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Sources of organic carbon in the Portuguese continental shelf sediments during the Holocene period

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ABSTRACT

Organic C (OC) and total N (TN) concentrations, and stable isotope ratios ($\delta^{13}C$) in muddy deposit sediments of the Northern and Southern Portuguese continental shelf were used to identify sources of fine-sized organic matter (<63 μm) during the Holocene period. Sedimentary columns off the Guadiana (core CRIDA 05), Tagus (core MD 992332) and Douro (core KSGX 57) estuaries are characterised by elemental and isotopic values that reflect distinct sources of organic matter (OC/TN and $\delta^{13}C$ ranging, respectively, from 8.5 to 21 and from −22.4‰ to −27‰). Intense supplies to the Guadiana continental shelf of fine terrigenous particles during the Younger-Dryas Event are closely linked with higher OC/TN values and lower $\delta^{13}C$ ratios. During the postglacial transgression phase, an increasing contribution of marine supplies (up to 80%) occurred. Higher $\delta^{13}C$ (up to −22.4‰) values and low OC/TN ratios (down to 8.5) are found as the sea level approaches the current one. The Upper Holocene records emphasize the return to enhanced terrestrial supplies except for the Little Climatic Optimum between the 11th and 15th centuries AD. This climatic event is especially obvious in the three cores as a return to marine production and a decrease in terrestrial sediment supply to the continental shelf. The return to a cooling event, the Little Ice Age, between the 15th and 19th centuries AD, is mirrored by decreased terrigenous supplies in core KSGX 57. Gradually increasing sedimentation in estuaries, as well as formation of coastal dune fields, have been hypothesized on the basis of increasing $\delta^{13}C$ and decreasing OC, TN and OC/TN values.

1. Introduction

The burial of organic C (OC) on continental margins depends intimately on OC supply, dilution effects of detrital material, and preservation and mineralization in sediments (Ogrinc et al., 2005). Detrital sedimentary material represents a complex mixture of biogenic substances introduced by a variety of marine and riverine inputs (Sigleo and Macko, 2002). Terrestrial organic C whose input to coastal margin sediments is largely controlled by riverine sources (Hedges et al., 1997) represents a significant fraction of total OC in coastal sediments (Prahl et al., 1994; Jia and Peng, 2003; Ogrinc et al., 2005). More recent evidence suggests that delivery and quantification of terrigenous organic matter in margin sediments is complicated by the heterogeneous nature of the riverine end-member (Goñi et al., 1998; Gordon and Goñi, 2003). Carbon isotope ratios ($\delta^{13}C$) and OC to total N ratios (OC/TN) have the potential to provide information as to the origin of organic material preserved in coastal environments (Megens et al., 2002). The usefulness of $\delta^{13}C$ and OC/TN to identify the various sources of C has led to their widespread use as tracers of C pathways and storage in coastal marshes (Chmura and Aharon, 1995; Middelburg et al.,

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1997) and marine sediments (Bird et al., 1995). More recently these techniques have been applied to Holocene sediments to distinguish changes in palaeocoastal environments and relative position of sea-level (Lamb et al., 2006; Wilson et al., 2005).

During the most recent postglacial transgression, coastal margin sedimentary records offer excellent opportunities to study the sequence of events which have led to the burial of organic matter. On century to millennium time scales, climatic patterns such as the cold phases associated with the Younger-Dryas Event and the Little Ice Age modulated stream flow and sediment discharge (Dias et al., 2000). On yet another time scale, during the past centuries, the marked changes in riverine sedimentary supply were brought by human activities (Stallard, 1998; Ver et al., 1999; Lal, 2003). There are several published studies dealing with OC contents in cores and surficial sediments on the Western Iberian shelf and Guadiana River estuary (Drago, 1995; Paiva et al., 1997; Oliveira et al., 1999; Jouanneau et al., 1998, 2002; Epping et al., 2002; Van Weering et al., 2002; González-Vila et al., 2003). However, no data have yet been published on the use of C isotopes and OC/TN ratios as an alternative proxy to interpret past ecosystems and environments in which sedimentary OC was produced and deposited.

In this study, a high-resolution elemental (OC and TN) and δ^{13}C record of fine-sized (<63 μm) particulate organic matter from the main muddy deposits of the Portuguese continental margin covering the Holocene period is provided. It was performed in order: (1) to estimate the contribution of terrestrial organic matter in ambient marine sediments, which have direct relevance to palaeoclimate, and (2) to discuss the potential alteration of geochemical signatures that may affect the reliability of δ^{13}C and OC/TN as accurate recorders of the source of organic material in sediments, as a result of decompositional processes.

2. Regional setting

The northern and southern Portuguese continental shelf is the catchment basin of strong fluvial inputs, as revealed by the presence of important muddy complexes located in the mid-shelf off the Douro, Tagus and Guadiana Rivers.

The Douro muddy deposits are located NW off the Douro River mouth as an elongated feature that is well defined and cover the mid-shelf area below the 60 m isobath. The Douro muddy complex seems to have developed as a consequence of a high amount of sediment input from the river to the shelf, favourable hydrodynamic conditions, and a morphological setting of the outer shelf edge on its western side that acts as a sediment trap (Fig. 1; cf. Dias et al., 2002). Maximum sedimentation rates previously determined using the ^{210}Pb technique ranged overall from 0.41 to 0.58 cm a^{-1} (Carvalho and Ramos, 1989; Drago, 1995; Drago et al., 1999; Jouanneau et al., 2002), emphasizing the high input in the Douro mud patch. The Tagus sedimentary deposit, located further south, offshore of the Tagus river basin, is quite narrow and covers the continental shelf from the river delta front up to the shelf-break, where several canyons intersect the outer shelf. The area is protected against swell from the NW and since the Tagus acts as an important source of fine particles, almost the entire continental shelf is covered by a large expanse of mud deposit (Fig. 1). Away from the estuary mouth, profiles of radionuclides measured in cores provided estimates of the maximum sedimentation rate of 0.16 cm a^{-1} (Jouanneau et al., 1998). Large bodies of sand and gravelly sands occur on restricted areas of the shelf, more typically in the northern sector where there are several rocky outcrops, and on the inner shelf, where there are strong littoral currents.

The Guadiana river's sediment contribution is particularly significant in the northern margin of the Gulf of Cadiz (Southwestern Iberian Peninsula) (Morales, 1997). The surface sediment distribution on the shelf off the Guadiana estuary consists of sandy deposits, dominating the shelf down to a depth of approximately 25 m. The outer infralittoral between 25 and 30 m consists of sand and sandy mud while the middle shelf is characterised by an extensive mud belt, consisting of very fine-sized clayey material (Fig. 1; cf. Gonzalez et al., 2004). On the outer shelf below 100 m, sediments are generally dominated by sand and silty clay.

The discharges from the Douro, Tagus and Guadiana rivers are by far the most important on the Portuguese coastal zone; the three rivers' basins are large and their sediment loads are great. The total annual sediment supply to the shelf from the Tagus, Douro and Guadiana river has been estimated to be about 1–5 × 10^6, 1.8 × 10^6 and 6.15 × 10^4 tonnes, respectively (Bettencourt, 1990; Dias et al., 2002; Morales, 1997).

3. Sampling and analytical methods

3.1. Sample collection

Sediment samples were recovered from a vibro core CRIDA 05 (37°1′54″N-7°20′44″W; water depth: 72 m; length: 351 cm; date of collection: April 2002) and from two gravity cores MD 992332 (38°33′05″N-9°22′W; water depth: 91 m; length: 303 cm; date of collection: September 1999) and KSGX 57 (41°14′33″N-9°01′44″W; water depth: 97 m; length: 270 cm; date of collection: July 1998), coming from the mud field of the Guadiana, Tagus and Douro continental shelf, respectively (Fig. 1).

Sampling was carried out from the top to the bottom, at a spacing of 1 cm for cores KSGX 57 and MD 992332 and for the first 50 cm of core CRIDA 05, and every 2 cm between 50 and 352 cm for core CRIDA 05. Subsamples were carefully picked among the continuous collection of samples for sedimentological, elemental and stable isotope measurements, and among CRIDA 05 and MD 992332 samples for radioisotopes analysis. In all tables and figures, sediment depths are reported using the upper boundary of each sampling interval.

3.2. Carbonate content

Calcium carbonate content was determined using a gasometric method (Hulseman, 1966), showing a fairly low

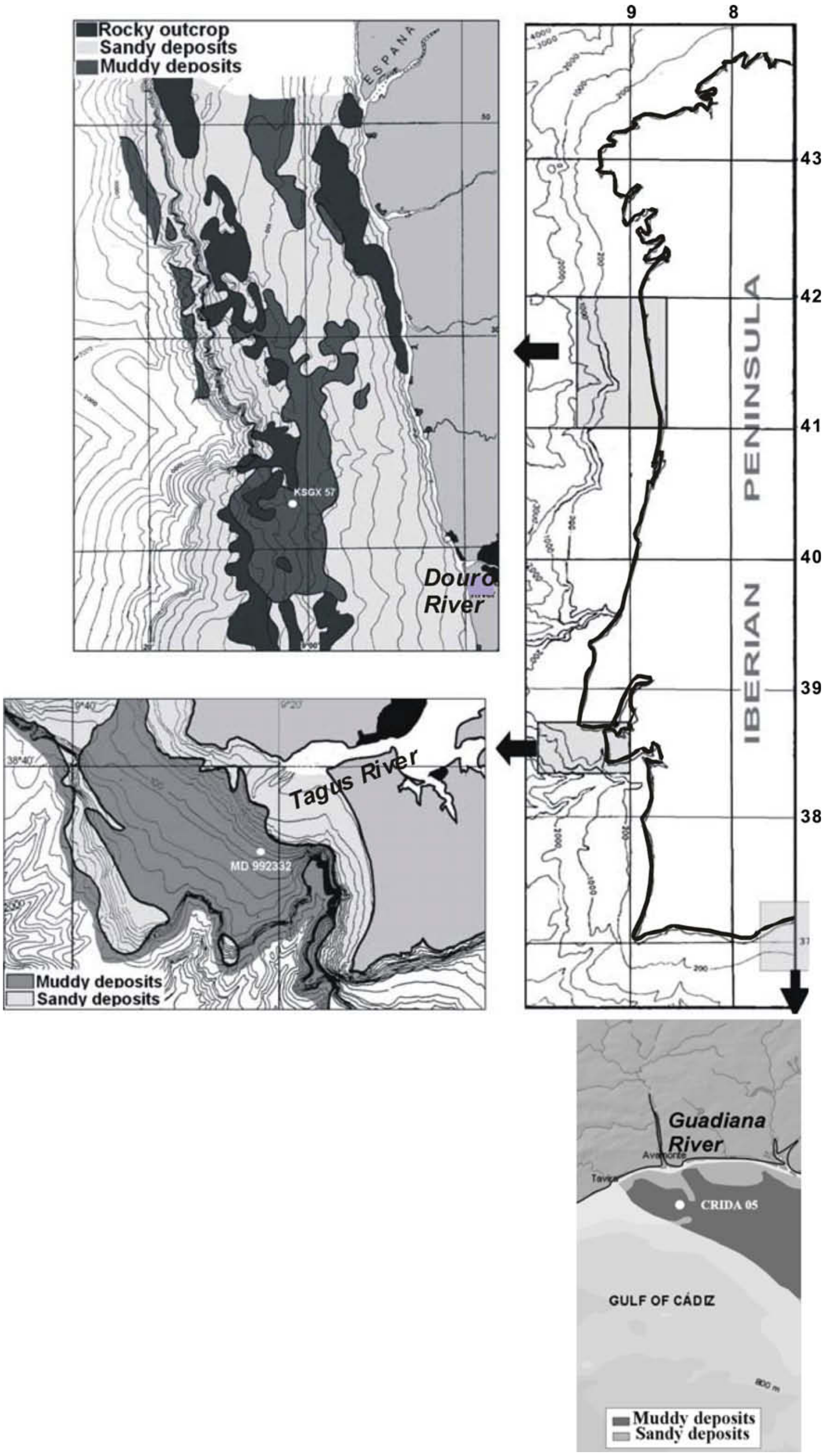

Fig. 1. Location of cores CRIDA 05, MD 992332 and KSGX 57 on the Portuguese continental shelf.

relative variation (<2%) in duplicate measurements. Hydrochloric acid is added to a sediment sample to decompose all the carbonates. The volume of CO_2 released is measured with a Bernard Calcimeter and compared with the volume of CO_2 released by pure $CaCO_3$. The carbonate content is expressed as the equivalent $CaCO_3$ concentrations.

3.3. *Grain size fractionation*

Grain size studies were performed with a Mastersizer S equipment (Malvern Instruments) using Laser Diffraction for Particle Size Analysis. The sediment type in terms of its dominant grain size components was determined using the classification of Folk (1954). Grain sizes <2 μm, between 2 μm and 63 μm and >63 μm correspond to the clayey, silty and sandy fraction, respectively.

3.4. *Radionuclides*

Radioisotopic measurements were made by gamma-spectrometry, using a high-resolution, low background low energy semi-planar hyperpure Ge detector (EGSP 2200-25-R from EURYSIS Mesures) coupled to a multi-channel (8000 channels) analyser. The use of the natural radionuclide ^{210}Pb (half-life = 22.3 a) is a well established technique to determine marine sedimentation rates during at least the past century (Koide et al., 1972; Nittrouer et al., 1979). Excess ^{210}Pb apparent sedimentation rates were estimated based on a CF:CS model (constant flux:constant sedimentation) (Goldberg, 1963). This model assumes a constant flux of excess ^{210}Pb from the atmosphere and a constant dry-mass sedimentation rate. Where these assumptions are satisfied, the ^{210}Pb concentration will vary exponentially in accumulating sediment.

3.5. *^{14}C ages*

^{14}C age values were determined using accelerator mass spectrometry (AMS) on benthic foraminiferal assemblages or liquid scintillation counting (LSC) on organic matter, following the methods described in Soares (2005, 2006). The ages are presented as conventional ^{14}C dates and also as calendar dates using the program CALIB Rev 5.0.1 (Stuiver and Reimer, 1993; Reimer et al., 2005), corrected by reservoir effect values for the Portuguese coast (Soares, 2006). Table 1 shows the specific horizons that were ^{14}C dated for each core and the materials used.

3.6. *Elemental and stable isotope measurements*

Bulk sediment samples were sieved at 63 μm because terrigenous organic matter, transported away from its continental source, is much more concentrated in the fine size fraction (Christensen, 1996). Furthermore, resistant soil organic matter is more concentrated in fine size fractions (Balesdent and Mariotti, 1996) and therefore, a better characterisation of continental sources of organic matter is expected. Organic C, TN and δ^{13}C isotope ratios were measured, after carbonate removal, on the same sample aliquot by EA-IRMS (EuroVector 3028-HT Elemental Analyser on line with a SIRA 10 Isotope Ratio Mass Spectrometer). In order to reduce possible leaching effects on organic matter during carbonate removal, the fine size fraction of sediment was carefully treated with 1 N HCl at 70 °C in a way that pH was always maintained at 3. A previous study, realized on particulate organic matter in North Atlantic deep-sea sediments (Huon et al., 2002), showed that complete dissolution of carbonates (calcite and dolomite) required heating. In such cases more than 90% recovery of the total OC content of the samples was attained. All samples were rinsed in deionised water to remove dissolved salts. The solid residue was recovered by high velocity centrifugation (20,000 revs min^{-1} for 1 h), dried at 35 °C and hand-grounded with a mortar. Results for isotope abundance are reported in‰ relative to Pee Dee Belemnite (PDB) standard for δ^{13}C. Organic C and TN are reported in mg g^{-1} of dry sample (equivalent to weight‰). During the course of this study, analytical precision (±1σ) was: ±0.2‰ for δ^{13}C, 0.1 mg g^{-1} for OC and 0.1 mg g^{-1} for TN. The uncertainty on OC:TN ratios averages 0.2. Data reproductibility was checked by replicate analysis of samples (50%) and of an acetanilide standard which yielded −30.6 ± 0.2‰, 710 ± 30 mg g^{-1} and 100 ± 1 mg g^{-1}, for δ^{13}C, OC and TN, respectively.

4. Results

4.1. *Stratigraphic framework*

Assuming constant accumulation rate for the intervals between dated horizons and over the remainder of the core, the calendar dates indicate that the sedimentary sequences accumulated under various rates of vertical accretion. An average sedimentation rate of 0.10 cm a^{-1} can be estimated for earlier Holocene sediments (between 351 and 207 cm depth) in core CRIDA 05 (Fig. 2a). With the calendar ages of foraminifera sampled above (151 cm), the sedimentation rate decreases to 0.010 cm a^{-1}. However, taking into account an additional date of 1113–1290 cal a BP measured at 103 cm depth, it shifts to 0.015 cm a^{-1}. An average sedimentation rate of 0.09 cm a^{-1} can be estimated for the remainder of the core.

Table 1
Information from C dating

Depth (cm)	Material	Laboratory code	^{14}C age (BP)	δ^{13}C (‰)	Calibrated BP (2σ)
351 (CRIDA 05)	Benthic foraminiferal assemblages	Beta-194504	10,400 ± 70	−3.1	11,218–11,826
207 (CRIDA 05)	Benthic foraminiferal assemblages	Beta-211324	9320 ± 50	−8.1	9976–10,276
151 (CRIDA 05)	Benthic foraminiferal assemblages	Beta-204306	4170 ± 40	−2.2	4126–4392
103 (CRIDA 05)	Benthic foraminiferal assemblages	Beta-211322	1650 ± 40	−2.6	1113–1290
285 (MD 992332)	Turritella	SacA-3020/3021	3570 ± 100	5.65	3221–3715
139 (KSGX 57)	Organic matter	Sac-1921	570 ± 80	−26.7	495–677

The ages are presented as conventional ^{14}C dates and also as calendar dates using the program CALIB Rev 5.0.1. Beta–Beta Analytic Radiocarbon Dating Laboratory, Miami, FL, USA; SacA-Laboratoire de Mesure du Carbone 14, CEN Saclay, Gif sur Yvette, France; Sac-Instituto Tecnologico e Nuclear, Sacavem, Portugal.

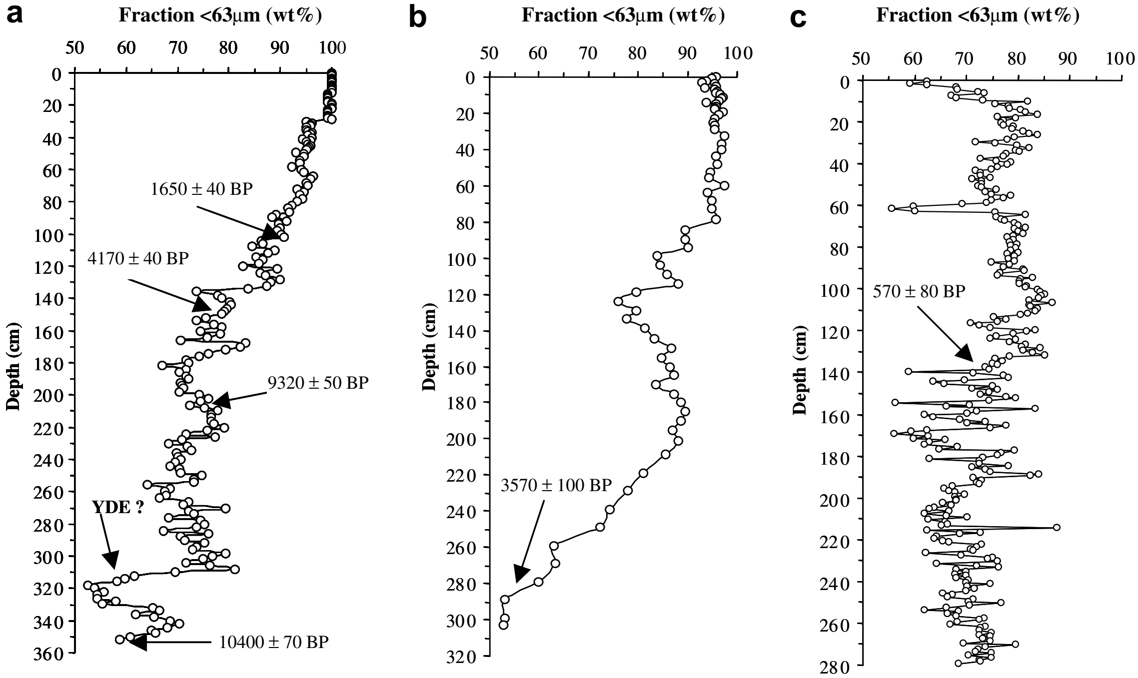

Fig. 2. Plot of down-core variations of fine size fraction (<63 µm) content. (a) CRIDA 05; (b) MD 992332; (c) KSGX 57. ^{14}C ages are from this study (detailed information about C dating is in Table 1).

The high uncertainty attached to these values is mainly due to the low resolution of the ^{14}C dates, with respect to the submillimetre successions of laminated deposits. The Younger-Dryas event (11,000–10,000 ^{14}C a BP, Lowe and Walker, 1997) could not be precisely positioned in core CRIDA 05 sedimentary record (Fig. 2a). Assuming a higher sedimentation rate during the Younger-Dryas event (in the range of the mean estimate for the bottom section), the upper boundary would be placed at ~300 cm, providing a thickness of ~50 cm. The use of a higher sedimentation rate is based on the assumption that this event is interpreted in the North Atlantic as a dry and cold climatic event, increasing aridity and reducing the vegetation cover (Roberts, 1998). The protection offered to the soil against erosion was affected, increasing the erosional activity (Walker, 1995).

4.2. Grain size and carbonate content

The core CRIDA 05 collected in the Guadiana mud patch is entirely clayey (Fig. 2a). The mean grain size does not exceed 30 µm and the percentage of the sandy fraction (>63 µm) is higher at the bottom with more than 40%. From the base to the top, the sedimentation is fining up. In the last decimetres, the sediment is fluid mud with a higher water content. Some shells can be observed at 90 cm and in the bottom part of the core where gastropods are visible (turitella ?).

The core MD 992332 collected in the Tagus mud patch displays a mean grain size always less than 50 µm (Fig. 2b). From the bottom to 250 cm, the sediment is relatively coarser and slightly more carbonated (12%) than between 250 and 180 cm, where mean grain size and carbonate content decrease (25 µm and 8%, respectively). Above, between 180 and 120 cm, a coarser layer displays increasing carbonate contents related to shelly fragments and intact gasteropods (*Turitella* sp.). Then, from 120 cm to the top, a general fining-up of size fraction and low carbonate contents (around 8% at the sediment surface) are observed.

The core KSGX 57 collected in the Douro mud patch can be divided into two sedimentary units according to their density, grain size and carbonate content (Fig. 2c). The upper unit (down to 180 cm depth), less dense, displays a mean fine fraction percentage of 75% and carbonate contents around 8%. One can note that the base of this unit, i.e. between 200 and 178 cm, corresponds to a medium to coarse sand level. The lower unit, denser, contains 10–30% of carbonates. In this unit, one can observe alternately muddy and sandy layers with clear limits. The fine fraction percentage decreases down to 62%. However, there is a perturbation induced by coring that is marked by an input of sand inside the clayey layers.

Compared to the two other Lusitanian mud patches, the Douro one appears to be the least fine.

4.3. Accumulation rate

The ^{210}Pb excess vertical distribution is represented in Fig. 3. Profiles mostly show a single gradient down-core (to values close to 10 Bq kg^{-1}) interrupted by several breaks in the decay profiles of ^{210}Pb excess activity as shown for CRIDA 05 and MD 992332. These disrupted profiles probably show several sequences of mixed deposition or indicate a massive input of sediment.

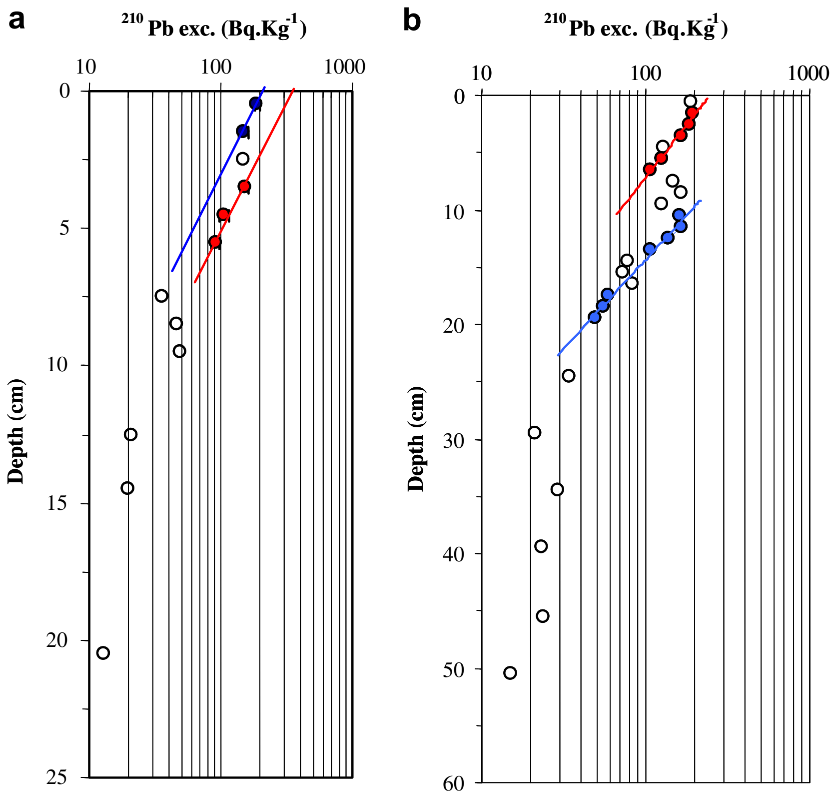

Fig. 3. ^{210}Pb excess activity profiles of the mud-field cores. (a) CRIDA 05 and (b) MD 992332.

Based on the single uninterrupted gradient of ^{210}Pb excess activity, according to Jouanneau et al. (2002), the maximum accumulation rate has been determined (Table 2). The results have also been compared with those reported by Carvalho and Ramos (1989), Drago et al. (1999) and Jouanneau et al. (1998, 2002).

It is evident that the accumulation rate calculated in the Tagus mud patch is higher than the one for the Guadiana mud patch. Whereas the core sampled at the Tagus mud patch yields values between 0.16 and 0.22 cm a^{-1}, the Guadiana one presents low and homogeneous values ranging between 0.12 and 0.13 cm a^{-1}.

4.4. Organic matter

4.4.1. Core CRIDA 05

The down-core variation of OC and TN concentrations is displayed for fine sedimentary organic matter, together

Table 2

Maximum sedimentation and long-term deposition rates for Portuguese continental shelf mud fields

Site	Core	Accum. rate (from ^{210}Pb) (cm a^{-1}) (g cm^{-2} a^{1})		SML[b] (cm)	SML content[c] (mg g^{-1}) OC TN		Accum. Rate[d] (mg cm^{-2} a^{-1}) OC TN		Authors
					OC	TN	OC	TN	
Guadiana mud patch	CRIDA 05	0.12 ± 0.01	0.10 ± 0.02	5	12.3 ± 0.3	1.5 ± 0.06	1.2 ± 0.3	0.15 ± 0.04	This paper
Tagus mud patch	MD 992332	0.22 ± 0.03	0.26 ± 0.03	20	15.7 ± 1.9	1.3 ± 0.2	4.1 ± 1	0.34 ± 0.09	This paper
	T25	0.16		–	–		–		Jouanneau et al. (1998)
Douro mud patch	KSGX 57	0.49[a] ± 0.11	0.49 ± 0.05	25[a]	6 ± 3.1	0.5 ± 0.2	2.9 ± 1.8	0.25 ± 0.1	This paper
	FF1GM92	0.57		–	–		–		Drago et al. (1999)
	CG15	0.58		–	–		–		Drago et al. (1999)
	KTB43	0.42		–	–		–		Jouanneau et al. (2002)
	MCC	0.41		–	–		–		Jouanneau et al. (2002)
	C32 (B)	0.55		–	–		–		Carvalho and Ramos (1989)

[a] Average values from Drago et al. (1999) and Jouanneau et al. (2002).

[b] SML, surface mixed layer.

[c] Calculated as the average over the SML.

[d] Calculated as the product of the OC (mg g^{-1}) and mass accumulation rate (g cm^{-2} a^{-1}).

with OC/TN and C isotope ratios, in Figs. 4 and 5a. Organic C concentrations of 2.2 mg g^{-1} to 12.5 mg g^{-1} and TN concentrations of 0.3–1.5 mg g^{-1} are obtained. These contents show a rapid decrease from 12.5 mg g^{-1} and 1.5 mg g^{-1} at the surface to 8.3 mg g^{-1} and 1 mg g^{-1} at 32 cm, respectively. Surface sediment contains twice as much OC and TN as found deeper. Organic C and TN concentrations are correlated (Fig. 6a). Such a correlation is required to check if the N content of samples is organic in nature with respect to OC (Stein and Rack, 1995). The intercept at 0 mg g^{-1} OC yields a value that is a fall to zero (0.019 mg g^{-1}). Therefore, it is estimated that the TN concentrations are organic in Nature.

The down-core variation of OC/TN molar ratios ranges between 8.5 and 14.3. Most of the values are out of the range of the mean ratio for marine phytoplankton (7.4 ± 1.3, Anderson and Sarmiento, 1994). High OC/TN are obtained for the deeper sediments, contrasting sharply with the values displayed by sediments younger than 4170 ^{14}C a (9.7 ± 0.4). Below this depth, the ratios increase up to 14.3, which are consistent with the lowest TN contents of the core.

The down-core variation of δ^{13}C values for fine sized organic matter ranges from −26.4‰ to −22.4‰. δ^{13}C values are almost invariable down to a depth of 80 cm (−23.5 ± 0.2‰) apart from the first 20 cm, where a slight δ^{13}C increase (~0.7‰) is observed. The highest δ^{13}C values are obtained below the 80 cm depth for sediments older than 4170 ^{14}C a. The lowest δ^{13}C values are recorded during the phase of enhanced coarse-size fraction corresponding to the first-order estimation of the Younger-Dryas event. The down-core δ^{13}C variation mirrors that of OC/TN ratios. The extremes in the δ^{13}C curve correspond rather well to those in the OC/TN ratios curve.

4.4.2. Core MD 992332

The down-core variation of OC and TN concentrations is illustrated for fine sedimentary organic matter, together with OC/TN and C isotope ratios, in Figs. 4b and 5b. Organic C and TN concentrations vary through the core from 2.9 mg g^{-1} to 38.4 mg g^{-1} and from 0.3 mg g^{-1} to 2.4 mg g^{-1}, respectively. These contents show a rapid decrease from 18.1 mg g^{-1} and 1.4 mg g^{-1}at the surface to 3.9 mg g^{-1} and 0.3 mg g^{-1} at 70 cm, respectively. Sediment below 70 cm displays increasing concentrations with depth (OC = 38.4 mg g^{-1} and TN = 2.4 mg g^{-1} at 175 cm). Noticeable decreases with sediment depth are also observed from 175 cm toward the core bottom. As was the case in the core CRIDA 05, the intercept value between OC and TN proves that TN is organic in nature (Fig. 6b).

High OC/TN are obtained between 155 and 200 cm, contrasting clearly with the values registered for younger and older sediments 14.6 and 12.8, respectively. Increases up to 19 are observed close to 175 cm.

δ^{13}C values, ranging between −26‰ and −24.7‰, are rather constant in the first 90 cm. In the following 70 cm, δ^{13}C becomes relatively enriched, reaching −24.3‰ at 134 cm. In the last 140 cm, there is a general increasing trend reaching the greatest value of −23.5‰ at the bottom sediment. Here again, the down-core δ^{13}C variation mirrors that of OC/TN ratios.

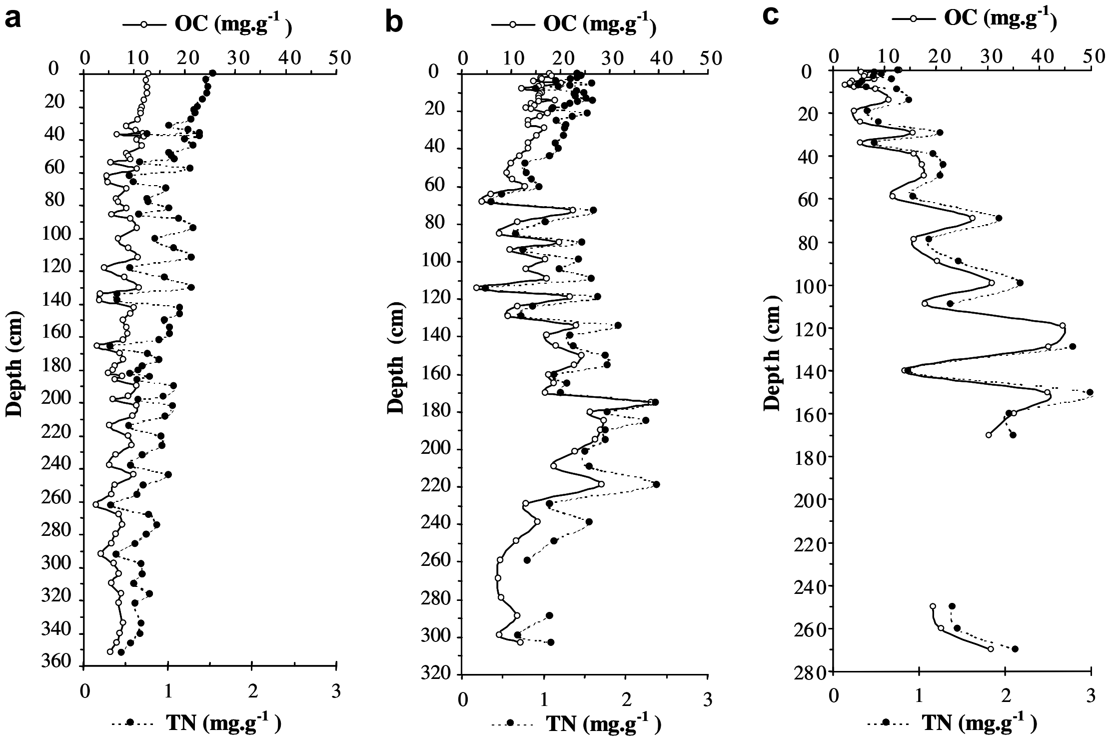

Fig. 4. Plots of down-core variation of OC and TN concentrations, for fine (<63 μm) size fractions of carbonate-free samples. (a) CRIDA 05; (b) MD 992332; (c) KSGX 57.

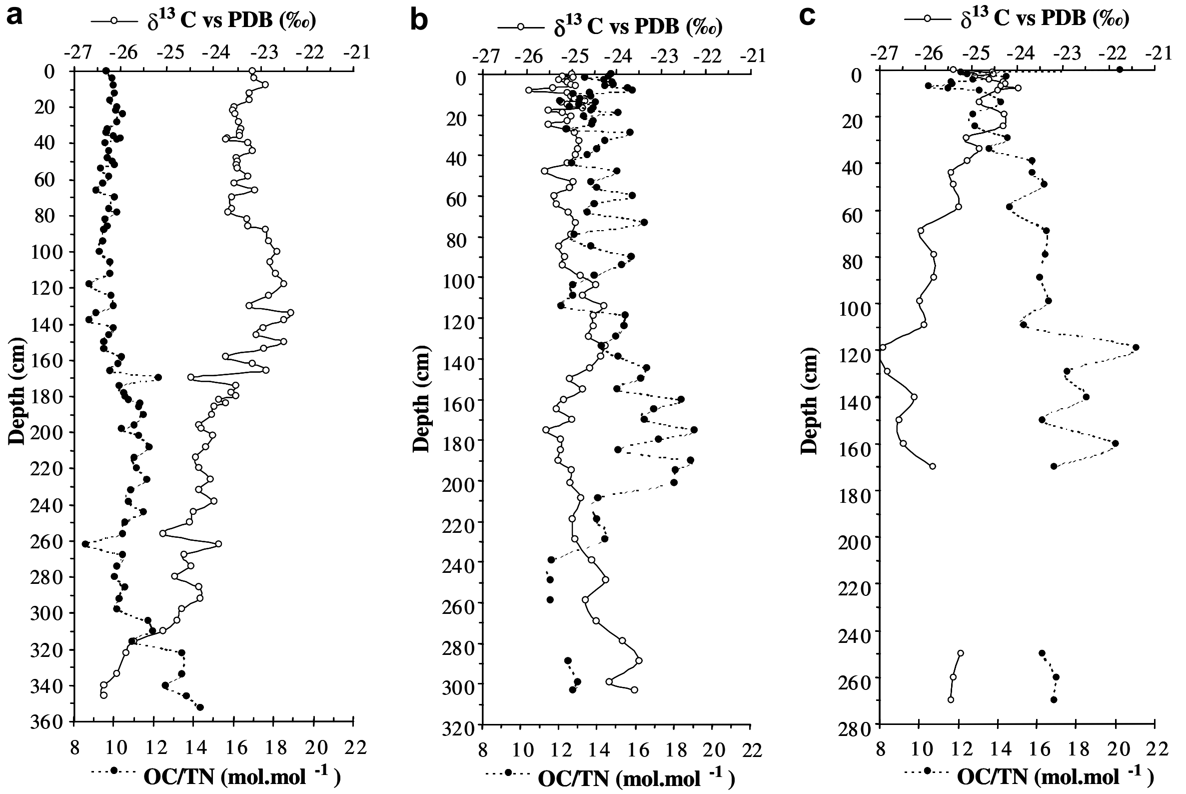

Fig. 5. Plots of down-core variation of OC/TN molar ratios and δ^{13}C, for fine (<63 μm) size fractions of carbonate-free samples. (a) CRIDA 05; (b) MD 992332; (c) KSGX 57.

4.4.3. Core KSGX 57

The down-core variation of OC and TN concentrations is illustrated for fine sedimentary organic matter, together with OC/TN and C isotope ratios, in Figs. 4c and 5c. Organic C and TN contents vary between 2.2 mg g^{-1} and 44.4 mg g^{-1} and between 0.3 mg g^{-1} and 3 mg g^{-1}, respectively. Organic C and TN contents show a general down-core trend toward higher values. The vertical distribution of both elements becomes more variable down the core. As observed in cores CRIDA 05 and MD 992332, OC and TN concentrations are correlated (Fig. 6c). The zero-intercept value indicates that TN concentrations are organic in nature.

Overall, OC/TN ratios decrease upward from 16.8 to 12.1, except the one at the surface, which is as high as deeper samples.

δ^{13}C values range between −27‰ and −24‰, with a down-core variation reflecting that of OC/TN ratios. The more depleted ^{13}C value is obtained at 120 cm depth corresponding to the higher OC/TN ratio.

5. Discussion

5.1. Long-term fine-sized organic matter accumulation

The increasing trend in ^{14}C dates of bottom sediments, 1400 ^{14}C a BP at 310 cm in a neighbour core of core KSGX 57 (FF1GM92; Drago, 1995), 3570 ^{14}C a BP at 285 cm in core MD 992332 (Fig. 2b) and 9320 ^{14}C a BP at 207 cm in core CRIDA 05 (Fig. 2a), would suggest sedimentation rates are lower for the muddy deposit off the Guadiana estuary than for those off the Tagus and Douro estuaries. Accumulation rates calculated here from ^{210}Pb excess profiles confirm this. Organic C mass accumulation rate (CAR) of fine fraction averages 1.2 ± 0.3 mgC cm^{-2} a^{-1} in core CRIDA 05 (Table 2). Due to the rise of sedimentation rate and OC concentration in core MD 992332, and partly in core KSGX 57, CAR increases to values greater than 1.2 mgC cm^{-2} a^{-1}. CAR values in sediments highlight the potential contribution of these rivers to the continental shelf sedimentary deposits in terms of terrestrial materials.

Organic C contents in sediments of the three cores vary greatly. The highest average value (44.4 mg g^{-1}) is found in core KSGX 57 (Fig. 4c), and the lowest (2.2 mg g^{-1}) in core CRIDA 05 (Fig. 4a). They fall into the range of values reported for other surface sediments of the Iberian margin (Epping et al., 2002; Jouanneau et al., 1998 and Jouanneau et al., 2002). Sedimentation rates have often been pointed out to be a major factor controlling preservation of organic matter (Muzuka and Hillaire-Marcel, 1999). Low accumulation rates (low sedimentation) cause large quantities of organic matter to be oxidized after reaching the sediment water interface, while the effect of oxidation is reduced

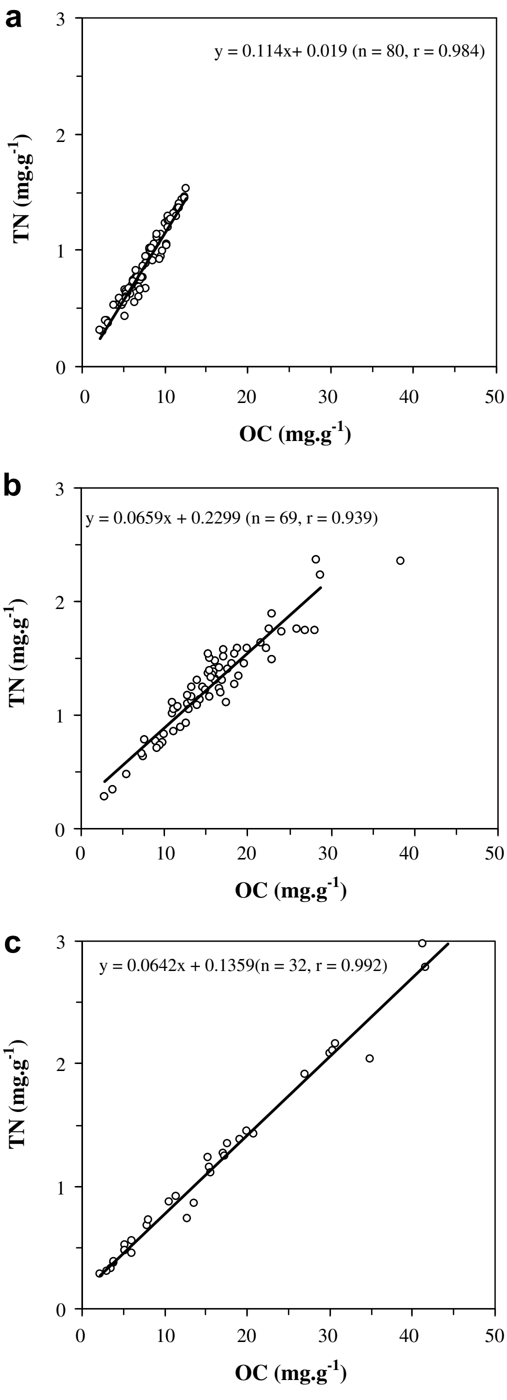

Fig. 6. Plots of OC vs. TN concentrations for fine (<63 μm) size fractions of carbonate-free samples. (a) core CRIDA 05; (b) core MD 992332; (c) core KSGX 57. All Pearson's *r* coefficients are significant from zero at 99.9.

when the sedimentation rate increases. The low sedimentation rate of the muddy deposit off the Guadiana estuary compared with the muddy deposit off the Tagus and Douro estuaries could be responsible for the much lower OC and TN contents observed in core CRIDA 05. However, in the present case, this assumption seems unlikely, as the higher sedimentation rate found in core KSGX 57 should induce higher OC and TN contents, which is not observed here.

Evidence of a changing sedimentary organic matter supply is shown by the OC/TN and the $\delta^{13}C$ values in all studied cores. The generally high OC/TN ratios of the sediment core off the Tagus and Douro estuaries compared with the muddy deposit off the Guadiana estuary correspond to an increase of fine OC concentrations with respect to TN, whose $\delta^{13}C$ values are depleted; a first order estimate of a changing source of organic matter.

5.2. Degradation vs. preservation for fine-sized sedimentary organic matter

Postdepositional decomposition of organic matter in continental shelf sediments during diagenesis has the potential to modify the original OC/TN ratios as well as the source isotope signatures of the organic matter that accumulates (Twichell et al., 2002; Gordon et al., 2001). Decompositional shifts in OC/TN, and particularly $\delta^{13}C$, can occur over a relatively short time-period; however, it is the way $\delta^{13}C$ and OC/TN change, rather than absolute values, that is key for interpreting geochemical changes. A decrease in OC/TN ratios over time of burial below the seafloor has been reported in open-ocean settings (François et al., 1997; Meyers et al., 1996) due to the absorption and retention of NH_3 and the release of CO_2 with concomitant ^{13}C enrichment from the sediment suffering the decomposition of organic matter. The down-core $\delta^{13}C$ and OC/TN records reflect an opposite trend in cores CRIDA 05, MD 992332 and KSGX 57 (Fig. 5). Moreover, no significant deviation from younger sediments is observed in cores CRIDA 05, MD 992332 and partly in core KSGX 57. If degradation under oxic conditions does not account for the observed major elemental and stable isotope changes, methanogenic bacteria could also be able to carry on the degradation process under low O_2 conditions that may prevail in deeper sections. For instance, the concomitant down-core $\delta^{13}C$ decrease and OC/TN increase in the upper half of core KSGX 57 and between 115 cm and 175 cm depth in core MD 992332 could be explained by selective degradation of more labile ^{13}C and N-rich organic molecules such as carbohydrates and amino acids (Ogrinc et al., 2005; Muzuka and Hillaire-Marcel, 1999).

But this assumption does not hold if OC/TN and $\delta^{13}C$ values are taken into account because the assumed degradation effect is no longer observed down-core. This does not mean that diagenetic effects are absent, but rather that fine-sized organic matter in the sediment is mainly composed of refractory OC, less inclined to postdeposition degradation.

Thus, it is unlikely that postdeposition diagenetic effects are responsible for the major elemental and stable isotope changes down-core. Therefore, the records represent the primary isotopic signature of the organic matter at the time of deposition.

5.3. Terrestrial versus marine sources of fine-sized organic matter

Sedimentary organic matter in continental shelf sediments can be derived from several possibles sources: land plants and soil material supplied by river flows; and marine organic matter derived from algae sources. Stable ($\delta^{13}C$) isotope signature of organic matter and OC/TN ratios can be used to identify these possible sources. A first-order linear correlation can be drawn between $\delta^{13}C$ values and OC/TN ratios in each core (Fig. 7A–C). Such a relationship is usually interpreted as a mixing trend between terrestrial and marine sources of organic matter, which, respectively, provide depleted and enriched isotope ratios (Huon et al., 2002; Jia and Peng, 2003; Ogrinc et al., 2005). In core CRIDA 05, the Upper Holocene samples would have an isotopic signature close to the marine end-member one, whereas Younger-Dryas samples would have an isotopic signature close to the terrestrial source end-member. In core MD 992332, the linear relationship corresponds to a binary mixture in which one end-member is best represented by sediments underlying the return of marine conditions (~175 cm depth), the second being a source enriched in ^{13}C (~−24‰) and in TN (OC/TN ~ 12), corresponding to the earlier Upper Holocene deposits. The third mixing trend, in core KSGX 57, links the most recent sediments on one side and deposits underlying the Little Ice Age (~495–677 cal a BP) on the other.

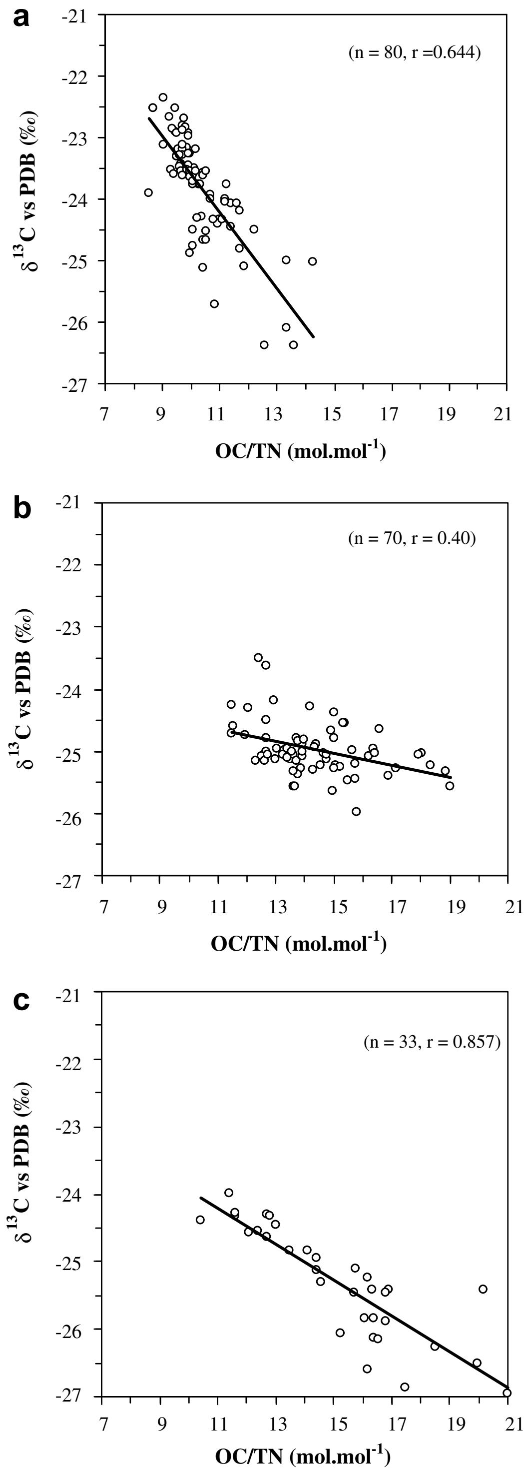

Fig. 7. Plots of $\delta^{13}C$ vs. OC/TN ratios for fine (<63 μm) size fractions of carbonate-free samples. (A) core CRIDA 05; (B) core MD 992332; (C) core KSGX 57. All Pearson's *r* coefficients are significant from zero at 99.9.

Significant collection of surface organic matter in the open ocean has shown that typical marine phytoplankton exhibit significantly enriched $\delta^{13}C$ values, in the range of −19 to −22‰ (Goñi et al., 2003; Dickens et al., 2004). Although practically no data have been reported for the location of cores CRIDA 05, MD 992332 and KSGX 57, the most enriched $\delta^{13}C$ values (Fig. 5) approach present-day marine surface organic matter values. Organic matter derived from the major Portuguese River drainage area should produce low $\delta^{13}C$ values. Indeed, soil, peat, and wetland sources of organic matter release material derived from terrestrial C_3 plants ($\delta^{13}C = -27 \pm 6‰$, Huon et al., 2002; Medina et al., 2005). Moreover, land plants and algae are diverse in their C/N ratios. Marine algae typically have C/N ratios between 4 and 10, whereas vascular land plants, due to the abundance of cellulose, have C/N ratios of 20 and greater (Jia and Peng, 2003).

All together, plots of $\delta^{13}C$ values against OC/TN show more precisely the mixing assumptions and suggest the following organic matter source estimates (Fig. 8): (a) a marine end-member whose composition is approached by the Upper Holocene sediments of core CRIDA 05 (averages ± 1σ: $\delta^{13}C = -23.2 \pm 0.4‰$; OC/TN = 9.7 ± 0.4); (b) a terrestrial source characterised by low $\delta^{13}C$ values (down to −27‰) and variable OC/TN ratios (18 < OC/TN < 21), corresponding to soil and lithic detritus inputs that culminate in samples underlying the Little Ice Age (~495–677 cal a BP) of core KSGX 57. Assuming constant $\delta^{13}C$ end-member values for marine and terrestrial fine-sized organic matter supply, a semi-quantitative estimation was made of the proportion of continental derived organic matter in cores CRIDA 05, MD 992332 and KSGX 57 using the following stable C isotope mass balance equation: $\delta^{13}C = f\delta^{13}C_t + (1 - f)\,\delta^{13}C_m$, where f is the proportion of terrestrial supply (%), $\delta^{13}C_t$ is the terrestrial end-member estimated with samples of core KSGX 57 (−27‰), and $\delta^{13}C_m$ is the assumed marine end-member value for Portuguese shelf sediments (−21‰). Results for these estimates are reported in Fig. 9a–c. Although the end-member values are only assumptions, they can describe the varying mixture of terrestrial and marine supplies in sediments. According

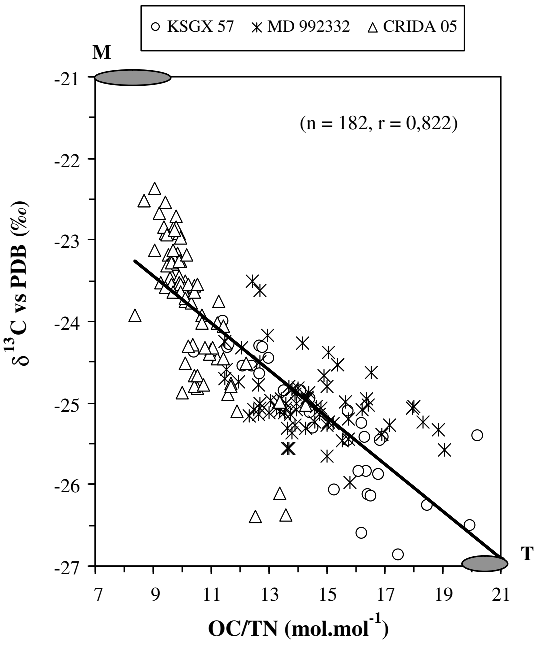

Fig. 8. Plots of δ^{13}C vs. OC/TN ratios for fine (<63 μm) size fractions of carbonate-free samples. Regression line is calculated for all samples using a least square fit. Pearson's *r* coefficient is significant from zero at 99.9%. Marine and terrestrial end-members are designated with *M* and *T*, respectively.

to the estimates, over 50% of fine size organic matter in sediments is of terrestrial origin in cores KSGX 57 and MD 992332, and in the lower half of core CRIDA 05.

5.4. Temporal variance of sedimented fine size organic matter

Considerable variation of δ^{13}C values along core CRIDA 05 (from −26.4‰ to −22.4‰; Fig. 5a) may be a consequence of temporal variability in sediment supply. Significant changes are observed at the bottom, where depleted values of ^{13}C isotope (−26.4‰) and high OC/TN ratios (14.3) are close to the terrestrial end-member. Moreover, a predominant coarse, sandy/gravelly granulometry size fraction content for these depths (Fig. 2a) suggest that this could be attributed to river erosion of the sedimentary infill of the estuary in response to the lowering sea level. Over the Gulf of Cadiz continental shelf, several backstepping successions of sedimentary units related to the post-glacial transgression have been identified, whose formation has also been linked to periods of sea-level rise deceleration or short-lived stillstands (Lobo et al., 2001). Of them, the Younger-Dryas Event, a major cooling event in the North Atlantic, would have modified vegetation patterns and erosion processes (Lowe and Walker, 1997). Lower temperatures increased aridity and reduced the vegetation cover (Roberts, 1998). The protection offered to the soil against erosion was reduced, increasing the erosional activity. As a result, the amount of sediment washing into the streams probably increased, leading to an associated

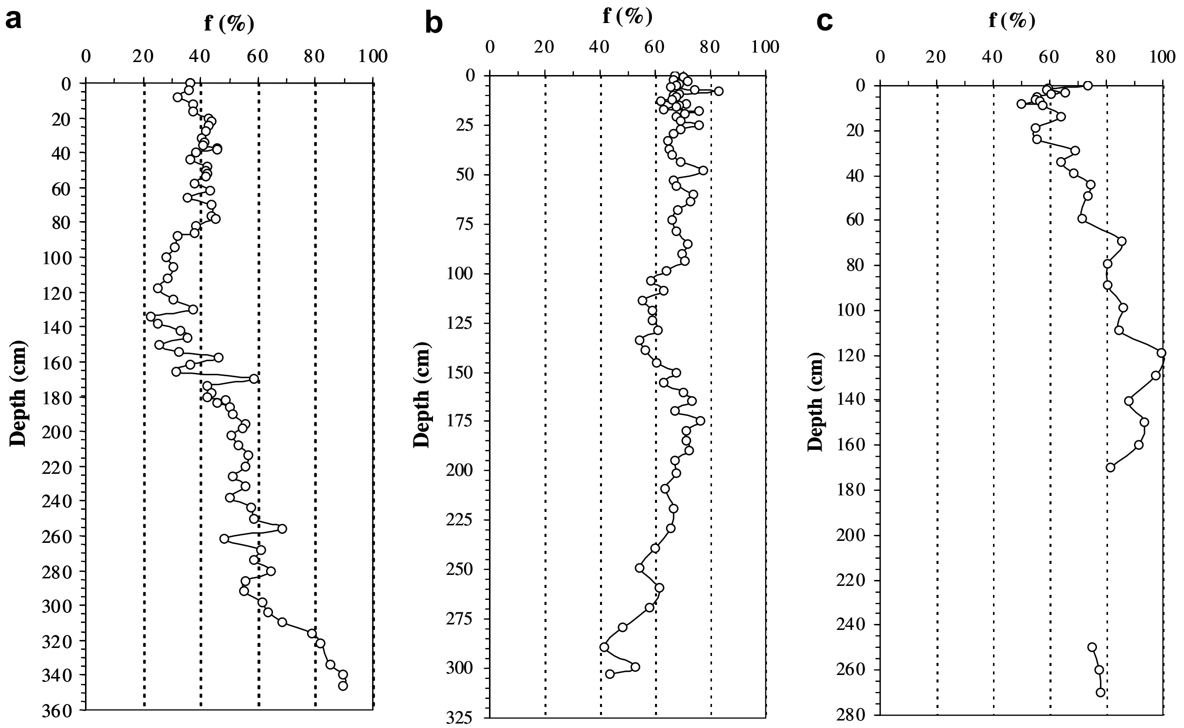

Fig. 9. Plots of down-core calculated continental fine size OC percentage (*f*). *f* values were calculated using $\delta^{13}C_t = -27‰$ and $\delta^{13}C_m = -21‰$. (a) CRIDA 05. (b) MD 992332. (c) KSGX 57.

increase in the terrigenous supply to the shelf (Gonzalez et al., 2004). Moreover, a dry-humid climate transition would result in a flow increase in bedload to the shelf due to the higher river discharge rates in relation to melt-water times and the adjustment of river equilibrium profiles (Bard et al., 1990). As shown by the changes in OC mass accumulation rates, most of the Holocene sedimentary OC (about 70%; Fig. 10) accumulated during the Younger-Dryas Event (11,000–10,000 ^{14}C a BP) and in the course of the deglacial warming occurring shortly after this cold event (10,000–9300 ^{14}C a BP). In return, low OC accumulation rates occurred afterwards up to ca. 3500 ^{14}C a BP. A progressive change toward marine source organic matter occurred in the deposited sediment, as reflected by the decreasing values of factor *f* (down to 20%; Fig. 9a). Such results are supported by the fact that there was an accelerated phase of estuary infilling by clayey sediment sequences during the postglacial transgression until the present sea level was reached (Boski et al., 2002). More recently, in the course of the Upper Holocene, the core location registered increasing OC accumulation rates. Additionally, concomitant accumulations of terrigenous components directly associated with a high fine size fraction content and factor *f* indicates that a large export of sedimentary load may have spilled material to an area as far as the mid-shelf off the Guadiana River. Whereas the eustatic sea level rise appears to be a principal factor in the contribution of marine supplies to the continental shelf by the postglacial transgression, the non-eustatic factor, such as the terrigenous sediment supply rate, became more dominating during the Upper Holocene. Evidence of large supplies of terrestrial sediment to the shelf is also shown by the total benthic foraminiferal assemblage record of this core (Mendes et al., 2004). Whereas total benthic foraminifera abundance increases progressively from the base of the core up to 130 cm, large-scale events in the course of the Upper Holocene could explain periods of minimum total foraminifera content (Fig. 11). Massive influx of terrestrial material could have been related to the dilution of total benthic foraminifera (low counts of foraminifera per gram of dry sediment) as a result of high energy flood events in the Guadiana River basin.

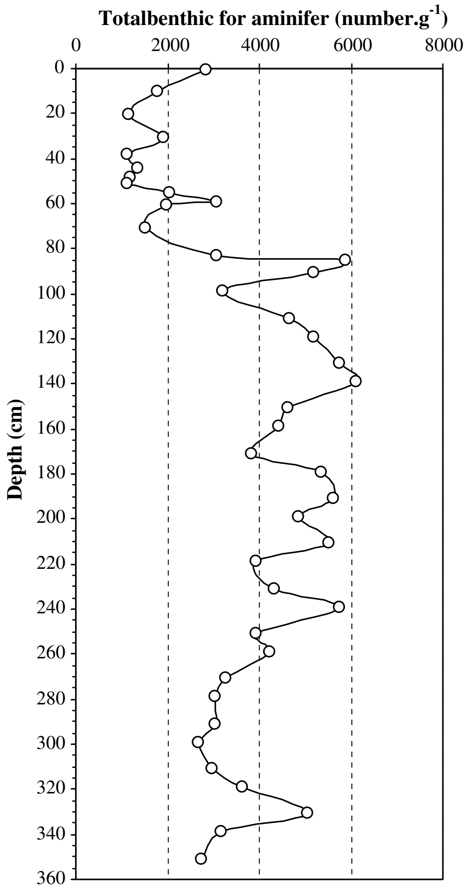

Fig. 11. Plots of down-core variations of total benthic foraminifera abundance. Benthic foraminifera data for core CRIDA 05 are from Mendes et al. (2004).

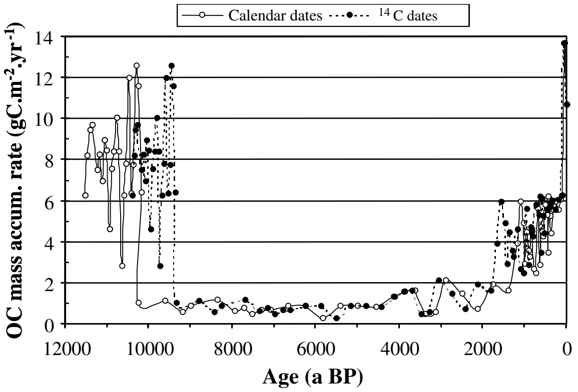

Fig. 10. Changes in OC mass accumulation rate during core CRIDA 05 sediment formation. The ages are presented as conventional ^{14}C dates and also as calendar dates.

Core MD 992332 covers a period of about 3221–3715 cal a BP (Table 1), corresponding to the stable period of sea level (Dias et al., 2000). The concomitant up-core increase of fine-grained fraction, factor *f*, OC and TN concentrations suggests a period of enhanced terrestrial supply from the Tagus estuary. However, a return of marine conditions is visible between 185 cm and 125 cm depth, as indicated by the increase in carbonate contents and coarse-size fraction (Fig. 2b). Such a sudden reversal of the situation is also obvious in the upper section of core CRIDA 05 where a slightly coarser section appears between 45 cm and 65 cm (Fig. 2a). According to the stratigraphic framework of the core CRIDA 05 and assuming a constant sedimentation rate during the Upper Holocene (in the range of 0.09 cm a^{-1}), the upper and lower boundary of the slightly coarser section would be dated between 525 cal a BP and 760 cal a BP, and may have been induced by climate fluctuation occurred during the Little Climatic Optimum between the 11th and 15th centuries AD (Dias, 1990). In that sense, the transition from a colder phase to the Little Climatic Optimum would have been marked by a decrease in terrestrial sediment supply to the shelf.

The core KSGX 57 profile also shows a period of enhanced marine depositional environment as carbonate content and coarse fraction percentage increase in the lower unit. The upper boundary of this event would be placed at 180 cm depth, corresponding to a dated horizon hardly any older than the date of 495–677 cal a BP measured at 139 cm depth. This limit is consistent with the upper boundary of the Little Climatic Optimum (15th century AD). The upper section of the core KSGX 57 deposits show in turn a reduction in the supply and/or accumulation of terrigenous organic matter as deduced from the concomitant decrease of factor *f*, OC and TN content (Fig. 9c). Such environments do not correspond to the periods of cooling events dominated by increased sediment supply on the continental shelf that prevailed during the Little Ice Age between the 15th and 19th centuries AD (Font Tullo, 1986). In fact this period is characterised by intense sedimentation in some Portuguese estuaries and formation of coastal dune fields, turning them into coastal lagoons (Dias et al., 2000). Additionally, some accelerated sediment infilling originated from the deforestation and increasing agricultural land use (Boski et al., 2002). Consequently, the proportion of marine production in ambient sediments is expected to increase. This trend is practically absent from cores CRIDA 05 and MD 992332, suggesting that local factors, namely the anthropogenic activities, become progressively a factor whose impact on continental shelf sediment budget equalled or even surpassed the effects of climate fluctuations.

6. Conclusions

Discrimination between sources of fine-sized organic matter in Portuguese continental shelf muddy deposits using OC and TN elemental concentrations and stable (δ^{13}C) isotope data is a difficult challenge due to the wide range of values. However, the use of diagrams that combine OC/TN and δ^{13}C values inform on the possible mixtures of terrestrial and marine organic matter. In the present case, diagenetic effects on the sediment organic matter seem of minor influence compared with the major change in organic matter supplies that has accompanied the Holocene period. Of the three cores considered, the sedimentary column of core CRIDA 05 borehole is the most representative of the Holocene. Two enhanced terrestrial-derived input units (the Younger-Dryas Event and the Upper Holocene) enclose the postglacial transgression sediments that experienced increased contribution of marine supplies corresponding to the eustatic sea level rise. Cross-correlations with cores CRIDA 05, MD 992332 and KSGX 57 were performed using the fine-sized fraction and carbonate content records. The Little Climatic Optimum was identified at core depths 45–65 cm, 125–185 cm and 180 cm to down-core, respectively for cores CRIDA 05, MD 992332 and KSGX 57.

On the other hand, the Little Ice Age was marked by a rapid decrease of terrigenous organic matter supplies in the core KSGX 57, and apparently not in cores CRIDA 05 and MD 992332. It is suggested that local factors, namely anthropic activities, become likely to equal or even to surpass the effects of climate fluctuations on the continental shelf.

Although as a general rule the highest continental supplies are found both in the Younger-Dryas Event and the Upper Holocene, it can not be affirmed that a complete breakdown of marine supply was attained. Further characterisation of organic matter of these sediments using ^{14}C and ^{15}N isotope analysis is needed to answer this question.

Acknowledgments

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