Chapter 24

Organic Sulfur Compounds and Other Biomarkers as Indicators of Palaeosalinity

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A number of selected molecular parameters obtained from analysis of immature crude oils and sediment extracts are evaluated as indicators of palaeosalinity. The nature of these parameters is discussed taking into account the role of intermolecular and intramolecular incorporation of sulfur into specific functionalized lipids. Specific distribution patterns of methylated chromans and C_{20} isoprenoid thiophenes and the relative abundance of gammacerane are excellent indicators for palaeosalinity, whilst other parameters such as 14α(H),17α(H)/14β(H),17β(H) -sterane ratios, the pristane/phytane ratio, the even-over-odd carbon number predominance of *n*-alkanes and the relative abundance of C_{35} hopanes and/or hopenes may indicate palaeohypersalinity but are affected by environmental factors other than hypersalinity and by diagenesis.

In a recent paper Evans and Kirkland (1) summarized important aspects of hypersaline (salinity > 4%) environments. Contrary to previous thoughts these environments, especially those with salinities varying between 4 and 12%, are very productive, sometimes up to 10 times more than upwelling environments. The species distribution in these environments is limited and consists in general mainly of sulfate reducing- and photosynthetic sulfur bacteria and halophilic Eubacteria, specific green algae such as *Dunaliella* species, certain diatom species and Protozoa (2-5). In extreme saline environments (brines) halophilic Archaebacteria such as *Halobacterium* may contribute significantly to the biomass.

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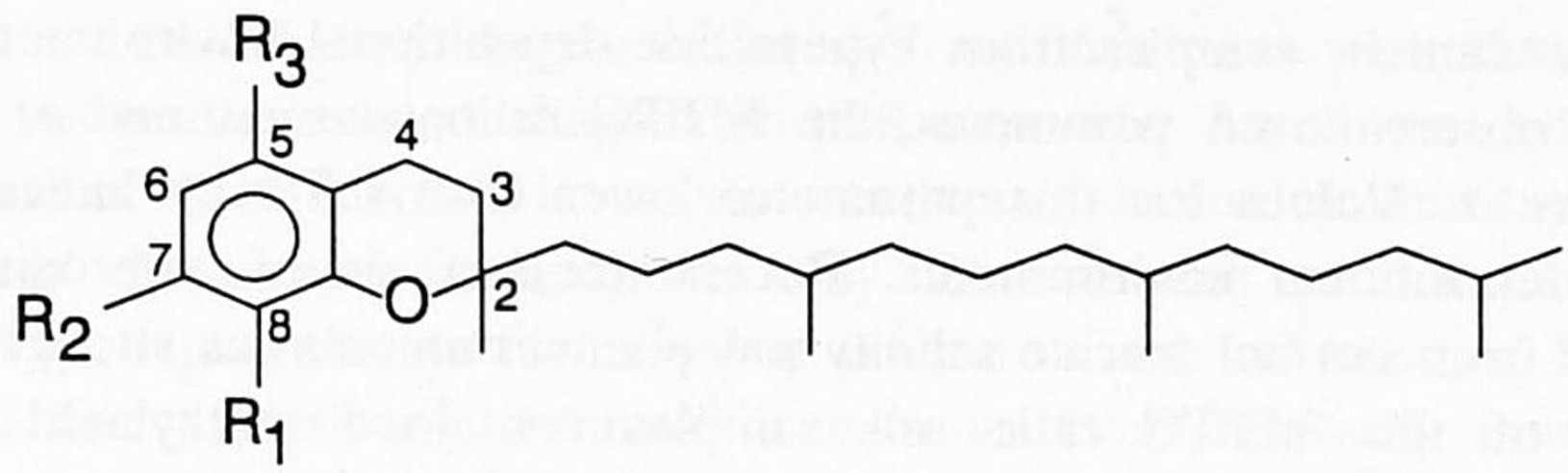
The surface waters are less oxygenated in these environments due to their enhanced salinities and water circulation is slowed down by its higher viscosity. Bacterial sulfate reduction can be very high (1,6). These aspects favour anoxia, especially when a halocline forms. The extremely high production of biomass combined with good preservation conditions make these hypersaline environments of particular interest in organic geochemical terms. It has been suggested that a significant proportion of the petroleum reserves may derive from organic matter produced in hypersaline environments (1).

The importance of these depositional environments makes it desirable that studies concerned with the reconstruction of palaeoenvironments from sediments or source rocks of oils also establish molecular parameters for palaeohypersalinity. Recently, ten Haven *et al.* (7-9) have summarized a number of "organic geochemical phenomena" related to hypersaline depositional environments. In addition to previously known parameters, such as an even-over-odd carbon number predominance of *n*-alkanes and a low pristane/ phytane ratio (<0.5), several new parameters were suggested. These parameters, however, are mainly based on empirical relations.

In this paper we discuss a selected set of molecular parameters which may indicate hypersaline palaeoenvironments. Attempts are made to explain the nature of most of these parameters taking into account recent results concerning the early stage diagenesis of Δ^5- and Δ^7-sterols (10-12) and the role and consequences of reactions of inorganic sulfur species with organic matter in Recent sediments (13-20). The selection of data is based on results obtained from studies of aliphatic and aromatic hydrocarbons, organic sulfur compounds and sulfur-rich high-molecular-weight substances occurring in sediment extracts and oils derived from organic matter deposited in both 'normal' marine salinity and hypersaline palaeoenvironments (13-26).

Chroman Distributions

In a recent paper Sinninghe Damsté *et al.* (27) have described the presence of a family of methylated chromans with an isoprenoid side chain (methylated 1-methyl-1-(4,8,12-trimethyltridecyl)chromans, MTTC) in a number of sediment extracts and crude oils. A diagenetic origin from tocopherols was thought to be highly unlikely and the authors speculated about an origin from Eu- or Archaebacteria. The distribution patterns of these chromans vary considerably and a correlation was found between the chroman distributions and the palaeosalinity of the sample (Figure 1). The palaeosalinity of the samples studied was assessed on the basis of geological and biomarker data (27). Chroman distributions of samples from normal marine salinity environments are dominated by the trimethyl chroman, whilst this chroman isomer is much



8-Me-MTTC	$R_1 = CH_3$, $R_2 = H$, $R_3 = H$
5,8-diMe-MTTC	$R_1 = CH_3$, $R_2 = H$, $R_3 = CH_3$
7,8-diMe-MTTC	$R_1 = CH_3$, $R_2 = CH_3$, $R_3 = H$
5,7,8-triMe-MTTC	$R_1 = CH_3$, $R_2 = CH_3$, $R_3 = CH_3$

$$\text{MTTC ratio} = \frac{[\text{ 5,7,8-triMe-MTTC }]}{[\text{ total methylated MTTC }]}$$

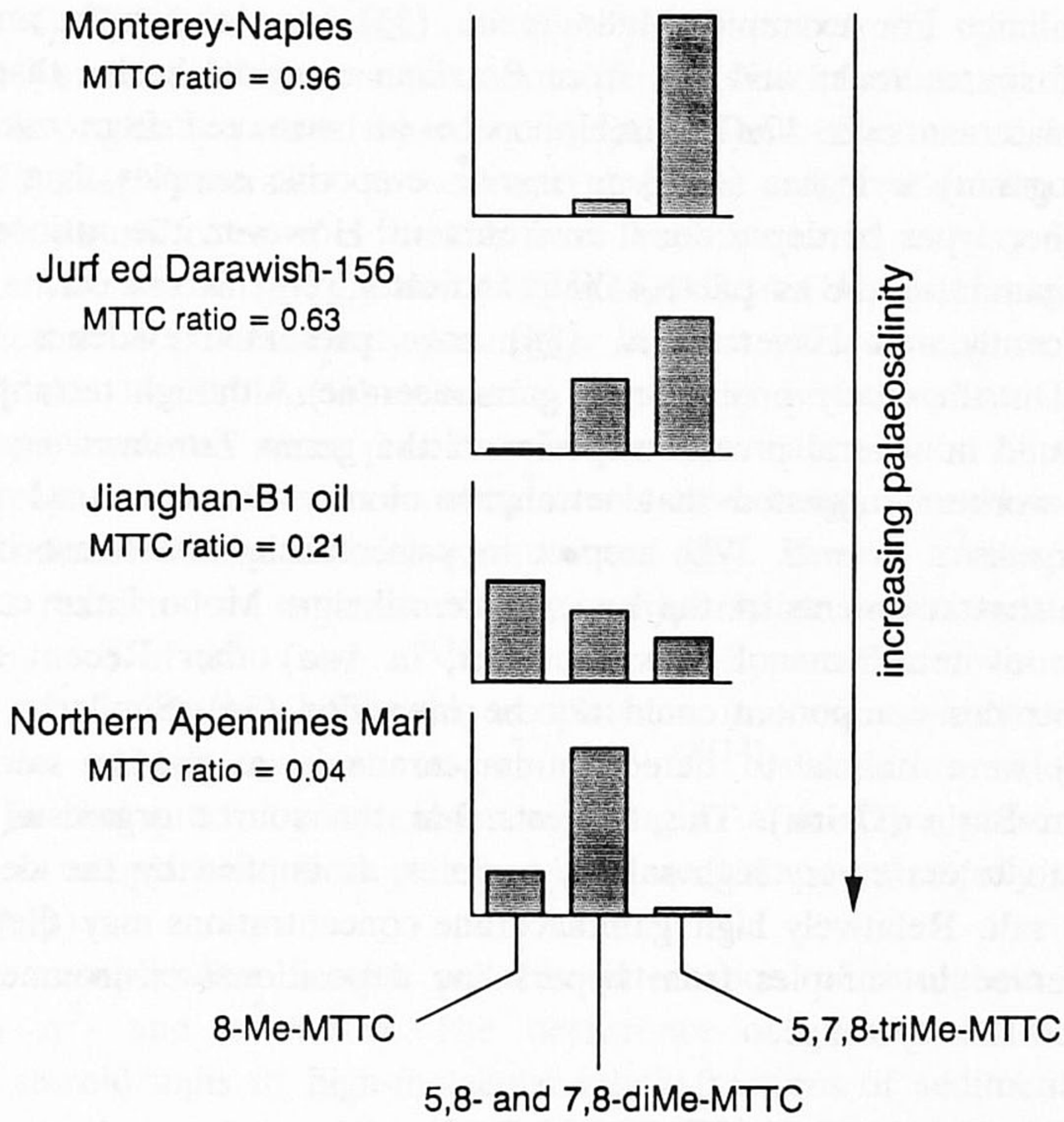


Figure 1. Methylated 1-methyl-1-(4,8,12-trimethyltridecyl)chromans (MTTC) as indicators of palaeosalinity: structures, definition of the MTTC ratio and typical methylated MTTC distributions in sediments and petroleums. Description of the samples is given elsewhere (16).

less abundant in samples from hypersaline depositional environments. Based on this observation a parameter, the MTTC ratio, was defined as indicated in Figure 1. Values for this parameter lower than 0.5 may indicate hypersaline depositional environments. Recent (re)analysis of approximately 85 samples from normal marine salinity palaeoenvironments has strengthened the validity of this MTTC ratio: all samples contained methylated chromans dominated by the trimethyl chroman (28,29). Although these chromans or their precursors have not yet been encountered in organisms we believe that the significant variations in their distribution patterns are due to marked changes in microbial populations as a result of variations in salinity.

Gammacerane

Gammacerane occurs widespreadly in sediments and oils from different palaeoenvironments (30,31). It has been noted that its concentration relative to other triterpanes is particularly high in sediments and oils from hypersaline palaeoenvironments (7,8,30-33) and therefore may be of use in assessing palaeosalinity. For example, Mello *et al.* (31) have shown in an extensive study of source rocks and oils from Brazilian marginal basins that the ratio of gammacerane over 17α(H),21β(H)-hopane (as measured from *m/z* 191 mass chromatograms) is higher (>0.7) in marine evaporitic samples than in samples from other types of depositional environment. However, the rationale for the use of gammacerane as palaeosalinity indicator remains unclear.

Recently, ten Haven *et al.* (34) have presented evidence that tetrahymanol is the likely precursor of gammacerane. Although tetrahymanol has been found in several protozoa species of the genus *Tetrahymena*, ten Haven and co-workers suggested that tetrahymanol may be a natural product of other organisms as well. With respect to palaeosalinity assessment it is worthy of note that sediments of the hypersaline, alkaline Mono Lake contain high amounts of tetrahymanol (35). However, in two other Recent hypersaline sediments this component could not be identified (34). Similarly, Brassell *et al.* (33) were unable to detect gammacerane in a glauber salt from the Jianghan Basin (China). This suggests that the source organism(s) may be unable to tolerate very high salinity regimes, as implied by the deposition of glauber salt. Relatively high gammacerane concentrations may therefore only be observed in samples from hypersaline depositional environments with a restricted salinity range.

14β(H),17β(H)/14α(H),17α(H)-Sterane Ratio

Based on molecular mechanics studies of sterenes and on reinterpretations of steroid data in the organic geochemical and chemical literature, corrected

and separate routes of early diagenesis for Δ^5- and Δ^7-sterols were postulated (11). The newly formulated diagenetic pathways are based on selective hydrogenation of double bonds in sterenes and on a limited isomerisation of double bonds *via* tertiary carbocations only. Sterane end products of the proposed diagenetic pathways for Δ^5- and Δ^7-sterols are indicated in Figure 2. The detailed analysis of steranes in extracts from relatively immature sediments and crude oils confirmed the proposed pathways in that: i) the distribution patterns of 14β(H),17β(H)-steranes are completely different from those of the 14α(H),17α(H)-steranes and ii) the 14β(H),17β(H)-steranes are fully isomerised at C_{20} whilst the 14α(H),17α(H)-steranes are not or only partly isomerised at C_{20} (10,12). A mass chromatogram of *m/z* 218 obtained from GC-MS analyses of the saturated hydrocarbon fractions of the Rozel Point Oil, an oil which is thought to originate from a hypersaline source rock (8,36), exemplifies this feature (Figure 3). In a study of an immature marl sample from the Northern Apennines (Italy) Peakman *et al.* (12) have recently shown that the assumed intermediate products in the isomerisation of Δ^7-sterols, the spirosterenes, indeed possess a distribution pattern similar to the 14β(H),17β(H)-steranes and completely different from that of the 14α(H),17α(H)-steranes. These considerations permit discrimination of the Δ^5- and Δ^7-sterols originally present based on measurements of ratios of 14β(H), 17β(H)/14α(H),17α(H) steranes in sediment extracts and crude oils. Since relatively high abundancies of Δ^7-sterols have been reported in very Recent hypersaline environments (37,38) the 14β(H),17β(H)/14α(H),17α(H) ratio can be rationalized as a palaeosalinity parameter at least in sediments or crude oils in which the 14α(H),17α(H)-steranes are not fully isomerised at C_{20}.

There are, however, some problems in the direct application of such a ratio. First, relative high abundances of Δ^7-sterols have been reported in Lake Kinneret, a normal marine salinity environment (39). Hence, Δ^7-sterols are obviously not restricted to organisms living in hypersaline environments. The relative abundance of Δ^7- (and $\Delta^{8(14)}$-) sterols in hypersaline environments may be due to the absence of grazing zooplankton in these environments. In normal marine salinity environments Δ^7- and $\Delta^{8(14)}$-sterols are selectively metabolised in the guts of zooplankton resulting in a selective preservation of Δ^5-sterols in zooplankton fecal pellets, which are transported rapidly to the sediment (40,41).

Another complication is the possible interaction of inorganic sulfur species with Δ^5- and Δ^7-sterols. The occurrence of thiosteroids and of sulfur-bound steroid units in high-molecular-weight fractions of sediments and oils has been observed recently (15,16,20,26). The thiosteroids with the thiophene ring condensed to the D-ring almost exclusively possess the 14β(H) configuration (26). Thiosteroids with a thiophene unit in the side chain mainly

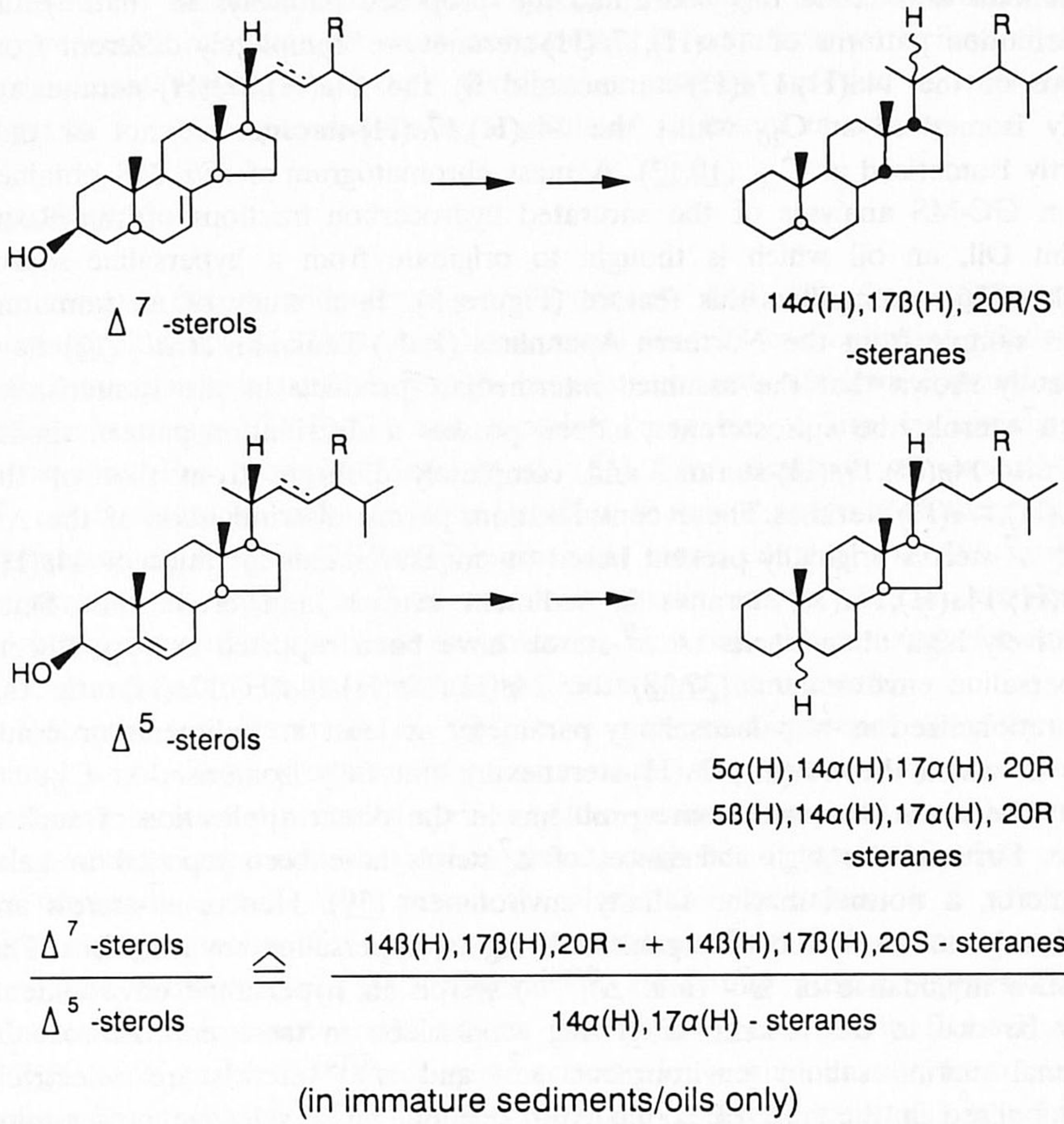


Figure 2. Sterane end products of the early diagenetic pathways of Δ^5- and Δ^7-sterols. Data from ref. 11.

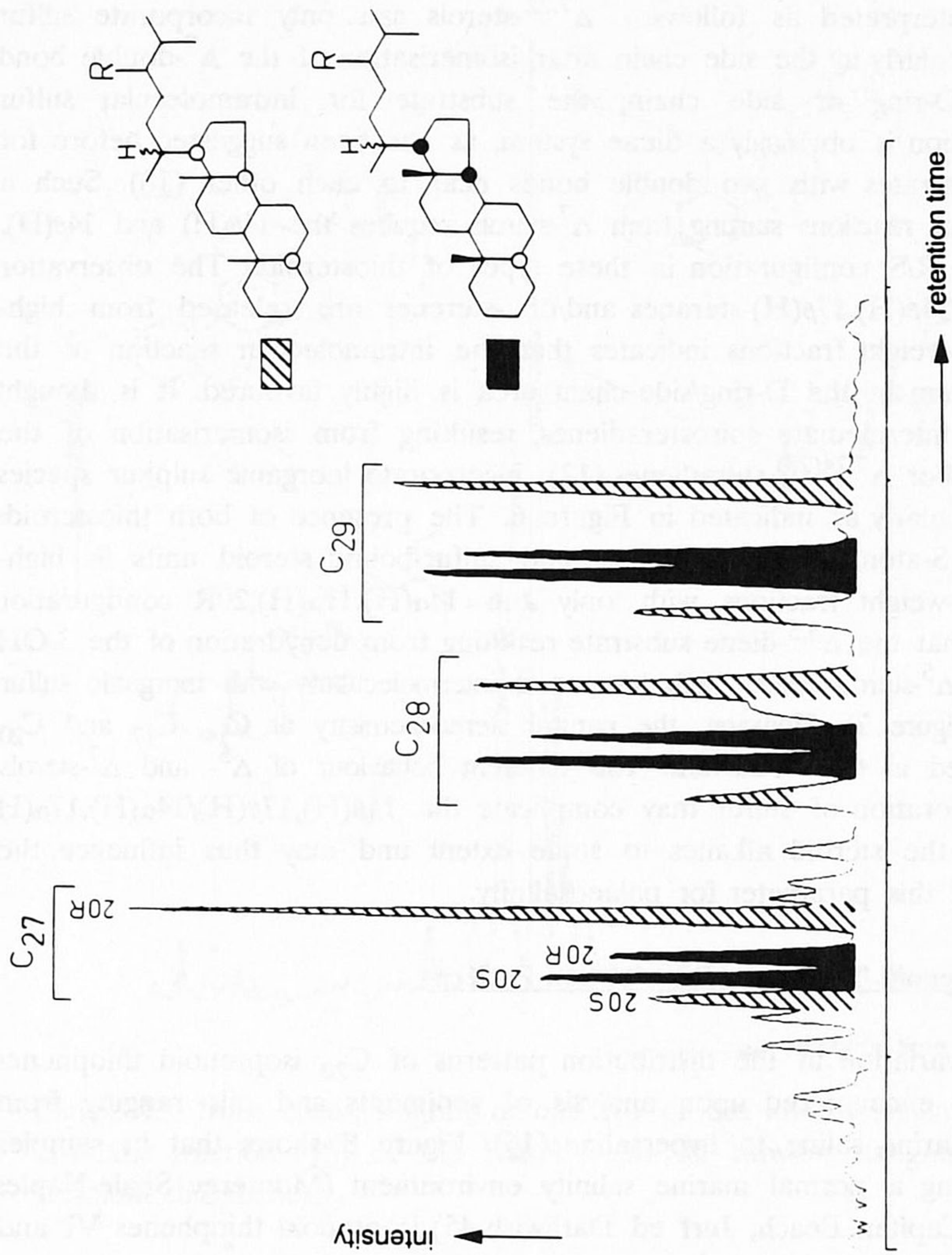


Figure 3. Mass chromatogram of *m/z* 218 of the saturated hydrocarbon fraction of the Rozel Point oil. 5α(H),14α(H),17α(H)- and 5α(H),14β(H),17β(H)-steranesare differentiated as shown.

have the 14β(H),17β(H),20R/S configuration (26; Figure 4). When the sulfur atom is located in the A/B-ring part of the molecule the compounds occur exclusively in the 14α(H),17α(H),20R configuration (26). After desulfurisation or flash-pyrolysis of the high-molecular-weight fraction of appropriate samples only 14α(H),17α(H),20R steranes are released and no 14β(H),17β(H),20R or 20S steranes are observed (20; Figure 5). These observations can be speculatively interpreted as follows: $\Delta^{7,22}$-sterols can only incorporate sulfur intramolecularly in the side chain after isomerisation of the Δ^{7}-double bond to the D-ring or side chain; the substrate for intramolecular sulfur incorporation is obviously a diene system, as has been suggested before for other substrates with two double bonds near to each other (18). Such a sequence of reactions starting from Δ^{7}-sterols requires the 14β(H) and 14β(H), 17β(H),20 R/S configuration in these types of thiosteroids. The observation that no 14β(H),17β(H)-steranes and/or -sterenes are released from high-molecular-weight fractions indicates that the intramolecular reaction of the diene system in the D-ring/side chain area is highly favoured. It is thought that the intermediate spirosteradienes, resulting from isomerisation of the $\Delta^{7,22}$- and/or $\Delta^{7,24(28)}$-steradienes (12), incorporate inorganic sulphur species intramolecularly as indicated in Figure 6. The presence of both thiosteroids with the S-atom in the A/B ring and sulfur-bound steroid units in high-molecular-weight fractions with only the 14α(H),17α(H),20R configuration suggests that the $\Delta^{3,5}$-diene substrate resulting from dehydration of the 3-OH group of Δ^{5}-sterols reacts both intra- and intermolecularly with inorganic sulfur species (Figure 7). However, the natural stereochemistry at C_{14}, C_{17} and C_{20} is preserved in these reactions. This different behaviour of Δ^{5}- and Δ^{7}-sterols on incorporation of sulfur may complicate the 14β(H),17β(H)/14α(H),17α(H) ratios of the steroid alkanes to some extent and may thus influence the validity of this parameter for palaeosalinity.

C_{20} Isoprenoid Thiophene Distribution Patterns

A large variation in the distribution patterns of C_{20} isoprenoid thiophenes has been encountered upon analysis of sediments and oils ranging from normal marine saline to hypersaline (16). Figure 8 shows that in samples representing a normal marine salinity environment (Monterey Shale-Naples and -El Capitan Beach, Jurf ed Darawish-45) isoprenoid thiophenes VI and VII are dominant whereas in samples from hypersaline palaeoenvironments (Sicily seep oil-E2, Rozel Point oil) isoprenoid thiophene V and the so-called midchain isoprenoid thiophenes (I-IV) are relatively abundant. C_{20} isoprenoid bithiophenes (VIII-X) only occur when the midchain isoprenoid thiophenes are relatively abundant (Figure 9).

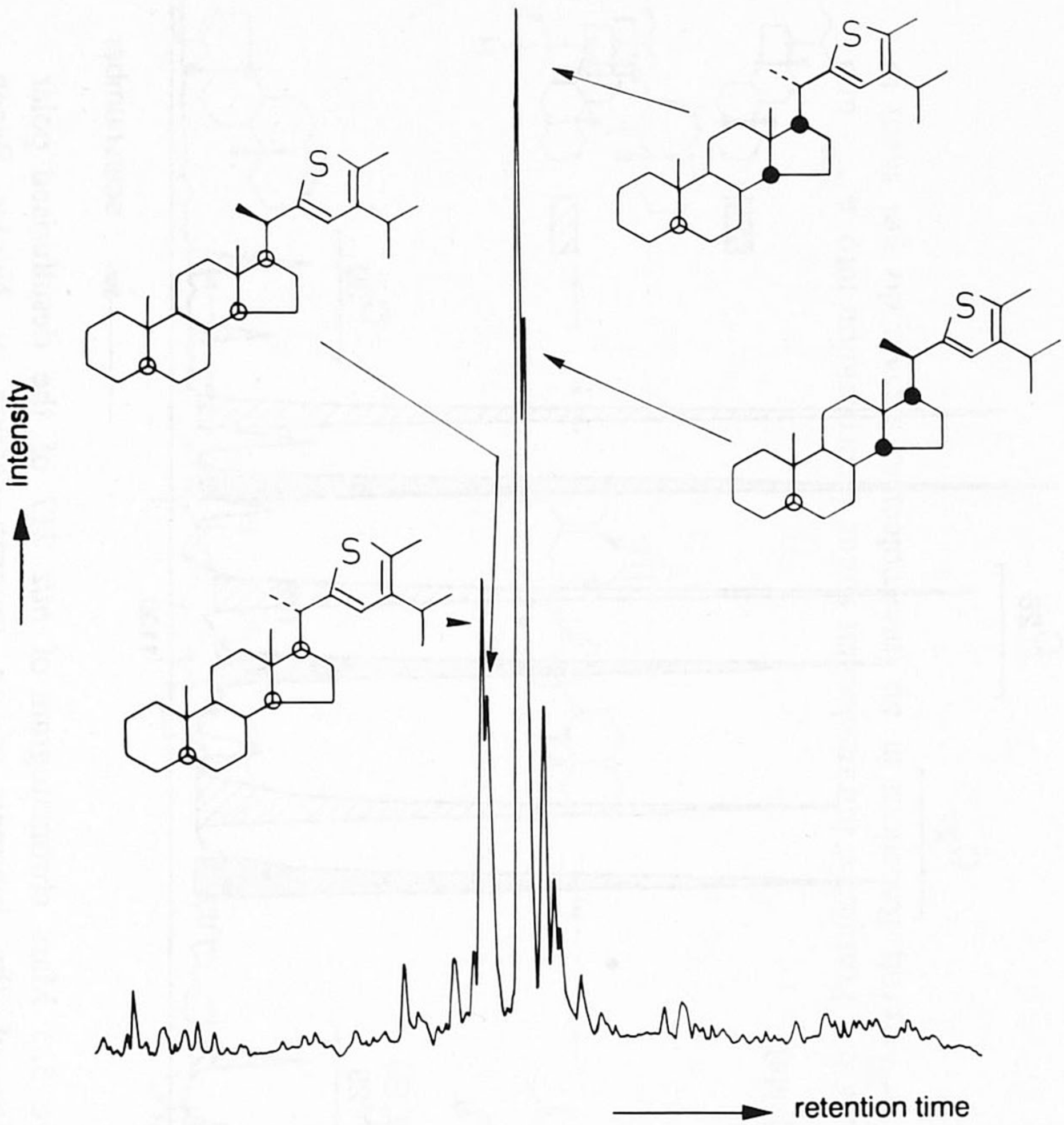


Figure 4. Mass chromatogram of *m/z* 167 of the low molecular weight aromatic fraction (15) of the Rozel Point oil showing assignments of steroidal thiophenes.

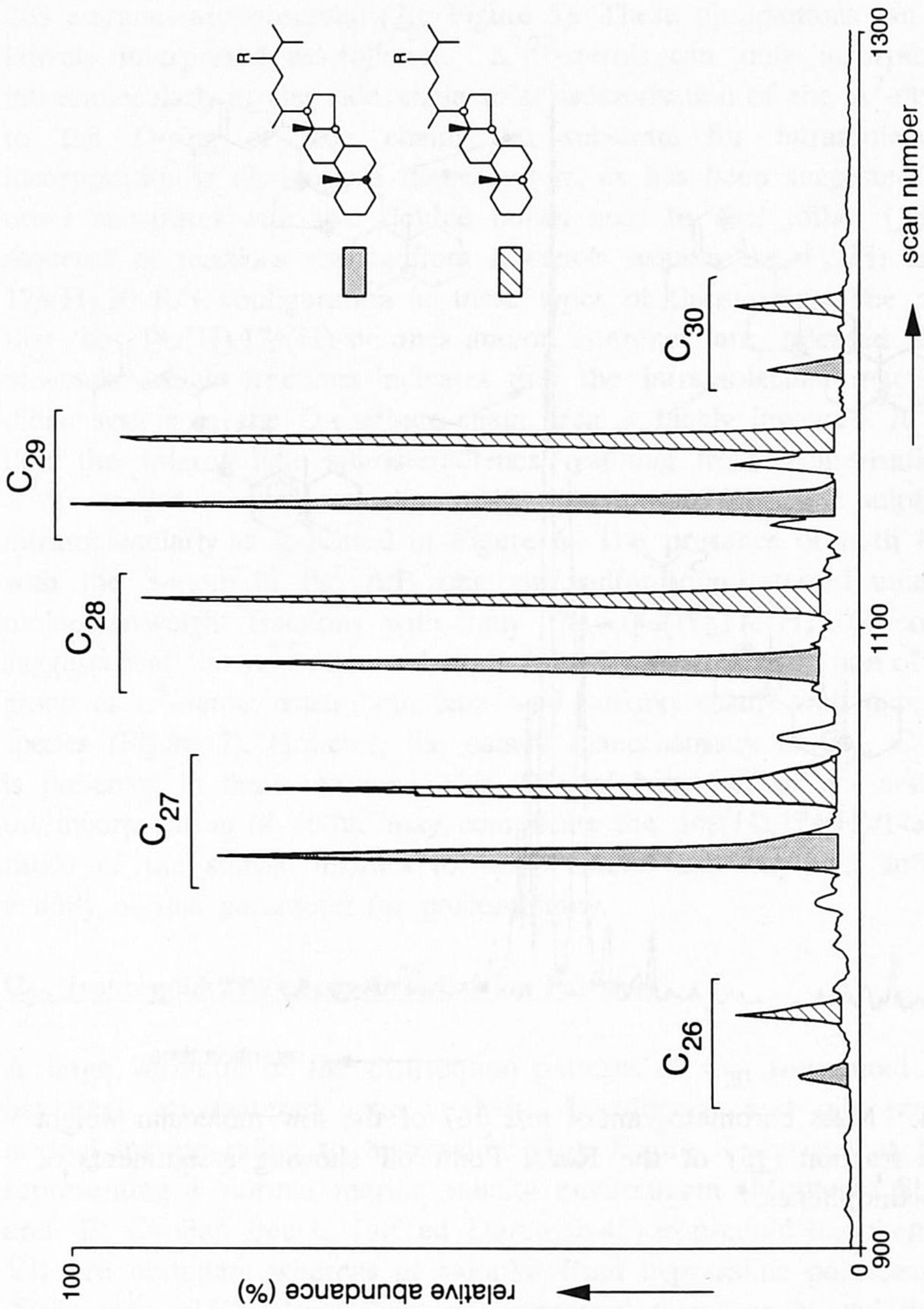


Figure 5. Mass chromatogram of *m/z* 217 of the desulfurised polar fraction of the bitumen of an outcrop section at Naples Beach (California, U.S.A.) of the Monterey Formation.

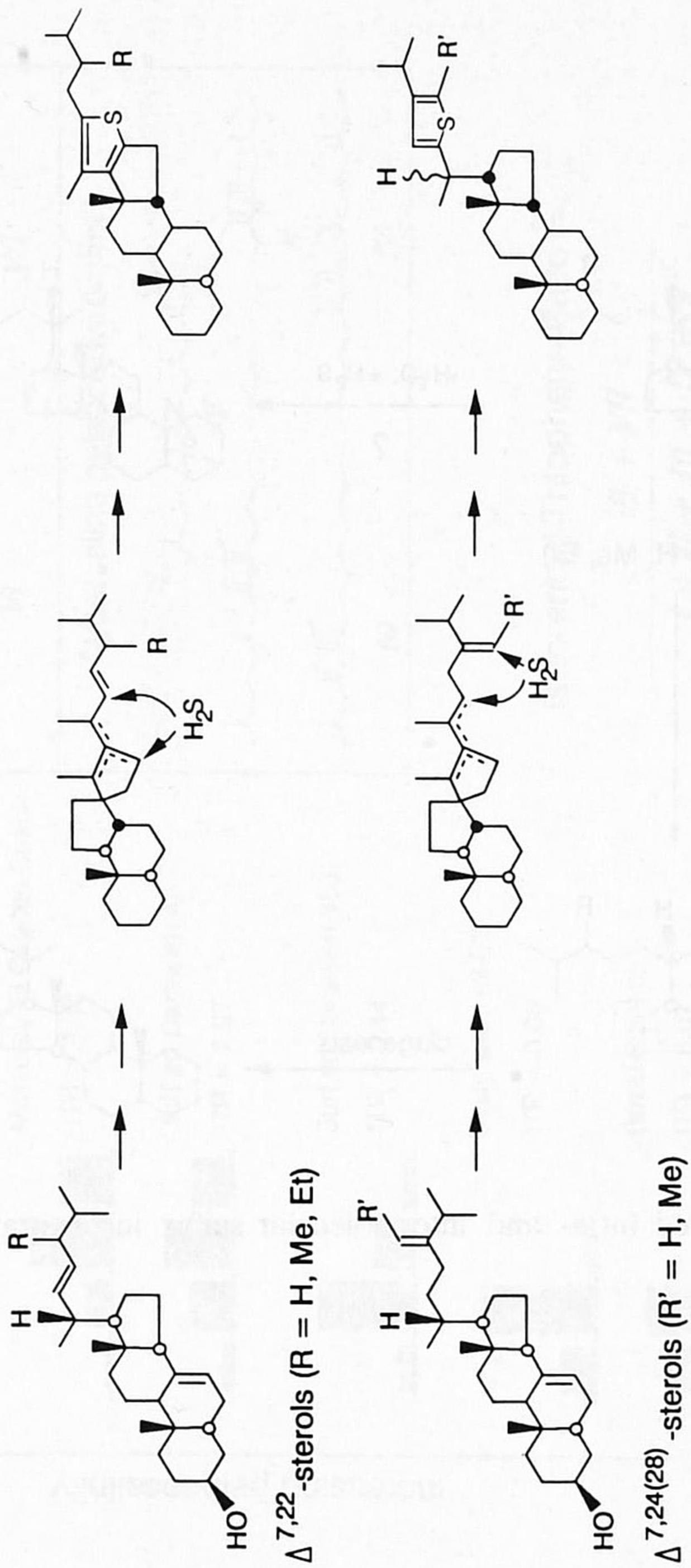


Figure 6. Postulated intramolecular sulfur incorporation into $\Delta^{7,22}$- and $\Delta^{7,24(28)}$-sterols. Reactions in an intermolecular fashion do not seem to occur.

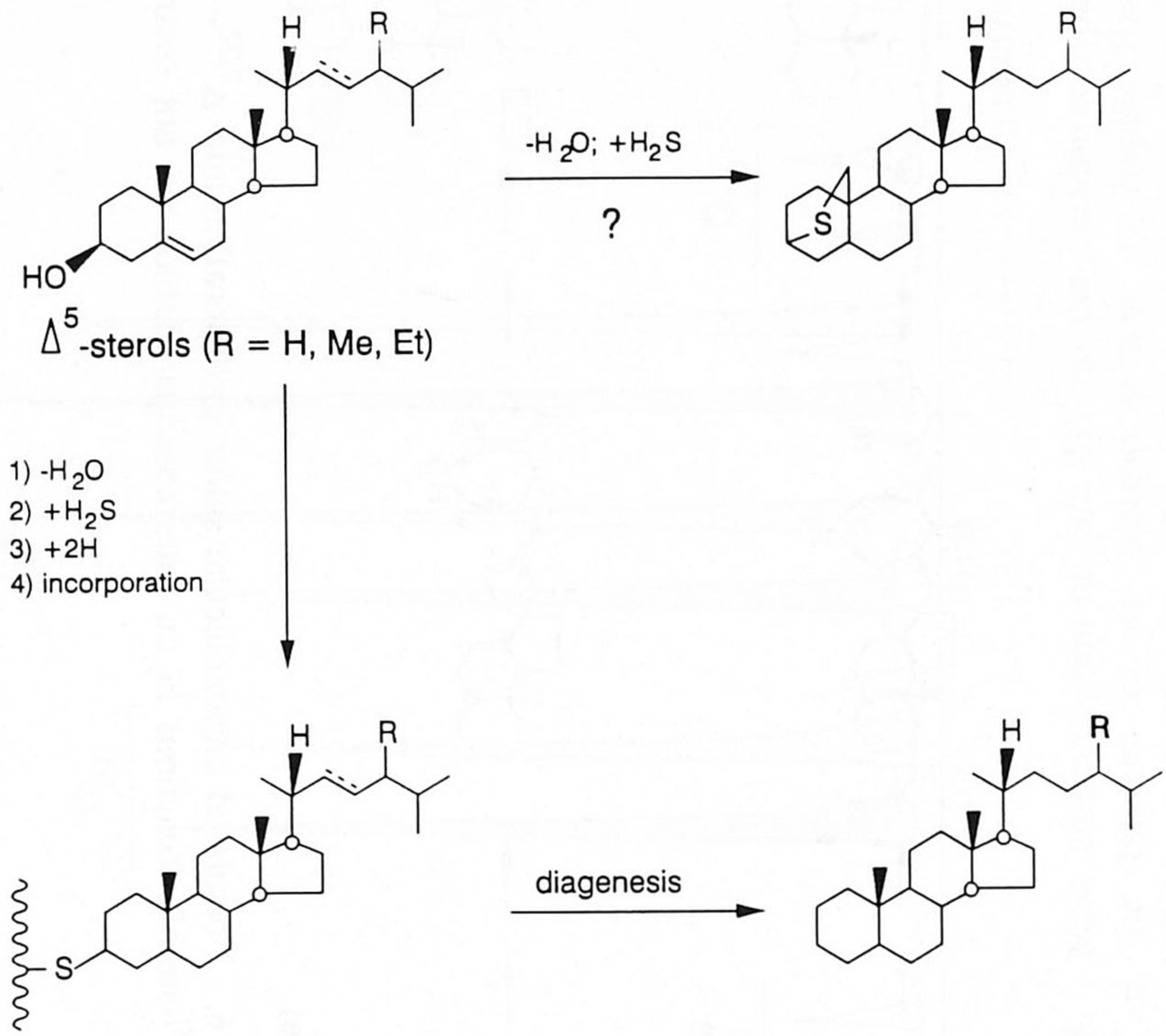


Figure 7. Proposed intra- and intermolecular sulfur incorporation into Δ^5-sterols.

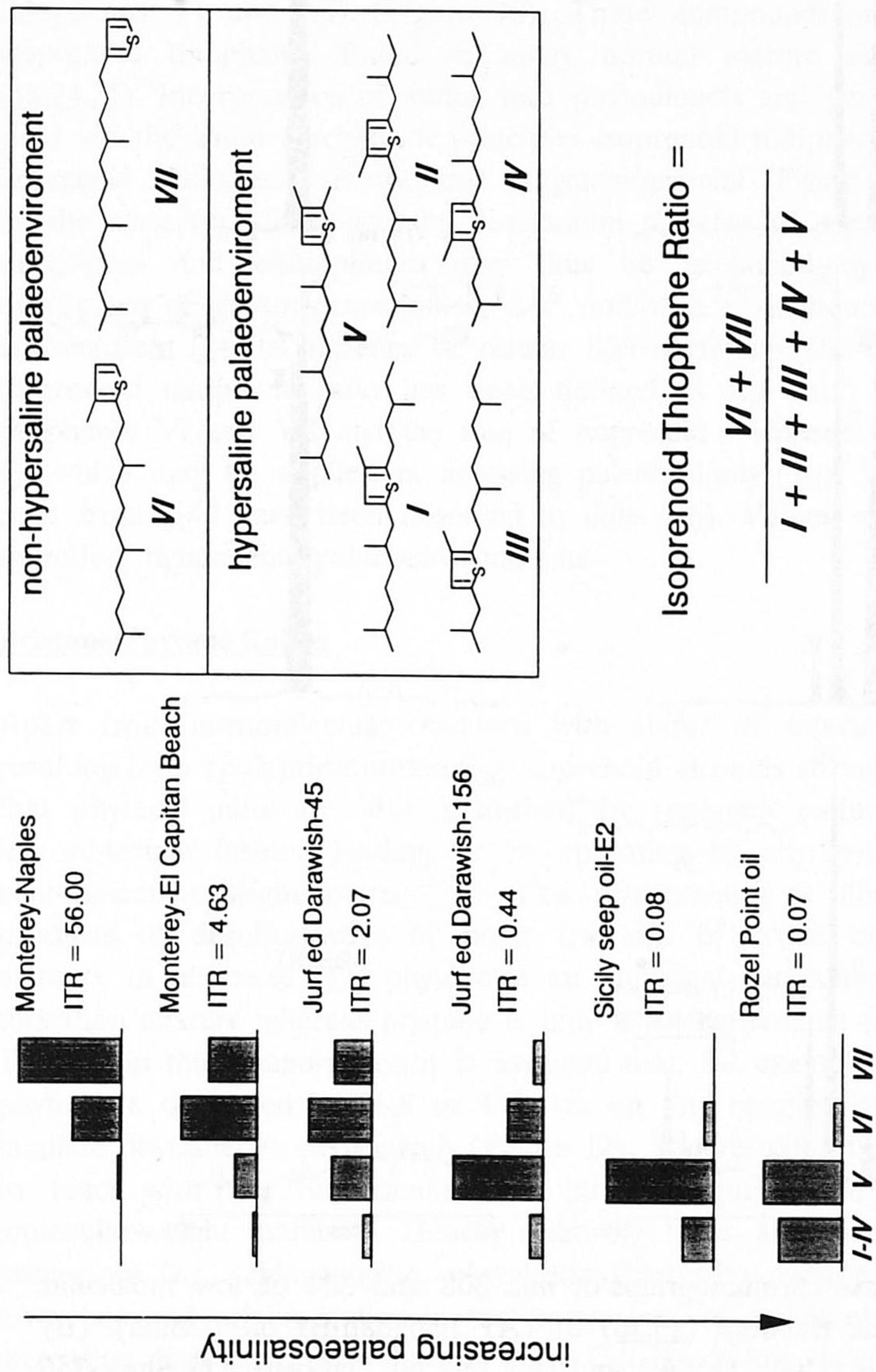


Figure 8. C_{20} isoprenoid tiophenes as indicators of palaeosalinity: structures, definition of the isoprenoid thiophene ratio (ITR) and some typical distributions (based on peak heights in *m/z* 308 mass chromatograms) in sediments and petroleums. Description of the samples is given elsewhere (16).

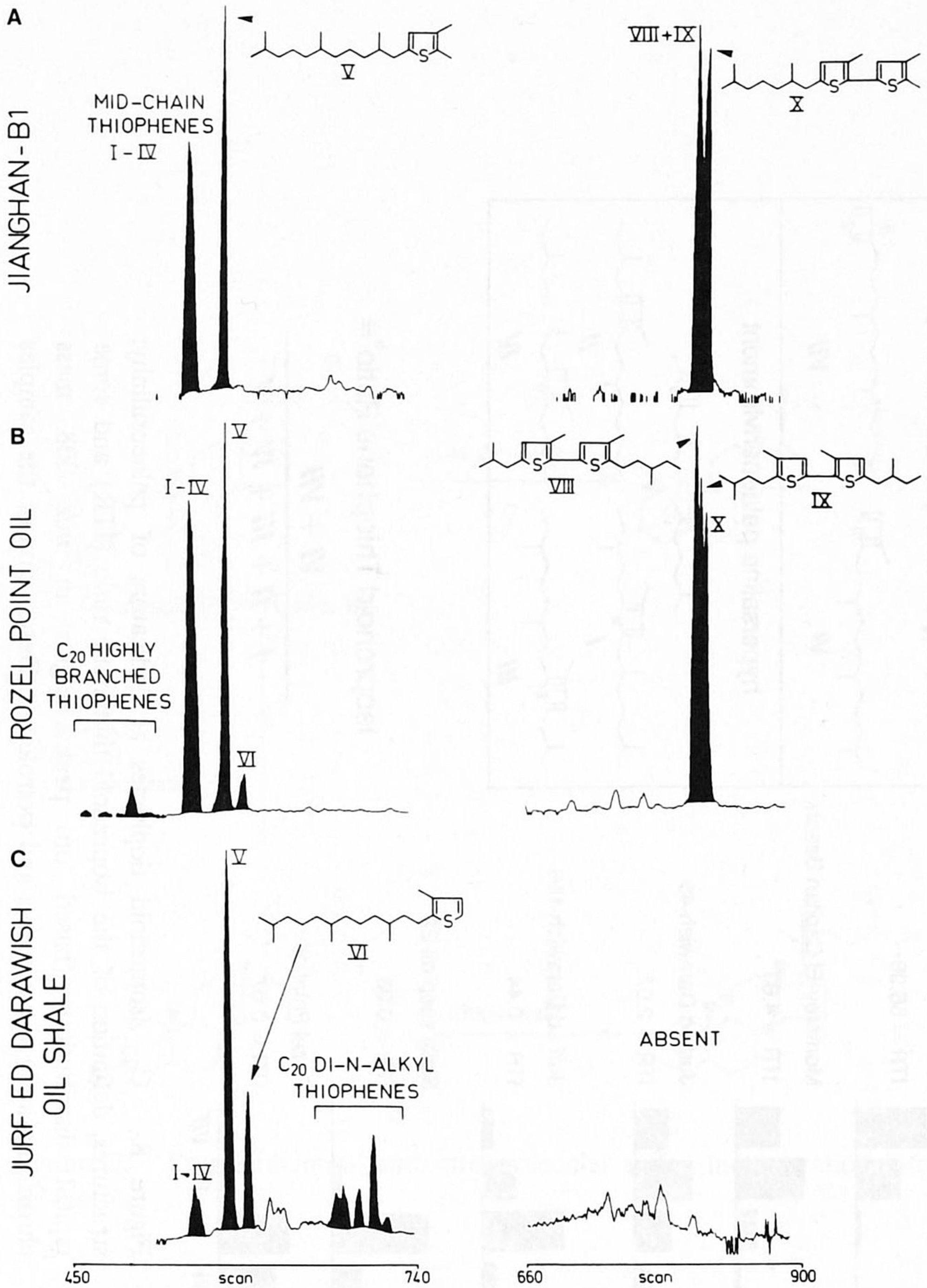


Figure 9. Mass chromatograms of *m/z* 308 and 334 of low molecular weight aromatic fractions (15,16) of (A) Jianghan-B1 oil (China), (B) Rozel Point oil (Utah, U.S.A.) and (C) Jurf ed Darawish Oil Shale-156 bitumen (Jordan). These examples show the co-occurrence of C_{20} mid-chain isoprenoid thiophenes I-IV with C_{20} isoprenoid bithiophenes VIII-X; if thiophenes I-IV are abundant the bithiophenes VIII-X also occur and if thiophenes I-IV are relatively minor the bithiophenes VIII-X are absent. Description of the samples is given elsewhere (16).

Isoprenoid thiophenes are formed by incorporation of sulfur into phytadienes and polyunsaturated phytenes (13,14). The differences in distribution patterns of C_{20} isoprenoid thiophenes may be explained as the result of differences in the abundance of the various precursors of these phytenes. Sulfur incorporation into phytol-derived phytadienes yields isoprenoid thiophenes VI and VII (Figure 10). These compounds are the common isoprenoid thiophenes found in many normal marine salinity sediments (13,24,25). Incorporation of sulfur into phytadienols and geranylgeraniol will yield *via* the same mechanistic principles isoprenoid thiophenes I-V and also isoprenoid bithiophenes in the case of geranylgeraniol (Figure 10). The nature of the observed differences in distribution patterns of the C_{20} isoprenoid thiophenes and bithiophenes may thus be explained by the restricted occurrence of geranylgeraniol and $\Delta^{2,6}$ and/or $\Delta^{2,10}$-phytenol in hypersaline environments (14) as moieties of certain bacteriochlorophylls. Consequently, an isoprenoid thiophene ratio has been defined as the ratio of the sum of thiophenes VI and VII and the sum of isoprenoid thiophenes I-V (see Figure 8), which may be applied in assessing palaeosalinity (16). Variation in this ratio from 0-40 have been observed to date (16). Values <0.5 are thought to reflect hypersaline palaeoenvironments.

Pristane/Phytane Ratios

Apart from intramolecular reactions with sulfur of intermediate phytenes resulting from (poly)unsaturated C_{20} isoprenoid alcohols strong evidence exists that phytanyl units are also 'quenched' by inorganic sulfur species in an intermolecular fashion leading to incorporation of phytanyl moieties in a high-molecular-weight matrix (20). This phenomenon is illustrated by the products of desulfurisation of polar fractions of crude oils or sediment extracts. In all cases (42) phytane is an abundant component of the desulfurisation mixture whereas pristane is only a minor product (*e.g.*, Figure 11). To explain this phenomenon it is assumed that, for example, phytolesters or phytol are quenched by H_2S or HS_x^- *via* an Sn_2 reaction or *via* the intermediate phytadienes, respectively (Figure 12). The resulting thiols are thought to react with the functionalities of other compounds to produce high-molecular-weight materials. Hence, relatively large amounts of the phytol precursors (*e.g.*, chlorophyll-*a*, phytylesters) probably escape from biotransformation and mineralisation in the upper part of sediments. Later on, on increasing diagenesis, the relatively weak C-S bonds are cleaved and phytane can be generated after hydrogenation of the intermediate phytenes or phytadienes. As a result of this selective preservation of phytol *via* sulfur

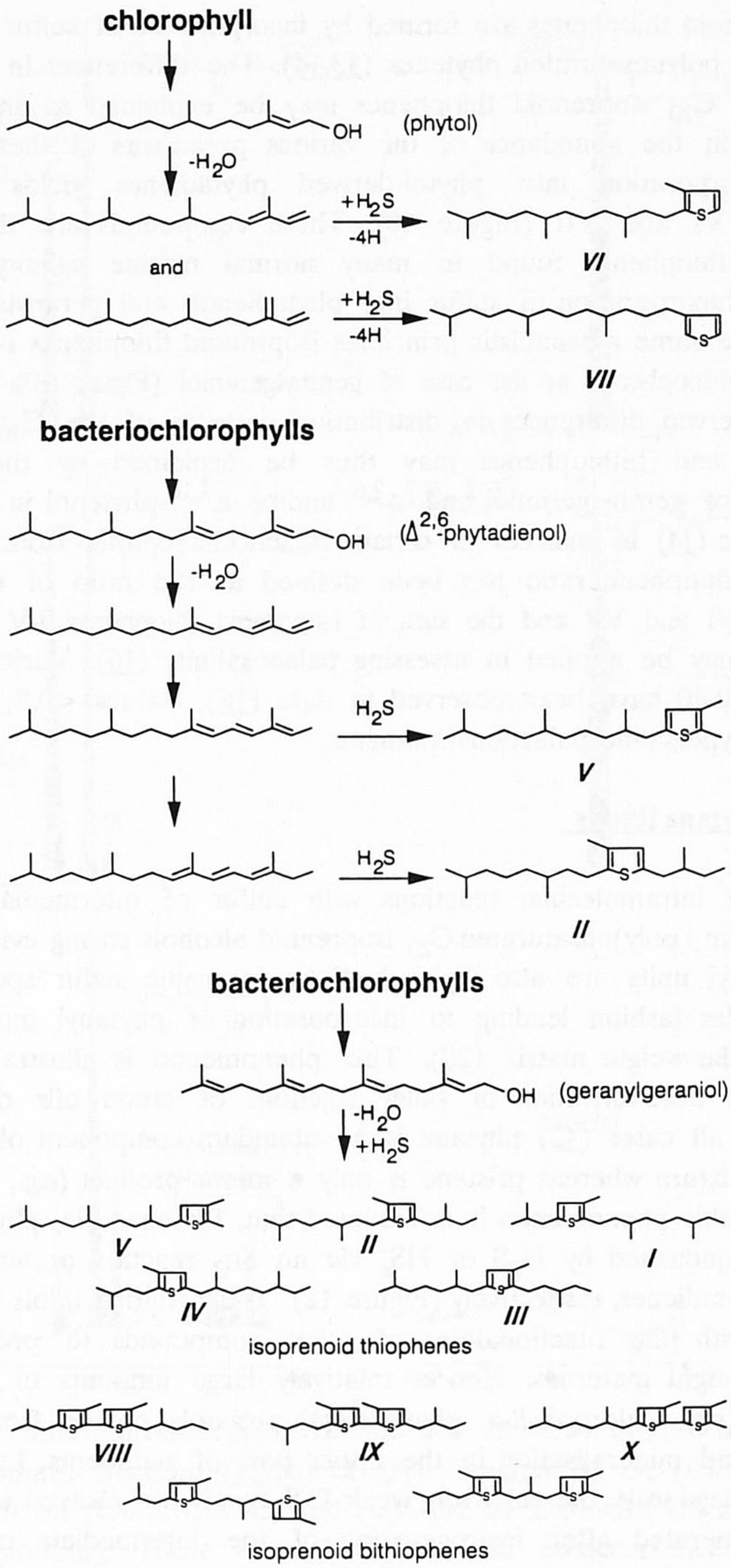


Figure 10. Postulated formation of C_{20} isoprenoid thiophenes and bithiophenes by incorporation of sulfur into phytenes. Different substrates lead to different thiophenes which is the major control for the thiophene ratio.

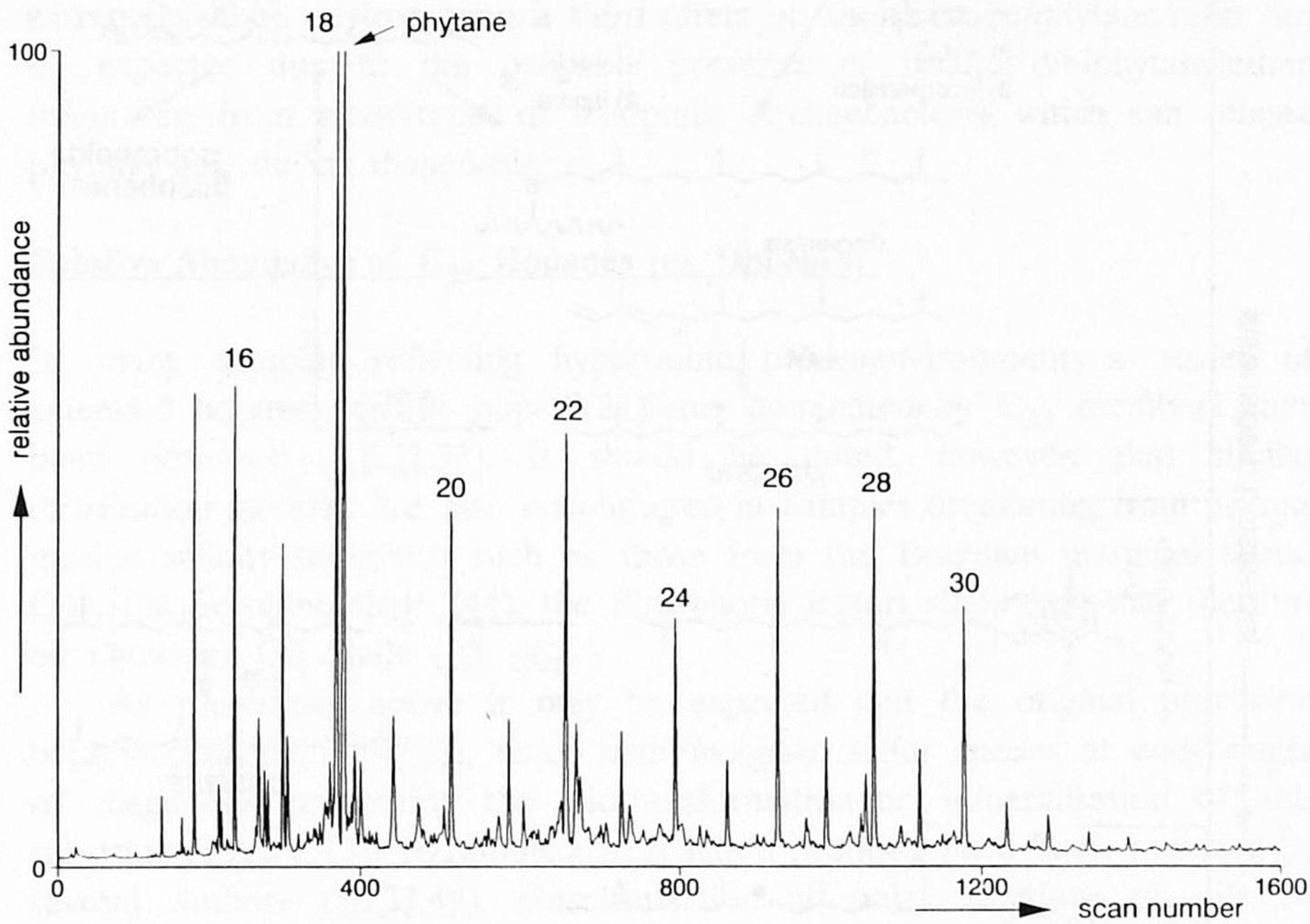


Figure 11. Mass chromatogram of *m/z* 57 of the desulfurised polar fraction of the Sicily seep oil-E2 (Italy).

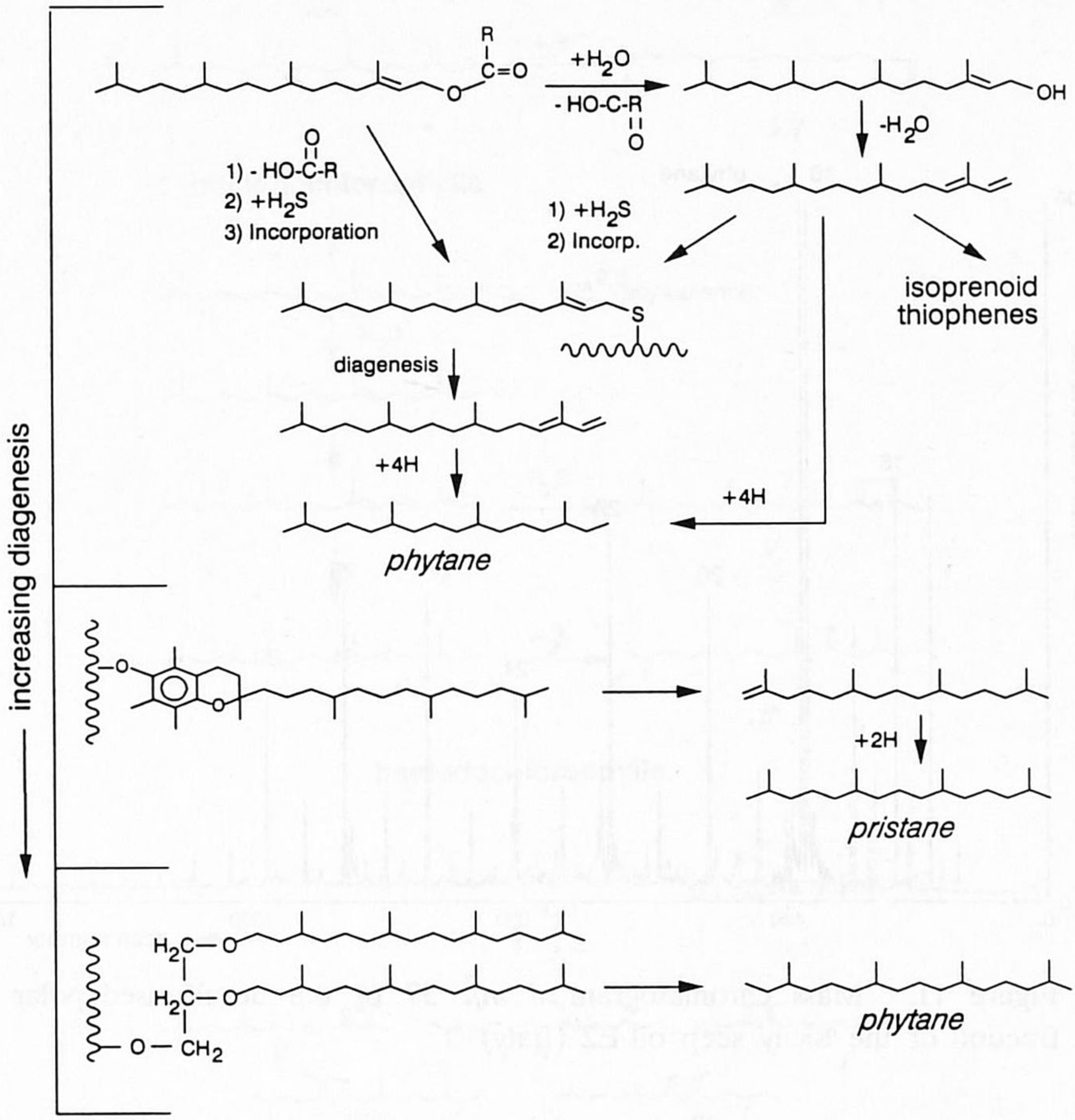


Figure 12. Formation of phytane and pristane from high-molecular-weight substances during increasing stages of diagenesis.

quenching very low pristane/phytane ratios can be expected in sedimentary environments where H_2S (or HS_x^-) can react with functionalised lipids such as phytol. H_2S and/or HS_x^- concentrations may be high in hypersaline environments due to the presence of high amounts of relatively well-preserved organic matter. Also, the relatively low concentration, or absence, of iron is highly favourable for the genesis of organic sulfur compounds (15,16,21). In addition, the pristane/phytane ratio may be influenced by increasing diagenesis. Tocopheryl units, present in the high-molecular-weight fractions of sediments, are thought to release pristane at a latter stage of diagenesis due to their higher relative stability (43, Figure 12). In sediments originating from extremely saline environments a third effect on the pristane/phytane ratio can be expected due to the probable presence of bound dibiphytanylethers originating from membranes of halophilic Archaebacteria, which can release phytane late during diagenesis.

Relative Abundance of C_{35} Hopanes (or Hopenes)

In many samples reflecting hypersaline palaeoenvironments a series of extended hopanes and/or hop-17(21)-enes dominated by C_{35} members have been observed (7,8,31,33). It should be noted, however, that similar distribution patterns are also encountered in samples originating from normal marine salinity sediments such as those from the Brazilian marginal basins (31), the Serpiano shale (44), the Phosphoria Retort shale (45) and the Jurf ed Darawish Oil Shale (23, 46).

As mentioned above it may be expected that the original precursor, bacteriohopanetetrol (47,48), reacts with inorganic sulfur species at early stages of diagenesis preventing the biotransformation or mineralisation of this substrate (Figure 13). Intramolecular reaction products have been reported by several authors (16,23,49). Desulfurisation of polar fractions of oils or sediment extracts releases exclusively C_{35} hopanes in relatively high amounts (20,42), as illustrated by the mass chromatogram of *m/z* 191 for the desulfurised polar fraction of an outcrop sample of the Monterey formation at Naples Beach (Figure 14). Obviously the C_{35} bacteriohopanetetrol is also quenched intermolecularly by sulfur. Because of the relatively weak C-S bonds C_{35} hopanes and hopenes can be generated rather early during diagenesis leading to extended hopane distributions with relatively abundant C_{35} components.

Even-Over-Odd Carbon Number Predominance of *n*-Alkanes

The phenomenon of even-over-odd carbon number predominance of *n*-alkanes has long been recognised in a number of Recent and ancient sediment

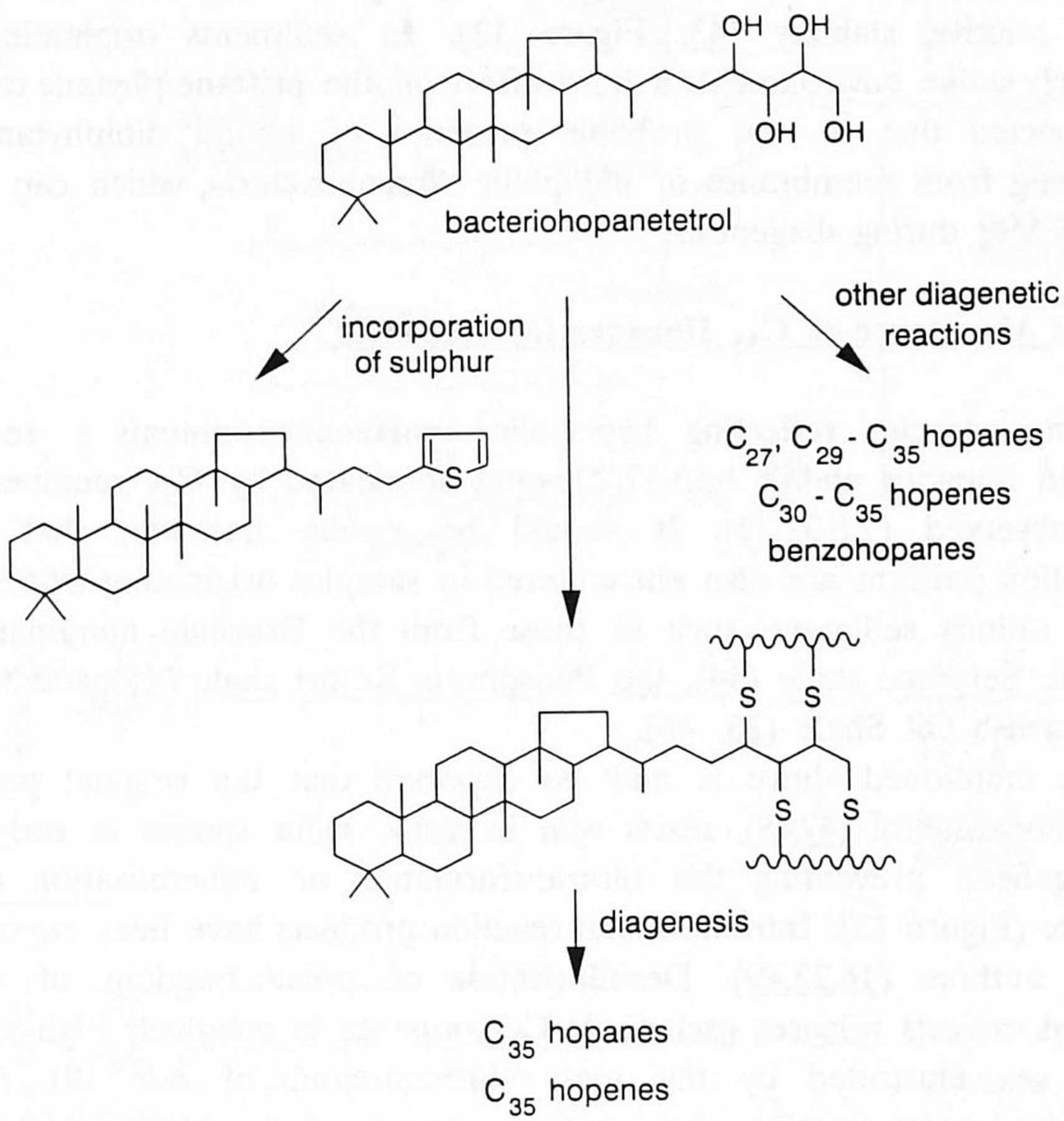


Figure 13. Proposed early diagenetic pathways of bacteriohopanetetrol.

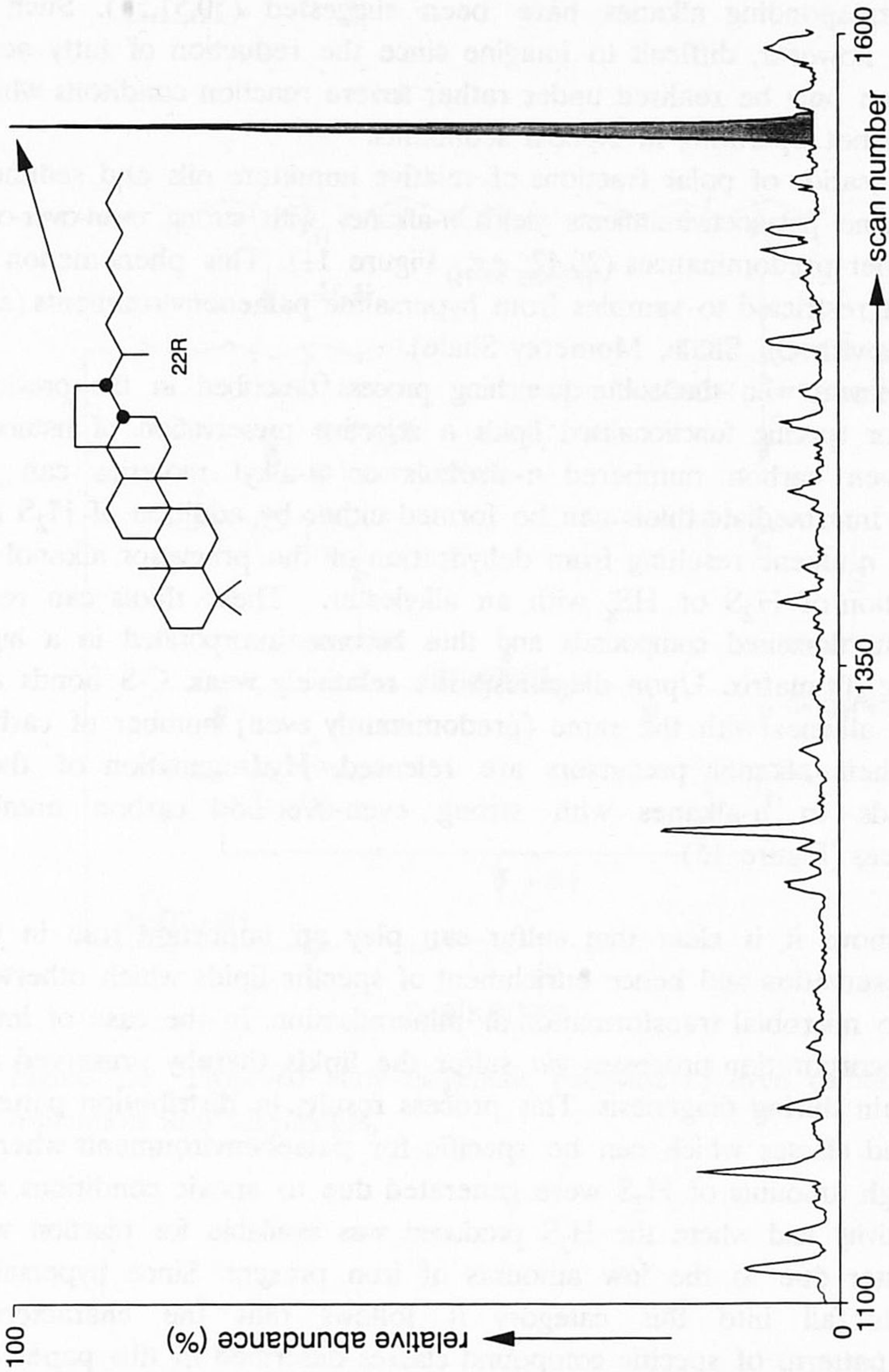


Figure 14. Mass chromatogram of *m/z* 191 of the desulfurised polar fraction of the bitumen of an outcrop section at Naples Beach of the Monterey Formation.

extracts and crude oils (50-58). Based on empirical correlations this even-over-odd carbon number predominance was associated with hypersaline palaeo-environments (50,53,54).

In most of these publications suggestions have been put forward to explain this phenomenon. Complete reduction of naturally occurring fatty acids to their corresponding alkanes have been suggested (50,51,55). Such a reduction is, however, difficult to imagine since the reduction of fatty acids to alkanes can only be realised under rather severe reaction conditons which are probably not operating in Recent sediments.

Desulfurisation of polar fractions of relative immature oils and sediment from hypersaline palaeoenvironments yields *n*-alkanes with strong even-over-odd carbon number predominances (20,42; *e.g.*, Figure 11). This phenomenon is, however, not restricted to samples from hypersaline palaeoenvironments (*e.g.*, Jurf ed Darawish Oil Shale, Monterey Shale).

In agreement with the sulfur-quenching process described in the previous paragraphs for specific functionalised lipids a selective preservation of naturally occurring even carbon numbered *n*-alcohols or *n*-alkyl moieties can be rationalized. Intermediate thiols can be formed either by addition of H_2S (or HS_x^-) to the *n*-alkene resulting from dehydration of the precursor alkanol or by Sn_2-reaction of H_2S or HS_x^- with an alkylester. These thiols can react with other functionalised compounds and thus become incorporated in a high-molecular-weight matrix. Upon diagenesis the relatively weak C-S bonds are cleaved and alkenes with the same (predominantly even) number of carbon atoms as their alkanol precursors are released. Hydrogenation of these alkenes leads to *n*-alkanes with strong even-over-odd carbon number predominances (Figure 15).

From the above it is clear that sulfur can play an important role in the selective preservation and hence enrichment of specific lipids which otherwise are prone to microbial transformation or mineralisation. In the case of inter-molecular incorporation processes *via* sulfur the lipids thereby preserved are released again during diagenesis. This process results in distribution patterns of compound classes which can be specific for palaeoenvironments wherein relatively high amounts of H_2S were generated due to anoxic conditions and high productivity and where the H_2S produced was available for reaction with organic matter due to the low amounts of iron present. Since hypersaline environments fall into this category it follows that the characteristic distribution patterns of specific compound classes described in this paper are observed in samples from hypersaline palaeoenvironments. It should be realised, however, that these environmental conditions are not restricted to

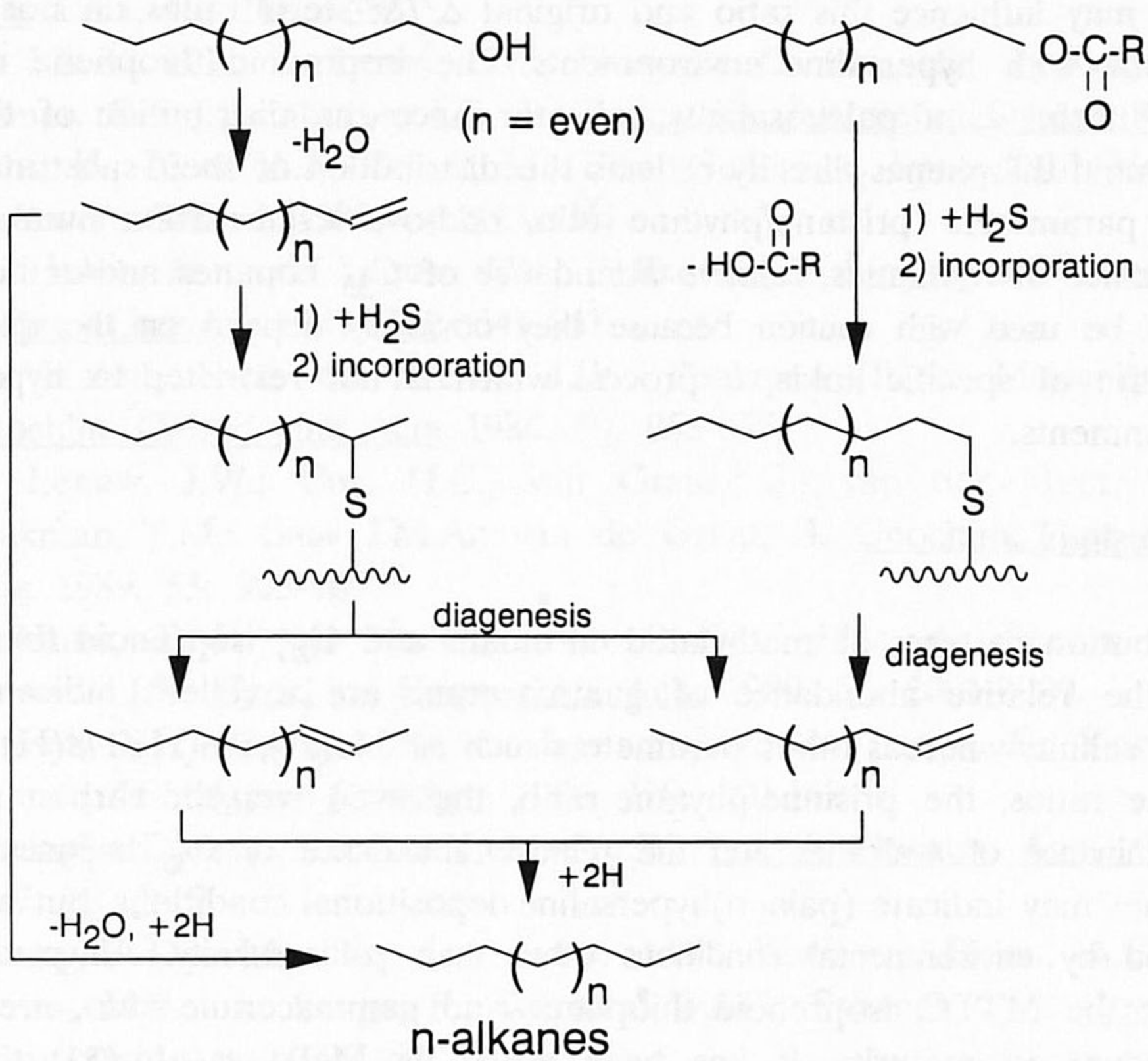


Figure 15. Proposed early diagenetic pathways of even carbon numbered *n*-alcohols and alkylesters.

hypersaline palaeoenvironments and, therefore, these characteristic distribution patterns may also be observed in samples from non-clastic, marine environments (*e.g.*, siliceous oozes, carbonates, phosphorites).

A more critical evaluation of the above mentioned ratios and phenomena reveals the usefulness of the various palaeosalinity indicators. Distribution patterns of methylated chromans and the relative abundance of gammacerane are not influenced by sulfur incorporation reactions and may directly reflect species distributions in the palaeoenvironment. To some extent this holds for 14α(H),17α(H)/14β(H),17β(H)-steraneratios as well, although incorporation of sulfur may influence this ratio and original Δ^7/Δ^5-sterol ratios do not always correlate with hypersaline environments. The isoprenoid thiophene ratio is highly useful as a palaeosalinity indicator since the distribution of the C_{20} isoprenoid thiophenes directly reflects the distribution of their substrates. The other parameters (pristane/phytane ratio, odd-over-even carbon number predominance of *n*-alkanes, relative abundance of C_{35} hopanes and/or hopenes) should be used with caution because they obviously depend on the quenching by sulfur of specific lipids, a process which is not restricted to hypersaline environments.

Conclusions

Distribution patterns of methylated chromans and C_{20} isoprenoid thiophenes and the relative abundance of gammacerane are excellent indicators for palaeosalinity whereas other parameters such as 14α(H),17α(H)/14β(H),17β(H)-sterane ratios, the pristane/phytane ratio, the even-over-odd carbon number predominance of *n*-alkanes and the relative abundance of C_{35} hopanes and/or hopenes may indicate (palaeo)hypersaline depositional conditions, but are also affected by environmental conditions other than palaeosalinity. All parameters, except the MTTC, isoprenoid thiophene and gammacerane ratio, are highly dependent on maturity. It has been noted by Mello *et al.* (31) that "no single biological marker property is sufficient to characterise and assess a specific environment of deposition" and this statement also holds for assessment of palaeosalinity. We, therefore, highly recommend the use of a combination of the various palaeosalinity indicators.

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