30. MOLECULAR INDICATORS OF THE SUPPLY OF MARINE AND TERRIGENOUS ORGANIC MATTER TO A PLEISTOCENE ORGANIC-MATTER–RICH LAYER IN THE ALBORAN BASIN (WESTERN MEDITERRANEAN SEA)\textsuperscript{1}

Marc Hauschildt,\textsuperscript{2} Joachim Rinna,\textsuperscript{2} and Jürgen Rullkötter\textsuperscript{2,3}

\textbf{ABSTRACT}

The organic matter in sediment series across two organic-matter–rich layers from Ocean Drilling Program Hole 977A drilled in the Alboran Basin of the Western Mediterranean Sea has been characterized by organic geochemical methods. Organic carbon contents reached more than 2% in the organic-matter–rich layer and was ~1% in the background sediment under and overlying it. Molecular compositions of the extractable bitumens in the organic-matter–rich layer for a wide range of compound groups are broadly similar to those of the background sediments. The organic matter in the organic-matter–rich layer is enriched in marine biomarkers, especially long-chain diols and keto-alcohols and particularly sterols. A higher supply of land-derived material to the sediment during formation of the organic-matter–rich layer is indicated by concentrations of long-chain alkanes and \( n \)-alcohols largely following the organic carbon profile. The elevated terrigenous runoff during times of more humid land climate may have fertilized marine biodiversity.

\textbf{INTRODUCTION}

The Alboran Sea is the key area to understand the Atlantic Ocean influence on the post-Messinian paleoceanography of the Mediterranean Sea. One of the more important results of Ocean Drilling Program (ODP) Leg 161 was the discovery of sapropel-like organic-matter–rich layers in this westernmost part of the Mediterranean Sea. Sapropels—dark-green to black, organic-matter–rich layers with total organic carbon (TOC) content >2% according to the definition of Kidd et al. (1978)—were known before to occur only in the eastern part of the Mediterranean Sea (e.g., Ryan, Hsü, et al., 1973; Hsü, Montadert et al., 1978) and in the Tyrrenhenian Sea (Kastens, Mascle, et al., 1990).

The Alboran Sea between Spain and Morocco is ~400 km long, 200 km wide, and 2000 m deep. It is bounded by the southern Betic Basin in the east and the Gibraltar Strait in the west. Through the Gibraltar Strait it is connected with the Atlantic Ocean surface water. It shows a complex morphology with many sub-basins, ridges, and seamounts. A local elevation shapes the tiny Spanish Alboran Island (Fig. 1).

The Atlantic water flowing into the Mediterranean Sea through the Gibraltar Strait develops two extensive anticyclonic gyres, one in the western part and the other in the eastern part of the Alboran Basin (Tintoré et al., 1988; Fig. 2). Whereas the western gyre can be explained by the topographical setting and the Coriolis force (EUROMODEL Group, 1975), the eastern gyre remains unexplainable.

On the southwest Spanish coast an upwelling system (Minas et al., 1984; Vergnaud-Graziinni and Pierre, 1991) is supplied with nutrients from both the outflowing Levantine Intermediate Water and Mediterranean Deep Water (Kinder and Parrilla, 1987) and from the inflowing Atlantic water (Minas et al., 1984). The primary production here has been estimated at >200 g C m\(^{-2}\) yr\(^{-1}\) (Minas et al., in pers. comm. to Vergnaud-Graziinni and Pierre, 1991). Because of a persistent density front (Almeria-Oran Front) along the eastern basin demarcation, the Atlantic water is accelerated in a southerly direction toward the Algerian coast and develops into a strong jet strictly toward the east (Tintoré et al., 1995). Along this narrow stream, nutrient-rich deep waters are locally upwelled and induce regional fertilization in the surface water (Prieur et al., 1993).

These signatures may be recorded in the underlying sediments, but may probably have varied during glacial/interglacial cycles. Abrantes (1988) deduced glacial/interglacial variations of productivity from paleoceanographic studies. Compared to the recent conditions, quite different atmospheric and wind systems prevailed during the last interglacial maximum (COHMAP Members, 1988). This different wind pattern may have led to an eastward shift of the gyres and to a modification of the upwelling system (Vergnaud-Graziinni and Pierre, 1991). The \( \Delta ^{13} \text{C} \) data suggest a nutrient depletion of Atlantic water during the last interglacial maximum (Zahn et al., 1987), which may have reduced the fertility of the Western Mediterranean Sea (Vergnaud-Graziinni and Pierre, 1991).

Terrigenous material is supplied to the Alboran Basin directly from the numerous rivers, essentially the Andarax, Rio Guadalhorce, Rio Guadalfeito, and Muluja effluents (Fig. 2). Indirectly, terrigenous material is transported from the Guadalquivir River over the Gulf of Cadiz with the Atlantic inflow (Grousset et al., 1988). Local winds transport terrigenous material into the Alboran Basin too, especially during the winter, by a strongly developed depression over the whole Mediterranean Sea. Sahara dust has been shown to be present in Holocene sediments of the Adriatic Sea (Tomadin et al., 1984).

This study attempts to provide information on variation in the supply of terrigenous and marine organic matter to the sediments of the Alboran Basin during the short time interval represented by a Pleistocene organic-matter–rich layer recovered at ~77 m depth in Hole 977A of Leg 161. For this purpose, nonpolar and polar lipids were extracted from the sediments and analyzed on a molecular level. A second interval covering an organic-matter–rich layer at about 164 mbsf from the same hole was only analyzed for total organic and carbonate carbon contents.

\textbf{ANALYTICAL METHODS}

We investigated a total of 18 core samples from Hole 977A (Table 1). After freeze-drying and grinding, the sediments were analyzed for total carbon (TC) content coulometrically in a Ströhlein Coulomat...
Figure 1. Bathymetric map of the Alboran Basin and location of Site 977 and other sites of Leg 161.

Figure 2. Anticyclonic gyres of the Alboran Sea (schematically after Arnone et al., 1990) and upwelling system on the South Spanish Coast (shaded; after Minas et al., 1984).
702. The results of elemental analysis for total organic carbon (TOC) and carbonate content in the two investigated sequences across organic-matter–rich layers in the Alboran Basin Hole 161-977A are compiled in Table 1 and Figure 3. The organic carbon contents in Sections 161-977A-18X-5 and -6 vary between 0.74% and 1.90% while in Section 977A-9H-5 they range from 0.88% to 2.27%. The more pronounced symmetric form of the TOC profile in the samples from Section 977A-9H-5 and the more regular sample spacing led us to investigate this sequence in greater detail on a molecular level. TOC content of organic-matter–rich layers in the Western Mediterranean Sea are distinctly lower than those in eastern Mediterranean sapropels, which, considering the proximity to the African and Spanish coasts, may mainly reflect a higher supply of clastic material from the continent and thus a higher degree of terrigenous dilution, but may also be a factor of lower primary productivity and inferior conditions for organic matter preservation in the Alboran Basin. In the background sediments below and above the organic-matter–rich layers, recovered in the Alboran Sea during Leg 161, the average TOC content is more than twice as high as the deep-ocean sediment average of 0.3% reported by McIver (1975) and distinctly higher than in nonsapropel background sediment of the Eastern Mediterranean Sea (Emeis, Robertson, Richter, et al., 1996). Maximum TOC values at the four sites occupied during Leg 161 in the Alboran Sea are in the range of 1.27% (Site 978) to 2.50% (Site 977; Comas, Zahn, Klaus, et al., 1996). The carbonate contents of the investigated samples are between 20%–50% and indicate varying influences of bioproductivity, dilution by noncarbonate material and post-depositional carbonization; the carbonate data are positively correlated with the TOC values.

**Molecular Composition**

Six of the ten samples from Section 161-977A-9H-5 (marked in Fig. 3) were selected for further molecular organic geochemical investigations. The sterols are quantitatively the most important group of compounds among those separated by liquid chromatography and analyzed quantitatively, while the n-aldehydes represent the least abundant group (Fig. 4). The data in Figure 4 represent the sum of concentrations of identifiable single compounds (together making up 4% to 9% of the total extracts), but are not identical to the amounts of total liquid chromatography fractions separated from the total extracts. Among the different compound groups, only the n-alkanes correlate positively with the TOC values of the entire interval studied. The long-chain n-alkenones, n-alkanols, fatty acids, and
squalene have a significant maximum in the 86- to 88-cm interval of Section 161-977A-9H-5, while the \( n \)-alkanolones and diols have a minimum there. The ketols and diols show a distinct positive correlation with each other \((R = 0.97)\).

**n-Alkanes**

The \( n \)-alkanes in the nonaromatic hydrocarbon fraction of the extracts cover a range of chain lengths between \( C_{17} \) and \( C_{40} \) (Fig. 5). The \( C_{23} \) and \( C_{35} \) \( n \)-alkanes dominate and exhibit a pronounced odd-over-even carbon-number preference typical of an origin of terrestrial higher plants (Eglinton et al., 1962). The \( n \)-alkanes between \( C_{15} \) and \( C_{23} \) have a low abundance and do not exhibit a characteristic pattern of an intense autochthonous supply of phytoplanktonic organic matter (Blumer et al., 1971). The distribution without any preference may be due to co-occurring phyto- and zooplankton signals, with the even-over-odd carbon-number preference of the latter (Giger and Schaffner, 1977) being superimposed on the odd-over-even carbon-number predominance of the phytoplankton (Blumer et al., 1971), but the broad and smooth distribution of short-chain \( n \)-alkanes may also be a result of the presence of a certain amount of recycled, more mature organic matter commonly found in deep-sea sediments (e.g., Tissot et al., 1980; Summerhayes, 1981). The \( n \)-alkanes with chain lengths beyond \( C_{36} \) may be a result of the incorporation of coccolithophore biomass into the sediments (Volkman et al., 1980c), which is likely to be also responsible for the presence of the long-chain \( n \)-alkenones (Volkman et al., 1980b).

Another aspect of the \( n \)-alkane distributions is the unexpectedly small variation of their distribution pattern over the organic-matter–rich layer. Together with the fact that organic-carbon–normalized concentrations of \( n \)-alkanes vary little, that is, they increase with the increase of total organic carbon, this shows that deposition of the organic-matter–rich layer is accompanied by an increase in the supply of terrigenous organic matter to the Alboran Basin.

**Fatty Acids**

While the \( n \)-alkanes show mainly a terrestrial influence, the fatty acids are dominated by short-chain marine or microbial components. The chain length of the fatty acids ranges from \( C_{11} \) to \( C_{30} \) with a distinct maximum at \( C_{16} \) and a strong even-over-odd carbon number predominance (Fig. 6). Diatoms may be the main contributors of the fatty acids in the Alboran basin sediments because they mainly produce \( C_{16} \) and \( C_{18} \) homologs (Volkman et al., 1980a). Dinoflagellates mainly biosynthesize \( C_{18}, C_{20}, \) and \( C_{22} \) fatty acids (Harrington et al., 1970),
while coccolithophores have C\(_{14}\) and C\(_{16}\) (Volkman et al., 1981), green algae C\(_{16}\) and C\(_{18}\) (Patterson, 1970), blue-green algae C\(_{14}\), C\(_{16}\), and C\(_{18}\) acids (Kenyon et al., 1972).

### n-Alkanols

The \(n\)-alkanols exhibit a mainly terrestrial carbon number distribution pattern (Fig. 7). The chain lengths range from C\(_{12}\) to C\(_{32}\) with a predominance of the higher-carbon-number homologs and a strong even-over-odd carbon-number preference. Noteworthy is the depth profile of the C\(_{22}\) \(n\)-alkanol. Algal mats have been reported to contain this compound as a major constituent (Cardoso et al., 1976), but the strong correlation with the long-chain fatty acids in the studied interval from the Alboran Basin (\(R = 0.95\); Fig. 8) favors a common terrestrial source of both the C\(_{22}\) alcohol and the long-chain fatty acids, possibly initially ester-linked.

### Ketols and Diols, Long-Chain Alkenones

The sum of the concentrations of 1-hydroxytriaconta-15-one and 1-hydroxydotriaconta-15-one and the sum of the concentrations of all long-chain diols (Table 2) correlate strongly with each other over depth, while both classes apparently do not have any relationship with the long-chain alkenones (Fig. 9). This lack of correlation of the long-chain alkenones with the other two compound classes corroborates earlier reports of different sources. Prymnesiophytes, and particularly coccolithophores, are well known as producers of heptatriaconta–8(E),15(E),22(E)-triene and heptatriaconta–15(E),22(E)-diene.

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**Figure 5.** Distribution of \(n\)-alkanes in selected sediments from Section 161-977A-9H-5.

**Figure 6.** Distribution of fatty acids in selected sediments from Section 161-977A-9H-5.
as well as other long-chain alkenones and alkenoates (Prahl and Wakeham, 1987). The source of the ketols and diols has been discussed controversially for a long time. While Morris and Brassell (1988) suggested cyanobacteria as a probable source, Volkman et al. (1992) identified specific marine green algae (Eustigmatophytes) as a more likely source of these compounds. The suggestion of de Leeuw et al. (1981) that coccolithophores may be the source of ketols and diols as of the \(n\)-alkenones could not be confirmed here.

Paleo–sea-surface temperatures based on the ratio of di- and tri-unsaturated long-chain ketones (Prahl and Wakeham, 1987) show a distinct increase from 19°C to 22°C over the short sediment interval studied here, with the main increase occurring after the deposition of the organic-matter–rich layer (Fig. 10).

Pentacyclic Triterpenoid Ketones

The concentrations of two angiosperm pentacyclic triterpenoid ketones, lup-20(29)-en-3-one and olean-12-en-3-one, closely correlate with each other (R = 0.98). In contrast to this, the concentration of friedelan-3-one has a different depth profile, with a decrease toward the top of the studied section. This is taken as evidence of different taxonomic sources of friedelan-3-one and the other two triterpenoid ketones. As a terrestrial biomarker friedelan-3-one, other than lup-20(29)-en-3-one and olean-12-en-3-one, is mostly associated with monocotyledons (Das and Mahato, 1983). Monocotyledons in general prefer open, thinly vegetated areas and are more robust under rough climatic conditions. The decreasing upward trend of friedelan-3-one concentration may indicate a climatic change to higher temperatures and increasingly dense wood vegetation on land during the deposition of the sediment interval studied. This would be consistent with the temperature trend calculated from the alkenone index.

Sterols

More than 50 different free sterols were detected and quantified (Tables 3, 4). Among them, cholesterol (I), 5α-cholestane-3β-ol (j), 24-methylcholesta-5,22(E)-di-en-3β-ol (A), 24-methyl-5α(H)-cholesta-22
Figure 9. Comparison of downhole trends of organic-carbon normalized concentrations of 1-hydroxy-n-alkan-1-ones, alk-1-ene-diols, and long-chain n-alkenones in selected sediments from Section 161-977A-9H-5.

(E)-en-3ß-ol (B), 24-ethylcholest-5-en-3ß-ol (M'), 23,24-dimethyl-5α(H)-cholestan-3ß-ol (N'; note that M' and N' coelute with fucosterol, L', but the former two compounds represent the main part of the peak), and 24-ethyl-5α(H)-cholestan-3ß-ol (P') are the main free sterols in the six samples together with the 4-methylsterols 4α,24-dimethyl-5α(H)-cholestan-3ß-ol (Q'; note that P' and Q' coelute with iso-fucosterol, R', but the former two compounds represent the main part of the peak), dinosterol (C'''), and two isomers of 4α,23,24-trimethyl-5α(H)-cholestan-3ß-ol (H'' and I'').

The summed concentrations of the lignin phenols are usually termed λ or Λ, where λ is defined as the sum of the vanillyl and syringyl phenols in mg/100 g TOC (Hedges and Parker, 1976), while Λ includes the cinnamyl phenols as well. The p-hydroxyphenols are not considered, because they can also come from marine sources. The lignin phenols show depth profiles similar to those of the straight-chain homologous series and the sterols, that is, during the deposition of the organic-matter–rich layer there is a slightly less allochthonous inflow, as revealed by the n-alkane concentration profile. The lignin phenols are usually termed λ or Λ, where λ is defined as the sum of the vanillyl and syringyl phenols in mg/100 g TOC (Hedges and Parker, 1976), while Λ includes the cinnamyl phenols as well. The p-hydroxyphenols are not considered, because they can also come from marine sources. The lignin phenols show depth profiles similar to those of the straight-chain homologous series and the sterols, that is, during the deposition of the organic-matter–rich layer there is a slightly less allochthonous supply than before and after this time (Fig. 12). It has to be noted, however, that the concentrations of lignin phenols measured in the Alboran Basin sediments are three orders of magnitude smaller than those reported for Holocene sediments by Hedges and Parker (1976) and Goñi and Hedges (1990); therefore, concentrations of λ and Λ are in μg/g TOC here.

CONCLUSIONS

Two sediment sequences across organic-matter–rich layers from ODP Sites 161-977 in the Alboran Basin (Western Mediterranean Sea), comprising about 3000 yr of sedimentation according to bulk-
sedimentation rates (Comas, Zahn, Klaus, et al., 1996), were investigated for bulk organic carbon and carbonate content; molecular analyses on the extractable bitumens were performed on the sequence in which a maximum organic carbon content of 2.27% had been determined. The TOC profiles clearly indicate a strong variation of deposition conditions with respect to organic matter supply and preservation, but this effect is not as pronounced as during times of sapropel formation in the Eastern Mediterranean Sea. Over the interval studied, alkenone-derived sea-surface temperatures increased by about 1°C. The molecular composition of GC-amenable biomarkers in the organic-matter-rich layer is broadly similar to the biomarker distributions in the underlying and overlying sediments. An elevated marine-organic–matter supply in the organic-matter–rich layer is indicated by an increase in the concentrations of sterols, long-chain diols, and keto-ols. Because concentrations of terrigenous long-chain n-alkanes and n-alcohols also rise in this layer, an increased terrigenous run-off may have fertilized marine bioproductivity. A change of continental climate to higher humidity may have been the driving force for this.

### ACKNOWLEDGMENTS

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### REFERENCES


ORGANIC MATTER MOLECULAR INDICATORS


Date of initial receipt: 21 May 1997
Date of acceptance: 22 September 1997
Ms 161SR-273
Table 4. Sterol concentrations in sediments from Section 161-977A-9H-4, intervals 63-65 cm, 73-75 cm, 80-82 cm, 86-88 cm, 92-94 cm, and 103-105 cm.

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<th>Symbol</th>
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Notes: See Table 3 for symbol key; n.d. = not detected; * = number of C atoms used for triangular diagram; ** = quantified by GC (otherwise by GC-MS by peak area ratios from the RIC [reconstructed ion current chromatograms]).

Figure 11. Huang-Meinschein diagram of sterol carbon number distributions for sediments from Section 161-977A-9H-5.

Figure 12. Downhole trends of organic-carbon–normalized concentrations of individual lignin phenols and of their sum (A) in Section 161-977A-9H-5.