"The Mediterranean is an absurdly small sea; the length and greatness of its history makes us dream it larger than it is."

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Chapter 8

Comparison of coeval organic carbon rich sediments in the Vrica section and in ODP Sites 967 and 969

I.A. Nijenhuis, J. Becker, G.J. de Lange

Abstract - The geochemistry of eastern Mediterranean sediments from the early Pleistocene insolation cycle i-156 was studied in the Vrica section (Calabria, Italy) and in ODP Sites 967 and 969. The ODP sediments are rich in carbonates and contain a sapropel with up to 20% organic carbon, whereas the Vrica sediments are rich in clays and contain a laminit with up to 1% organic carbon. Processes that affected the land section but not the ODP sediments can only partly account for these differences. In the land section, dessication and compaction resulted in higher dry bulk densities. Subsurface weathering caused oxidation in sediments surrounding conductive planes constituted by ash layers, resulting in lower organic carbon and total nitrogen contents, and lower C/ N ratios and organic carbon isotopic values. Subaerial weathering resulted in higher Na and K contents because of evaporation at the outcrop surface.

Other geochemical differences are thought to be due to the different settings: the Vrica sediments have been deposited closer to land, in shallower water, with a higher sedimentation rate and in a more western part of the Mediterranean than the ODP sediments. This resulted in higher aluminium and organic carbon accumulation rates, lower "terrestrial" and redox-sensitive element to aluminium ratios, lower barium contents and more negative organic carbon isotopic values in the sediments of Vrica compared with those of ODP.

Formation of a laminite enriched in organic carbon at Vrica, and of laminated sapropels at the ODP sites can be explained by one model combining higher productivity and better preservation. The occurrence of an interval enriched in organic carbon immediately above and below the anoxic laminit provides evidence for the hypothesis that organic carbon production increased before anoxia developed. The inferred duration of the laminit is shorter than that of the sapropels, indicating that anoxia probably lasted longer in deep water than in shallow environments.

This chapter has been submitted for publication in Palaeogeography, palaeoclimatology, palaeoecology.
Introduction
In the Mediterranean area, particularly on islands like Sicily, Crete and Gavdos, outcrops of
Neogene marine sediments can be found, which are characterized by an alternation of light-
coloured marls and darker layers with a higher clay and organic matter content. These dark
layers are occasionally called sapropels, although they generally contain less organic carbon
($C_{org}$) than implied by that term (at least 2% [Olsson, 1961]). Their cyclic occurrence coincides
with minima in the index of the precession of the Earth’s equinoxes [Hilgen, 1991a, b; Hilgen et
al., 1995]. Similar layers have been recovered from the present-day Mediterranean seafloor in
piston-, box- and gravity-cores. These layers generally seem to be better developed than those
found in land sections, in the sense that they are more enriched in $C_{org}$, more depleted in
carbonate, and have better developed lamination. On the other hand, they are usually thinner.
Unfortunately, a direct comparison between age-equivalent sediments recovered with
traditional marine coring techniques (younger than approximately 1 Ma) and astronomically
tuned sapropels in land sections (older than 1.2 Ma) has not been possible until now. During
ODP Leg 160 to the eastern Mediterranean, sapropel-containing sediments of a Recent to
Miocene age were recovered from several sites by hydraulic coring techniques, offering the
opportunity to compare abyssal, well-developed sapropels from ODP sites with shallower
equivalents in land sections. We sampled the coeval sapropels of insolation cycle i-156 in ODP
Sites 967 and 969 and laminite "o" [Selli et al., 1977] in the Vrica section (Calabria, Italy; Fig. 8.1)
in high resolution. We show that the geochemical differences between the sapropels and the
laminite are due to the dissimilarity of the settings and to the combined results of compaction,
weathering and oxidation. Additionally, comparison between these diverse settings provides new information on the palaeoceanographic aspects of sapropel formation.

**Material and methods**

At the Vrica section, sampling took place in a recently (less than a year before sampling) excavated building site. As a result, we obtained fresh, blue-coloured samples after removing less than one metre of sediment from the outcrop surface. However, within the laminite there were five bedding-parallel intervals of a few mm to 7 cm which retained a red-brown colour. Using a stainless steel chisel, 156 'fresh' samples were taken, with a resolution varying between 1 cm in laminite "o" and 4-15 cm in the adjacent homogeneous intervals (Table 8.1). For twenty-one of these samples, stratigraphically equivalent, but slightly weathered (40 cm from the edge of the outcrop) and strongly weathered (edge of the outcrop) samples were also taken. From the ODP split cores, slices with a thickness of 0.5 to 2 cm were taken using Teflon cutters (Table 8.1). Lourens et al. [1996b] demonstrated by astronomical tuning that the Vrica laminite and the ODP sapropels are age-equivalent and were deposited during precession cycle i-156. At Site 964 samples from this sapropel were not available, and the younger cycle i-152 (equivalent to Vrica laminite "p") was studied instead (Table 8.1).

All samples were transferred to the laboratory within a few days, where they were freeze-dried, after which subsamples were taken. These subsamples were powdered in an agate mortar, and subsequently used for geochemical analyses. After removing inorganic carbon with 1 M HCl, C$_{org}$ and remaining nitrogen (N$_{tot}$) contents were measured with a Fisons NA

<table>
<thead>
<tr>
<th>Site</th>
<th>Interval (cm)</th>
<th>Sapropel (cm)</th>
<th>Depth (m)</th>
<th>Sedimentation rate (cm/kyr)</th>
<th>Cycle</th>
<th>Age (Ma)</th>
<th>$\rho_{hom}$ (g cm$^{-3}$)</th>
<th>$\rho_{sap}$ (g cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vrica</td>
<td>0-755</td>
<td>519-575</td>
<td>500-800</td>
<td>20.85</td>
<td>i-156</td>
<td>1.603</td>
<td>2.1</td>
<td>2.1</td>
</tr>
<tr>
<td>160-964D-5-7</td>
<td>1-84</td>
<td>19-39</td>
<td>3660</td>
<td>2.05</td>
<td>i-152</td>
<td>1.564</td>
<td>1.3</td>
<td>1.0</td>
</tr>
<tr>
<td>160-969D-4-5</td>
<td>0-80</td>
<td>35-52</td>
<td>2192</td>
<td>2.69</td>
<td>i-152</td>
<td>1.603</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>160-967B-6-2</td>
<td>95-150</td>
<td>115.5-134</td>
<td>2555</td>
<td>2.91</td>
<td>i-156</td>
<td>1.603</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 Arbitrary top (0 cm) 519 cm above laminite "o"
2 Laminated interval for Vrica; interval enriched in C$_{org}$ extends between 438 and 620 cm
3 Estimated depositional water depth for Vrica [Colalongo et al., 1981]; current water depth for ODP sites
4 Calculated by dividing the cycle thickness by the duration of the accompanying astronomical cycle
5 Midpoint of the sapropel (Lourens et al. [1996b]; continuous model)
Comparison of coeval organic carbon rich sediments

$\rho_{\text{hom}}, \rho_{\text{sap}}$: dry bulk density of the homogeneous and sapropel (or laminated) intervals
NCS analyser. Stable carbon isotopes of organic matter ($^{13}$C$_{org}$) were determined with a Stable Isotope Ratio Analyser (VG SIRA 24), and are reported relative to the PeeDee Belemnite (PDB) standard. On the Vrica samples, the carbonate content was determined gas-volumetrically. For the ODP samples, the CaCO$_3$ content was calculated from the amount of inorganic carbon present (determined with the NCS analyser).

For major, minor and trace element analyses, a 250 mg sample was digested in 10 ml of a 6.5 : 2.5 : 1 mixture of HClO$_4$ (60%), HNO$_3$ (65%) and H$_2$O, and 10 ml HF (40%) at 90°C. After evaporation to dryness on a sand bath at 190°C, the residue was dissolved in 50 ml 1 M HCl. The resulting solutions were analysed with a Perkin Elmer Optima 3000 inductively coupled plasma atomic emission spectrometer (ICP-AES) for Al, Fe, K, Na, Mg, Sr, Ba, Mn, V, Mo, Cu, Ni, Zn, Cr, Ti and Y. In the ODP sapropel samples, Ba was determined separately in solutions prepared by the same procedure, but using only 40 mg sample to prevent BaSO$_4$ precipitation. On selected Vrica samples, As and Se were measured with a Perkin Elmer 3100 hydride Atomic Absorption Spectrometer (AAS), and Mo with a Perkin Elmer 4100 ZL ZGFAAS (AAS with Zeeman correction). From other selected samples of the Vrica section, pyrite was extracted following the methods in Passier et al. [1997], and analysed for its stable sulphur isotopic composition ($^{34}$S$_{pyr}$, reported relative to the Vienna-Canyon Diablo troilite) by means of combustion isotope ratio monitoring mass spectrometry (C-irmMS [Böttcher et al., 1998]). Opal was analysed on selected samples following the method of Müller and Schneider [1993], using a Technicon TRAACS 800 auto-analyser.

All results were checked with international and house standards. Relative standard deviations in duplicate C$_{org}$ and N$_{tot}$ measurements are <5%. The absolute standard deviation in $^{13}$C$_{org}$ and $^{34}$S$_{pyr}$ analyses are below 0.2‰ and 2‰, respectively. Relative standard deviations in duplicate measurements are <1% for carbonate analyses. ICP duplicate measurements have relative standard deviations <5% for all elements. Molybdenum, As and Se (Vrica) were measured in triplicate with a standard deviation of, respectively, <10%, <3%, and <10% for samples that contain more than 1 ppm Se.

**Results**

**Vrica**

Microscopic analysis of thin sections revealed that the laminites consists of 0.2-0.5 mm thick calcareous-clayey layers separated by 0.01-0.1 mm thick organic strands. Foraminifera shells are present in the clay layers, and are sometimes filled in by pyrite. In the laminated intervals, this pyrite occurs mainly in shells as 5-10 µm large framboids composed of crystals of ~0.5 µm in diameter. In more homogeneous intervals, pyrite occurs both as framboids (but unrelated to foraminifera shells), and as larger (ø 5-8 µm) euhedral crystals. $^{34}$S$_{pyr}$ ranges from -30.2 to -39.6‰ (Table 8.2). The red-brown intervals in the laminites are located around very thin (<1 mm) layers of fine-sand-sized, angular grains of plagioclase, amphibole and quartz, which are interpreted as volcanic ash deposits. Laminae are continuous around the ash layers, but
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appear darker in colour. Non-laminated intervals appear homogeneous, with some small organic strands or pyrite aggregates.

The background C\textsubscript{org} content of the sediments is 0.28%. Enrichment of C\textsubscript{org} in a 179 cm thick interval is indicated by a lightly shaded area (Fig. 8.2). Highest C\textsubscript{org} contents (up to 1%) are reached in the 56 cm thick laminite (indicated by dark shading in Fig. 8.2), located within the C\textsubscript{org}-enriched interval. In the laminite, red-brown intervals around the thin ash layers (indicated by horizontal lines in Fig. 8.2) are characterized by lower C\textsubscript{org} contents. The N\textsubscript{tot} profile (not shown) is virtually identical in shape to that of C\textsubscript{org}; N\textsubscript{tot} values range from 0.05 to 0.1%. C\textsubscript{org}/N\textsubscript{tot} and \textsuperscript{13}C\textsubscript{org} profiles show the same pattern (Fig. 8.3). Barium is shown relative to aluminium (Fig. 8.2) in order to correct for relative variations in detrital input. Ba/Al values are virtually constant except for some local spikes, especially in the laminite. No opal was detected in six selected samples coming from within and around the laminite. The carbonate content of the Vrica sediments (Fig. 8.4) is relatively low compared with most Mediterranean Neogene sections, namely approximately 23%, with even lower values (~18%) in the C\textsubscript{org}-enriched interval. Sr/Ca values (Fig. 8.5) are also lower in this interval, but higher again in the actual laminite. Because the carbonate content is rather low, most of the sediment consists of clays, which is confirmed by the high Al content (Fig. 8.4). The laminite contains less of other “terrestrial” elements (Fe, K, Mg, Na, Ti, Y and Zr) relative to Al than the homogeneous sediments (Table 8.3; Na/Al and K/Al shown graphically in Fig. 8.6), except for Fe/Al (Fig. 8.5), which is high in the C\textsubscript{org}-enriched interval. Redox-sensitive and chalcophilic trace elements (As, Cr, Cu, Mo, Ni, Se, V) are also high in this interval (relative to Al), but especially in the laminite (Ni/Al and V/Al shown as examples; Fig. 8.7). Manganese contents, on the other hand, are lower in the C\textsubscript{org}-enriched interval. Weathered samples only differ geochemically from their fresh equivalents by higher Na/Al and K/Al values (Fig. 8.6).

**ODP Sites**

Compared with the Vrica section, the ODP sapropels are characterized by substantially higher C\textsubscript{org} and N\textsubscript{tot} contents (up to 20% and 1.1%, respectively), sharper and larger changes in C\textsubscript{org}/N\textsubscript{tot} values, and a reversed pattern of the \textsuperscript{13}C\textsubscript{org} profile (Figs. 8.2 and 8.3; Table 8.4). Ba/Al is higher in the sapropels than in the homogeneous intervals (Fig. 8.2). Ash layers are not present except

<table>
<thead>
<tr>
<th>sample location (cm)</th>
<th>description</th>
<th>( \delta^{34} \text{S}_{\text{pyr}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>363</td>
<td>homogeneous sediment</td>
<td>-33.1</td>
</tr>
<tr>
<td>531</td>
<td>upper part laminite</td>
<td>-36.5</td>
</tr>
<tr>
<td>575</td>
<td>bottom laminite</td>
<td>-30.2</td>
</tr>
<tr>
<td>620</td>
<td>bottom C\textsubscript{org} enriched interval</td>
<td>-31.7</td>
</tr>
</tbody>
</table>
Table 8.3  Average Al contents and terrestrial element to Al ratios of homogeneous and sapropel (shaded) intervals of the Vrica section and the ODP sites.

<table>
<thead>
<tr>
<th>Site</th>
<th>Al</th>
<th>Fe/Al</th>
<th>K/Al</th>
<th>Mg/Al</th>
<th>Na/Al</th>
<th>Ti/Al (ppm/%)</th>
<th>Y/Al (ppm/%)</th>
<th>Zr/Al (ppm/%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vrica</td>
<td>7.42</td>
<td>0.51</td>
<td>0.29</td>
<td>0.22</td>
<td>0.12</td>
<td>561</td>
<td>2.96</td>
<td>12.8</td>
</tr>
<tr>
<td></td>
<td>7.74</td>
<td>0.55</td>
<td>0.27</td>
<td>0.22</td>
<td>0.10</td>
<td>528</td>
<td>2.70</td>
<td>11.5</td>
</tr>
<tr>
<td>969</td>
<td>3.58</td>
<td>0.55</td>
<td>0.32</td>
<td>0.45</td>
<td>0.31</td>
<td>609</td>
<td>5.04</td>
<td>17.6</td>
</tr>
<tr>
<td></td>
<td>2.99</td>
<td>1.06</td>
<td>0.32</td>
<td>0.55</td>
<td>0.62</td>
<td>548</td>
<td>9.01</td>
<td>23.0</td>
</tr>
<tr>
<td>967</td>
<td>4.74</td>
<td>0.68</td>
<td>0.23</td>
<td>0.29</td>
<td>0.23</td>
<td>714</td>
<td>4.39</td>
<td>19.4</td>
</tr>
<tr>
<td></td>
<td>5.08</td>
<td>1.27</td>
<td>0.21</td>
<td>0.32</td>
<td>0.29</td>
<td>632</td>
<td>4.78</td>
<td>19.3</td>
</tr>
</tbody>
</table>

at Site 967, just above the middle of the sapropel (indicated by a horizontal line in Figs. 8.2-4 and 8.7). The carbonate content varies between less than 1% in the sapropels to almost 70% in the homogeneous intervals (Fig. 8.4). The Al content of the ODP sediments varies inversely with CaCO$_3$ and is, with values between 2.3% and 6.5% (except for a maximum of 8.9% in the ash layer at Site 967), lower than in Vrica (Fig. 8.4; Table 8.3). With respect to Al, all terrestrial elements are higher in the sapropel (Table 8.3). Redox-sensitive trace element contents are considerably higher in the ODP sapropels than in the Vrica laminites (Fig. 8.7). The geochemistry of sapropel i-152 in ODP Site 964 is comparable to that of sapropel i-156 in Site 967 and 969 [Chapter 7]. Of the i-152 sapropel, only the $C_{org}/N_{tot}$ ratio and the $\delta^{13}C_{org}$ values are reported (Table 8.4).

Table 8.4  Average $C_{org}/N_{tot}$ and $\delta^{13}C_{org}$ values of homogeneous and sapropel (shaded) intervals of the Vrica section and the ODP sites. $C_{org}$ accumulation rates for these intervals calculated under the assumption that sedimentation rate did not change during deposition (not shown for Site 964). n.d.: no data

<table>
<thead>
<tr>
<th>Site</th>
<th>$C_{org}/N_{tot}$</th>
<th>$\delta^{13}C_{org}$ ($\‰$)</th>
<th>acc. rate $C_{org}$ (g m$^{-2}$ yr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vrica</td>
<td>5.8</td>
<td>-23.95</td>
<td>-23.67</td>
</tr>
<tr>
<td>964</td>
<td>5.5</td>
<td>-22.83</td>
<td>-23.21</td>
</tr>
<tr>
<td>969</td>
<td>3.0</td>
<td>-21.64</td>
<td>-22.11</td>
</tr>
<tr>
<td>967</td>
<td>4.7</td>
<td>-19.02</td>
<td>-20.70</td>
</tr>
</tbody>
</table>
Comparison of coeval organic carbon rich sediments
Figure 8.2  $C_{\text{org}}$ and Ba/Al versus depth profiles in Vrica, ODP Sites 969 and 967. For Vrica, light grey denotes the area enriched in $C_{\text{org}}$, dark grey the laminite. For the ODP sites, dark grey denotes the sapropel. Horizontal lines in Vrica and ODP Site 967 indicate the position of ash layers. The graphs have been arranged so that the bases of the $C_{\text{org}}$-enriched layers are aligned. The vertical axes have been scaled according to sedimentation rate: the three axes have equal length, representing 36,000 years. Note that the scale of the horizontal axes is different.
Figure 8.3  $C_{\text{org}}/N_{\text{tot}}$ and $\delta^{13}C_{\text{org}}$ versus depth profiles (like Fig. 8.2).
Figure 8.4  CaCO$_3$ and Al versus depth profiles (like Fig. 8.2).
Figure 8.5  Fe/Al, Mn/Al and Sr/Ca versus depth profiles in the Vrica section.
Chapter 8

Discussion

Marine sediments in a land section have been subject to a series of events that may have changed their initial composition with respect to their counterparts that have remained subaqueous. The processes involved are (1) uplift, dessication and compaction, (2) subsurface weathering and oxidation, and (3) erosion and subaerial weathering. These processes might be responsible for the differences observed between the Vrica and the ODP sediments. Alternatively, these differences may be original and result from dissimilar palaeoceanographic settings. This discussion will first deal with these aspects, and subsequently focus on implications for sapropel formation models.

Land section versus marine cores

1. Uplift, dessication and compaction - Marine sediments are compacted during the deposition of younger strata on the seafloor. During this process, marine pore waters are squeezed out of the sediment. When sediments are uplifted above sea level, original pore waters may be retained or exchanged for groundwater. The major element chemistry of the sediments will not change much as a direct result of such an exchange, but a change in pore water pH and Eh may affect the chemical reactions taking place during weathering. Uplift of sediments above groundwater level may result in further dessication and compaction. This is probably the reason for the observed dry bulk density difference between the ODP and Vrica sediments (Table 8.1).

2. Subsurface weathering and oxidation - Subsurface weathering can affect sediments deep in sections by percolation of oxidizing fluids along fault planes or other conductive areas. Studies investigating subsurface weathering mainly focused on changes that may occur in the organic matter fraction [e.g. Leythaeuser, 1973], but other changes, such as the dissolution of carbonates and oxidation of pyrites [e.g. Littke et al., 1991], and leaching and precipitation of iron/manganese oxides and associated trace elements [e.g. Van Os et al., 1996] have also been reported.

The laminite has a blue colour, except for the red-brown sediments a few centimetres directly above and below the ash-layers. This difference in colour suggests that oxidation of reduced iron (presumably as pyrite) to iron (hydr)oxides has taken place around the ash layers. Oxidation of organic matter is likely to have occurred as well. Indeed, the red-brown sediments around the ash layers have lower C$_{org}$/N$_{tot}$, $^{13}$C$_{org}$ and C$_{org}$/N$_{tot}$ values (Figs. 8.2,3), apparently resulting from subsurface weathering. The nature of these changes in C$_{org}$/N$_{tot}$ and $^{13}$C$_{org}$ values is consistent with data reported for subsurface weathering in a laminated interval in the Sicilian marls of the Narbone formation [Van Os et al., 1996], whereas the observed decrease in C$_{org}$/N$_{tot}$ ratio can also be expected upon organic matter oxidation because of the relative increase of inorganic N. Except for these differences, the bulk geochemistry of the red-brown sediments around the ash layers cannot be distinguished from the rest of the laminite.
Comparison of coeval organic carbon rich sediments

Subsurface weathering probably occurred around the ash layers because they are relatively course-grained and, therefore, more permeable for fluids. Laminated intervals may also provide a pathway for fluids, but the blue colour of the Vrica laminite indicates that the sediments still are in a reduced state. Littke et al. [1991] report that perhaps the most reliable indicator of weathering is the microscopic appearance of pyrite, since pyrites are easily oxidized and subsequently show dull, red-brown rims of iron(hydr)oxide. Our microscopic studies revealed that the pyrites in the laminated interval appear fresh, and are perfectly shaped cubes and framboids. Therefore, if oxidation of organic matter occurred in the laminite with respect to the homogeneous interval, it must have been by means of sulphate reduction (the sulphate being supplied by other fluids and in an earlier phase compared with oxidation around the ash layers). As a result of such subsurface weathering, $C_{org}$, $N_{tot}$, $^{13}C_{org}$ and $C_{org}/N_{tot}$ may have decreased in the laminite if the effect of oxidation is similar as observed in the red-brown sediments around the ash layers. Such changes cannot be inferred from a comparison with the homogeneous intervals, because these have been deposited under conditions dissimilar to those during laminite formation, and which may have led to very different (initial) values for these parameters. Therefore, a comparison is made with the ODP sapropels, which were not affected by subsurface weathering. The accumulation rates of $C_{org}$ (Table 8.4) and $N_{tot}$ in the Vrica laminite are higher than those in the ODP sapropels. $^{13}C_{org}$ values of the Vrica laminite are lighter than in the ODP sapropels (Table 8.4). However, in ODP sapropels...
Figure 8.6  Na and K/Al versus depth profiles in the Vrica section. "Fresh" samples (80 cm into the section) are indicated by solid dots, "slightly weathered" samples (40 cm from the edge of the outcrop) by open dots, and "strongly weathered" samples (edge of outcrop) by crosshairs.
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Figure 8.7 Profiles of Ni/Al and V/Al versus depth (like Fig. 8.2).
13C\textsubscript{org} values are more negative than in the over- and underlying homogeneous sediments (Fig. 8.3; Table 8.4), whereas in cycle i-152 in Vrica, the laminite has less negative 13C\textsubscript{org} values than the adjacent homogeneous intervals. If these 13C\textsubscript{org} values of the laminite in Vrica have decreased because of subsurface weathering, then the initial values would have been even less negative than they are now. This would contrast strongly with the shift to more negative values not only observed in the ODP sapropels, but also in the older laminite "h" of the Vrica section [Howell et al., 1988; Meyers, 1993]. Therefore, it is not likely that oxidation of organic matter in the Vrica laminite did occur with respect to the homogeneous intervals.

There are no indications that leaching and precipitation of iron/ manganese oxides has occurred in the Vrica section: no fronts of these elements such as observed in the Narbone marls [Van Os et al., 1996] have been found in the laminite. The one iron peak in the laminite (Fig. 8.5) correlates with sulphur and can be ascribed to iron sulphide occurrences. Although manganese contents are higher in the laminite (Fig. 8.5), no localized fronts are observed. The Sr content is higher in the laminite with respect to the sediments around it, even relative to Ca (Fig. 8.5) and Al. This is remarkable, since in the ODP cores Sr contents are lower in the sapropels than in the homogeneous sediments. Van Os et al. [1996] attribute high Sr contents in the Narbone marls to precipitation of celestite that formed as a result of oxidation of pyrite. In the Vrica sediments of this study, there are no indications for pyrite oxidation, and the Sr enrichment is cooccurring with Ca enrichments. This may indicate a relative increase in Sr-containing carbonates (such as aragonite).

We conclude that there is no evidence for substantial subsurface weathering in the Vrica section except around some thin ash layers in the laminite.

3. Erosion and subaerial weathering - Outcropping sediments are exposed to subaerial weathering, which may be effective up to a few metres into a section. Littke et al. [1991] did not find geochemical (organic matter content and composition; silicate, carbonate and sulphide content) differences between outcrop surface samples and samples taken 30 cm into the rock. Clayton and Swetland [1978] did find lower C\textsubscript{org} contents near the outcrop surface of the Phosphoria Formation, but no such change for the Pierre Shale.

The bulk geochemistry of the weathered samples from the Vrica laminite is not different from that of the fresh samples. The only exceptions are Na and K/ Al (Fig. 8.6), which are higher in samples closer to the edge of the outcrop. Similar observations have been made by Van der Weijden [1993], also in the Vrica section, and by Nijenhuis and Schenau [1994] for the Miocene Faneromeni section on Crete (Greece). This phenomenon can be explained by evaporation of water at the outcrop surface drawing pore fluids to the surface. When this water evaporates, the salt remains, enriching the sediment in Na, K, Mg, SO\textsubscript{4} and Cl. This is most clearly visible in the K and Na profiles, because the background content of the sediment is lowest for these elements. The strong visual difference between fresh (blue, immature clays) and weathered samples (grey/ beige, dry and hard sediments) is not reflected by other changes in bulk geochemistry. This is probably best explained by the relatively short aerial exposure of the sediments after the recent excavation of the building site. The short-term effect of
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subaerial weathering is apparently limited to physical changes (mainly further dessication of the sediments).

Near-coastal versus abyssal sites

Now that we have established that most differences between the ODP sapropels and the Vrica laminites are not due to uplift and weathering of the land section, we can explain them in terms of different environments and palaeoceanographic settings. There are four main differences: the Vrica section has been deposited (1) closer to land, (2) in shallower waters, (3) with a higher sedimentation rate, and (4) in a more western part of the eastern Mediterranean than the ODP sites (Table 8.1). We will discuss these four factors in relation to the observed geochemical differences.

The Al content (which is representative of the clay fraction) of the Vrica sediments is 150-250% higher than that of the ODP sediments (Table 8.3). A higher clay input is expected in a setting closer to land, but the difference in Al content between Vrica and the ODP sites is relatively small because the accumulation rate of carbonates is also higher than at ODP Sites 967 and 969. Ratios of "terrestrial" elements to Al are higher in ODP than in Vrica (Table 8.3). For Ti/Al and Zr/Al, this can be explained by a relatively higher fluviatile contribution in Vrica, and a more dominant aeolian input in the ODP sediments. The heavy mineral fraction, of which Ti and Zr are representative, is thought to be predominantly transported to marine sediments by wind [Boyle, 1983; Shimmield, 1992]. The higher Fe/Al values in the ODP sediments, especially in the laminites, are most likely explained by the presence of more pyrite in the latter. For other terrestrial elements, the lower abundance relative to Al in Vrica is remarkable. For example, sediments at Sites 964 (Fig. 8.1; western part of the eastern Mediterranean) and 969 are characterized by high K/Al and Mg/Al values (resulting from supply of illite by bottom currents from the Aegean and Adriatic Seas), whereas sediments at Sites 966 and 967 are more influenced by the Nile (supply of kaolinite and smectite), resulting in low K/Al and Mg/Al values [Wehausen and Brumsack, 1998; Chapter 7]. This east-west trend also applies to sapropel i-156 in ODP Sites 967 and 969, but the Vrica sediments do not show the expected higher K/Al and Mg/Al values. This is probably best explained by a different, local terrestrial source that influenced the Vrica sediments.

In the homogeneous intervals of the Vrica sediments, the Ba contents (Fig. 8.2) are about twice as high as in the ODP cores. In the laminites, however, the Ba content does not increase, whereas very high values (almost 2,200 ppm in Site 969) are reached in the ODP sapropels. Since Ba can be used as a palaeoproductivity indicator [Dehairs et al., 1980; Dymond et al., 1992], this suggests that productivity increased during sapropel formation at the ODP sites, but not during deposition of the laminites in the Vrica section. Bishop [1988] proposed a model in which barite precipitates in microenvironments containing decaying organic matter during transit from surface waters to the seafloor. As a result, barite may not be enriched in shallow highly productive areas, whereas it is increased in deeper sites with similar productivity [von Breymann et al., 1992]. This may explain the contrasting Ba contents in the
ODP sapropels and the Vrica laminite. Alternatively, the low Ba contents in Vrica may indicate that productivity was never high, or that barite was present but dissolved under conditions of sulphate reduction. Evidence that sulphate reduction did occur in the laminite comes from microtextures and sulphur isotopic values of pyrite, which are very similar to those reported by Passier et al. [1997] for the eastern Mediterranean Holocene S1 sapropel. This is indicative for pyrite forming during sulphate reduction in sediments still in contact with oxic or dysoxic seawater (“open system”). Under such conditions, barite may become undersaturated. Thus, Ba may become mobilized, and precipitate outside the zone of sulphatereduction [e.g. De Lange et al., 1994]. Such “mobilization peaks” may have escaped detection because they can be thinner than the sample resolution of 1-15 cm. 

\[ C_{\text{org}} \text{ accumulation rates are higher in Vrica than in the ODP sediments (Table 8.4). The flux of } C_{\text{org}} \text{ to the sediment is influenced by factors such as detrital (terrestrial) organic matter input, export productivity, water depth, sedimentation rate, and oxygen conditions of the water column. Both in Vrica and in the ODP cores, the homogeneous sediments were probably deposited under oxic conditions. This can be inferred from the absence of laminae and the low redox-sensitive and chalcophilic trace element contents. Therefore, we can use an equation relating } C_{\text{org}} \text{ flux to productivity, water depth and sedimentation rate to estimate the effects of these factors on the differences in sedimentary } C_{\text{org}} \text{ content between Vrica and the ODP sediments. The basic formula of Sarnthein et al. [1992] will serve for the calculations:} \]

\[ P_{\text{exp}} = 9.354 C_{\text{A}}^{0.493} S_{\text{B-C}}^{-0.105} z^{0.300} \]

in which \( P_{\text{exp}} \) is the export productivity in \( \text{gC m}^{-2}\text{yr}^{-1} \), \( C_{\text{A}} \) the \( C_{\text{org}} \) accumulation rate (\( \text{g m}^{-2}\text{yr}^{-1} \)), \( S_{\text{B-C}} \) the \( C_{\text{org}} \) free sedimentation rate (in \( \text{g m}^{-2}\text{yr}^{-1} \)), and \( z \) the water depth in metres. For the homogeneous ODP sediments this gives an export productivity of 19.3 gC m² yr⁻¹ (average of both sites). If we assume that the export productivity for the Vrica sediments was comparable, we obtain an accumulation rate of 0.16 gC m² yr⁻¹ for these sediments, whereas the actual value is 1.51 gC m² yr⁻¹ (Table 8.4). Thus, the fact that \( C_{\text{org}} \) accumulation rates are higher in the Vrica sediments than in the ODP cores can only for a small part be attributed to the differences in water depth and sedimentation rate. The largest part of the difference must be due to higher productivity and/or higher terrestrial organic matter input at Vrica. The latter factor is often constrained by using \( ^{13}C_{\text{org}} \) and C/ N values as indicators for terrestrial/ marine

\[ ^{13}C_{\text{org}} \text{ accumulation rates} \]

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\[ ^{13}C_{\text{org}} \text{ accumulation rates} \]
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organic matter [e.g. Jasper and Gagosian, 1990; Tyson, 1995]. However, a simple two end-member mixing model with terrestrial organic matter characterized by high C/N and light $^{13}$C$_{org}$ values, and marine organic matter characterized by low C/N and heavy $^{13}$C$_{org}$ values, does not seem to apply in the eastern Mediterranean [Chapter 7]. There is, however, a distinct east-west trend in $^{13}$C$_{org}$ values in the eastern Mediterranean, with lighter values in the west and heavier values in the east [Chapter 7]. This may explain why $^{13}$C$_{org}$ values are lower in Vrica than in the more eastern ODP cores. Consequently, we cannot determine the relative proportions of terrestrial and marine organic matter in Vrica and in ODP Sites 967/969 using these parameters. Organic geochemical research, however, indicates that in both settings the major portion of organic matter is of marine origin [Meyers, 1993; Bosch et al., 1998].

The high contents of redox-sensitive trace elements in the abyssal ODP sapropels have been explained by effective scavenging from an anoxic water column by sulphides and organic matter [Nijenhuis et al., 1998]. Trace element accumulation rates in Vrica are higher, but the trace element to Al ratios are lower, especially in the sapropels. This may be the result of the shallower water depth, because higher amounts of trace elements can be scavenged from a larger water column. Alternatively, anoxic conditions were more restricted at Vrica than at the ODP sites. In addition, a signal of trace elements scavenged from the water column will be more diluted in the Vrica section because of the higher sedimentation rate.

Concluding, the differences in the geochemistry of cycle 1-156 in Vrica and ODP Site 967/969 can partly be explained by the different settings. In Vrica, both the clay and carbonate input are higher than at the ODP sites. The clay fraction is more dominant in the near-coastal Vrica sediments, resulting in higher Al contents than in the open marine ODP sediments of this study. Lower Ti/Al and Zr/Al ratios indicate a stronger fluvial relative to aeolian input throughout the Vrica section compared with the ODP sediments. The shallower water depth may partly explain the lower trace element to aluminium ratios and higher homogeneous C$_{org}$ accumulation rates in the Vrica section, but factors like water column oxygen level and productivity are thought to have been more important.

Palaeoceanographic implications

Productivity versus preservation - Since the Crotone-Spartivento Basin in which the Vrica section was deposited had an open connection with the Ionian Sea in the early Pleistocene [e.g. Moretti, 1993], laminite deposition in this basin and sapropel deposition in the eastern Mediterranean should be explained in one model. Schenau et al. [1999] (Chapter 3) suggest one basic model for eastern Mediterranean sapropel formation since the middle Miocene: at times of precession minima (Northern Hemisphere insolation maxima) enhanced continental runoff and Atlantic-born depression activity lead to increased productivity and reduced water circulation, the combination of the latter two resulting in reduced bottom water oxygen levels. The intensity of productivity, dilution and diagenesis will vary with time and place, depending on factors like proximity to land, depositional environment, intensity of the astronomical forcing, etc. For the Plio-Pleistocene sapropels recovered by ODP, it was shown that both productivity and
preservation were strongly enhanced [Chapter 7]. In contrast, the Vrica laminites were thought to have formed as a result of improved preservation, not of increased productivity [Howell et al., 1988; Meyers, 1993; V an der Weijden, 1993]. However, the planktonic fauna of Vrica laminites "o" is characterized by an increase in Neogloboquadrina sp. [Spaak, 1983; Howell et al., 1990; Lourens, 1994]. This foraminifera species is often linked to eutrophic conditions [Tolderlund and Bé, 1971; Howell et al., 1990; Thunell and Sautter, 1992]. The uniform occurrence of increased Neogloboquadrina abundance in Miocene to Pliocene sapropels is, therefore, interpreted as an indication of higher productivity during their formation [Schenau et al., 1999 (Chapter 3)]. Thus, productivity may have been an important factor in the formation of the Vrica laminites as well. Evidence for higher productivity in the ODP sapropels comes from the very high C$_{org}$ accumulation rates, Ba contents, and the presence of opal in some sapropels [Chapter 7]. Opal is not found in all sapropels: it is prone to dissolution since both seawater and sedimentary pore waters are usually undersaturated with respect to silica. Barium is a useful palaeoproductivity indicator, but as we have indicated before it may not be enriched in shallow sediments. The absence of opal and Ba enrichments in the Vrica laminites, therefore, does not exclude high productivity during its formation. There is no direct evidence that palaeoproductivity was not increased during the formation of laminites "o" in Vrica, so the model proposed for the abyssal sapropels can be extended to the shallower environments. The observed enrichment in redox-sensitive and chalcophilic trace elements, the absence of benthic foraminifera [Howell et al., 1990; Lourens, 1994], the indications for sulphate reduction and the presence of pyrite in the laminites, added to the preservation of the laminae themselves, confirm that the oxic-anoxic interface was located at a shallower depth in the sediment, or perhaps even in the water column during formation of laminites "o" and of the ODP sapropels [Chapter 7]. Preservation of laminae and high redox-sensitive trace element contents do not occur outside the laminites. The C$_{org}$-rich interval around the laminites, then, may have resulted mainly from increased productivity, whereas anoxic (bottom) water conditions and associated improved preservation of organic matter resulted in laminites deposition. This seems to support the idea that anoxia developed as a result of increased productivity in the Plio-Pleistocene sapropels [Passier et al., in press (Chapter 5); Chapter 7].

**Duration of sapropel and laminites formation** - Is the period of sapropel formation comparable to laminites duration? It has been suggested that sedimentation rates did not change much during Plio-Pleistocene sapropel formation [Chapter 7]. An indication that this might also be the case in the Vrica section comes from the thickness of the laminae (0.2-0.5 mm). If we assume that each lamina represents a year (varve-like sedimentation), the 56 cm thick laminites would have been deposited in 1,100 to 2,800 years. The 2,700 years obtained by simply dividing the laminites thickness by the average sedimentation rate of one precession cycle is within this range. Both ODP sapropels were formed in about 6,300 years [Chapter 7], i.e. a considerably longer period. However, the C$_{org}$-rich interval in the Vrica section represents 8,700 years. Thus, the laminites was deposited in a considerably shorter period than the sapropels, but the
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$C_{\text{org}}$ enriched interval lasted longer, if indeed sedimentation rate did not change during sapropel and laminite formation.

The discrepancy between the abyssal and near-coastal sites may indicate that anoxia was limited to deep water most of the time, and only reached the shallow areas of Vrica part of the time (namely in the period of laminite deposition). However, the decrease of the terrestrial element to Al ratios in the laminite, which do not occur in the sapropels, suggests an additional change, namely that in terrestrial influence. This may be a local variation in the Crotone-Spartivento basin. Indeed, the large and frequent variations of many parameters in the laminite indicate that the Vrica section was deposited in a dynamic environment that changed from year to year, whereas the abyssal sapropels formed in a more constant, stable environment.

Conclusions

The insolation maximum of cycle i-156 is expressed by a sapropel in ODP Sites 967 and 969, and by a laminite in the Vrica section. There is a strong difference in the geochemistry of the land section on the one hand, and the marine sediments on the other hand. Uplift, dessication, weathering and erosion of the marine sediments in the Vrica section resulted in a higher dry bulk density, oxidation of $C_{\text{org}}$ and an associated decrease in $N_{\text{tot}}, C_{\text{org}}/N_{\text{tot}}$, and $^{13}C_{\text{org}}$ values in intervals along conductive planes, and in salt precipitation near the outcrop surface. Other differences between the Vrica section and the ODP sites are the result of different palaeoceanographic settings. A relatively stronger river input in the Vrica section resulted in higher clay content and lower Ti/Al and Zr/Al values. Shallower water depth may account for the low Ba/Al values in Vrica, and partly for the lower trace element to Al ratios and higher $C_{\text{org}}$ accumulation rates. Lower $^{13}C_{\text{org}}$ values in Vrica than in the ODP sediments are coherent with the east-west trend of this parameter in the eastern Mediterranean. The formation of laminite "o" in the Vrica section is thought to be not only a preservation event, but also the result of increased productivity. Therefore, our results for the Vrica section fit in the general model for sapropel formation in the eastern Mediterranean.

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