

C_{20} , C_{25} and C_{30} Highly Branched Isoprenoid Alkenes in The Branched and Cyclic Hydrocarbon Fractions of Qinghai Lake Sediments^①

¹ Li Jinggui ¹ Fan Pu ¹ Cui Mingzhong ¹ Li Zhenxi

² R. P. Philp, J. Allen

¹ (Lanzhou Institute of Geology, Academia Sinica, Lanzhou 730000 China)

² (University of Oklahoma, School of Geology and Geophysics, Norman, OK 73019 USA)

ABSTRACT The very abundant highly branched isoprenoid (HBI) alkenes (C_{20} , C_{25} and C_{30}) have been detected in four cores of Qinghai Lake recent sediments. This is the first report of these compounds in Chinese recent lake sediments. Diatoms may be the biological source of these sedimentary HBI alkenes.

Key words: BHI alkenes HBI thiophenes diatoms petroleum origin

INTRODUCTION

Qinghai Lake in Qinghai province, China, is the biggest inland plateau lake in China at an altitude of 3193m above sea level. The lake is 106km in length from east to west and 62 km in width from north to south with an area of 4278km², and maximum water depth of 26.5m. The pH value of the lake water is approximately 9.2 and the average salinity of the water is 14.15‰. Since there are no sources of industrial pollutants being discharged in the vicinity of the lake, it provides an ideal situation for studying biogeochemical characteristics of recent lacustrine sediments.

Over the past few years considerable interest has arisen in the biological and geological occurrence of a group of hydrocarbons, the so-called highly branched isoprenoid (HBI) hydrocarbons.

HBI alkanes and alkenes are widely distributed in a vast variety of recent sedimentary settings such as recent lacustrine, marine and hypersaline sediments (for a review see Rowland

^① Separations and identifications of these compounds were carried out at laboratory of Prof. R. P. Philp, University of Oklahoma, U. S. A. This work was partly supported by Lanzhou Branch, Academia Sinica (1994)

and Robson, 1990). The fully saturated C_{20} (I, see Appendix), C_{25} (II) and C_{30} (III) alkanes have been unambiguously identified by synthesis of standards (Yon et al., 1982; Robson and Rowland, 1986, 1988a). The unsaturated counterparts of these compounds, with 1–6 double bonds, are often abundant hydrocarbons in recent sediments (Rowland and Robson, 1990). Moreover, a novel C_{35} HBI alkenes with 7 double bonds has been found in recent Indian Ocean sediments (Hoefs et al., 1995). More recently it has become clear that diatoms may be the biological source of the C_{20} , C_{25} and C_{30} sedimentary HBI alkenes.

The positions of the double bonds in biological and sedimentary HBI alkenes have been unambiguously determined in a few cases only. By epoxidation Yruela et al., (1990) were able to assess the double bond positions in a C_{25} HBI diene occurring in lacustrine sediments. Hird et al., (1992) determined the double bond positions in several sedimentary C_{20} and C_{25} HBI monoenes. Belt et al., (1994) determined the double bond positions in a C_{25} HBI diene, isolated from sediments of the Caspian Sea, by means of NMR spectroscopy and mass spectrometry.

SAMPLES AND EXPERIMENTAL

Samples: The samples examined in this paper were obtained from four cores collected in 1989 and 1990, and whose locations are shown in Fig. 1. A brief summary of the core locations is: Core QH was collected from near the Heima River mouth, water depth: 0.5m, core length: 30cm; core Q-16A collected from the SE corner of the lake, water depth: 23.5m, core length: 72cm, water salinity: 12‰; core QG from an area currently isolated from the main lake with water depth: 9m, core length: 230cm, and with the highest

level of water salinity: 33‰; and finally core QE: also isolated from the main body of the lake, water depth: 4m, core length: 30cm, in a fresh water environment.

Experimental: The core samples were freeze dried and selected samples from the cores crushed to 100 mesh size and extracted with chloroform and methanol (1 : 1) for 48hrs. Elemental sulphur in the samples was removed using activated copper wires following which the extracts were fractionated on an Al_2O_3/SiO_2 column after precipitation of any asphalticlike material with *n*-hexane. Aliphatic hydrocarbons were eluted with *n*-hexane, aromatic hydrocarbons with benzene, and polar fractions with methanol. *N*-Alkanes were removed using S-115 molecular sieves from aliphatic fractions to obtain branched and cyclic hydrocarbon fractions prior to analysis by GC/MS.

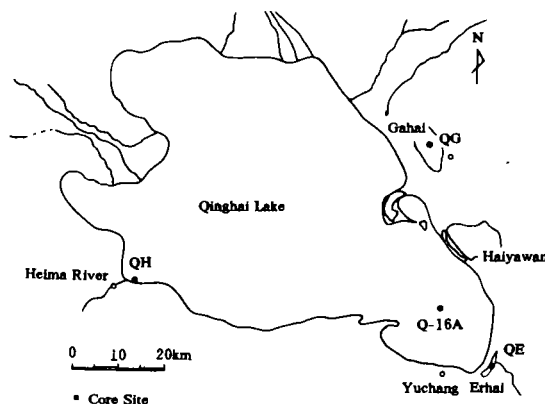


Fig. 1 location of the sediment cores taken in the Qinghai Lake

The aliphatic fractions were analyzed initially using a HP 5890 gas chromatograph with an on-column injector. A fused silica capillary column coated with DB-1 (25m × 0.25mm i. d. ; 0.25μm film thickness) was temperature programmed from 40°C to 130°C at 15°C min⁻¹ and then to 300°C at 4°C min⁻¹. The branched and cyclic hydrocarbon fractions selected for GC/MS analyses were analyzed using a Finnigan TSQ 70. The TSQ 70 was equipped with a Varian 3400 gas chromatograph fitted with a fused silica capillary column coated with DB-5 (25m × 0.25mm i. d. ; 0.25μm film thickness) which was temperature programmed from 40°C to 140°C at 15°C min⁻¹ and then to 300°C at 1.8°C min⁻¹.

RESULTS AND DISCUSSION

(1) The distributions of C₂₀, C₂₅ and C₃₀ HBI alkenes

The C₂₀, C₂₅ and C₃₀ HBI alkenes are widely distributed in recent sediments from various environments. Robson and Rowland (1988b) proposed that the abundance of these compounds in surface sediments may be explained in part by their resistance to biodegradation, relative to n-alkanes.

The identifications of these compounds studied in this paper are in Table 1.

Table 1 Peak identifications in Fig. 2a and 2b

Peak No.	Identification
1	HBI C ₂₀ monenes (br 20 : 1)
2	HBI C ₂₅ alkenes (br 25 : 2, br 25 : 3)
3,4	HBI C ₃₀ alkenes (br 30 : 4)
5,6	HBI C ₃₀ alkenes (br 30 : 4)
7,8	HBI C ₃₀ alkenes (br 30 : 4)
9	steroid and pentacyclic triterpenoid hydrocarbons
10	Perhydro-β-carotene (C ₄₀ H ₇₈)

The extracts from the QG (saline water) and QE (fresh water) cores were found to contain the C₂₀ monoenes (peak 1 in Fig. 2a). The C₂₅ (peak 2 in Figs. 2a, 2b) and C₃₀ (mainly peaks 3, 8 in Figs. 2a, 2b) alkenes were found in all four cores (Figs. 2a and 2b). In the branched and cyclic hydrocarbon fractions of the lake sediments, the relative concentrations of the C₂₀, C₂₅ and C₃₀ HBI alkenes are very high. The C₂₀ monoene is a major component of the QG-6 extracts (Fig. 2a) and a major constituent from the QE-1 and QE-3 sediment extracts; the C₂₅ alkene is the predominant compound in some of the surface sediments such as QH-1 and QG-1 sections (Figs. 2a and 2b) and the C₃₀ alkene is the most abundant component in virtually all sections of the four cores in the lake (Figs. 2a and 2b).

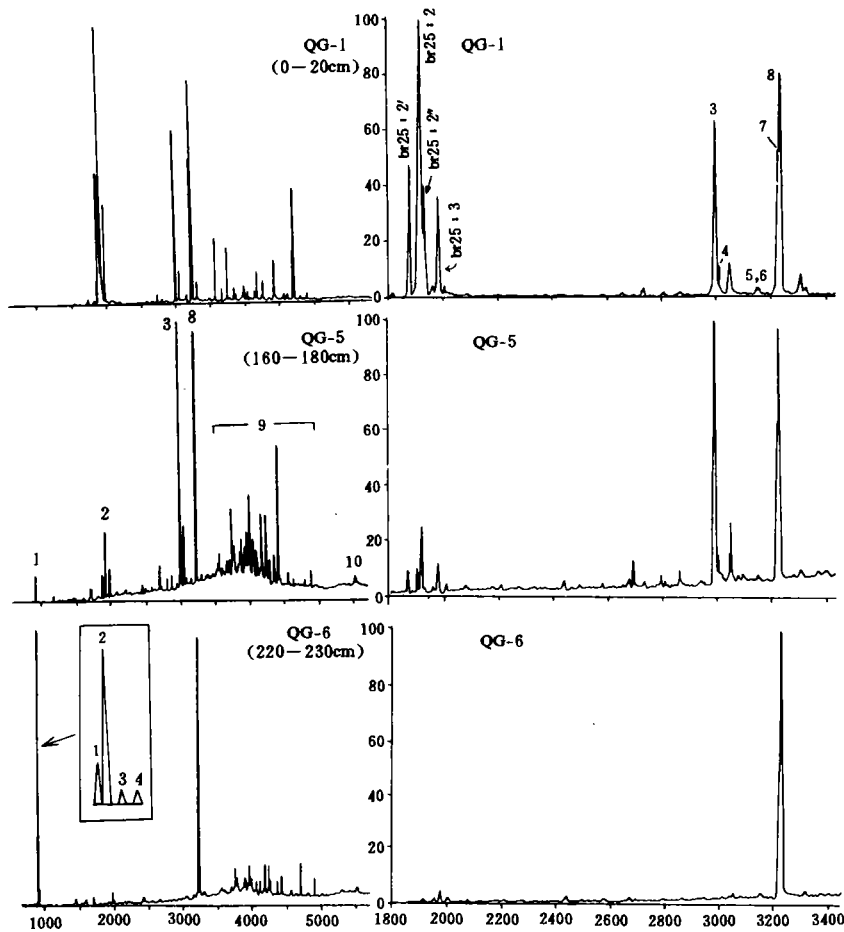


Fig. 2a C_{20} , C_{25} and C_{30} HBI alkene distributions of QG core sediments
(Peak identifications are in Table 1)

The HBI C_{20} monoene ($M^+ = 280$) [a C_{20} isoprenoid alkane has been isolated from Rozel Point Crude oil (Yon et al., 1982)] has been reported previously as having one or two isomers (Cranwell, 1982; Barrick et al., 1980). The C_{20} monoene coeluting with $n-C_{17}$ alkane found in these lake sediments occurs as either two (QE-3, QG-5) or four (QE-1, QG-6) isomers (Fig. 2a), among which the second isomer is the highest Peak, and the mass spectra of the four isomers are shown in Figure 3. It has been shown by Yon et al., (1982), from synthesis of the corresponding C_{20} alkane, that one of these C_{20} monoenes has a structure analogous to 2, 6, 10-trimethyl-7(3-methylbutyl)-dodecane (1). The C_{20} monoenes has also been identified in field specimens of the green alga *Enteromorpha prolifera* by Rowland et al., (1985). The mass spectral features of the C_{20} monoenes in the Qinghai Lake sediments shown in Fig. 3 are very similar to those previously reported for the monoene of the green alga

(Rowland et al., 1985).

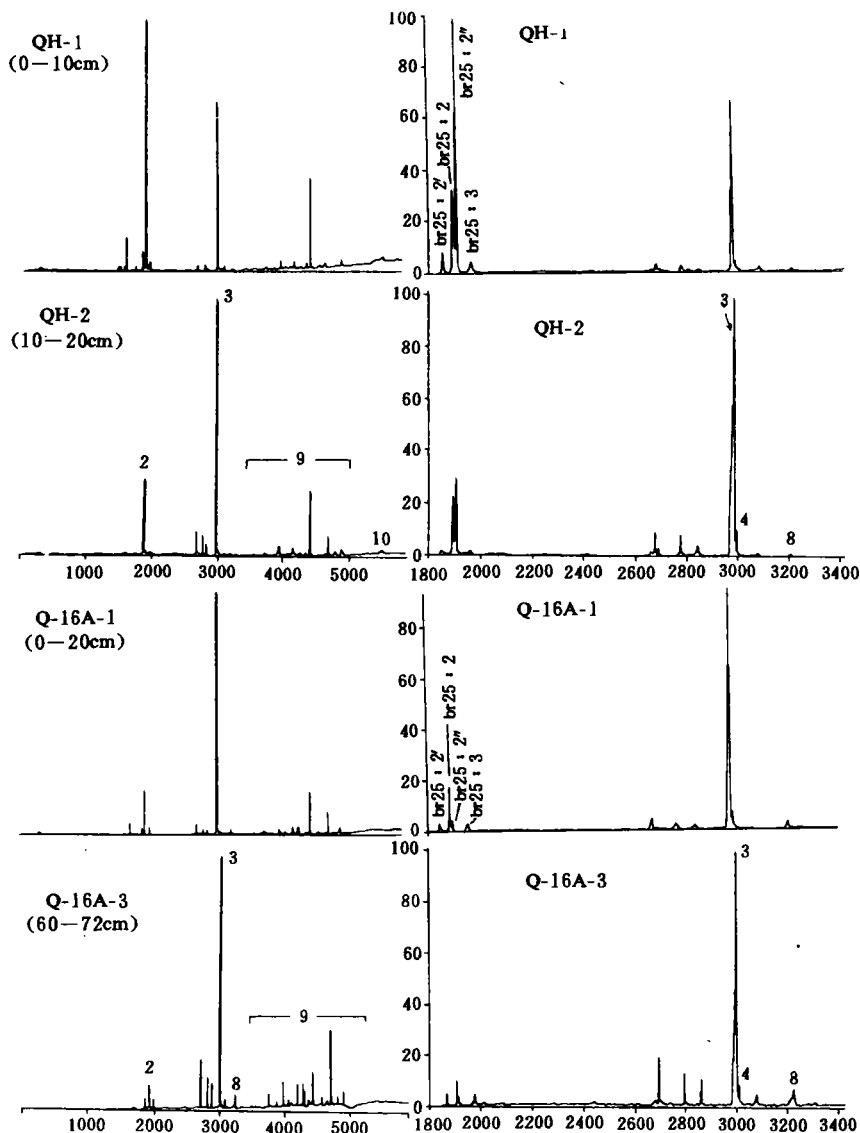


Fig. 2b C_{25} and C_{30} HBI alkene distributions of QH and Q-16A core sediments
(Peak identifications are in Table 1)

The cluster of C_{25} HBI alkenes eluting in the vicinity of the $n-C_{21}$ saturated hydrocarbon in extracts from the lake sediments consist of C_{25} dienes ($M^+ = 348$) and a C_{25} triene ($M^+ = 346$).

To designate the structural characteristics of the C_{20} , C_{25} and C_{30} alkenes, the notation system introduced by Barrick and Hedges (1981) is used throughout this paper. In this notation system, c or br denotes either a cyclic or a branched acyclic skeleton, respectively, followed by the number of carbon atoms; number of double bonds; number of rings. A superscript symbol ' or ' is used to designate compounds having the same hydrocarbon skeleton but

different locations of the double bonds and/or geometrical configuration.

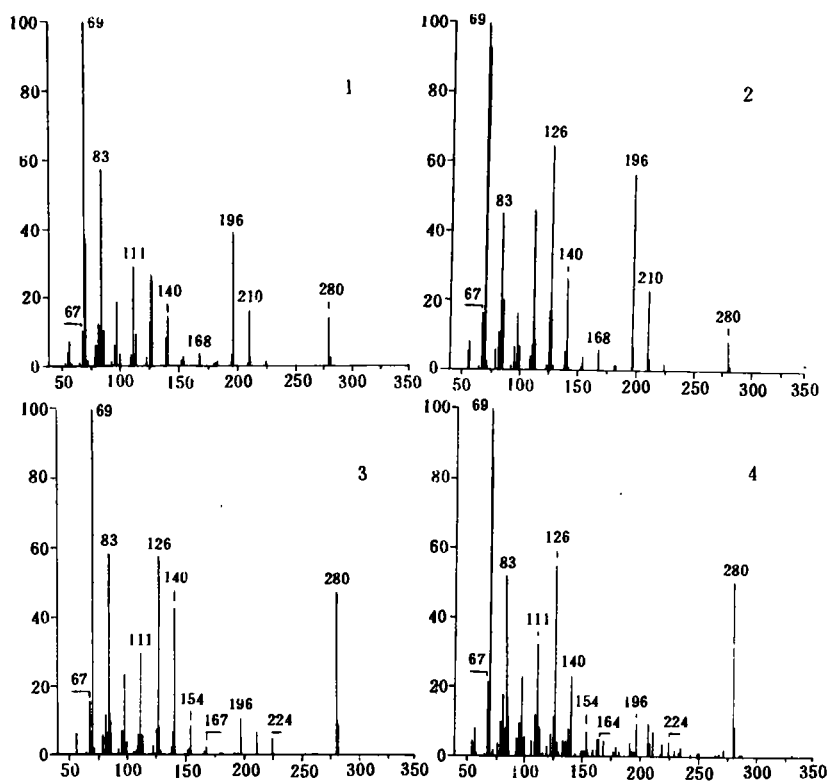


Fig. 3 Mass spectra of C_{20} HBI monoene four isomers of QG-6 (220–230 cm) in Fig. 2a

The C_{25} diene in the extracts of the lake sediments comprises three isomers, designated as br 25 : 2', br 25 : 2 and br 25 : 2'' and C_{25} triene expressed as br 25 : 3 (Figs. 2a, 2b). The mass spectra of the C_{25} dienes (Fig. 4) from the lake sediments are virtually identical to those reported for the C_{25} dienes isolated from a sediment core from the Pettaquamscutt River, USA (Requejo et al., 1984). A C_{25} diene of this type has also been found in the green alga *Enteromorpha prolifera* (Rowland et al., 1985) and in sea-ice diatoms (Nichols et al., 1988).

The mass spectrum for one of the C_{25} dienes in the lake sediment extracts is virtually identical to that of a C_{25} diene previously published by Rowland et al., (1985). The mass spectrum of the C_{25} triene in the lake is identical to that of a C_{25} triene ($C_{25:3}$) from diatom *Haslea ostrearia* (Volkman et al., 1994). Robson and Rowland (1986) showed that the C_{25} compounds possess a 2, 6, 10, 14-tetramethyl-7(3-methylpentyl)-pentadecane structure (I).

The distribution of the C_{30} alkenes ($M^+ = 414$) (br 30 : 4) in the lake sediments consists of at most 6 isomers (three pairs) (peaks 3, 4, 5, 6, 7, 8 in Figs. 2a, 2b), with the first isomer coeluting with $n-C_{25}$ and the sixth isomer coeluting with $n-C_{26}$. The first or sixth isomer is a major constituent. The mass spectra of these alkenes are very similar to those obtained for the c 30 : 2 : 2 isolated from sediments of Narragansett Bay (Requejo and Quinn, 1983). Robson and Rowland (1986) speculated that the c 30 : 2 : 2 identified by Requejo and Quinn

(1983) was pseudohomologous with the C_{20} and C_{25} HBI alkenes and that the $c\ 30 : 2 : 2$ has a 2, 6, 10, 14, 18-pentamethyl-7(3-methylpentyl)-nonadecane structure (III). Some question remains about the structure of the C_{30} diene in sediments, Although the C_{30} alkenes which are structurally homologous to the C_{20} and C_{25} compounds have been reported previously in sediment (Robson and Rowland, 1988a).

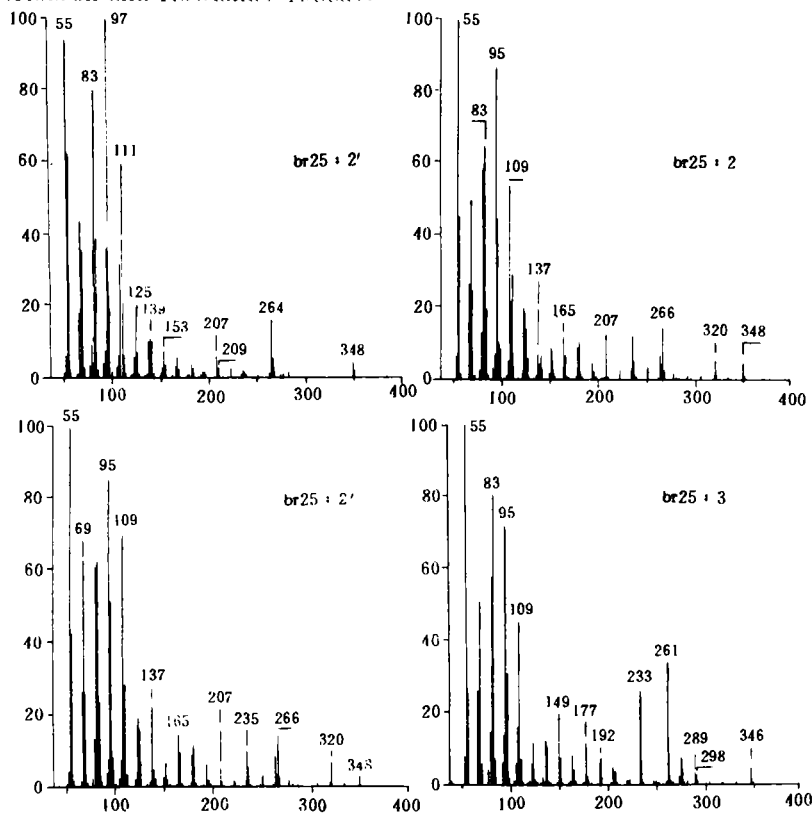


Fig. 4 Mass spectra of C_{25} HBI dienes and triene of Qinghai lake sediments.

(2) The biological source of C_{20} , C_{25} and C_{30} HBI alkenes

More recently, it has become clear that diatoms may be the biological source of the C_{20} , C_{25} and C_{30} sedimentary HBI alkenes. Nichols et al., (1988) reported a C_{25} HBI alkadiene as a major hydrocarbon in natural populations of Antarctic sea-ice diatoms. This finding was further substantiated by the work of Volkman et al., (1994) who identified C_{25} HBI alkenes with 3-5 double bonds and C_{30} HBI alkenes with 5-6 double bonds in laboratory cultures of the diatoms *Haslea ostrearia* and *Rizosolenia setigera*, respectively. Hird and Rowland (personal communication) also reported the presence of saturated and unsaturated C_{20} and C_{25} HBI alkenes in the diatom *Navicula* sp. isolated from field samples of the Tamar Estuary (Sinninghe Damste and Rijpstra, 1993). It is believed that the presence of a C_{20} HBI monoene and a C_{25} HBI diene in field samples dominated by the green macroalga *Enteromorpha prolifera* (as mentioned in the distribution section) is most likely due to the presence of epiphytic diatoms. So,

some species of diatoms abundant in Qinghai Lake water may be the biological source of the C_{20} , C_{25} and C_{30} HBI alkenes in the lake recent sediments.

(3) The Geochemical significance of C_{20} , C_{25} and C_{30} HBI alkenes.

The presence of double bonds in the biologically produced HBI components make them prone to natural sulfurization during early diagenesis, leading to formation of HBI thiophenes, thiolanes and macromolecularly sulfur-bound HBI skeletons. Eight C_{20} and three C_{25} HBI thiophenes were identified in sediments (Pleistocene, Miocene and Cretaceous) and immature oils (Miocene, Paleogene) from different geographical locations (Sinninghe Damste et al., 1989; Sinninghe Damste and Rijpstra, 1993). Kohnen et al., (1990) reported the co-occurrence of C_{25} and C_{30} HBI polyenes and unsaturated C_{25} and C_{30} HBI thiolanes possess-

ing two double bonds less than the corresponding HBI polyenes in a recent sediment from the Black Sea, strongly suggesting that the HBI thiolanes were formed by reaction of inorganic sulphur species with double bonds of the HBI polyenes. Hence, the study of these HBI alkenes in recent sediments has a certain geochemical significance for petroleum origin.

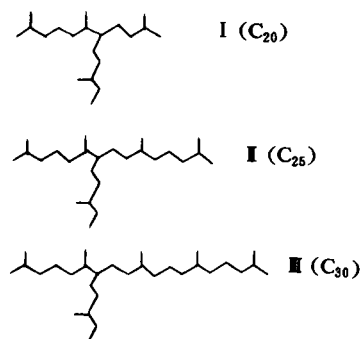
CONCLUSIONS

(1) There are abundant C_{20} , C_{25} and C_{30} HBI alkenes in Qinghai Lake recent sediments.

(2) The C_{20} , C_{25} and C_{30} HBI alkenes originate from some species of diatoms abundant in the lake water.

REFERENCES

- [1] Barrick R. C., Hedges J. I. and Peterson M. L. (1980) Hydrocarbon geochemistry of the Puget Sound region - I. Sedimentary acyclic hydrocarbons. *Geochim. Cosmochim. Acta* 44, 1349-1362.
- [2] Barrick R. C. and Hedges J. I. (1981) Hydrocarbon geochemistry of the Puget Sound region - II. Sedimentary diterpenoid, steroid and triterpenoid hydrocarbons. *Geochim. Cosmochim. Acta* 45, 381-392.
- [3] Belt S. T., Cooke D. A., Hird S. J. and Rowland S. (1994) Structural Determination of a highly branched C_{25} sedimentary isoprenoid biomarker by NMR spectroscopy and Mass spectrometry. *J. Chem. Soc., Chem. Commun.* 2077-2078.
- [4] Cranwell P. A. (1982) Lipids of aquatic sediments and sedimentary particulates. *Prog. Lipid Res.* 21, 271-308.
- [5] Hird S. J., Evans R. and Rowland S. J. (1992) Isolation and characterization of sedimentary and synthetic highly branched C_{20} and C_{25} monoenes. *Mar. Chem.* 37, 117-129.
- [6] Hoefs M. J. L., Sinninghe Damste J. S. and de Leeuw J. W. (1995) A novel C_{35} highly branched isoprenoid polyene in



APPENDIX

Structures of C_{20} , C_{25} and C_{30}
branched isoprenoid alkanes

- recent Indian Ocean sediments. *Org Geochem.* 23, 263—267.
- [7] Kohnen M. E. L., Sinninghe Damste J. S., Rullkötter J., ten Haven H. L. and de Leeuw J. W. (1990) Origin and transformation of C₂₅ and C₃₀ highly branched isoprenoid sulphur compounds; further evidence for the formation of organically bound sulphur during early diagenesis. *Geochim. Cosmochim. Acta* 54, 3053—3063.
- [8] Nichols P. D., Volkman J. K., Palmisano A. C., Smith G. A. and White D. C. (1988) Occurrence of an isoprenoid C₂₅ diunsaturated alkene and high neutral lipid content in Antarctic sea—ice diatom communities. *J. Phycol.* 24, 90—96.
- [9] Requejo A. G. and Quinn J. G. (1983) Geochemistry of C₂₅ and C₃₀ biogenic alkenes in sediments of the Narragansett Bay estuary. *Geochim. Cosmochim. Acta* 47, 1075—1090.
- [10] Requejo A. G., Quinn J. G., Gearing J. N. and Gearing P. J. (1984) C₂₅ and C₃₀ biogenic alkenes in a sediment core from the upper anoxic basin of the Pettaquamscutt River (Rhode Island, U. S. A.). *Org. Geochem.* 7, 1—10.
- [11] Robson J. N. and Rowland S. J. (1986) Identification of novel widely distributed sedimentary acyclic sesterterpenoids. *Nature* 324, 561—563.
- [12] Robson J. N. and Rowland S. J. (1988a) Synthesis of a highly branched C₃₀ sedimentary hydrocarbon. *Tetrahedron Lett.* 29, 3837—3840.
- [13] Robson J. N. and Rowland S. J. (1988b) Biodegradation of highly branched isoprenoid hydrocarbons: A possible explanation of sedimentary abundance. In *Advances in Organic Geochemistry 1987*, *Org. Geochem.* 13, 691—695.
- [14] Rowland S. J., Yon D. A., Lewis C. A. and Maxwell J. R. (1985) Occurrence of 2, 6, 10—trimethyl—7(3—methylbutyl)—dodecane and related hydrocarbons in the green alga *Enteromorpha prolifera* and sediments. *Org. Geochem.* 8, 207—213.
- [15] Rowland S. J. and Robson J. N. (1990) The widespread occurrence of highly branched acyclic C₂₀, C₂₅ and C₃₀ hydrocarbons in recent sediments and biota—a review. *Mar. Environ. Res.* 30, 191—216.
- [16] Sinninghe Damste J. S., Van Koert E. R., Kock—van Dalen A. C., de Leeuw J. W. and Schenck P. A. (1989) Characterization of highly branched isoprenoid thiophenes occurring in sediments and immature crude oils. *Org. Geochem.* 14, 555—567.
- [17] Sinninghe Damste J. S. and Rijpstra W. I. C. (1993) Identification of a novel C₂₅ highly branched isoprenoid thiophene in sediments. *Org. Geochem.* 20, 327—331.
- [18] Volkman J. K., Barrett S. M. and Dunstan G. A. (1994) C₂₅ and C₃₀ Highly branched isoprenoid alkenes in laboratory cultures of two marine diatoms. *Org. Geochem.* 21, 407—413.
- [19] Yon D. A., Ryback G. and Maxwell J. R. (1982) 2, 6, 10—Trimethyl—7(3—methylbutyl) dodecane, a novel sedimentary biological marker compound. *Tetrahedron Lett.* 23, 2143—2146.
- [20] Yruela I., Barbe A. and Grimalt J. O. (1990) Determination of double bond position and geometry in Linear and highly branched hydrocarbons and fatty acids from gas chromatography—mass spectrometry of epoxides and diols generated by stereospecific resin hydration. *J. Chromatogr. Sci.* 28, 421—427.

青海湖沉积物支链和环烷烃组分中 C₂₀, C₂₅和 C₃₀高度支链类异戊二烯烯炔^①

¹李景贵 ¹范璞 ¹崔明中 ¹李振西 ²R. P. Philp ²J. Allen

¹ (中国科学院兰州地质研究所, 兰州 730000)

² (University of Oklahoma, School of Geology and Geophysics, Norman, OK., 73019, U. S. A)

摘要 在青海湖不同盐度的四孔近代沉积物岩芯(Q-16A, QH, QE 和 QG)(图 1)抽提物支链和环烷烃组分中检出了非常丰富的 C₂₀, C₂₅和 C₃₀高度支链类异戊二烯烯炔 (highly branched isoprenoid alkenes), 简称 HBI 烯炔。这是在我国近代湖泊沉积物发现这类化合物的首次详细报导。

由于 C₂₀, C₂₅和 C₃₀ HBI 烯炔比正构烷烃具有较强的抵抗生物降解的能力 (Robson and Rowland, 1988b), 因此, 它们广泛分布于各种近代环境中, 如湖泊、海洋和高盐环境的近代沉积物中 (Rowland and Robson, 1990)。并且, 具有 1~6 个双键的 C₂₀, C₂₅和 C₃₀烯炔经常是现代沉积物中丰富的烃类。最近在印度洋现代沉积物中又发现了一个新的具有 7 个双键的 C₃₅ HBI 烯炔 (Hoefs *et al.*, 1995)。全饱和的 C₂₀(I, 附图)、C₂₅(II, 附图)和 C₃₀(III, 附图) HBI 烷炔已通过标样的合成确切地确定了它们的结构。

在青海湖 QG 孔(尕海, 咸水)和 QE 孔(耳海, 淡水)抽提物中发现了 C₂₀单烯(1 号峰, 图 2a)。C₂₅烯炔(2 号峰, 图 2a、2b)和 C₃₀烯炔(主要是 3 号和 8 号峰, 图 2a、2b)存在于所有四孔沉积物中。在支链和环烷烃组分中, C₂₀, C₂₅和 C₃₀ HBI 烯炔的丰度相当高。C₂₀单烯是 QG-6 层段的最高峰(图 2a), 在 QE-1 和 QE-3 层段中也是一个主要成分; C₂₅烯炔在一些表层沉积物(QH-1 和 QG-1)中为最高峰(图 2a、2b); C₃₀烯炔在所有四孔岩芯各层段中丰度都非常高(图 2a、2b)。

青海湖沉积物中的 C₂₀单烯(与 nC₁₇烷烃共逸出)具 2 个(QE-3, QG-5)或 4 个(QE-1, QG-6)异构体。其中第二个异构体丰度最高(图 2a)。该 C₂₀HBI 烷炔已从 Rozel Point 原油中分离出来 (Yon *et al.*, 1982)。Yon *et al.*, (1982)通过合成该 HBI 烷炔表明 C₂₀单烯具有 2,6,10-三甲基-7(3-甲基丁基)-十二烷结构 (I, 附图)。该 C₂₀单烯在绿藻 *Enteromorpha prolifera* 中鉴定出 (Rowland *et al.*, 1985)。青海湖沉积物中的 C₂₀单烯的质谱图特征(图 3)与该绿藻中的 C₂₀单烯质谱图特征完全一致。

青海湖沉积物中的一组 C₂₅HBI 烯炔(在 nC₂₁烷烃附近逸出)由 C₂₅二烯(M=348)和 C₂₅三烯(M=346)组成。为了表示 C₂₀, C₂₅和 C₃₀烯炔的结构特征, 本文采用 Barrick 和 Hedges(1981)使用的符号系统。在该系统中, c 表示具环状骨架; br 表示无环、具支链骨架; 其后是碳原子数、双键数和环数。(')和('')表示不同的异构体。青海湖沉积物中的 C₂₅二烯由三个异构体组成。用以上符号系统其结构分别被表示为 br25 : 2', br25 : 2 和 br25 : 2''。C₂₅三烯被表示为 br 25 : 3(图 2a、2b)。青海湖沉积物中的 C₂₅二烯的质谱图(图 4)与美国 Pettaquamscutt River 上部缺氧盆地沉积物岩芯中的 C₂₅二烯的质谱图特征完全一致。这种类型的一个 C₂₅二烯也发现于绿藻 *Enteromorpha prolifera* 中 (Rowland *et al.*, 1985)。青海湖沉积物中的 C₂₅二烯的质谱图和该绿藻中的 C₂₅二烯的质谱图特征也完全相同。C₂₅二烯也发现于海-冰硅藻中 (Nichol *et al.*, 1988)。Robson 和 Rowland (1986) 指出该 C₂₅烯炔具 2,6,10,14-四甲基-7(3-甲基戊基)-十五烷结构 (II, 附图)。

青海湖沉积物中的 C₃₀ HBI 烯炔(M=414)(br : 4)最多可由 6 个(三对)异构体组成(3,4; 5,6; 7,8 号

① 化合物的分析和鉴定在美国俄克拉何马大学 Philp 教授实验室完成, 该课题得到中国科学院兰州分院(1994)部分资助。

峰,图2a)。其中第一个(与 nC_{25} 烷烃共逸出)或第六个(与 nC_{26} 烷烃共逸出)异构体丰度最高。这些烯烃的质谱图与美国Narragansett Bay沉积物中的 $c\ 30:2:2$ 的质谱图(Requejo and Quinn, 1983)非常类似。Robson和Rowland(1986)认为被Requejo和Quinn(1983)确定的 $c\ 30:2:2$ 是 C_{20} 和 C_{25} HBI烯烃的同系物,认为 $c\ 30:2:2$ 中的两个环是由于不完全氢化引起的。并推断该 $c\ 30:2:2$ 具2,6,10,14,18-五甲基-7(3-甲基戊基)-十九烷结构(Ⅱ,附图)。该 $c\ 30:2:2$ 的确切结构尚存疑问(Robson and Rowland, 1988a)。

最近研究日趋清楚表明硅藻可能是这些 C_{20} , C_{25} 和 C_{30} HBI烯烃的生物来源。Nichols *et al.*, (1988)报导了一个 C_{25} 二烯为南极州天然海-冰硅藻群中的一个主要烃类。Volkman *et al.*, (1994)在两种硅藻*Haslea ostrearia*和*Rizosolenia setigera*的实验室培养物中鉴定出了具有3~5个双键的 C_{25} 烯烃和5~6个双键的 C_{30} 烯烃。Hird和Rowland从Tamar Estuary野外样品(field samples)分离出的硅藻*Navicula* sp.中也报导了这类饱和的和不饱和的 C_{20} 和 C_{25} 烃类的出现(Sinninghe Damste and Rijpstra, 1993)。因此一些有机地球化学家推断出现于以绿藻*Enteromorpha prolifera*占优势的野外样品中的一个 C_{20} 单烯和一个 C_{25} 二烯可能是由于附生硅藻的存在。所以,青海湖水体中某些种类的硅藻可能是该湖沉积物中这类化合物的生物来源。

由于这类化合物双键的存在,使得这些化合物在早期成岩作用期间易于天然硫化,导致高度支链类异戊二烯噻吩的形成。已从不同地理位置的沉积物(更新世,中新世,白垩纪)和不成熟原油(中新世,早第三纪)中鉴定出8个 C_{20} 和3个 C_{25} HBI噻吩,并且认为这些噻吩类化合物也可能来自硅藻(Sinninghe Damste *et al.*, 1989; Sinninghe Damste and Rijpstra, 1993)。因此,近代沉积物中高度支链类异戊二烯烯烃的研究对石油成因、演化具有一定意义。

关键词 高度支链类异戊二烯烯烃(HBI 烯烃) 高度支链类异戊二烯噻吩(HBI 噻吩) 硅藻 石油成因

第一作者简介 李景贵,52岁,副研究员,有机地球化学