STUDY OF HEAVY MINERALS FROM THE VJOSA AND MATI RIVER DELTA SEDIMENTS IN ALBANIA

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Abstract

This research is focused on the determination of the heavy minerals (HM) load of the Vjosa and Mati river delta deposits along the Albanian coastline and it is based on X-ray Diffractometry. The Albanian coastline consists of sandy beaches at the north (Adriatic coastline) and rocky escarpments at the south (Ionian coastline). Several layers of heavy mineral deposits, up to 50 cm thick, with heavy mineral fraction up to 95% and 88% of total sample for Vjosa and Mati sediments respectively, are identified. The layers enriched in heavy minerals from Vjosa delta deposits are almost black in colour, while at Mati delta these layers are dark green coloured. Separation of the heavy from the light fraction was performed, in order to compare the different fractions between the two studied delta areas. The accumulation of HM occurs mainly in the fraction of 125-250 µm in the sediments of both deltas. The HM dominate in the magnetic field of 0.4-0.8 A/m. XRD analysis results show a great variety of minerals present in the delta samples which can be attributed to the wide variety of geological zones and lithologies that are intersected by the Vjosa and Mati rivers, respectively. In the 63-425 µm fraction rich in heavy minerals of both delta systems considerable amounts of magnetite (up to 39.4% in Vjosa samples), chromite (up to 20.2% in Vjosa samples), garnet (up to 13.6% in Vjosa samples), ilmenite (up to 8.3% in Mati samples), rutile (up to 4.7% in Mati samples), hematite (up to 2.2% in Mati samples), and zircon (up to 2.1% in Vjosa samples) are observed. Rock forming minerals such as pyroxene,
amphibole, and epidote compose significant percentages of this fraction. In addition, the presence of gold grains in Vjosa delta sediments is remarkable. Both catchment areas consist to a great extent of similar formations such as the Mirdita Ophiolite Zone and the Pindos Ophiolite complex, providing thus a similar HM fingerprint at both delta areas. Minerals that occur in higher abundances reflect the extensive presence in the drained areas of related parent rocks which are rich in these minerals and which are often more vulnerable to weathering. The samples of Vjosa river delta show high percentage of carbonate constituents, which is related to the presence of carbonate rocks of the Ionian and Kruja tectonic zones within which the hydrographic network of the Vjosa River has been developed. The samples of Mati river delta show lower abundance of carbonate minerals, reflecting the limited presence of carbonate rocks at the Kruja Zone, which occur in the catchment area of the river near its mouth.

Keywords: River Delta Deposits, HM Concentrations, Magnetic Susceptibility, X-ray Diffractometry.
aimatita (εως 2,2% σε δείγματα Mat) και ζιρκονίου (εως 2,1% σε δείγματα Mat). Επιπρόσθετα, πετρογενετικά ορυκτά όπως πυρόξενος, αμφίβολος και επίδοστο αποτελούν σημαντικά ποσοστά αυτού του κλάσματος. Η παρουσία κόκκων χρυσού στα ιζήματα του δέλτα του Αώου είναι αξιοσημείωτη. Οι δύο λεκάνες απορροής αποτελούνται σε μεγάλο βαθμό από παρόμοιους σχηματισμούς όπως αυτοί των οροφιλιθικών συμπλεξιμάτων των Ζώνων Mirdita και Πίνδου, παρέχοντας έτσι παρόμοιες συγκεντρώσεις βαρέων ορυκτών και στους δύο περιοχές. Ορυκτά που εμφανίζονται σε μεγαλύτερες ποσότητες αντικατοπτρίζουν την εκτεταμένη παρουσία των μητρικών πετρωμάτων στις λεκάνες αποστράγγισης. Σαν ορυκτά αυτά τείνουν να είναι πιο ευάλωτα στις αλλοιώσεις λόγω καιρικών συνθηκών. Τα δελταϊκά δείγματα του ποταμού Αώου παρουσιάζουν υψηλές συγκεντρώσεις ανθρακικών ορυκτών, οι οποίες συνδέονται με την παρουσία ανθρακικών πετρωμάτων των Ιόνιας Ζώνης και της Ζώνης Κρύμα εντός των οποίων έχει αναπτυχθεί το υδρογραφικό δίκτυο του ποταμού. Από την άλλη πλευρά, τα δελταϊκά δείγματα του ποταμού Ματ εμφανίζουν χαμηλότερη υψηλότερη αφθονία ανθρακικών ορυκτών, αντανακλώντας την περιορισμένη παρουσία ανθρακικών πετρωμάτων της Ζώνης Κρύμα, στην περιοχή της λεκάνης απορροής του ποταμού.

1. INTRODUCTION

The Adriatic coastline consists of several river delta systems and sandy beaches characterized by the presence of dark-coloured heavy mineral accumulations, some of which are studied in this contribution. Heavy minerals (HM) are sensitive indicators of provenance. Consequently, their analysis is most widely used in the determination of the provenance. Because of their diversity and characteristic origin of several HM, they play a key role in the interpretation of sediment provenance (Morton, 1985). They have been used as an important tool to understand sedimentary processes and to identify operating factors that control depositional environments (Morton and Hallsworth, 1999). Heavy mineral fractions in sediments are often composed of diverse mineral species, in which each grain conveys its own history. It is the sedimentary petrologist's task to decipher the message encoded in the assemblages allowing to: 1) determine provenance; 2) trace sediment transport paths; 3) map sediment distributions; 4) delineate sedimentary petrological provinces; 5) outline, and in suitable cases correlate, various sand bodies; 6) indicate the action of particular hydraulic regimes and concentrating processes; 7) locate potential economic deposits (Mange and Mauer, 1992). The use of heavy minerals for constraining sediment provenance, source lithology and palaeotransport was recognised early on, while the range of heavy mineral applications increased progressively through the 20th century and up to the present day, in parallel with the application of modern technology (Mange and Wright, 2007). Heavy
mineral assemblages are influenced by physical properties such as: size, density and shape which affect selective sorting due to hydraulic effects. Each assemblage contains diverse heavy minerals with unique grains that convey its palaeo-history. The reliability of heavy mineral analyses is affected by source area climate, physiographic settings, hydraulic factors, diagenesis, pH, and abrasion during transportation (Garzanti et al., 2013, Etimita and Beka, 2019).

Li and Komar (1992) have undertaken a series of flume experiments to investigate the processes of selective entrainment and differential transport of sand containing a mixture of light and heavy minerals, from the ocean beach near the Columbia river mouth, at the northwest coast of the USA. Their study documented the grain sorting and sediment transport along shore away from the Columbia River, leaving black sand as a lag deposit on the beaches near the river mouth. Hamilton and Collins (1998) studied the Minninup placer deposits in Western Australia. These sediments form a Late Holocene transgressive barrier sequence with placer development occurring in transgressive dunes, beaches, near shore units and contemporary environments. They described the grain scale processes of differential entrainment and transport as well as shear shorting within Minninup placers. They also presented a model of deposit formation, based on the geomorphological concepts, which may assist in the search of new economic reserves. In their study area, ilmenite content of 89.5% in beach samples and 75.3% in dune samples was observed. Other minerals within these deposits were leucoxene (1.7% and 2.3%, respectively), zircon (4.7% and 4.9%, respectively), monazite (0.8% and 0.2%, respectively) and garnet (3.3% and 17.2%, respectively). The sediments are well sorted and mean grain sizes vary around 150 µm for ilmenite, 100 µm for zircon and 200 µm for garnet.

Lotfy (1999) reviewed the size distribution of heavy minerals, texture, and composition of some modern Nile Delta coastal sands (river, coastal dune, beach-face, and nearshore marine). Textural analysis of unseparated bulk samples indicates that the examined four types of sands differed in their mean grain sizes and degree of sorting. Heavy mineral distribution in the Nile delta coastal sands appear to depend on: range of grain size fractions in each sample, relative availability of heavy mineral in each size grade of the sample, specific gravity of minerals comprising these sands, and some other unknown factor or factors. The heavy mineral assemblage in the Nile River, beach, coastal dune and nearshore marine include: biotite, tourmaline, hornblende, augite, epidote, garnet, rutile, zircon, magnetite, ilmenite and monazite.
Komar (2007) reviewed the contrasting hydrodynamic properties (density, diameter and shapes) of heavy minerals in comparison to quartz and feldspar grains. He concluded that hydrodynamic sorting visibly separates the heavy from the light minerals, producing heavy-mineral black-sand concentrates and in some cases valuable placers. Komar (2007) explained the entrainment, transport and sorting of heavy mineral by waves and currents, mainly in the context of the placers formation found in rivers, beaches and continental shelf sands. He concluded that a better understanding of the physical processes that control mineral sorting is necessary to assist in provenance interpretations of heavy mineral analyses.

Significant advances have been made in understanding the formation of black-sand mineral concentrates on beaches, demonstrating that occurrences in the swash zone are due primarily to selective entrainment and bedload transport, while grain suspension by the surf and breaking waves can have a counter effect of homogenizing the different minerals. The processes of waves and currents in these marine environments can also account for large-scale sorting patterns, while longshore transport of the sand leads to a concentration of heavy minerals adjacent to a river-mouth source or next to a headland, or waves may ‘sweep’ the heavy minerals from continental shelf sands and concentrate them in landward beaches (Komar, 2007).

Cascalho and Fradique (2007) treated the sources and hydraulic sorting of heavy minerals on the Northern Portuguese continental margin. They studied 358 samples of shelf and upper slope and 146 samples from the major rivers. The main assemblages consisted of biotite (up to 81%), andalusite (up to 21%), tourmaline (up to 15%), amphibole (up to 17%), garnet (19% in the shelf and upper slope; 3% in the rivers), staurolite (up to 7%), zircon (up to 7%) and apatite (up to 4%). These minerals were sourced from metamorphic and igneous rocks (mainly granites, gneisses and schists), which are widespread in the drainage basins of all northern Portuguese rivers. Minor mineral suites include orthopyroxene, clinopyroxene and olivine, which were probably eroded from basic igneous rocks, located offshore in the outer shelf or upper slope, south of Porto canyon.

Setiady and Aryanto (2009) studied the distribution of heavy minerals in placer deposits in Singkawang waters, west Kalimantan, which commonly originated from felsic igneous rocks and were deposited on the seafloor. They analysed 36 samples by microscopy and categorized the HM in oxides, hydroxides and sulphides. The minerals found were magnetite, cassiterite (up to 15%), hematite (up to 60%) and ilmenite (up to 45%), silicates (zircon up to 4.5%, tourmaline up to 15%, topaz up to 5.5% and epidote.
up to 4%), sulphides (pyrite up to 4.2%) and carbonate groups. Pupienis et al. (2011) have studied the distribution of the heavy mineral concentrations along the southeast Baltic Sea coast where quartz and feldspars-rich sands contain variable amounts (1-8%) of heavy minerals such as garnet, rutile, zircon, magnetite, ilmenite, hornblende, and other accessory minerals. In addition, they documented the lithological differences between heavy mineral concentration and background quartz-rich sands focused on coastal environments with different sedimentary regimes.

At a great number of Adriatic coasts the presence of heavy minerals is mentioned in many studies, where attention is paid to their distribution, to the most interesting placers and to the interpretation of the provenance of these minerals. In the past, many studies focused on the shore placers of the Albanian coastline, for exploration of metal deposits (Sinoimeri, 1966; Sinoimeri et al., 1966; 1970; Ostrosi, 1977; Ostrosi et al., 1998). In 1964 a pilot project plant was set up in Durres Albania which was producing on average 10,000 tons of heavy mineral concentrates per year. Activities continued till 1994 with a great economical profit, producing zircon, rutile, ilmenite, chromite, magnetite, garnet, etc. Sinoimeri (1966) identified three different types of deposits: i.e. shore placers, dune placers and underwater marine placers. Ostrosi et al. (1998) have studied the heavy mineral placers along Adriatic Sea shore, the genetic types of the placers, their mineralogical composition and their potential economic importance. However, recent studies are sparse and questions related to the composition still remain. The aim of this article is to determine by XRD analysis the mineralogical composition of the heavy mineral concentrates from samples of the Vjosa and Mati delta sediments. A comparison between both deltas will be made and an assessment on the provenance of the heavy minerals will be presented. For this reason, the separation of the heavy from the light fractions of the studied sediments was necessary.

2. STUDY AREA

The Albanian coastline comprises about 454 km of rocky and sandy beaches along the Adriatic Sea and rocky escarpments along the Ionian coastline (Durmishi et al., 2005). The Adriatic coastline hosts several delta river systems and sandy beaches characterized by the presence of dark-coloured heavy mineral concentrations in its sediments. The study areas include the Vjosa and Mati river deltas systems.

Vjosa River has a length of 272 km, of which the first 80 km are in Greece and the rest 192 km in Albania. Its drainage basin covers an area of 6706 km² (Fig. 1a) and its most part is located in the Pindus Mountains in Greece (where the river is called Aoos). The
The surface area of the Vjosa delta is 317 km$^2$. It stretches from the Hoxhara channel to the Narta lagoon, forming a littoral area with a length of 22 km. The delta mainly consists of sandy sediments; several small beaches were formed by the dynamic movements of Vjosa river mouth during the Holocene Period (Durmishi et al., 2018). In the Vjosa delta several sedimentary layers rich in heavy minerals are identified. These deltaic sediments are characterized by a large variation in minerals content. Chromite, rock forming minerals such as pyroxenes, amphiboles, olivine and epidote, as well as ilmenite, zircon, rutile, garnet and to a less extent gold grains are reported (Xhaferri et al., 2014). Mati River is found in North Albania with its delta situated near the Rodoni Gulf. Its sediment sources are located in the Bulqiza District (Fig. 1: a) Map of the drainage basins of the studied Rivers; b and c) Geological map of the Vjosa River delta and Mati River delta). The river has a length of 115 km and its drainage basin covers an area of 2450 km$^2$. The delta of the river is composed of sandy sediments and several nice beaches are found at it. In addition, in the Mati delta deposits, several layers of black coloured sediments, rich in chromite, magnetite, pyroxenes, amphiboles, ilmenite, epidote, rutile, etc., are reported (Xhaferri et al., 2014).

Vjosa river delta is of particular interest because its sediments are related to a great variety of rock formations of Triassic to Quaternary Age. Its drainage basin consists mainly of flysch and molasse deposits developed in several sub-basins. Magmatic rocks, carbonates, clastic sediments and some ophiolitic units (mainly ultramafic), are exposed in spectacular outcrops that actually are subject to the erosive activity of the Vjosa river network. These weathering materials, transported and deposited on the shore, consist of gravels, sands, silts and clays most of which reflect relatively high hydraulic activity (Durmishi et al., 2018). Miocene and Pliocene molasses of the Peri-Adriatic depression make up the lower part of the drainage basin, which are covered by Quaternary deposits (Fig. 1 1 and 2). Westwards rocks of the Ionian tectonic zone follow, consisting of flysch, carbonates in the form of anticlines, carbonates with radiolarite intercalations and dolomite deposits. Then, a lower land cutting flysch, carbonate and dolomite deposits of the Kruja tectonic zone, follows. Subsequently, the river erodes the rocks of the Krasta tectonic zone which consists of carbonate and flysch deposits. Then Vjosa drains the Mirdita tectonic zone composed of ophiolitic formations (mainly peridotite and serpentinite) associated by radiolaritic cherts, carbonates, turbidity sediments and mélange units. Mélange rocks are the protolith of the metamorphic sole, resulting in metabasic and metasedimentary rock of amphibolite to greenschist facies (Fig. 1).
Fig. 1: a) Map of the drainage basins of the studied Rivers; b and c) Geological map of the Vjosa River delta and Mati River delta, respectively (ISPGJ-IGJN, 1983).

Mati River crosses the molasses of Peri-Adriatic depression and the flysch and carbonate deposits of Kruja and Krasta tectonic zones, in the western part (Fig. 1c). Further upstream it crosses the Mirdita tectonic ophiolites and an associated mélange. Mirdita tectonic strata are exposed over a wide belt making up a significant part of Mati drainage basin. This belt represents a synform structure (Nicolas et al., 1999) with two ultrabasic massif ranges in the western and eastern sides, with approximately N-S strike, often referred as western and eastern ultrabasic belts, whereas in the central part oceanic crust sequences are developed. The eastern ophiolites are constituted by thick harzburgitic tectonites, followed by dunitic and pyroxenitic cumulates, gabbros and plagiogranites, a well-developed, but not classical, sheeted dyke complex and volcanic sequence that consists of low-Ti basalts and andesites, dacites and rhyodacites. The western ophiolites are composed of harzburgitic and lherzolitic tectonites, as well as plagioclase-bearing lherzolitic and dunitic cumulates. The majority of ophiolites are of the Western type, but a part of the Eastern type is also drained by Mati River.
Further to the east, it crosses the molasses of Burreli basin located to the top of ophiolites (Fig. 1 and 2). The most important sediment contributor to Mati River is the Fani River which transects volcanic and sulphide-bearing rocks and crosses the large copper mining area of the Mirdita tectonic zone (Milushi, 2015).

**Fig. 2:** Tectonic map of Albania, with extension to the southwest in the border with Greece (modified by Velaj, 2015).
3. MATERIALS AND METHODS

Samples were taken from the Vjosa and Mati river deltas, mainly from layers along the coastline enriched in heavy minerals, from the area that follows the shore and from the dune system (Fig. 2 1b, c and Fig. 3). Half kilogram to 1.5 kg from each dried original sample was quartered and about 250 g of it was used for the analyses. A sufficient amount of each sample was placed in a beaker and dilute HCl (5%) was added for acid digestion and boiled until no reaction was anymore observed. Subsequently, the sample was washed several times and placed into an ultrasonic bath for 15 minutes to disintegrate the remaining sediment, clean its grains from clays or cement materials and disperse the flocculated particles. Each sample was weighted before and after acid treatment to quantify its carbonate content. For mineral identification, the grain size 63-425 µm was used (Mange and Maurer, 1992), after sieving with Endecotts ASTME11 laboratory sieve – steel mesh. This wide grain size allows a greater variety of heavy mineral grains to be mineralogically determined. Grains <63 µm in size were omitted as being very impractical to identify. They were negligible in any case, due to their low content in this fraction (about 0.02%). Grains with sizes >425 µm are absent in Vjosa sediments while in Mati sediments, such grains are composed mainly of lithic fragments. The separation of the heavy fraction (63-425 µm) was performed by immersion in high density liquids using LOC 100 (Laboratory Overflow Centrifugation) developed by Ijlst (1973), with a speed of 5000 rpm, in the laboratory of the Vrije Universiteit Amsterdam. For sample preparation, the applied heavy liquid consisted of a mix of Diodomethane (AcrosCas 75-11-6) and Orthodichloro-benzene (AcrosCas 5-50-1) solution to obtain a density of 2.9 g/cm³. In between separations, the liquid density was checked with a density gauge (Densito 30PX, Mettler Toledo). For a general assessment on the magnetic susceptibility of the HM fraction, we performed magnetic separation of it based on the classification of Rosenblum and Brownfield (1999). Because magnetic separation works better when a sample is split over narrow grain sizes, in order to facilitate the mineralogical determination, each treated sample was separated by sieving in three fractions: coarse, medium and fine sand, corresponding to the >250 µm, 125-250 µm, and <125 µm fractions. Then each fraction was divided in 5 other fractions considering its magnetic susceptibility. After separation of the hand magnet fraction, 4 other magnetic field fractions were separated using Franz Isodynamic Separator (Oberteuffer, 1974), by modifying the magnetic field. Each of the obtained fractions was weighted on an electronic weighing balance.

Mineral composition analyses were conducted by X-Ray Diffraction (XRD) analysis. The procedure is based on studies of Buhrke et al. (1998) and Webster et al. (2003), for
the total HM concentration. McChrone Micronizing Mill was used to reduce to 10 μm the particle size of the material to be set under XRD analysis. In its canister 2.7 grams of HM concentrate from each sample and 0.3 grams of ZnO as internal standard (10 wt%) were placed and 5 ml of ethanol were added. The grinding time was fixed to 5 minutes, after several tests. The obtained sample was washed with ethanol and subsequently dried for at least 48 hours. The dried sample was subsequently disaggregated by hand in an agate mortar and analysed by XRD. The analysis was performed by a Phillips PW 1830 diffractometer, while the XRD patterns were processed with Diffrac plus Eva software using a Master database. Mineral quantification was performed by Topaz Academic for Rietveld quantitative phase determination. The locations of the examined samples are presented in Fig. 3 and 4 and their description in Table 1.

| Sample | N/E | Description |
|--------|-----|-------------|
| VS01   | 40°38'24.22" 19°18'54.7" | The sample was taken from a black coloured layer, near the mouth of the Vjosa River, at a depth of 20 cm. |
| VS07 A/B/C | 40°40'37.9" 19°21'07.3" | The samples were taken about 1000 m from the shoreline. The profile was cleaned from the vegetation and three different horizons were sampled. |
| VS28   | 40°38'44.2" 19°18'47.4" | A section parallel to the coast was excavated and a regular layer enriched in HM was sampled. |
| VS33B  | 40°39'44.9" 19°18'56.1" | The sample was taken from a depth of 50 cm of a section where four different layers could be distinguished. Sample 33B was collected from a black layer enriched in HM. |
| VS34 A/B/C/D/E/F | 40°39'54.7" 19°18'59.4" | The samples were taken from a section with alternating dark coloured layers enriched in HM and lighter coloured ones. The layers dip towards the sea perpendicular to the excavated section. |
| VS38   | 40°37'15.9" 19°20'30.8" | The sample was taken from an aeolian sand ripple developed along a dune. |
| VS 57, 58, 59, 60 | 40°37'17.48" 19°20'29.62" | The sample VS60 corresponds to a 10 cm thick top layer with irregular black coloured thin layers of fine sand enriched in HM. |
| MA08   | 41°37'23.9" 19°34'42.3" | The sample was taken from a depth of 20 cm along the shoreline of Mati river delta. |
| MA11   | 41°37'36.1" 19°34'33.3" | The sample was taken from a depth of 20 cm, two meters from the excavated shoreline. Only two black layers, each 1 cm in thickness, were visible. |
| MA14   | 41°41'42.4" 19°34'52.6" | The sample was taken 2 m from the shoreline. Black coloured thin layers are visible. |
| S.MA18A | 41°41'08.9" 19°34'44.9" | The sample was taken from a sand ridge parallel to the coast covered by vegetation with an elevation of one meter above the beach. |
| MA19   | 41°41'08.5" 19°34'45.6" | Green coloured sand with parallel black layers was sampled at a depth of 20 cm. |
| MA21 A/B/C | 41°40'50.0" 19°34'38.5" | The samples were taken from an excavated sand ridge, 4 m from the shoreline along an East to West section with three consecutive cycles of deposition. The elevation is 80 cm above the sea level. |
| MA23   | 41°39'41.0" 19°34'14.5" | Beach sand sample was taken from a depth of 20 cm at the northern shore of Mati mouth, near an abandoned mouth. |
| MA26   | 41°39'58.2" 19°34'18.1" | The sample was taken from a depth of 30 cm of a black coloured layer enriched in HM. |
Fig. 3: Sample locations at Vjosa River and Mati River Deltas.

Fig. 4: Illustrations of sample locations. Vjosa delta: a) samples VS57-60; b) sample VS38; c) sample VS34 taken within an excavated dune. Mati delta: d) sample MA08; e) sample MA21 taken from the shoreline.

4. RESULTS

During field work, it was noticed that the colour of layers with a significant presence of HM in the Vjosa deltaic deposits is almost black while at Mati deposits these layers are
almost dark green. The layers with higher concentration of HM at Vjosa are thicker than those at Mati. Comparison of the weight percentage of HM fraction within samples from Vjosa delta to those from Mati delta (Table 2) leads to the conclusion that both delta samples contain sufficient amounts of HM. Furthermore, the granulometry of Vjosa deltaic deposits is finer than that of Mati deposits. The finer granulometry of the Vjosa delta sediments can be explained by the longest distance this river flows on a flat downstream terrain. Consequently, the hydrodynamic sorting leads to finer grain size fractions that can reach the delta. The downstream Mati river length is rather short and therefore less effective to impose fine granulometry. Consequently, the sorting is not as good as at Vjosa delta. Layers enriched in significant amounts of HM have been observed in areas with continuous coastline erosion. These facts fit with the finding of Komar (2007) that the shoreline may be receded after river mouth and create ideal conditions for HM accumulation. The greater rate of erosion, the higher is the concentration of HM and the finer is the mean grain size of sand. In areas with higher HM concentrations, coastal processes have selectively removed the grains of lower density and coarser size, leaving behind grains of high density and smaller size; the end result of such processes is the formation of black-sand placer deposits (Frihy, 2007).

Table 2. Weight percentages (wt%) of treated samples from Vjosa delta sediments.

| Sample | Dissolved1 | >425 µm2 | 425-63 µm3 | 425-63 µm4 Sank | 425-63 µm4 Floated |
|--------|------------|----------|-----------|----------------|-----------------|
| 1      | 3.00       | 0.00     | 95.45     | 1.55           |
| 7A     | 43.20      | 0.00     | 9.29      | 47.51          |
| 7B     | 18.32      | 0.00     | 60.25     | 21.43          |
| 7C     | 40.96      | 0.00     | 11.88     | 47.16          |
| 28     | 39.4       | 0.00     | 23.34     | 37.26          |
| 33B    | 18.87      | 0.00     | 67.86     | 13.27          |
| 34A    | 42.38      | 0.00     | 19.9      | 37.72          |
| 34B    | 12.72      | 0.00     | 80.49     | 6.79           |
| 34C    | 31.17      | 0.00     | 47.37     | 21.46          |
| 34D    | 7.04       | 0.00     | 90.16     | 2.80           |
| 34E    | 37.2       | 0.00     | 29.10     | 33.7           |
| 34F    | 33.35      | 0.00     | 43.56     | 23.09          |
| 38     | 26.76      | 0.00     | 30.13     | 43.11          |
| 60     | 36.46      | 0.00     | 34.68     | 28.86          |

1wt% of dissolved materials, 2wt% after sieving, 3wt% of heavy minerals after immersion in heavy liquid, 4wt% of light fraction after immersion in heavy liquid

Vjosa river delta samples show higher percentages of dissolved materials, indicating a higher contribution of carbonate grains (Table 2). This is related to the presence of limestone formations in the anticlines and synclines of the Ionian and Kruja tectonic zones on which the drainage network of Vjosa River was developed. As shown in Figure 5a, after the HCl (5%) treatment, the percentages of the dissolved and floated (light) materials are in positive correlation in all samples. However, a slight deviation
from this fact is noticed in sample 38 that corresponds to a sample taken from a dune cordon.

The situation is completely different for the Mati delta samples. The total percentage of the dissolved materials is very low and there exists no relationship between the percentages of the dissolved and floated materials (Fig. 5b). However, a good relationship is noticed between the percentages of the floated materials and the coarser fraction (>425 μm). The dissolved materials mainly belong to the carbonate constituents which are related to the limited presence of the limestone formations of Kruja tectonic zone at the adjacent area of the Mati river delta.

The separation of the heavy fraction from each sample was performed by immersion in high density liquids. This heavy part was thoroughly cleaned and separated by sieving in three fractions (>250 μm, 250-125 μm, <125 μm). Then each fraction was subjected to magnetic field susceptibility. The grain size distribution (wt%) of the treated samples is presented in Tables 4 and 5. It is shown that the medium size fraction (125-250 μm) predominates in both delta sediments. In extension of this finding this fraction must be the richest in HM. Nevertheless, differences are observed between these two river delta deposits. The coarser fraction (>250 μm) of sands from Vjosa shows lower percentage and thus lower concentration of heavy minerals, whereas at Mati River lower concentration of HM exists in the finer fraction (<125 μm). The latter is probably related to the extended presence of ophiolitic rock formations in the Mati river drainage basin; such rocks are more resistant to mechanical weathering.

| Sample | Dissolved$^1$ | >425 μm$^2$ | 425-63 μm$^3$ Sank | 425-63 μm$^4$ Floated |
|--------|---------------|-------------|---------------------|----------------------|
| 8      | 4.44          | 0.00        | 88.17               | 7.39                 |
| 11     | 4.30          | 1.40        | 69.43               | 24.87                |
| 14     | 5.71          | 0.73        | 73.67               | 19.89                |
| 18A    | 4.14          | 0.96        | 55.61               | 39.29                |
| 19     | 8.00          | 10.17       | 42.41               | 39.42                |
| 21A    | 5.56          | 8.85        | 36.83               | 48.76                |
| 21B    | 3.96          | 3.74        | 65.52               | 26.78                |
| 21C    | 3.20          | 0.62        | 82.65               | 13.53                |
| 23     | 5.80          | 13.26       | 38.29               | 42.65                |
| 26     | 7.17          | 3.83        | 49.95               | 39.05                |

1 wt% of dissolved materials, 2 wt% after sieving, 3 wt% of heavy minerals after immersion in heavy liquid, 4 wt% of light fraction after immersion in heavy liquid.
Fig. 5: Variation of weight percentages of the dissolved, >425 µm, sank (425-63 µm) and floated (425-63 µm) fractions from each sample analyzed from the Vjosa (a) and Mati (b) river deltas.

Table 4. Grain size distribution (wt%) of the treated samples which are enriched in Heavy Minerals from Vjosa delta sediments.

| Fraction | Mean | 1   | 7/A | 7/B | 7/C | 28 | 33/B | 34/A | 34/B | 34/C | 34/D | 34/E | 34/F | 38 | 60 |
|----------|------|-----|-----|-----|-----|----|------|------|------|------|------|------|------|----|----|
| >250 µm  | 5.7  | 0.4 | 3.9 | 2.4 | 2.5 | 5.1 | 7.4  | 14.4 | 4.6  | 12.5 | 2.1  | 6.0  | 7.1  | 4.9 | 7.0 |
| 125-250 µm| 83.0 | 76.3| 83.1| 78.9| 80.0| 83.0| 85.6 | 80.4 | 88.7 | 79.8 | 89.1 | 86.5 | 83.5 | 83.6| 84.0|
| <125 µm  | 11.2 | 23.3| 13.0| 18.7| 17.5| 11.9| 7.0  | 5.2  | 6.7  | 7.7  | 8.8  | 7.5  | 9.4  | 11.5| 9.0 |

Table 5. Grain size distribution (wt%) of the treated samples which are enriched in Heavy Minerals from Mati delta sediments.

| Fraction | Mean | 8    | 11   | 14   | 18/A | 19   | 21/A | 21/B | 21/C | 23   | 26   |
|----------|------|------|------|------|------|------|------|------|------|------|------|
| >250 µm  | 18.9 | 3.4  | 12.8 | 19.0 | 10.9 | 23.6 | 23.7 | 22.8 | 14.1 | 38.0 | 20.6 |
| 125-250 µm| 76.1 | 86.6 | 82.7 | 75.3 | 83.4 | 70.9 | 73.1 | 73.6 | 80.2 | 60.2 | 75.3 |
| <125 µm  | 5.0  | 10.0 | 4.5  | 5.7  | 5.7  | 5.5  | 3.2  | 3.6  | 5.7  | 1.8  | 4.1  |

Finally, each sample fraction (>250 µm, 250-125 µm, <125 µm) was subjected to magnetic separation under different magnetic field (Tables 6 and 7). The following conclusions are drawn:

- In the fraction >250 µm from both delta sediments, higher percentages are noticed in the magnetic field of 0.4-0.8 A/m (Ampères/metre) where probably the highest accumulations of HM occur and to a less extend in the magnetic field of 0.8-1.7 A/m.
- In the fraction 125-250 µm from both delta sediments, HM are mostly concentrated in the magnetic field of 0.4-0.8 A/m and to significant percentages in the magnetic field of <0.4 A/m and hand magnet fraction.
- In the fraction <125 μm of Vjosa samples, HM are found in higher concentrations in the magnetic field of 0.4-0.8 A/m and in significant amounts in the magnetic field of <0.4 A/m and hand magnet fraction.
- In the fraction <125 μm of Mati samples, HM are found in higher concentrations in the hand magnet fraction.

The hand magnet fractions from both delta sediments are mainly composed of magnetite, easily recognizable by its black colour and metallic lustre and by its surrounded grains. In addition, a large amount of rock-forming minerals with magnetite inclusions (particularly in the coarser fractions) as well as grains of ilmenite and magnetitic chromite are also present.

| Grain size | Magnetic field (A/m) | 1 | 7/a | 7/b | 7/c | 28 | 33/B | 34/A | 34/B | 34/C | 34/D | 34/E | 34/F | 38 | 60 |
|------------|---------------------|---|-----|-----|-----|----|------|------|------|------|------|------|------|----|----|
| >250 μm    | Hand magnet         | 0.2 | 0.3 | 0.2 | 0.2 | 0.4 | 0.5  | 0.9  | 0.6  | 0.9  | 0.2  | 0.4  | 0.4  | 0.5 | 0.3 | 0.5 |
|            | <0.4                | 0.0 | 0.3 | 0.2 | 0.2 | 0.5 | 0.8  | 1.3  | 0.8  | 0.9  | 0.3  | 0.5  | 0.7  | 0.3 | 0.6 |    |
|            | 0.4-0.8             | 0.1 | 1.8 | 1.1 | 1.1 | 2.3 | 2.9  | 6.1  | 1.9  | 5.3  | 0.8  | 2.8  | 3.0  | 1.6 | 2.6 |    |
|            | 0.8-1.7             | 0.0 | 1.2 | 0.7 | 0.8 | 1.5 | 2.1  | 4.7  | 1.0  | 3.5  | 0.6  | 1.8  | 2.0  | 1.1 | 1.8 |    |
|            | >1.7                | 0.1 | 0.3 | 0.2 | 0.2 | 0.4 | 1.1  | 1.4  | 0.3  | 1.9  | 0.2  | 0.5  | 0.9  | 1.6 | 1.5 |    |
| <125 μm    | 125-250 μm          | 20.6 | 7.6 | 11.4 | 9.8 | 11.0 | 17.4 | 9.3  | 20.0 | 13.6 | 19.6 | 10.7 | 14.5 | 7.4 | 14.6 |    |
|            | >1.7                | 0.1 | 0.3 | 0.2 | 0.2 | 0.4 | 1.1  | 1.4  | 0.3  | 1.9  | 0.2  | 0.5  | 0.9  | 1.6 | 1.5 |    |
|            | 0.4-0.8             | 22.1 | 10.0 | 19.1 | 10.9 | 11.9 | 21.6 | 13.1 | 26.4 | 15.9 | 26.6 | 15.2 | 17.9 | 12.5 | 19.3 |    |
|            | 0.8-1.7             | 29.5 | 42.1 | 35.8 | 38.6 | 41.1 | 37.9 | 39.6 | 36.5 | 36.6 | 36.6 | 44.4 | 36.5 | 35.9 | 37.8 |    |
|            | >1.7                | 21.2 | 2.7 | 6.5 | 1.8 | 4.5 | 7.2  | 2.7  | 1.8  | 4.2  | 2.0  | 2.8  | 3.9  | 14.0 | 4.5 |    |
|            | 0.8-1.7             | 6.5 | 2.6 | 4.2 | 3.5 | 3.7 | 2.2  | 1.3  | 2.1  | 2.3  | 2.7  | 1.9  | 2.8  | 2.2 | 2.5 |    |
|            | >1.7                | 6.4 | 3.0 | 5.4 | 6.2 | 2.9 | 1.6  | 1.5  | 1.4  | 2.5  | 1.8  | 2.1  | 2.8  | 2.7 | 2.8 |    |
| <125 μm    | 0.4-0.8             | 9.0 | 5.9 | 8.2 | 6.1 | 4.1 | 2.8  | 2.0  | 2.9  | 2.9  | 3.4  | 3.3  | 3.9  | 5.0 | 3.2 |    |
|            | 0.8-1.7             | 0.1 | 0.9 | 0.1 | 0.9 | 0.7 | 0.0  | 0.2  | 0.0  | 0.1  | 0.0  | 0.2  | 0.1  | 0.4 | 0.1 |    |
|            | >1.7                | 1.3 | 0.6 | 0.8 | 0.8 | 0.5 | 0.4  | 0.2  | 0.3  | 0.4  | 0.2  | 0.3  | 0.5  | 1.1 | 0.4 |    |

| Grain size | Magnetic field (A/m) | 8 | 11 | 14 | 18/a | 19 | 21/a | 21/b | 21/c | 23 | 26 |
|------------|---------------------|---|----|----|------|---|------|------|------|----|----|
| >250 μm    | Hand magnet         | 0.4 | 1.6 | 2.6 | 1.7 | 3.7 | 4.2  | 3.4  | 1.7  | 5.5 | 3.1 |
|            | <0.4                | 0.4 | 2.1 | 3.1 | 3.1 | 3.9 | 3.9  | 3.7  | 2.1  | 6.7 | 3.2 |
|            | 0.4-0.8             | 1.2 | 5.9 | 8.4 | 4.6 | 11.1 | 11.4 | 9.8  | 6.7  | 19.2 | 9.8 |
|            | 0.8-1.7             | 0.4 | 2.2 | 3.6 | 1.8 | 4.4 | 4.0  | 4.0  | 2.6  | 6.4 | 3.6 |
|            | >1.7                | 1.0 | 1.0 | 1.2 | 0.5 | 0.2  | 1.9  | 1.0  | 0.2  | 0.9 |    |
| <125 μm    | 125-250 μm          | 38.4 | 24.5 | 15.3 | 17.9 | 18.8 | 15.2 | 20.3 | 12.2 | 18.3 | 17.4 |
|            | >1.7                | 15.7 | 14.8 | 11.1 | 11.1 | 14.3 | 11.2 | 14.1 | 12.5 | 9.7 | 12.2 |
|            | 0.4-0.8             | 27.4 | 33.7 | 35.3 | 39.6 | 28.4 | 35.8 | 28.4 | 41.3 | 25.7 | 34.4 |
|            | 0.8-1.7             | 4.5 | 8.4 | 11.0 | 11.3 | 8.1 | 10.5 | 8.8  | 11.2 | 6.2 | 9.4 |
|            | >1.7                | 0.6 | 1.3 | 2.6 | 3.5 | 1.3 | 0.4  | 2.0  | 3.0  | 0.3 | 1.9 |
| <125 μm    | 0.4-0.8             | 6.3 | 2.7 | 3.4 | 2.8 | 3.2 | 1.8  | 2.0  | 2.2  | 1.0 | 1.8 |
|            | 0.8-1.7             | 0.1 | 0.1 | 0.1 | 0.2 | 0.1 | 0.1  | 0.2  | 0.0  | 0.2 | 0.2 |
|            | >1.7                | 0.1 | 0.1 | 0.0 | 0.1 | 0.0 | 0.0  | 0.0  | 0.1  | 0.0 | 0.1 |
The low magnetic field fraction (<0.4 A/m) is composed mainly of chromite and minor amounts of ilmenite and hematite grains. Garnet grains from Vjosa sediments present higher magnetic susceptibility in comparison with those from Mati sediments. The highest concentration of chromite at Vjosa sediments is found in the 0.4-0.8 A/m magnetic field fraction, which is not evident at the Mati deposits. This likely reflects a difference in the chromite presence at the parent rocks of the drainage basins of Vjosa and Mati rivers. The magnetic field fraction of 0.8-1.7 A/m is composed almost entirely by rock-forming minerals such as pyroxenes, amphiboles, less olivine and rutile, and rarely some zircon. In the Vjosa deposits some chromite is still present, probably because of its low Fe-content. Rutile and zircon are concentrated in the magnetic field fraction of >1.7 A/m of both delta sediments. However, in the Vjosa deposits zircon content is higher than in Mati delta samples. In addition, in this fraction some carbonate and quartz grains are found meaning that the acid treatment and the heavy liquid processing were incomplete.

The results of the XRD analysis of the rich in heavy minerals fraction of 63-425 μm from the Vjosa and Mati delta sediments are presented in Table 8 and 9, respectively. These results show a great variety of minerals present in the delta samples which can be attributed to the wide variety of geological zones and rock formations that are intersected by the Vjosa and Mati rivers, respectively. Given the fact that the catchments of both rivers are developed on similar formations exposed in the Mirdita Ophiolite Zone and Pindos Ophiolite Zone, the similar HM fingerprint can be explained (Table 10).

In addition, both catchments contain some carbonate formations, weathering products of which compose a significant part of the delta sediments. However, they were dissolved during the sample processing. The differences in relative mineral contribution reflect the source lithologies in the drainage basins of both rivers. Zircon and garnet (accessory minerals in igneous and metamorphic rocks), are present in significant amounts in the Vjosa samples. The parent rocks of the catchment area drained by this river include ophiolitic rocks, flysch and molasses. From the weathering of these rocks zircon and garnet tiny crystals could be detached, transported and discharged at the river’s mouth with other weathering products.
Table 8. Mineralogical composition (wt%) of the 63-425 µm fraction rich in heavy minerals from the Vjosa delta sediments.

| Sample | Magnetite | Chromite | Ilmenite | Hematite | Pyroxenes | Olivine | Amphiboles | Epidote | Garnet | Rutile | Zircon | Quartz | Other |
|--------|-----------|----------|----------|----------|-----------|---------|------------|---------|--------|--------|--------|--------|-------|
| 1      | 39.4      | 18.0     | 3.8      | 1.7      | 14.3      | 1.7     | 1.7        | 2.0     | 8.0    | 1.5    | 2.1    | 1.4    | 4.4   |
| 7A     | 12.2      | 16.8     | 1.7      | 0.8      | 24.7      | 11.0    | 11.9       | 2.9     | 6.9    | 2.6    | 0.9    | 2.1    | 5.5   |
| 7B     | 21.8      | 20.2     | 1.9      | 1.4      | 17.9      | 4.2     | 10.8       | 1.6     | 8.9    | 1.8    | 0.9    | 1.3    | 7.3   |
| 7C     | 18.8      | 5.8      | 3.4      | 0.0      | 23.6      | 7.1     | 18.2       | 6.6     | 5.4    | 1.7    | 0.4    | 3.2    | 5.9   |
| 28     | 8.5       | 2.3      | 2.3      | 0.0      | 31.5      | 5.1     | 23.3       | 7.8     | 4.6    | 2.4    | 0.4    | 5.3    | 6.5   |
| 33B    | 25.8      | 10.2     | 3.5      | 0.6      | 22.4      | 2.0     | 12.3       | 3.3     | 7.7    | 1.3    | 0.6    | 2.9    | 7.4   |
| 34A    | 8.5       | 6.7      | 1.6      | 0.4      | 31.8      | 6.7     | 22.5       | 5.2     | 4.2    | 2.2    | 0.4    | 1.2    | 8.6   |
| 34B    | 25.4      | 10.8     | 1.7      | 1.8      | 19.2      | 3.9     | 6.2        | 4.5     | 13.6   | 5.3    | 0.6    | 1.4    | 7.6   |
| 34C    | 23.4      | 13.1     | 1.7      | 1.0      | 25.3      | 2.6     | 7.2        | 6.5     | 8.6    | 3.0    | 0.6    | 1.9    | 5.1   |
| 34D    | 27.6      | 15.2     | 3.8      | 2.1      | 20.3      | 1.2     | 7.7        | 1.6     | 10.8   | 2.1    | 0.9    | 1.2    | 5.5   |
| 34E    | 11.0      | 7.8      | 3.4      | 1.0      | 37.7      | 5.6     | 11.0       | 2.4     | 7.1    | 1.7    | 0.6    | 1.5    | 9.2   |
| 34F    | 14.6      | 9.1      | 2.8      | 1.0      | 29.2      | 6.4     | 11.4       | 6.9     | 8.6    | 3.8    | 0.5    | 2.8    | 2.9   |
| 38     | 4.9       | 3.6      | 0.0      | 0.0      | 33.3      | 6.3     | 17.2       | 3.6     | 5.7    | 3.0    | 0.2    | 7.6    | 14.6  |
| 60     | 25.7      | 12.6     | 3.1      | 1.8      | 21.9      | 4.4     | 7.4        | 3.5     | 8.9    | 2.3    | 0.4    | 6.2    | 1.8   |

Other: (magnesite, titanite, clinopchlore, sphalerite, dolomite, calcite and ankerite).

Table 9. Mineralogical composition (wt%) of the 63-425 µm fraction rich in heavy minerals from the Mati delta sediments.

| Sample | Magnetite | Chromite | Ilmenite | Hematite | Pyroxenes | Olivine | Amphiboles | Epidote | Garnet | Rutile | Zircon | Quartz | Other |
|--------|-----------|----------|----------|----------|-----------|---------|------------|---------|--------|--------|--------|--------|-------|
| 8      | 16.8      | 14.6     | 8.3      | 2.2      | 22.0      | 1.5     | 16.7       | 7.0     | 2.5    | 2.8    | 0.6    | 2.0    | 3.0   |
| 11     | 8.2       | 6.6      | 2.2      | 0.0      | 33.9      | 5.4     | 19.5       | 7.6     | 4.9    | 2.3    | 0.3    | 2.8    | 6.3   |
| 14     | 3.7       | 3.3      | 2.1      | 0.0      | 44.2      | 9.0     | 19.3       | 5.1     | 0.0    | 3.9    | 0.4    | 3.8    | 5.2   |
| 18A    | 5.0       | 5.0      | 2.2      | 0.0      | 31.8      | 5.0     | 22.9       | 8.6     | 0.0    | 3.3    | 0.9    | 8.3    | 7.0   |
| 19     | 4.8       | 0.8      | 0.9      | 1.0      | 40.0      | 4.4     | 25.4       | 6.0     | 2.1    | 3.0    | 0.8    | 5.7    | 5.1   |
| 21A    | 4.6       | 1.8      | 1.1      | 1.9      | 37.9      | 6.6     | 20.5       | 9.4     | 0.0    | 4.2    | 0.7    | 2.0    | 9.3   |
| 21B    | 13.0      | 5.3      | 2.8      | 1.2      | 34.1      | 6.0     | 18.3       | 6.4     | 0.0    | 3.3    | 0.8    | 2.3    | 6.5   |
| 21C    | 9.2       | 4.7      | 3.3      | 1.2      | 37.6      | 6.0     | 17.9       | 9.2     | 0.0    | 4.1    | 0.3    | 2.0    | 4.5   |
| 23     | 5.6       | 4.4      | 3.4      | 1.1      | 40.7      | 3.6     | 20.4       | 6.0     | 0.0    | 2.1    | 0.5    | 1.0    | 11.2  |
| 26     | 7.9       | 4.0      | 0.0      | 1.8      | 44.6      | 4.7     | 20.7       | 4.5     | 0.0    | 4.7    | 0.7    | 3.1    | 3.3   |

Other: (magnesite, titanite, clinopchlore, sphalerite, dolomite, calcite and ankerite).

Magnetite, chromite and ilmenite are present in almost all samples of Vjosa and Mati delta sediments. The black colour of the layers rich in HM is induced by chromite and magnetite grains. There are important differences between the chromite content of both delta sediments. The ratio chromite/rock-forming minerals at Vjosa sediments is by average 0.33 (maximum ratio 1.02 in sample no. 1, from the river mouth) whereas at Mati sediments this ratio is 0.09 (maximum ratio 0.4 in sample no. 8, near the river mouth). The presence of magnetite, ilmenite and chromite is justified by the extensive presence of ophiolites and peridotites at their drainage basins.
Pyroxenes, amphiboles, olivine and epidote are the main rock-forming minerals that compose the majority of HM fractions in both deltas. They are more predominant in Mati delta sediments where 90% of them are composed by >55% of these rock-forming minerals, while in the Vjosa delta sediments only 25% of the samples contain a similar mineral assemblage. The high percentages of rock-forming minerals are more evident in Mati deposits since this river drains mafic and ultramafic rocks from its drainage basin. These high percentages explain the absence of black coloured layers in Mati delta sediments.

### Table 10. Overview of similarities and differences between the sediments of both river deltas.

| Similarities                                      | Differences                                      |
|--------------------------------------------------|--------------------------------------------------|
| **Terrain observation**                          |                                                  |
| - HM enriched layers;                            | - Black coloured layers;                        |
| - Ancient channels visible;                      | - Thicker enrichment layers;                    |
| - Successive layers;                             | - Dark green coloured layers;                   |
| - Considerable wt% floated;                     | - Thinner enrichment layers;                    |
| - High wt% of 125-250 µm;                        |                                                  |
| **Analysis observation**                         |                                                  |
| - High wt% sank;                                 | - Higher wt% dissolved;                         |
| - Considerable wt% floated;                     | - Wt% of >425 µm = 0;                           |
| - Considerable wt% of <125 µm;                  | - Lower wt% dissolved;                          |
| - Dominated by medium magnetic field fractions for grains of >125 µm; | - Wt% of >425 µm > 0;                           |
| - Presence of Rock forming minerals (RFM), average of olivine and epidote fraction is similar; | - Considerable wt% of >250µm;                  |
| - Magnetite and chromite;                        | - Coarser grain size of sediments;              |
| - Ilmenite and hematite possess equal average concentrations; |                                                  |
| - Lower percentage of pyroxenes and amphiboles; | - Higher percentage of pyroxenes and amphiboles; |
| - Lower percentage of RFM;                      | - Higher percentage of RFM;                     |
| - Higher percentage of garnet and lower percentage of rutile; | - Lower percentage or absence of garnet and higher percentage of rutile; |
| **Drainage basin**                               |                                                  |
| - Adriatic depression molasses;                  | - Wide extent of Mirdita Zone (2 types of ophiolites comprising a large peridotite massif composed of plagioclase and plagioclase-spinel lherzolites to spinel harzburgites); |
| - Ophiolite homologues;                          | - Ultramafics and gabbros;                      |
| - Flysch, carbonate and dolomite deposits of Kruja Zone; | - Volcanic extrusives (basalt, andesite, dacite, rhyolite); |
| - Carbonate and flysch deposits of Krasta Zone;  | - Limited felsic igneous rocks;                  |
| - Two separate ophiolitic zones;                 | - Plutonic rocks (pyroxenite, gabbro, quartz diorite, intrusions of plagiogranite, amphibole gabbro); |
| - Kolonja area ophiolites containing blocks of ultramafic rocks; | - Metamorphic rocks (amphibolites, greenschists and micaschists); |
| - Pindos Ophiolite complex in Greece (sheets imbricated together with carbonates, turbidites and mélange units); | - Molasses of Albania-Thessaly trough; |
| - Ultramafic and mafic cumulates;                | - Limited presence of Kruja and Krasta Zone;    |
| - Harzburgite mantle tectonites with pyroxenes;  | - Absence of Ionian Zone;                       |
| - Peridotite overlain by ultramafic cumulates;   |                                                  |
| - Mélange rocks;                                 |                                                  |
| - Significant part of drainage basin occurs in Ionian, Kruja and Krasta Zones; |                                                  |
| - Limited presence of Albania-Thessaly trough;  |                                                  |
sediments compared to Vjosa ones. The greatest abundance of epidote and amphiboles in Mati delta deposits is due to the great variety of ophiolitic and metamorphic rocks present at its catchment area which extends over several hundred square kilometres. On the contrary, Vjosa River intersects some magmatic rocks only at the upper part of its drainage basin.

Garnets are more abundant in Vjosa delta sediments (up to 13.6% of the heavy fraction with average 7.8%) compared to Mati samples. The flysch deposits which exist extensively at Vjosa catchment area may be considered as parent rocks. According to XRD analyses, most garnets possess an almandine (up to 5%) or spessartine (up to 8%) mineralogy. Garnet is observed in minor amounts (up to 5% of the heavy fraction) or is absent from the Mati delta sediments, which is explained by the limited presence of metamorphic rocks and flysch at the drainage basin of the river. Rutile is present in all samples of Vjosa deposits (up to 3.8% of heavy fraction with average 2.3%) and in all samples of Mati deposits (up to 4.7% of heavy fraction with average 3.4%). It can be correlated to the occurrence of igneous rocks and schists of the drainage basins of both rivers. Zircon is omnipresent but it is found in higher amounts in Vjosa delta deposits, with a maximum of 2.1% in the heavy fraction of sample no. 1, while the highest amount of zircon detected in Mati delta deposits is 0.9% in the heavy fraction of sample no. 18A. The presence of zircon in Vjosa delta sediments is related to the flysch deposits of its catchment area. The zircon in Mati delta sediments is related to plagiogranitic rocks and ophiolitic sequences of its drainage basin. In addition, the presence of gold grains in Vjosa delta sediments is remarkable, besides tourmaline and pyrite grains.

5. DISCUSSION

The shore placers of the Adriatic Sea have been explored as potential economic deposits. Ostrosi et al. (1998) reviewed the sources of minerals from rocks of the Albanides, the transportation of shredded materials from the hydrologic mountain network to the shore of the Adriatic Sea and the location of the formation of HM shore placers. The latter are located within Quaternary sands of the Albania seashore, with a 200 km length from Buna in the North to Vlora in the South. These deposits make up the zone of fields and seashore with a width from some meters till 16 km. Ostrosi et al. (1998) have estimated that the heavy fraction makes up 8-16% of the sand mass. At the Vjosa river sediments this fraction contains 2.8% titano-magnetite, 26.6% chromite, 5.2% ilmenite, 0.41% zircon, 0.77% rutile, 10.65% garnet, 0.82% leucoxene, and 0.91% barite. At the Mati river sediments this fraction contains 43.6% titano-magnetite, 10.5% chromite, 4.2% ilmenite, 0.06% zircon, 0.07% rutile, 0.9% garnet, 0.25%
leucoxene, and 0.01% barite. In addition, two other river deltas along the Albanian coast with placers were studied by these authors namely the Erzen River (central-northern shore) and Shkumbin-Kavaje River (central-southern shore). The Erzeni river sediments consist of 0.5% titano-magnetite, 12.5% chromite, 7.7% ilmenite, 0.6% zircon, 0.6% rutile, 10.7% garnet, 0.6% leucoxene and 0.1% barite, while the Shkumbini river sediments consist of 2.6% titano-magnetite, 16.6% chromite, 5.0% ilmenite, 0.2% zircon, 0.3% rutile, 6.9% garnet, 0.3% leucoxene and 0.1% barite.

Ostrosi (1977) reported that heavy fraction minerals of Adriatic placers are associated with pyroxene, amphibole, epidote, kainite, tourmaline, limonite, pyrite, and small amounts of monazite. In the northern beaches the main heavy minerals are chromite and titan-magnetite, in contrast with the southern beaches where chromite, zircon, rutile, ilmenite and garnet are more dominant, while the light fraction makes up 84-92% of the samples. In northern beaches quartz and feldspars are present in small amounts while the largest part of the sediments consists of serpentine-chlorite which gives the sand a grey to green colour, while the southern seashore sediments are quartz-carbonate rich (Ostrosi et al., 1998).

The heavy minerals fraction has a mean diameter of 0.22 mm in the north and 0.17 mm in the south. The diameter of the largest part of heavy minerals varies between 0.40 mm and 0.11 mm (Sinoimeri, 1966). Shore placers were formed from the weathering and transportation of shredded rocks of the Albanides by the hydrographic network of rivers (Ostrosi et al., 1998). They classified the sources in 2 types; the first sources are the ophiolitic rocks and their presence is confirmed by the high content of titano-magnetite and chromite in the northern beaches, where rivers erode such rock formations; the second sources are those of accessory shredded minerals of Palaeozoic to Tertiary.

In this study, titanite is present only in few samples, concretely in the Vjosa samples 7A, 7C (located at 1100 m from the shoreline), 34A and 34E with percentages up to 2.8%, while in the samples 23C and 21C of Mati titanite makes up 5.0% of the heavy fraction. Leucoxene and barite are not accounted in this study. Samples were selected from the dark coloured sediment layers of both deltas. XRD analysis was focused in the 63-425 μm fraction that is the richest in heavy minerals. Ostrosi et al. (1998) evaluated the heavy minerals content from the total sand used for metal exploration, including the dunes, shore and marine placers. This can explain the differences encountered, because of the different study procedures.

Considering the tectonic units which intersect the Mati and Vjosa river drainage basins and the fact that Vjosa basin extends into Greece, other publications on heavy minerals...
of Albanian and Greek sediments have been taken into account. Faupl et al. (2007) have synthesized the heavy mineral results from studies conducted on flysch successions at the different tectonic units of the Hellenides to incorporate them into the geodynamic model of the Hellenic orogeny. The studied Hellenides tectonic units were: Pelagonian; Parnassos-Ghiona; Pindos (corresponding with Albanian Krasta-Çukali Zone) and Ionian-Gavrovo (corresponding with Albanian Ionian and Kruja Zones). For each unit an average heavy mineral composition of the sediments analyzed, was given. Zircon, tourmaline, rutile, apatite, garnet and chrome spinel are observed as frequent constituents in the turbidite sandstones of Hellenic flysch successions. Staurolite, chloritoid, epidote, amphiboles and pyroxenes occur in low amounts, sometimes as traces (1 or 2 grains/200). The authors indicated the presence of green and blue varieties of amphiboles. In addition, they applied ternary diagrams to illustrate the HM composition, defining provenance controlled genetic suites: i.e. ultra-stable group (zircon-tourmaline-rutile), metamorphic group (garnet, staurolite, chloritoid, blue amphibole) and ophiolite group (chrome spinel, pyroxene), excluding apatite and epidote because of their wide percentage as accessories in different rock types.

In the Krasta-Çukali Zone (Pindos Zone in Greece), the HM within the flysch succession older than Middle Eocene present relative uniform distribution, with a predominance of garnet, associated sometimes with blue amphiboles and low amounts of chromite. In the samples from mainland, of Middle Eocene to Late Oligocene age, an important change occurred in HM assemblage with increase of ophiolite formations and decrease of metamorphic rocks. This indicates the onset of tectonic activity and ophiolite emplacement, which later formed the extended “ophiolite nappe” of the Pindos Zone. In the Ionian and Kruja (Gavrovo-Tripolitza Zone in Greece) Zones, the flysch stage started in Late Eocene, with garnet-dominated assemblages. In the Ionian Zone of the mainland, in contrast with the Gavrovo-Tripolitza Zone, an influx of ophiolite minerals can be observed in some samples. The sedimentary material of flysch succession deposited in the Ionian – Gavrovo basin, was derived to a great extent from erosion of the newly formed nappe complex in the east. Faupl et al. (2007) proposed the reworking of the Pindos flysch; this is explained by the heavy mineral assemblages. Garnet-rich heavy mineral associations, characteristic of the Pindos flysch, are also typical for the flysch of the Gavrovo-Tripolitza and Ionian Zones. Even detrital blue amphiboles, known from the Pindos flysch, are present in trace amounts in the new foreland basin. Authors have evidenced that the Pindos flysch provenance is from metamorphic basement, exhumed ophiolitic bodies and outcropped blueshists. They have concluded that considerable clastic components of Gavrovo-Tripolitza flysch were recycled from the Pindos flysch. The Ionian flysch of Oligocene to Early Miocene
shows similar characteristics to that of the Gavrovo-Tripolitza Zone, but the influence of ophiolitic bodies becomes more important towards higher stratigraphic levels (Faupl et al., 2007).

The contribution of both the ultrastable group minerals and garnets in the flysch is related with the abundant garnet and granitoid formations being exposed in the east of Albania. Additional garnet contribution can be delivered by the metamorphic basement rocks, but the presence of Greek flysch with abundant garnet and small amounts of chromite seems to indicate non-ophiolitic derived garnets, because the basement rocks and ultramafics provide a simultaneous input of garnets and chromite. The heavy minerals present in the sediments of Vjosa and Mati river deltas show a rich assemblage of granitoid, metamorphic and ophiolite derived mineralogies. The majority of the latter could be accounted for by present day erosion of ophiolites and related rocks in the headwater of both rivers. Zircon and garnet show a marked variability which is assumed to be at least partly derived from the flysch and molasse sediments of the lower drainage basin of Vjosa River which were later concentrated in the beach placers. The dominance of present-day input by the Mirdita and Pindos ophiolites is likely to reflect a possible ophiolitic derived component in the flysch and molasse sediments. Due to the limited metamorphism of the Korabi zone in Albania, a more internal provenance area seems likely. The literature on the Pelagonian terrain allows explanation of the observed characteristics of both zircons and garnets, while at the same time sufficient siliciclastic material was provided to make up the thick flysch and molasse deposits. These proximal to distal sources can also provide the flysch with other observed minerals like rutile, staurolite and tourmaline. Heavy mineral assemblages determined for the corresponding Greek flysch deposits to the south (Faupl et al., 2007) confirm the interpretation of an important garnet and zircon component in the flysch sediments.

6. CONCLUSIONS

The HM content of the 63-425 μm fractions of the Vjosa and Mati delta sediments in Albania are studied on the basis of different magnetic field fractions and XRD analysis. The following conclusions are drawn:

- The layers enriched in heavy minerals from Vjosa delta deposits are almost black in colour because of the high concentration of magnetite and chromite in them, while at Mati delta these layers are coloured dark green due to the high concentration of rock forming minerals with green colour, such as pyroxenes, amphiboles, and olivine.
- The high percentage of dissolved materials in the Vjosa deposits indicates the significant presence of carbonate constituents. This is related to the extended presence of carbonate rocks of the Ionian and Kruja tectonic zones on which the hydrographic network of the Vjosa River has been developed. The low percentage of dissolved materials in Mati deposits reflects the limited presence of carbonate rocks at the Kruja Zone, near the river mouth.

- The lower granulometry of the Vjosa delta sediments can be attributed to the greater distance this river flows downstream on a flat terrain. The higher granulometry of the Mati deposits is related to the extended presence of ophiolites at its drainage basin and their resistance to mechanical weathering.

- The accumulation of HM occurs mainly in the fraction of 125-250 µm in the sediments of both deltas. The HM dominate in the magnetic field of 0.4-0.8 A/m.

- The XRD analysis of the 63-425 µm fraction showed that the minerals present in the delta sediments, can be attributed to a great variety of lithological formations which are intersected by the Vjosa and Mati rivers. Both catchment areas consist to a great extent of similar formations such as the Mirdita Ophiolite Zone and the Pindos Ophiolite complex, providing thus a similar HM fingerprint at both delta areas. Minerals that show significantly higher abundances reflect the extensive presence at the drained areas of such parent rocks which are rich in these minerals and more vulnerable to weathering.

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