Discovery of low-mature hydrocarbon in manganese nodules and ooze from the Central Pacific deep sea floor

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Abstract **Extracts from manganese nodules and ooze from the Central Pacific deep sea floor were analyzed using the chromatogram-mass spectrum, and it was found that most of the biomarker molecules are of the low-mature type (some have characteristics of mature): the ratio of "A"/C is high between 11.4%—19.75%; CPI is 1.22—1.23; C_{31}-22S/(22S+22R) hopane is 0.59—0.60, Tm/Ts is 0.99—1.99; βα moretane/(αβ+βα) hopane is 0.12 — 0.14; C_{29} sterane 20S/(20S+20R) is 0.35—0.41; ββ/(ββ+αα) is 0.38—0.45; arene TA(I)/TA(I+II) is 0.16—0.21; methyl-phenanthrene index (MPI1) is 0.35—0.67. According to the geological settings of the sampling area and its organic geochemical characteristics, it is considered that the hydrothermal activities on the ocean floor facilitate the decomposition of organic matter in the sediment, which leads to the generation and migration of hydrocarbon into manganese nodules and ooze. This discovery is important for understanding the mechanisms of hydrocarbon generation in the ocean floor and for expanding the potential of oil and gas exploration in the ocean.**

Keywords: manganese nodules, ooze, biomarker, low-mature hydrocarbon.

The organic matter in manganese nodules and ooze in the Central Pacific deep sea floor was studied with emphasis on the analysis of dissociative hydrocarbon. It was found that the composition of biomarkers in the extracts of this research and the extracts of modern life-forms (algae, bacterium and plankton) reported in literature, are completely different. However, the composition of the former is consistent with the biomarker molecule in low-mature hydrocarbon or source rocks, some organic geochemical indexes of which even exist in the range of mature hydrocarbon. This indicates that the processes of hydrocarbon generation may occur under ocean floor conditions thus widening the possibilities for oil and gas exploration.

All samples were colleced from the Chinese Exploration Area (7°—14°N, 138°—152°W) in CC districts of the Central Pacific. The area is located between two EW-strike fault belts, Clarion and Clipperton faults, respectively, with substantive sub-ruptures, active tectonic movements, and violent magmatism. Sediment of the ocean floor is siliceous clays and siliceous ooze[1], basalt debris, tuff, plagioclase crystal debris and volcanic hydrothermal minerals such as fluorite[2,3], etc. Some manganese nodules grow surrounding the core of volcanic rock detritus[2,4]. The O-isotope geochemistry indicates that main metal elements of manganese nodules also derive from volcanic hydrothermal fluid[1,5—7]. The water temperature on the ocean floor is about 1.45℃, and salinity is about 3.47%[8].

Studies show that many microorganisms have been found in ocean floor ooze, including remnants of plankton and the dermarsal biological community[9,10]. Some manganese nodules have been proven to be constructed by microbes and there still remain nodules made of such organisms[11—13]. This study focused on the manganese nodules containing microrganisms and peripheral ooze containing organic matter in the ocean floor. The dissociated hydrocarbon was discovered in two groups of samples. The first group was collected in 1997, and included two kinds of manganese nodules: potato-like manganese nodules (#5107) with a smooth surface, sampled from the western CC district (10°07.50 N, 154°07.50 W) at a water depth of 5107 m; cauliflower-like manganese nodules (#4862) with a rough surface, sampled from ooze at the eastern CC district (11°45.3 N, 139°31.86 W) at a water depth of 4862 m. The second group of samples was collected in August 1999, and included cauliflower-like manganese nodules (sample 9510-Mn, 10°21.46 N, 145°11.46 W) and gray ooze containing organic matter (sample 9510-11, 13°41.22 N, 139°7.65 W).

1 Methods

The experimental methods in this study were consistent with routine organic geochemistry methods. Based on the analysis of total content of organic carbon (TOC) in sediment, dissolvable organic matter was extracted using chloroform extraction (chlorlform asphaltum A), and was separated into group components. Fractions of saturation hydrocarbon were analyzed using both gas chromatography and chromatogram-mass spectrum analysis; arene fractions were analyzed using the latter only.

(i) Chloroform extraction. Samples were dried below 80℃, crushed, and put into an LJ4 type extraction instrument. Temperature was held constant between 75—78℃ and samples were processed with chloroform for 48 h until the fluorescence level of extracted residue was below the third class. Dissolvable organic materials, chlorlform asphaltum A, were collected after volatilization.

(ii) Separation of organic group component. Using hexane preciptation, bitumen was separated from chlorlform asphaltum A. With the silica gel alumina chromatography column for dissoluble matter, a 2∶1 mixture of dichloromethane and hexane, absolute ethyl alcohol, and chloroform were used to separate saturation hydrocarbon, arene and nonhydrocarbon in turn. The fractions of saturation hydrocarbon and arene make up the fraction of dissociated hydrocarbon.

(iii) Chromatogram analysis of saturation hydrocarbon. Used HP6869 chromatogram with FID, equipped with HP-5 5% methyl silicone, 30 m×0.22 mm×0.25 μm elastic quartz capillary, and nitrogen as **supporting gas**. Temperature settings: initial temperature 80℃, rising at 3 ℃/min, reaching a maximum temperature of 310℃.

(iv) Chromatogram-mass spectrum analysis of saturation hydrocarbon. Used HP GC/MS/IRD, equipped with DB5-MS 60 m×0.25 mm×0.25 μm capillary. Samples were directly transfused into the diffluence infuse equipment at 320℃, analysis temperature was 325℃. Temperature settings: initial temperature 100℃, rising at 4℃ /min, reaching a maximum temperature of 320℃.

(v) Chromatogram-mass spectrum analysis of arene.

Used 5890II GC/5970B MSD, equipped with BPX5 30 m×0.22 mm×0.25 μm capillary, and nitrogen was used as the supporting gas. Temperature of gasification room and transmission line was 320℃. Temperature settings: initial temperature 80℃, rising at 3℃/min, reaching a maximum temperature of 325℃. Temperature was held constant for 13 min.

2 Results

(i) Composition of dissolvable organic matter and paraffin. Analysis results indicate that the content of organic material in manganese nodules and ocean floor ooze is very low: TOC is about 0.05%, dissolvable organic matter is 0.0057%—0.0079%, value of A/C is high at 11.4%—19.75% (table 1), which is similar to the characteristics of migration. Based on the results of chromatogram-mass spectrum and gas chromatography of saturation hydrocarbon, carbon numbers of normal alkane are distributed between nC_{17}-nC_{33} (fig. 1), and nC_{17} hydrocarbon decreases due to the high temperature in the former treatment. The distribution of normal alkane presents two peaks; the carbon number of the first main peak is nC_{18}, and is preponderant with the value of $C_{21}^-/\Sigma C_{22}^+$ at 0.58—1.09, which is characteristic of microorganism input. The carbon number of the second peak is nC_{25} or nC_{29}, and has obvious odd even dominance, CPI is 1.22—1.23, which shows representative low-mature hydrocarbon character[14—16]. Dvi-iso-pentylene paraffin shows distinct phytane dominance, Pr/Ph is 0.18—0.33, Pr/n-C_{17} 0.69—0.64, and Ph/n-C_{18} is 1.08—0.92 (table 1), which implies that hydrocarbon is formed in strong deoxidized conditions.

(ii) Composition of terpenoid. The distribution of

Table 1 Organic geochemistry index of some manganese nodules

Sample No.	Main index								
	C (wt%)	"A"(wt%)	"A"/C (%)	Main Peak	$\Sigma C_{21}^-/\Sigma C_{22}^+$	CPI	Pr/n-C17	Ph/n-C18	Pr/Ph
5107	0.04	0.0079	19.75	18	1.09	1.22	0.69	1.08	0.18
4862	0.05	0.0057	11.40	18	0.58	1.23	0.64	0.92	0.33

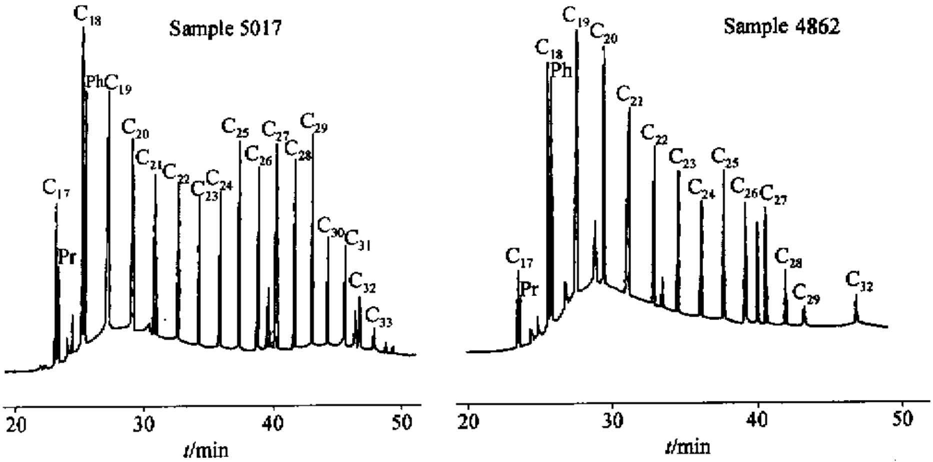

Fig. 1. Chromatogram-mass spectrum of saturation hydrocarbon of organic material in manganese nodules. C_{17}~C_{33}, Normal alkane; Pr, pristane; Ph, phytane.

terpenoid compound in saturation hydrocarbon distillation from two samples of manganese nodules and ocean floor ooze (fig. 2) have the following characteristics: rich in C_{19}—C_{28} (lack of C_{27}) 13β(H)-14α(H) series of three-ring terpane (series Ⅰ in fig 2), C_{27}—C_{35} (lack of C_{28}) 17β(H), 21α (H)-series of hopane, and C_{27}—C_{32} (lack of C_{28}) 17α (H), 21β(H)-series of moretane (series Ⅱ in fig. 2). The series of four-ring terpane do not develop, and there is a trace of C_{24} found in ooze (C_{24}* in fig. 2). All measured terpenoid compounds result from bacterium and alga microbe input: three-ring terpane is the input of alga, hopane and four-ring terpane are the input of bacterium. The abundance of three-ring terpane is relatively high (ratio of three-ring terpane/hopane is 0.6—1.3), which indicates the role of alga input.

According to the relative abundance of all terpenoid compounds in fractions of saturation hydrocarbon, indexes of terpane biomarkers have been caculated. 20S/(20S+20R) of homohopane in the series of hopane $C_{30}\alpha\beta$ is 0.58—0.60, and has reached equilibrium termination of isomerization; value of C_{30} βα moretane/(αβ hopane+βα moretane) is 0.12—0.15, value of C_{31}-22S/22(S+R) is 0.5—0.54, Tm/Ts is 0.99—1.19 (after change to Ts/(Ts+Tm), the value is about 0.5). Considering the qualities of organic maturity[14,16—18], it belongs to low-mature hydrocarbon.

(iii) Composition of sterane and aromatization sterane. Sterane is mainly composed of regulation sterane, a few of 5α (H)-pregnane and pregnane, with a lack of rearranged sterane. C_{27}—C_{29} regulation sterane show “V” distribution on mass-chromatogram, that is $C_{27} > C_{28} < C_{29}$, which is the dominant characteristic of the input of alga. Based on the isomerization degree of different allothreo configuration of cholane, some indexes of main terpane biomarker have been calculated: C_{29}5α-20S/20(S+R) is 0.34—0.41, C_{29}-ββ/(ββ+αα) is 0.38—0.45. The former study shows that fraction values of manganese nodules and ocean floor ooze are around 0.4[16], the margin between low-mature and mature hydrocarbon; it suggests that the extracts belong to low-mature hydrocarbon as a whole.

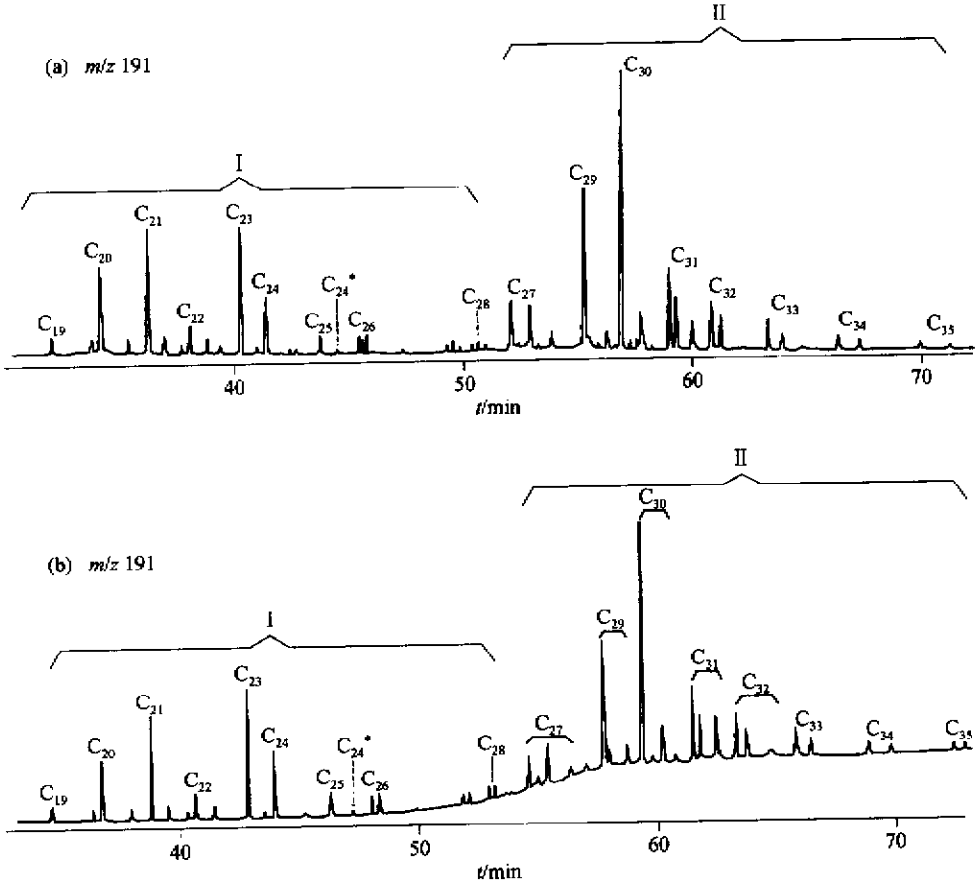

Fig. 2. The distribution of terpenoid compound in saturation hydrocarbon distillation (*m/z* 191 chromatogram-mass spectrum). (a) Sample 5107 (nodule); (b) Sample 9510-11 (ooze); I, three-ring terpane series; Ⅱ, 17α (H), 21β series of hopane and 17β (H), 21α(H) series of moretane; C_{24}*, four-ring terpane.

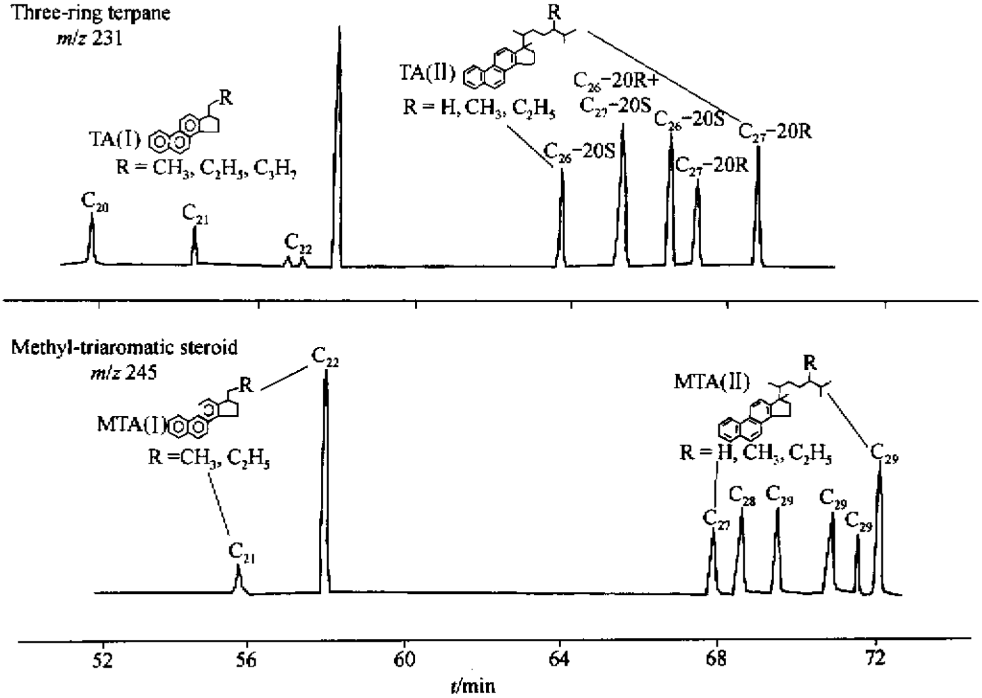

Fig. 3. The distribution of aromatization sterane in the arene fraction of dissociate hydrocatbon (*m/z* 231, 245 chromatogram-mass spectrum, sample 5017).

In the arene fraction of dissociated hydrocatbon, there is much aromatization sterane, involving predominantly two series of triaromatic steroid and methyl- triaromatic steroid, as well as phenanthrene steroid. Series of triaromatic steroid is composed of C_{20}—C_{22} triaromatic pregnane (TA(Ⅰ) in fig. 3) and C_{26}—C_{28} triaromatic steroid (TA(Ⅱ) in fig. 3). The distribution of triaromatic pregnane ($C_{20}>C_{21}>C_{22}$) is lower than triaromatic steroid ($C_{26}\approx C_{27}<C_{28}$) which results from the difference between their input sources. The ratio of TA(I)/TA(Ⅰ +Ⅱ) is 0.16—0.21, which is characteristic of the low-mature hydrocarbon maturity parameter[14]. Series of methyl-triaromatic steroid contain the dominant methyl-triaromatic pregnane C_{21}—C_{22} and methyl- triaromatic steroid C_{27}—C_{29}. Series of triaromatic steroid and methyl-triaromatic steroid are the outcome of aromatization of pregnene and methyl-pregnene, two precursors of sterene which belong to products of alga.

(ⅳ) Composition of multiring arene. Fractions of arene mainly consisted of many multiring arenes, including integrated series of naphthalene, phenanthrene, and series of biphenyl, fluorene, dibenzothiophene, biphenylene oxide and a trace of multiring hydrocarbons such as fluoranthene and pyrene.

Because of different sampling sites and preservation conditions in ocean floor, as well as the loss of some low carbon number hydrocarbon and dissociated hydrocarbon during the 48-h extraction period at 75—78℃, there is a slight difference in preservation degree and the distribution model of naphthalin series among arene samples. In two manganese nodule samples collected in 1997 (＃4862 and #5017), series of C_0-naphthalene—C_4-naphthalene were retained completely, but the abundance of low carbon number hydrocarbon is low, and C_2-naphthalene is dominant; the distrubution model is C_0-naphthalene$<C_2$-naphthalene $<$ C_3-naphthalene $>$ C_4-naphthalene. Conversely, in manganese nodule (#9510-Mn) and ocean floor ooze collected in 1998, there was a lack of C_0-naphthalene, and C_1-naphthalene and C_2-naphthalene also seem to be lost to some extent; the distrubution model is C_0-naphthalene$<C_1$-naphthalene$<C_2$-naphthalene.

Series of phenanthrene ranged from C_0-phenanthrene to C_2-phenanthrene. In manganese nodules (# 9510-Mn) and ocean floor ooze (#9510-11), phenanthrene series were dominated by C_0-phenanthrene. With an increase of substitution groups on the rings of phenanthrene, there was a subsequent decrease from C_0-phenanthrene to C_2-phenanthrene. The distrubution model is C_0-phenanthrene $>C_1$-phenanthrene$>C_2$-phenanthrene (fig. 4).

3 Discussion

(ⅰ) Determination of low-mature hydrocarbon from the ocean floor. Results of the analysis show that the manganese nodules from the ocean floor and the biomarker molecules of dissolvable organic materials in the ooze have the biomarker moleculeized specificity of low-mature hydrocarbon species as a whole. Some have

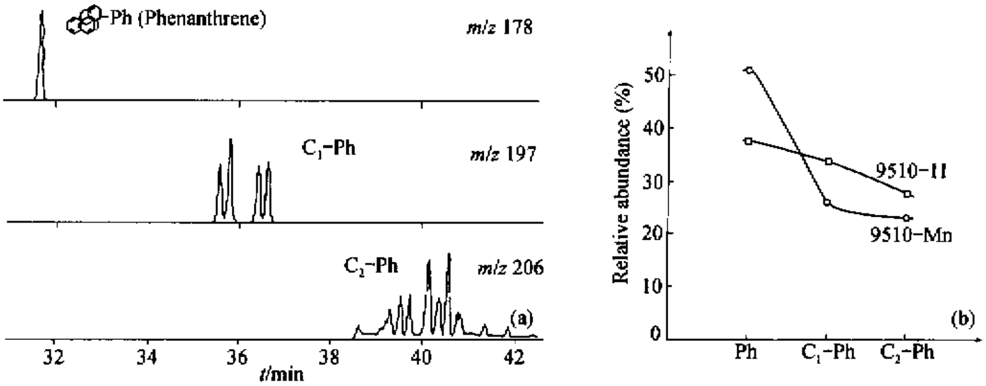

Fig. 4. The distribution of phenanthrene series in the arene fraction of dissociate hydrocatbon.

the characteristics of mature hydrocarbon. Recently, Sheng from the Guangzhou Research Institute of Geochemistry consigned by Prof. Lin, studied the biomarker molecules of hydrocarbon species from a set of manganese nodules, and the results were consistent with this research. Thus the data imply that the biomarker characteristics are not incidental but have an explanable cause which is discussed below.

As previously noted, there are many animalcules that grow in the sludge of the ocean floor, including a variety of plankton and communities of life-forms that dwell on the bottom and in manganese nodules. The environment on the ocean floor has ample capacity for hosting life-forms and the conditions are well conserved. Some alkyl hydrocarbon biomarker molecules (pristane or phytane) are also signs of the strong character of the deoxidized environment. Thus, the area where the sediments accumulate thickly can provide the material foundation for the bio-hydrocarbon from the ocean floor.

According to the biomarker molecule character stated in this note, the hydrocarbon formed on the ocean floor has some differences from the regular sea facies oil that has been found. Firstly, it has low-mature hydrocarbon character, and the changing range of the biomarker molecule is wide; it also differs from typical low-mature hydrocarbon from the land facies basin. Secondly, the manganese nodules that provide the hydrocarbon and sludge of the shallow layer, have a low content of organic carbon. However, the translation rate of the hydrocarbon generation is high and the value of A/C is abnormally high, which are characteristics of migrating hydrocarbon. Perhaps the low-mature hydrocarbon develops from the sludge in a deeper layer of the ocean floor and is carried to the shallower layer under particular circumstances, eventually entering the manganese nodules and the shallow layer sludge by diffusing and imbuing.

It should be noted that the low-mature hydrocarbon from ocean floor sediments cannot be caused by artificial pollution. Leakage from oil tankers would be the obvious source, however, it is largely mature oil, which does not explain the low-mature hydrocarbons found in sediment. Additionally, the components of hydrocarbons of several biomarker molecules have a wide range of variation (figs. 1, 2; table 1). If, on the other hand, hydrocarbon presence were caused by external pollution, one would expect mainly coherent components. Evidence is strong that the low-mature hydrocarbon from manganese nodules and ocean floor sludge is formed under the depths of the ocean floor and not externally.

(ii) Mechanism of hydrocarbon generation in the ocean floor. The generation of the low-mature hydrocarbon in the ocean floor is related to hydrothermal activity. According to the geologic background mentioned above, the samples were collected from areas with tectonic activity, intensive volcano-magma action, and frequent hydrothermal activity with mass pyroclast, silica ooze and fluor a kind of volcanic hydrothermal mineral[1—3]. Based on these facts, despite the low water temperature of the ocean floor, there must have been one or more historical thermal actions at which time the temperature would have been very high, and even surpassed the threshold temperature for oil generation. The organic matter in the ocean floor ooze decomposed into hydrocarbon during pyrogenation due to the extreme heat flow.

In fact, some "thermal petroleum" that was generated by the volcano-magma activities has been found. For example in Guaymas rift valley of California Gulf, "thermal petroleum" was found in the ocean floor at a depth of 2000 m[19]. Hydrothermal action decomposes organic matter that is rich in diatom pyrogenation and generates an abundance of multi-ring arenes, phytanes, pristanes, alkenes and tars. Hou et al. also found the liquid inclusion in hydrothermal sediment at Okinawa Trough[20]. This indicates that "sudden" hydrocarbon generation from organic matter that is effected by thermal events in deep crust, is crucial to the generation of hydrocarbons in nature.

Some of the biomarker molecules in this note also display traces of thermal events in the ocean floor. For example, the content of aromatic phenanthrene (table 2) in samples 9510-Mn (manganese nodules) and 9510-11 (ooze of ocean floor), changes from high to low, with low carbon number substituted phenanthrene (C_0-phenanthrene) to high carbon number substituted phenanthrene (C_3-phenanthrene); the distrubution model is C_0-phenanthrene > C_1-phenanthrene > C_2-phenanthrene. Based on lectures by Prof. Sinoneit in 1990, the above characteristics of phenanthrene only appear in the hydrocarbon generated by "sudden" thermal events, which are different from the hydrocarbons generated in the long geological history that have completely different change series; the highest peak appearing at C_3-phenanthrene, not at C_0-phenanthrene. Moreover, the triaromatic terpane/17α(H)-hopane ratio in manganese nodules is 0.6—1.30, compared with 0.1—0.2[14] of inmature oil (source rocks). By heating and hydrolyzing, Peter et al. studied Monterey shale and found more triaromatic terpane than 17α(H)-hopane[21], which may evidence that the very high value of triaromatic terpane/17α(H)-hopane is related to organic hydrothermal hydrolyzing effects.

Table 2 Representative aromatic hydrocarbon combinations with relative content and distribution

Component		Relative abundance (%)	
		9510-Mn	9510-11
Phenan-threne genus	phenanthrene	50.3	37.1
	C_1-phenanthrene	26.4	34.8
	C_2-phenanthrene	23.3	28.1
	C_3-phenanthrene	–	–
	*methyl phenan-threne exponent Ⅰ	0.35	0.54

Blank entries indicate the absence of data or uncertainty.

(iii) Significance. There are hundreds of thousands of heat points and hydrothermal areas on the ocean floor, in which mineralization is taking place[22]. If this effect coincides with an area spread thick with sediments and high organic content (i.e. at marginal sea basin and deep sea basin), decomposition, migration, and trapping will take place under favorable conditions. The discovery of low-mature hydrocarbon in manganese nodules and ocean floor ooze is significant to furthering the theory and study of hydrocarbon generation, and promoting petroleum exploration.

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