glass cylinder that contained 90 ml of a saturated solution of BaOH. Some acidic components (e.g. organic acids, phenols) were probably partially or totally removed by this procedural step. A 5 μ l sample of the remaining gas was injected into a Carlo Erba G.C. (split, 5:1) equipped with a 30 m \times 0.25 mm i.d. fused silica capillary column coated with SE-54 [oven temperature: 35°C for 5 min, then 35–85°C at 0.5°C/min, held for 15 min at 85°C; carrier gas (He) 0.5 ml/min]. A Kratos MS-25 mass spectrometer equipped with a Nova 4X computer and a DS-55 data system served as the detector. Mass spectra of individual components were obtained in the electron impact (EI) mode with a 70 eV electron beam energy and an accelerating voltage of 2 kV.

After the above described gas analyses, the remaining materials in bombs A and B were extracted with chloroform:methanol (9:1). Portions of the solvent extracts were evaporated to dryness under N₂ at 40°C and the residues were combusted for stable carbon isotopic analyses as described above. Similarly, portions of the dry, solvent extracted, pyrolyzed melanoidin were analyzed for their respective stable carbon isotopic compositions. A portion of the pyrolyzed melanoidin recovered from bomb A was also analyzed for its elemental composition. Finally, aliquots of the solvent extract of bomb A were analyzed directly by GC and GC/MS. The analytical conditions were similar to the ones used for the headspace gas in bomb A with the exception of the oven temperature program for GC/MS (100°C for 5 min, then 100–290°C at 2.5°C/min).

RESULTS AND DISCUSSION

The reactants, L-lysine, L-histidine, L-arginine and D-glucose were selected for this synthesis because (1) the basic amino acids react rapidly with reducing sugars to form insoluble melanoidin polymers; a consequence, in part, of the presence of additional, reactive amine functional groups (Engel and Hare, 1982), (2) the reactions of basic amino acids and glucose to form melanoidins have been previously studied (e.g. Engel and Hare, 1982; Rubinsztain *et al.*, 1984), (3) basic amino acids are present in significant concentrations in sea waters (Mopper and Lindroth, 1982) and (4) free glucose has been reported as one of the more common monosaccharide constituents in acid hydrolyzates of Recent marine sediments (Cowie and Hedges, 1984; Klok *et al.*, 1984) and, more recently, in acid hydrolyzates of woody tissues preserved in Recent marine sediments (Hedges *et al.*, 1985). An excess of glucose was used as it has previously been reported that carbohydrates appear to be more abundant than peptides in Recent marine sediments (Klok *et al.*, 1983).

A. Stable isotopes

The stable carbon isotopic compositions of the reactants and products are listed in Table 1. In contrast to the initial solution ($\delta^{13}\text{C} = -10.76\text{‰}$), the melanoidin polymer was depleted in carbon-13 ($\delta^{13}\text{C} = -13.50\text{‰}$), while the mother liquor was enriched ($\delta^{13}\text{C} = -7.13\text{‰}$). The $\delta^{13}\text{C}$ values of the reactants (Table 1) might lead to the speculation that histidine, the precursor that was most depleted in carbon-13, was preferentially incorporated into the melanoidin polymer. The overall complexity of the condensation, decomposition and rearrangement re-

Table 1. Stable carbon isotope values for reactants and products

Samples	(‰*) $\delta^{13}\text{C}$
Reactants	
L-lysine	-11.58
L-arginine	-12.01
L-histidine	-18.81
D-glucose	-9.82
Initial solution (D-glucose, 0.5 M; L-lys, 0.05 M; L-his, 0.05 M; L-arg, 0.05 M)	-10.80† -10.76‡
Products	
A. Melanoidin synthesis (288 h, 100°C)	
1. Mother liquor	-7.13
2. Melanoidin polymer	-13.50
B. Hydrous pyrolysis (72 h, 325°C)	
1. Solvent extract (bomb A)	-12.55
2. Pyrolyzed melanoidin (bomb A)	-13.33
3. Solvent extract (bomb B)	-13.20
4. Pyrolyzed melanoidin (bomb B)	-13.43
5. Gases (bomb B)	
a. CO ₂	-13.0
b. CH ₄	-22.8
c. C ₂ H ₆	-17.9
d. C ₃ H ₈	-17.4

*Data are reported as $\delta^{13}\text{C}$, ‰ relative to PDB standard and corrected for ¹⁷O contribution.

†Calculated value based on the concentration of the individual components in the solution.

‡Actual measured value.

actions taking place during melanoidin formation, however, preclude evaluation of the stable carbon isotopic composition of the mother liquor and melanoidin polymer based on a simple mass balance.

The only sources for nitrogen in the melanoidin polymer are the amino acids. It may therefore be inferred from elemental nitrogen composition (Table 2) that a higher molar ratio of amino acids to glucose was incorporated in the polymer product than was present in the starting solution. A similar observation has been previously reported by Hedges (1978). Since the reactant amino acids are depleted in carbon-13 relative to glucose, this may partially explain the observed carbon-13 depletion of the melanoidin polymer.

An additional mechanism that may be responsible for the $\delta^{13}\text{C}$ depletion of the melanoidin relative to the starting solution could be the decarboxylation of the amino acids. Amino acid decarboxylation via Strecker degradation during melanoidin formation is well documented (Hodge, 1953). Abelson and Hoering (1961) have shown that, in general, the carboxyl group(s) of an amino acid is significantly enriched in carbon-13. The loss of the carboxyl group would, therefore, leave behind a molecule depleted in

Table 2. Elemental compositions

Samples	% Composition				Atomic ratios		
	C	H	N	O*	H/C	O/C	N/C
Initial solution†	41.1	6.9	5.5	46.5	2.01	0.85	0.11
Melanoidin polymer	57.7	5.2	7.2	30.9	1.08	0.40	0.11
Pyrolyzed melanoidin	72.8	4.3	7.2	15.7	0.71	0.16	0.08

*Oxygen determined by difference.

†Initial solution: D-glucose, 0.5 M; L-lys, 0.05 M; L-his, 0.05 M; L-arg, 0.05 M.

carbon-13. A similar mechanism has been invoked for natural systems. Nissenbaum (1974) has reported a depletion in carbon-13 for humic materials resulting from the condensation of amino acids and sugars in marine environments. He attributed the depletion of carbon-13 in the resultant polymeric material to the loss of carbon-13 enriched carboxyl groups during synthesis.

While the melanoidin polymer was depleted in carbon-13, the mother liquor was enriched. A possible explanation for this phenomenon may be the presence of carboxy- and/or carbonyl-containing compounds in the mother liquor. The carbon of these functional groups is reported to be enriched in carbon-13 (Abelson and Hoering, 1961; Galimov, 1980). Although the mother liquor was not analyzed for compounds containing these functional groups, their presence as products of the Maillard reaction has been reported (Hodge, 1953). Moreover, the drop in pH (7.5 to 3.4) of the aqueous solution during melanoidin formation cannot be accounted for entirely by CO₂ production, thereby suggesting the formation of other acidic species.

After hydrous pyrolysis, the remaining residues in bombs A and B were, at most, only slightly enriched in carbon-13 ($\delta^{13}\text{C} = -13.33\text{‰}$ and $\delta^{13}\text{C} = -13.43\text{‰}$, respectively) relative to the melanoidin starting material ($\delta^{13}\text{C} = -13.50\text{‰}$). This observation is in agreement with previous findings of no change or only very slight enrichment in carbon-13 abundances for naturally occurring marine kerogens and humic materials that were subjected to thermal alteration (Nissenbaum, 1974; Ishiwatari *et al.*, 1977; Lewan, 1983).

With respect to the stable carbon isotopic compositions of light gases that evolved during hydrous pyrolysis of the melanoidin polymer, CO₂ was slightly enriched in carbon-13 ($\delta^{13}\text{C} = -13.0\text{‰}$). A significant isotope depletion effect, however, was observed for CH₄ ($\delta^{13}\text{C} = -22.8\text{‰}$), and, to a lesser extent, for C₂H₆ ($\delta^{13}\text{C} = -17.9\text{‰}$) and C₃H₈ ($\delta^{13}\text{C} = -17.4\text{‰}$). This observed depletion in carbon-13 for CH₄ generated via the hydrous pyrolysis of a synthetic melanoidin is similar to the depletion in carbon-13 for CH₄ derived from thermally altered marine kerogens (Hoering and Abelson, 1963; Ishiwatari *et al.*, 1977; Rohrback *et al.*, 1984). The slight enrichment in carbon-13 observed for C₂H₆ and C₃H₈ relative to CH₄ in the present study, has also been observed for

the pyrolysis of natural marine kerogens (Ishiwatari *et al.*, 1977), and is consistent with most natural gases of thermal origin (Erdman and Morris, 1974).

B. Elemental analysis

Elemental compositions and atomic ratios for the initial solution, the melanoidin polymer and the polymer residue after hydrous pyrolysis are reported in Table 2. Elemental analyses indicate a kerogen evolution pathway similar to that observed for natural samples (Tissot and Welte, 1984) and for kerogens subjected to laboratory simulated thermal alteration (Ishiwatari *et al.*, 1977; Schiefelbein, 1983). The H/C and O/C atomic ratios for the synthetic melanoidin decreased substantially upon hydrous pyrolysis; the N/C ratio, however, decreased only slightly.

C. Hydrocarbon analyses

The principal gaseous component generated from bombs A, B and C was CO₂, with minor amounts of N₂. The distributions and abundances of light alkanes generated from the synthetic melanoidin are listed in Table 3. The relative abundance of light alkanes generated from bombs A, B and C were the same, i.e. $C_1 > C_2 > C_3 > n-C_4 > i-C_4$. A minor amount of propylene was also detected in the headspace gas of the bombs. No hydrocarbons were detected in the headspace gas of bomb D, which contained only water. A gas chromatogram of the light alkanes isolated from bomb A is shown in Fig. 2. With respect to the structural evolution of natural kerogens, the light alkanes generated in the present study are comparable to a wet gas that would be expected to evolve from marine kerogen during the latter stages of catagenesis (Tissot and Welte, 1984).

Evans and Felbeck (1983b) reported that hydrous pyrolysis of cellulose, a glucose polymer, resulted in a higher yield of CH₄ [$C_1/(C_2 + C_3 + C_4) = 2.27$] than hydrous pyrolysis of protein [$C_1/(C_2 + C_3 + C_4) = 0.85$]. In the present study, the average amount of CH₄ generated from the synthetic melanoidin [$C_1/(C_2 + C_3 + C_4) = 1.08 \pm 0.17$] appears to be more closely related to the pyrolysis product of pure protein. A comparison of the present study with the previous work of Evans and Felbeck (1983b) is, however, tenuous, as the present experiments were conducted at 325°C, while the experiments of Evans and Felbeck (1983b) were conducted at 440°C, which is above the critical temperature of water (374.1°C).

Table 3. Light hydrocarbon abundances (ml at STP)*

Samples	C ₁	C ₂	C ₃	i-C ₄	n-C ₄	C ₅₊	Total C ₁ -C ₄	Total C ₂ -C ₄	% wetness†
Bomb A	1.93	1.23	0.46	0.02	0.21	1.16	3.85	1.92	49.9
Bomb B	0.39	0.27	0.09	0.01	0.04	0.28	0.80	0.41	51.3
Bomb C	0.16	0.09	0.02	trace	0.01	0.08	0.28	0.12	42.9

*Hydrocarbon abundances are an average of three analyses of a single gas sample taken from each bomb.

†% wetness = $\frac{(C_2-C_4)}{(C_1-C_4)} \times 100$.

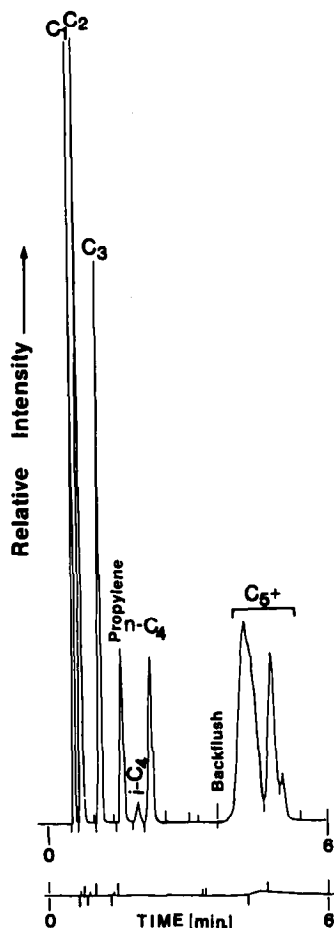


Fig. 2. Gas chromatogram of the light alkanes present in the headspace gas of bomb A. The lower chromatogram is the blank from bomb D run at the same attenuation. Analytical conditions are provided in the text.

In addition to light gas analyses, the headspace gas of bomb A and the solvent extractable organic matter from bomb A were analyzed for gasoline range hydrocarbons by GC. While preliminary results indicate the presence of subordinate amounts of higher molecular weight *n*-alkanes e.g. C_5 – C_8 , the majority of the compounds that have been identified in these fractions consist of complex, heterocyclic structures that will be discussed below. The presence of higher molecular weight *n*-alkanes (C_{10} – C_{24}) and isoprenoids (e.g. pristane, phytane), which have been previously reported to evolve during hydrous pyrolysis of pure cellulose and protein at 400°C (Evans and Felbeck, 1983b), were not detected in this study.

D. Gas chromatography/mass spectrometry

Analyses of the headspace gas and the solvent extractable organic matter from bomb A by GC/MS resulted in the detection of a variety of unsaturated aliphatic, aromatic and complex, heterocyclic compounds, the identities of which have been tentatively confirmed by comparison with standard mass spectra. In the headspace gas, toluene and xylenes have been identified, in addition to a complex mixture

of unsaturated, aliphatic compounds, including alkynes, e.g. 5-methyl-3-heptyne, and alkadienes, e.g. 1,4-hexadiene. While the absence of unsaturated products, e.g. alkenes, from hydrous pyrolysis of kerogens has been reported (e.g. Lewan *et al.*, 1979), the mechanisms of hydrocarbon generation during pyrolysis in the presence of water are undoubtedly complex, a case in point being the recent report by Tannenbaum and Kaplan (1984) of the presence of a similar distribution of unsaturated hydrocarbon products resulting from the pyrolysis of kerogens in the presence and absence of water. Since very few "anhydrous" pyrolysis experiments are actually conducted under vacuum conditions (e.g. Zumberge *et al.*, 1978), at least some of the previous anhydrous experiments may have had a certain amount of water present, leading to the speculation that the presence or absence of unsaturated hydrocarbon products may be a consequence of several factors, including starting material, sample preparation and experimental conditions e.g. time, temperature, vessel pressure and moisture content.

The following classes of compounds have been tentatively identified by GC/MS in the extractable organic matter of bomb A: indane, indole, 1-indanone, alkyl phenol, xylene, methoxy benzene and quinoline. The total ion current chromatogram is shown in Fig. 3. Of particular interest are the presence of quinoline and phenolic compounds. The presence of nitrogen in higher molecular weight fractions of crude oils has been commonly associated with the occurrence of quinoline and related compounds (Miller, 1982; Schmitter *et al.*, 1982; Tissot and Welte, 1984). While the presence of phenolic compounds in sediments is commonly associated with an input of terrestrial organic matter, e.g. lignin (Ertel and Hedges, 1983), it is interesting to observe that, in the present study, alkyl substituted phenols and methoxy benzenes are readily synthesized via the direct thermal alteration of a simple melanoidin synthesized from non-aromatic amino acids and sugar in the presence of water.

SUMMARY

The analog employed in this study for recent marine geopolymers is a very simple one, based on the condensation reaction between sugars and amino acids. Nevertheless, it fulfills the demands imposed upon the model system, i.e. it exhibits many of the properties of the natural product (kerogen).

1. Compared to the starting solution ($\delta^{13}C = -10.76\%$), the melanoidin polymer is depleted in carbon-13 ($\delta^{13}C = -13.50\%$). This is comparable to the evolution of organic matter during diagenesis and the formation of geopolymers.

2. The stable carbon isotopic composition of the melanoidin polymer ($\delta^{13}C = -13.50\%$) changes only slightly during catagenesis ($\bar{\delta}^{13}C = -13.40\%$ after hydrous pyrolysis).

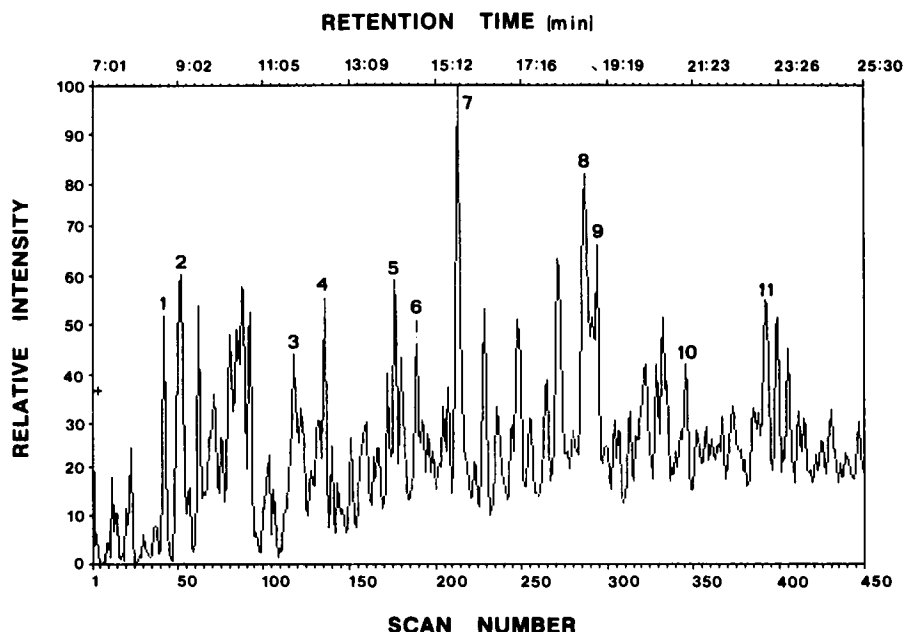


Fig. 3. Total ion current of the GC/MS analysis of the chloroform:methanol extractable organic matter of bomb A. Analytical conditions are provided in the text. The following compounds have been tentatively identified by comparison with the NIH mass spectral library: 1. ethyl-phenol; 2. 2,6-dimethyl phenol; 3. 1,2-dimethoxy benzene; 4. quinoline or isoquinoline; 5. 2,3-dihydro-1H-inden-1-one; 6. indole; 7. 5,6-dimethyl indane; 8. 5-methyl-1H-indole or 2-methyl indolizine; 9. 5- or 3-methyl-1H-indole or 1-methyl indolizine; 10. 2,3-dihydro-3,3-dimethyl-1H-inden-1-one; 11. 2,3-dimethyl indole.

3. The light hydrocarbon gases generated from the melanoidin polymer during hydrous pyrolysis exhibit (1) a wetness characteristic of hydrocarbon gases generated from natural marine kerogens during the latter stages of catagenesis and (2) a significant isotope depletion effect with respect to carbon-13 abundance. This depletion effect is largest for methane, and is typical for thermally generated natural gases.

4. In addition to gaseous products, hydrous pyrolysis of this melanoidin resulted in a complex mixture of saturated and unsaturated organic compounds some of which, e.g. quinoline, are common crude oil constituents and others, e.g. alkyl phenols, methoxybenzenes, which are commonly employed as terrigenous source indicators.

Acknowledgements—The authors wish to thank S. Sellers and J. Williamson, Cities Service Research, for technical assistance and M. Starr, School of Geology and Geophysics, O.U., for typing this manuscript. M. H. Engel wishes to acknowledge the Energy Resources Institute (O.U.), the National Science Foundation, Division of Earth Sciences (Grant No. EAR-8352055) and the Donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant No. 16144-AC2) for support of this research. M. H. Engel wishes to dedicate this paper to the memory of his student and friend, Gary E. Cox.

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