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Cenomanian–Turonian organic sedimentation in North-West Africa: A comparison between the Tarfaya (Morocco) and Senegal Basins

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Abstract

The Cenomanian–Turonian Oceanic Anoxic Event was recognised in North Western Africa in various depositional settings from abyssal areas to continental shelves. To derive information on environmental conditions in these different settings and define a depositional model, a petrographical and geochemical study of the organic matter was performed on sediments from the Tarfaya (Morocco) and Senegal Basins. The results obtained for these two locations were compared to those of previous studies, namely from DSDP wells.

Petrographic and geochemical data allow the differentiation of two main organofacies: a shallow depositional facies (continental shelf) is characterised by low total organic carbon (TOC) contents (< 4%). As attested by low hydrogen index (HI) values (100 to 400 mg HC/g TOC), the organic matter (OM) is moderately preserved. Petrographically, this facies is composed of mixed OM with high proportions of reworked vitrinite indicating detrital material influence. The depositional environment is typical of dysoxic conditions (S/C < 0.36) exposed to high mineral inputs and oxygenated water currents.

The second organofacies deposited in the deep marine environment (slope and abyssal) shows a high TOC content (> 7%). The predominance of fluorescing amorphous OM combined with high HI values suggests good preservation conditions. The S/C ratio (> 0.36) and abundance of organic-sulphur compounds support this interpretation and indicate a development of anoxic conditions.

To explain the organic contrast between both environments a depositional model has been developed which is based on limited water exchange between both depositional settings. The main factor which has determined black shale sedimentation is the restricted water circulation related to the presence of isolated depositional environment during Atlantic Ocean opening. Compared to present upwelling zones, the palaeoproductivity in the studied area was relatively moderate during Cenomanian–Turonian and seems not to be the only determining factor of organic matter accumulation.

Keywords: Tarfaya Basin; Senegal Basin; Organic matter; Primary productivity; Euxinic

1. Introduction

On the North African continental margin Cenomanian–Turonian (C–T) sediments have been recognised in present-day shelf and slope areas (Herbin et al., 1986, Leine, 1986, El Albani et al., 1999 and Kolonic et al., 2002). These formations have also been penetrated by several ODP and DSDP wells (138, 367, 368 Sites) and petroleum exploration boreholes (CM7, CM10) in offshore Senegal. C–T sediments also occur at outcrops along the Moroccan Atlantic coast (Herbin et al., 1986) and in Bahloul Formation in Tunisia (El Albani et al., 1999). Since the introduction of the concept of Oceanic Anoxic Events (OAE) by Schlanger and Jenkyns (1976), aiming to explain the organic richness of these units, there are still active controversies on the origin and the extension of this event. Many authors have discussed the main factors which are responsible for high OM contents usually found in these sedimentary formations (Lancelot, 1980, Waples, 1983, Busson and Cornée, 1996 and de Graciansky et al., 1984).

Euxinic conditions in a large part of the water column are presently considered one of the most susceptible mechanisms to explain black shale sedimentation in the North Atlantic area (Kuypers et al., 2002 and Lüning et al., 2003). This assumption is essentially supported by the presence of molecular biomarkers (isorenieretane) derived from photosynthetic green sulphur bacteria (chlorobiaceae) found both in the Tarfaya Basin (Kolonic et al., 2002) and the Senegal offshore (DSDP 367) (Sinningh  Damst  and K ster, 1998).

Based on recent work (Nzoussi-Mbassani et al., 2003) we assume that the supposed global anoxic conditions did not affect all depositional environments in the North Atlantic area and that organic matter sedimentation was also dependent on local paleogeographic and environmental factors. In addition, most of the work that has been done on C–T series lacked a comparison between shallow and deep environments that makes the establishment of a global depositional model for these formations difficult. The similarity of the geological evolution between the sedimentary Basins of Morocco and Senegal gives us the opportunity to compare the C–T sediments in these two areas, along the Western coast of the Atlantic Ocean.

The present study includes petrographic and geochemical analyses from both the Senegal platform and the Tarfaya Basin (Morocco) in order to compare sediment characteristics, and especially organic matter contents. These data are compared to other C–T occurrences in the study area to propose a depositional model for the North African margin area.

2. Regional geological setting

The geological evolution of the North African domain was controlled by the Late Triassic–Jurassic break-up of the supercontinent Pangaea, resulting in the opening of oceanic Basins forming the Western NeoTethys and the central Atlantic (Baudin, 1995) (Fig. 1).

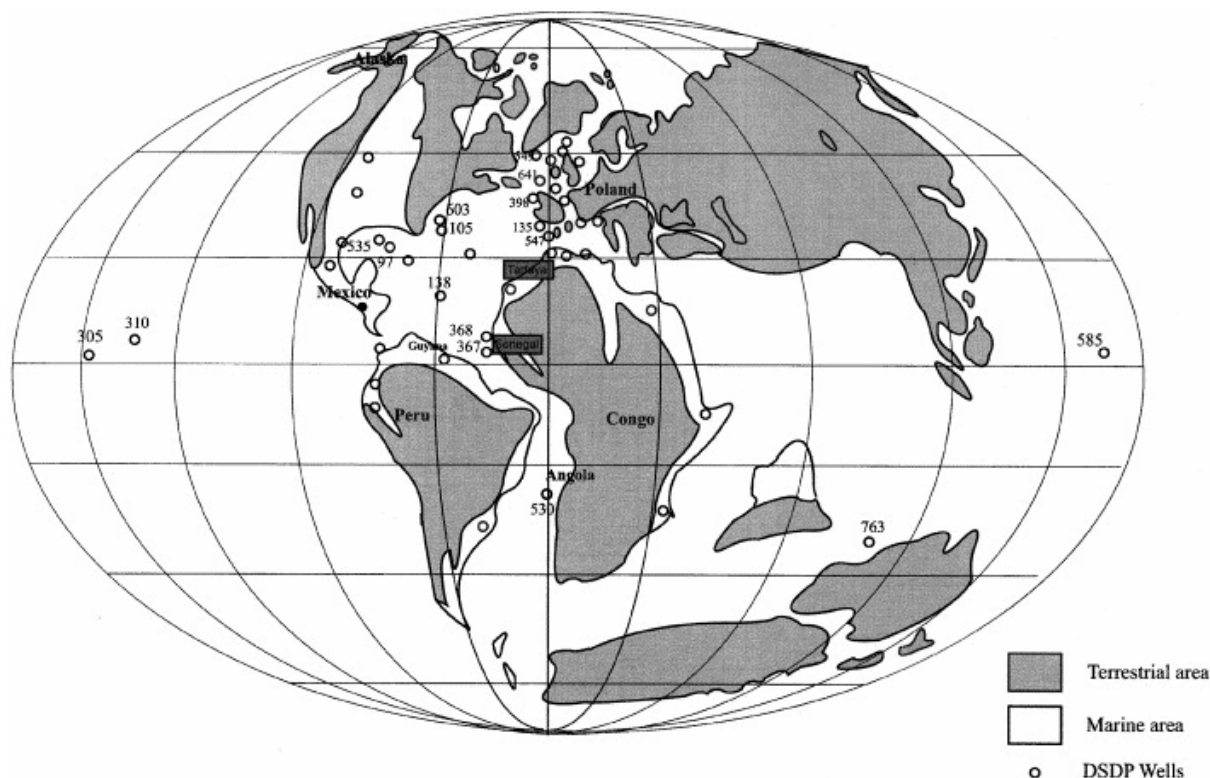


Fig. 1. Paleogeographic map during Cenomanian–Turonian period with DSDP sites according to Schlanger et al. (1987), Herbin et al. (1986) and Arthur et al. (1990).

During the Cenomano–Turonian, the Tethys and the Atlantic Ocean showed sluggish oceanic circulations due to limited connection to the neighbouring oceans (Handoh et al., 1999). These conditions contributed to the development of anoxic bottom waters (Philip et al., 1993 and Philip et al., 2000). During the Late Cretaceous, a major oceanic reorganisation occurred when the direction of the deep water circulation reversed from Equator-wards to Pole-wards (Hay, 1982). Accordingly, the establishment of water exchange in response to the deepening and the widening of the Atlantic Ocean had an important impact on the resulting sedimentary facies due to the influence of oxic water currents (Herbin et al., 1986).

2.1. Senegal Basin

The Senegal Basin covers an area of 340,000 km² between 11 and 17°N latitudes (Fig. 2) occupying the central part of the large North-Western Africa Basin which extends along Senegal, Gambia, Guinea-Bissau, Mauritania and the Moroccan coastal areas. It opens westward to the Atlantic Ocean and is limited by the Panafrican to Hercynian Mauritanide chain to the east (Villeneuve and Da Rocha Araujo, 1984). This Basin contains more than 14 km thick Paleozoic to Tertiary sediments. Outcrops are rare and any known stratigraphy is based on deep wells. The thickness of the Meso-Cenozoic sediments partly exceeds 10,000 m in the western part of the Basin. It consists of transgressive and regressive series: (i) a Jurassic–Lower Cretaceous carbonate platform, (ii) a Cretaceous clastic wedge and (iii), a cap of Tertiary carbonates and shales (Michaud, 1984).

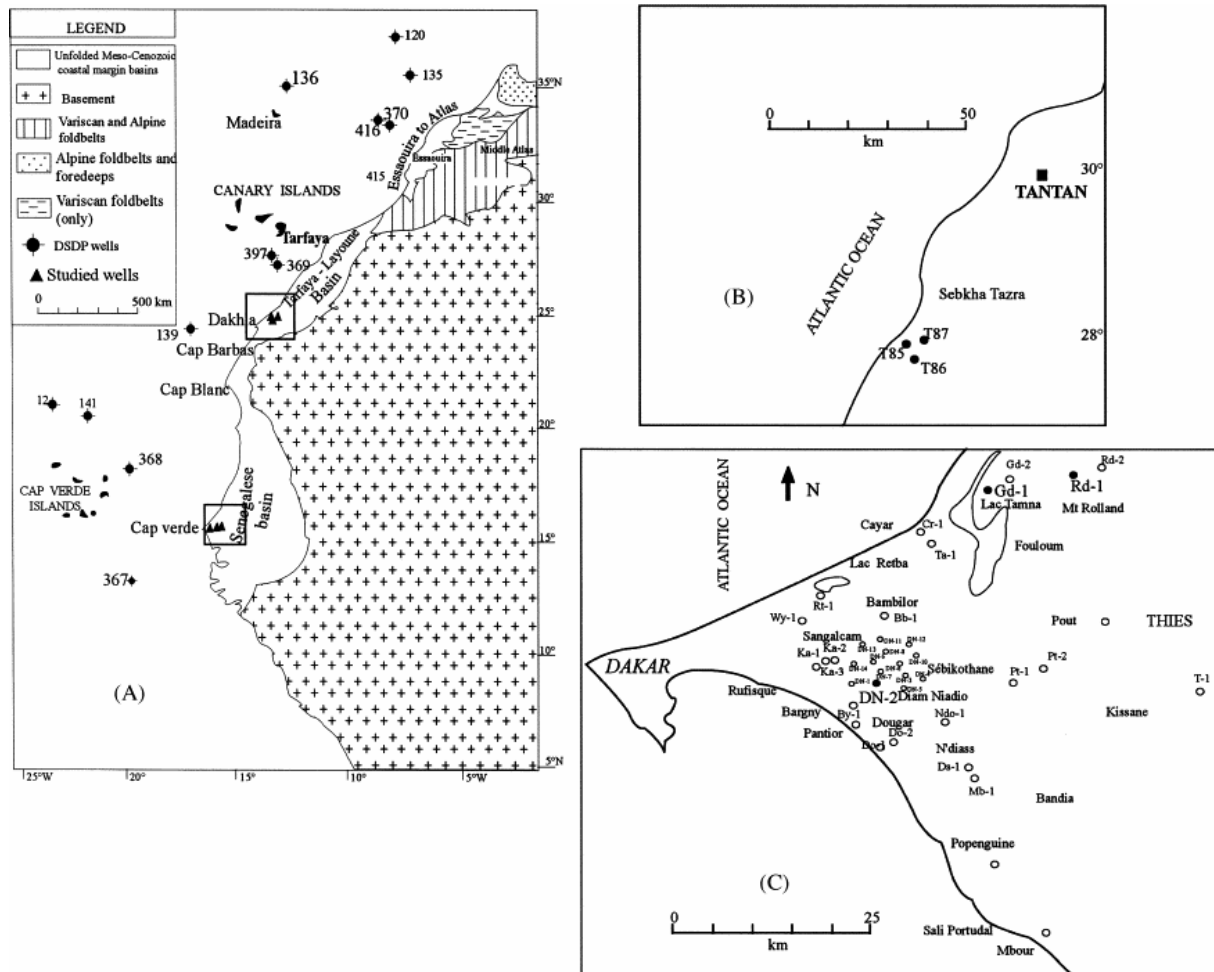


Fig. 2. (A) Map showing generalised geological setting of West African margin and the location of the Senegalese and Tarfaya (Morocco) basins. (B) Location of studied boreholes (T85, T86, T87) within the Tarfaya basin. (C) Location of studied boreholes within the Senegal platform (full circles show the three studied wells, i.e. DN-2, Gd-1, Rd-1).

Three facies characterise the lateral variations of the C–T sediments. The first consists of homogenous black shales deposited in the fully marine environment. This facies dominates the western part of the Thies-Diam Niadio area and reaches maximum thickness in Casamance. No well has reached the base of this facies in the study area. However seismic profiles suggest a Basinward increase in thickness. The second facies is characterised by a succession of calcareous and shaly calcareous sediments typical of a transitional neritic environment. The third facies, typical of a sub-littoral to nearshore marine environment, is composed of shales with shaly siltstone intercalations. These sediments become increasingly rich in siltstone towards the shoreline.

2.2. Tarfaya Basin

The Tarfaya Basin (Fig. 2) is a tectonically stable Mesozoic Basin, which extends along the southern Moroccan coast between latitudes $27^{\circ}40'$ and $28^{\circ}40' N$ and covers an area of $10,000 \text{ km}^2$. It is bounded by the Anti-Atlas Mountains to the North, the

Precambrian Reguibat Massif in the east and the Atlantic Ocean to the West. Studies based on correlations between deep onshore and offshore (DSDP 369, 397) wells allow to make a synthesis of the stratigraphy and of tectonic evolution of the Basin (Wiedmann et al., 1982). During Triassic times, a synrift continental megasequence (1000 m) was deposited. The sediments include evaporite horizons followed by sills of dolerite basalts. The post rift phase started with the Jurassic marine transgression, which only affected the northern part of the Basin. Maximum transgression was reached in Late Cenomanian–Early Turonian times. The Cenomanian–Turonian sediments are composed of hemipelagic facies (Leine, 1986). The strata consist of dark brownish and greyish laminated kerogeneous chinks, alternating with non laminated lightly coloured, often nodular limestones having low kerogen content. The same strata were found far toward the east (Well 75) and the west of the basin (Kuhnt et al., 1990 and Kolonic et al., 2002). Kerogen-rich chinks contain abundant fossils (foraminifera tests) and a carbonate matrix mainly composed of coccoliths and micrite (Leine, 1986 and El Albani et al., 1999).

3. Material and methods

In the Tarfaya Basin, 94 core samples were obtained from three wells (T85, T86 and T87) (Fig. 2) drilled in the western part of the Sebkha Tazra anticline (Fig. 2). Palaeontological investigations attribute them to Upper Cenomanian–Lower Turonian age (Leine, 1986) according to upper *Rotalipora cushmani* to lower *Whiteinella archaeocretacea* biozone (Kuhnt et al., 2001). Concerning the Senegal Basin, 115 samples of drill cuttings were collected from three wells (DN-2, Gd-1, Rd-1) (Fig. 2) which penetrated one of the main facies of the C–T succession in the area (Nzoussi-Mbassani et al., 2003). DN-2 corresponds to distal environment, while Rd-1 represents the proximal one.

3.1. Bulk geochemical analyses

Total Organic Carbon (TOC) contents (wt.%), Hydrogen Index (HI, mg HC g⁻¹ TOC), Oxygen Index (OI, mg CO₂ g⁻¹ TOC), Tmax (°C) and Petroleum Potential (PI) were determined by Rock-Eval 6 pyrolysis (Espitalié et al., 1977 and Lafargue et al., 1998). The analyses were carried out on 100 mg of crushed sample under standard conditions. The Tarfaya Basin samples were first analysed using Rock-Eval II. However, for a better comparison between both basins, some of these samples were re-analysed with the model 6 device. Elemental analyses have been performed on bulk material with a Leco CNS2000 analyser in order to determine Total C (TC), N and S contents.

3.2. Microscopic observations

OM petrographic studies were performed using a Leica DMR XP microscope under different illumination modes: identification and counting of organic constituents (palynofacies) were carried out under transmitted light on total organic matter (TOM) obtained after acid hydrolysis of carbonates and silicates. Specific characterisation (maceral analysis) of land-derived organic particles, i.e. mainly from vitrinite and inertinite groups, was performed on polished sections of OM densimetric concentrates under reflected light and fluorescence. Identifications were made

following the nomenclatures of Stach et al. (1982) and the International Commission for Coal Petrology procedures (ICCP, 1971). Random vitrinite measurements (R_r expressed in %) were made on the same densimetric concentrates under reflected light using a $\times 50$ oil immersion objective (ICCP, 1971).

The microtexture of selected samples showing geochemical and sedimentological contrasts was studied using a Scanning Electron Microscope (SEM, Hitachi S4200 apparatus) in backscattered electron (BSE) mode combined with energy dispersive X-ray spectrometry (EDS). The obtained imaging depends on atomic number (Z) contrasts between the different constituents of the sample, i.e. organic matter and mineral matrix. Investigations were carried out both on polished sections of bulk rocks and of palynofacies residues, previously coated with carbon, with an accelerating voltage of 15 kV.

3.3. Flash pyrolysis–gas chromatography/mass spectrometry (Py–GC–MS)

The kerogens used for flash pyrolysis–gas chromatography/mass spectrometry analyses were isolated by HCl/HF treatment according to the Durand and Nicaise (1980) method. Py–GC–MS analyses were carried out on a Thermofinnigan GCQ TRACE gas chromatography–mass spectrometer equipped with Fischer GSG pyrolysis unit set at 300 °C.

The samples were applied to a ferromagnetic wire with a Curie temperature of 650 °C. Pyrolysis is a thermal degradation in an inert atmosphere which generates products with different weights depending on the temperature of pyrolysis and the type of molecular bounds within the macromolecular network. Only 10% of the pyrolysed products can be analysed by Py–GC–MS. However, NMR and other studies have shown that structural information which can be recovered is, in most cases, representative of bulk material subjected to pyrolysis (Gelin, 1996, Larter and Horsfield, 1993, Horsfield, 1989 and Goth et al., 1988). Even if a precise chemical structure of the macromolecules involved cannot be elucidated by Py/GC/MS, the structural elements in the pyrolysis products can still provide information concerning the origin and the preservation state of sedimentary OM. In this study, pyrolysis products generated between 300 and 650 °C were analysed by Py–GC–MS according to the following oven temperature program: 40 °C during 2 min, then 40–100 °C at 30 °C/min, 100 °C–300 °C at 3 °C/min, and finally 30 min hold at 300 °C. Helium was used as a carrier gas. Separation was achieved using a fused silica capillary column (30 m $\times$ 2.5 mm) with 0.25 mm of stationary phase. The mass spectrometer operated at 70 eV in the electron ionisation mode with a mass range of m/z 50–650.

4. Results

4.1. Senegal Basin

4.1.1. Petrographic and bulk geochemical characteristics

C–T sediments are characterised by low to moderate TOC contents, which does not exceed 4% (Fig. 3D). HI values are generally low ($< 300 \text{ mg HC g}^{-1} \text{ TOC}$) except in some samples originating from the distal part of the Basin. When plotted in a HI/OI diagram (Espitalié et al., 1977), the data points are mainly located in the type III OM field (Fig. 3B) thus suggesting an OM of predominant terrestrial origin (Tissot and Welte, 1984 and Bordenave, 1993). Nevertheless, the high values observed toward the distal part of the Basin indicate marine OM influences. C/N ratios also depend on depositional area. In the proximal areas they are generally higher than 10 in contrast to the distal part where some intervals present C/N values lower than 10 (Fig. 3C). High C/N ratios could indicate terrestrial OM precursor, but should normally not be interpreted separately for OM source characterisation because of possible alteration impact. S/C ratio values are generally lower than 0.36 (Fig. 3D), thus suggesting that the deposition mostly occurred under medium oxic conditions (Raiswell and Berner, 1985 and Morse and Berner, 1995).

As illustrated in a HI–Tmax diagram and by reflectance values, the studied C–T series have reached a degree of thermal evolution globally corresponding to the first part of the oil window, i.e. from its onset to its middle part. Such a moderate maturity suggests a limited thermal alteration of OM quality, e.g. depicted by Hydrogen Index values (Fig. 3A).

Two samples originating from the proximal (Rd-1) and distal area (DN-2) (Fig. 2), respectively, were selected for Scanning Electron Microscopic (SEM) observations. No major distinction in OM distribution has been made between these two samples. In both cases, the OM shows two main morphological features. Firstly, it occurs as thin laminated bands interbedded within the mineral matrix. In the second case, the OM occurs as rounded to subrounded structures/particles finely dispersed/disseminated in the mineral matrix.

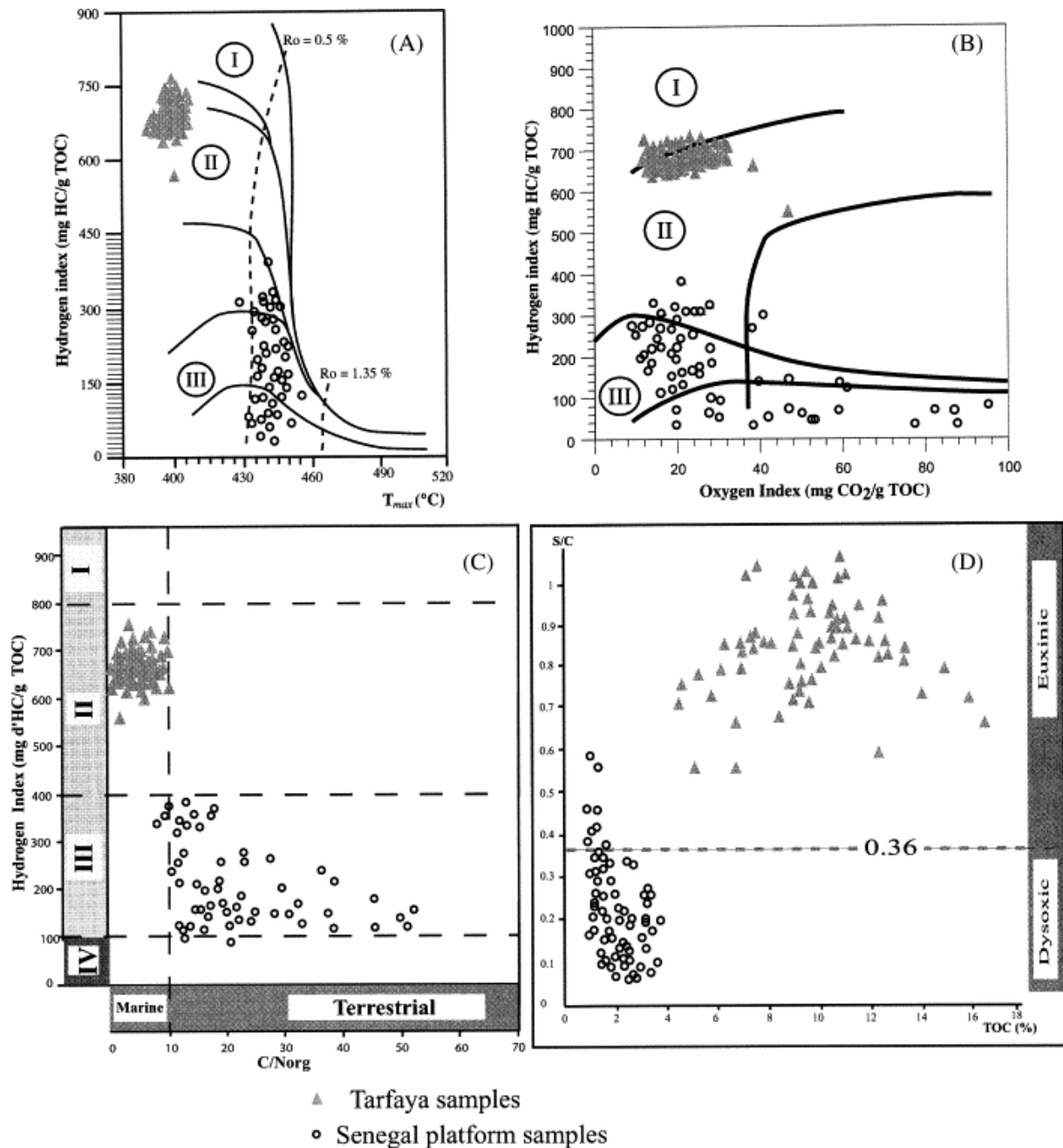


Fig. 3. Bulk geochemical characteristics of studied samples. HI-Tmax diagram (A); HI vs. OI diagram (B); total organic carbon (TOC) and nitrogen ratio vs. HI (C); sulphur and carbon ratio vs. TOC (D).

EDS microanalysis (Fig. 4) shows that, unlike the particulate OM (Fig. 4B), the laminated OM systematically presents sulphur enrichment (Fig. 4A). Such results suggest that (i) sulphurisation reaction does not affect all of OM particles and/or (ii) particulate and laminated OM do not have the same origin.

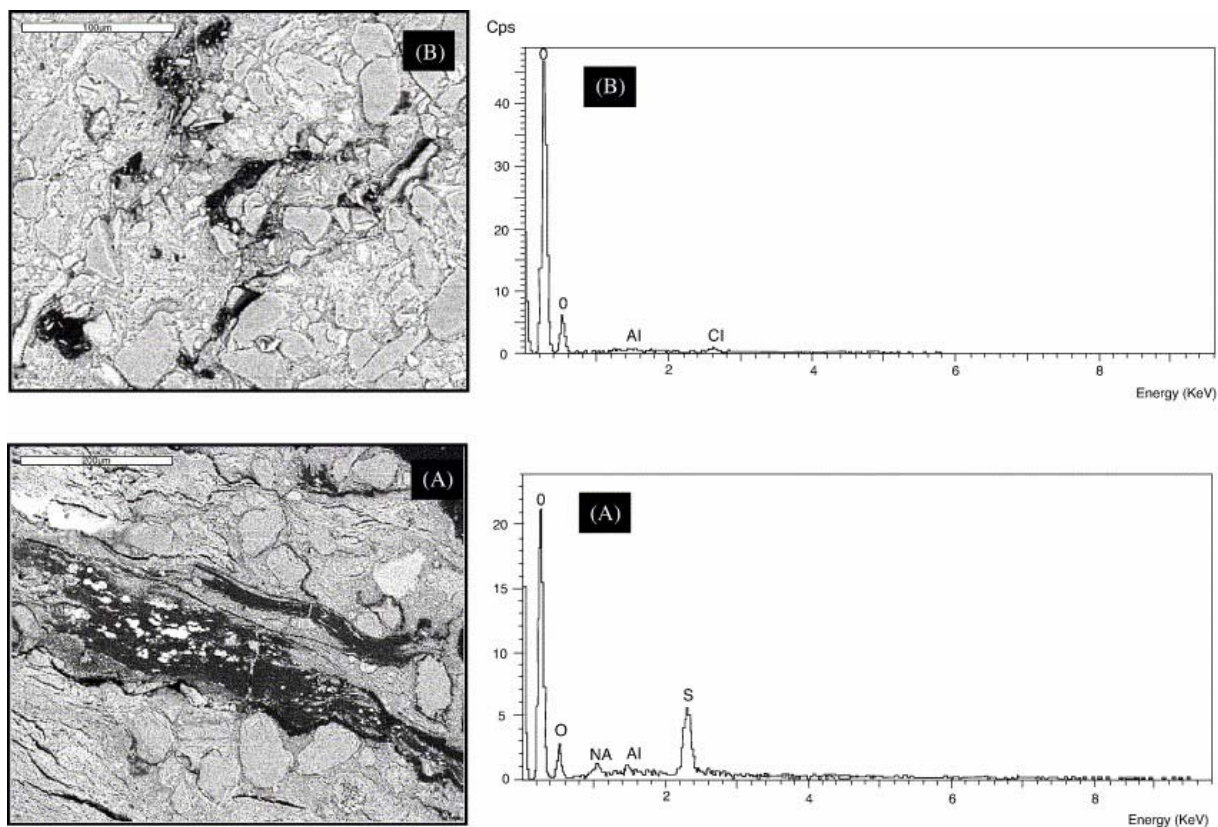


Fig. 4. SEM images of Senegal samples showing two OM morphological features with corresponding EDS analyses: (A) thin laminated bands with sulphur enrichment; (B) dispersed OM without sulphur presence.

The mineral matrix is dominated by Al, Fe, K, Si while Ca is rare (Fig. 5A). The notable presence of Titanium indicates terrigenous influences (Latimer and Filippelli, 2002). Element chemical mapping that have been performed in order to gain a more comprehensive view of elemental distribution, mostly confirms the association of sulphur either with OM or iron in pyrite (Fig. 5B).

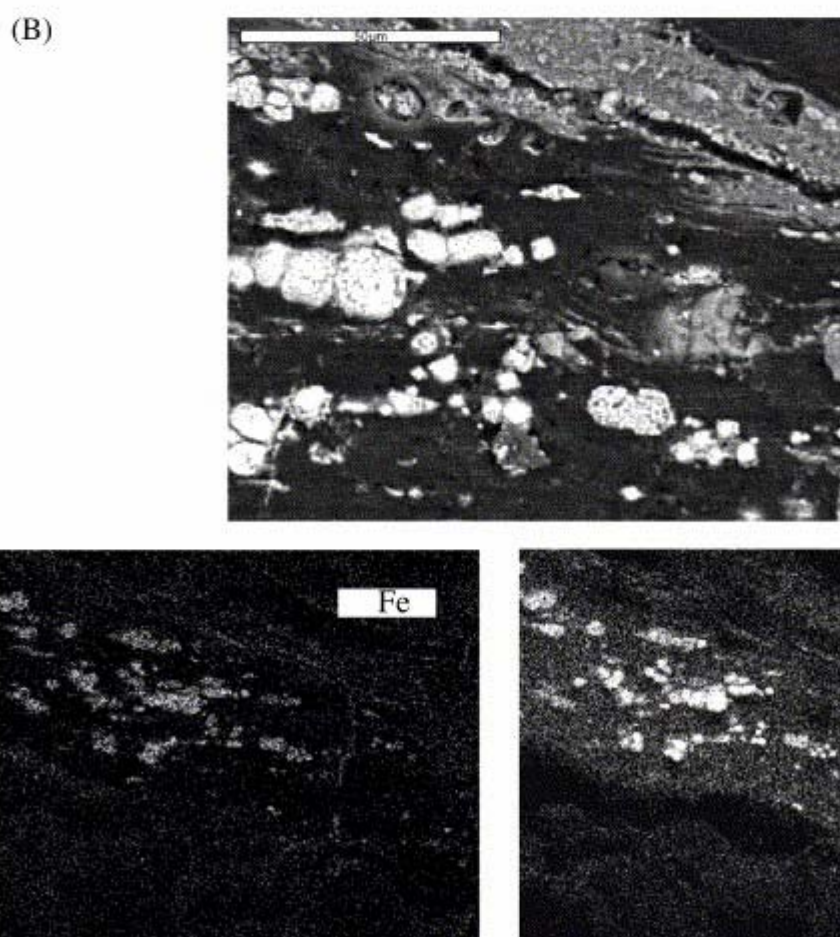
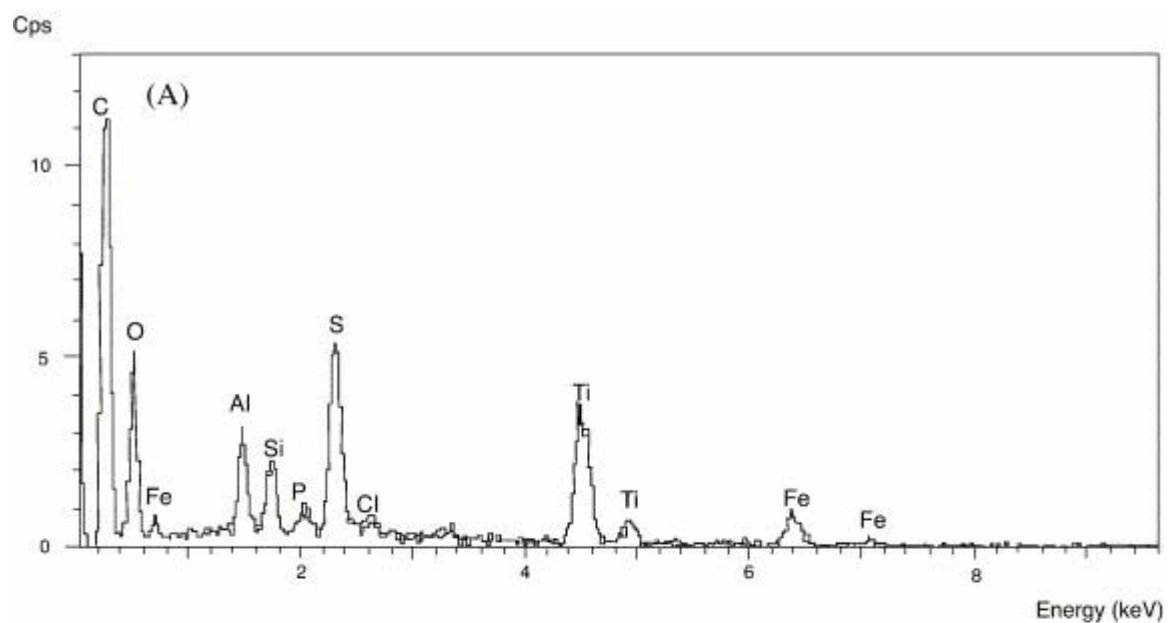


Fig. 5. (A) EDS analysis spectra showing mineral composition of Senegal sediments; (B) an example of elemental (Fe, S) fingerprints of Senegal samples.

4.1.2. Molecular organic geochemical data

The distributions of the major classes of compounds found in the pyrolyzates can be appreciated in the chromatograms displayed in Fig. 6. These latter ones comprise alkylbenzenes, *n*-alkanes and alkylnaphthalenes (Table 1 and Table 2). There is a slight predominance of alkylbenzene compounds, which show similar distribution in the proximal and the distal Senegal areas. Ethylbenzene is the dominant alkylbenzene compound. The occurrence of these compounds in the pyrolysates could result from the cyclisation and further aromatisation of primary linear functionalised lipid precursors such as fatty acids and fatty alcohols (Largeau et al., 1986 and Derenne et al., 1990).

Table 1. : Alkylbenzenes identified in Senegal samples

Peak	Compounds
1	Methyl benzene
2	1,2 Dimethylbenzene
3	Ethylbenzene
4	1-Ethyl-3 methylbenzene
5	1,3 Dimethylbenzene
6	1-Methyl -3 ethylbenzene
7	1-Ethyl -2 methlybenzene
8	Propylbenzene

Table 2. : Naphthalene identified in Senegal samples

Peak number	Compounds
1	Naphthalene
2	Methylnaphthalene
3	Dimethylnaphthalene
4	Trimethylnaphthalene
5	Ethylnaphthalene

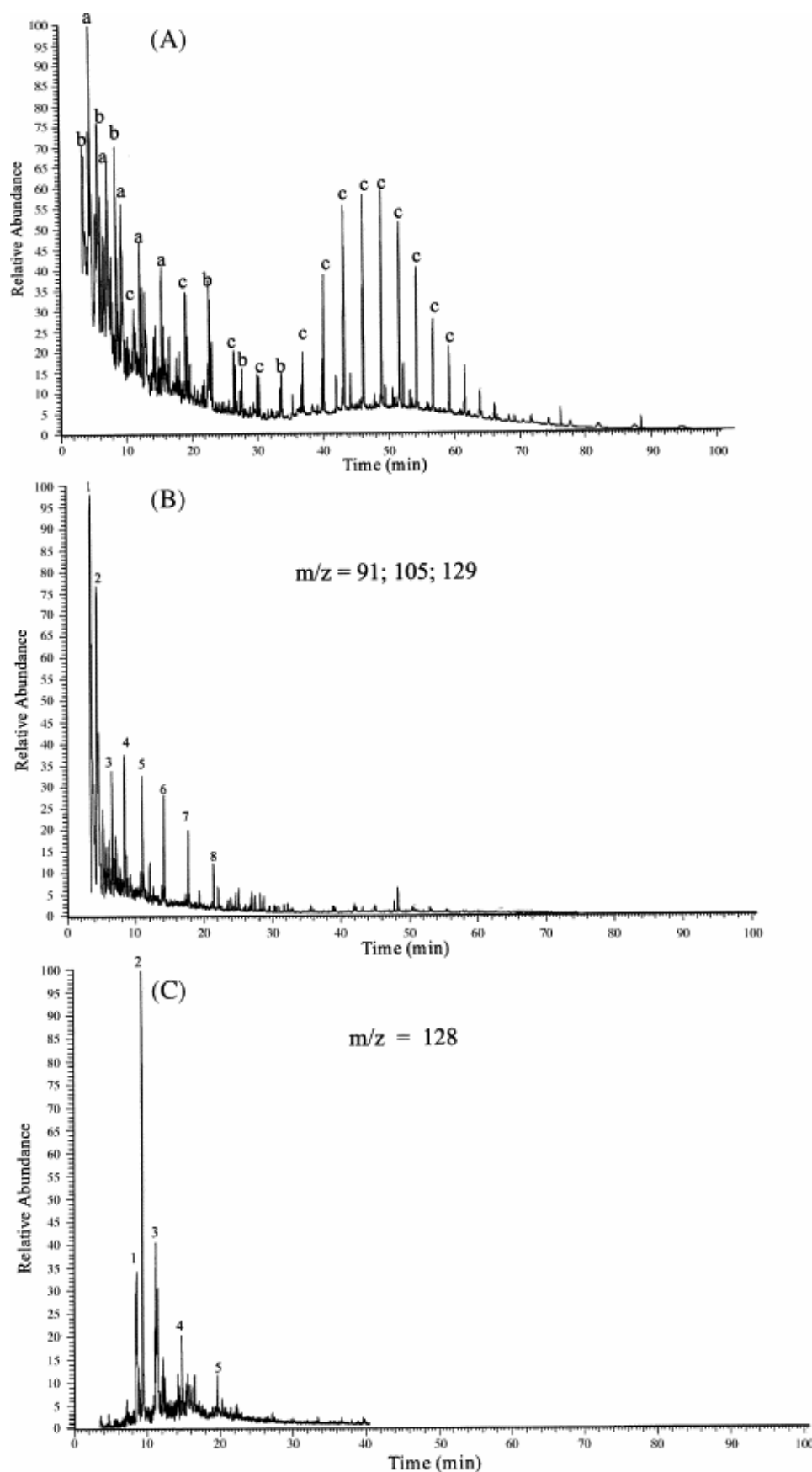


Fig. 6. (A) Gas chromatogram showing relative abundance of major compounds in Senegal samples. (a) Alkylbenzene; (b) naphthalene; (c) alkane. (B) Gas chromatogram showing distribution of the alkylbenzene series (see Table 1 for identification). (C) Gas chromatogram showing the distribution of the naphthalene series (see Table 2 for identification).

The *n*-alkane distributions (Fig. 7) differ between the distal to the proximal sites. The chromatogram from the proximal environment shows a bimodal distribution with a major mode centred on nC_{13} , and the second one on nC_{23} , with no obvious odd–over–even predominance in the C_{23} – C_{29} range. The classical *n*-alkane bimodal distribution in sample pyrolysates indicates a mixed terrestrial and marine-derived OM.

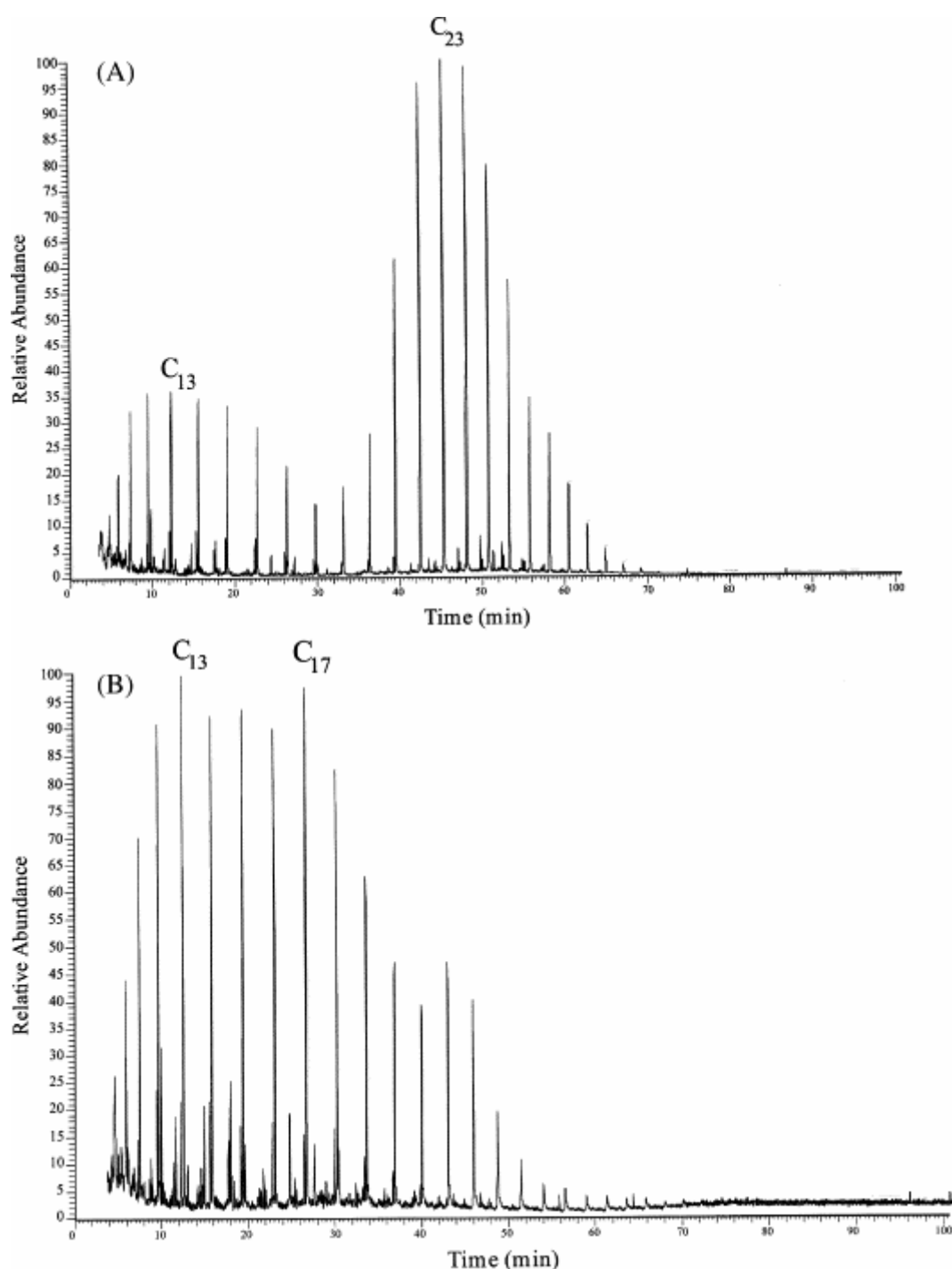


Fig. 7. Gas chromatograms showing *n*-alkane distributions in Senegal samples. (A) Proximal area with bimodal distribution; (B) distal showing unimodal distribution.

In contrast, the chromatogram from the distal environment is characterised by a unimodal *n*-alkane distribution pattern centred on compounds in C₁₃–C₁₇, fully representative of a marine-derived OM.

In addition to alkylbenzene compounds, aromatic fractions also comprise alkylnaphthalenes (Fig. 6) and minor alkylphenanthrenes. These compounds, which are particularly well represented in the sample from the proximal environment, confirm the importance of terrestrial OM inputs in this area. Minor amounts of hopanoids (C₂₇–C₃₁), which were identified in the distal area sample (Fig. 8) witness the development of anaerobic bacteria in the deposition environment (Peters and Moldowan, 1993).

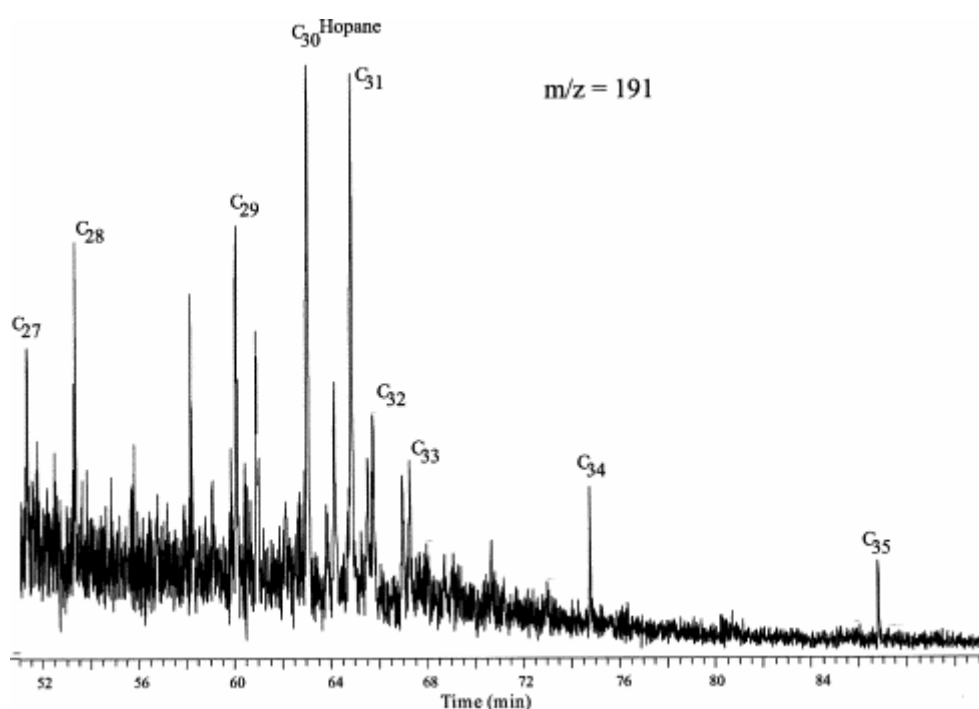


Fig. 8. Gas chromatogram showing the hopane series in distal part of Senegal platform.

4.2. Tarfaya Basin

4.2.1. Petrographic and bulk geochemical characteristics

Tarfaya sediments show much higher TOC contents than lateral equivalent samples from the Senegal (Fig. 3). As a matter of fact, despite some organic-poor levels (ca. 1.5% TOC), the mean TOC contents of these sediments is about 7.5% and can reach up to 16% in some samples (Fig. 3D). HI values vary from 500 to 850 mg HC g⁻¹ TOC with an average around 600 mg HC g⁻¹ TOC. According to HI vs. OI as well as HI vs. Tmax diagrams, OM fall close to the maturation pathways typical for type I and type II kerogens (Fig. 3A,B). Such high TOC and HI contents suggest high primary phytoplanktonic productivity and/or favourable OM preservation conditions (Tissot and Welte, 1984).

In this general context, C/N ratios lower than 10 (Fig. 3C) could be indicative of a notable contribution of nitrogen-rich OM of marine origin and/or OM alteration. S/C

ratios (Fig. 3D) greater than 0.36 suggest euxinic conditions in the depositional environment (Raiswell and Berner, 1985 and Morse and Berner, 1995).

Organic particles observed under photonic microscope (Fig. 9) consist mainly of liptinite (90–95%). The prevailing liptinite groups are alginite and bituminite, while liptodetrinite is seldom observed. Alginite occurs as small (usually less than 20 μm long) elongated particles (lamalginite). In marine sediments, alginite and liptodetrinite, respectively, represent the morphologically well and little preserved remains of marine plankton. Bituminite is commonly regarded as a microbial degradation product of more labile OM that can only be (partly) preserved under exceptional conditions such as anoxic bottom waters (Teichmüller, 1982 and Tyson, 1995). Thus, in addition to other indicators such as the abundance of organic carbon and high S/C ratios, high proportions of bituminite witness the establishment of anoxic bottom waters during deposition. A subordinate proportion of particles of inertinite or vitrinite of terrigenous origin was also observed. The scarcity of such terrigenous particles indicates low inputs of eroded material in the Basin.

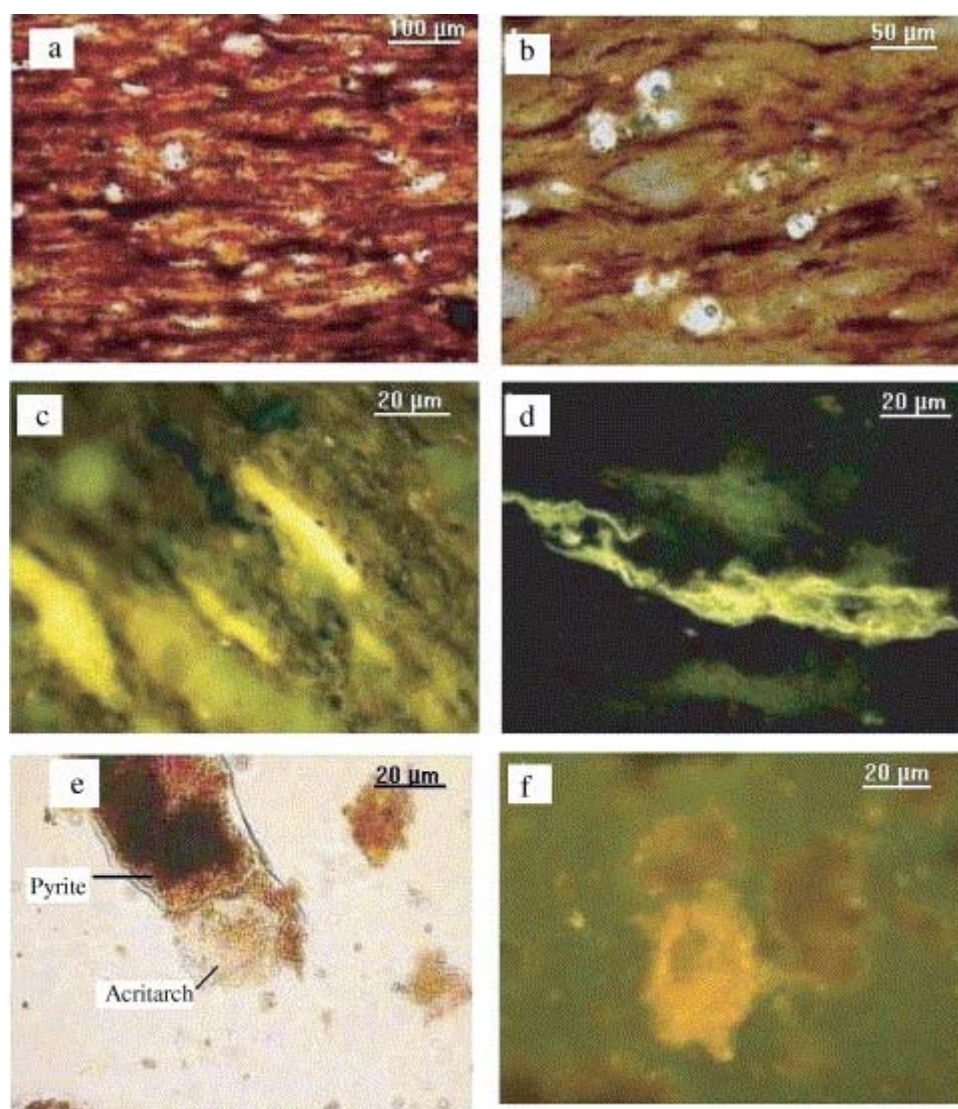


Fig. 9. Photomicrographs illustrating the typical maceral composition of Tarfaya samples. (a) Organic-rich sample showing high OM bands. (b) Organic poor sample with dense mineral. (c) and (d) Strong fluorescing alginite. (e) Reddish brown amorphous organic matter (AOM) and (f) fluorescing AOM.

Under transmitted light (Fig. 9), OM particles isolated by destruction of the mineral matrix (palynofaciès extracts), appear highly dominated by homogenous reddish-brown gelified AOM flakes with frequent inclusions of pyrite flamboids. AOM flakes present variable morphologic appearance and often fluoresces under blue incident light. This fluorescence suggests an oil-prone composition and favourable OM depositional conditions (Lewan, 1986). Rare opaque debris can be identified as inertinite and vitrinite particles. The palynomorphs also contain algal remains and dinocysts and acritarchs. The absence of contrasted OM composition suggests the existence of a single OM source (i.e. marine).

Vitrinite reflectance values determined from the very few particles observed usually vary between 0.3% and 0.45%. These values are in general agreement with Tmax data which range between 419 °C and 422 °C and thus indicate that the OM is still immature (Fig. 3A).

SEM investigations show that the microtexture of Tarfaya sediments is similar to that of the Senegal samples, except for the predominance of thick OM laminations in organic-rich sediments. The main difference between the two series concerns sulphur distribution, since EDS microanalyses reveal that the whole OM here is enriched in this element (Fig. 10). This observation points out the role of sulphurisation processes in OM preservation in Tarfaya. The analyses of the mineral fraction (Fig. 11) and elemental X-ray mapping show the predominance of Ca, and in a lesser extent, the presence of carbonate formations.

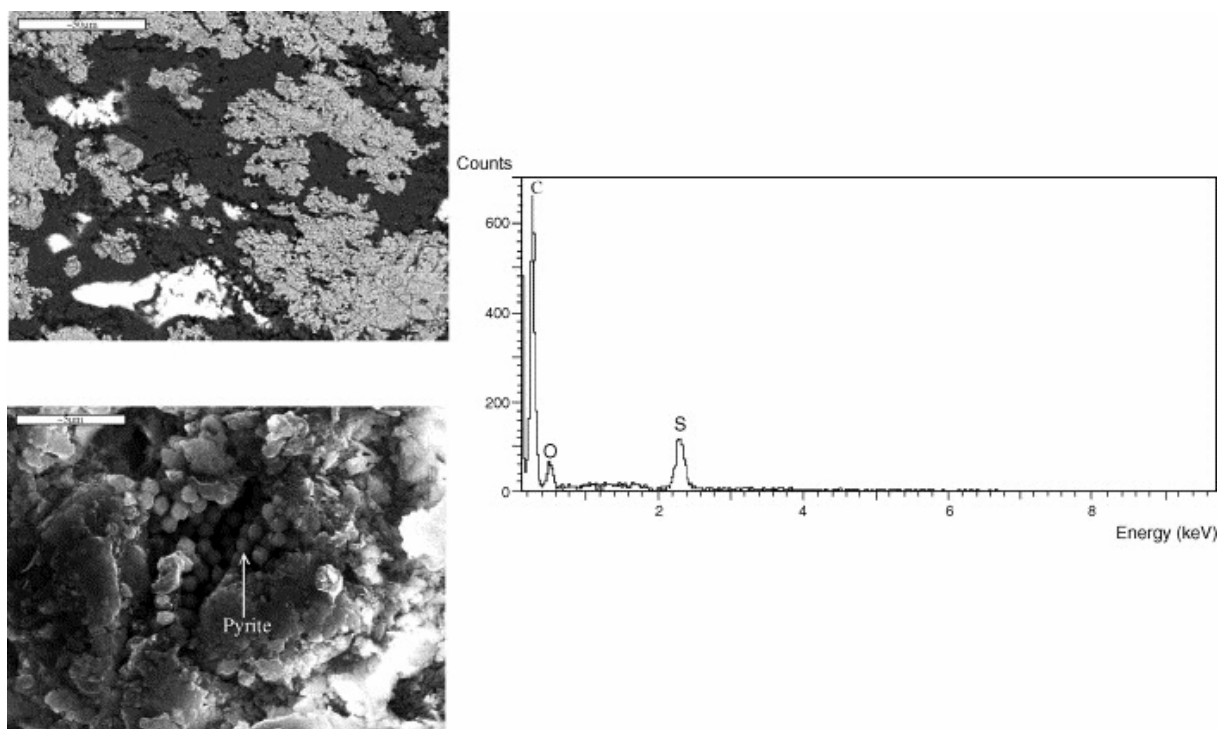


Fig. 10. SEM images of Tarfaya samples showing both OM and mineral matrix relationship and pyrite distribution in mineral matrix. The EDS spectra show the presence of sulphur in OM.

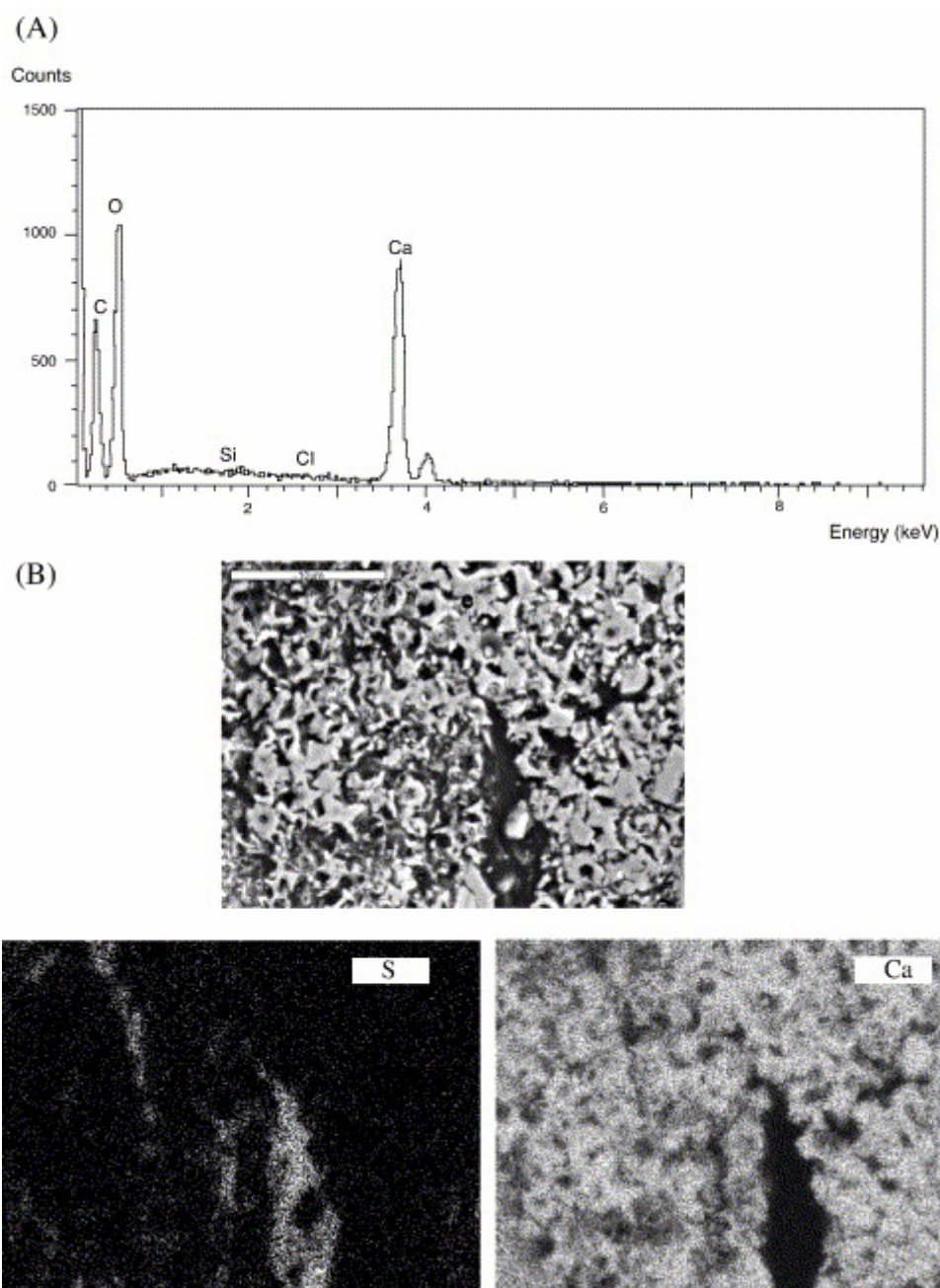


Fig. 11. (A) EDS analysis spectra showing the mineral composition of Tarfaya sediments; (B) an example of elemental (S, Ca) fingerprints of Tarfaya samples.

5. Molecular organic geochemical proxies

The gas chromatogram obtained from samples of the Tarfaya formations are shown in [Fig. 12](#) ([Table 3](#) and [Table 4](#) for identification). The major compounds comprise a long series of alkylthiophenes dominated by 2-ethyl 5-butyl thiophene. A high alkylthiophene content is characteristic of type II-S kerogens ([Sinningh  Damst  et al., 1989](#)). According to various authors (e.g. [Boussafir et al., 1995](#), [Boussafir and Lallier-Verg s, 1997](#) and [Riboulleau et al., 2000](#) and references therein), the abundance of sulphur-containing compounds results from the sulphurisation of planktonic lipids and carbohydrates during early diagenesis. Rare benzothiophenes are also observed.

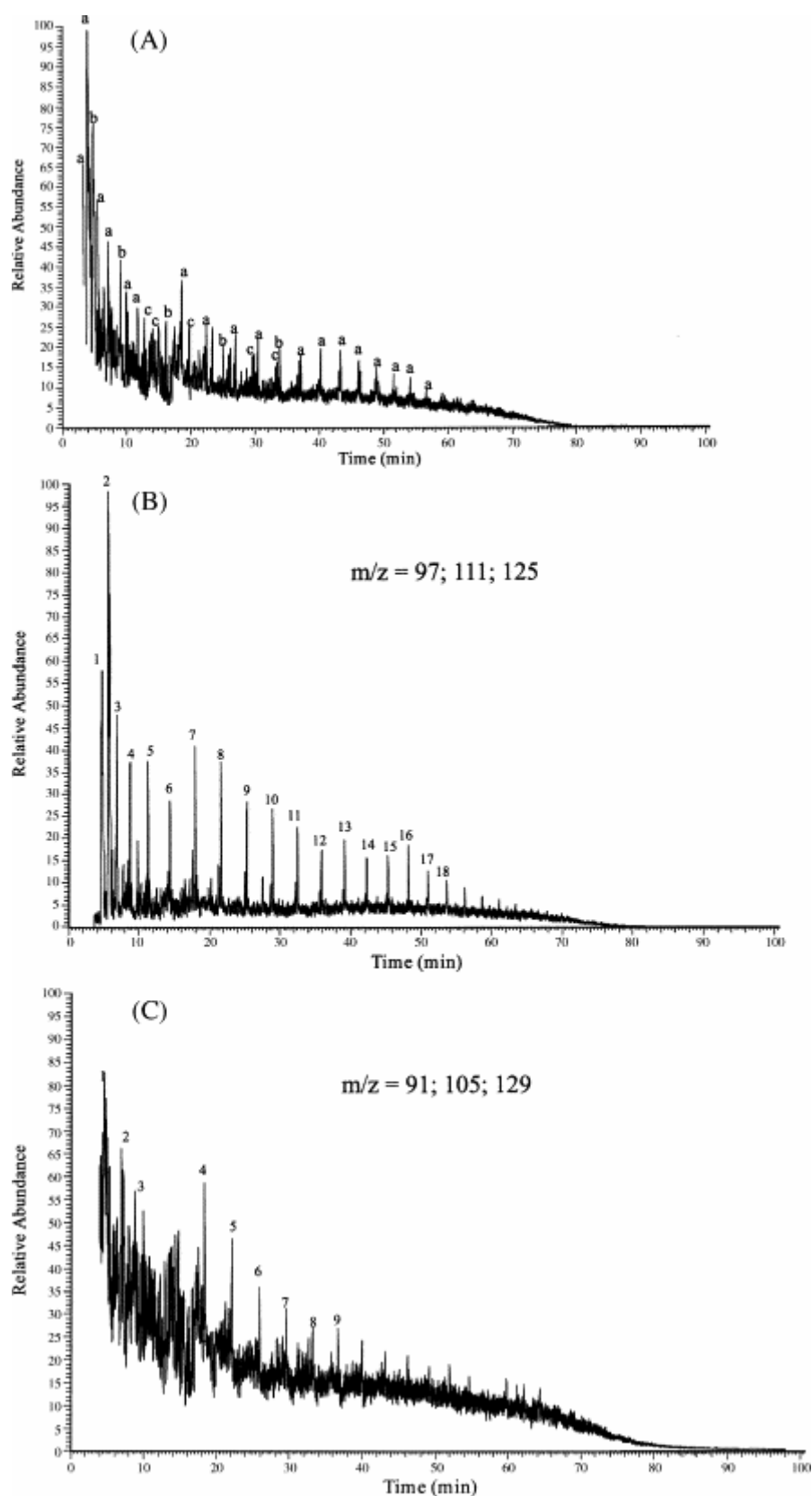


Fig. 12. (A) Gas chromatogram showing relative abundance of major compounds in Tarfaya samples. (a) Alkylthiophene; (b) alkylbenzene; (c) alkane. (B) Gas chromatogram showing distribution of the alkylthiophene series (see Table 3 for identification). (C) Gas chromatogram showing the distribution of the alkylbenzene series (see Table 4 for identification).

Table 3. : Alkylthiophene identified in Tarfaya samples

Peak	Compounds
1	2-Hexyl thiophene
2	2-Ethyl 5-butyl thiophene
3	2-Ethyl 5-methyl thiophene
4	2-Butyl 5-ethyl thiophene
5	2,5 Diethyl thiophene
6	2-Pentyl thiophene
7	2-Isopropyl thiophene
8	2-Butyl thiophene
9	Benzothiophene
10	3-Methyl 2-butyl thiophene
11	Benzothiophene
12	3-Pentyl 3 methyl thiophene
13	2-Hexyl 3-ethyl thiophene
14	3-Methyl 2-butyl thiophene
15	Benzothiophene
16	Propylthiophene
17	2,3,5 Trimethylthiophene
18	2-Propyl 3-methyl thiophene

The *n*-alkane series (Fig. 13) shows short chain predominance with a maximum abundance at C₁₃. This distribution indicates a predominance of marine OM. Pentacyclic triterpane biomarkers are low abundant or even absent. Hopanoids mainly occur as trisnorhopane (Fig. 13), higher homologues in C₂₈–C₃₂ are not well developed. Steranes, usually rare in flash pyrolysis products, are not present in high level enough to be identified.

Table 4. : Alkylbenzenes identified in Tarfaya samples

Peak	Compounds
1	2-Butyl benzene
2	Ethylbenzene
3	1,4 Dimethylbenzene
4	1,2,3,4 Tetramethylbenzene
5	1-Methyl 4-methylbenzene
6	Propylbenzene
7	Hexylbenzene
8	3-Methyl 2-ethylbenzene
9	1,2,4-Trimethylbenzene

6. Discussion

Comparison between Senegal and Tarfaya Basins ([Table 5](#)) shows large contrast in OM abundance and characteristics. Senegal sediments exhibit mixed OM composition from terrestrial and marine origin. This feature is corroborated by bimodal *n*-alkane distributions, generally high C/N ratio values and medium to low HI values. Unlike Senegal, Tarfaya sediments show nearly homogenous OM composition highly dominated by marine-derived amorphous organic matter (AOM). High HI values, rather low C/N ratio values and *n*-alkane distributions dominated by short-chain compounds, all support the predominance of phytoplanktonic-derived OM.

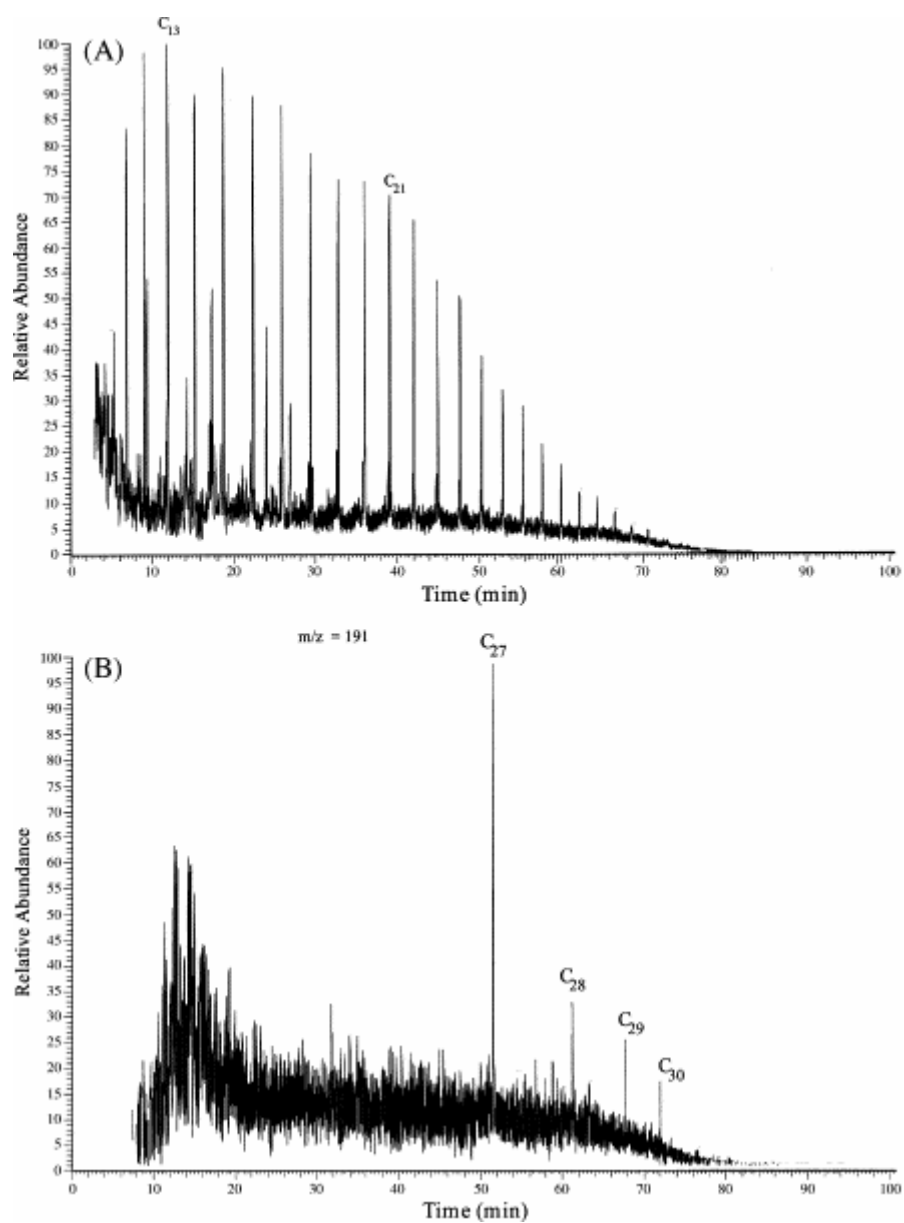


Fig. 13. Gas chromatograms showing *n*-alkane unimodal distribution (A) and hopane distribution (B).

Table 5. : Synthesised petrographic and geochemical data of Cenomanian–Turonian sediments North-Western Atlantic margin area

Samples	Senegal onshore (shelf environment) ^a	Tarfaya (hemipelagic) ^a	Senegal offshore (CM7) (hemipelagic) ^b	DSDP 367 (pelagic) ^c
Thickness (m)	500–2050	100–150	300	150
Sedimentation rate (cm/1000 year)	10–22	1.1–1.7	3.3	Ca. 0.1
TOC (%)	< 4%	1.5–16%	1.27–8.72	10–40%
HI (mg HC/g TOC)	< 400	500–850	152–660	300–900
Kerogen type	II and III	II	II rarely III	II
C/N	> 10	< 10		
S/C	< 0.36	> 0.36		
Liptinite	Very low	90–95% (alginite; bituminite)		
AOM	> 60%	Highly predominant		Highly predominant
Vitrinite I	Notable	Very low		rare
Vitrinite II	Notable	Very low		rare
Inertinite	Notable	Very low		rare
Molecular predominance	Alkyl benzene	Alkylthiophenes		Benzothiophene
Tmax (°C)	435–445	419–422	434–438	396–431
R ₀	0.3–0.9	0.3–0.4	0.57–0.64	0.24

^a This study and Nzoussi-Mbassani (2003).

^b Lancelot (1980).

^c de Graciansky et al. (1982), Herbin et al. (1986) and Müller et al. (1983).

Senegal and Tarfaya Basins also differ on another fundamental factor that is OM preservation conditions. The low S/C values and the lack of organo-sulphur compounds observed on the Senegal platform suggest that C–T sediments were deposited in suboxic medium conditions little favourable to OM preservation. These unfavourable conditions were most probably at least partly counterbalanced by a relatively rapid burial due to a high sedimentation rate (> 10 cm/ky; Nzoussi-Mbassani, 2003) (Table 5). Nevertheless, the latter factor also entailed a notable dilution of the organic inputs. Finally, a poor preservation conditions and high inorganic inputs globally result in the observed low TOC contents. Such features are

not observed in Tarfaya where high S/C ratio values and the abundance of molecular organo-sulphur compounds typify anoxic depositional conditions whereas a low sedimentation rate (ca. 0.1 cm/ky; de Graciansky et al., 1982, Herbin et al., 1986 and Müller et al., 1983) excludes a dilution of the organic inputs by the mineral matter. In addition, it is worth underlying that the high sulphur content of Tarfaya sediments is mostly due to S-bearing organic compounds. This is clearly indicative of high reduced sulphur production and incorporation in the OM, during early diagenesis, and thus necessarily of pronounced anoxic medium conditions.

In order to determine a more coherent depositional model for NW Africa margin, the results obtained on Tarfaya and the Senegal Basins are compared to other C–T occurrences in the study area (Table 5). The first of these sites is the DSDP 367 well drilled offshore Senegal (Fig. 1) which penetrated a C–T series consisting of alternating black and green claystones deposited in pelagic environment (Lancelot and Seibold, 1977). At this site the sediments show the highest TOC contents (about 40%) recorded on the NW African margin, with HI values comprised between 300 to 900 mg HC g⁻¹ TOC (Herbin et al., 1986). The second site, the CM7 exploration well in the Senegal Basin is also situated offshore Senegal, in southern Casamance. It is representative of a slope or a hemipelagic environment, and thus could be compared to the Tarfaya Basin. The sediments from this site exhibit moderate TOC values (1% to 8%, Table 5) (Lancelot, 1980).

The comparison of OM data from these two sites with those of Tarfaya and Senegal onshore area (Table 5) suggests a northward increase in OM productivity and/or preservation from the shelf (Senegal platform), to the transitional slope (Tarfaya and South Casamance) and the abyssal area (DSDP 367). Such evolution contrasts with the distribution of organic carbon contents observed in major recent and present depositional marine settings (Suess, 1980, Tissot and Welte, 1984 and Bordenave, 1993). Indeed, the OM export flux from the euphotic zone decreases exponentially with depth throughout the water column (Suess, 1980), even in the case of high primary productivity such as in upwelling areas (Bertrand et al., 2003). This process necessarily results in the deposition of OM depleted sediments in deep water settings (abyssal area) compared to shelf areas. The processes that might have influenced OM accumulation in the NW African margin during the C–T period are discussed below, and conflict with those observed by many authors in modern high OM sedimentation environments.

6.1. C–T primary productivity on the NW African margin: comparison with present-day upwelling areas

The reconstruction of primary palaeoproductivity in general poses a number of problems. One of the main enigmas concerns the source of nutrients that must have supported high OM production. Generally, an abundant supply of nutrients to the surface photic layer can originate from terrestrial environments with riverine transport to the sea and/or directly from the sea, by upwelling currents.

The importance of terrestrial material inputs can be assessed by the rate of sediment accumulation (Waples, 1983). The average rate of sediment accumulation (Table 5) during C–T black shale deposition is estimated to ca. 0.1 cm/ky for deep areas (DSDP 367; de Graciansky et al., 1982; Herbin et al., 1986, consistently with

datations provided by Müller et al., 1983) and to ca. 1.1 to 1.7 cm/ky at Tarfaya, and around 10 to 22 cm/ky for continental shelves (Nzoussi-Mbassani, 2003). In comparison, sediment accumulation in modern high productivity areas such as the Peruvian margin is about 19 cm/ky (Oberhänsli et al., 1990 and Wefer et al., 1990) and about 30 to 120 cm/ky for the Namibian continental margin (Calvert and Price, 1983). However, the relatively low terrestrial inputs observed in hemipelagic and abyssal areas cannot explain the high OM productivity of these latter sites.

The other possible mechanism for nutrient supply and therefore high bioproductivity in marine area is the upwelling process. The assumption concerning the existence of a palaeo-upwelling regime along the NW African coast during C–T was initially mainly based on the existence of high OM contents in the sediments (Herbin et al., 1986). A key to the identification of this process in ancient series requires the identification of some characteristic markers within the sediments. In this respect, recent studies emphasise the distinction between nutrient markers (e.g. nitrates, phosphates, silicates...) and those related to OM production (e.g. diatomaceous ooze, microfossils...) (Romero and Hebbeln, 2003). For example, particular benthic foraminifera assemblages support the existence of palaeoecological conditions specific to upwelling regime in slope to shelf margin environments in NW Africa (Kuhnt and Wiedmann, 1995). Thus, the abundance of *Gabonita* (typical benthic foraminifera of high productivity areas) in Tarfaya sediments is considered as a proxy of considerable paleoproductivity due to upwelling system (Kuhnt and Wiedmann, 1995).

Other arguments can also be found in modern, supposedly comparable depositional settings. Two areas presently well known to be the site for efficient coastal upwelling responsible of high primary productivity are here considered: the Peruvian margin and the Namibian shelf. Both occur under vigorous costal upwelling system responsible of high primary productivity in the photic zone (Devries and Percy, 1982, Calvert and Price, 1983 and Dingle, 1995). On the Peruvian margin, OM-rich sediments are accumulating on the continental shelf (depth lower than 300 m) along the eastern Pacific Ocean coast. The sedimentation rate of about 19 cm/ky contributes to a maximum sediment organic carbon content of about 12% (Dingle, 1995). Such values strongly contrast with the low TOC content of the Senegal platform deposits despite a roughly similar sediment accumulation rate. On the Namibian shelf, recent studies have evidenced the presence of OM-rich sediments deposited in hemipelagic and pelagic environment with an average TOC content of 3.5% (Bertrand et al., 2003). On the platform (i.e. below 150 m depth) TOC contents reach 9% in an average, but they locally reach 25% (Calvert and Price, 1971). Some authors proposed that the abyssal OM-rich sediments might be composed of material redeposited from slope, after having been transported to depth by turbidity currents (Huc et al., 2001 and Stow et al., 2001). This assumption is supported by absence of features characteristic of anoxic environment such as laminations and benthic foraminifers (Giraudeau et al., 2002).

There are some similarities in term of high OM content in deep sea sediments between present sedimentation from Namibia and NW African C–T series. However, in contrast to Namibian sediments, the abyssal black shales investigated in NW Africa exhibit fine laminations and no evidence of bioturbation (Herbin et al., 1986 and Lancelot and Seibold, 1977). Such features are typical for anoxic depositional

conditions. In addition, the absence of carbonates indicates that these black shales were deposited below the carbonate compensation zone (CCD), in pelagic environment (Lancelot and Seibold, 1977).

Assuming a preservation factor of 2%, Bralower and Thierstein (1984) estimated the primary productivity to ca. 50 g C m⁻²/year corresponding to the middle Cretaceous North Atlantic black shale. Such a value is markedly lower to that measured in present-day upwelling systems and which amounts to 200–360 g C m⁻²/year (Pedersen and Calvert, 1990).

In light of the above discussion which throws some doubts on the role of upwelling systems in the formation of OM-rich sediments we suggest that this process probably did not control the deposition of C–T sediments on NW African coastal area.

6.2. Euxinic depositional conditions: role of isorenieratane

The discovery of isorenieratane in sediments from Cenomanian–Turonian in North Atlantic Ocean (Sinningh  Damst  and K ster, 1998), the Pliocene from Mediterranean Sea (Bosch et al., 1998 and Passier et al., 1999) and recently, in the Tarfaya Basin (Kolonic et al., 2002) shed some new light on the conditions of black shale deposition. This molecule derives from the reduction of isorenieratene, a carotenoid uniquely biosynthesized by the brown-colored strains of photosynthetic green sulphur bacteria (*chlorobiaceae*). In modern environments like the Black Sea the *chlorobiaceae* proliferate only in sulphate and sulphide-rich waters below the oxic/anoxic boundary (Repeta, 1993 and Sinningh  Damst  et al., 1993). Their presence in sediments thus strongly suggests that water-column euxinia extended into the photic zone at the time of their deposition (Sinningh  Damst  et al., 1993).

The absence of such a marker in the Senegal platform series suggests the inexistence of Photic Zone Euxinia and corroborates previous studies suggesting global suboxic depositional conditions in this Basin (Nzoussi-Mbassani, 2003). In contrast to Kolonic et al. (2002), we did not directly identify any isorenieratene derivative in the pyrolysates of our Tarfaya samples. However, the 1,2,3,4 tetramethylbenzene (TMB) molecule found in the alkylbenzene series could be related to the presence of isorenieratene in these sediments (Hartgers et al., 1994). Indeed, the 1,2,3,4 tetramethylbenzene (TMB) could be considered as originating from the β cleavage of aromatic carotenoid moieties such as isorenieratene during pyrolysis (Hartgers et al., 1994). Various studies such as in the Western Canada sedimentary Basin (Fowler et al., 1993), in the Bakken Formation (Muscio et al., 1994) and more recently in Holocene series (Aycard et al., 2003) established the possible link of this compound and isorenieratene presence. However, its real diagnostic value depends on alkylbenzene distribution (Hartgers et al., 1994 and Hoefs et al., 1995). More explicitly, Hartgers et al. (1994) considered the abundance of TMB as an indicator of isorenieratene incorporation during early diagenesis, when coupled to the co-occurrence of 1-ethyl-2,3,6-trimethylbenzene. The abundance of TMB in our samples coupled to high content in alkylbenzene compounds may strongly link to isorenieratene (Hoefs et al., 1995). The development of an anoxic column can then be regarded as a global phenomenon that affected only deep waters as suggested by similar evidences of anoxic deposition medium found in Tarfaya and Senegal offshore sediments. In this context, the presence of benthic

fossil suggested by Kuhnt and Wiedmann (1995) could indicate temporary or periodic development of dysoxic and oxic bottom waters (Kening et al., 2004).

6.3. Depositional model

The appraisal of Cenomanian–Turonian depositional conditions also requires taking into account the whole Basin evolution since the rifting period. The development of a rifting system such as that initiated by Gondwana break up during Early Cretaceous times, usually results in the development of normal faults bounding downthrown and upthrown sides (Anders and Schlische, 1994). As the faults increase in length and displacement, the system attains a typical half-graben geometry, which results in the formation of many isolated Basins delimited by high accommodation zone (Anders and Schlische, 1994 and Gawthorpe, 1999). The existence of a half-graben system responsible of isolated and rift related Basins has been recognised by numerous authors at the North African margin (Orgeval, 1994). The implication of such a tectonic system for further sediment filling and OM accumulation is investigated here after according to the depositional model summarised in Fig. 14.

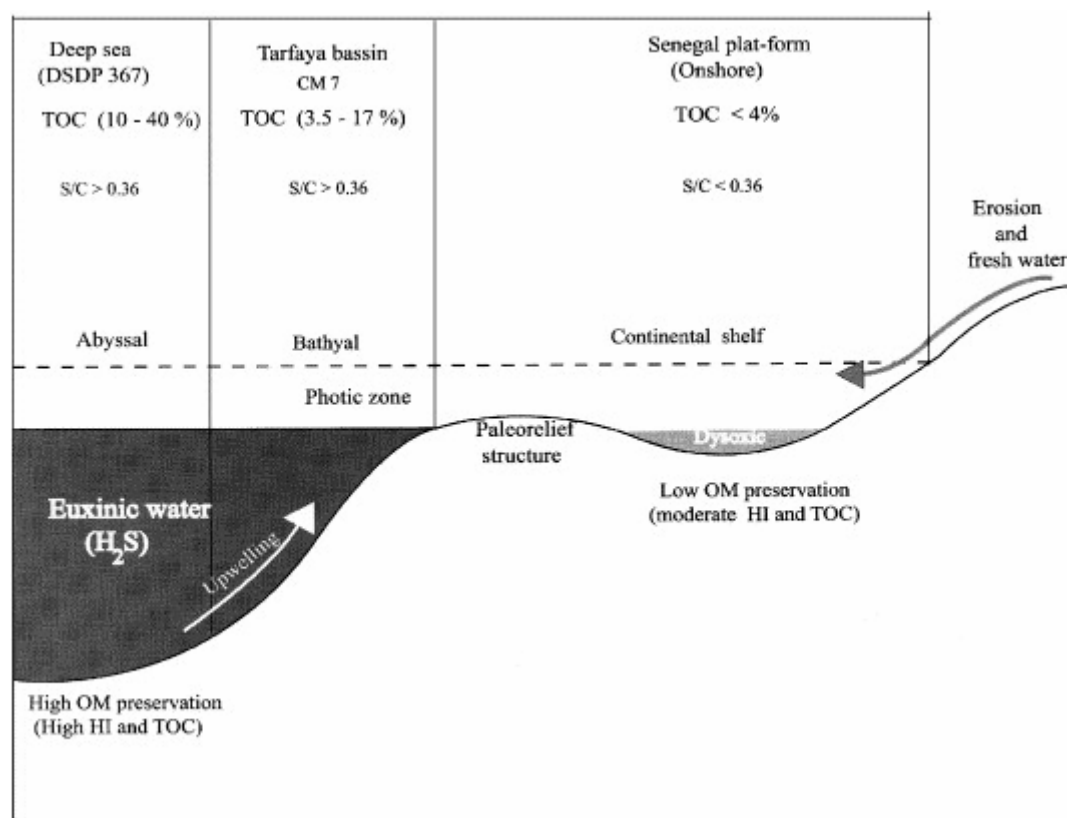


Fig. 14. Paleoceanography and depositional setting during Cenomanian–Turonian time. Note the presence of paleorelief structure between the continental shelf and the bathyal and abyssal environment. This structure restricted water exchange between both depositional settings.

In the general framework of the geological evolution of the whole study area, the different expressions of the so-called C–T anoxic events in the various sites examined led us to suggest that positive palaeorelief features might have isolated deep and anoxic areas from the platform and related suboxic environments. This palaeorelief could have been the relict of the upthrown side/compartiment formed

during rifting. This structural element might have played a key role in limiting exchanges between water bodies and especially in isolating the deep environment (Tarfaya, CM7, DSDP 367) and open shallow marine settings (Senegal shelf). This latter area was characterised by full water circulation and high terrigenous inputs from hinterlands (siliciclastics, plant material). This detrital material mostly originated from Mauritanides chain to the East and the Reguibat structure to the North.

The described model agrees with some previous observations concerning C–T sediment distribution (Orgeval, 1994, Latil-Brun and Lucazeau, 1988, Braun and Beaumont, 1989 and Arthur et al., 1987). Those authors observed that C–T strata in West and North Africa was restricted to a marine facies deposited under minimum water depth and with a distribution that followed palaeoreliefs that existed at that time. This feature appears susceptible to explain the East–West increase in organic carbon content observed from platform to hemipelagic and pelagic environment.

7. Conclusion

Organic-rich strata of two North Western African Atlantic Basins were compared through organic petrography and bulk and molecular geochemistry approaches. Each setting revealed specific features of these strata related to depositional environment conditions during Cenomanian–Turonian period. At the scale of North Africa margin those differences may be attributable to paleogeographic configuration and particular geodynamic evolution. The OM-rich sediments were most probably preferentially deposited in isolated and stagnant basins, with oxygen depleted bottom waters. The main factor, which has determined and further increased OM preservation conditions, was certainly the limited communication between southern oxygenated water (opened platform) and northern confined ones (mini-basins). Water stratification, salinity increase, H₂S production related to sulphuration processes have certainly contributed to preservation conditions increase. Confined environments are rift related basins originating from horst and graben structures resulting from Atlantic Ocean formation.

One implication of our results is that the occurrence of black shale is a consequence of interaction between particular Middle Cretaceous climate and *local factors* (paleogeographic conditions). Consequently, behind apparently homogenous facies of black shale sediment, there are many disparities in terms of organic matter composition, depositional environment and preservation conditions. Additionally, primary productivity was certainly not the key factor of C–T black shale deposition. This productivity mainly appeared moderate, especially when compared to present-day upwelling areas.

Finally, according to this study, the conditions that prevailed along the NW African margin during Cenomanian–Turonian times probably differed from those found in the environment of modern upwelling cells.

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