MINERALOGY OF THE BOTTOM SEDIMENTS IN THE CENTRAL AREA OF THE BLACK SEA SHELF

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Abstract. GeoEcoMar Programmes (Acronyms: GEOMAND and FLUDITMAR) represented the financial support for the marine scientific activities, including the mapping of the Romanian shelf area. The drawing of the sedimentological maps, scale 1:50.000, includes the mineralogical analyses of the bottom sediments of the Black Sea, with a special attention for the heavy minerals associations. For the central part of the Black Sea shelf area, the main contributors in heavy minerals are the solid discharge of the River Danube and, partially, the northern longitudinal marine current. Source areas of heavy minerals are the geological basement of the River Danube drainage basin and the old geological formations of the Scythian Platform. The distribution of the sandy sediments, siliciclasts and heavy minerals are presented in some thematic maps. The erosion of the palaeo-beaches, located in the basement of the Holocene sediments of the Danube Delta complex, favours the diversity of the heavy minerals associations.

Key words: marine sediments, siliciclasts, sand, heavy minerals, Black Sea

1. INTRODUCTION

Marine researches carried out under the aegis of the core programmes (GEOMAND and FLUDITMAR) of GeoEcoMar, represented the basis for elaboration of the sedimentological map sheets K-35-144-C, K-35-12-A and K-35-11-B, 1:50.000 scale, located within central area of the Romanian Black Sea continental plateau (Fig. 1). The data used to prepare this work resulted from systematic analysis of 300 bottom sediment samples collected in the 2006-2008 time interval, at the interface water / sediment, using a Van Veen type grab sampler. To prepare this paper, the author used some older data she had, collected in the 1982-2008 time interval (Fulga & Fulga, 1996, 1998, 1988-2008; Fulga, 2005 a, b).

2. MATERIALS AND METHODS

The samples taken were processed and analysed in the laboratory of mineralogy of GeoEcoMar - Constanta branch by the author. The method of investigation is based on the microscopic mineralogical determination guide, especially "Les mineraux en grains" (Parfenoff & Pomerol, 1970)

All samples prepared for mineralogical studies were sieved, extracting the arenitic granoclasts - fine and very fine sand (class 0.250-0.063 mm). Carbonates and siliclasts + oxides + sulphides contents of the chosen arenitic class were calculated from data obtained by weighing the samples before and after removal of carbonate by treatment with hydrochloric acid, of 16% concentration. Decarbonated granoclasts, generally siliciclasts, were separated with bromoform (density 2.9 g/cm^3) and each were studied on heavy and the light subfractions. Also, the Frantz Isodynamic magnetic separator was used in order to obtain various classes of heavy minerals, depending on their magnetic susceptibility level. The author calculated each subfraction content, but without reporting it to the entire sample, because the carbonates and siliciclasts may exist in the coarse and shelly sand, siltites or lutites, as well.

Mineralogical study of the sediment samples, collected from the map sheets K-35-144-C, K-35-12-A and K-35-11-B was performed qualitatively and quantitatively on the arenitic granoclasts, with special regard to the heavy minerals.

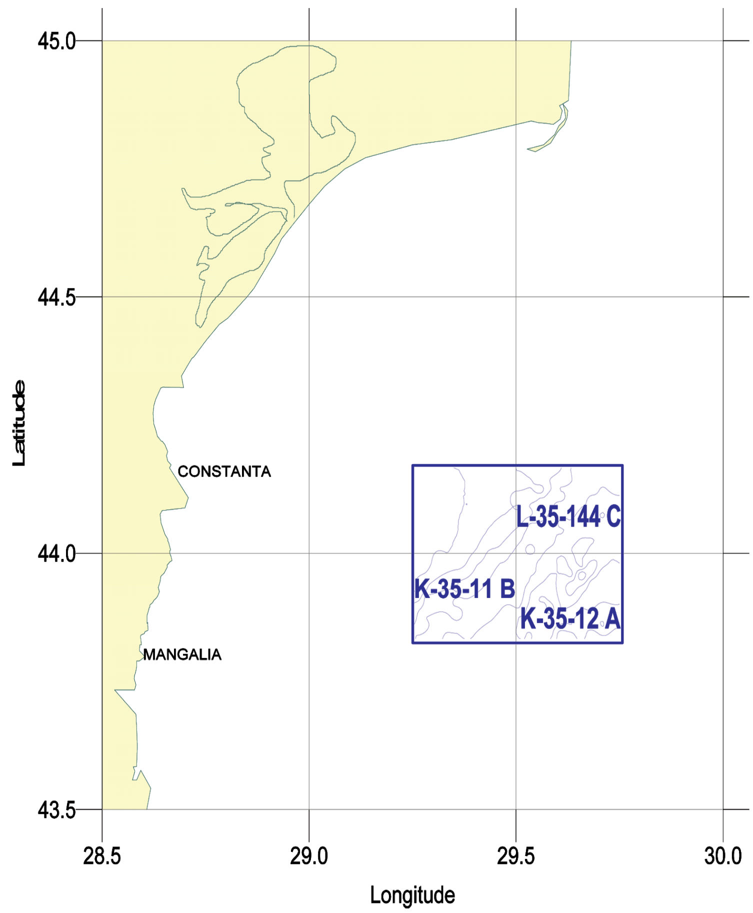

Fig. 1 Map sheets location: K-35-144-C, K-35-12-A, K-35-1-B.

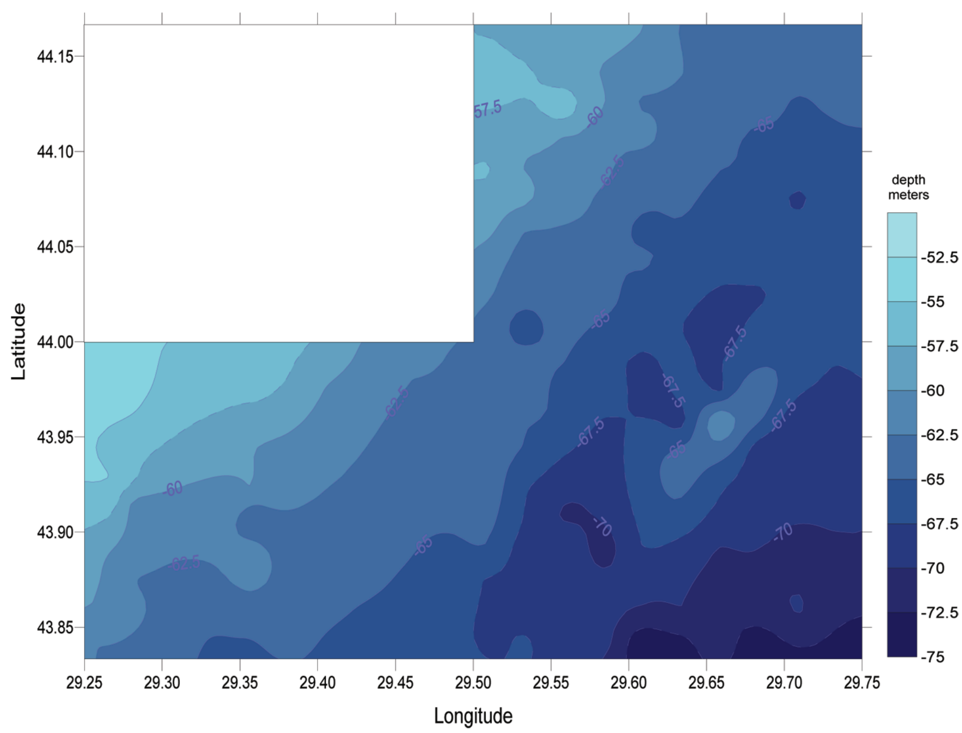

Fig. 2 Water depth to the upper layer of sediments measured in the sampling locations.

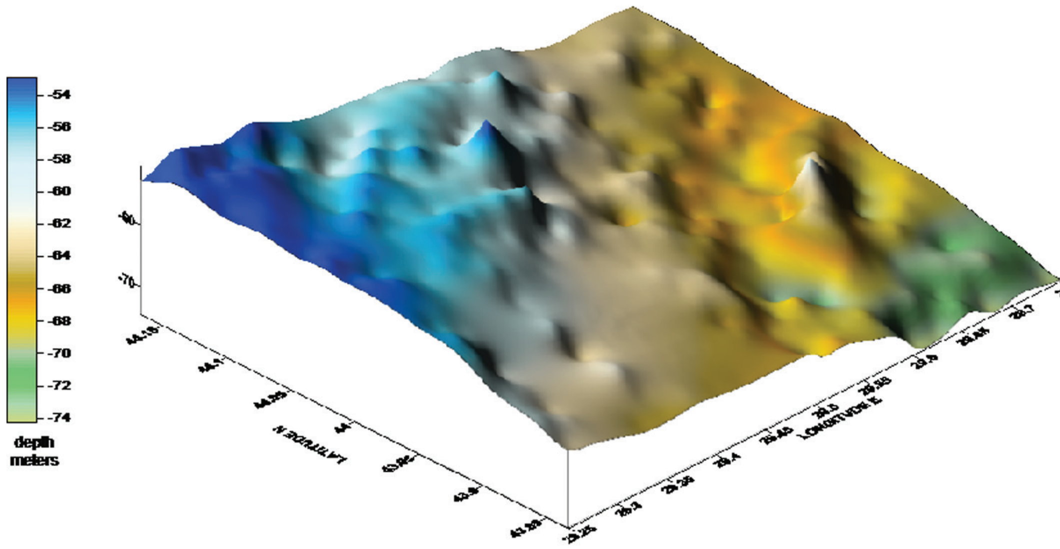

Fig. 3 Water depth to the upper layer of sediments, measured in the sampling locations – 3D image.

For details, particularly for the study of the subordinated heavy minerals, the polarizing microscope was used, by glycerin immersion method. All details concerning the mineralogical composition of fine and very fine sand, with special regard to the heavy minerals, were represented as a percentage, creating the distribution maps for each mineralogical parameter. The percentage of each mineral has been reported to the heavy fraction, considered as the total heavy minerals content.

The heavy minerals associations of the sands from the sediments collected in the years 2006 – 2008 at depths ranging between 52 and 75 m (Figs 2 and 3) are represented on the distribution maps with no quantitative meaning, only the most frequent mineral in the heavy fraction is taken into account as a determinant for each association.

3. MINERALOGICAL COMPOSITION OF THE SEDIMENTS

The main factors affecting the mineralogical composition are selective sorting of minerals under equivalent hydrodynamic influence, the resistance of different minerals to abrasion, the chemical post-depositional changes, the rate of sedimentation in different times, the maturity of the sediments and the progressive dilution depending on the distance to the source of alluvia.

Analysing the fine sandy fraction content (Table 1, Fig. 4) and watching, in particular, the grain size distribution of the ranges 0.250-0.125 mm and 0.125-0.063 mm, the following trends have been noted:

1) sandy fraction content increases to over 20%, in the northwestern and northern areas of the sheet K-35-144-C, in conjunction with the water depth, from inshore till the isobath of 62.5 m; in central and eastern parts of the map sheet, around 65-67.5 m, the minimum values are obvious;

2) in the northwestern and central-northern area of the sheet map K-35-12-A, from the shore till 65 m depth, the fine sandy fraction content increases to over 30-60%; in central and south-eastern parts of the sheet, around 65 m depth and over 72.5 m, minimum values are obvious;

3) within the map sheet K-35-11-B, the sediments contain more than 20% fine and very fine sand, on a large area, between 55 - 65 m depth.

Main constituents of the sandy fraction are:

1. **bioclasts** – shells and shell debris, or skeletal fragments of molluscs, foraminifera, ostracoda, which give the coarse terms, and print the carbonated characteristic to sediment; the areal distribution can be inferred from the image distribution of siliciclasts, their maximum and minimum concentrations being inversely correlated to the carbonates (Fig. 5).
2. **lithoclasts** – represented by the petrographic terms characteristic for various sources of detrital material (schists, limestone, quartzite, etc.), and showing lower contents due to the long distance from the main source of alluvia;
3. **authigenic** minerals – glauconite, more abundant around the 67.5 m isobath, exceeding 1%, in the western third part of the area; pyrite, showing spherical forms, which appears more abundant in correlation with bathymetry: there are two alignments in the north-western area, around 65 m depth, and around 67.5 m and another

one at 65 m, in the south-eastern area, all of them, characteristic to the external continental shelf;

4. **terrigenous minerals (**generally **siliciclasts)** – consisting of light and heavy fractions, concentrated mainly in the grain size subfractions 0.250-0.125 mm and 0.125-0.063 mm, reaching averages of 15.79%, in the north map sheet, 40.49%, in the south map sheet and 59.35%, in the west one. It is a different distribution on the surface of the 3 map sheets. Maximum values have been found around 67.5 m depth, and between 67.5-70 m water depths, in the middle of the south map sheet (Table 1, Fig. 5)

Analysing in detail the grain size subfractions 0.250-0.125 mm and 0.125-0.063 mm, we found an average content of calcium carbonate in the fine and very fine sand, reaching 84.21%, in the north map sheet, 59.51%, in the south map sheet and 40.65%, in the west one. An important part of the sediments, collected from the west and south map sheets area, is characterised by fine and very fine sand with over 40% carbonates (Table 1, Fig. 5)

Light fraction

The light fraction exceeds 96% of the 0.250-0.063 mm grain size subfraction. The terrigenous fraction predominates among light minerals, and the heavy fraction may be absent in some samples.

The light fraction consists of magmatic/volcanic and metamorphic quartz, feldspar, micas and chlorite.

In general, the total feldspars and micas contents decrease with water depth and distance from the shore. The zone up to 65 m water depth is characterized by an enrichment in micas over 1%, especially in the northern area, and feldspars content increases towards the south to over 15%; the contents are relatively constant to the open sea. There is also a correlation between these characteristics of light fraction and the heavy minerals associations dominated by amphiboles.

Quartz, which predominates quantitatively in the light fraction, appears generally as subrounded grains; the granules with a more intense processing appear in two areas, west and central, of old sandy belts, placed around 65 m and 67.5 m water depth.

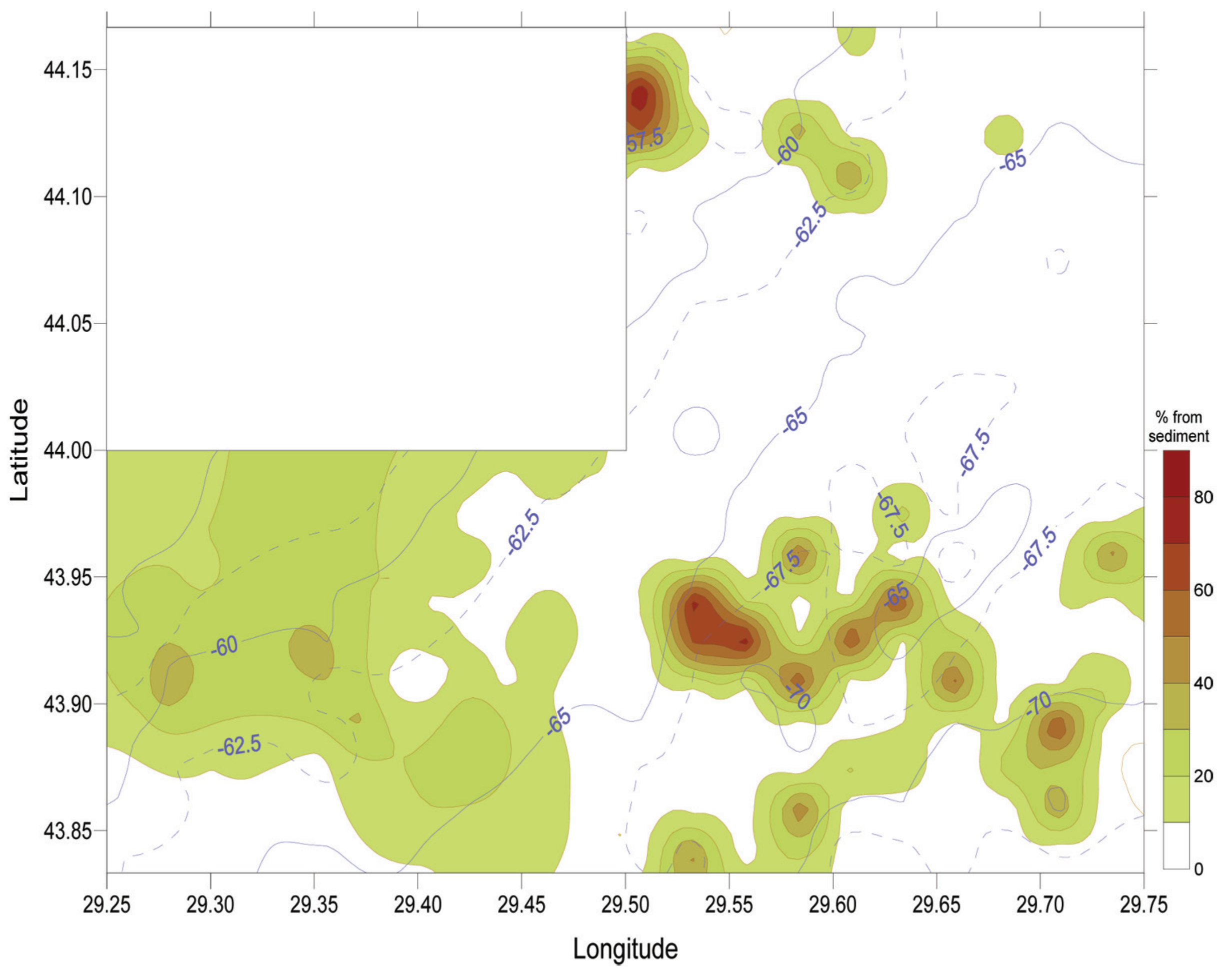

Fig. 4 Distribution of the fine and very fine sand (map sheets location as in Fig. 1)

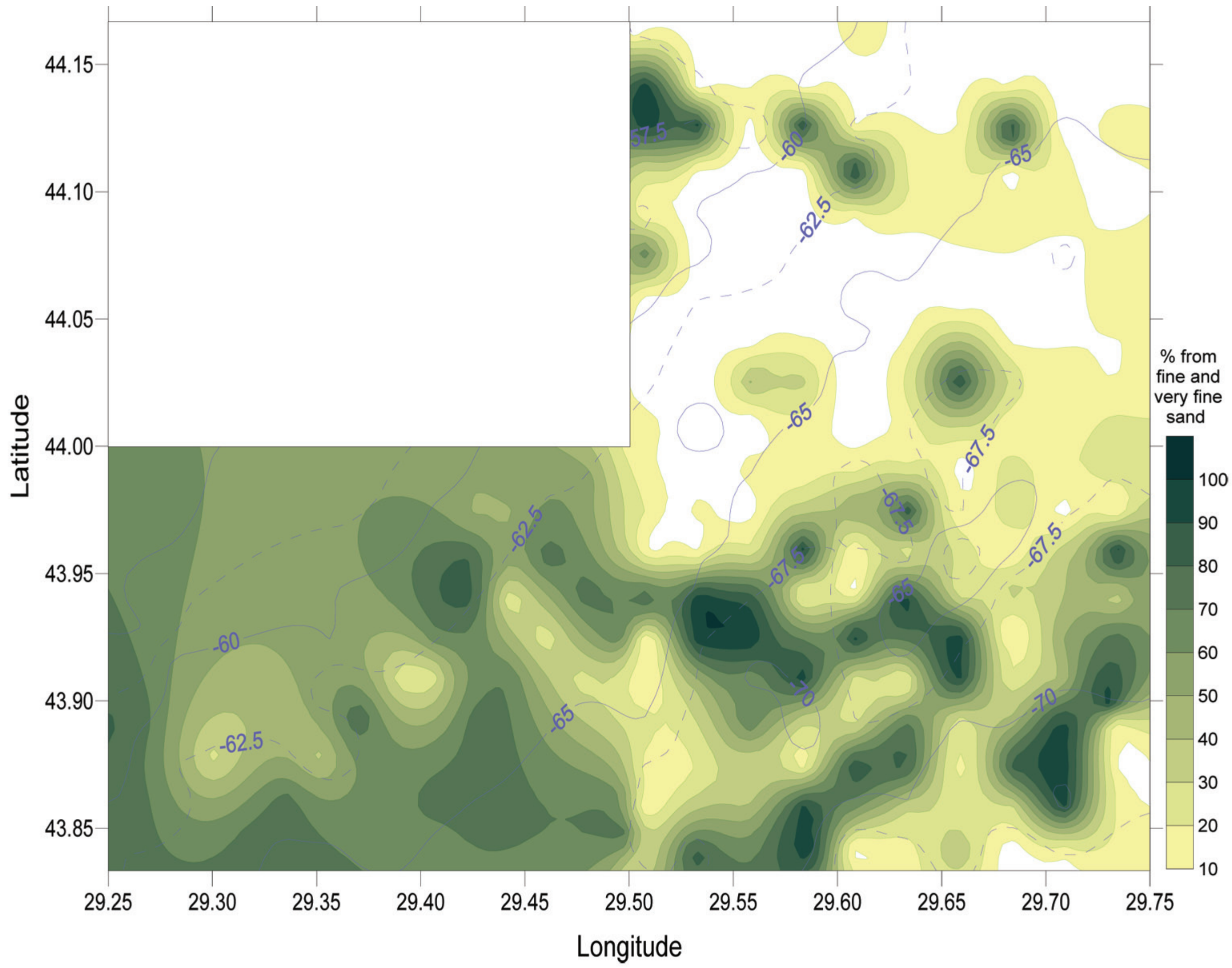

Fig. 5 Siliciclasts distribution included in fine and very fine sands (map sheets location as in Fig. 1).

Heavy fraction

The heavy fraction contributes with an average content of 1.75-3.40% in the fine and very fine sands (Table 1, Fig. 6), but in some samples, around 67.5 m and 70 m water depth, it exceeds 10% of the sandy fraction. In the north-western area, central part, and southeast quarter of the map sheet K-35-12-A, the maximum values appear. Generally, the heavy fraction represents a small part of the entire sample collected – average values are 1.28-0.18%, but these minerals are important in terms of their genesis (Table 1, Figs 8 and 9).

About 35 different heavy minerals have been identified. Most of them have scarce or occasional contribution; just six heavy minerals constitute more than 90% of the heavy fraction.

Opaque minerals (Opacites) - *ilmenite* ($FeTiO_3$), *magnetite* (Fe_3O_4), *leucoxene* (TiO_2), *hematite* (Fe_2O_3), *limonite* ($Fe_2O_3.n\ H_2O$) and rarely *chromite* ($FeCr_2O_4$). –are predominant minerals in many locations, exceeding 30% of the heavy fraction in most samples taken from the upper layer of sediment, and showing averages of 42.85% - 32.98% - 18.42% for the three map sheets (Table 1, Fig. 7). The roundness of the opaque minerals, due to their processing is more advanced at about 67.5-65 m water depth, outlining two west - east alignments, situated approximately in the north-eastern and western parts of the map sheet K-35-12 A.

Amphiboles - $(Na,K)Ca_2(Mg,Fe,Al)_5[Si_7AlO_{22}](OH,F)_2$, are represented mainly by *green hornblende*; *brown basaltic hornblende* is rare, appearing accidentally in the south. *Tremolite* and *actinote* are present in all samples, but with little participation. Content values (Table 1, Fig. 7) are increasing in the south, around 70 m and 67.5 m isobaths, the amphiboles becoming, in several places, the second mineral of the heavy-mineral associations, in central and southern areas of the map sheet K-35-12-A. We emphasize that the distribution map of the main heavy minerals is not identical to the map of the heavy minerals associations.

Garnets - *almandine* variety – $Fe_3Al_2[SiO_4]_3$ – are dominant among heavy minerals in a few samples. *Pirope* is rarely present. Quantitatively, the averages recorded in the sediments of the three map sheets are 10.67% - 14.71% - 42.07% of heavy fraction, (Table 1, Figs 7, 8 and 9).

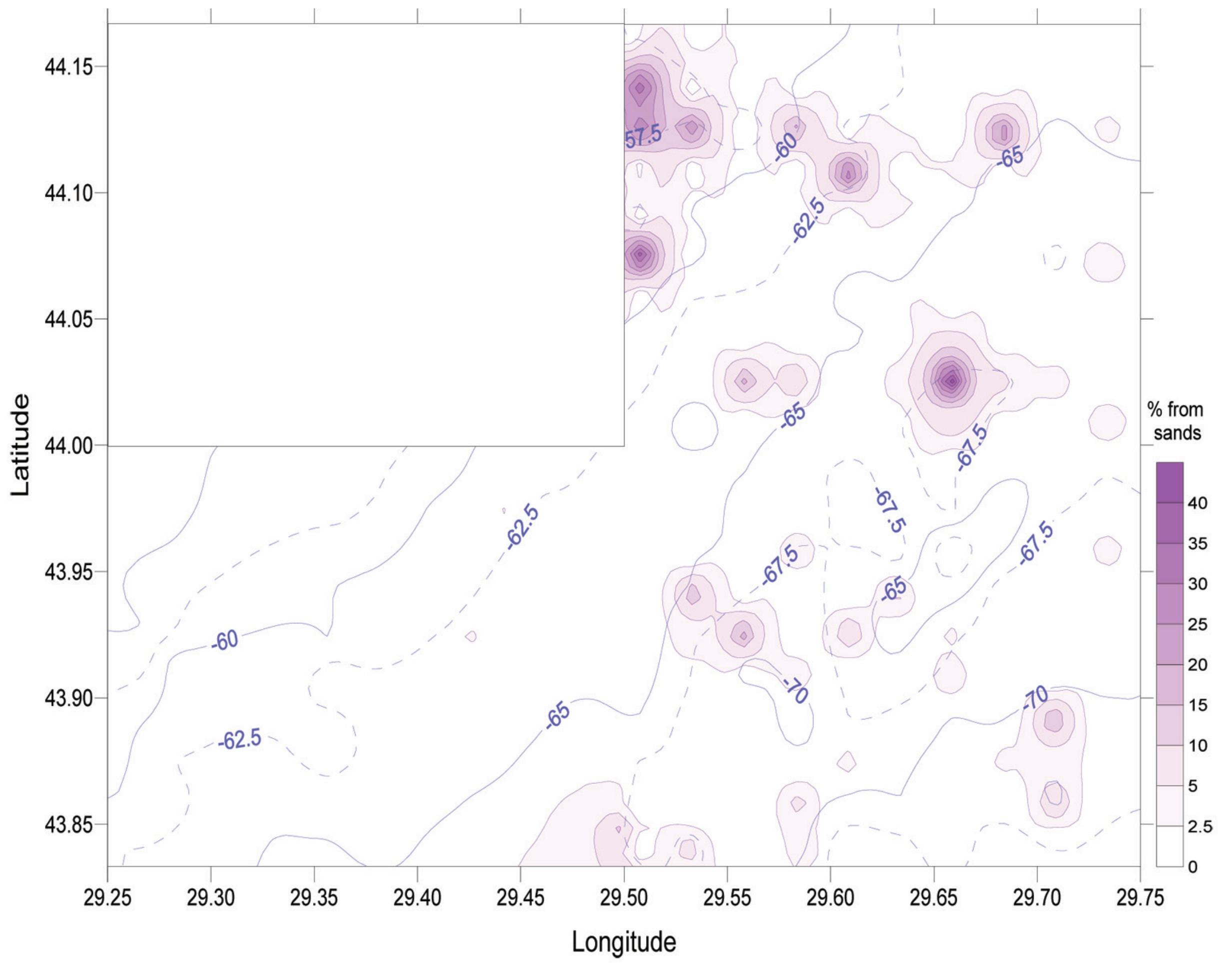

Fig. 6 Distribution of heavy minerals in the fine and very fine sand fractions of sediments (map sheets location as in Fig. 1)

There is a trend of increasing garnet contents on the map sheet K-35-11-B, although these sediments are poorer in heavy fraction. A tendency to roundness of the garnet grains is marked in two areas of the map sheet K-35-12-A, located in north-eastern and central parts, around isobaths of 67.5 m and 65 m, (provenance could be from relict belt) although, generally, granoclasts appear as subangular and subrounded grains.

Epidote - *pistacite* variety - $Ca_2FeAl_2O.OH[Si_2O_7][SiO_4]$, together with *zoizite*, and rarely *clinozoizite*, is the fourth important mineral in the mineral composition. Values over 20% are rare in the studied area, averaging 5.05% - 8.27% - 16.53% within the three map sheets (Table 1). Its enrichment trends are inversely correlated to opaque mineral. Maxima are placed around isobaths of 67.5 m, in north-western part of the mapped area, 70 m, in the centre of the map sheet K-35-12-A, and reach higher values on the map sheet K-35-11-B.

Pyroxenes - $(Na,Ca)(Fe,Mg,Al)[Si_2O_6]$, are represented by *augite*, *hyperstene* and, rarely, *aegirin*, *diopside*, *enstatite*, *bronzite*. The mean contents calculated on every sheet map are 4.68% - 4.84% - 2.84%. There is a percentage increase of the pyroxenes content in central, eastern and southern zones of the sheet map K-35-12-A, reaching over 8% of the entire heavy fraction (Table 1).

Tourmaline - $Na(Mg,Fe,Li,Al)_3Al_6[Si_6O_{18}](BO_3)_3(OH,F)_4$ has an average, relatively uniform, participation of 2.05%, with a maximum of 5% in the south-eastern part of the mapped area, around the isobath 72.5 m.

Zircon – $Zr[SiO_4]$ shows more than 1% from the entire heavy fraction only around the isobaths of 65 and 70 m (Table 1). *Zircon* grains are perfect crystals, and seldom are the crystal extremities rounded; these minerals originated in old relict belt. Rarely was pointed out the variety *malacon*.

Kyanite – $Al_2O[SiO_4]$, is accounting for more than 1% and shows an enrichment trend in similar areas as zircon.

Staurolite – $Fe,Mg)_2(Al,Fe)_9O_6[SiO_4]_4(O,OH)_2$, was described on the map sheets K -35-12-A and K-35-11-B, showing, sometimes, more than 3% from the heavy fraction, (Table 1).

Rutile (TiO_2) and **titanite** – $CaTi[SiO_4](O,OH,F)$, specific minerals for the primary magmatic source areas, are quantitatively reduced (Table 1). The presence of perfect crystals can

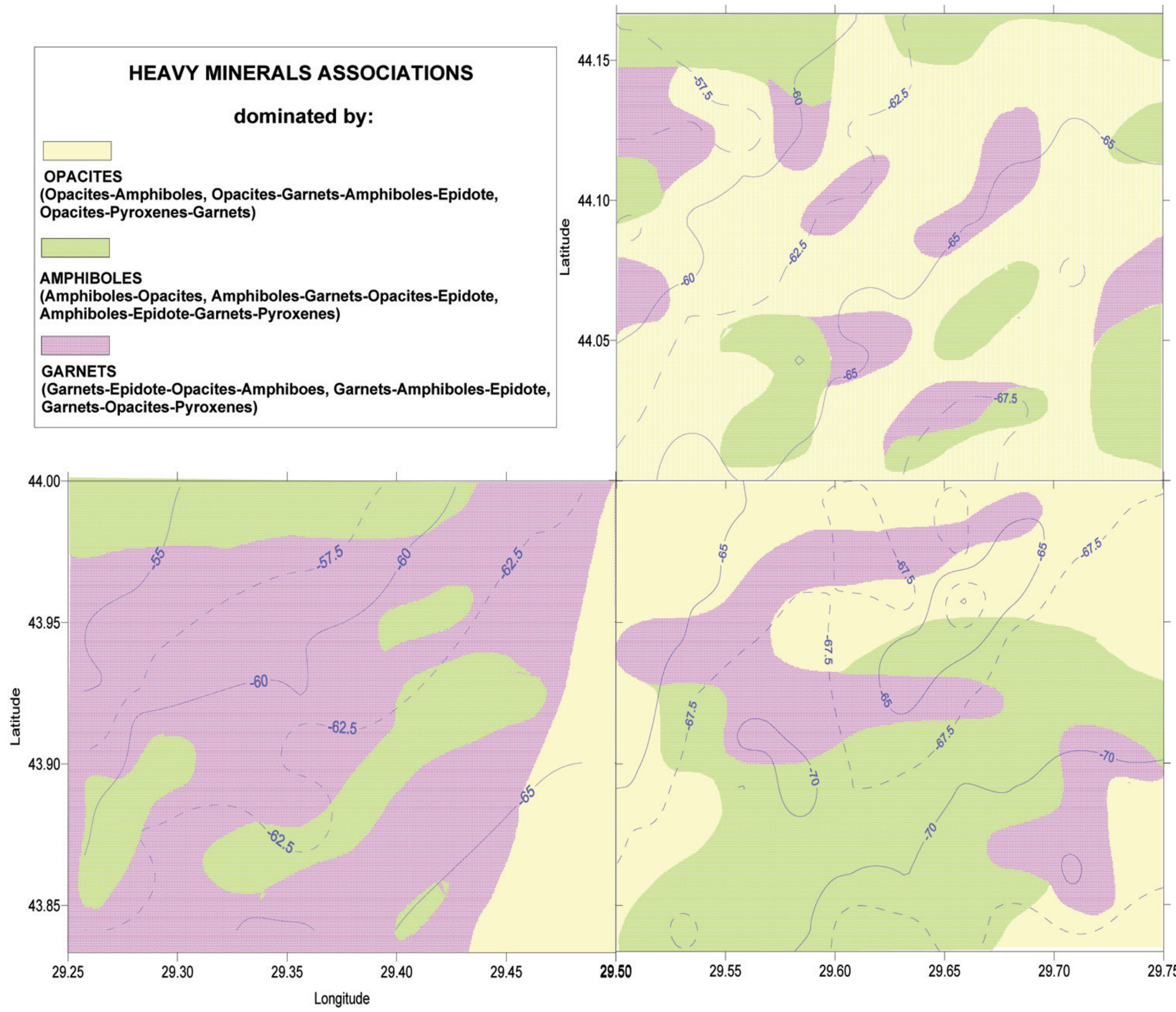

Fig. 7 Heavy minerals associations (map sheets location as in Fig. 1)

be remarked, but often the grains are rounded. The higher contents have a spatial distribution similar to that of zircon.

Heavy-mineral associations

Heavy minerals represent accessory minerals of the pre-existent rocks, sometimes being relict minerals, which concentrate themselves in the fine arenites. Their chemical and morphological characteristics, reflecting almost standard crystallisation conditions, allow the use of the heavy minerals as important markers of the source areas. At the same time, their mechanical and chemical resistance and the high resistance of some of them to abrasion make them good indicators of the sediment maturity. The highly rounded granoclasts represent, regularly, recycled products from old epiclastic deposits.

The fluctuations in the spreading of different mineralogical associations are determined by the hydrodynamic regime, proximity of alluvial sources, morphology of the sedimentation basin, factors leading to the coexistence of actual deltaic sediments with predominantly marine ones, relict or palimpsest sediments.

Following laboratory analyses, three major associations of heavy minerals were separated, depending on the percentage of every mineral species in the entire heavy mineral fraction:

1. **Opacites** - Amphiboles - Pyroxenes - Garnet - Epidote + zoizite;
2. **Amphiboles** - Garnet - Opacites - Epidote + zoizite - Pyroxenes;
3. **Garnet** - Amphiboles - Epidote + zoizite - Opacites - Pyroxenes;

Also, there are the heavy-mineral associations in which one of the above prevails, but the order of the indicator mineral is changed (Fig. 7).

The first association was dominated by **Opacites**, evidenced in most samples collected from the upper layer of

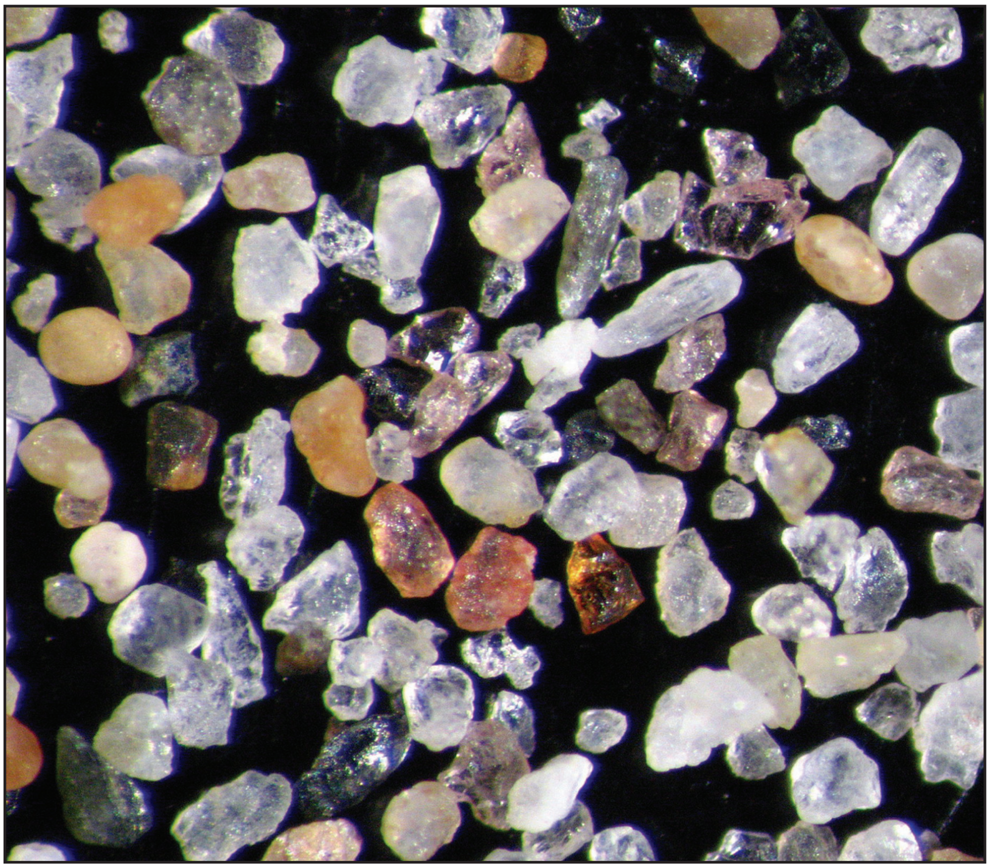

Fig. 8 Image of some minerals from the sands, viewed with stereomicroscope.

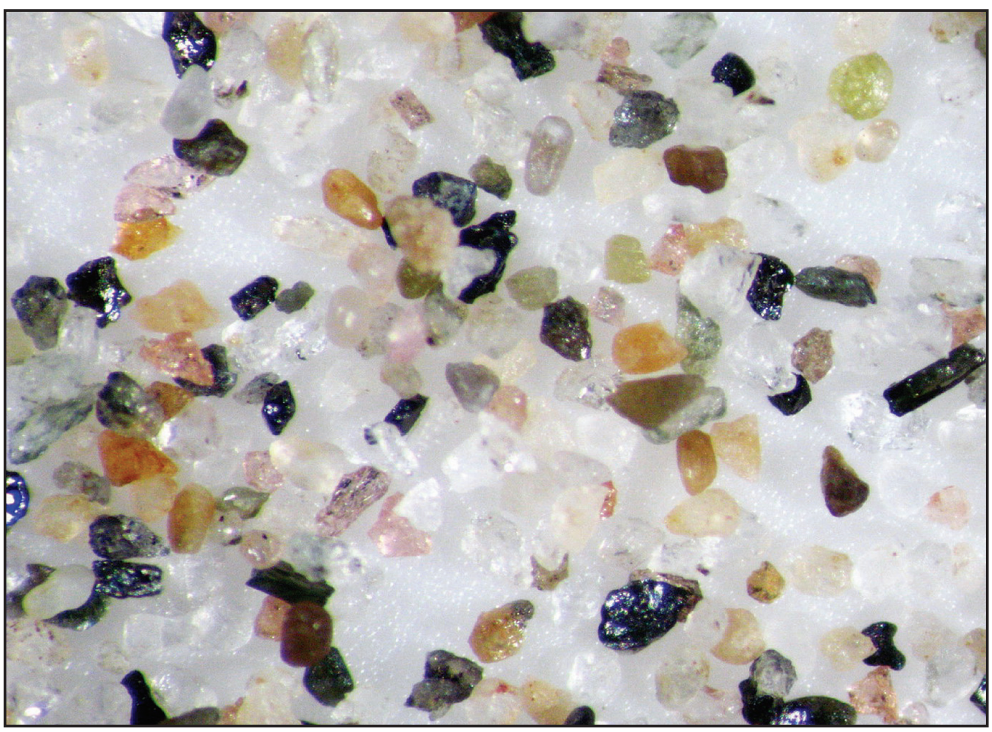

Fig. 9 Naturally concentrated heavy minerals, viewed with stereomicroscope.

Table 1. Statistical characteristics of sandy fraction and heavy minerals in sediments of the map sheets L-35-144-C, K-35-12-A and K-35-11-B.

	L-35-144-C				K-35-12-A				K-35-11-B			
Fraction (%)	**Mean**	**Median**	**Minim**	**Maxim**	**Mean**	**Median**	**Minim**	**Maxim**	**Mean**	**Median**	**Minim**	**Maxim**
Fine and very fine sand in sample	5.83	3.00	0.72	81.02	12.74	5.00	1.30	78.50	13.32	9.99	2.99	35.00
Siliciclastes in fine and very fine sand	15.79	5.80	0.00	97.80	40.49	29.85	3.00	99.50	59.35	66.98	21.02	83.09
Carbonate in fine and very fine sand	84.21	94.20	2.20	100.00	59.51	70.15	0.50	97.00	40.65	33.02	16.91	78.98
Heavy fraction in fine and very fine sand	3.40	0.13	0.00	43.89	3.31	0.37	0.00	24.00	1.75	1.05	0.18	11.57
Heavy fraction in sample	0.89	0.00	0.00	27.17	1.28	0.02	0.00	17.75	0.18	0.10	0.01	1.29
Heavy minerals in heavy fraction (%)	**Mean**	**Median**	**Minim**	**Maxim**	**Mean**	**Median**	**Minim**	**Maxim**	**Mean**	**Median**	**Minim**	**Maxim**
Garnet	10.67	8.63	0.00	33.33	14.71	13.81	0.00	48.67	42.07	42.00	25.50	56.10
Opacites	42.85	42.38	2.91	80.65	32.98	30.73	0.00	87.72	18.42	18.50	10.40	32.00
Epidote	5.05	1.96	0.00	77.67	8.27	6.46	0.00	48.67	16.53	16.10	6.40	27.60
Amphiboles	29.32	31.25	13.16	50.00	31.14	31.34	1.77	56.70	11.90	11.90	6.60	19.90
Pyroxenes	4.68	4.46	0.00	13.33	4.84	3.79	0.00	15.56	2.84	2.60	1.00	6.10
Staurolide	0.31	0.00	0.00	2.67	0.97	0.69	0.00	3.91	1.88	1.70	0.60	4.40
Kyanite	0.30	0.00	0.00	2.13	0.45	0.14	0.00	2.08	0.82	0.70	0.00	2.10
Rutile	0.62	0.00	0.00	2.51	1.03	1.09	0.00	2.90	1.03	1.09	0.00	2.90
Titanite	0.83	0.00	0.00	4.88	1.55	1.73	0.00	3.77	1.34	1.30	0.00	2.90
Zircon	0.29	0.00	0.00	2.44	0.52	0.55	0.00	2.42	0.48	0.40	0.00	1.90
Tourmaline	2.12	2.09	0.00	5.71	2.05	2.11	0.00	6.00	1.42	1.30	0.40	4.30
Glauconite	1.31	0.90	0.00	5.88	0.19	0.00	0.00	1.68	0.01	0.00	0.00	0.20
Pyrite	1.58	0.00	0.00	10.00	0.95	0.00	0.00	9.30	0.00	0.00	0.00	0.00

sediment. This is the main heavy minerals background of the sediments from north and south map sheets.

The second association is dominated by **Amphiboles** and occurs in northern and southern areas of the map sheet K-35-12-A. This association, together with the third, described below, are located along the coastal zone, on a possible relict belt.

The third association, dominated by **Garnet**, is less extensive in the upper layer of sediments. Even if on the map sheet K-35-11-B, garnets dominate quantitatively the heavy fraction, generally speaking, the content is the lowest one as compared to the other contents, evidenced within the Black Sea shelf sediments on other map sheets.

4. CONCLUSIONS

Comparing the data collected in the 2006-2008 time interval with earlier data from the 1984-2005 interval (Fulga & Fulga, 1996, 1998; Fulga, 2005 a, b), the author evidences a diminution ratio of the heavy minerals fraction among the sandy fraction constituents, including some changes in heavy-mineral associations.

Generally, the heavy-mineral associations have as primary major source of siliciclastic material the solid discharge of the Danube River, especially its bed-load. The coexistence of the recent sediments, characteristic to the shelf, coastal or deltaic areas, with relict sediments, is to be noted. The influence of a southern heavy minerals source is quite obvious, this fact being supported by enrichment of analysed samples with feldspars, epidote, pyroxenes and tourmaline, and by the changing of the granoclasts morphology, garnet and quartz occurring, mainly, as subrounded to rounded grains.

By comparing the new data with the existing mineralogical database we can observe a constantly decreasing of the terrigenous, siliciclastic minerals content, including heavy minerals. Correlated with oldest data, obtained on samples collected from some sediment cores, we can say that within the area of the shelf zone, mapped in the framework of GeoEcoMar recent programs, fossil alignments of coastal belts can be evidenced between isobaths 60 and 75 m, which runs parallel to the present beach line. We presume the existence of a paleovalley, too.

Taking into account that the source area for the studied zones is represented by the geological substratum of the Danube River catchment area, the spread of various associations of heavy minerals is determined by the hydrodynamic regime dominated by marine currents, but also, by the direction of the waves generated by wind.

The Danube terrigenous mineralogical province is characterised by a mixture of old and new sediments, marine and deltaic palimpsest sediments. The variety of the heavy-mineral associations is due to the existence of a multicycled material proving a coastline migration. The influence of a supplementary supply, the erosion of old sediment belts and the direction of the currents changed the distribution of the heavy minerals.

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