Sedimentology and geochemistry of surface sediments in a semi-enclosed marine area. Central Aegean-Greece



Sediment Geochemistry Central Aegean Shallow water Factor analysis

Sédiment Géochimie Mer Egée centrale Eau côtière Analyse factorielle

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ABSTRACT

A suite of 68 surface sediment samples from the South Evvoikos (SEG), North Petalion (NPG) and South Petalion (SPG) gulfs was analysed for grain size, mineralogy, major and minor elements in the bulk sample and the $< 2 \mu m$ fraction. Grain size analysis distinguished two sedimentary provinces: i) SEG with fine grained sediments; and ii) NPG, SPG dominated by relict sandy sediments. Abundant minerals are quartz, feldspars, calcite and Mg-calcite. Heavy minerals identified were epidote, hornblende, zircon and glaucophane. Factor analysis revealed that chemical elements of the total sample are mainly of terrigenous origin, supplied by the Asopos river, which discharges in SEG. The southern part is dominated by residual Si and biogenic components. Metals are generally present in low concentrations. Igeo index computation for the trace elements indicated relatively high concentrations of Ni and Cr in the SEG area, which are in all probability related to the erosion of laterite formations and ultramafic rocks.

RÉSUMÉ

Sédimentologie et géochimie des sédiments superficiels dans un bassin semi-fermé de la mer Egée.

Une série de 68 échantillons de sédiments superficiels, prélevés en mer Egée dans les golfes sud d'Eubée (GSE), nord de Pétalioi (GNP) et sud de Pétalioi (GSP), a été analysée en termes de granulométrie, minéralogie, éléments majeurs et mineurs dans l'échantillon brut et dans la fraction de taille inférieure à deux micromètres. La granulométrie conduit à distinguer deux domaines sédimentaires: 1) GSE avec des sédiments de grain fin et 2) GNP, GSP à dominante de reliquats sableux correspondant à des dépôts de l'époque würmienne. Les minéraux les plus abondants sont le quartz, le feldspath, la calcite et la Mgcalcite. Les minéraux lourds identifiés sont l'épidote, la hornblende, le zircon et le glaucophane. L'analyse factorielle révèle que les éléments chimiques de l'échantillon brut sont essentiellement terrigènes, charriés par le fleuve Asopos qui les dépose dans le GSE. La partie sud est dominée par la silice détritique et par des composants biogènes. Les métaux-traces sont généralement présents à faibles concentrations. L'indice de calcul I_{geo} pour les métaux-traces indique des concentrations fortes en Ni et Cr dans la région GSE; ces concentrations élevées sont vraisemblablement liées à l'érosion des formations latéritiques et des roches ultramafiques qui affleurent en Eubée centrale.

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INTRODUCTION

The area under investigation (Fig. 1) is located between the Attica mainland, Evvoia island and the North Kyklades islands. It has three parts: i) South Evvoikos Gulf (SEG); ii) North Petalion Gulf (NPG); and iii) South Petalion Gulf (SPG).



Figure 1

Location of the study area, surface sediment sampling stations and ultramafic rock outcrops.

Both the coastal zone and the marine area are of high interest, since over the past 10-20 years this region has seen the expansion of tourism, especially for the inhabitants of the neighbouring capital –Athens. Therefore, a detailed geochemical investigation is important for the determination of the physical processes which control chemical element distribution, together with the examination of possible pollution problems. This initial identification of the sediment geochemical characteristics could be regarded as a reference point, while increased urbanization is expected in the near future and the human impact on the coastal-marine environment will be reinforced.

Geographical and oceanographic setting

The studied area is a part of a post-alpine basin system related to the general evolution of the Kyklades plateau. Land geological formations comprise non-metamorphic alpine and post-alpine structures in the central and northern parts, while metamorphic rocks are observed in SE Attica, central and southern Evvoia island.

Rainfalls in the area are low, varying between 400-800 mm/y (Karapiperis, 1974). Attica and the Kyklades islands are among the most arid areas of the Hellenic territory. The drainage system is generally poor and the main contributor in terms of suspended load is the Asopos river, with an annual water discharge of 23×10^6 m³ (Therianos, 1974).

Water circulation in the area is cyclonic (Hopkins, 1978). The narrow strait (~ 60 m width) between the South and North Evvoikos gulfs (Fig. 1) generates a rare phenomenon known as the "Evripos channel tide". This tidal current reaches a speed of nine knots and produces a sea-level oscillation up to 80 cm in SEG, whereas the Petalion gulfs are not affected. The Greek Meteorological Service reports dominating north winds, especially during the summer. Wave height is 1-1.5 m in SEG and 2-4 m in NPG, and SPG.

The sea-bed topography (Fig. 2) is characterized by shallow depths – up to 68 m – in SEG. The bed gradient is steeper in the coastal zone and the sea floor is flat in the inner part. A wide circular basin is formed in SPG, with a maximum depth of 162 m and a relatively low bed gradient.





Bathymetric map of the area. SEG is a shallow semi-enclosed embayment (depths up to 68 m). SPG contains a circular basin (maximum depth 162 m), with a low bed gradient.

A set of 68 surface sediment samples was collected (Fig. 1) with a Reineck stainless steel grab, during three cruises of R/V *Aegaeo*, between October 1986 and December 1988. Positioning was obtained by the Integrated Navigation System of the vessel, comprising GPS, Loran-C, gyro compass and speedlog.

Sample preparation for the grain size analysis involved successive treatments with H_2O_2 10% and HCl 5%, to remove the organic matter and the carbonates, respectively (Folk, 1974). The fraction < 2 μ m for the geochemical and clay mineral analyses was separated in settling tubes, dried at 70°C and ground to a fine powder in an agate mortar.

The mineralogical composition was determined by X-Ray Diffraction and microscope examination. The XR-D system was a Rigaku D/MAX B, employing CuKa radiation and graphite monochromator. Powder samples were analysed for bulk mineralogy, in the range $2^{\circ}-40^{\circ}$ 2θ . For the identification of the clay minerals, glass slide mounts were prepared and analysed sequentially in four stages: normal, glycolated, heated at 375 °C and 500 °C, in the range $2^{\circ}-14^{\circ}$ 2θ . The other diffractometer settings were: scan speed 1°/min, voltage 40 kV, current 20 mA, DS 1°, RS 0.3 mm, SS 1°. Coarse-grained sandy samples were mounted in synthetic resin and thin sections were prepared for microscope examination, together with several smear slides. Heavy minerals were separated using CHBr₃.

Major and minor elements were determined by a Philips PW 1400 X-Ray Fluorescence system, following the procedure described in Stoffers *et al.* (1983). Total carbonates were determined by a LECO CS-125 carbon analyser.

In order to compare present-day heavy metal concentrations with pre-European background values, we computed the "Index of Geoaccumulation", as introduced by Müller (1979):

$$I_{geo} = \log_2 \frac{C_n}{1.5^* B_n}$$

 C_n is the measured concentration of the element "n" in the pelitic sediment fraction ($\emptyset < 2 \ \mu$ m) and B_n represents the geochemical background concentration of element "n" for the "average shale" referenced from Turekian and Wedepohl (1961). The factor 1.5 is introduced to take account of possible variations in the background values due to lithogenic effects. Therefore, I_{geo} value is assumed to be a measure of heavy metal enrichment, and is defined in the following scale:

I _{geo} value	I _{geo} class	Designation of sediment quality		
> 5	6	Extremely contaminated		
4-5	5	Strongly to extremely strongly contaminated		
3-4	4	Strongly contaminated		
2-3	3	Moderately to strongly contaminated		
1-2	2	Moderately contaminated		
0-1	1	Uncontaminated to moderately contaminated		
< 0	0	Uncontaminated		

In order to examine the relationships among the various chemical elements, we performed multivariate statistical

analyses. Computation of correlation coefficients and R-mode factor analysis with Varimax Rotation was carried out using a Statgraphics 3.0 software package (Statistical Graphics Corporation, 1988). A commendable review of factor analysis and other eigenvector methods together with the mathematical equations utilized for the factor models and the factor scores computation, is given by Davis (1986).

RESULTS AND DISCUSSION

Surface sediment grain size distribution

The grain-size properties of the surface sediments are nicely represented by the sand fraction (> 63 μ m) spatial distribution (Fig. 3). In the area under investigation, two sedimentary provinces are clearly distinguished: i) South Evvoikos gulf (SEG), characterized by fine grain sediments with less than 20% sand; and ii) North and South Petalion gulfs (NPG, SPG), covered by sandy sediments. The source of the fine-grained sediments is the Asopos river. Due to the semi-enclosed morphology of SEG, sediments are trapped and rapidly deposited in this small sedimentary basin. In the southern part, comparing the bathymetry (Fig. 2) and the sand distribution (Fig. 3), we observe that sand percentage is very high in the deepest parts of SPG. Apparently, these sands are of relict type, deposited during the late Wurmian glacial period (25,000-18,000 yrs BP), when the sea level was about 100 m below the present one (Chappell and Shackleton, 1986). The relict sands represent the coastal deposits of this period. The absence of important rivers, and the subsequent low sedimentation rate, have left the relict sands uncovered by modern sediments.





Detrital sand distribution map (> 63 μ m, after treatment with H₂O₂ and HCl 5 %). Fine sediments characterize SEG, while coarse relict sands dominate NPG and SPG.

Surface sediment mineralogy

Quartz is the most abundant mineral in the area under investigation. Its grain size varies between 10-50 μ m in SEG, while in NPG and SPG, grains up to 200 μ m are observed. Plagioclase represents the feldspars and is also widely distributed. Calcite, Mg-calcite and aragonite are present, mainly related with the biogenic facies.

Clay minerals are mainly represented by illite, which shows a clear peak at 10 Å, remaining unaffected during the sequential treatments. Chlorite and kaolinite are both present. Chlorite was identified at the 25° 2θ area, where kaolinite (3.58 Å) and chlorite (3.54 Å) peaks were clearly separated. Finally, a randomly interstratified illite/smectite, rich in illite, was identified. It was identified on the ethylene glycol-solvated diffraction patterns, by a strong but broad reflection near 17 Å, which was added to the illite peak at 10 Å, after the 375 °C heating.

Heavy minerals do not exceed 1 % of the sediment, but they exhibit a wide variety. The most abundant heavy mineral is epidote, followed by hornblende, zircon and glaucophane, which is an amphibole with very characteristic bluemagenda pleochroism.

The biogenic facies is represented mainly by foraminifera, diatoms and sponge needles. In the coarse sandy sediments of NPG and SPG, bivalves and gastropods are also present. Their size ranges from a few millimetres up to 5 cm.

The mineralogical composition of the surficial sediments for SEG, NPG and SPG, in so far as it concerns the identified minerals, is considered to be uniform. This illustrates the homogenous detrital supply of the marine area and also reflects the petrology of the catchment basins' rock formations. The only areal differentiation is the higher heavy mineral concentration in NPG and SPG than in SEG, which is related to the presence of the relict sediments.

Geochemistry of the bulk sample

Summary statistics from the XR-F results for major, minor elements and carbonates are presented in Table 1. Among major components, SiO₂, CaO and Al₂O₃ exhibit the greatest variability, varying between 3.19 and 48.79%, 7.61 and 52.82% and 0.60 and 15.28%, respectively. Among the minor elements, Sr varied between 163 and 2927 ppm and Mn between 77 and 1162 ppm. Chromium and nickel show significant variability (20-342 ppm and 15-301 ppm respectively). Statistical analyses were performed on carbonate-free-basis data (c.f.b.), in order to eliminate the dilution phenomenon of element concentrations due to the carbonate content. Strontium data were not recalculated in c.f.b., because Sr is strongly related to the carbonate fraction. The first attempt to recognize groups of chemical elements-variables was the computation of the correlation coefficient matrix (Table 2).

Silicon and aluminium

Silicon, deriving from terrigenous alumino-silicates, quartz and siliceous skeletons, is the element with the greatest variability (Table 1). The Si/Al ratio in SEG varies between 2.53 and 4.49 (mean value 3.05) and between 2.78 and

Table 1

Summary statistics of SEG, NPG and SPG surface sediments: major and minor elements, carbonates and Si/Al ratio (significance level 0.05, n = 68).

	Mean	Standard deviation	Minimum	Maximum
SiO ₂ (%)	28.00	13.07	3.19	48.79
Al ₂ O ₃ (%)	6.56	4.42	0.60	15.28
Fe_2O_3 (%)	3.37	1.89	0.70	6.99
CaO (%)	28.09	12.33	7.61	52.82
K ₂ O (%)	0.66	0.57	0.07	2.35
Na ₂ O (%)	1.37	0.57	0.38	2.75
TiO ₂ (%)	0.33	0.20	0.04	0.73
MgO (%)	2.86	0.88	1.66	4.64
Mn (ppm)	510	275	77	1162
Cu (ppm)	12	12	1	91
Pb (ppm)	22	10	7	59
Zn (ppm)	55	28	7	102
Cr (ppm)	138	103	20	342
Ni (ppm)	110	92	15	301
Sr (ppm)	1272	807	163	2927
Carbonates (%)	51.4	22.3	14.5	91.5
Si/Al	4.10	1.55	2.53	9.06

9.06 (mean value 5.16) in NPG, SPG, indicating higher Si concentration in the latter areas. Excess silicon should be derived either from detrital quartz or siliceous skeletons (Shankar *et al.*, 1987; Nath *et al.*, 1989). In the area under investigation, the higher Si/Al values were observed in NPG and SPG, where the bottom is covered by relict sandy sediments. Therefore, the main source of silicon in excess is presumably terrigenous quartz. The presence of diatom shells could be a minor Si source (Karageorgis, 1992; Karageorgis *et al.*, 1993). SiO₂ shows a slight positive correlation with the elements Al, Na, Ti, Cu and Cr (Table 2).

Aluminium is derived mainly from alumino-silicates, generally of terrigenous origin, and is extremely immobile in the marine environment (Bischoff *et al.*, 1979). Consequently, it is regarded as one of the best indicators of a terrigenous contribution to marine sediments. Higher concentrations of Al_2O_3 are observed in SEG, an enclosed area of a terrigenous sediment entrapment and rapid deposition. Aluminium is positively correlated with Fe, K, Ti, Zn, Cr and Ni, forming the group of elements related to the continental alumino-silicates.

Calcium, carbonates, magnesium and strontium

The elements Ca, Mg and Sr and the carbonates are highly inter-correlated (Table 2), because of their common genetic origin, which is principally in the skeletons of marine organisms (Calvert, 1976). Many of the latter build their shells with CaCO₃ or MgCO₃, while the substitution of Ca²⁺ by Mg²⁺ during the formation of (Ca,Mg)CO₃ is very common. Sr in marine sediments is also related to the carbonate phase and especially in the skeletons of foraminifera, coccoliths, corals and sponges (Buchardt, 1977; Goreau, 1977). The elements of this authigenic biogenic group are negatively correlated with the former alumino-silicates group.

CaO carbonates K ₂ O Na ₂ O TiO ₂ MgO Mn Cu Pb Zn Cr Ni Sr	$ \begin{array}{c} 10000\\ 0.9170& 1.0000\\ 0.5170& 1.0000\\ 0.5249& 0.7714& 0.6720& 0.2311\\ 0.0228& 0.0228& 1.0000\\ 0.3096& 0.5474& -0.1251& 0.5944& -0.1156\\ 0.3096& 0.5474& -0.1251& 0.5944& -0.1156& 1.0000\\ 0.3096& 0.2463& 0.0200& 0.3422& 0.0799& 0.5425& 1.0000\\ 0.0124& 0.0950& 0.6364& 0.3165& 0.3874& 0.3038& 1.0000\\ 0.2206& 0.4466& -0.0140& 0.3422& -0.1023& 0.7710& 0.5992& 0.2426& 1.0000\\ 0.0035& 0.0025& 0.6364& 0.3165& 0.3874& 0.3333& 0.01190& 0.5395& 1.0000\\ 0.0035& 0.0124& 0.0350& -0.0172& 0.0572& 0.1190& 0.5992& 0.2426& 1.0000\\ 0.0035& 0.0853& 0.4736& 0.3402& 0.1123& 0.3353& 0.4128& 0.3645& 0.0692\\ 0.0035& 0.0785& 0.2420& 0.1157& -0.6853& 0.2011& 0.0420& 0.5776& 0.4463& 1.0000\\ 0.08953& 0.9624& -0.6420& 0.1577& -0.6853& 0.5038& 0.2011& 0.0420& 0.4626& -0.0724& -0.0725& -0.6346& 1.0000\\ 0.0405& 0.6874& 0.0420& 0.1577& -0.6853& 0.5038& 0.2011& 0.0420& 0.4626& -0.0725& -0.6346& 1.0000\\ 0.0405& 0.6674& -0.6722& 0.1577& -0.6853& 0.5038& 0.2011& 0.0420& 0.4626& -0.0724& -0.0725& -0.6346& 1.0000\\ 0.0405& 0.6774& -0.0722& -0.6344& -0.0725& -0.6346& 1.0000\\ 0.0405& 0.4626& -0.0724& -0.0725& -0.6346& 1.0000\\ 0.0405& 0.4626& -0.0724& -0.0725& -0.6346& 1.0000\\ 0.0405& 0.4626& -0.0724& -0.0725& -0.6346& 1.0000\\ 0.0405& 0.4626& -0.0724& -0.0725& -0.6346& 1.0000\\ 0.0405& 0.4626& -0.0725& -0.6346& 1.0000\\ 0.0405& 0.4626& -0.0724& -0.0725& -0.6346& 1.0000\\ 0.0405& 0.4626& -0.0724& -0.0725& -0.6346& 1.0000\\ 0.0405& 0.4626& -0.0724& -0.0725& -0.6346& 1.0000\\ 0.0405& 0.4626& -0.0725& -0.6346& 1.0000\\ 0.0405& 0.4626& -0.0724& -0.0725& -0.6346& 1.0000\\ 0.0405& 0.4002& 0.4002& 0.4002& 0.4002& 0.4002& 0.4002& 0.4004& 0.0002\\ 0.0405& 0.4002& 0.4002& 0.4002& 0.4002& 0.4004& 0.0002& 0.4004& 0.0002\\ 0.0405& 0.4002& 0.4002& 0.4000& 0.4000& 0.4000& 0.4000& 0.4000& 0.4000& 0.4000& 0.4000& 0.4000& 0.4000& 0.4000& 0.4000& 0.4000& 0.4000& 0.4000& 0.4000& 0.4000& 0.0000& $
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S	SiO ₂ SiO ₂ Al ₂ O ₃ Co ₂ Cao Carbonates

Titanium and iron

Titanium is highly correlated with aluminium (r = 0.94). Both Ti and Al, very immobile in the marine environment, are indicators of the terrigenous contribution to marine sediments (Emelyanov *et al.*, 1979). The relatively high positive correlation of Fe with the terrigenous elements (Fe-Al r = 0.63, Fe-Ti r = 0.63) indicates that, in principle, iron is of terrigenous origin.

Factor analysis

The results of R-mode factor analysis for the geochemical data of the bulk sample are presented in Table 3. A model of three factors, which explains 90.2% of the total data variability, has been chosen in order to interpret the element geochemical behaviour.

The first factor accounts for 48.4% of the total data variability. This factor is characterized by the high positive relation between Al, Fe, K, Ti, Ni and the negative correlation between Ca, carbonate, Sr and Mg. The strongly bipolar character illustrates the antithesis between the detrital alumino-silicates and the authigenic biogenic phase. The factor scores distribution for the "alumino-silicates factor" is presented in Figure 4. As higher factor scores dominate in the SEG area and the lower NPG and SPG areas, it is inferred that SEG receives a greater terrigenous supply, mainly due to the Asopos river. Southwards, the supply decreases, and factor scores are lower, in contrast with the biogenic carbonate content.

The second factor (30.2%) is characterized by positive loadings for almost all variables. Variables can be separated into two groups according to their geochemical relationship, but it would appear that both groups attract a part of the metals. The first group involves the elements Fe, Mn and one part of the metals (Pb, Cr, Cu, Zn, Ni). The hydrogenous origin ferro-manganese oxides have a great absorption capacity and are important scavengers of metals (Förstner and Wittman, 1983). The second is the

Table 3

R-mode factor analysis results after Varimax rotation.

Variable	Factors					
-	1	2	3			
SiO ₂	0.15	-0.01	0.89			
Al ₂ O ₃	0.95	0.20	0.05			
Fe ₂ O ₃	0.39	0.81	-0.04			
CaO	-0.91	-0.01	-0.32			
carbonates	-0.93	0.27	-0.09			
K ₂ O	0.82	0.13	-0.24			
TiO ₂	0.85	0.29	0.22			
MgO	-0.35	0.77	-0.17			
Mn	-0.06	0.75	-0.10			
Cu	0.09	0.52	0.31			
Pb	-0.24	0.75	- 0.39			
Zn	0.33	0.52	-0.53			
Cr	0.33	0.68	0.11			
Ni	0.83	0.21	-0.37			
Sr	-0.89	0.27	-0.14			
Variance (%) cumulative	48.4	30.2	11.6			
Variance (%)	48.4	78.6	90.2			

Table





Factor scores distribution map for the "alumino-silicates factor". Higher values for this factor are observed in SEG, indicating a detrital origin of the chemical elements Al, Fe, K, Ti, Ni. The authigenic biogenic phase expressed by Ca, carbonates, Sr and Mg, dominates the Petalion gulfs.

biogenic group of the elements Mg, carbonates, Sr and another part of the metals. The correlation of the latter elements of the biogenic group with the metals (Pb, Cr, Zn, etc.) may be due to: i) metal adsorption by carbonate minerals (Emelyanov and Shimkus, 1983); ii) the formation of oxide coatings on carbonate grains (Salomons and Förstner, 1984); or iii) Ca, Mg, Sr substitutions. Higher loadings are observed for the elements Fe and Mn, hence this factor will be termed the "Fe-Mn oxides factor".

Higher factor scores for the second factor are observed in SPG. This area is dominated by relict sediments with increased percentage of biogenic carbonates and heavy minerals. Finally, the third factor shows high loading on Si (0.89) and represents residual quartz. Factor scores are lower in SEG and significantly higher in SPG, confirming the relation of Si with the relict sediments.

Geochemistry of the fraction \emptyset < 2 μ m

Table 4 summarizes the results of the XR-F analyses and the computed I_{geo} values. I_{geo} values for Mn, Cu and Zn classify the sediments in class 0, *i.e.* the uncontaminated class. For Mn, only one sample is classified in class 2 ($I_{geo} = 1.13$). For Pb, the SPG area is classified in class 2, while SEG and NPG present classes 0 and 1. From the former factor analysis, it is induced that Pb is connected with the carbonate fraction, which dominates this area. Consequently, its relatively high I_{geo} values seems to be unrelated to human impact.

All I_{geo} values for chromium vary between 0.93 and 1.6, *i.e.* almost all samples are classified in class 2 (moderately to

Table 4

Heavy metals and Geoaccumulation Index in the fraction $< 2 \mu m$ of SEG, NPG and SPG surface sediments (significance level 0.05, n = 68).

	Mean	Standard deviation	Minimum	Maximum 6.78 -0.06	
Fe (%) I _{geo}	5.60 -0.35	0.70 0.18	4.01		
Mn (ppm)	1137	500	542	2791	
I _{geo}	- 0.28	0.57	-1.23	1.13	
Cu (ppm)	19	7	6	44	
I _{geo}	- 1.95	0.64	- 3.49	-0.62	
Pb (ppm)	45	12	22	80	
I _{geo}	0.54	0.39	-0.46	1.41	
Zn (ppm)	114	18	67	190	
I _{geo}	-0.33	0.23	1.09	0.42	
Cr (ppm)	355	40	258	411	
I _{geo}	1.39	0.16	0.93	1.6	
Ni (ppm)	246	68	88	415	
I _{geo}	1.22	0.41	-0.21	2.15	

strongly contaminated). This uniform distribution in SEG, NPG and SPG alike, suggests a detrital origin rather than anthropogenic influence.

The areal distribution of the I_{gco} classes for Ni is presented in Figure 5. Nickel is the only element showing I_{gco} index in the third class. Those sediment samples are located in SEG and especially in the central part of the gulf, close to the industrialized city of Aliveri. A possible Ni source



Figure 5

Areal distribution of the I_{geo} classes for nickel. The highest (class 3 - moderately to strongly contaminated) is observed in the central part of South Evvoikos gulf. The high concentrations of Ni are possibly related to the erosion of laterite and ultramafic rocks of Central Evvoia.

could be the Aliveri aluminium factory. Nevertheless, values of I_{geo} index for Ni also imply an increased detrital supply. It is possible that high Ni values in SEG are due to the erosion of laterite and ultramafic rocks, which are present in Central Evvoia (Albadakis, 1980). This opinion is also supported by some previous studies in SEG (Angelidis *et al.*, 1980; Scoullos and Dassenakis, 1983; Karageorgis *et al.*, 1994), which consider South Evvoikos gulf as a non-polluted marine area.

In comparison with other gulfs in Greece (Table 5), such as North Evvoikos (Voutsinou-Taliadouri and Varnavas, 1993), Elefsis (Sioulas *et al.*, 1990), Geras (Sioulas and Anagnostou, 1989), Thermaikos and Pagassitikos (Chester and Voutsinou, 1981) and also with average shale data (Turekian and Wedepohl, 1961), the area under investigation generally appears to be free of metal pollution.

CONCLUSIONS

In the marine area between Attica, Evvoia and the North Kyklades islands, surface sediments were studied for their grain size and mineralogical and geochemical properties. Grain-size analysis revealed two sedimentary provinces in the area. The first one is SEG, characterized by fine grained silty sediments, supplied by the Asopos river. The second involves NPG and SPG, areas dominated by relict sandy sediments rich in heavy minerals and deposited during the last glacial period. The relict sediment presence is associated with the poor drainage system in the area and the low sedimentation rate.

The most abundant minerals identified are quartz, feldspars, calcite, Mg-calcite, chlorite and biotite. Heavy minerals are represented by epidote, hornblende, zircon and glaucophane. The mineralogical composition is uniform throughout SEG, NPG and SPG, differentiated only by the increase of heavy minerals in the southern part of the area, which is dominated by relict sandy sediments.

The distribution of major and minor elements in the surface sediments of the South Evvoikos and Petalion gulfs is controlled by three major parameters. The first

Table 5

Comparison of the trace elements composition of South Evvoikos, North and South Petalion gulfs, with those of other sediments.

Area	Fe	Mn	Cu	Pb	Zn	Cr	Ni
	(%)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
Area average							
bulk (1)	2.4	510	12	22	55	138	110
SEG bulk	3.8	730	18	31	86	248	217
NPG bulk	1.6	395	5	18	42	94	62
SPG bulk	1.7	401	16	15	32	61	41
Area average							
$< 2 \ \mu m$ (1)	5.6	1130	19	45	115	354	245
SEG < 2 μ m	6.3	939	17	36	111	378	308
NPG < 2 μ m	5.5	1087	18	50	109	357	206
SPG < 2 μ m	4.7	1506	25	51	130	314	217
North							
Evvoikos (2)	5.1	3979	34	-	64	592	1367
Elefsis < 2 μ m (3)	5.6	1079	99	194	523 [·]	181	118
Geras < 2 μ m (4)	3.4	1309	29	56	134	723	318
Thermaikos (5)	-	751	18	56	73	65	66
Pagassitikos (6)	-	654	10	20	21	26	38
Average							
Shale (7)	4.7	850	45	20	95	90	68

(1) Present study; (2) Voutsinou-Taliadouri and Varnavas (1993); (3) Sioulas *et al.* (1990); (4) Sioulas and Anagnostou (1989); (5), (6) Chester and Voutsinou (1981) and (7) Turekian and Wedepohl (1961).

relates to the terrigenous supply, which is definitely higher in SEG, where the Asopos river discharges, as a consequence of which alumino-silicate concentration is also increased, associated with the enclosed system and rapid deposition.

The second parameter is related to the relict quartz, whose presence characterizes the sediments of SPG. Finally, the third parameter is the biogenic factor, which appears to concentrate a part of the metals.

Compared to other Greek gulfs, the area under investigation has, in general, no significant load of heavy metals. Only a small area in SEG shows considerable concentrations of Ni, which are related to the increased terrigenous natural supply.

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