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DISTRIBUTION OF CARBONATE AND ORGANIC CARBON CONTENTS IN LATE QUATERNARY SEDIMENTS OF THE SOUTHERN MARMARA SHELF

GÜNEY MARMARA ŞELFİNİN GEÇ KUVATERNER ÇÖKELLERİNDE KARBONAT VE ORGANİK KARBON DAĞILIMI

M. NAMIK ÇAĞATAY, OYA ALGAN, NURAY BALKIS AND MEHMET BALKIS

Institute of Marine Sciences and Management, University of Istanbul

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Abstract

A total of 165 surface and 81 core samples from four gravity cores were analyzed for their total carbonate and organic carbon contents. The sediments are generally low in carbonate content (<10% $CaCO_3$) along the inner shelf. Relatively higher values (>10% $CaCO_3$) are found on the outer shelf to the north, along a belt extending from the Bozburun Peninsula to west of Marmara Island. Patches of >20% $CaCO_3$ values occur between the İmralı Island and Bozburun Peninsula, NE of the Kapıdağ Peninsula, and in a belt extending west from the Kapıdağ Peninsula, through the Avşa Island to Karabiga. The high carbonate areas generally correspond to the sandy sediments with high contents of shell material.

Total organic carbon content of the surface sediments ranges from 0.10-2.50%, with the high values being located in shallow areas along the coast and decreasing values occurring in the offshore direction. This distribution pattern suggests that the organic-carbon matter is mainly of terrestrial origin.

Depth profiles of organic carbon values along the core samples indicate the presence of a sapropel layer in two cores (No.22 and 13) in the Gemlik Gulf. The highest carbonate (8-12% $CaCO_3$) and organic carbon values (1.7-2.11%) are found in a phosphorescent green, plastic, clayey sapropelic mud horizon at a depth ranging from 1.75 to 2.15 m. This layer is enriched in planktonic foraminifera but depleted in benthic foraminifera species, suggesting both the high surface organic productivity and bottom unoxic conditions. It was probably

deposited following the Holocene transgression during a pluival period when increased quantities of nutrients were supplied by rivers into the Sea of Marmara and when water stratification was established. Radiometric carbon, organic and isotope geochemical studies are in progress on this layer.

Introduction

Carbonate minerals and organic matter are the important components of sediments and sedimentary rocks, and thus, play a significant role in the major- and trace-element geochemisty of these deposits. Total carbonate content of sediments depend on the amount of carbonate minerals that may be present in biogenic and lithogenic forms. Except for a few trace elements, such as Sr and Ba, the carbonate minerals in sediments have a diluting effect on the concentrations of most trace elements. On the other hand organic-carbon material is significant in adsorbtion, transportation and deposition of many trace elements, and therefore, acts as a concentrator. Organic-carbon content of marine sediments depends on the primary organic productivity, rate of sedimentation, grain size and composition of the matrix material, oxygen content and depth of water column, and on the amount of land- and marine-based organic pollutants (Müller and Suess, 1979; Demaison and Moore, 1980; Thunell et al., 1989; Pederson and Calvert, 1990; Calvert et al., 1992). Therefore, the vertical distribution profiles of organic carbon contents in marine sediments, together with other geochemical and paleontological evidence, could provide important clues about the paleo-oceanographic conditions.

Being an intracontinental sea on a waterway between the Mediterranean Sea and Black Sea, the sediments of the sea of Marmara are believed to have been a rather sensitive recorder of climatic, biological and chemical changes and water-mass movements in the region. In this paper, we discuss the distribution of the total-carbonate and organic-carbon contents in surface sediment samples and four gravity cores from the southern shelf of the Sea of Marmara (Fig. 1). Three of the cores are located in the Gulf of Gemlik and one core on the central part of the inner southern shelf.

This work is a part of a comprehensive geochemical programme undertaken by the Institute of Marine Sciences and Management (IMSM-IU) on the Late Quaternary sediments of the Sea of Marmara, which is itself part of the TÜBİTAK YDABÇAG 241/G project being carried out under the National Marine Geological and Geophysical Programme. Reconstruction of the Late Quaternary history of the Sea of Marmara is the main objective of the geochemical studies. More specific objectives of this part of this geochemical study are the reconstruction of the paleo-oceanographic conditions and the timing of the water-mass exchanges between the Sea of Marmara, Black Sea and the Aegean sea via the straits of İstanbul and Çanakkale (Dardanelles) (e.g., see Stanley and Blanpied, 1980).

Present-day Oceanography of the Sea of Marmara

The Sea of Marmara is an intra-continental basin between Thrace and Anatolia, having an east-west length of about 210 km and a width of 75 km. It has a relatively broad shelf (40 km) in the south and a narrow one (10 km) in the north. In between these shelves are a serious of deep basins having a maximum depth of 1265 m. The shelf break is located at depth of about 110 m. The Marmara Sea is connected to the Brackish Black Sea in the northeast via the Istanbul Strait (Bosphorus) and to the saline Aegean sea in the southwest via the Canakkale Strait (Dardanelles). This results in a permanent two-layer flow system with a halocline at a depth of 20-25 m (Ünlüata et al. 1990). The stratification of the water column, together with the topographic restriction of the two straits, prevents the efficient circulation of the sub-halocline layer. As a result, the dissolved oxygen content of the bottom waters decrease by microbial oxidation of organic matter from 7-10 mg/l near Çanakkale Strait towards east to about 1 mg/l above the deep basins and 2.5-5 mg/l near the Istanbul Strait (Ünlüata and Özsoy, 1986).

In terms of primary production, the sea of Marmara is intermediate between the Black Sea and the Aegean Sea, with values of 60-160 gCm^{-2} $year^{-1}$ (Yılmaz, 1986; Ergin 1993); the highest velues being located in the inner southen shelf. The main phytoplanktons contributing to the primary productivity are diatoms and dinoflagellate (Ünsal and Uysal, 1988).

The only major rivers flowing into the Sea of Marmara are from the south. These are the Biga, Gönen and Kocasu rivers that are responsible for high input of nutrients and alloctonous organic matter to the southern shelf.

Sampling and Analytical Methods

The samples were collected by using a grab and a gravity corer on board the R/V Seismic-1 of the General Directorate of the Mineral Research and Exploration (MTA) during August 1995. The grab samples represent the top 15-20 cm of the recent sediment column, which may show colour and textural change with depth in some stations. Such grab samples were further subsampled as surface and subsurface for the purposes of studying the changes in the metal concentrations during the early diagenesis. The gravity cores were sampled at a density of about 1 sample per 10 cm of core depth, based on lithological variation.

A total of 165 surface and 65 core samples from four stations (no.1, 13, 22, and 88; Fig. 1) were analyzed for their total carbonate and organic carbon contents. Total carbonate contents were determined by a gasometric-volumetric method after a 4M HCl treatment (Loring ve Rantala, 1992). Organic carbon contents were analyzed by the Walkey-Blake method, which involves the titration with ferrous aluminium sulphate of the dichromate left after a wet combustion of the sample with potassium dichromate (Gaudette, 1974; Loring ve Rantala, 1992).

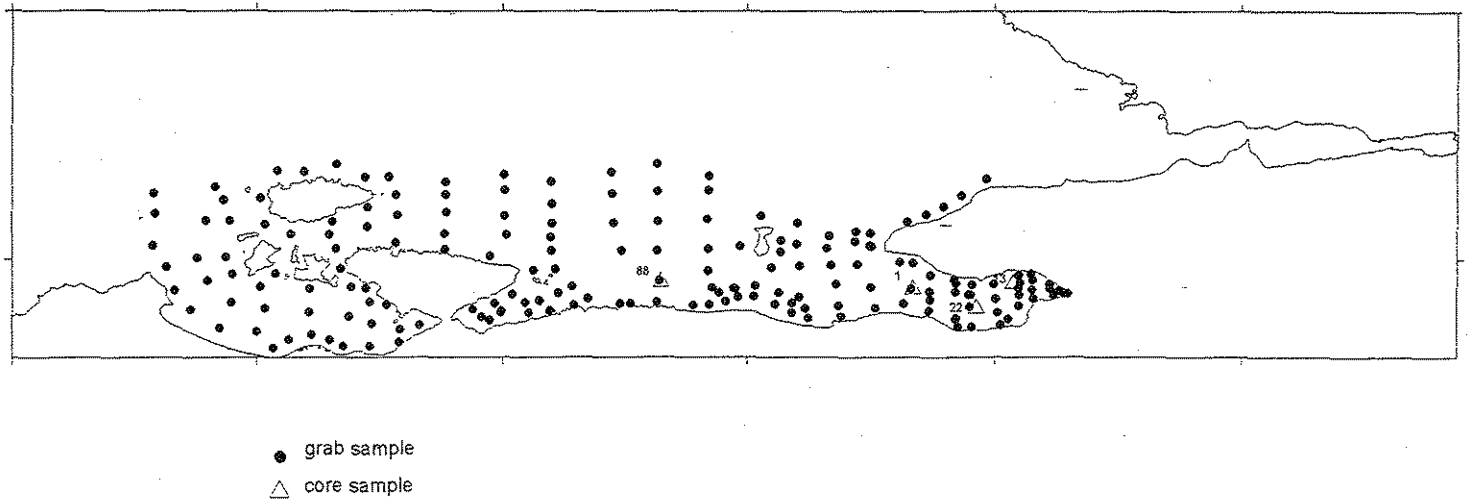

Figure 1 : Grab and core sample locations on the southern shelf of the Sea of Marmara.

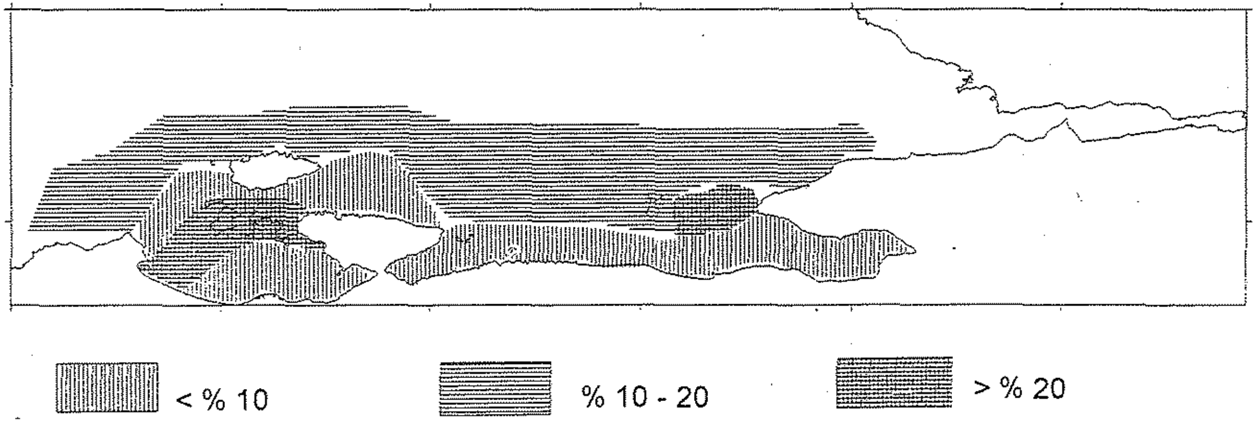

Figure 2 : Total carbonate content (as % CaCO3) distribution of surface sediments from the southern shelf of the Sea of Marmara.

The organic-carbon content of the surficial sediments averages 1.2% and ranges between 0.1% and 2.5% (Table 1). The high values (>2%) being located in a narrow band along the shore, with gradually decreasing values occurring towards the outer shelf (Fig. 3).

The average annual primary organic production rates, as calculated from chlorophyll-a measurements, are 161 $gCm^{-2}year^{-1}$ for the inner southern shelf, 107 $gCm^{-2}year^{-1}$ for the outer southern shelf, and 64 $gCm^{-2}year^{-1}$ for the Erdek Bay (Ergin et al., 1993). As these autors have indicated and as seen from the results of the present study, there is no direct relationship between the distribution of the primary organic production rates and the organic carbon distribution in the sediments of the study area. The anticipated relationship may have been complicated by the allochtonous organic matter supplied by rivers, variable oxidation state of the bottom waters on the shelf, or by grazing activity of organisms. The distribution pattern of the organic carbon values shown in Fig. 3 suggests that the organic matter in the sediments of the inner southern Marmara shelf is mainly of allochtonous organic origin supplied mostly by the major riverine input from the south.

Total carbonate and Organic Carbon Distributions in Sediment Cores

The three sediment gravity cores (Numbers 1,13 and 22; see Fig. 1 for locations) from the Gulf of Gemlik are up to 2.60 cm long, and consists of various tints of brown, gray and green, texturally homogeneous, plastic, clayey muds (Figs. 4, 6, and 7). They locally contain some benthic shells and plant debris. Approximately the top 10 cm parts of the cores No. 1 and No.22 show various tints of brown and represents the oxidation zone. The lower parts with different tones of green and gray mark the reducing zones. In core 13 the oxidation zone is about 30 cm long.

The total carbonate and organic carbon contents of the core samples vary between 7.6-12.6% $CaCO_3$ and between 0.2-2.4%, respectively (Figs. 4, 5, 6 and 7). In Core No. 1 the total carbonate and organic-carbon contents show an increasing tren with depth (Fig. 4). In core 88 located in the central inner shelf area (Fig. 5) total carbonate values range between 5.75-9.75% $CaCO_3$ and organic carbon values between 0.70-1.50 %. The highest organic carbon values are located at a core depth of about 100 cm. In Core No. 13, the highest carbonate (12.55% $CaCO_3$) and organic carbon (1.7%) values are found in a phosphorescent green, plastic, clayey mud horizon at a depth of 1.75-1.93 m (Fig. 6).

The organic carbon values in Core No. 22 varies from 0.70 to 2.41%, with the highest values being found in the phosphorescent green to brownish grey-green, plastic, hemi-pelagic, clayey mud at a depth interval of 1.75-2.15 m (Fig. 7). The organic-carbon rich levels of this core is enriched in planktonic foraminifera species of Meditterranean affinity and rather depleted in benthic foraminifera species (Sakınç, pers. communication); the most abundant planktonic foraminifera species include *Globigerina calida Parker, Globigerina rubra* d'Orbigny, *Globigerina ruber* (d'Orbigny) and *Orbiluna universal* d'Orbigny. This enrichment

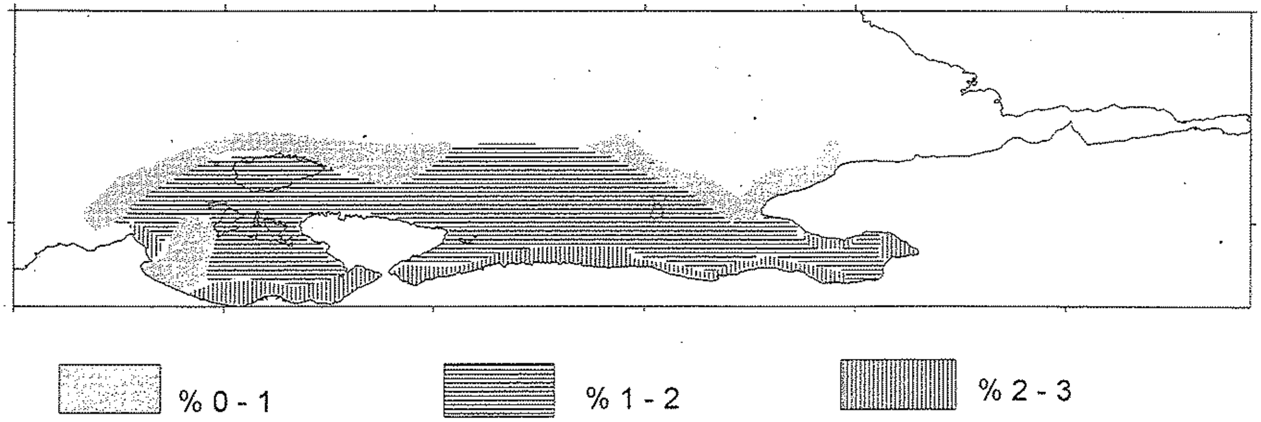

Figure 3 : Organic carbon (%) content distribution of surface sediments from the southern shelf of the Sea of Marmara.

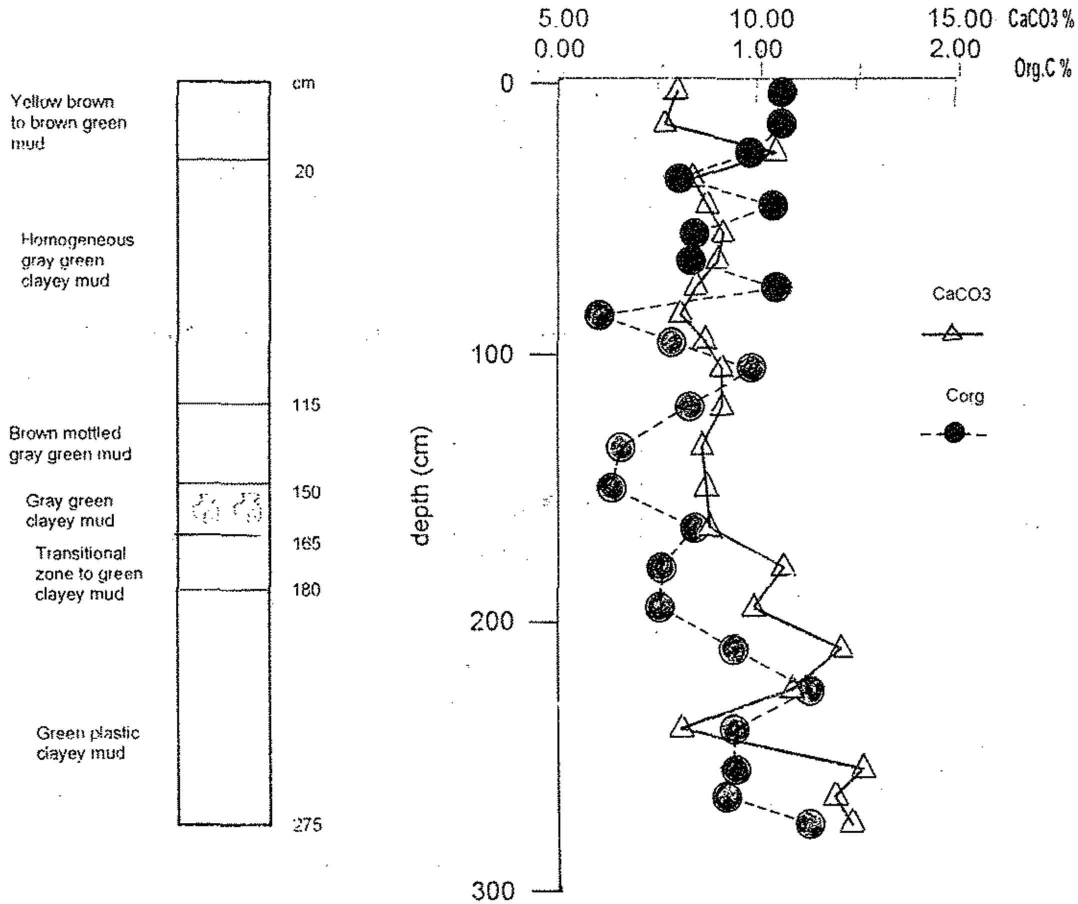

Figure 4 : Vertical distributions of CaCO3 (%) and organic carbon (&) contents in core 1 from Gemlik Gulf.

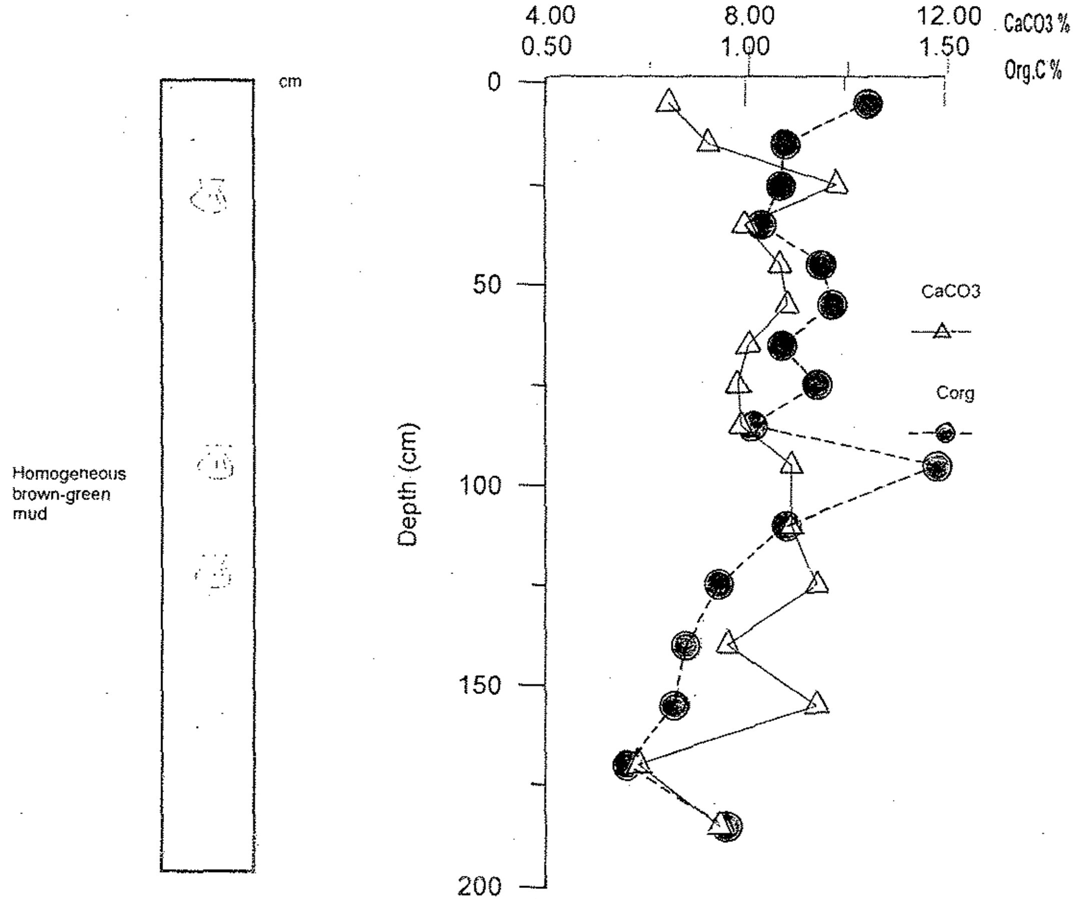

Figure 5 : Vertical distributions of CaCO3 (%) and organic carbon (%) contents in core 88.

in the planktonic foramininfera suggests increased primary organic productivity during the deposition of the organic-rich layer. Scarcity of the benthic forms, together with high content of pyrite suggests anoxic bottom-water conditions.

Marine sediments containing greater than 2% and 0.5% organic carbon are known repectively as 'sapropel' and 'sapropelic' sediments (Kidd et al., 1978). Accordingly the the organic-carbon-rich horizons especially in Cores Nos. 13 and 22 can be classified as sapropel and sapropelic sediments. The critical requirements for the deposition of such organic-rich sediments are some combination of (1) increased surface-water productivity, (2) restricted bottom water circulation, and (3) anoxic bottom-water circulation (Demaison and Moore, 1980; Schrader and Maderne, 1981; Calvert, 1983; Thunnel and Williams, 1989; Pederson and Calvert, 1990; Calvert et al, 1992). Establishment of these conditions may in turn be related to climatic control. These organic-rich sediments, are therefore, important indicators of paleoenvironmental conditions.

With their relatively low organic-carbon contents and phosphorescent green-gray colors and textural appearance the newly discovered Marmara sapropels show many similarities with descriptions of the Mediterranean sapropels (Stanley et al., 1975; Cita et al., 1977; Calvert, 1983; Shaw and Evans, 1984; Anastasakis and Stanley, 1984; Calvert et al., 1992; Rohling, 1994; Emeis et al., 1996). About 12 sapropel horizons have been formed in the eastern Mediterranean in the past 400 ka (Cita et al., 1977). The youngest of the sapropel layers (S1) formed between 8300-6300 a B.P., according to AMS ^{14}C datings (Jorisson, et al., 1993; Rohling, 1994). The Black Sea sapropel is about 30 cm-thick and formed between about 7000-3000 a B.P. (Degens and Ross, 1974; Calvert, 1990).

It is highly possible that the Marmara sapropel formed following the Holocene transgression. The present geochemical study and the preliminary micropaleontological data (M. Sakınç, pers. communication) presented above indicate that the sapropel was deposited during a period of high organic productivity and bottom water anoxia. These conditions were established, probably by high input of fresh waters during.a pluvial period.

Geochemical studies have been initiated to date the sapropel horizon by a radiocarbon method and to characterize the organic matter making up the sapropelic layers by organic, inorganic and isotope geochemical methods. It is anticipated that these studies will contribute to a better understanding of the Late Quaternary paleo-oceanographic history of the Sea of Marmara by correlation of these sapropels with those in the Aegean Sea and the Black Sea and by establishing the water-mass exchange between them via the straits of Dardanelles and Bosphorus.

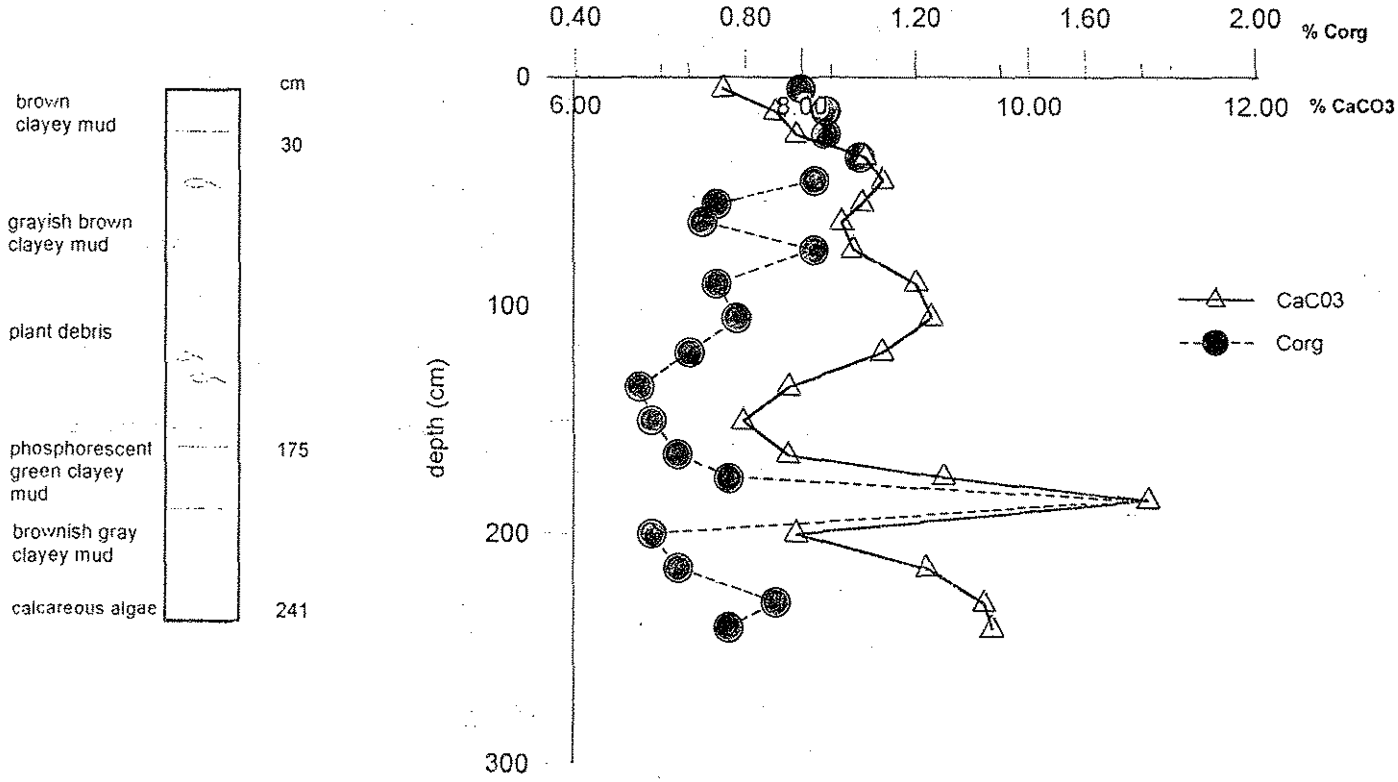

Figure 6 : Vertical distributions of CaCO3 (%) and organic carbon (%) contents in the core 13 from Gemlik Gulf.

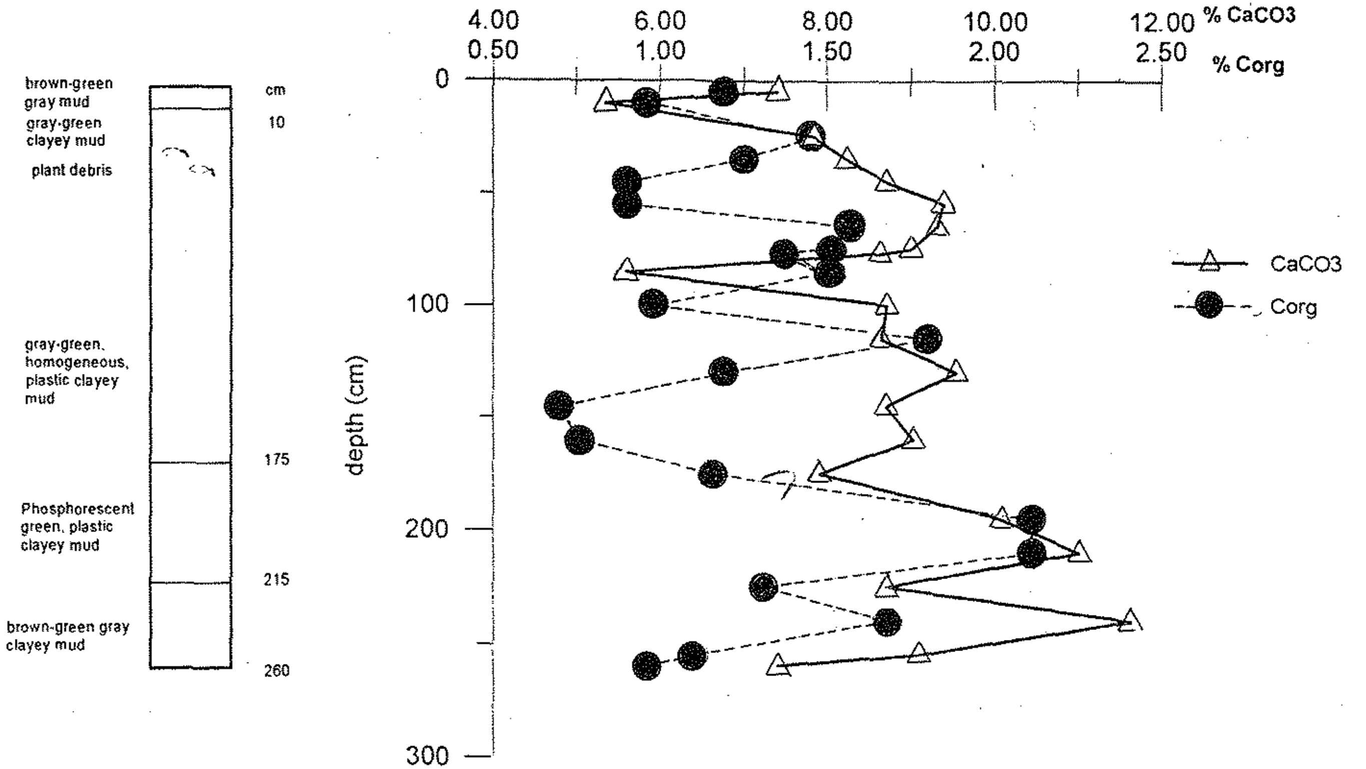

Figure 7 : Vertical distributions of CaCO3 (%) and organic carbon (%) contents in core 22 from Gemlik Gulf.

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Özet

Marmara Denizi'nin güney şelfinden 165 yüzey ve dört karottan 81 sediment örneğinin toplam karbonat ve organik karbon analizleri yapılmıştır. İç şelf bölgesi sedimentlerinin karbonat içerikleri genellikle düşüktür (<%10 $CaCO_3$). Daha yüksek karbonat değerleri (>%10 $CaCO_3$), Bozburun Yarımadası'ndan batıya uzanan dış şelf bölgesinde izlenmiştir. %20'den daha yüksek $CaCO_3$ değerleri İmralı adası ile Bozburun Yarımadası arasında, Kapıdağ Yarımadası KD'sunda ve aynı yarımadadan Avşa Adası ve Karabiga'ya uzanan bir koridor boyunca bulunmuştur. Yüksek karbonat içerikli alanlar çoğunlukla kavkılı, kumlu sedimentlerin bulunduğu alanları temsil etmektedir.

Yüzey sedimentlerinin organik karbon içerikleri %0.10 ile %2.50 arasında değişir. Yüksek değerler kıyı boyunca dar bir şeritte görülmüştür. Kıyı açıklarına doğru değerlerde bir azalma izlenir. Bu dağılım şekli güney şelfi yüzey sedimentinde organik maddenin kökenin büyük ölçüde karasal olduğunu göstermektedir.

Organik madde değerlerinin iki karot (No.22 and 13) uzunluğu boyunca değişen profilleri 1.75-2.15 m karot derinliğinde bir sapropel tabakasının varlığını göstermiştir. En yüksek karbonat (%8-12 $CaCO_3$) ve organik karbon (%1.7-2.11) değerleri fosforlu yeşil renkteki plastik killi çamur özelliğindeki sapropelli seviyede bulunmuştur. Bu sapropel seviyesi zengin bir planktonik foraminifer ve çok fakir bir bentik foraminifer faunası içermektedir. Zengin planktonik foraminifer faunasının varlığı yüksek organik üretime; fakir bentik foraminifer faunası ise anoksik dip suyu koşullarının varlığına işaret etmektedir. Adı geçen sapropel tabakasının olasılıkla Holosen transgresyonunu izleyen yağışlı bir iklimde, nehir besin girdilerinin ve su tabakalanmasının oluştuğu koşullarda çökeldiği düşünülmektedir. Bu birim üzerinde radyometrik karbon yöntemi ile yaşlandırma, organik ve izotop jeokimyası çalışmaları devam etmektedir.

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