Application of biological markers in the recognition of palaeo-hypersaline environments

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SUMMARY: In this study the saturated and aromatic hydrocarbon fractions of a marl sample from a Messinian (late Miocene) evaporitic basin located in the northern Apennines, and four oils, Rozel Point oil (Utah, USA; Miocene) and three seep oils from Sicily (Messinian), have been studied by GC with simultaneous FID and FPD detection and by GC-MS. All samples show characteristics which might be linked to hypersaline conditions prevailing during the time of deposition. Some of these characteristics are: a very low pristane/phytane ratio (<0.1), a relatively high abundance of docosane (C_{22}) and gammacerane and a series of extended hopanes and/or hop-17(21)-enes maximizing at C_{35}. The aromatic hydrocarbon fraction of all samples is dominated by organic sulphur compounds of which 2,3-dimethyl-5-(2,6,10-trimethylundecyl) thiophene is the most abundant compound. The suggestion of Meissner *et al.* (1984), that the source rock of Rozel Point oil was deposited under hypersaline conditions in a playa-lake system, is supported by the organic geochemical characteristics of this oil.

Introduction

Biological markers, compounds which originate from specific structures occurring in living organisms, are widely used in petroleum exploration. Mostly, they are applied to discriminate between a continental versus a marine origin, for oil/source rock correlations and for thermal maturity estimates of source rocks (e.g., Tissot & Welte 1984). The different sources of marine input can, at present, be specified most exactly by biological markers. For example, it is believed that 4-methylsteranes are the diagenetically altered imprints of dinoflagellates (Boon *et al.* 1979; Robinson *et al.* 1984; de Leeuw 1986).

Recently several characteristic biological markers and their specific distribution patterns have been correlated with hypersaline conditions prevailing during time of deposition (ten Haven *et al.* 1985; Sinninghe Damsté *et al.* 1986).

It is the intention of this paper to present data with similar characteristics observed in a marl layer from the northern Apennines (NAM) and seep oils from Sicily (SSO E1 and E5), the depositional conditions of which are known, and to apply this information to reconstruct the palaeoenvironmental facies of the source rock of the Rozel Point oil (RPO). We will, therefore, discuss only those compounds which are relevant.

Detailed descriptions of the geological setting of the northern Apennines marl layer and of the saturated hydrocarbon fraction extracted from this sample are given by ten Haven *et al.* (1985). The aromatic hydrocarbon fraction is described by Sinninghe Damsté *et al.* (1986). Some preliminary geochemical results of the Sicily seep oils (SSO) and their geological setting were published by Palmer & Zumberge (1981). The Italian samples are all Messinian (late Miocene) in age. It is thought that during the late Miocene the most geographically widespread anoxic event since the Cretaceous took place (Thunell *et al.* 1984), resulting in the deposition of organic-rich sediments, such as the Monterey shale and its contemporary deposits from the circum Pacific. In and around the Mediterranean area the late Miocene is characterized by thick evaporatic deposits, interbedded with organic-rich layers (Cita 1982). The origin and age of the Rozel Point oil is not exactly known. Meissner *et al.* (1984) suggested that this oil is sourced by playa-lake deposits of the Miocene Salt Lake group.

Experimental

The extraction procedure and the separation of the extracts and oils into saturated hydrocarbon, aromatic hydrocarbon and polar fractions are described by Sinninghe Damsté *et al.* (1986). Prior to gas chromatography the elemental sulphur was removed with activated copper. Gas chromatography of the saturated hydrocarbon fractions was performed using a Carlo Erba 4160 instrument with on-column injection, equipped with a 25 m fused silica column (0.32 mm) coated with CP-sil 5, programmed from 125 to 330°C at 4°/min with H_2 as carrier gas. Gas chromatography of the aromatic hydrocarbon fraction

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was performed using a Varian 3700 instrument with simultaneous flame ionization detection (FID) and flame photometric detection (FPD), equipped with a 50 m fused silica column (0.22 mm) coated with CP-sil 5. The conditions of the gas chromatography–mass spectrometry analyses are described by Sinninghe Damsté *et al.* (1986). Identifications of compounds are based on comparison of relative retention times and mass spectra with those of standards and data reported in the literature (e.g., Sinninghe Damsté *et al.* 1986; Philp 1985 and references cited therein).

Results and discussion

Saturated hydrocarbon fraction

The gas chromatograms of the saturate fraction of four samples are shown in Figure 1. The numbers in this figure indicate n-alkanes and correspond with their number of carbon atoms. The R_{22} index, defined as $2 \times C_{22}/(C_{21}+C_{23})$, is greater than one for all samples (RPO = 1.7; NAM = 1.9; SSO E1 = 3.0; SSO E5 = 3.1). This predominance of docosane is interpreted as a marker for hypersaline environments (ten Haven *et al.* 1985) and is also observed in Chinese oils, the source rock of which was deposited in saline lakes (Wang *et al.* this volume). Tetracosane is even more abundant than docosane in the RPO sample, a phenomenon sometimes also observed in Chinese oils (Wang *et al.* this volume). The alkanes of RPO show an even over odd predominance ($CPI_{(24-34)} = 0.82$) in contrast with those of the NAM (CPI = 2.20) and SSO E5 (CPI = 1.20). It has been postulated several times that an even over odd predominance of n-alkanes characterizes a hypersaline environment (see ten Haven *et al.* 1985 and references cited therein). Sometimes, though, such an even over odd predominance can be obscured due to an additional input of continentally-derived alkanes. We believe, therefore, that the R_{22} index is a better criterion for hypersaline environments as heneicosane (C_{21}) and tricosane (C_{23}) are relatively low components among continentally-derived hydrocarbons.

Monomethyl branched alkanes, such as 2-methylpentadecane (A in Fig. 1) and 2-methylhexadecane (C) are relatively abundant and are thought to reflect the original presence of heterotrophic bacteria. Also in the RPO sample 7-methyl- and 8-methylheptadecane were observed and these compounds are thought to be derived from cyanobacteria (Gelpi *et al.* 1970).

Isoprenoid alkanes are abundant and phytane (G) is the most abundant compound in the saturate fraction of all samples. The pristane/phytane ratio is very low (<0.1), which is indicative of hypersaline environments (ten Haven *et al.* 1985; see also Albaiges & Torradas 1974; Fu Jiamo *et al.* this volume; Wang *et al.* this volume). The C_{25} isoprenoid (K), either 2,6,10,14,18- and/or 2,6,10,14,19-pentamethyleicosane, is also present in all samples and it is noteworthy to mention that the 2,6,10,14,18-C_{25} isoprenoid has been suggested as a biological marker for hypersaline environments (Waples *et al.* 1974). The 2,6,10,15,19-C_{25} isoprenoid is virtually absent. The presence of squalane (L) suggests that halophilic bacteria were present in the original depositional environment, although a contribution from other bacteria such as methanogenic bacteria cannot be precluded. Recently large quantities of highly branched

TABLE 1. *Selected compounds identified in the saturated hydrocarbon fraction*

A	2-methylpentadecane
B	2,6,10-trimethylpentadecane
C	2-methylhexadecane
D	3-methylhexadecane
E	2,6,10-trimethyl-(3-methylbutyl) dodecane
F	2,6,10,14-tetramethylpentadecane (pristane)
G	2,6,10,14-tetramethylhexadecane (phytane)
H	2,6,10,14-tetramethylheptadecane
I	2,6,10,14-tetramethyloctadecane
J	5α(H),14α(H),17α(H)- + 5α(H),14β(H),17β(H)-pregnane
K	2,6,10,14,18- and/or 2,6,10,14,19-pentamethyleicosane
L	2,6,10,15,19,23-hexamethyltetracosane (squalane)
M	5β(H),14α(H),17α(H)-20R-cholestane + 5α(H),14α(H),17α(H)-20S-cholestane (esp. RPO)
N	5α(H),14β(H),17β(H)-20R-cholestane + 5α(H),14β(H),17β(H)-20S-cholestane
O	5α(H),14α(H),17α(H)-20R-cholestane
P	5α(H),14β(H),17β(H)-20R-24-methylcholestane 5α(H),14β(H),17β(h)-20S-24-methylcholestane
Q	5α(H),14α(H),17α(H)-20R-24-methylcholestane
R	4α,24-dimethyl-5α(H),14β(H),17β(H)-20R-cholestane + 5α(H), 14α(H), 17α(H)-20S-24-ethylcholestane (esp. RPO)
S	4α,24-dimethyl-5α(H),14β(H),17β(H)-20S-cholestane + 5α(H), 14β(H), 17β(H)-20R-24-ethylcholestane + 5α(H), 14β(H), 17β(H)-20S-24-ethylcholestane
T	5α(H), 14α(H),17α(H)-20R-24-ethylcholestane
U	4α-methyl,24-ethyl-5α(H),14α(H),17α(H)-20R-cholestane + 17α(H),21α(H)-hopane
V	gammacerane
W	22R-pentakishomohop-17(21)-ene 22S-pentakishomohop-17(21)-ene
X	17α(H),21β(H)-22R-pentakishomohopane 17α(H),21β(H)-22S-pentakishomohopane

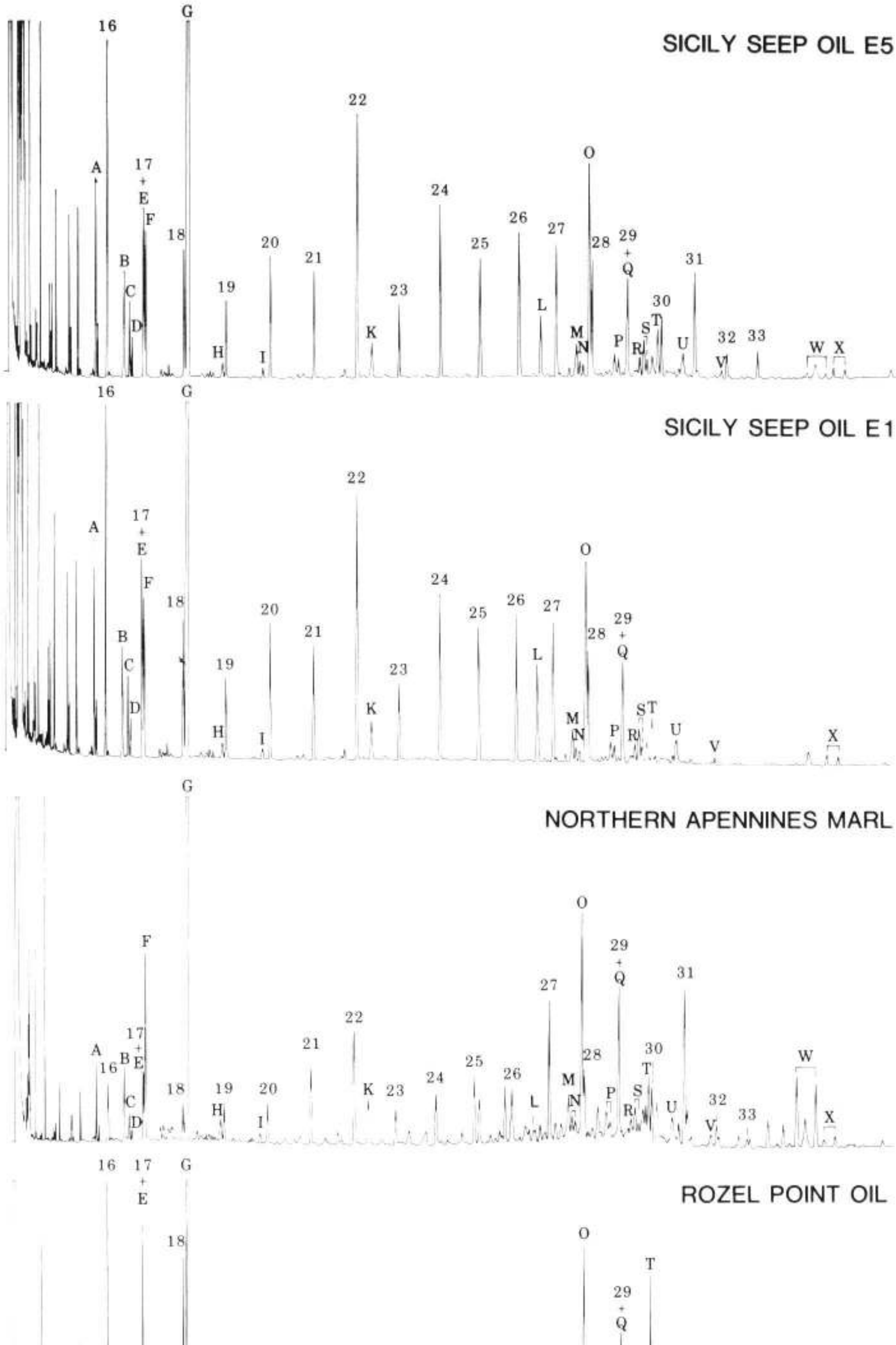

FIG. 1. Gas chromatograms of the saturated hydrocarbon fractions of Sicily seep oils E1 and E5 (E2 and E5 gave identical gas chromatograms), northern Apennines marl sample, and Rozel Point oil. Identifications of letter-labelled compounds are given in Table 1.

alkanes and alkenes were found in sediments from some hypersaline basins of Western Australia (Dunlop & Jefferies 1985). The isoprenoid alkane 2,6,10-trimethyl-7-(3-methylbutyl) dodecane (E) is an important compound occurring in the RPO (Yon *et al.* 1982) and is also present in small quantities in the other samples. This compound might be a biological marker for *Enteromorpha prolifera* (Rowland *et al.* 1985), a species which is known to have a salinity tolerance up to 65‰ (Ehrlich & Dor 1985).

Figure 2 shows mass chromatograms of m/z 191 and 367 of the RPO. The distribution patterns of the extended hop-17(21)-ene series, exemplified by the m/z 367 trace, and the extended 17α(H),21β(H)-hopane series are very similar if not identical and maximize at C_{35}. This phenomenon is thought to be very typical for hypersaline environments (ten Haven *et al.* 1985). Similar distribution patterns of the hopanoids are observed in the other samples (Fig. 1) and also in marl extracts from Sicily evaporitic deposits (Palmer & Zumberge 1981) and in some Chinese oils derived from salt lake evaporitic formations (Fu Jiamo *et al.* this volume). There are, however, some similar distribution patterns reported from non-hypersaline environments (e.g., McEvoy 1983). A reduction of hopenes to the corresponding hopanes was suggested to explain the similar distribution patterns of these compounds (ten Haven *et al.* 1985, 1986). Another feature which all samples have in common, is the presence of gammacerane (V in Fig. 1; see also Fig. 2). Gammacerane is also ubiquitous in Chinese oils derived from saline environments (Fu Jiamo *et al.* this volume; Xie Taijun *et al.* 1986). In the RPO 5α(H),14α(H),17α(H)- and 5α(H),14β(H),17β(H) pregnane (J), homopregnane and 4-methylpregnane were encountered, but only in small amounts. Sometimes pregnanes and homopregnanes are present as the major steranes in samples from hypersaline environments (ten Haven *et al.* 1985; see also Fu Jiamo *et al.* this volume).

The sterane composition and distribution of the Italian samples (NAM, SSOs) are almost identical (Fig. 1), supporting the presumed origin of the seep oils from Messinian formations in Sicily (Palmer & Zumberge 1981). One remarkable characteristic is the almost complete absence of 20S 5α(H),14α(H),17α(H) sterane isomers, whereas the 20S and 20R 5α(H),14β(H),17β(H) steranes (N, P, S) are present in relatively high amounts. This 'maturity' discrepancy can be explained by an alternative diagenetic pathway of steroids, assuming precursor steroids with a Δ^7, Δ^8 and/or $\Delta^{8(14)}$ double bond (ten Haven *et al.* 1986). Other relatively important steranes are 4-methylsteranes (R, S, U). These compounds may point to an input of dinoflagellates (Boon *et al.* 1979; Robinson *et al.* 1984; de Leeuw 1986), which is not surprising considering the wide salinity tolerance of dinoflagellates (Wall & Dale 1974). However, a bacterial origin for the 4-

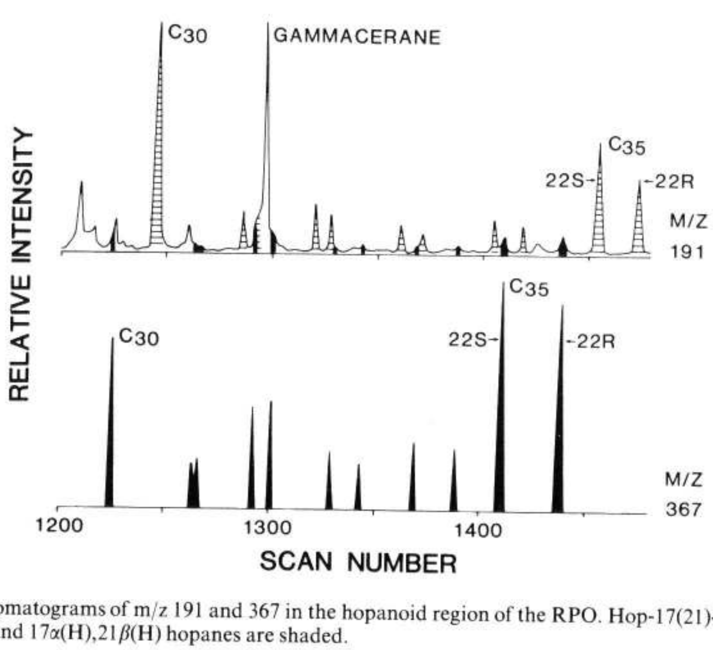

FIG. 2. Mass chromatograms of m/z 191 and 367 in the hopanoid region of the RPO. Hop-17(21)-enes are indicated black and 17α(H),21β(H) hopanes are shaded.

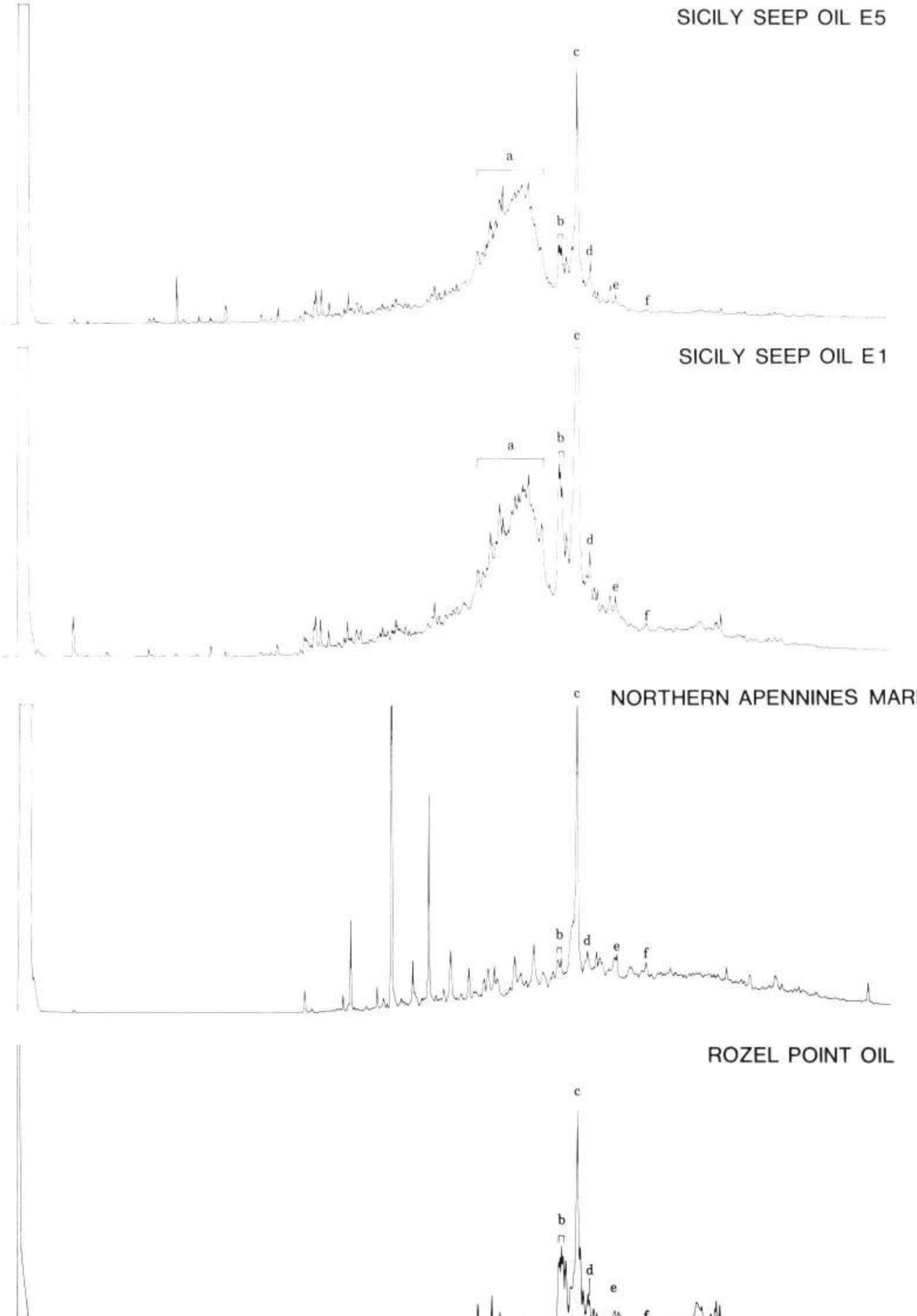

FIG. 3. FPD–gas chromatograms of the aromatic hydrocarbon fraction of Sicily seep oils E1, E5, northern Apennines marl and Rozel Point oil. Identifications of selected compounds are given in Table 2.

TABLE 2. *Selected compounds identified in the aromatic hydrocarbon fraction*

a	unresolved hump of a.o. thiolanes
b	mixture of mid-chain C_{20} isoprenoid thiophenes
c	2,3-dimethyl-5-(2,6,10-trimethylundecyl) thiophene
d	3-methyl-2-(3,7,11-trimethyldodecyl) thiophene
e	3,5-dimethyl-2-(3,7,11-trimethyldodecyl) thiophene
g	5-ethyl-3-methyl-2-(3,7,11-trimethyldodecyl) thiophene

methyl steranes can at present not totally be precluded, since Bouvier *et al.* (1976) reported the occurrence of a 4-methyl-$\Delta^{8(14)}$-sterol and a 4-methyl-$\Delta^{8(14),24}$-sterol in the bacterium *Methylococcus capsulatus*.

Aromatic hydrocarbon fraction

The majority of compounds present in the so-called aromatic hydrocarbon fraction consists of organic sulphur compounds (OSC). In view of this it is noteworthy that Thompson (1981) reported a sulphur content of 13.95% for the RPO and Colombo & Sironi (1961) measured up to 10.10% sulphur in Messinian seep oils. Figure 3 shows the gas chromatograms as recorded with an FPD giving a selective response for OSC. A detailed description of the OSC of the NAM sample is reported by Sinninghe Damsté *et al.* (1986) and OSC of the RPO are reported by de Leeuw (1986) and by Sinninghe Damsté and de Leeuw (1986). The most abundant compound in all samples is identified as 2,3-dimethyl-5-(2,6,10-trimethylundecyl) thiophene (c in Fig. 3). The co-occurrence of this C_{20} isoprenoid thiophene and phytane as the most important compounds in the respective component classes, seems to favour the hypothesis that this isoprenoid thiophene results from an early diagenetic incorporation of sulphur in, for example, archaebacterial phytenes (Brassell *et al.* 1986). In the RPO a mixture of uncommon isoprenoid thiophenes is observed with the 2,6,10-trimethyl-7-(3-methylbutyl) dodecane carbon skeleton (Sinninghe Damsté *et al.* 1987). These types of sulphur compounds are relatively abundant in the aromatic fraction. In the saturated fraction the corresponding alkane, 2,6,10-trimethyl-7-(3-methylbutyl) dodecane, is an important compound, which supports the incorporation theory. More information concerning the OSC of the seep oils investigated here is published elsewhere (Sinninghe Damsté *et al.* 1987; Schmid *et al.* 1987).

As the precise nature of the OSC is still poorly understood, a direct link with the depositional environment seems rather speculative. However, in view of their dominant presence in all samples, the suggestion of Sinninghe Damsté *et al.* (1987) that these OSC characterize hypersaline depositional environments, seems to be justified. Moreover the existence of high-sulphur petroleums has been ascribed to sulphur incorporation into organic matter in carbonate–evaporate environments (Tissot & Welte 1984).

Conclusions

All samples show similar biological marker characteristics, which can be attributed to the environment of deposition. Table 3 summarizes these biological markers and their typical distribution patterns.

TABLE 3. *Organic geochemical phenomena related to hypersaline depositional environments*

- Phytane ≫ pristane
- $R_{22} = \dfrac{2 \times n\text{-}C_{22}}{n\text{-}C_{21} + n\text{-}C_{23}} > 1.5$
- High abundance of regular C_{25} isoprenoid
- High abundance of squalane
- High abundance of organic sulphur compounds especially 2,3-dimethyl-5-(2,6,10-trimethylundecyl) thiophene
- 14β(H),17β(H)-sterane concentration relatively high in comparison with the 14α(H),17α(H)-20S steranes
- Relatively high abundance of gammacerane
- Typical distribution patterns of C_{31}–C_{35} hop-17(21)-enes and 17α(H),21β(H)-hopanes, both maximizing at C_{35}

The Rozel Point oil has been suggested to be sourced by playa-lake deposits of the Miocene Salt Lake group (Meissner *et al.* 1984), and based on the distribution of biological markers and their relative quantities observed in the saturated and aromatic hydrocarbon fractions, we support this suggestion. It seems that the phenomena as described in Table 3, can be used as a key to the past to recognize palaeo-hypersaline environments.

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