

The Discovery of Retene in Precambrian and Lower Paleozoic Marine Formations

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Abstract: Microscopic and SEM observations of thin sections and kerogens and GC-MS analyses of aromatic fractions in sediment extracts and pyrolysis products of kerogens provide strong evidence suggesting that in the Lower Yangtze Valley area the Sinian and Lower Paleozoic carbonate formations of marine facies received no higher plant input, but there was produced abundant retene during diagenesis and abietic acid substances are still its precursors.

Key words: retene; abietic acid; Precambrian; Lower Paleozoic formation; aromatic hydrocarbon

Introduction

The analyses of aromatic fractions in terrestrial sedimentary rocks showed that they contain abundant phenanthrene and phenanthrene-family compounds. Retene, namely 1-methyl, 7-isopropyl phenanthrene, is thought to be an important member of the phenanthrene family, and can be used as a source indicator in organic geochemistry (Simoneit et al., 1986; Grimalt et al., 1988; Jiang et al., 1994)

B. R. T. Simoneit (1986, 1991) suggested that the precursor of retene be abietic acids and abietadienes, secreted from some higher plants (Fig. 2). Abietadiene was first transformed into dehydroabietane during diagenesis, then into simonellite, and finally into more stable retene. It can also be seen from Fig. 2 that abietadiene might be changed into dehydroabietane, then into 1, 2, 3, 4-tetrahydroretene, and finally into retene.

Dehydroabietic acids derived from abietic acids under diagenesis and aromatization conditions followed the three paths through different mediums, and finally also transformed into retene.

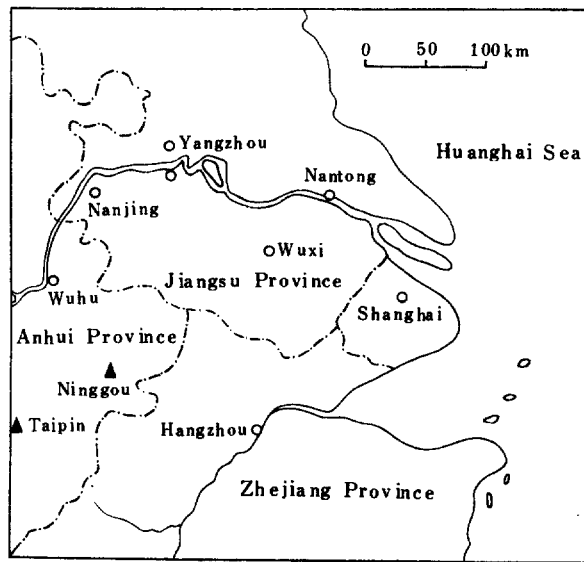


Fig.1. Sketch map showing the sample localities.

▲ stands for sample locality.

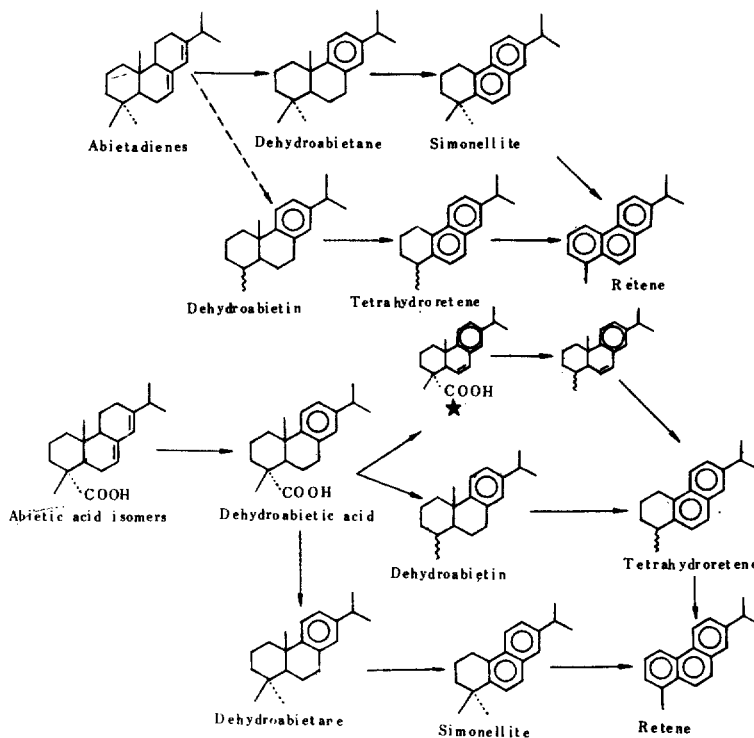


Fig.2. Diagenesis of the abietane-type diterpenoids. (After B. R. T. Simoneit, 1991)

*-13-isopropyl-5 α (H)-abietane-6, 8, 11, 13-tetraene-16-carboxyl.

The idea that retene was derived from some higher plant-secreted resins during diagenesis has been commonly accepted by geochemists. But whether retene exists in the Precambrian

and Lower Paleozoic carbonate formations of marine facies with no higher plant input in the periods before land plants appeared is still an open question.

GC-MS analyses of the aromatic fractions isolated from these carbonate formations showed that retene was highly concentrated, even higher than phenanthrene, methyl phenanthrene, pyrene and chrysene. So it is reasonable to cast doubt on the hypothesis that retene was derived only from some higher plant-secreted resins.

Experimental

Sedimentary-rock samples were taken from Ningguo County, Anhui Province, China (Fig.1). The samples are lithologically characterized by limestone, marl, siltstone and mudstone (Table 1). The standard-sample preparation methods including the isolation of saturated and aromatic fractions (edited by China National Petroleum Corporation) were employed. Then, both the fractions were taken for GC-MS analysis.

Finnigan MAT TSQ-700 GC/MS/MS coupled with Varian 3700 GC was used. Operating conditions: injection at 300°C, column 30m in length and 0.25mm in i.d., temperature programming at 70°C holding 1 min: 70–310°C, 3°C/min for aromatic fraction analysis and 70–160°C, 6°C/min and 160–310°C, 2°C/min for saturated fraction analysis. Carrier gas was He. MS analytical conditions: EI ion source; filament current, 200 μ A; multiplier voltage, 1200V. MID and full scan mode were used.

The standard methods for the isolation of kerogen (edited by CNPC) were employed. SEM observation of kerogen was made on a Shimadzu EPM-810 electron probe microanalyzer with an electron gun voltage of 20kV.

The procedure of kerogen pyrolysis is described as follows: 1–10mg of kerogen was taken from each sample and was extracted for 72 h using Soxhlet apparatus to remove those remaining soluble substances. The kerogen was put into a glass tube measuring 6mm in diameter and 15cm in length with one end being sealed. Then the tube was exhausted for 10 min under 10⁻³mm Hg vacuum conditions, and simultaneously the other end was sealed. The tube was placed in a pyrolysis furnace and heated at 370°C for 48 h. After heating, the tube was cut into two parts for extracting the soluble substances with dichloromethane. Finally these soluble substances were separated into saturated and aromatic hydrocarbon fractions using the methods described above.

In addition, microscopic observations were made of the thin sections prepared from sedimentary rock samples to reveal their compositional, structural and bio-fossil characteristics.

Results and Discussion

Lithology and paleontology of the stratigraphic formations under investigation

Formation Z₁ (Lower Sinian) composed mainly of pebble marls and phyllites is characterized by light metamorphism and depletion in organic carbon (Compiling Group for the Stratigraphy of Anhui Province, 1978). Formation Z₂ (Upper Sinian) consists of thin-bedded calcareous

shales and siliceous marls. Formation ϵ_2y is built up of thick-bedded muddy limestones and siliceous mudstones, and fossilized by trilobites *Agnostus sp.*, brachiopoda *Obolus sp.* and sponges *Protospongia sp.* Formations ϵ_3h and ϵ_3x are made up of grayish-black carbonaceous shales, limestones and dolomitic limestones, intercalated with minor silty shales, and are fossilized by trilobite *Agnostus sp.* and brachiopoda *Palaeobolus sp.* Formations O_1t and O_1n are comprised of black siliceous and grayish-green shales, with graptolites *Asaphopsis sp.* and *Dendrograptid* being dominant. Formation O_2h is lithologically similar to O_1t and O_1n , with graptolites, trilobites and orthoceras as the dominant fossils. Formations O_3h and O_3x consist of grayish-green silty shales and shales, intercalated with siltstones and are fossilized by graptolites and trilobites.

Table 1. The geochemical parameters of n-alkanes, isoprenoids, steranes, and terpanes in the sedimentary rock extracts

Sample No.	6079	6078	6077	6076	6075	6083	6074	6082	6073	6072
Lithology	DMS	DM	DM	BM	DSM	DML	BL	BM	BM	BSLM
Stratigraphy	O_3x	O_3h	O_2h	O_1n	O_1t	ϵ_3x	ϵ_3h	ϵ_2y	ϵ_1h	Z_2l
n-alkanes and isoprenoids:										
Main carbon No.	C ₁₉	C ₁₈	C ₁₉	C ₂₁	C ₂₀	C ₁₉	C ₂₀	C ₁₉	C ₁₉	C ₁₈
Pr/n-C ₁₇	1.07	1.55	0.59	0.48	1.15	0.82	0.85	0.96	1.72	0.93
Ph/n-C ₁₈	2.14	1.61	0.94	0.81	0.37	1.19	1.29	0.85	3.24	1.62
Pr/Ph	0.59	0.90	0.41	0.42	1.43	0.57	0.73	1.40	0.56	0.58
Steranes:										
C ₂₁ Preg/C ₂₉ $\alpha\alpha$ 20R	0.99	1.45	0.75	0.47	0.67	0.67	0.43	2.08	0.82	0.77
C ₂₇ Rear/C ₂₉ $\alpha\alpha$ 20R	0.21	0.21	0.19	0.14	0.18	0.14	0.18	0.20	0.15	0.16
C ₂₉ 20S/(20S+20R)	0.49	0.50	0.47	0.41	0.43	0.47	0.42	0.48	0.49	0.46
Hopanes:										
Ts/Tm	0.67	0.80	1.00	0.90	1.11	0.91	1.00	1.00	0.89	1.00
C ₂₉ $\beta\alpha$ /C ₂₉ $\alpha\beta$	0.07	0.07	0.09	0.07	0.07	0.07	0.07	0.07	0.08	0.07
C ₃₀ $\beta\alpha$ /C ₃₀ $\alpha\beta$	0.12	0.10	0.12	0.14	0.10	0.12	0.12	0.09	0.12	0.12
C ₃₁ 22S/(22S+22R)	0.60	0.59	0.61	0.64	0.64	0.62	0.60	0.62	0.64	0.59
Terpanes:										
Gammacerane/ C ₃₀ Hop.	0.16	0.17	0.17	0.17	0.17	0.19	0.19	0.14	0.16	0.17
C ₂₀ Tric/C ₃₀ Hop.	1.08	0.59	1.00	0.33	0.34	0.74	0.17	2.14	0.70	0.81

Note: Main carbon number stands for the carbon number of the most intensive n-alkane in a gas chromatogram; Pr—pristane; Ph—phytane; Preg—pregnane; C₂₉ $\alpha\alpha$ 20R—C₂₉ 5 α , 14 α , 17 α , 24-ethylcholestane 20 R; C₂₇ Rear—13 β , 17 α , discholstane 20S; C₂₉ 20S/(20S+20R)—C₂₉ 5 α , 14 α , 17 α , 24-ethylcholestane 20S/(20S+20R); C₂₉ $\beta\alpha$ —C₂₉ 17 β , 21 α normoretane; C₃₀ $\beta\alpha$ —C₃₀ 17 β , 21 α moretane; C₂₉ $\alpha\beta$ —C₂₉ 17 α , 21 β hopane; C₃₀ $\alpha\beta$ —C₃₀ 17 α , 21 β hopane; DMS—dark grey muddy siltstone; DM—dark grey mudstone; BM—black mudstone; DSM—dark grey sandy mudstone; DML—dark grey marl; BL—black limestone; BSLM—black siliceous mudstone; C₃₁ 22S/(22S+22R)—C₃₁ 17 α , 21 β 30-homopane 22S/(22S+22R); C₃₀ Hop.—C₃₀ 17 α , 21 β , hopane; C₂₀ Trica—C₂₀ tricyclic terpane.

The above lithology and paleontology data provide evidence suggesting that these formations are associated with the marine depositional environments with no higher plant input.

Observations of sedimentary rock thin sections by microscope and kerogen by SEM

A variety of algae assemblages were observed in the Z₂l samples under the microscope; carbonaceous material is of laminated distribution and algae and their slack assemblages are recognized in the ϵ_{2y} formation. The laminated and lens-like distributions of algae and their slacks and the assemblages of dolomite, carbonaceous slacks and algae and their slaks are commonly seen in the Lower Paleozoic formations, but their morphological features could not be seen clearly under the optical microscope.

SEM examinations of kerogen-bearing samples 6072(Z₂l), 6077(O₂h) and 6078(O₃h) were performed. The rest samples have not been examined because of too small amounts of kerogen in them. Almost only algae and algae fragments were seen in the three samples. There would exist other kinds of fossils, but they are too small to be recognized. Shown in the photos (Photos a-d) are some relatively distinct and intact algae fragments. These algae are morphologically similar to the alga *Gloeocapsomorpha Prisa*, which is widely distributed in the Ordovician formations in North America, Australia and North Europe and contributed a lot of organic material. No higher plant fossils including pollens were observed under the microscope and SEM.

Geochemistry of n-alkanes, isoprenoids, steranes, terpanes and aromatics in the sedimentary rock extracts

The carbon numbers of the most intensive GC peaks of n-alkanes for the 7 samples ranging in age from Z₂1 to O₂ are within the range of C₁₈-C₁₉ (Table 1), with the exception of samples 6074(ϵ_{3h}), 6075(O_{1t}) and 6076(O_{1n}). The ratios of Pr/Ph are mostly less than 1.0. These values are similar to those of crude oils produced in the O₁ and O₂ formations in the middle part of North America (Derenne, S. et al., 1992; Longman, M. N. and Palmer, S. E., 1987).

Pregnane is highly concentrated in steranes with the ratios of pregnane/C₂₉ $\alpha\alpha\alpha$ 20R ranging from 0.43 to 2.08 (Table 1), suggesting these sedimentary rocks would be related with the hypersaline depositional environment (Ten Haven et al., 1986). Low rearranged sterane concentrations are in agreement with marine carbonate environments (Rubinstein et al., 1975). C₂₉ $\alpha\alpha\alpha$ steranes 20S/(20S+20R) ratios are in the range of 0.41-0.50, suggesting the maturation of those samples, but the parameter cannot be used to determine the maturity of these samples in detail.

The high abundance of C₂₀-C₂₄ tricyclic terpanes (Table 1) is also indicative of a marine carbonate depositional environment (Palacas et al., 1984). The terpane maturity parameters including Tm/Ts, C₂₉ $\beta\alpha$ normortane/C₂₉ $\alpha\beta$ norhorpane, C₃₀ $\beta\alpha$ mortane/C₃₀ $\alpha\beta$ hopane and C₃₁ 22S/(22S+22R) are also indicative of the maturation of those samples and those parameters could not distinguish the maturities in detail either.

GC-MS analyses of the aromatic fraction are more useful than those of the saturated hy-

drocarbon fraction. Firstly, MPR, MPI₁ and MPI₂, as listed in Table 2, not only indicate that these samples have been mature, but also distinguish their maturity differences. The degree of maturation tends to decrease from Z₂l (high) to O₃ (low) and such a trend can be regarded as a correct maturation series. The MPR, MPI₁ and MPI₂ of two O₃ samples appear to be a little higher, which may be the result of magmatic activity since volcanic tuffs have been found in the O₃ formation.

Secondly, relatively high retene has been detected in these samples, indicating that retene can occur not only in the formations with intensive higher plant input, but also in the formations deposited before land plants appeared.

Fig. 3 shows there is abundant retene present in the Z₂l, ε₃h and O₃h formations. The extremely high concentration of retene was detected in sample 6074(Z₂l). Although the sample is Precambrian in age with a predominance of primitive algae, retene abundance is higher than that in all the other aromatic compounds detected.

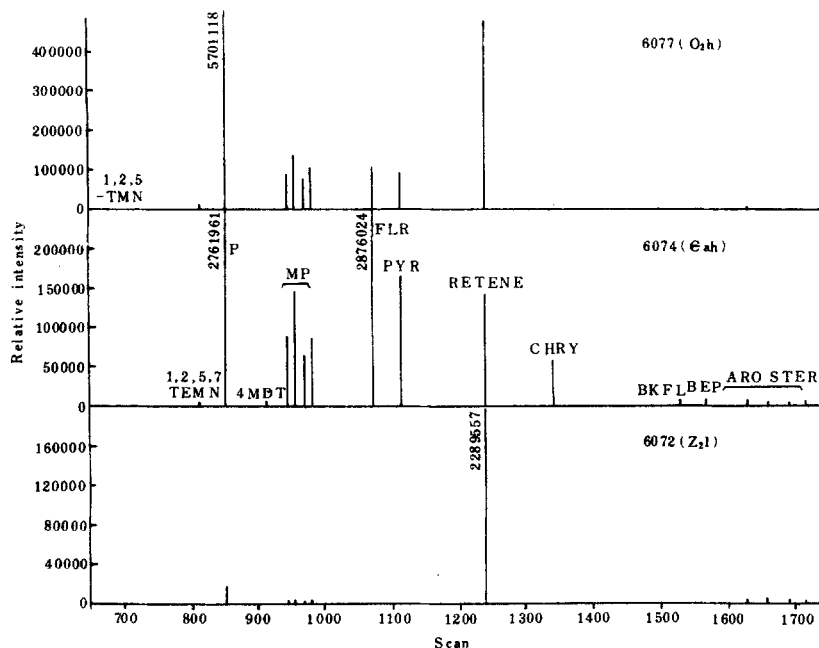


Fig.3. The molecule-ion chromatograms of main aromatic components in samples 6072(Z₂l), 6074(ε₃h) and 6077(O₂h).

TMN—trimethyl naphthalene; TEMN—tetramethyl naphthalene; P—phenanthrene; MP—methyl phenanthrene; FLR—fluoranthene; PYR—pyrene; CHRY—chrysene; BKFL—benzo [K] fluoranthene; BEP—benzo [e] pyrene; BAP—benzo[a]pyrene; ARO STER—triaromatic steroid.

GC-MS analyses of the pyrolysis products of kerogen

In order to further confirm that retene was produced in the Z₂l (Precambrian) and Lower Paleozoic formations, GC-MS analysis of the pyrolysis products of kerogen was carried out. Before pyrolysis, kerogen was put into a Soxhlete extractor to remove soluble substances.

Table 2. The geochemical parameters of aromatics

Sample No.	6079	6078	6077	6076	6075	6083	6074	6082	6073	6072
Stratigraphy	O _{3x}	O _{3h}	O _{2h}	O _{1n}	O _{1t}	ε _{3x}	ε _{3h}	ε _{2y}	ε _{1h}	Z _{2l}
MPR	1.83	1.47	0.32	0.88	1.37	0.99	1.64	1.55	1.53	1.56
MPI ₁	1.57	1.26	0.71	0.88	1.12	0.93	1.64	1.12	1.40	1.33
MPI ₂	1.44	1.65	0.37	0.85	1.24	0.66	1.99	1.17	1.41	1.68
1,2,5-TMN/Sum	0	0	0.01	0	0	0.22	0	0.01	0.01	0.01
1,7-DMP/Sum	0.28	0.49	0.65	2.20	2.03	0.27	0.56	0.35	0.22	0.50
Retene/Sum	0.13	8.03	2.83	12.91	6.02	13.09	1.08	4.59	1.01	33.9
FLR/Sum	1.67	1.10	0.65	1.49	1.47	0.42	2.20	1.74	0.60	0.15
Pyrene/Sum	0.91	0.97	0.55	0.78	1.15	0.23	1.26	0.90	0.30	0.15
B[k]FLR/Sum	0.03	0	0	0.38	0.02	0	0.08	0	0	0
4-MDBT/Sum	0.08	0.10	0.10	0.03	0.07	0.04	0.05	0	0.06	0.17
Chrysene/Sum	0.36	0.04	0.02	0.32	0.36	0.03	0.47	0.34	0.02	0
ARO STER/Sum	0.18	1.15	0.05	0.18	0.37	0.58	0.24	2.01	3.97	3.18

MPR-[2-MP]/[1-MP]; MPI₁(modified)-([2-MP]+[3-MP])/([1-MP]+[9-MP]); MPI₂(modified)-2*[2-MP]/([1-MP]+[9-MP]); MP-methylphenanthrene; P-phenanthrene; TMN-trimethylnaphthalene; Sum-(P+[1-MP]+[2-MP]+[3-MP]+[9-MP])/5 as a reference for the contents of aromatic compounds; DMP-dimethylphenanthrene; FLR-fluoranthene; B[k] FLR-benzo[k] fluoranthene; 4-MDBT-4-methyl dibenzothiophene; ARO STER-triaromatic steroid.

The distributions of n-alkanes, isoprenoids, steranes and terpanes in the pyrolysis products of kerogen are more similar to those of the extracts from sedimentary rocks. C₂₀-C₂₄ tricyclic terpanes, pregnane and homopregnane show a small difference in amounts in the pyrolysis products of kerogen.

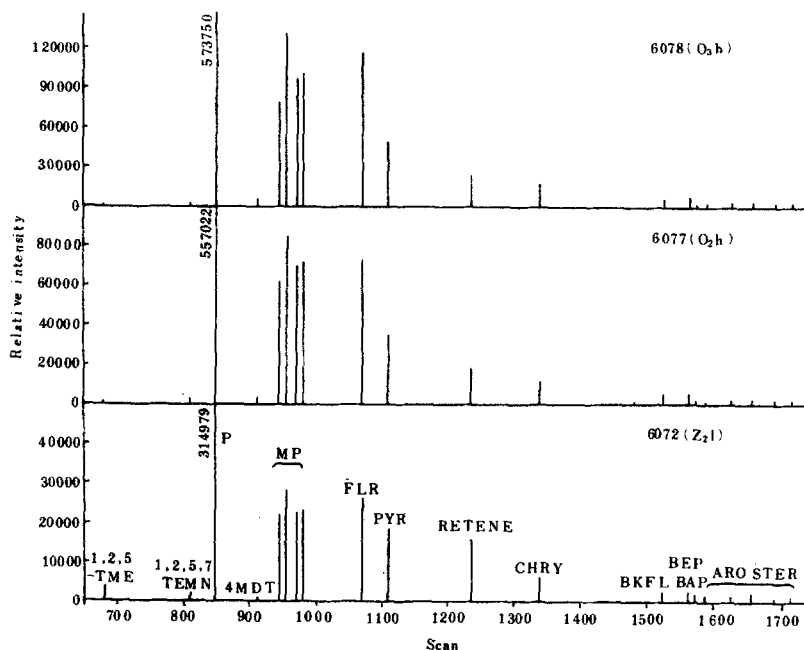


Fig.4. The molecule-ion chromatograms of main aromatic components in the pyrolysis products of kerogen from samples 6072(Z_{2l}), 6077(O_{2h}), 6078(O_{3h}). The explanations are the same as in Fig.3.

The distribution of aromatics in the pyrolysis products of kerogen is still similar to that in the extracts from sedimentary rocks but the phenanthrene concentration is obviously increased (Fig. 4). However retene in the pyrolysis products of kerogen is less than in the sedimentary rock extracts from the same sample, but this compound was detected in significant amounts. This provides strong evidence for the formation of retene from the pyrolysis of kerogen isolated from marine sedimentary rocks without higher plant input rather than from aromatics derived from other formations.

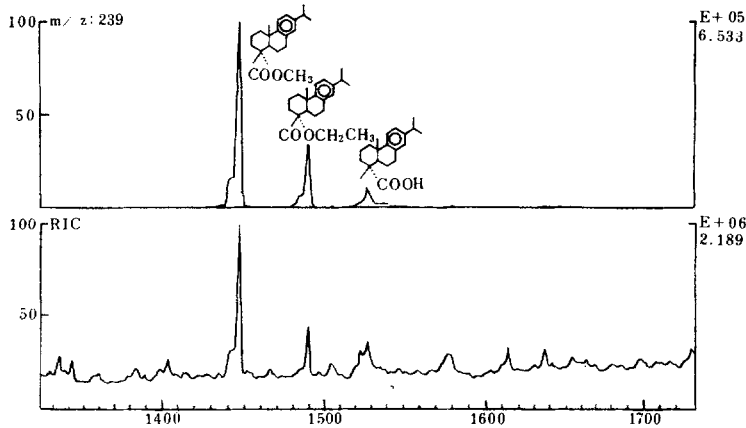


Fig.5. m/z 239 mass chromatograms showing the distribution of methyl dehydroabietate, ethyl dehydroabietate and dehydroabietic acid in the weak polarity fraction of the pyrolysis product of kerogen from sample 6077(02h).

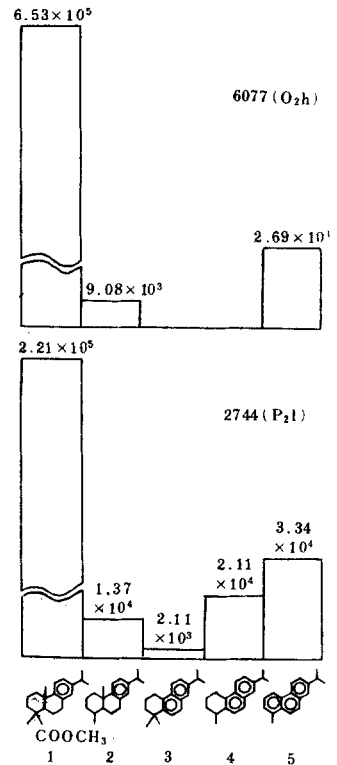


Fig.6. The relative concentrations of abietic acid derivatives in the pyrolysis products of kerogen from samples 6077(02h) and 2744(P21).

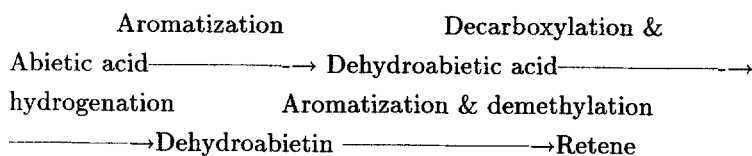
The values at the top of the columns are the intensities of basic fragment mass spectra of the compounds. The numbers at the bottom: 1. methyl dehydroabietate; 2. dehydroabietin; 3. simonellite; 4. tetrahydroretene; 5. retene.

The relatively high concentrations of methyl dehydroabietate, ethyl dehydroabietate and dehydroabietic acid have been detected on the m/z 239 mass chromatograms (Fig. 5) in the three samples. This provides strong evidence for reasonable precursors of retene. Dehydroabietin is another kind of abietic acid derivative detected, but no simonellite and tetrahydroretene have been discovered (Fig. 6).

The discovery of methyl and ethyl dehydroabietate and dehydroabietic acid in the pyrolysis products of kerogen is a clear indication that the precursors of retene are still abietic acid sub-

stances because these compounds might be derived from abietic acid through aromatization and esterification. This implies that abietic acid substances could come not only from higher plant resins, but also from primitive algae and other organisms (probably including archeobacteria).

Kerogen isolated from sediments with a predominance of primitive algae and other lower organisms but no terrestrial plants might produce abietic acid derivatives, but the path of transformation of these compounds during diagenesis is different from what was proposed by Simoneit (1986, 1991). As viewed from these abietic acid derivatives detected in the pyrolysis products of kerogen (Fig. 6), the transformation path is assumed as follows;



To be compared with the formation mechanism of retene in coal-measure strata, a kerogen pyrolysis experiment was performed under the same conditions as described above. The kerogen was isolated from coal with abundant higher plant fossils such as *Gigantopteris sp.* and *Neuropteris sp.* in the P₂l formation, Taiping County, Anhui Province, China. A variety of abietic acid derivatives were obtained including methyl and ethyl dehydroabietates, dehydroabietic acid, tetrahydroretene, simonellite, dehydroabietin and retene (Fig. 6). These abietic acid derivatives lend considerable support to the suggestion by Simoneit (1986, 1991) on the transformation path of abietic acid and its derivatives during diagenesis.

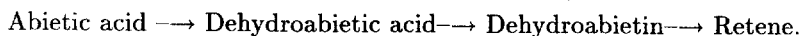
Conclusions

1. The discovery of fossils in the Precambrian (Z₂l) and Lower Paleozoic formations, including algae, trilobite, orthoceras, brachiopoda, sponge, graptolite and other primitive organism fragments and the lack of higher plant fossils demonstrate that these formations were deposited in the marine environment.

2. More abundant retene was detected in the samples taken from the formations mentioned above. The extremely high concentration of retene was recognized in the Z₂l (Precambrian) formation, suggesting that retene may be produced in the formations with no higher plant input but with a predominance of algae.

3. Significant amounts of retene, methyl and ethyl dehydroabietates and dehydroabietic acid (small in size) have been detected in the pyrolysis products of kerogen present in the formations. This suggested that abietic acid substances are still the precursors of retene.

The path of transformation from abietic acid substances to retene is somewhat different from that proposed by Simoneit (1986, 1991; Fig. 2), which is assumed to be:

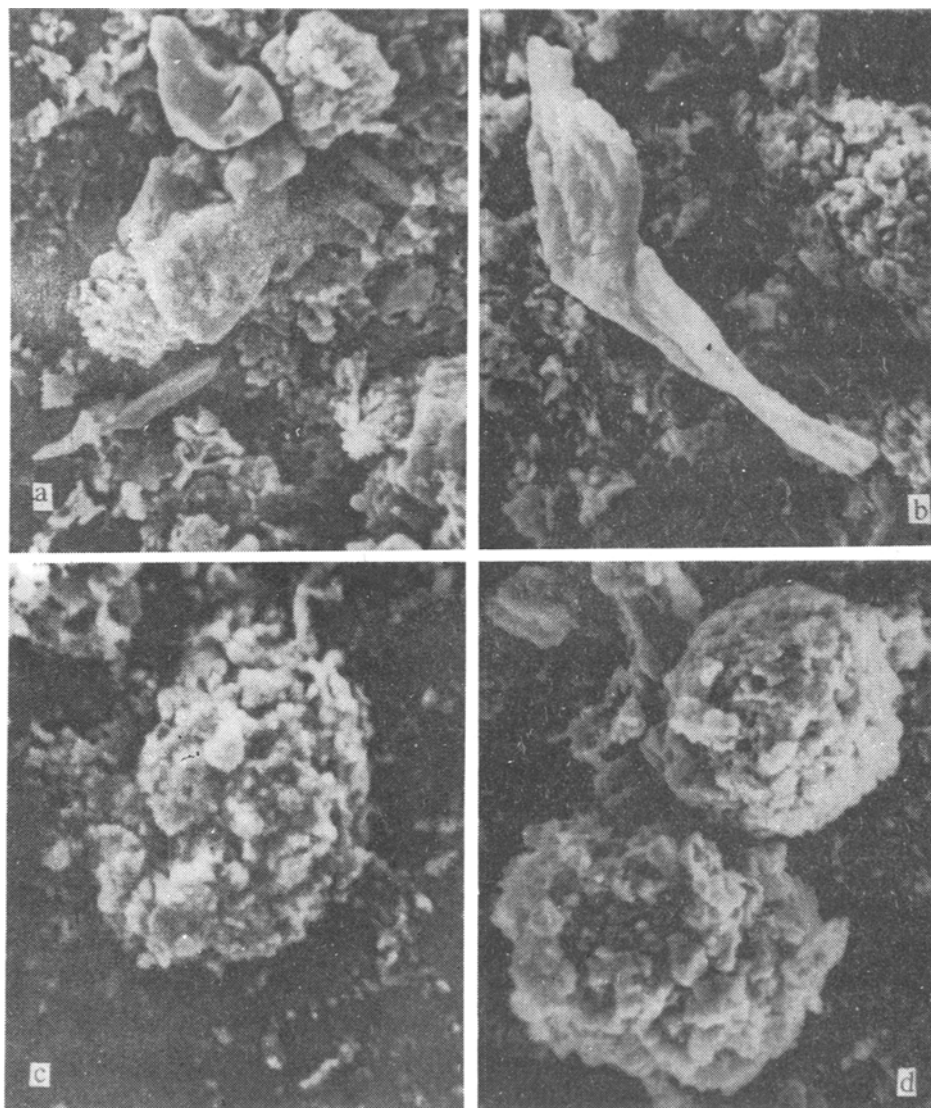


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Photos a-d: Algae microfossils observed by SEM in the kerogen isolated from the Z₂l and O₂h formations.

- a. Algae in the Z₂l formation ($\times 4800$).
- b. Algae in the Z₂l formation ($\times 4300$).
- c. Algae in the O₂h formation ($\times 7000$).
- d. Algae in the Z₂l formation ($\times 5000$).