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Composition and sources of sedimentary organic matter in the deep Eastern Mediterranean Sea

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Abstract

Surface sediments collected from deep slopes and basins (1018–4087 m depth) of the oligotrophic Eastern Mediterranean Sea have been analysed for bulk elemental and isotopic composition of organic carbon, total nitrogen and selected lipid biomarkers, jointly with grain size distribution and other geochemical proxies. The distribution and sources of sedimentary organic matter (OM) have been subsequently assessed and general environmental variables, such as water depth and currents, have been examined as causative factors of deep-sea sediment characteristics. Lithogenic and biogenic carbonates are the dominant sedimentary fractions, while both bulk and molecular organic tracers reflect a mixed contribution from autochthonous and allochthonous sources for the sedimentary OM, as indicated by relatively degraded marine OM, terrestrial plant waxes and anthropogenic OM including degraded petroleum by-products, respectively. Wide regional variations have been observed amongst the studied proxies, which reflect the multiple factors controlling sedimentation in the deep Eastern Mediterranean Sea. Our findings highlight the role of deep Eastern Mediterranean basins as depocentres of organic-rich fine-grained sediments (mean $5.4 \pm 2.4 \mu m$), with OM accumulation and burial due to aggregation mechanisms and hydrodynamic sorting. A multi-proxy approach is hired to investigate the biogeochemical composition of sediment samples, which sheds new light on the sources and transport mechanisms along with the impact of preservation vs. diagenetic processes on the composition of sedimentary OM in the deep basins of the oligotrophic Eastern Mediterranean Sea.

1 Introduction

The burial of organic matter (OM) in marine sediments constitutes the main link between “active” pools of carbon in the oceans, atmosphere and landmasses and carbon pools that cycle on much longer, geological time scales (Burdige, 2007). Therefore, in-
investigating the processes that control the composition of sedimentary OM that is buried in deep-sea sediments is crucial for understanding carbon cycling on a global scale.

The deep sea receives inputs of organic particles from multiple sources, both autochthonous (e.g. biogenic particulate matter from primary production in ocean surface waters) and allochthonous (i.e. land-sourced OM from soils, plant debris, riverine phytoplankton and man-made compounds transported by runoff and atmospheric deposition into the marine domain). Consequently, sedimentary OM constitutes an heterogeneous and complex mixture of organic compounds with a wide range of chemical and physical properties (Mayer, 1994; Hedges and Oades, 1997; Hedges et al., 1997; Goñi et al., 1998). Due to the heterogeneity and complex nature of sedimentary OM sources, the combined use of bulk geochemical indicators such as total nitrogen (TN) to organic carbon (OC) ratios, stable isotopes of OC and TN, and molecular proxies such as lipid biomarkers is required to assess the origin, delivery and preservation of OM in marine sediments (Bouloubassi et al., 1997; Meyers, 1997; Goñi et al., 2003; Volkman, 2006).

The biogeochemical composition of sediments in deep basins of the oligotrophic Eastern Mediterranean Sea (EMS), as well as the sources, transport and preservation of sedimentary OM, have been scarcely investigated so far. Some studies have shown that the composition of surficial sediments is principally controlled by the geochemical characteristics of the source areas, the prevailing metoceanic conditions on the adjacent shelves, the contribution of atmospheric aerosols and the dominant regional circulation (e.g., Weldeab et al., 2002; Ehrmann et al., 2007; Hamann et al., 2008). Nevertheless, the factors involved in the supply, distribution and fate of sedimentary OM are still poorly known. The reason for this lack of knowledge lies on the complex interactions amongst the various physical, chemical and biological factors that altogether control OM cycling (Francois et al., 2002; Lutz et al., 2002; Danovaro et al., 2010).

In the present study, surface sediments collected from deep slopes and basins of the EMS have been analysed for physical and geochemical parameters such as grain size distribution, lithogenic, calcium carbonate (CaCO$_3$), opal, OC and TN contents, along with TN/OC ratios, stable isotopic ratios of OC ($\delta^{13}$C) and selected lipid biomarkers.
Our main goal is to investigate the spatial distribution and main sources of sedimentary OM and to evaluate the impact of autochthonous vs. allochthonous contributions in the study area. We also examine whether and up to which point general environmental factors, such as currents and water depth, could explain the observed deep-sea sediment geochemical properties.

2 Oceanographic setting

The EMS is a land-locked sea with a complex topography including shelves, slopes, ridges, seamounts, trenches and four main basins: the Adriatic Sea, the Ionian Sea, the Aegean Sea and the Levantine Sea (Fig. 1) (Amblàs et al., 2004; Medimap Group, 2007). The Ionian Sea to the west and the Levantine Sea to the east are longitudinally connected and cover most of the EMS area. They are also the largest and deepest basins in the EMS, with the maximum depth (5267 m) achieved at the Hellenic Trench, south of the Cretan Arc. The Aegean Sea and, especially, the Adriatic Sea represent the northern extensions of the EMS. Both are relatively shallow, in particular the Adriatic Sea, which is dominated by a broad shelf and a slope sub-basin shallower than 1200 m. In the Aegean Sea, which has a particularly complex topography with tenths of depressions, highs and islands, water depths up to 2500 m are found in its southernmost part north of the island of Crete (Amblàs et al., 2004; Medimap Group, 2007). The southern Aegean Sea, often referred to in the literature as the “Cretan Sea”, is the sea area comprised between the Cyclades Archipelago to the north and the island of Crete to the south, which also includes the western Cretan Straits.

The general circulation pattern in the EMS is anti-estuarine, which results from interactions of basin, sub-basin and mesoscale flow (Bethoux, 1979). The EMS communicates with the Western Mediterranean Sea through the Sicily Strait, with an inflow of low-salinity Modified Atlantic Water (MAW) at the upper 100–150 m of the water column (Rabitti et al., 1994; Malanotte-Rizzoli et al., 1997). MAW flows in an easterly direction getting progressively saltier and warmer till transforming into Levantine Intermediate
Water (LIW) into the Levantine Sea where it sinks to mid depths, largely in the Rhodes gyre (Milliff and Robinson, 1992; Lascaratos et al., 1993).

The Eastern Mediterranean Deep Water (EMDW) is a relatively well oxygenated water mass, likely as a result of the formation and sinking of warm deep-water that ventilates the deepest levels in the EMS (Schlitzer et al., 1991; Roether and Well, 2001; Meador et al., 2010). Waters from the Adriatic Sea (Adriatic Deep Waters, ADW) have been classically considered as the main contributor of deep and bottom waters to the EMS (Malanotte-Rizzoli and Hecht, 1988). ADW outflows over the sill of Otranto Strait and circulates along the deep western boundary of the Ionian Sea before entering into the Levantine Basin (Robinson et al., 1992). Nevertheless, the Aegean Sea constitutes a sporadically significant contributor to EMDW through the Cretan Deep Water (CDW), as shown during the Eastern Mediterranean Transient (EMT) anomaly in the 1990s (Roether et al., 1996; Lascaratos et al., 1999; Theocharis et al., 1999). Additionally, the Aegean Sea constitutes a possible secondary source of intermediate waters to the adjacent Ionian and Levantine seas, through outflows across the Cretan Arc straits (Robinson et al., 2001).

Key factors that control the exchanges through the Cretan Arc straits are the thermohaline properties of water masses and mesoscale variability. For example, the Ierapetra anticyclonic gyre, which is located off the southeast corner of Crete (Ierapetra Basin), exhibits a strong seasonal signal that is linked to variations of the outflow across the eastern Cretan Arc straits (Theocharis et al., 1993; Larnicol et al., 2002). Actually, the several permanent and/or recurrent eddies in each of the EMS sub-basins enhance exchanges between continental shelf and slope waters (Robinson et al., 1992; Malanotte-Rizzoli et al., 1997; Millot and Taupier-Letage, 2005), which in turn influence primary productivity and the settling of OM to the deep-sea floor (Danovaro et al., 2010).

Thermohaline circulation and overall environmental conditions make the EMS one of the most conspicuous ultra-oligotrophic environments in the world ocean (Psarra et al., 2000; Tselepides et al., 2000; Krom et al., 2005; Thingstad et al., 2005; Gogou et al., 2014). The EMS (except the Adriatic Sea) is characterized by very low concentrations
of nutrients reflected by low overall chlorophyll $a$ concentrations and low levels of primary production. Within the EMS, the Ionian Sea and the Levantine Sea are the most nutrient-depleted basins (Bosc et al., 2004). Annual particulate primary production in the EMS averages between 121 and 145 g C m$^{-2}$ yr$^{-1}$ (Bosc et al., 2004; Gogou et al., 2014). However, the fraction of primary production exported below 2000 m water depth averaged 0.3 % (Gogou et al., 2014).

The low autochthonous contribution to OM fluxes to the deep open EMS is counterbalanced by allochthonous inputs resulting from long-range atmospheric transport and deposition of nutrients by aerial dust (Jickells, 1995; Gogou et al., 1996; Tsapakis and Stephanou, 2005). The Saharan dust flux, which follows a general westward direction, is a relevant contributor to sedimentation in the open EMS (Guerzoni et al., 1997). The Saharan dust spreads rather uniformly across the EMS (Rutten et al., 2000; Jickells et al., 2005). Riverine inputs have a rather minor influence on the open EMS sedimentation as they are small and localized (Weldeab et al., 2002; Statham and Hart, 2005; Garcia-Orellana et al., 2009). The overall sedimentation rate in the deep areas of the open EMS is low (i.e. 2–5 cm ky r$^{-1}$) (Van Santvoort et al., 1996, 2002; Garcia-Orellana et al., 2009; Stavrakakis et al., 2013).

3 Materials and methods

3.1 Sampling

Short sediment cores were collected with a multicorer at 29 stations, ranging from 1018 to 4087 m water depth, during six oceanographic cruises in the Ionian Sea, the southern Aegean Sea (Cretan Sea) and the northwestern Levantine Sea from January 2007 to June 2012 (Fig. 1 and Table 1). Only the undisturbed top centimetre of each sediment core is considered in this study, as our target is the most recent record of OM fluxes in the study area.
Once onboard, multicores were visually described and sliced at 1 cm intervals. Subsamples collected for grain size, elemental and stable isotopic composition were stored in sealed plastic bags at 4 °C, while those collected for the analysis of lipid biomarkers were stored in pre-combusted aluminium foils at −20 °C.

3.2 Analytical procedures

3.2.1 Particle size characterization

The grain size distribution of sediment samples was determined using a Coulter LS230 Laser Diffraction Particle Size Analyzer, which measures sizes between 0.04 and 2000 µm. Prior to analysis, freeze-dried samples were oxidized with a 10% H₂O₂ (v/v) solution in order to remove OM. Each sample was then divided into two subsamples, one of which was treated with 1 M HCl to remove carbonates and thus obtain the grain size distribution of lithogenic (siliciclastic) particles. Subsequently, both bulk and lithogenic fractions were dispersed into 20 cm³ of a 5% NaPO₅ (v/v) solution and mechanically shaken for 4 h, and then introduced into the particle size analyzer after using a 2000 µm sieve to retain occasional coarse particles that might obstruct the flow circuit of the instrument.

The measured particle size spectrum is presented as % volume in a logarithmic scale, where volume is calculated from particle diameter, assuming spherical shapes. Results were recalculated to percentages of clay (< 4 µm), silt (4–63 µm) and sand (63 µm–2 mm).

3.2.2 Elemental and stable isotopic analysis of carbon and nitrogen

For the determination of total carbon (TC), TN, OC contents and stable isotopic composition of OC (δ¹³C) freeze-dried and grounded sediments were analysed using a Flash 1112 EA elemental analyser interfaced to a Delta C Finnigan MAT isotope ratio mass spectrometer. Samples analyzed for %OC and δ¹³C were initially de-carbonated using...
repetitive additions of a 25% HCl (v/v) solution, separated by 60°C drying steps, until no effervescence was observed (Nieuwenhuize et al., 1994). Stable isotope data are reported using the conventional per thousand δ¹³C notation relative to the Pee Dee Belemnite standard. Uncertainties for elemental composition were lower than 0.1%, while uncertainty for δ¹³C was lower than 0.05‰.

In consistency with published data in the Mediterranean Sea we assumed OM as twice the OC content (e.g., Heussner et al., 1996; Masqué et al., 2003). The inorganic carbon content was calculated from the difference between TC and OC measurements. Assuming all inorganic carbon is contained within calcium carbonate, CaCO₃ content was determined using the molecular ratio of 100/12.

Atomic TN/OC ratios were also calculated. TN/OC is plotted in order to constrain the elemental ratios of N-depleted samples (i.e. TN/OC ≈ 0 rather than OC/TN ≈ 0) following Goñi et al. (2006), and to avoid the underestimation of the terrestrial-derived carbon fraction (Perdue and Koprivnjak, 2007).

3.2.3 Biogenic opal and lithogenic fraction analysis

The biogenic silica content was analysed using a two-step 2.5 h extraction with a 0.5 M Na₂CO₃ solution, separated by centrifugation of the leachates. Si and Al contents of both leachates were analysed with a Perkin–Elmer Optima 3200RL Inductive Coupled Plasma Optical Emission Spectrometer (ICP-OES), correcting the Si content of the first leachate by the Si/Al ratio of the second one. All values are reported as opal (SiO₂ × 0.4H₂O), a parameter defined by 2.4 times the weight percentage of biogenic Si content determined for each sample (Mortlock and Froelich, 1989). The opal detection limit, associated to the detection limit of the ICP-OES system, is approximately 0.2%.

The lithogenic fraction was estimated by subtracting the concentration of the major constituents from total dry weight (%lithogenic = 100 – [%OM + %CaCO₃ + %opal]). This fraction represents the residual component of particles such as quartz, feldspars, clay minerals and aluminosilicates (Mortlock and Froelich, 1989).
3.2.4 Lipid biomarkers analysis and definitions of molecular indices

Freeze-dried sediment samples were solvent-extracted three times by sonication with a dichloromethane: methanol mixture (4 : 1, v/v). Combined extracts were fractionated on a silica column (modified after Gogou et al., 1998) into three fractions, containing aliphatic hydrocarbons (F1), ketones (F2) and alcohols, sterols and diols (F3), respectively. Instrumental analysis of F1 and F3 fractions was carried out by Gas Chromatography–Mass Spectrometry (GC-MS) on an Agilent 7890 GC coupled to an Agilent 5975C Mass Selective Detector, while F2 fractions were analyzed on an Agilent 7890 GC equipped with a Flame Ionization Detector (FID). Details regarding the instrumental analysis are reported elsewhere (Gogou et al., 2007).

A range of selected lipid biomarkers are reported in this study, namely long chain n-alkanes and n-alkanols, long-chain alkenones, long-chain diols and a suite of sterols, along with lipid biomarkers’ indices, as proxies of organic matter sources and/or degradation. As OC can vary due to the supply of inorganic material (dilution effect) the concentrations of the reported lipid compounds were normalized to OC contents.

The sum of the concentrations of the most abundant high molecular weight n-alkanes and n-alkanols, which are major components of epicuticular higher plant waxes (Eglington and Hamilton, 1967; Ohkouchi et al., 1997), are defined, respectively, as:

\[ \sum \text{TerNA} = \sum n-C_{27,29,31,33} \]  
\[ \sum \text{TerN-OH} = \sum n-C_{24,26,28,30} \]  

The sum of the concentrations of the considered lipid biomarkers having a clear marine (algal) origin (see Sect. 5.1.2) was calculated as follows:

\[ \sum \text{Mar} = \sum \left( 28\Delta^5,22E + 30\Delta^{22E} + C_{30} \text{ diols & keto-ols} + \text{alkenones} \right) \]  

The abundance of the Unresolved Complex Mixture (UCM) of aliphatic hydrocarbons, a commonly observed persistent contaminant mixture in marine sediments consisting
of branched alicyclic hydrocarbons (Gough and Rowland, 1990), is used as an indicator of the contribution from degraded petroleum products, i.e. chronic oil pollution (Wang et al., 1999).

The Carbon Preference Indices of long chain \( n \)-alkanes (CPI\(_{\text{NA}} \)) and \( n \)-alkanols (CPI\(_{\text{N-OH}} \)) have been used as indicators of terrestrial OM degradation with CPI values in fresh leaves being typically > 4, although the occurrence of petroleum hydrocarbons bias (lower) CPI\(_{\text{NA}} \) values with increasing petroleum contribution, since petroleum products present CPI\(_{\text{NA}} \) values \( \sim 1 \) (Wang et al., 1999). The indices were calculated, respectively, as:

\[
\text{CPI}_\text{NA} = \frac{\sum ([n-C_{25}] - [n-C_{33}])}{\sum ([n-C_{26}] - [n-C_{34}])} \tag{4}
\]

\[
\text{CPI}_\text{N-OH} = \frac{\sum ([n-C_{24}] - [n-C_{30}])}{\sum ([n-C_{23}] - [n-C_{29}])} \tag{5}
\]

Finally, the abundance ratio of \( \sum \text{TerNA} \) to \( \sum \text{TerN-OH} \) is used as a proxy of the proportion of labile vs. refractory terrestrial components because the former are more resistant to degradation than their alcohol counterparts (Eglinton and Hamilton, 1967; Ohkouchi et al., 1997). The ratio is defined as:

\[
\frac{\text{[NA]}}{\text{[N-OH]}} = \frac{\left[ \sum \text{TerNA} \right]}{\left[ \sum \text{TerN-OH} \right]} \tag{6}
\]

### 3.2.5 Data analysis and presentation

Statistical treatment of grain size data was carried out using the GRADISTAT v. 8.0 software (Blott and Pye, 2001). Median diameter \( (D_{50}) \), sorting and skewness were calculated geometrically (in metric units) following the approach of Folk and Ward (1957), which is most appropriate when data are non-normally distributed, as in the case of polymodal sediments from the study area.

\( D_{50} \) was calculated as the average equivalent diameter, which is the diameter where 50\% of the sediment sample has a larger equivalent diameter and the other 50\%
has a smaller equivalent diameter. Sorting (expressed by the standard deviation) indicates the fluctuation in the degree of kinetic energy and the depositional regime on grain size characteristics. Skewness measures the degree of asymmetry onto particle distribution. The skewness for a normal distribution is zero, and any symmetric data should have skewness near zero. Positive values indicate skewness towards the finer grain sizes (skewed left) and negative values indicate skewness towards the coarse grain sizes (skewed right). The results of grain size distribution analysis were hierarchically clustered (using IBM SPSS Statistics 18.0) according to the above statistical parameters (autoscaled prior to cluster analysis), in order to determine the similarity of samples within each station measuring the squared Euclidean distance.

Principal component analysis (PCA) was performed on grain size and elemental composition data (%clay and sorting of lithogenic and bulk fractions, lithogenic, CaCO$_3$, OC, TN contents), on bulk organic matter signatures (TN/OC ratios and $\delta^{13}$C) and on indices and mass-normalized concentrations of lipid biomarkers. Through linear combinations PCA assigns a loading value to each variable on each factor (principal component, PC), while the same assignment is given to scores, representing sample location. Factors determine the percentage of data variance explanation. A subroutine, the Varimax rotation, was applied to the first three factors in order to maximize or minimize loadings within each factor, and thus simplify the visual interpretation of PCA projections (Yunker et al., 2005). While loadings reflect the influence of variables on sample patterns, site scores reveal the distance from the origin to each sample point along each PCA axis. Correlation analysis was also performed using the same variables. This statistical technique allows identification of the similarity amongst samples as well as the specificity of each individual compound in tracing OM (Fernandes et al., 1999; Goñi et al., 2000).

Spatial distributions of the various geochemical parameters’ contents, bulk OM signatures and selected lipid biomarkers’ concentrations/indices considered in this study were visualized using Ocean Data View (ODV) (Schlitzer, 2011).
4 Results

4.1 Grain size characteristics

The grain size composition (% clay, silt and sand) and the sedimentary parameters ($D_{50}$, sorting and skewness) are presented in Table 2, while the statistical dendrogram, type-averaged grain size spectrum and spatial distributions of grain size types are presented in Fig. 2.

Silt- and clay-sized particles dominate the bulk sediment, accounting for up to 76.7 and 57.1% of the total weight, respectively (Table 2). The lowest values (< 40%) for the silt fraction are found in the upper slope of the western Cretan Straits (station Red3) and the northwestern Levantine Sea (station BF19), while the highest values (> 65%) correspond to the Ionian Sea (stations H12 and H03). The lowest clay contents (< 20%) are also found in the upper slope of the western Cretan Straits (station Red3) but also in the northeastern Ionian Sea (station H12), while top values (> 55%) are recorded at the northwestern Levantine Sea (station Red1.1 in Ierapetra Basin, an abyssal basin a maximum depth of 4420 m) and the western Cretan Straits (station H01). Sand contents show large variations, i.e. from 0 to 47.7% (station Red3 in the upper slope of western Cretan Straits), with values less than 2% in most of the stations (Table 2). Rather high values (> 10%) are also obtained in the northwestern Levantine Sea (stations Red2, BF19 and BF24). $D_{50}$ values range between 3.5 and 56.6 µm (Table 2).

Sorting of bulk sediment range from 3.0 to 5.2 (Table 2). Most of the northwestern Levantine Sea and western Cretan Straits’ stations are very poorly sorted and all stations within the southern Aegean Sea and most of the Ionian Sea are poorly sorted (Table 2 and Fig. 2a). Skewness values for the investigated samples range from –0.45 to 0.27 (Table 2), varying from a very clear negative skewness in in the upper slope of the western Cretan Straits (station Red3), to positive skewness in the northwestern Levantine Sea (stations Red2.1, BF19, BF22 and BF24).
The hierarchical cluster analysis of all bulk sediment samples resulted into seven grain-size types (Fig. 2a). Most of the samples group into cluster types I \((n = 11)\), II \((n = 6)\) and III \((n = 6)\), with grain size profiles almost symmetrical and poorly sorted, and a dominance of clay and silt fractions. Type V includes three very poorly sorted and positive skewed samples from the northwestern Levantine Sea, which consist mainly of clay and silt fractions. Types IV, VI and VII include only one sample each (Red2, H12 and Red3, respectively). Samples Red2 and Red3, dominated by coarse silt fractions \(D_{50} 11.1\) and 56.6 µm, respectively), are both very poorly sorted but with different types of skewed distributions (symmetrical and negatively skewed, respectively). Finally, sample H12, composed mostly of fine silt, is poorly sorted and slight positive skewness.

As in the bulk sediment, silt- and clay-sized particles dominate the lithogenic fraction, accounting for up to 73.5 and 50.8 % of the total weight, respectively. The hierarchical cluster analysis of the lithogenic fraction identified six grain size types (clusters) (Fig. 2b). A majority of samples are highly similar (types I-V), with an average composition of 35.2±5.6 % clay, 63.5±5.3 % silt and 1.3±2.3 % sand, a \(D_{50}\) of 6.6±1.3 µm and a bimodal or trimodal, symmetrical, poorly sorted grain size distribution. Sample Red3 from the upper slope of western Cretan Straits is an exception, in which belongs to type VI. The composition of its lithogenic fraction is 10.3 % clay, 34.6 % silt and 55.1 % sand, with a \(D_{50}\) of 78.1 µm and a bimodal, very poorly sorted and negatively skewed grain size distribution (Fig. 2b and Table 2).

4.2 Bulk geochemical sediment composition

The spatial variability of lithogenics, CaCO\(_3\), OC and TN contents within the study area is presented in Fig. 3a–c. The lithogenics content in the analyzed surface sediments range between 32.5 and 85.4 % (Fig. 3a). Higher percentages (> 70 %) are found in stations of the Ionian Sea (with the exception of station H02), while the lowest percentages (< 40 %) are found in the southern Aegean (stations Red4 and Red5) and northwestern Levantine seas.
(stations Her01 and BF19) (Table 2). The CaCO$_3$ contents also show a wide range of values throughout the study area, from 13.2 to 66.5 % (Fig. 3b and Table 2). Stations in the western Ionian Sea (H04, BF27, H03, BF15, BF13 and H07) have the lowest CaCO$_3$ contents (< 22 %), whereas most stations in the southern Aegean and northwestern Levantine seas and in the western Cretan Straits have elevated CaCO$_3$ contents (> 40 %).

Opal contents are very low, ranging from below detection limits to a maximum of 0.24 % in the southern Aegean and northwestern Levantine seas (stations Red5 and Red13) (Table 2). Since opal contents are very close to the detection limits, those can be considered as negligible. Therefore inorganic geochemical fraction of the investigated deep EMS sediments consists only of lithogenic (terrigenous) and carbonate components.

OC contents in the studied samples range from 0.15 to 1.15 %, with an average value of 0.47 % (Table 2). The lowest values are recorded in the northeastern Ionian Sea, south of Otranto Strait (station H12), while the highest values are found not too far off the Gulf of Taranto (station H07), followed by other stations also in the Ionian Sea (stations BF27, H04 and H03). However, the overall distribution of OC contents is rather patchy and does not seem to have any clear pattern, as stations with higher and lower contents appear close one to each other (Fig. 3c). TN contents range from 0.01 to 0.11 % with an average value of 0.06 %. TN display a pattern similar to OC, also with the highest values recorded off the Gulf of Taranto (station H07) and the lowest south of Otranto Strait (station H12), both in the northern Ionian Sea.

4.3 Elemental and stable isotopic composition of sedimentary OM

The spatial distribution of TN/OC ratios and $\delta^{13}$C within the study area is presented in Fig. 3d and e.

TN/OC atomic ratios of the sedimentary OM range from 0.08 to 0.16 (Fig. 3d and Table 2). The highest TN/OC ratios values (> 0.14) are recorded in the southern Aegean (station Red8) and northwestern Levantine (stations Her01, BF22 and BF24) seas,
whereas the lowest TN/OC ratios (< 0.09) are recorded in stations from the northwestern Levantine Sea (station Red15.1), the western Cretan Straits (stations Red3 and Red3.1) and the northern Ionian Sea (stations H07 and H12). However, there is no clear spatial trend (Fig. 3d).

The spatial distribution of δ¹³C values shows that relatively lower values are more common in the Ionian Sea than in the northwestern Levantine Sea, the southern Aegean Sea and the south Ionian Sea (Fig. 3e). δ¹³C values range from −18.3 to −24.6 ‰ (Fig. 3e and Table 2), with stations from the Ionian Sea (stations H03, H07 and H12) yielding relatively depleted δ¹³C values (< −24 ‰) and stations from the western Cretan Straits (station Red3) and the northwestern Levantine Sea (Ierapetra Basin, stations BF22, Red1.1 and Ier01) having relatively enriched δ¹³C values (> −22 ‰).

4.4 Lipid biomarkers

The analysed sedimentary aliphatic hydrocarbons comprise of a series of resolved compounds, mainly n-alkanes, and a UCM (Parinos et al., 2013). The UCM dominate amongst aliphatic hydrocarbons in concentrations ranging between 0.50 and 6.64 mg g OC⁻¹ (Fig. 4a and Table 3). Maximum concentrations (> 5 mg g OC⁻¹) are recorded in the northwestern Levantine Sea (station Red2.1) followed by the deep central Ionian Sea (station H03). The lowest UCM values (< 1.0 mg g OC⁻¹) are obtained in the northern Ionian Sea (station H12) and in the western Cretan Straits (station H01), while rather low values are also recorded in the southern Aegean Sea and west of Crete.

The molecular profile of the n-alkanes is dominated by long chain homologues (Cₙ ≥ 24), maximizing at n-C₃₁, with elevated CPIₙₐ values (4.9 ± 1.6) (Table 3). ∑TerNA range between 40.8 and 483 µg g OC⁻¹, with an average value of 172 µg g OC⁻¹ (Fig. 4b and Table 3). The station with the highest concentration (station Red2.1) is found in the northwestern Levantine Sea, while the stations with the lowest ones (< 110 µg g OC⁻¹) are located in the northern Ionian Sea (stations H07 and H12) and in the southern Aegean Sea (station Red9). Furthermore, relatively elevated ∑TerNA concentrations...
(> 210 µg g OC\(^{-1}\)) are recorded at the deep station of the western Cretan Straits’ (station Red3.1) and the deep central Ionian Sea (stations H03 and H05).

The aliphatic alcohol fraction is dominated by a series of \(n\)-alkanols ranging from \(n\)-C\(_{22}\) to \(n\)-C\(_{30}\), with maxima at \(n\)-C\(_{26}\), and elevated CPI\(_{N-OH}\) values (4.5 ± 0.8) (Table 3).

\(\Sigma\)TerN-OH range from 13.4 to 105 µg g OC\(^{-1}\), with an average of 40.4 µg g OC\(^{-1}\), displaying similar distribution with \(\Sigma\)TerNA (Fig. 4c and Table 3). The [NA]/[N-OH] ratios for the analysed sediments range between 2.9 and 6.9, with an average of 4.3 ± 0.9 (Table 3).

Long-chain di- and tri-unsaturated C\(_{37}\) and C\(_{38}\) methyl ketones and C\(_{38}\) ethyl ketones, commonly referred to as long-chain alkenones, are present in all samples with total concentrations ranging from 3.41 to 30.5 µg g OC\(^{-1}\), 13.0 µg g OC\(^{-1}\) on average. The major C\(_{27}\)–C\(_{30}\) sterols considered in this study, i.e. cholesterol (cholesta-5-en-3\(\beta\)-ol; \(27\Delta^5\)), brassicasterol (24-methylcholesta-5,22-dien-3\(\beta\)-ol; \(26\Delta^5,22\)), \(\beta\)-sitosterol (24-ethylcholesta-5-en-3\(\beta\)-ol; \(29\Delta^5\)) and dinosterol (4\(\alpha\),23,24-trimethyl-5\(\alpha\)(H)-cholesta-22(E)-en-3\(\beta\)-ol -\(30\Delta^{22}\)), have total concentrations ranging between 10.3 and 62.4 µg g OC\(^{-1}\), averaging 31.7 µg g OC\(^{-1}\). Long-chain C\(_{30}\) \(n\)-alkan-1,15-diols and the corresponding C\(_{30}\) keto-ols are also found in concentrations ranging from 7.30 to 35.81 µg g OC\(^{-1}\), with an average of 20.3 µg g OC\(^{-1}\) (Table 3).

\(\Sigma\)Mar range between 18.2 to 72.6 µg g OC\(^{-1}\), 43.6 µg g OC\(^{-1}\) on average (Fig. 4d and Table 3), displaying a generally increasing eastward trend with maximum concentrations (> 55 µg g OC\(^{-1}\)) recorded in the deep northwestern Levantine Sea (stations Red2.1, Her01, Ier01 and Red7). Elevated \(\Sigma\)Mar values are also recorded at stations Red3 in the upper slope of western Cretan Straits, but also stations H04 and H05 in the deep Ionian Sea. The lowest values (< 40 ug g OC\(^{-1}\)) are obtained in the southern Aegean Sea (stations Red8, Red9), the northern Ionian Sea (station H12) and the western Cretan Straits (station H01).
4.5 Multivariate analysis of geochemical parameters

Grain size, lithogenics, CaCO$_3$, OC and TN contents, TN/OC ratios, stable isotopic compositions ($\delta^{13}$C) and lipid biomarkers’ concentrations and indices provide a robust database to assess the composition of sediments and the provenance of sedimentary OM in the investigated areas, which cover a large part of the EMS. The PCA allow the identification of similarities amongst samples, as well as the value of each individual proxy in tracing the composition of surface sediments of the deep EMS.

Three main principal components (PCs) are identified, accounting for 64.3% of the variation within the data set (23.8, 22.8 and 17.7% for PC1, PC2 and PC3, respectively). PC1 is characterised by positive loadings for water depth, $\sum$TerNA, $\sum$TerN-OH, $\sum$Mar, UCM and negative loadings for CPI$_{NA}$ and CPI$_{N-OH}$. The highest positive loadings on PC2 are associated to %CaCO$_3$, %clay in the bulk sediment and TN/OC values, while negative loadings are associated to %lithogenics. Finally, the geochemical parameters with high positive loadings on PC3 are %OC, %TN, and %clay of the lithogenic fraction, while those with negative loadings are $\delta^{13}$C and sorting of bulk sediment (Fig. 5a).

Factor scores on each PC display significant variability amongst the studied stations, both within the same area and from one area to another (Fig. 5b). High positive factor scores on PC1 are observed both in stations to the west (Ionian Sea) and east (western Cretan Straits and northwestern Levantine Sea). For PC2, an eastward increasing contribution of positive factor score values seems to exist, with the highest ones located in the southern Aegean Sea and the northwestern Levantine Sea. In contrast, the prevalence on PC3 is recorded in stations of the Ionian Sea and in parts of the northwestern Levantine Sea (Ierapetra Basin).

PCA results mirror the composition of surface sediments. Indeed, the contents of CaCO$_3$ show an increasing north-south and west–east gradient (Figs. 3b and 5). In the southern Aegean Sea, the northwestern Levantine Sea and the western Cretan Straits’ stations CaCO$_3$ contents are positively correlated to %clay of the bulk sediment.
(r = 0.48, p < 0.05) and to alkenone concentrations (r = 0.62, p < 0.05). Lithogenic contents are higher in the north and west (Ionian Sea) while being significantly positively correlated to OC and TN contents (r = 0.65 and r = 0.72 and p < 0.05, excluding stations BF15, H07 and H12 of the Ionian Sea). Furthermore, OC and TN contents of stations deeper than 2100 m show a significant positive correlation to water depth (r = 0.54 and r = 0.70, respectively, p < 0.05). However, this is not highlighted by the PCA. A significant positive correlation is also observed for OC and TN contents in the analysed samples (r = 0.87, p < 0.0001).

Surface sediments of the Ionian Sea show a significant (p < 0.05) positive correlation of OC and TN contents with %clay (r = 0.80 and r = 0.73), and a negative correlation with %silt (r = −0.75 and r = −0.65) and D_{50} of the lithogenic fraction (r = −0.79 and r = −0.83). δ^{13}C values (excluding station Red3 of the western Cretan Straits) are significantly (p < 0.05) and positively correlated to CaCO_{3} contents (r = 0.53), %clay of the bulk sediment (r = 0.65) and TN/OC ratios (r = 0.53), and negatively correlated to %OC (r = −0.46), %silt (r = −0.66) and D_{50} (r = −0.59) of the bulk sediment.

Terrestrial lipid biomarker concentrations (ΣTerNA and ΣTerN-OH) display a significant positive correlation amongst them (r = 0.95, p < 0.0001), but also to %clay (both with r = −0.55, p < 0.05) and D_{50} (r = 0.62 and r = 0.58, respectively, p < 0.01) of the bulk lithogenic fraction. ΣTerNA and ΣTerN-OH show a significant positive correlation (p < 0.05) to β-Sitosterol (29Δ^5) (r = 0.71 and r = 0.56, respectively, excluding stations H07 and H12 of the Ionian Sea). ΣTerNA and ΣTerN-OH (not normalized to OC contents) are also significantly correlated to OC (r = 0.81 and r = 0.76, respectively, p < 0.001), again excluding stations H07 and H12 of the Ionian Sea. Moreover, ΣMar (not normalized to OC contents) display a significant positive correlation with OC (r = 0.7, p < 0.001), with a significant positive correlation (r > 0.65, p < 0.005 in all cases) also found amongst the concentration of cholesterol (27Δ^5) and marine algal markers (28Δ^{5,22E}, 30Δ^{22E}, C_{30} diols&keto-ols and alkenones; see Sect. 5.2.1).
5 Discussion

5.1 Sources of sedimentary material in the deep Eastern Mediterranean Sea

Clearly the surface sediments of the deep EMS mostly consist of lithogenics and carbonates, have low OC contents and opal is nearly absent (Table 2). The range of lithogenics, carbonates and opal contents recorded in our samples are in agreement to those previously reported in the Eastern Mediterranean Sea (Emelyanov and Shimkus, 1986; Bethoux, 1989; Cros, 1995; Kemp et al., 1999; Rutten et al., 2000; Struck et al., 2001). The OC contents are also comparable to those for the Eastern Mediterranean Sea (0.23–0.99 %, Bianchi et al., 2003; 0.30–0.82 %, Gogou et al., 2000; 0.25–1.73 %, Polymenakou et al., 2006) as well as the western Mediterranean Sea (0.8–1.6 %, Kaiser et al., 2014; 0.47–1.53 %, Masqué et al., 2003; 0.23–1.85 %, Roussiez et al., 2006).

5.1.1 Lithogenics and carbonate

Generally speaking, lithogenics can be supplied from different sources through aeolian and riverine transport, discharge and deposition. Several studies have highlighted that deposition of mineral aerosol particles may have a profound influence on the geochemistry and sedimentology of the open Mediterranean Sea (Buat-Menard et al., 1989; Rutten et al., 2000; Guerzoni and Molinaroli, 2005). The grain size of the lithogenic fraction found in the studied sediments is very similar to Saharan dust particles, which mainly consist of clayey silts and silty clays, with particle diameters ranging from 0.5 to 60 µm \((D_{50} \sim 5 \mu m)\) and two main modes at 3–4 and 60 µm (Guerzoni and Molinaroli, 2005 and references therein). This strongly suggests that the Sahara desert is the main source of lithogenics to the deep EMS. Such a view is supported by observations pointing to Saharan dust transported by southerlies blowing over the great North African desert as the main lithogenic input to the EMS (Guerzoni et al., 1999; Rutten et al., 2000; Weldeab et al., 2002; Jickells et al., 2005). Furthermore, volcanic
ash deposition into the EMS represents another external source of fine-grained particles (<5–50 µm) (Kelepertsis et al., 2003). Mount Etna, located on the island of Sicily (Italy) in the central Mediterranean Sea, generates volcanic ash plumes that are transported by the wind hundreds of kilometers over the Mediterranean Sea reaching as far as Greece and Libya (Olgun et al., 2013 and references therein).

In contrast to the atmospheric deposition, the influence of terrigenous riverine/estuarine inputs in deep-sea surface sediments of the EMS is limited and localized (Statham and Hart, 2005; Garcia-Orellana et al., 2009). The high lithogenic contents found in most Ionian Sea stations (Fig. 3a and Table 2) points to fluvial inputs reaching the area from the Adriatic Sea and local rivers. The main source of riverine inputs is the Po River, opening into the northernmost end of the Adriatic Sea, but inputs from some smaller rivers draining the Apennines can be also relevant (Weldeab et al., 2002). In the Ionian Sea, river-sourced particles are carried by both surface and deep currents flowing southwards along the Italian Peninsula as part of the overall anticlockwise circulation in the Adriatic Sea (Orlic et al., 1992). It should be noted that dense water formation takes place seasonally in the northern Adriatic Sea (and also in the southern), which triggers episodes of fast flowing, sediment-loaded dense water near-bottom currents that cascade into the deeper Meso Adriatic depression before passing through the Otranto Strait, subsequently spreading into the Ionian Sea where their particle load settles to the bottom (Zocolotti and Salusti, 1987; Manca et al., 2002; Vilibic, 2003; Trincardi et al., 2007a, b; Canals et al., 2009).

The grain-size variability of the carbonate particles recorded in the studied sediment samples is indicative of calcareous skeletons of primary producers. While the abundance of particles <8 µm is attributable to coccoliths, which is the most abundant primary producer in the EMS (Emelyanov and Shimkus, 1986), coarser carbonate particles mostly correspond to shells and fragments of calcareous dinoflagellates and planktonic foraminifers, in agreement with Ziveri et al. (2000) and Frenz et al. (2005). Despite part of the carbonate fraction might also have a terrestrial provenance as transported, for instance, with Saharan dust (Chester et al., 1977; Correggiari et al., 1989;
Rutten et al., 2000), this does not seem to be the case with our samples. Like other aeolian particles, aeolian carbonates typically are better sorted than those formed in situ, as usually shown by a well-sorted unimodal distribution due to gravitational settling during atmospheric transport (Skonieczny et al., 2013). The predominance of very poorly sorted grain-size distributions within the bulk sediment samples (Fig. 2a) and the highly variable CaCO$_3$ contents (Fig. 3b) in our samples, suggests that even within such a highly oligotrophic environment biogenic carbonates are the main source of CaCO$_3$ in the deep EMS.

5.1.2 Sources of sedimentary organic matter

Bulk geochemical proxies such as elemental (TN/OC) and stable isotopic ratios of OC ($\delta^{13}$C) have been widely used to assess the sources of OM in marine sediments, by taking advantage of the distinct signatures of marine and terrestrially sourced OM (Meyers, 1994; Goñi et al., 2003; Hu et al., 2006). Marine-derived OM is characterized by high TN contents yielding TN/OC ratio values $>0.12$, while vascular plants are N-depleted due to the predominance of nitrogen-free biomolecules, thus yielding TN/OC ratio values $<0.08$ (Redfield et al., 1963; Hedges and Oades, 1997).

$\delta^{13}$C values in marine algae from low- to mid-latitude temperate seas vary from $-18$ to $-22$‰ (Goericke and Fry, 1994; Meyers, 1994; Harmelin-Vivien et al., 2008), whereas most terrestrial OM inputs from C3 plants show depleted $\delta^{13}$C values ranging from $-25$ to $-28$‰ (Hedges et al., 1997). The contribution of C4 vascular plants can be considered negligible throughout the study area because C4 plants are generally absent in the Mediterranean climate (e.g., Teeri and Stowe, 1976; Collatz et al., 1998). The $\delta^{13}$C range obtained in this study also provides evidence of absence of C4 plants in the EMS.

Sedimentary TN/OC ratios $\delta^{13}$C values determined in this study are consistent with previously reported values for surface sediments of the deep EMS (Tesi et al., 2007; Meyers and Arnaboldi, 2008; Carlier et al., 2010; Goudeau et al., 2013). In order to constrain the origin of sedimentary OM and assess the spatial variability in its marine-
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Lipid biomarkers have often been used as molecular proxies to identify specific biological precursors of sedimentary OM (Meyers, 1997; Volkman, 2006). The concentrations of sedimentary lipid biomarkers reported in this study are fairly comparable to those previously reported in areas devoid of significant fluvial influence both in the Eastern and Western Mediterranean basins (Grimalt and Albaigés, 1990; Gogou et al., 2000; Gogou and Stephanou, 2004; Kaiser et al., 2014).

The patterns of long-chain \( n \)-alkanes and \( n \)-alkanols with elevated CPI\(_{NA} \) and CPI\(_{N-OH} \) values, respectively, indicate the presence of allochthonous natural (terrigenous) inputs from epicuticular higher plant waxes (Eglinton and Hamilton, 1967). Terrestrial plant waxes are major components of EMS aerosols (Gogou et al., 1996), which are highly relevant vectors for the transport of terrestrial OM into the open EMS given the relatively minor direct influence of riverine inputs (Gogou et al., 2000).

Lipid biomarkers preserved in the surface sediments of the study area also highlight the contribution from autochthonous marine OM derived from in situ phytoplankton production. Brassicasterol \( (28\Delta^{5,22E}) \) is the major sterol in many diatoms and prymnesiophytes, while dinosterol \( (30\Delta^{22E}) \) is a major compound in dinoflagellates and is commonly used as source-specific biomarker for these algae (Volkman, 1986). The presence of long-chain alkenones reflects the productivity from algal species of the Prymnesiophyte class, e.g. \textit{Emiliania huxleyii} (Marlowe et al., 1984), which constitute the dominant primary producers across the Mediterranean Sea (Ziveri et al., 2000; Triantaphyllou, 2004). Regarding the long-chain C\(_{30} \) \( n \)-alkan-1,15-diols and the cor-
responding C_{30} keto-ols, although their major sources remain unknown, microalgae of the genus Nannochloropsis (class *Eustigmatophyceae*) are potential sources, while C_{30} keto-ols might result from oxidation of the corresponding C_{30} diols (Volkman, 1986; Volkman et al., 1999; Rampen et al., 2007). Cholesterol \( (27\Delta^5) \) is mainly considered as a biomarker for consumer organisms and a proxy for zooplankton and benthic animals (Grice et al., 1998), while \( \beta \)-Sitosterol \( (29\Delta^5) \) may derive from both terrigenous and marine sources (Volkman, 1986). In the study area, the positive correlation between \( \sum \text{TerNA} \) (and \( \sum \text{TerN-OH} \)) and \( \beta \)-Sitosterol argues for a dominant terrestrial origin for this compound.

Aside from natural sources, the abundance of UCM in the investigated sediments indicates a contribution of anthropogenic OM resulting from degraded petroleum hydrocarbons. Two main pathways have been identified for the introduction of petroleum hydrocarbons in the deep EMS, which are direct discharges from merchant shipping and oil transportation (UNEP, 2010) and atmospheric transport and deposition (Gogou et al., 1996; Castro-Jiménez et al., 2012; Parinos et al., 2013).

### 5.2 Regional variability and oceanographic control on the geochemical composition of deep Eastern Mediterranean Sea surface sediments

The PCA provide a robust overview of the variables and processes controlling the geochemical composition of the investigated deep-sea surface sediments (Fig. 5).

The significant positive loadings of \( \sum \text{TerNA}, \sum \text{TerN-OH}, \sum \text{Mar}, \) UCM and depth on PC1 are indicative of a considerable contribution from both natural (marine and terrestrial) and anthropogenic (degraded petroleum products) OM preserved in deep-sea surface sediments of the EMS. The negative PC1 loading of CPI_{N-OH} ratios on PC1 indicates that the terrestrial OM is relatively altered, while the negative PC1 loading of CPI_{NA} ratios is indicative of an enhanced contribution of petroleum products. Furthermore, the non-zero intercept of the TN to OC ratio values suggests that inorganic IN is present (see Sect. 5.2.1). Overall, PC1 represents the degradation processes and fate of the sedimentary OM in the study area.
The second PC separates samples with high carbonate contents, TN/OC ratios and enhanced contribution of clay-sized particles from those with high lithogenic contents. Therefore, samples with positive loadings of PC2 are enriched in fine marine carbonate particles, while those with negative loadings are enriched in lithogenic particles (see Sect. 5.2.2).

Finally, PC3 separates samples with high contents of OC, TN and clays from those with high values of δ^{13}C. Consequently, positive loadings are associated to sediments with an enhanced contribution of OC-rich fine particles, thus pointing to hydrodynamic processes that control grain size sorting and remobilization/deposition of sedimentary material with different OC contents (see Sect. 5.2.2).

5.2.1 Processes modulating the biogeochemical signal of the sedimentary organic matter

The quantity of OC and TN buried in marine sediments depends on the rate of OM supply, the degree to which this fraction is diluted by other sediment components and the degree of preservation of the deposited material (Calvert and Pedersen, 1992). The low OC and TN contents in the surface sediments of the study area reflects the oligotrophic character of the EMS (e.g., Krom et al., 2003). However, it should be taken also into account that some processes may have further pushed TN to OC ratios towards low values (Fig. 8a). These include the preferential degradation of N-rich proteinaceous components of algal OM during early diagenesis (Meyers et al., 1996; Meyers, 1997; Hopmans et al., 2004) and the enrichment of OC relative to TN due to the input of petroleum residues (Friligos et al., 1998). Furthermore, a significant contribution of inorganic N, presumably as NH₄⁺ adsorbed on clays (Müller, 1977; Meyers, 1997), is inferred from the positive intercept on the N axis at around 19 % (Fig. 8a).

We assume that the diagenetic isotopic fractionation during sinking and burial of OM in the study area is minor since previous studies Mediterranean sea have shown that the isotopic composition of sedimentary OM is fairly conservative, reflecting the isotopic signatures of the sources. (e.g., Di Leonardo et al., 2009). However, isotopic signatures
can be potentially shifted by inputs of anthropogenic OM. $\delta^{13}C$ values for crude oil and petroleum products are around $-28.5$ and $-28.9\%_{oo}$, respectively (Rumolo et al., 2011 and references therein). In the study area, the negative PC1 loadings of the CPI$_{NA}$ ratio values together with the positive PC1 loadings of depth and UCM indicate an enhanced contribution of petroleum products with increasing water depth. This points to an enrichment of the sediments in petroleum hydrocarbons in the deep Ionian Sea and western Cretan Straits stations H03 and Red3.1 where such an isotopic shift is observed (Figs. 3e and 7), in addition to maximum concentrations of UCM along with relatively low TN/OC ratios ($< 0.11$) (Table 2, Figs. 3d and 4a).

Lipid biomarkers provide further information on the natural sources of sedimentary OM. The significant positive correlation of $\Sigma\text{TerNA}$ and $\Sigma\text{TerN-OH}$ (not normalized to OC) to OC contents suggests a close association of terrestrial OM to OC, while the significant positive correlation of $\Sigma\text{TerNA}$ and $\Sigma\text{TerN-OH}$ to %clay suggests that the transport and accumulation of terrestrial OM is associated to fine particles (see Sect. 5.2.2). Furthermore, the relatively uniform spatial distribution of [NA]/[N-OH] and CPI$_{N-OH}$ ratios (Fig. 8), together with the negative PC1 loadings of CPI$_{N-OH}$ ratios vs. depth are overall indicative of an existent but non intensive reworking of the terrestrial OM in the deep EMS, which is rather consistent with its long-range atmospheric transport and long residence time in the water column and into the sediments (Gogou and Stephanou, 2004).

On the contrary, while a significant positive correlation is observed for $\Sigma\text{Mar}$ concentrations (not normalized to OC contents) and OC, indicating that the latter exerts an important control on the distribution of algal markers’ concentrations in the study area, no significant correlation is observed between $\Sigma\text{Mar}$ and grain size. These correlations together with the deviation trend observed for TN/OC ratios from the classical Redfield ratio (16/106) with increasing water depth, which is more evident for the deep Ionian Sea stations (Fig. 8a), probably reflect the preferential degradation processes during the transport and deposition of marine labile sedimentary OM, that probably also masks the association of marine OM to fine particles. The observations above, jointly with the
presence of cholesterol ($27\Delta^5$) and its significant positive correlation with the concentrations of marine algal markers, are altogether indicative of the re-working of algal OM by zooplankton that produces faecal pellets rapidly sinking in the water column and by benthic invertebrates (Volkman et al., 1990; Gogou and Stephanou, 2004).

5.2.2 Sediment transport and deposition and processes

The second and third PCs of the PCA allowed us to determine the main processes that affect sediment dispersal and deposition. These relate to pelagic settling of marine skeletons (corresponding to PC2) from surface waters and to the hydrodynamic sorting of organic-rich fine sediment by bottom currents (corresponding to PC3).

Particulate matter exported from the upper layers of the water column in the EMS is primarily composed of biogenic particles and atmospheric dust, which while settling to the seabed are able to transfer OC, other nutrient elements, and OC-associated organic pollutants (e.g., Stavrakakis et al., 2000, 2013; Theodosi et al., 2013). In the deep EMS, the distribution of pelagic carbonates (second PC) seems to be mainly influenced by planktonic contributions. In the study area, the phytoplankton biomass and primary production are relatively higher in the cyclonic regions where the nutricline ascends to the base of the euphotic zone. The Rhodes cold-core gyre, situated in the southeast of the Rhodes Island (NW Levantine Sea), is the most prominent dynamic feature in the EMS and is the main source area of the LIW. In this cyclonic gyre, which is enhanced during winter period, dense water masses from deeper layers tend to upwell at its centre, feeding the upper layers with nutrient-rich masses (Salihoglu et al., 1990). Therefore, this gyre plays an important role in the productivity of the Levantine Sea.

The third PC separated samples with high OC, TN and clay contents, which is indicative of a close OM-mineral association. This is in agreement with the high OC contents found in the fine-grained sediment samples from the deeper stations representing an essentially quiet environment (Figs. 2, 3 and 7). This is in contrast with the lower OC contents observed in coarser samples ($D_{50} > 14 \mu m$) from shallower depths where cur-
rents up to 20 cm s\(^{-1}\) occur commonly (Kontoyiannis et al., 2005; Ursella et al., 2014). Fine-grained particles have high capacity for OM adsorption due to their large specific surface area, and thus enhanced OM contents relatively to coarse-grained particles (Mayer, 1994; Hedges and Keil, 1995). Physical processes such as hydrodynamic sorting remobilize and transport sedimentary material with different OC contents, with the OC-rich finest ones easily reaching the deep EMS. A similar situation has been reported in other land-locked seas or marginal settings such as the the Western Mediterranean Sea (Pedrosa-Pàmies et al., 2013) the Gulf of Mexico (Goñi et al., 1998), or the Eel River margin (Wakeham et al., 2009). In short, the deep EMS behaves as a sink for OM-rich fine particles.

Grain-size provides additional information on sediment sources, transport mechanisms and depositional processes that affect sedimentary particles including their OM load (Folk and Ward, 1957; Hedges and Keil, 1995; Sun et al., 2002; Wakeham et al., 2009). What we found, as a general pattern, in the EMS is that bulk sediments show a poorer sorting than the lithogenic fraction (Fig. 2), which is caused by the presence of coarse biogenic carbonate particles in bulk samples or the effective hydrodynamic sorting linked to the prevailing depositional conditions in such deep low-energy environments (Friedman, 1969).

The poor sorting and positive skewness found in grain-size types I, II, IV and V of the bulk sediment samples (Fig. 2a) in the southern Aegean Sea and the northwestern Levantine Sea is explained by the prevalence of pelagic biogenic sedimentation, as shown by the high positive score values observed on PC2 (Fig. 5b). Accordingly, high percentages of CaCO\(_3\) have been measured in stations of the southern Aegean Sea, the northwestern Levantine Sea and western Cretan Straits’, which correlate with %clay fraction of the bulk sediment samples and the concentrations of alkenones (Table 3). This links to the formation of clay-carbonate concretions that have been reported in particularly large amounts in the southern Aegean Sea (Emelyanov and Shimkus, 1986). Vertical mixing and upward transport of nutrients in the eddies and gyres, such as the Rhodes gyre, may trigger first primary production and then the sinking and dom-
inance of pelagic biogenic particles over particles from other sources in the northwestern Levantine Sea (Siokou-Frangou et al., 1999). The $\sum_{\text{Mar}}$ distribution is indicative in that respect as it shows a general eastward increasing trend with peak concentrations in deep basins of the northwestern Levantine Sea.

Surface sediments in the Ierapetra Basin (stations Red15, Red1.1 and Ier01) also show positive scores in PC3 (Fig. 5b), which point to an influence of hydrodynamic sorting processes. The relatively high OC content in these stations (Fig. 7), along with the elevated values of the associated natural and anthropogenic lipid concentrations (Table 3), suggests that the Hellenic Trench is a sink of OC associated to fine particles transferred by the active outflows of the Cretan Straits, besides the pelagic sedimentation related to the well-known semi-permanent Ierapetra anticyclone (Larnicol et al., 2002; Taupier-Letage, 2008).

Sediments with grain size types I-III of the bulk sediment samples (Fig. 2a) in the Ionian Sea show lower CaCO$_3$ contents due to the dilution by lithogenic components, with the only exception of station H02. High positive score values on PC3 (Fig. 5b), and the significant positive correlation for OC and TN contents with %clay of the lithogenic fraction, suggest again a significant influence of hydrodynamic sorting processes, which largely determine a differential distribution of OM in surface sediments according to grain size. In this area, the Otranto Strait may act as a preferential conduit by funnelling sedimentary material and associated OM from the Adriatic Sea towards the deep basins of the adjacent Ionian Sea, which may eventually reach the Levantine Sea. Cascading of North Adriatic dense water and subsequent propagation and outflow through the Otranto Strait (Bensi et al., 2013) may feed the deep Ionian Sea with fine OC-rich particles. Our Ionian samples off the southern mouth of the Adriatic Sea present relatively enhanced contributions of terrestrial OM as indicated by low $\delta^{13}$C values (Fig. 3e) and terrestrial biomarkers concentrations (Figs. 4b–c and Table 3). This probably also reflect the preferential degradation of labile marine OM in deep Ionian Sea basins due to slower sedimentation rates and longer residence time of organic matter occurring in these sites. Low OC content (Fig. 3c), poor sorting, very negatively
skewed, high % sand of grain size type VI (Fig. 2a) at the shallower station H12 just south of Otranto Strait supports winnowing of fine OC-rich particles due to episodic events of high current speed exiting the Adriatic Sea (Bignami et al., 1991; Gacic et al., 1996; Poulos et al., 1999).

Finally, station Red3 from the upper slope of western Cretan Straits representing grain size type VII of the bulk sediment samples (Fig. 2a) shows the highest contents of sand (47.7 %), which is poorly sorted. This is in agreement with the occurrence of the topographically restricted deep outflow of the western Cretan Straits. In these straits, a seasonal signal is characterized by intensification in the outflow speeds during winter and minimum speeds during fall (Kontoyiannis et al., 2005). The turbulent, fluctuating outflow current should normally trigger sediment resuspension and induce selective transport, thus leaving coarse OC-poor particles in the upper slope of the western Cretan Straits (negative factor scores of PC2 and PC3) and carrying fine OC-rich particles to the lower slope. A similar pattern has been also observed in some submarine canyon settings of the Mediterranean Sea, such as the Cap de Creus Canyon (Sanchez-Vidal et al., 2008) and the Blanes Canyon (Pedrosa-Pàmies et al., 2013). The top δ13C values found in the upper slope (Fig. 7 and Tables 2–3) indicates high contribution of marine OC, which is not supported by the lipid biomarkers results. Winnowing of fine particles loaded with terrestrial OC, thus shifting the isotopic signal of the remaining coarse particles towards high and more marine values seems to be the most plausible explanation.

6 Conclusions

Surface sediments collected from deep oligotrophic EMS were investigated using a multi-proxy approach that involved elemental composition, grain size, stable isotopes and selected lipid biomarkers’ analyses resulting in a robust database to determine sediment sources, the degradation and preservation state of OM, and transport and depositional processes. The PCA analysis helped to identify the main controlling fac-
tors of the observed geochemical variability in the investigated sediments. Such factors are sediment sources in terms of allochthonous vs. autochthonous, a highly variable physiography, the thermohaline structure and the regional and local circulation, leading to hydrodynamic sorting and regulating particle settling and deposition, and OM preservation state.

Surface sediments of the investigated part of the EMS mostly consist of airborne lithogenic particles and biogenic carbonate particles derived from primary production in surface waters. Sedimentary OM appears in rather low contents (0.15–1.15 % OC), as derived from both natural and anthropogenic sources, namely marine algae, terrestrial plants and degraded petroleum products. Samples from locations in the Ionian Sea and the western Cretan Straits that are under the direct influence of the Adriatic Sea outflow of dense waters through the Otranto Strait and of currents exiting the southern Aegean Sea are appreciably sorted. Current regime impacted not only grain size but also OC loadings in each region within the study area, with winnowing of fine OC-rich particles to the deepest EMS. In contrast, coarse OC-poor particles tend to occur in upper slope settings. While OC associated to fine particles was relatively non-degraded terrestrial OM, marine OM was found to be mostly degraded and reworked during transport processes and before reaching the deep seafloor.

The spatial variability in the yields of sedimentary OC and lipid biomarkers presented in this study highlights the heterogeneous nature of the particle load exported to the deep basins of the Eastern Mediterranean Sea. Such variability must be taken into account during the development of quantitative carbon budgets for this area.

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Table 1. Location, depth and collection date of surface sediments.

| Sample Code | Latitude (N) | Longitude (E) | Water depth (m) | Date of collection | Physiographic regions |
|-------------|--------------|---------------|-----------------|--------------------|-----------------------|
| Ionian Sea  |              |               |                 |                    |                       |
| North       |              |               |                 |                    |                       |
| H12         | 39.30        | 19.30         | 1450            | Jan 2007           | Otranto Valley         |
| H07         | 39.17        | 17.75         | 1866            | Jan 2007           | Taranto Valley         |
| Central     |              |               |                 |                    |                       |
| BF27        | 38.22        | 16.63         | 1264            | Jun 2009           | Calabrian Slope        |
| BF13        | 37.66        | 16.56         | 2012            | Jun 2009           | Calabrian Arc          |
| BF15        | 36.20        | 16.35         | 3335            | Jun 2009           | Ionian Basin           |
| H04         | 35.92        | 16            | 3750            | Jan 2007           | Ionian Basin           |
| West        |              |               |                 |                    |                       |
| H02         | 35.75        | 21            | 3008            | Jan 2007           | Ionian Basin           |
| H05         | 37.50        | 16.00         | 3154            | Jan 2007           | Ionian Basin           |
| H03         | 35.70        | 21.00         | 4087            | Jan 2007           | Ionian Basin           |
| S. Aegean Sea (Cretan Sea) | | | | | |
| Red5        | 35.68        | 25.10         | 1018            | May 2010           | Cretan Trough          |
| Red9        | 36.00        | 23.89         | 1200            | May 2011           | Cretan Trough          |
| Red4        | 35.76        | 25.10         | 1615            | May 2010           | Cretan Trough          |
| Red8        | 36.07        | 25.28         | 1715            | May 2011           | Cretan Trough          |
| W Cretan Straits | | | | | |
| H01         | 35.70        | 23.00         | 2117            | Jan 2007           | Kithira Strait         |
| Red3        | 35.40        | 23.40         | 2976            | May 2010           | Antikithira Strait     |
| Red3.1      | 35.30        | 23.32         | 3317            | May 2010           | Antikithira Strait     |
| Red7        | 34.60        | 24.15         | 3589            | May 2011           | Ptolemy Strait         |
| NW Levantine Sea | | | | | |
| Ierapetra Basin | | | | | |
| Red13       | 34.95        | 25.93         | 1101            | Jun 2012           | Cretan-Rhodes Ridge    |
| BF19        | 34.51        | 25.76         | 1200            | Jun 2009           | Hellenic Trench        |
| BF22        | 34.48        | 25.87         | 2015            | Jun 2009           | Hellenic Trench        |
| Red15.1     | 34.61        | 25.92         | 2428            | Jun 2012           | Hellenic Trench        |
| Red1.1      | 34.40        | 26.25         | 3568            | Jun 2012           | Hellenic Trench        |
| Ier01       | 34.44        | 26.19         | 3626            | Jan 2007           | Hellenic Trench        |
| Open Sea    |              |               |                 |                    |                       |
| Rho02       | 35.62        | 27.70         | 1305            | Jan 2007           | Rhodes Strait          |
| Her01       | 33.92        | 27.74         | 2680            | Jan 2007           | EM Ridge               |
| Red2        | 33.74        | 26.15         | 2717            | May 2010           | EM Ridge               |
| Red2.1      | 33.71        | 26.34         | 2720            | May 2010           | EM Ridge               |
| BF24        | 34.15        | 25.57         | 2902            | Jun 2009           | Pliny Trench           |
| Her03       | 33.67        | 29.00         | 3090            | Jan 2007           | Herodotus Basin        |

January 2007 samples were collected during the M71 (Leg 3) cruise onboard the R/V Meteor (University of Hamburg, Germany), June 2009 samples during the Biofun1 cruise onboard the R/V Sarmiento de Gamboa (CSIC-UB, Spain), and May 2010, 2011 and June 2012 samples during the ReDEco cruises onboard the R/V Aegaeo (HCMR, Greece).
Table 2. Bulk composition and sedimentological parameters of investigated surface sediments.

| Sample Code | Clay<sub>bulk</sub> (%<sub>4 µm</sub>) | Silt<sub>bulk</sub> (%<sub>4–63 µm</sub>) | Sand<sub>bulk</sub> (%<sub>63 µm–2 mm</sub>) | Sorting<sub>bulk</sub> | Sorting<sub>litho</sub> | Skewnes<sub>bulk</sub> | D<sub>50 bulk</sub> (µm) | Lithogenic | CaCO<sub>3</sub> (%) | Opal (%) | OC (%) | TN/OC (%) | δ<sup>13</sup>C (%) |
|-------------|------------------|------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-------------|---------|-------------|--------------|
| **Ionian Sea** | [Data Table]**North** | [Data Table]**Central** | [Data Table]**West** | [Data Table]**S. Aegean Sea (Cretan Sea)** | [Data Table]**W Cretan Straits** | [Data Table]**NW Levantine Sea** | [Data Table]**Ierapetra Basin** | [Data Table]**Open Sea** |
| H12 | 18.1 | 76.7 | 5.24 | 3.47 | 3.31 | −0.13 | 14.6 | 71.2 | 28.5 | 0.03 | 0.15 | 0.08 | −24.2 |
| H07 | 41.2 | 58.8 | 0.00 | 3.01 | 4.12 | −0.07 | 5.34 | 75.7 | 22.0 | 1.16 | 0.08 | −24.4 |
| BF27 | 52.8 | 46.1 | 1.04 | 3.38 | 2.83 | −0.04 | 3.97 | 80.8 | 17.8 | 0.16 | 0.64 | 0.12 | −23.0 |
| BF13 | 50.8 | 48.1 | 1.08 | 3.41 | 2.92 | −0.05 | 4.17 | 76.7 | 22.0 | 0.21 | 0.58 | 0.12 | −22.9 |
| BF15 | 39.1 | 57.0 | 3.98 | 4.01 | 2.91 | 0.03 | 5.88 | 77.9 | 21.6 | 0.28 | 0.14 | −22.5 |
| H04 | 41.6 | 58.4 | 0.04 | 4.69 | 3.53 | −0.23 | 5.52 | 85.4 | 13.2 | 0.04 | 0.65 | 0.13 | −23.6 |
| H02 | 53.3 | 46.7 | 0.00 | 2.99 | 6.16 | −0.07 | 3.92 | 47.7 | 51.3 | 0.04 | 0.45 | 0.1 | −22.5 |
| H05 | 41.6 | 58.4 | 0.00 | 2.98 | 3.48 | −0.01 | 5.34 | 60.7 | 38.2 | 0.57 | 0.10 | −23.7 |
| H03 | 34.5 | 65.5 | 0.08 | 3.11 | 3.49 | −0.04 | 7.03 | 77.6 | 21.0 | 0.11 | 0.63 | 0.10 | −24.6 |
| **Red5** | 54.0 | 46.0 | 0.00 | 3.32 | 3.61 | −0.01 | 3.88 | 32.5 | 66.5 | 0.24 | 0.39 | 0.10 | −22.4 |
| **Red9** | 50.1 | 49.9 | 0.00 | 3.24 | 3.28 | −0.01 | 4.23 | 46.6 | 52.2 | 0.15 | 0.55 | 0.12 | −22.6 |
| **Red4** | 52.6 | 47.4 | 0.00 | 3.26 | 3.58 | −0.06 | 4.17 | 39.3 | 56.6 | 0.08 | 0.59 | 0.13 | −22.6 |
| **Red8** | 53.1 | 46.9 | 0.00 | 3.12 | 3.36 | −0.03 | 4.00 | 44.0 | 55.3 | 0.08 | 0.33 | 0.15 | −22.0 |
| **H01** | 55.1 | 44.9 | 0.00 | 4.74 | 4.77 | −0.11 | 3.65 | 42.8 | 56.6 | 0.29 | 0.12 | −22.6 |
| **Red3** | 41.5 | 57.7 | 0.88 | 4.32 | 3.82 | −0.07 | 6.74 | 55.7 | 43.0 | 0.12 | 0.58 | 0.09 | −22.9 |
| **Red7** | 14.5 | 37.9 | 0.88 | 4.71 | 5.23 | 0.45 | 56.6 | 59.2 | 39.9 | 0.15 | 0.37 | 0.08 | −18.3 |
| **BF22** | 13.7 | 65.5 | 0.00 | 3.55 | 3.57 | −0.07 | 6.37 | 51.8 | 47.1 | 0.05 | 0.54 | 0.1 | −22.9 |
| **H07** | 36.0 | 63.5 | 0.00 | 3.69 | 3.67 | −0.03 | 4.59 | 51.8 | 46.9 | 0.8 | 0.61 | 0.08 | −20.2 |
| **Red3.1** | 47.5 | 44.0 | 0.00 | 3.32 | 3.58 | −0.06 | 4.17 | 39.3 | 56.6 | 0.08 | 0.59 | 0.13 | −22.6 |
| **Red8.1** | 57.1 | 42.8 | 0.00 | 3.73 | 2.61 | −0.13 | 3.53 | 51.8 | 47.1 | 0.05 | 0.54 | 0.1 | −21.5 |
| **BF15** | 41.9 | 50.4 | 0.00 | 3.84 | 2.67 | 0.03 | 4.35 | 55.6 | 43.3 | 0.80 | 0.52 | 0.10 | −21.7 |
| **Her01** | 43.0 | 51.8 | 0.00 | 4.43 | 3.25 | −0.14 | 5.24 | 58.4 | 40.6 | 0.16 | 0.47 | 0.12 | −22.7 |
| **Red2** | 48.2 | 51.8 | 0.00 | 4.38 | 4.89 | 0.04 | 4.44 | 35.8 | 63.4 | 0.13 | 0.31 | 0.15 | −22.7 |
| **Red3.1** | 47.5 | 51.8 | 0.00 | 3.84 | 3.25 | −0.14 | 5.24 | 58.4 | 40.6 | 0.16 | 0.47 | 0.12 | −22.7 |
| **BF24** | 43.1 | 45.0 | 11.9 | 5.25 | 3.51 | 0.2 | 5.34 | 45.0 | 44.3 | 0.11 | 0.50 | 0.16 | −22.3 |
| **Her03** | 39.8 | 60.2 | 0.00 | 4.30 | 3.20 | −0.20 | 5.81 | 55.0 | 55.0 | 0.10 | 0.49 | 0.11 | −22.4 |

Empty cell = not determined.
Table 3. Concentrations (OC-normalized) and indices of considered lipid biomarkers.

| Station | ∑TerNA<sup>a</sup> (µg g<sup>−1</sup> OC) | ∑TerN-OH<sup>a</sup> (µg g<sup>−1</sup> OC) | ∑Mar<sup>a</sup> (µg g<sup>−1</sup> OC) | ∑Alkenones<sup>a</sup> (µg g<sup>−1</sup> OC) | ∑C<sub>30</sub> diols<sup>b</sup> (µg g<sup>−1</sup> OC) | ∑Sterols<sup>d</sup> (µg g<sup>−1</sup> OC) | CPI<sub>NA</sub> | CPI<sub>N-OH</sub> | [NA] [N-OH] |
|---------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|--------------------------------|--------------------------------|-----------------|-----------------|-----------------|
| **Ionian Sea** | | | | | | | | | |
| North | | | | | | | | | |
| H12 | 54.9 | 19.0 | 29.4 | 6.75 | 14.7 | 62.4 | 29.7 | 3.22 | 24.8 | 4.72 | 4.14 | 4.00 | 2.90 |
| H07 | 40.8 | 13.4 | 34.5 | 5.97 | 14.6 | 35.6 | 6.77 | 5.52 | 14.9 | 8.37 | 4.39 | 4.14 | 3.03 |
| **Central BF27 BF13 BF15** | | | | | | | | | |
| H04 | 169 | 52.1 | 54.1 | 12.3 | 21.5 | 59.6 | 10.6 | 8.57 | 28.6 | 11.7 | 4.04 | 5.95 | 3.24 |
| **West** | | | | | | | | | |
| H02 | 176 | 35.2 | 34.2 | 8.14 | 19.7 | 17.1 | 3.67 | 2.36 | 7.06 | 3.96 | 3.57 | 3.73 | 5 |
| H05 | 211 | 42.8 | 47.2 | 12.5 | 25 | 24.2 | 4.12 | 3.43 | 10.4 | 6.28 | 4.07 | 3.63 | 4.93 |
| H03 | 214 | 37.0 | 35.7 | 8.77 | 25.5 | 25.2 | 6.04 | 3.65 | 9.62 | 5.92 | 2.80 | 4.08 | 5.00 |
| **S. Aegean Sea (Cretan Sea)** | | | | | | | | | |
| Red5 | 206 | 50.7 | 45.3 | 20.1 | 15.9 | 40.1 | 10.8 | 4.74 | 20 | 4.51 | 5.07 | 4.89 | 4.06 |
| Red9 | 101 | 14.7 | 22.2 | 9.85 | 7.3 | 17.7 | 3.77 | 2.66 | 8.83 | 2.42 | 7.25 | 5.12 | 6.88 |
| Red4 | 196 | 48.4 | 41 | 17.4 | 14.8 | 38.6 | 11.5 | 4.63 | 20 | 4.15 | 5.36 | 5.21 | 4.05 |
| Red8 | 127 | 29.4 | 41.0 | 16.8 | 7.30 | 26.3 | 5.62 | 3.23 | 14.2 | 3.20 | 6.40 | 4.97 | 4.32 |
| **W Cretan Straits** | | | | | | | | | |
| H01 | 127 | 26.2 | 18.2 | 3.41 | 11.3 | 10.3 | 2.22 | 1.35 | 4.55 | 2.22 | 6.64 | 6.13 | 4.84 |
| Red3 | 120 | 30.4 | 70.1 | 21.2 | 28.1 | 34.4 | 7.85 | 9.33 | 5.79 | 11.4 | 2.9 | 4.27 | 3.93 |
| Red3.1 | 218 | 50.0 | 29.0 | 10.8 | 11.8 | 20.7 | 3.87 | 3.15 | 10.4 | 3.3 | 3.63 | 4.02 | 4.37 |
| Red7 | 184 | 43.7 | 59.2 | 30.5 | 19.4 | 28.6 | 6.17 | 3.61 | 13.1 | 3.30 | 2.90 | 4.63 | 4.21 |
| **NW Levantine Sea** | | | | | | | | | |
| Ierapetra Basin | | | | | | | | | |
| Red13 | 156 | 36.8 | 38.8 | 14.1 | 16.1 | 34.5 | 10.20 | 4.97 | 15.8 | 3.60 | 7.95 | 5.82 | 4.24 |
| BF19 BF22 | | | | | | | | | |
| Red15.1 | 126 | 28.3 | 32.6 | 11.5 | 14.1 | 21.3 | 4.20 | 3.21 | 10.1 | 3.88 | 5.26 | 5.03 | 4.44 |
| Red1.1 | 166 | 38.6 | 36.9 | 14.1 | 14.1 | 23.9 | 5.14 | 3.67 | 10.7 | 4.39 | 6.07 | 4.79 | 4.3 |
| Ier01 | 206 | 44.4 | 59 | 11.1 | 35.0 | 29.8 | 4.94 | 4.69 | 11.9 | 8.3 | 6.37 | 3.68 | 4.63 |
| **Open Sea** | | | | | | | | | |
| Rh02 | 166 | 49.9 | 59.0 | 5.92 | 33.2 | 30.2 | 5.56 | 4.90 | 12.6 | 7.17 | 6.88 | 4.68 | 3.33 |
| Her01 | 195 | 52.2 | 66.3 | 14.2 | 35.8 | 46.5 | 11.3 | 7.59 | 18.9 | 8.71 | 4.43 | 3.70 | 3.74 |
| Red2 | 483 | 105 | 72.6 | 23.6 | 35.5 | 47.8 | 7.86 | 6.54 | 26.4 | 6.97 | 1.93 | 4.23 | 4.59 |
| BF24 | | | | | | | | | |
| Her03 | 157 | 39.7 | 45.7 | 7.96 | 29.5 | 22.2 | 4.57 | 3.05 | 9.39 | 5.23 | 3.69 | 3.49 | 3.96 |

Empty cell = not determined.

<sup>a</sup> Reported by Parinos et al. (2013).
<sup>b</sup> Sum of the concentrations of C<sub>37</sub> : 3M, C<sub>37</sub> : 2M, C<sub>36</sub> : 2FAME, C<sub>38</sub> : 3E, C<sub>38</sub> : 3M, C<sub>38</sub> : 2Et, C<sub>38</sub> : 2M (the corresponding unsaturated homologues are indicated with the number of their carbon atoms (n) and the number of double bonds (x) – (C<sub>n</sub>:<sub>x</sub>); M: methyl; Et: Ethyl; FAME: Fatty acid methyl ester).
<sup>c</sup> Sum of the concentrations of C<sub>30</sub> n-alkan-1,15-diols and C<sub>30</sub> keto-ols.
<sup>d</sup> Sum of the major C<sub>27</sub> : C<sub>30</sub> sterols considered in this study i.e., cholesterol (cholest-5-en-3β-ol; 27<sup>Δ5</sup>), brassicasterol (24-methylcholesta-5,22-dien-3β-ol; 28<sup>Δ22</sup>), β-sitosterol (24-ethylcholesta-5-en-3β-ol; 29<sup>Δ5</sup>) and dinosterol (4α,23,24-trimethyl-5α (H)-cholesta-22(E)-en-3β-ol 30<sup>Δ22</sup>).
Figure 1. (a) Location of sampling sites across the open Eastern Mediterranean Sea (see also Table 1). The map was produced using GEBCO Digital Atlas (IOC, IHO and BODC, 2003). (b) Plot of longitude vs. water depth of sampling stations.
Figure 2. Statistical dendrogram of type-averaged grain-size profiles and geographical distribution of grain-size compositional types for (a) the lithogenic fraction and (b) the bulk fraction of the investigated sediments.
Figure 3. Spatial distribution of (a) lithogens, (b) CaCO₃ contents, (c) OC contents, (d) TN/OC ratios, (e) and δ¹³C values in surface sediments of the deep Eastern Mediterranean Sea.
**Figure 4.** Spatial distributions of the OC-normalized concentrations of (a) Unresolved Complex Mixture (UCM), (b) $\sum$TerNA, (c) $\sum$TerN-OH and (d) $\sum$Mar in surface sediments of the deep Eastern Mediterranean Sea. Abbreviations of lipid biomarkers are defined in the text.
Figure 5. (a) Scatter plot of the factor loadings of the three principal components obtained in the Principal Component Analysis, and (b) plot of the scores found at each station. Abbreviations of lipid biomarkers are defined in the text.
Figure 6. Plot of TN/OC atomic ratio vs. $\delta^{13}C$, in surface sediments of the deep Eastern Mediterranean Sea. The compositional ranges of organic matter sources illustrated in plots (boxes) derive from previously published studies (see Sect. 5.1).
Figure 7. Distribution of OC content and bulk sediment tracers (TN/OC and $\delta^{13}$C) in surface sediments of the deep Eastern Mediterranean Sea. The histogram reflects a spatially variable mixture of marine and terrestrial sources for sedimentary OM.
Figure 8. (a) Co-plot of the weight percent content of nitrogen (TN) vs. organic carbon (OC) for the deep-sea surface sediments analysed. The linear fit of the data is shown (dotted line) along with the Redfield ratio $N_{16}/C_{106}$ associated with the fresh marine phytoplankton (0.17 wt. wt.$^{-1}$). Spatial distribution of lipid biomarker indexes (b) $[\text{NA}]/[\text{N-OH}]$ and (c) $\text{CPI}_{\text{N-OH}}$. Abbreviations of lipid biomarker indices are defined in the text.