

The occurrence and significance of C₂₅HBI in Cenozoic saline lacustrine source rocks from the Western Qaidam Basin, NW China

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The saline lacustrine deposit of the Oligocene Lower Ganchaigou Formation is the main source rock for the Western Qaidam Basin, NW China. In this study, abundant highly branched isoprenoids with 25 carbon atoms (C₂₅HBI) were detected in the upper section of the Lower Ganchaigou Formation. C₂₅HBI is a biomarker for diatoms, and can provide information regarding biogeochemical processes during production and preservation of sedimentary organic matter. The carbon isotopic values of C₂₅HBI in these source rocks were in the range of –18‰ to –20‰. The relative enrichment in ¹³C of C₂₅HBI suggests that these isoprenoids were derived from diatom blooms. In this case, the diatoms used HCO₃[–] as an additional carbon source to dissolved CO₂ in water column due to their high biological productivity. Conversely, the diatom blooms indicated an abundant nutrient supply to the environment and high primary productivity. Thus, the occurrence of ¹³C-enriched C₂₅HBI could be an ideal marker for good source rocks. The decreased concentration of CO₂ (aq) in the water column induced by diatom blooms can result in an enrichment in ¹³C of organic matter synthesized by primary producers. This may be a possible reason for the occurrence of ¹³C-enriched organic matter in the Cenozoic source rocks of the Western Qaidam Basin. Previous studies have shown that the high carbon number *n*-alkanes sourced from diatoms have no carbon preference. Hence, the sources of *n*-alkanes in regional source rocks are complex, and should be considered when discussing the sources of organic matter in future studies.

C₂₅HBI, diatoms, high carbon number *n*-alkanes, molecular stable carbon isotopic composition, Qaidam Basin

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The 2,6,10,14-tetramethyl-7-(3-methylpentyl)-pentadecane (Figure 1(c)) and its unsaturated homologous are usually termed C₂₅HBI by organic geochemists, and they represent diatom biomarkers. Previous studies have shown that these compounds are enriched in four diatom genera *Rhizosolenia*, *Haslea*, *Navicula* and *Pleurosigma*, including diatom of benthic, planktonic, marine, and freshwater habits [1–6]. C₂₅HBI compounds were first identified from sediments in the Gulf of Mexico [7,8], and then were widely detected in marine and lacustrine sediments, petroleum source rocks and crude oils [8–35]. The sulfurization of C₂₅HBI com-

pounds formed during early diagenesis was also characterized in sediments and source rocks [9,11]. Initially, the HBI compounds were considered to be markers of hypersaline environments, where they are widely distributed [13,14]. However, further studies have detected them in other environments suitable for diatom growth. The distribution of HBIs in sediments also depends on preservation, which often involves degradation during the early diagenetic process [15].

Saline lacustrine sediments provide one of the most important depositional settings for source rock development in China. Cenozoic saline lacustrine source rocks of the Jifan and Qaidam basins are the most representative saline depositional settings, and also are the most important

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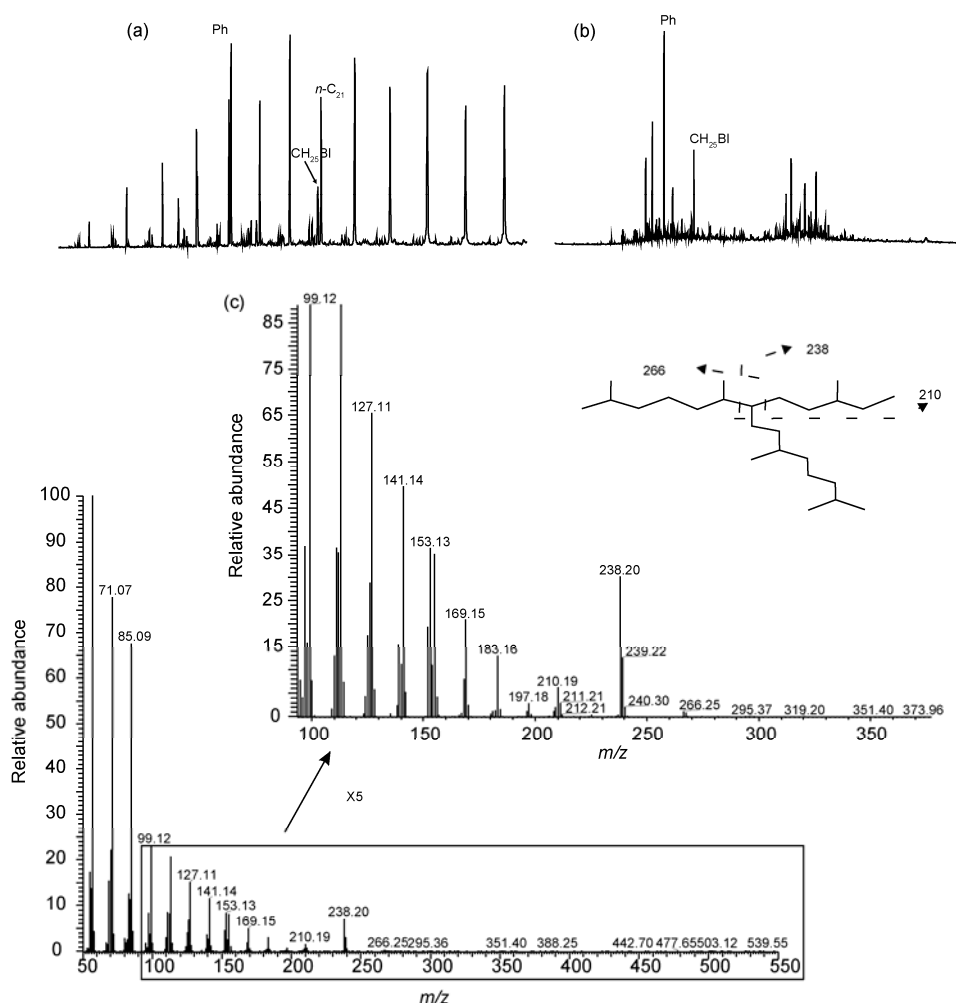


Figure 1 (a) Total ion chromatogram (TIC) of the aliphatic fraction of CDM3 (partly stretching); (b) branched/ cyclic fraction of the aliphatic hydrocarbon of CDM3; (c) the mass spectrum of C₂₅HBI in CDM3.

source rocks in these petroliferous basins [36,37]. Because C₂₅HBI compounds are believed to be sourced from diatoms and usually found in sediments from saline depositional settings, Chinese organic geochemists have been searching for these compounds in these source rocks for the last two decades (Peng Pingan, personal communication). However, there have been no reports on the identification of C₂₀ or C₂₅HBI compounds from these particular strata until now. Even so, several studies have reported HBIs from the modern sediments of Qinghai Lake and Nansha Yongshu reef lagoon [19,38]. The lack of fossil evidence for these biomarkers therefore may indicate that the particular biogeochemical processes involved in deposition of ancient saline lacustrine strata in China were unique, or that diatom did not grow in these ancient saline lakes. Resolving this issue is of critical importance for the evaluation of important saline lacustrine petroleum systems in the area, and for the identification of mechanisms that form good source rocks from these depositional environments.

Recently, we found a relatively high abundance of C₂₅HBI in saline lacustrine source rocks from the upper

section of the Oligocene Lower Ganchaigou Formation in Western Qaidam Basin, NW China. The stable carbon isotopic composition and retention time and mass spectrometry characters of our samples confirmed that this compound is C₂₅HBI. The significance of the biogeochemical process associated with the input of diatoms is discussed in this paper using the distribution of the C₂₅HBI we measured in the source rocks.

1 Samples and experimental design

Six core samples of calcareous mudstone were collected within the Oligocene Upper Section of the Lower Ganchaigou Formation from well Yuehui-103, Western Qaidam Basin, NW China. The sample location is described in the published literature [39]. The six samples were numbered as CDM1 to CDM6 from the top to the bottom (Table 1). The core samples were ground into powder, which were used to determine total organic carbon (TOC), and to conduct Rock-Eval pyrolysis analyses. About 100 g of powered

sample were extracted with dichloromethane and methanol (97:3) for 72 h in a Soxhlet apparatus. Asphaltenes were removed from the extracted organic matter by precipitation with petroleum ether, followed by filtration. The de-asphalted extracts were then separated into aliphatic, aromatic and polar (NSO) fractions by column chromatography packed with a mixture of pre-activated silica gel and alumina (9:1, v/v), using petroleum ether, benzene, and ethanol as solvents, respectively. The aliphatic fraction was further separated into straight chain and branched/cyclic hydrocarbon fractions by urea adduction.

Gas chromatography-mass spectrometry (GC-MS): Aliphatic hydrocarbon and the branched/cyclic fractions in aliphatic hydrocarbon were analyzed by GC-MS using a Thermo Scientific DSQ II mass spectrometer coupled to a Thermo Scientific Trace gas chromatograph. Chromatographic separation was achieved using a 50 m × 0.25 mm i.d. fused silica capillary column coated with a 0.25 μm film of DB-5. The oven temperature program started at 80°C (2 min), and then was changed from 80°C to 220°C at 4°C/min. Subsequently, the rate was changed at 2°C/min until a temperature of 300°C was achieved. This temperature was maintained for 30 min. Helium was used as the carrier gas at a flow rate of 1.0 mL/min. The ion source temperature was 250°C. The ion source was operated in the electron impact (EI) mode at 70 eV. Full scanning and the selected ion monitoring (SIM) mode were used simultaneously.

Gas chromatography-isotopic ratio mass spectrometry (GC-IR-MS): Stable carbon isotopic analyses of *n*-alkanes and branched/cyclic hydrocarbon fractions were performed on a GV Isoprime system interfaced to a Hewlett-Packard 6890 gas chromatograph. The GC was fitted with a 30 m × 0.25 mm id. A DB-5 fused silica capillary column with a film thickness of 0.25 μm leading directly into the combustion furnace was used. For the *n*-alkanes fraction, the GC oven temperature was programmed from 70°C (5 min) at 4°C/min to 295°C (30 min hold time). For the branched/cyclic fraction, the GC oven temperature was programmed from 80°C (5 min) at 3°C/min to 295°C (30 min hold time). Helium was used as the carrier gas. The isotopic values were calibrated against the reference gas, and are reported in the usual “del” notation relative to VPDB. The precision of the measurements was typically <0.5‰. The accuracy of the instrument was tested two to three times daily, by

analyzing a mixture of *n*-alkanes with known δ¹³C values acquired from Indiana University.

2 Results and discussion

2.1 Bulk geochemical characters of source rocks

The Oligocene Upper Section of the Lower Ganchaigou Formation in Western Qaidam Basin was deposited in a saline lacustrine environment interbedded with grey and dark grey mudstone, calcareous mudstone and peridotite. The grey mudstone, dark grey mudstone and calcareous mudstone of this section comprise important hydrocarbon source rocks for the Qaidam Basin during the Cenozoic. The thickness of the section deposited is about 182 to 2000 m [40]. Because of measurement difficulties of vitrinite reflectance in the collected samples, T_{max} values from Rock-Eval pyrolysis and molecular maturity parameters were used to evaluate the maturity of the source rocks. The T_{max} values of the six source rocks all were below 435°C (Table 1), indicating a marginally mature level [41]. The C₃₁ homohopane isomerization parameter 22S/(22S+22R) was in the range of 0.49 to 0.55. Furthermore, the sterane isomerization parameter C₂₉ 5α,14α,17α(H)-sterane 20S/(20S+20R) was below 0.3, which also suggests a marginal maturity level of organic matter in the source rocks. Thus, it is interpreted that the thermal maturity process had little influence on the carbon isotopic composition of the organic matter and the molecular geochemical parameters, and these primitive informations preserved can be used to delineate the biogeochemical process involved [42]. The hydrogen index (HI) and oxygen index (OI) derived from Rock-Eval pyrolysis can be used to classify types of kerogen. All six samples were type II kerogen. The kerogen of the four samples in the middle section were better in hydrocarbon production potential than the other two samples, and can be ascribed to type IIA kerogen. Samples CDM1 and CDM6 have relatively low HI and high OI. This may be due to a relatively high input of terrestrial organic matter or to bacterial reworking of organic matter during sedimentation and early diagenesis [41].

The molecular geochemical characteristics of the six samples had a similar patterns to that of saline lacustrine source rocks [23,37]. These can be summarized as follows.

Table 1 The gross geochemical parameters of source rocks in bore cores of Yuehui-103, Western Qaidam Basin

Sample No.	Rock	Depth (m)	TOC (%)	carbonate ^{a)} (%)	S1 (mg/g)	S2 (mg/g)	S3 (mg/g)	HI (mg/g TOC)	OI (mg/g TOC)	T _{max} (°C)	δ ¹³ C Bitumen (‰)
CDM1	mudstone	2831.6	1.07	34.8	0.09	1.82	0.96	172	91	435	-25.3
CDM2	mudstone	2845.32	3.52	15.0	0.57	11.24	0.94	418	35	420	-24.1
CDM3	mudstone	3018.14	2.69	18.3	1.29	9.56	0.92	439	42	432	-26.5
CDM4	mudstone	3022.16	2.13	20.9	0.72	6.63	0.77	356	41	428	-26.2
CDM5	mudstone	3043.77	2.37	30.5	2.18	8.31	0.80	444	43	433	-26.6
CDM6	mudstone	3053.83	1.11	34.7	0.24	2.15	0.84	187	73	427	-24.6

a) Carbonate contents were determined by X-Ray diffraction.

The concentration of Ph is abnormally high, and it is always the most abundant compound in the aliphatic fraction. The Pr/Ph values are in the range of 0.22 to 0.37. Steranes are more abundant than the hopanes (steranes/hopanes values higher than 4), and relatively abundant gammacerane may be observed. The *n*-alkanes dominate in *n*-C₂₀ or *n*-C₂₂, and usually have even-odd carbon predominance in the range of *n*-C₂₁ to *n*-C₂₉ with OEP values lower than one. Abundant β -carotane also was found in the CDM3 and CDM5 samples. Collectively these biomarker distributions indicate that the source rocks were deposited in a saline lacustrine environment.

2.2 Identification of C₂₅HBI

The C₂₅HBI was identified by comparing GC retention time and mass spectrometry characteristics of the sample with those of published C₂₅HBI data. The retention time of C₂₅HBI in the gas chromatogram was around *n*-C₂₁, although the retention time of C₂₅HBI changed relative to *n*-C₂₁ with a different stationary phase of the capillary column. The mass spectrum of C₂₅HBI can be found in the literature [20–22]. In general, the molecular ion of C₂₅HBI is weak, and also showed mass fragments of the common isoprenoid hydrocarbon. C₂₅HBI was characterized by fragmentation at about the tertiary carbon followed by deprotonation. This process resulted in a series of double ions, which produced deprotonation fragments more abundant than the parent fragment. The main mass fragments of C₂₅HBI were 238 and 239, and the *m/z* 238 response was approximately twice that of *m/z* 239. However, *m/z* 210–211 and 266–277 were minor compared with *m/z* 238–239 [23]. Figure 1 shows the total ion chromatogram (TIC) of the aliphatic fraction and the branched/cyclic fraction of the aliphatic hydrocarbon of sample CDM3. The mass spectrum of C₂₅HBI in CDM3 also is shown in Figure 1. C₂₅HBI in CDM3 had a very similar retention time and mass spectrum characteristics compared to the published literature. Usually, organic matter sourced from diatoms is enriched in ¹³C relative to other algae [25,34]. Thus, the C₂₅HBI sourced from diatoms should be enriched in ¹³C (greater than –20‰ in general according to published reports). The carbon isotopic values of C₂₅HBI in the studied source rocks were in the range of –18‰ to –20‰, and are consistent with their diatom sources. In summary, the compound found in the Cenozoic saline lacustrine source rocks of the Western Qaidam Basin was recognized as C₂₅HBI.

2.3 Abundance and geochemical significance of C₂₅HBI in source rocks

Because of the marginal maturity of the source organic matter, the C₂₅HBI/*n*-C₂₁ value was calculated, and used to characterize the relative abundance of C₂₅HBI in the source rocks. Figure 2 shows the total ion chromatograms (TIC) of

the aliphatic fraction of the six source rocks. Samples CDM3 and CDM5 had a relatively high abundance of C₂₅HBI, followed by sample CDM4. The relative abundance of C₂₅HBI was low in sample CDM6, which was collected from the lowest part of the section, and also was low in sample CDM1 and sample CDM2 collected from the top part of the section. Interestingly, there was no odd or even carbon preference for the high carbon number *n*-alkanes in sample CDM3 and sample CDM5, which had a relatively high abundance of C₂₅HBI. In sample CDM3 and sample CDM5, the *n*-C₂₂₊/*n*-C_{21–} ratios were 2.26 and 1.77, and the *n*-alkanes had a bimodal distribution pattern with maximum *n*-alkanes at *n*-C₂₀ and *n*-C₂₇, respectively. This pattern differs from that of the other samples, and may indicate a source input change or depositional environment change. It is well known that the *n*-alkanes of immature saline lacustrine source rocks exhibit even carbon number preference, with an OEP value less than one. This information suggests a microorganism source input or a control by the depositional environment. Table 2 shows that the OEP values calculated from *n*-C₂₅ to *n*-C₂₉ alkanes were slightly greater than one in samples CDM3 and CDM5. However, OEP values in the other four samples were less than one, with significant even carbon preference, which is typically indicative of organic matter deposited in saline lacustrine environments [43].

Table 2 Molecular geochemical parameters of the source rocks

Parameters ^{a)}	CDM1	CDM2	CDM3	CDM4	CDM5	CDM6
Pr/ <i>n</i> -C ₁₇	0.78	0.48	0.77	0.80	0.70	1.25
Ph/ <i>n</i> -C ₁₈	2.20	1.41	2.60	3.12	1.67	4.73
Pr/Ph	0.29	0.37	0.23	0.24	0.29	0.22
OEP(1)	0.78	0.74	0.76	0.84	0.88	0.64
OEP(2)	0.72	0.93	1.04	0.77	1.08	0.70
<i>n</i> -C ₂₂₊ / <i>n</i> -C _{21–}	0.65	0.50	2.26	0.61	1.77	0.99
Ts/Tm	0.30	0.40	0.45	0.81	0.24	0.52
C ₃₅ /C ₃₄ Hop	1.03	1.14	1.46	1.61	1.42	3.86
GI	0.54	0.88	0.90	1.40	0.64	0.67
C ₃₁ S/S+R	0.53	0.55	0.53	0.49	0.59	0.50
C ₂₇ %	0.45	0.41	0.35	0.33	0.30	0.36
C ₂₈ %	0.25	0.31	0.31	0.23	0.33	0.35
C ₂₉ %	0.31	0.29	0.34	0.44	0.37	0.29
C ₂₉ S/S+R	0.22	0.17	0.19	0.16	0.29	0.15
Sterane/Hopane	5.58	6.84	8.89	13.26	4.01	9.00
C ₂₅ HBI/ <i>n</i> -C ₂₁	0.04	0.05	0.59	0.21	0.45	0.07
β -carotane ^{b)}	–	–	++	+	++	–

a) OEP (1) = (*n*-C₂₁+6*n*-C₂₃+*n*-C₂₅)/4(*n*-C₂₂+*n*-C₂₄); OEP (2) = (*n*-C₂₅+6*n*-C₂₇+*n*-C₂₉)/4(*n*-C₂₆+*n*-C₂₈); C₃₅/C₃₄Hop: C₃₅homohopane/C₃₄homohopane; GI, Gammacerane Index, that is Gammacerane/C₃₀hopane; C₃₁S/S+R, C₃₁homohopane 22S/(C₃₁homohopane 22S+C₃₁homohopane 22R); C₂₇%, C₂₇sterane/(C₂₇sterane+C₂₈sterane+C₂₉sterane); C₂₈%, C₂₈sterane/(C₂₇sterane+C₂₈sterane+C₂₉sterane); C₂₉%, C₂₉sterane/(C₂₇sterane+C₂₈sterane+C₂₉sterane); C₂₉S/S+R, C₂₉ $\alpha\alpha\alpha$ 20S/(C₂₉ $\alpha\alpha\alpha$ 20S+C₂₉ $\alpha\alpha\alpha$ 20R). b) –, not detected; +, low abundance; ++, high abundance.

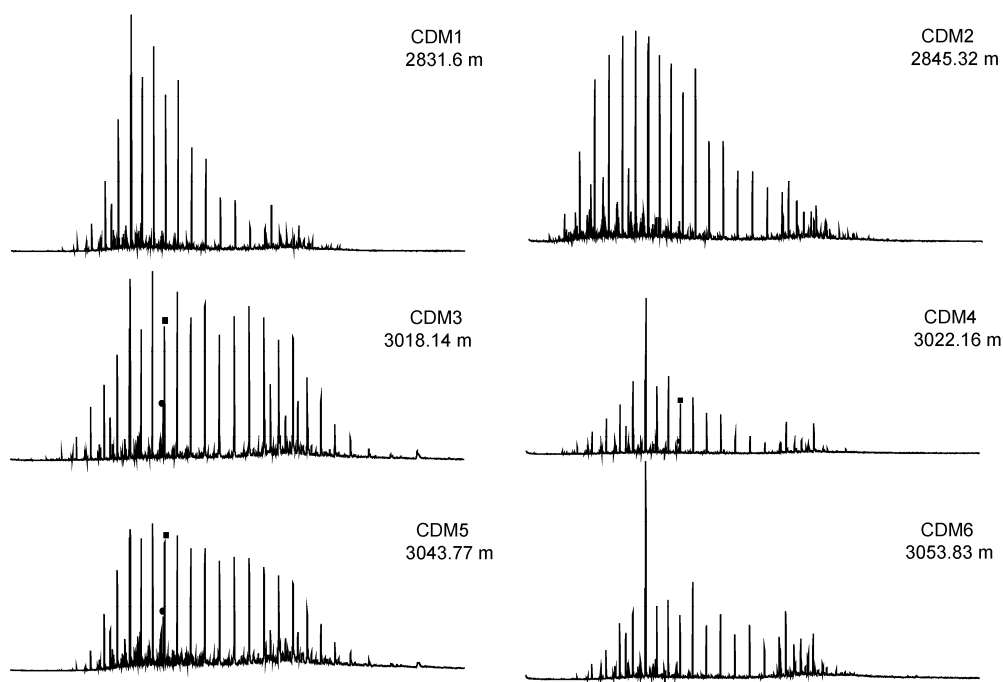


Figure 2 Total ion chromatogram (TIC) of the aliphatic fraction of six source rocks.

The relatively high abundances of high carbon number *n*-alkanes with no carbon preference in samples CDM3 and CDM5 were not consistent with their terrestrial higher plant organic sources. This is because the latter usually show a strong odd carbon preference of *n*-alkanes in its immature to marginally mature levels, and the presence of terrestrial terpenoids. The high carbon number *n*-alkanes distribution with an OEP value of about one in the range of *n*-C₂₅ to *n*-C₂₉ is consistent with *n*-alkanes distribution characteristics of diatom sources. Several previous studies have demonstrated that there is no carbon preference ($>n$ -C₂₁) in the range of high carbon number *n*-alkanes in the extracts of diatom cultures and in sea-ice diatom lipids [18,24,44]. The high carbon number *n*-alkanes (*n*-C₂₀ to *n*-C₃₅) with no carbon preference in the Peru upwelling zone also may be sourced from diatoms [15,24]. Analyses of pyrolysis products of diatom cultures made by Wu revealed that diatoms can produce high carbon number *n*-alkanes with no carbon preference (an OEP value of 1.01 in the range of *n*-C₂₅ to *n*-C₃₂) [45]. Following this idea, the high carbon number *n*-alkanes in samples CDM3 and CDM5 could be partly sourced from diatoms. If we use the n -C₂₂₊/*n*-C₂₂₋ value as one parameter to characterize the abundances of high carbon number *n*-alkanes relative to low carbon number *n*-alkanes in the source rocks, there is a good linear relationship with $R^2=0.86$ between the ratios of n -C₂₂₊/*n*-C₂₂₋ and C₂₅HBI/*n*-C₂₁ throughout the section (Figure 3). This relationship further suggests a contribution of diatoms to the high carbon number *n*-alkanes.

The contribution of diatoms to high carbon number *n*-alkanes in saline lacustrine deposition settings may be one

of the reasons for the lack of carbon preference in the range of high carbon number *n*-alkanes in marginally mature source rocks from some regions of the Western Qaidam Basin. These results may help explain the phenomenon of even carbon and no carbon preference of *n*-alkanes in this region, although microorganism inputs and/or influence of a particular depositional setting to *n*-alkane distributions still cannot be excluded [46]. Indeed, the preservation of sedimentary organic matter from diatoms is controlled by depositional environment. A high abundance of β -carotane was found in samples CDM3 and CDM5 and a relatively high abundance of C₂₅HBI has also been detected. The high abundance β -carotanes and C₂₅HBI in the same source rock suggests that reducing conditions were suitable for the preservation of C₂₅HBI and the diatom source *n*-alkanes. This is because β -carotanes only can be preserved in highly reducing conditions, and are used to indicate anoxic saline lacustrine or highly restricted marine depositional settings [23]. However, the presence of high carbon number *n*-alkanes with no carbon preference does not mean that diatoms are the main source of organic matter preserved in the source rocks. It is well known that diatoms are an important source of C₂₈ sterane in sedimentary organic matter [47]. However, there is no abnormally high abundance of C₂₈ sterane in the source rocks studied here. Thus, the phenomenon of high carbon number *n*-alkanes with no carbon preference may be partly induced by the overlap of the diatom sourced *n*-alkanes and other sourced *n*-alkanes with even carbon preference. Other studies also have shown that the *n*-alkanes with even carbon number preference mainly are distributed in the range of *n*-C₂₁ to *n*-C₂₆ [46].

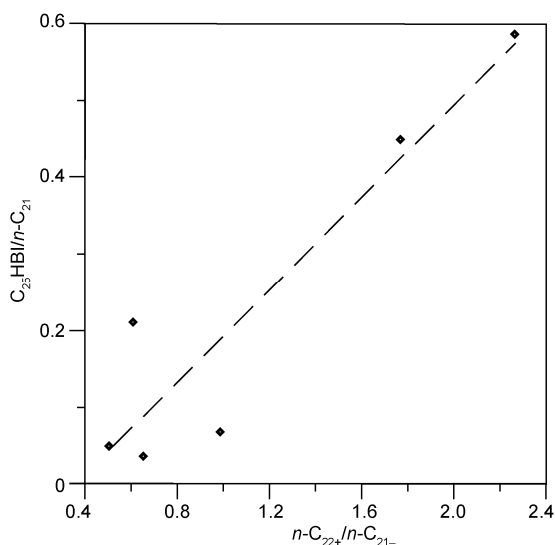


Figure 3 Relationships between $n\text{-C}_{22+}/n\text{-C}_{21-}$ and $\text{C}_{25}\text{HBI}/n\text{-C}_{21}$ values in extracts of the source rocks.

2.4 Characteristics and significance of carbon isotopic values of C_{25}HBI

The abnormal distribution of carbon isotopic values of C_{25}HBI has been known for a long time. Generally, fast-growing diatoms and the utilization of HCO_3^- by diatoms can result in ^{13}C enrichment of their organic matter. Thus, the stable carbon isotopic composition of C_{25}HBI sourced from the diatoms also is ^{13}C enriched relative to that of lipids from other primary producers. It has been shown that the carbon isotopic values of C_{25}HBI are generally higher than -20‰ . These conditions have occurred in modern and ancient aquatic ecosystems and sediments, such as in Hamelin Pool, Arabian Sea, Black Sea, black shale of the Menilite Formation of Poland and Miocene Monterey Formation sediments [25–31,33]. However, ^{13}C -depleted C_{25}HBI (-33‰) relative to other primary producers lipids also was found in Conception Bay of the Atlantic, and explained to not have been a biosynthesized compound by diatoms in blooms, in this situation the low-growing diatoms had strong carbon isotopic fractionation during the carbon utilization process, which resulted in the ^{13}C -depleted C_{25}HBI present [32]. The stable carbon isotopic compositions of n -alkanes and the biomarkers are listed in Table 3 and shown in Figure 4. The $\delta^{13}\text{C}$ of C_{25}HBI s were in the range of -18‰ to -20‰ , which are much more enriched in ^{13}C than bitumen, n -alkanes and other biomarkers. The Pristane (Pr) and Phytane (Ph) sourced from the primary producers had carbon isotopic values of -24‰ to -27‰ . The $\delta^{13}\text{C}$ of C_{27} $\alpha\alpha\alpha\text{20R}$ sterane sourced from algae were in the range of -23‰ to -25‰ . The C_{29} $\alpha\alpha\alpha\text{20R}$ sterane can be sourced from terrestrial plants or algae, but the similar carbon isotopic values of C_{29} $\alpha\alpha\alpha\text{20R}$ sterane with C_{27} $\alpha\alpha\alpha\text{20R}$ sterane indicate low inputs of land plants to the source organic matter. The $\delta^{13}\text{C}$ of C_{28} $\alpha\alpha\alpha\text{20R}$ ster-

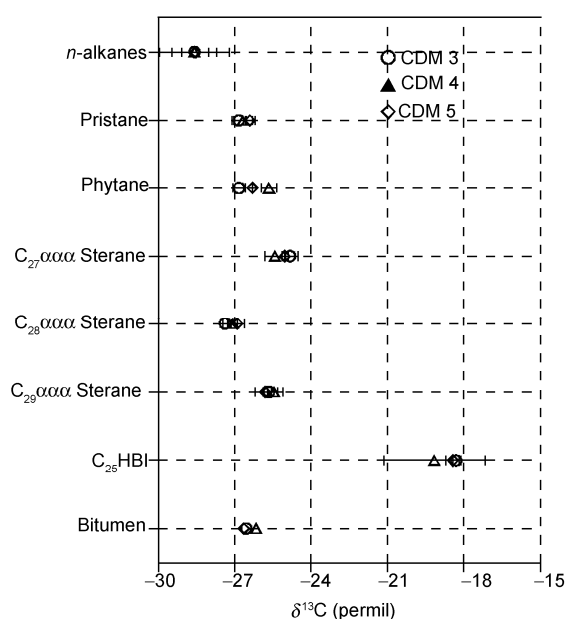
ane was about -27‰ in most of the source rocks. It is clear that the carbon isotopic values of C_{25}HBI were enriched in ^{13}C by 5‰ compared to other biomarkers, which is consistent with its diatom bloom source. Fry and Wainright found that diatoms in spring blooms and in well-mixed summer waters were relatively enriched in ^{13}C in the Georgen Bank ecosystem. This system had $\delta^{13}\text{C}$ values in the range of -15‰ to -19‰ for diatom, while other phytoplankton were depleted in ^{13}C , with $\delta^{13}\text{C}$ values in the range of -21‰ to -25‰ . High abundance of nutrients in the water is the main cause of diatom blooms and ^{13}C enrichment [34]. Thus, C_{25}HBI is usually used to map distribution of nutrients in rich upwelling zones which are suitable for diatom blooms [17,23]. Normally, the carbon isotopic composition of biomass is controlled by the carbon sources utilized, the carbon isotopic fractionation associated with carbon assimilation, metabolism and biosynthesis, and cell carbon budgets [48]. The ^{13}C enrichment of diatoms has been ascribed to the utilization of ^{13}C -enriched HCO_3^- and the weak carbon isotopic fractionation associated with carbon assimilation of fast-growing diatoms [25–34]. Carbonate contents were in the range of 15% to 30% in the source rocks studied here (Table 1). The carbonate must have been abundant in the water when the organic matter was produced and deposited. It is possible that HCO_3^- could have been assimilated by diatoms to maintain high productivity. Conversely, fast growing diatoms can decrease the carbon isotopic fractionation associated with carbon assimilation, metabolism and biosynthesis. Integration of these factors results in the enrichment of ^{13}C in C_{25}HBI .

2.5 Significance of C_{25}HBI occurrence in source rocks, Western Qaidam Basin

The oil and source rock organic matter of the Western Qaidam Basin was characterized by a relatively high enrichment of ^{13}C [36,46]. It generally has been accepted that the particular depositional environments and the high productivity of photosynthetic organisms present in saline lakes can cause a decrease in the amount of dissolved CO_2 available for photosynthesis. This further results in a decreased fractionation of ^{13}C during CO_2 assimilation [46,49,50]. The presence of ^{13}C -enriched C_{25}HBI in the source rocks of the Western Qaidam Basin suggests that diatom blooms occurred in the ecosystem, which can induce a decrease of dissolved CO_2 available for photosynthesis. This is because the fast growing diatoms assimilate more CO_2 in the water [27]. The impact of diatom blooms and other geochemical processes can cause a decrease in the amount of dissolved CO_2 available for photosynthesis and fractionation of ^{13}C during CO_2 assimilation. Thus, sedimentary organic matter with ^{13}C enrichment formed over time. This process differs from that of other terrestrial depositional settings. The contribution of ^{13}C of diatom biomass to the total ^{13}C in sedimentary organic matter strongly depends on the amount

Table 3 Carbon isotopic values of *n*-alkanes and biomarkers (‰, VPDB)

Compound	CDM1	CDM2	CDM3	CDM4	CDM5	CDM6
<i>n</i> -C ₁₅	-27.3	-27.3	-28.6	-28.5	-28.4	-28.1
<i>n</i> -C ₁₆	-27.3	-27.2	-28.9	-28.6	-28.6	-28.5
<i>n</i> -C ₁₇	-26.7	-26.7	-28.2	-28.2	-28.3	-27.7
<i>n</i> -C ₁₈	-26.9	-26.6	-28.1	-28.3	-28.5	-27.3
<i>n</i> -C ₁₉	-26.9	-26.8	-28.4	-28.3	-28.1	-27.1
<i>n</i> -C ₂₀	-26.3	-26.3	-26.2	-27.3	-27.2	-26.3
<i>n</i> -C ₂₁	-27.4	-26.9	-29.0	-29.3	-28.9	-28.2
<i>n</i> -C ₂₂	-27.5	-26.6	-29.0	-29.5	-28.9	-28.0
<i>n</i> -C ₂₃	-28.7	-27.0	-30.3	-31.2	-29.4	-29.9
<i>n</i> -C ₂₄	-28.1	-27.0	-29.3	-30.8	-28.9	-28.4
<i>n</i> -C ₂₅	-28.2	-26.9	-29.2	-30.1	-28.8	-28.0
<i>n</i> -C ₂₆	-27.6	-26.8	-28.6	-28.6	-28.7	-27.0
<i>n</i> -C ₂₇	-27.5	-27.6	-29.3	-28.5	-29.3	-26.7
<i>n</i> -C ₂₈	-25.9	-25.9	-27.9	-26.8	-28.3	-26.1
<i>n</i> -C ₂₉	-25.7	-26.1	-28.2	-26.3	-28.6	-25.9
<i>n</i> -C ₃₀	-26.4	-26.8	-28.1	-27.0	-28.1	-25.2
Average carbon isotopic values of <i>n</i> -alkanes	-27.1	-26.8	-28.6	-28.6	-28.6	-27.4
Pristane	-26.6	-26.6	-26.8	-26.7	-26.4	-24.5
Phytane	-25.3	-25.7	-26.8	-25.7	-26.3	-23.6
C ₂₅ HBI	-	-	-18.3	-19.2	-18.4	-
C ₂₇ 5α(H)14α(H)17α(H)20R sterane	-25.0	-23.5	-24.8	-25.4	-25.0	-23.8
C ₂₈ 5α(H)14α(H)17α(H)20R sterane	-26.7	-26.2	-27.4	-27.1	-26.9	-26.6
C ₂₉ 5α(H)14α(H)17α(H)20R sterane	-23.9	-24.8	-25.7	-25.5	-25.8	-23.7

**Figure 4** Carbon isotopic values of biomarkers in three source rocks with relatively high abundances of C₂₅HBI.

of diatoms preserved in the sediments. This process is highly complicated, and it is the focus of an on-going study. Theoretically, if diatom blooms are well-preserved in sediments, relatively abundant C₂₈ sterane (an indicator of diatoms) should be observed in the biomarker distributions,

and an enrichment of ¹³C in other related biomarkers. In fact, there was no abnormal distribution of C₂₈ sterane in the source rocks studied, and the carbon isotopic compositions of the steranes also were similar to those observed in the Jiangnan saline lacustrine source rocks [51]. The detection of ¹³C-enriched C₂₅HBI in source rocks of the Western Qaidam Basin may indicate only the presence of diatom blooms. Thus, the contribution of diatoms to sedimentary organic matter could be limited. As shown in Tables 1 and 3, the stable carbon isotopic compositions of bitumen and *n*-alkanes from source rocks with relatively high abundance of C₂₅HBI were depleted in ¹³C. This provides further support for the poor preservation of diatom biomass and its limited contribution to sedimentary organic matter. Because diatom-sourced *n*-alkanes show no carbon preference in their high homologues, the contribution of diatoms to sedimentary organic matter makes the distribution of high carbon number *n*-alkanes in source rocks from the Western Qaidam basin complicated. Of course, the distribution of *n*-alkanes also can be controlled by halophilic bacteria, inputs from other microorganisms, and influence of depositional setting [46]. The relative depletion in ¹³C of bulk organic matter in sediments may be due to a decrease of preferential utilization of ¹²CO₂ by diatoms during their fast-growing stage [27].

The occurrence of ¹³C-enriched C₂₅HBI in organic matter within sediments can be a marker for good source rocks in

the Western Qaidam Basin. This is because diatom blooms reflect a high abundance of nutrients in the water column, and high primary productivity. The detection of C₂₅HBI in source rocks also may be an indication of highly reducing conditions that are good for organic matter preservation. As showed in Table 1, all samples, except sample CDM2, which contained a relatively high abundance of C₂₅HBI (CDM3, CDM4 and CDM5) also have high TOC contents and HI values. These characteristics also indicate good source rocks.

3 Conclusions

C₂₅HBI was detected and identified in the Cenozoic Oligocene Lower Ganchaigou Formation source rocks of the Western Qaidam Basin. The detection was achieved using gas chromatography, gas chromatography-mass spectrometry, and gas chromatography-isotope ratio-mass spectrometry techniques. The relatively high abundance of C₂₅HBI in the cyclic/branched hydrocarbons makes it possible to determine its carbon isotopic compositions accurately. The C₂₅HBI in the source rocks of the Western Qaidam Basin is enriched in ¹³C and its stable carbon isotopic compositions are in the range of -18‰ to -20‰. These results are consistent with carbon isotopic values of C₂₅HBI reported in other zones around the world. The relatively high abundance of C₂₅HBI suggests that diatoms are one of the important primary producers in the saline lacustrine ecosystems in the Western Qaidam Basin. The enrichment of ¹³C in C₂₅HBI, relative to the biomarkers from other primary producers, indicates high diatom productivity. Biogeochemical processes deduced from diatom-sourced biomarkers can help to explain the observed phenomena. The enrichment of ¹³C in bulk organic matter and lack of carbon preference in high carbon number *n*-alkanes (>*n*-C₂₅) can then be applied to regional petroleum geochemistry studies. Conversely, the occurrence of ¹³C-enriched C₂₅HBI could be an ideal marker to search for the development of good source rocks in the Western Qaidam Basin.

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