Journal of Coastal Research	SI 39	165 - 169	ICS 2004 (Proceedings)	Brazil	ISSN 0749-0208

The Meaning of Heavy Minerals in the Recent Sedimentary Record of the Douro Estuary (Portugal)

C. Fradique†; J. Cascalho‡; T.Drago?; F. Rocha§ and T.Silveira¤

†Museu Nacional de História Natural, Lisboa, 1600-250, Portugal, catfradique@hotmail.com

‡Museu Nacional de História Natural, Lisboa, 1600-250, Portugal, jpcascalho@fc.ul.pt

∞ Instituto de Investigação das Pescas e do Mar-CRIPSUL, Olhão, 8700-305, Portugal, tdrago@ipimar.pt

§Universidade de Aveiro, Departamento de Geociências, Campus de Santiago, Aveiro, 3810-193, Portugal, frocha@geo.ua.pt

¤Instituto de Investigação das Pescas e do Mar-CRIPSUL,Olhão, 8700-305, Portugal, tanyasilveira@hotmail.com

ABSTRACT

FRADIQUE, C.; CASCALHO, J.; DRAGO, T.; ROCHA, F. and SILVEIRA, T.; 2006. The meaning of heavy minerals in the recent sedimentary record of the Douro Estuary (Portugal). Journal of Coastal Research, SI 39 (Proceedings of the 8th International Coastal Symposium), 165 - 169. Itajaí, SC, Brazil, ISSN 0749-0208.

The relative abundance of the different heavy mineral species may be used as a tool to deduce the provenance signal of the sediment and the dominant transport mode that occurred just prior to sedimentation. In this work, the sedimentary infilling of the Douro estuary was analysed using Principal Components Analysis (PCA) in order to characterize the sedimentary sequence over the past 14 000 years. Three cores were obtained by rotary drilling in this estuary and several samples were collected. Heavy minerals were separated using SPT (sodium poly-tungstate); different species were identified and the non-opaque minerals were counted. The mineralogical composition of the fines was analysed by X-ray diffraction (CuK radiation) on random-oriented powder samples. A simple relation was obtained: the finer sediment levels are less mature and the heavy mineral assemblage, transported mainly as suspended load, is composed by minerals with platy and lamellar forms. Levels with coarser sediment have a high maturity index and much rounder, denser heavy minerals transported as bedload. In the lower levels it is detected a high abundance of euhedral heavy minerals assemblages reflecting the provenance signal of the granite and gneissic bedrock. With this information we can determine episodes where the fluvial influence was stronger and where a marked marine influence was sensed. The first episodes are represented by the finer levels and the marine influence is testified by the coarser levels.

ADDITIONAL INDEX WORDS: *PCA, selection processes, sediment maturity*

INTRODUCTION

Heavy minerals have long been used as a tool to interpret sedimentary deposits. Generally, they are used in determining provenance, tracing transport paths, mapping dispersal patterns, depicting the action of hydraulic regimes and selection processes, locating potential economic deposits and understanding diagenetic processes (KOMAR, 1989; MORTON and HALLSWORTH, 1999). In the present work, heavy mineral analysis is applied as a contributor to the interpreting of recent sedimentary infilling of the Douro estuary (Portugal), along with other mineralogical and sedimentological attributes.

For this purpose, data were obtained within the "Envi-changes" project, whose main objective is to outline an evolutionary model for this estuary since 14000 BP (DRAGO *et al.*, 2002).

The Douro estuary is located in the northern Portuguese coast, south of Porto. This narrow funneled estuary is partly barred by a sand barrier (*Cabedelo*) that develops from the south and shelters the S.Paio Bay (DRAGO *et al.*, 2002).

Three cores were obtained by rotary drilling in this estuary: Core 1 (+3.5/-4.4m depth), 1B (-6.6/-16.2m depth) and 2 (-15.16/ -39.66m depth) (Fig. 1). These cores can be considered as being representative of the continuous sedimentary sequence present in the southern margin of Douro estuary (DRAGO *et al.*, 2002).

METHODS

The study of the heavy minerals was carried out in a total of 90 samples in three grain-size classes, medium (ϕ1-2), fine (ϕ2-3) and very fine (ϕ3-4) sand, in the sand rich levels of each of the three cores that represent the sedimentary infilling.

The acquisition of heavy mineral data involved the following laboratory procedure: a) the samples were washed, oven dried at 70º and sieved at 1 interval in order to obtain the entire grain size sand distribution and its respective parameters; b) light and heavy minerals from the referred grain-size classes were separated using sodium poly-tungstate (density 2.82g/cm^3) (CALLAHAN, 1987); c) heavy minerals from each fraction were mounted on microscope slides in Canada balsam; d) three hundred mineral grains were counted in each slide and the non-opaque minerals were identified (DRYDEN, 1931).

The presence of immature together with mature grains was analysed by grain angularity/roundness evaluation of several heavy mineral species. Three roundness classes were defined: round, subrounded/subangular and angular (adapted from roundness classes defined by POWERS, 1953). Attention was also given to the relationship between sediment/heavy mineral grain-size in order to deduce the conditions at the time of deposition.

The mineralogical composition of the finer fraction (<63µm) was analysed by X-ray diffraction (CuK radiation) on random-oriented powder samples. Semi quantitative determinations followed criteria recommended by BARAHONA (1974), SCHULTZ (1964), THOREZ (1976), MELLINGER (1979) and PEVEAR and MUMPTON (1989).

Three mineralogical indexes (VIDINHA *et al.*, 1998) were computed in fraction <63µm: FineDetrital/CoarseDetrital

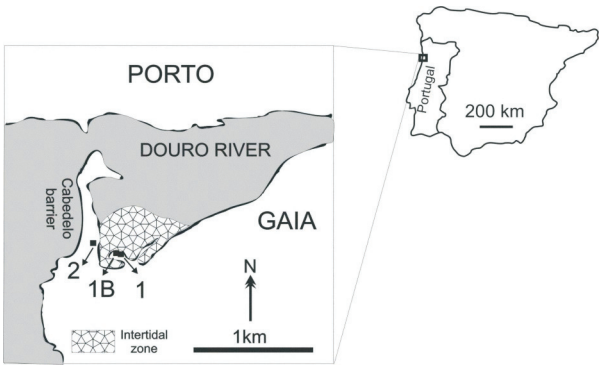

Figure 1. Core location (adapted from DRAGO *et al.*, 2002).

Table 1. *Mean heavy mineral distribution.*

	Mean (%)				
Minerals	SED1	SED2	SED3	SED4	SED4a
Andalusite (AN)	8.2	4.5	3.6	4.8	12.5
Amphibole (AMP)	10.4	10.9	6.6	17.6	4.9
Apatite (APA)	2.1	1.6	1.7	1.1	0.8
Biotite (BIO)	37.7	45.3	48.6	32.0	12.6
Kyanite (KYA)	0.2	0.2	0.2	0.1	0.6
Staurolite (STA)	0.6	0.6	0.5	0.4	5.2
Garnet (GAR)	2.7	2.7	2.5	1.1	14.6
Sillimanite (SIL)	0.2	0.3	0.2	0.2	0.1
Tourmaline (TOU)	2.6	2.7	2.4	1.7	7.9
Zircon (ZIR)	0.4	0.4	0.5	0.1	0.2
Monazite (MON)	0.4	0.5	0.1	0.1	0.3
Epidote (EPI)	0.2	0.2	0.21	0	1.5
Opaques (OPA)	32.9	29.5	32.8	39.6	38.3
Non Identified (NI)	1.2	0.7	0.3	0.9	0.3
Others (OTH)	0.1	0.1	0	0.2	0.1
Total	100	100	100	100	100

(FD/CD - phyllosilicates/(quartz+K-feldspars+plagioclases), Carbonate minerals/Detrital minerals (CM/DM) and Maturity Index (quartz/(feldspars+mica) M.I.) expressing the relative importance, intensity and hydrodynamics of the terrigenous supply as well as marine versus continental influences. The content in feldspar and mica was also considered.

Principal Component Analysis (PCA), described by Davis (1986), was used on the data set in order to understand the relationships between variables. Several sets of variables were considered: sediment grain-size, heavy mineral frequency and grain shape and, fine sediment M.I.. In order to simplify the relationships between variables two different approaches were used. The first approach considers the variables sediment grain-size and heavy mineral frequency and the second includes sediment grain-size, heavy mineral shape and fine sediment M.I..

RESULTS

Sedimentary Units

The sedimentological, geochemical and paleoecological study of Core 1, 1B and 2 reveal the existence of four sedimentary units referred by DRAGO *et al*. (2002) as SED1, SED2, SED3 and SED4 (Figure 2).

The sedimentary sequence begins with a slightly muddy sand sequence - SED1 (according to Flemming, 2000) sediment classification. It is comprised between 13750 and 10310 BP, and it has a continental signature. SED1 is followed by succession of slightly sandy mud, sandy mud and muddy sand sediments (core 2) and an alternated succession of sandy mud and muddy sand interbedded layers (core1) - SED2, comprised between 10310 and 5780 BP. This unit is present in both cores 2 and 1B. The lower section of this unit represents a low saline estuarine environment with intensification of marine influence towards the top (DRAGO *et al.*, 2002). The third unit (SED3), deposited after 5750 BP, is a gravel layer, which was probably deposited under a climate of torrential rains favouring the coarse clastic supply. The morphometric study of the gravel components suggests fluvial transport and a littoral reworking, this unit being interpreted as a shingle barrier (DRAGO *et al*., 2002).

Table 2. *Mean fine fraction data Distribution.*

	Mean				
	SED1	SED2	SED3	SED4	SED4a
M.I.	3	4	7	3	5
FD/CD	0.2	0.1	0.07	0.1	0.04
CM/DM	0.02	0.03	0.04	0.02	0.07
Feldspars (%)	18	15	12	16	14
Mica (%)	8	6	4	7	3
Quartz (%)	63	69	75	67	74

The last unit (SED 4), deposited from 1600 BP till present, consists of sands with few interbedded mud represented essentially at the bottom and top of this unit. Micropaleontological data, obtained in the finer levels of this unit, suggests a brackish intertidal environment with low salinity that rapidly acquired fluvial and/or subaerial characteristics towards the top (DRAGO *et al*., 2002). This unit appears on the top of core 1 and 2.

Heavy Mineral Data

The mean percentage of each heavy mineral species along the different sedimentary unit is represented in Table 1.

In the lower levels of SED 1, the heavy mineral suite is dominated by biotite (20%), andalusite (27%) and apatite (6%), with euhedral forms, reflecting the presence of the bedrock (granites and gneisses). Opaque minerals correspond to 44% and all other species range between 0.1 and 3% (Table 1). In the medium and upper levels, the heavy mineral suites are essentially composed by biotite (40%), amphibole (12%) and andalusite (6%) with platy and lamellar forms. Tourmaline and garnet appear both with contents of 3%. (Table 1). The other minerals occur in negligible amounts ranging between 0.2 and 1.7% except for opaque minerals (32%).

The SED 2 heavy mineral assemblage is dominated by biotite (45%), amphibole (10%) and andalusite (4%). Tourmaline and garnet contents are 3% and the other minerals range between 0.2 and 1.6% (Table 1). The levels with high content of biotite (> 50%) match the muddy sand/sandy mud sequences in these cores.

In SED 3, heavy minerals appear only in Core 2 (less coarse). The heavy suite is mainly composed by lamellar and platy minerals such as biotite (49%) and amphibole (7%) and by rounded, spherical and ellipsoidal grains such as garnet (3%), andalusite (4%) and tourmaline (2%) (Table 1).

The SED 4 heavy mineral suite is composed by biotite (32%), amphibole (18%) and andalusite (5%) (Table 1). The other non-opaque minerals range between 0 and 1.7%.

The distinct heavy mineral suites that characterize the upper levels of Core 1 and 2 can be used to define a sub-unit classified as SED 4a. This sub-unit is included in the SED 4 defined by DRAGO *et al.* (2003) and is represented in the top of Core 2 and in a small part of Core 1 (Figure 2). The heavy mineral suite is composed by rounded grains of garnet (15%), andalusite (13%), tourmaline (8%) and staurolite (5%) (Table 1). Biotite (13%) and amphibole (5%) have platy and lamellar forms. These particles are included in medium to coarse sand levels and no micropaleontological analysis could be made in this unit (SED 4a).

Finer Sediment

The mineralogical analysis of the <63 μm fraction shows the

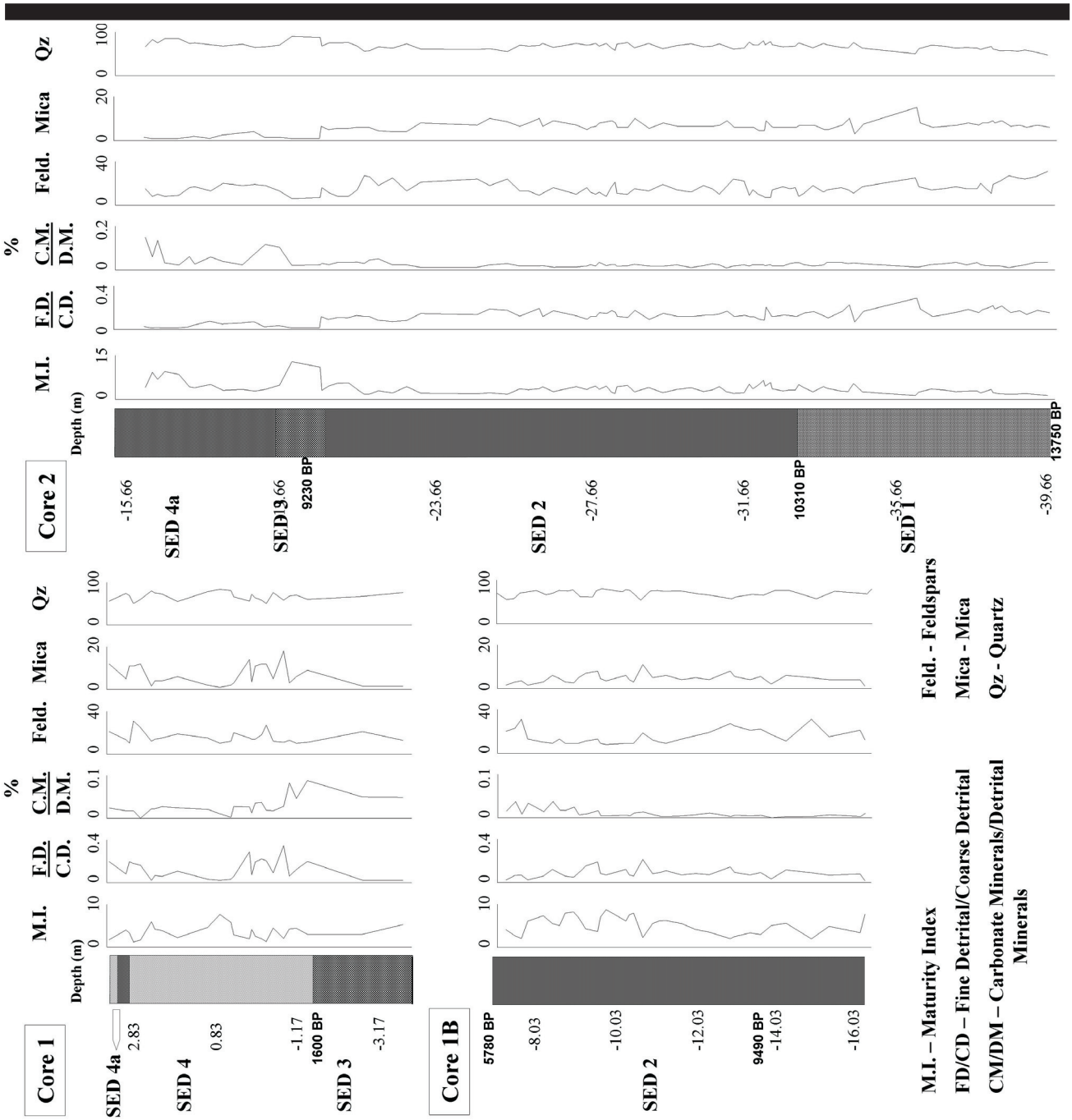

Figure 2. Sedimentary units and their relation with very fine sediment data (adapted from Drago *et al*., 2002).

predominance of the detrital minerals, such as quartz, feldspars and phyllosilicates (mainly micas), followed by a group of accessory minerals that includes calcite, dolomite, opal C/CT and pyrite. Some layers contain anhydrite, zeolites (mainly, clinoptilolite/heulandite), siderite and hematite. The four defined sedimentary units show different composition (Figure 2), by the evolution of the three selected mineralogical ratios:

In the lower levels of SED 1 and SED 2 of Core 1B the bedrock signature is detected in the finer grain-sizes by high feldspar content (namely 26% and 16% in average).

SED 4a and SED3 have the higher M.I., higher CM/DM, lower FD/CD (Table 2) and higher content in quartz.

SED1, SED 2 and SED 4 reveal high content in mica (>5%) and the muddy sand/sandy mud sequences of these units have the highest content in mica (<10%). The FD/CD index evolution along the cores is similar to the mica content. Levels with finer sediment have higher mica percentage.

In the upper levels of Core 2 the fine sediment reveals a high average M.I. value of 5 in SED 4a and of 9 in SED 3. In SED 3 of Core 1, M.I. is equal to 4.

Principal Component Analysis (PCA)

When applying the "varimax normalized" rotation to the data correlation matrix used for the first PCA approach, 5 components were obtained explaining almost 70% of the data variance (Figure 3A). The first and fourth components show a strong correspondence between the platy and lamellar minerals such as biotite and amphibole with the very fine sand (ϕ3-4), silt and clay fractions.

On the contrary, the more equant grains such as garnet, tourmaline and staurolite are correlated with the coarser fractions (ϕ-1 to 2).

The second component represents the opposition between fine (ϕ1 to >4) and coarse sediment (ϕ-1 to 0), all other variables being weighted near zero.

The third component reflects the differences between mineral densities. Opaque minerals, zircon, monazite and the non identified minerals (most of them iron coated) are in the denser group and are related with fine and coarse sand. Component 5 relates apatite with sillimanite probably due to their tabular and euhedral form.

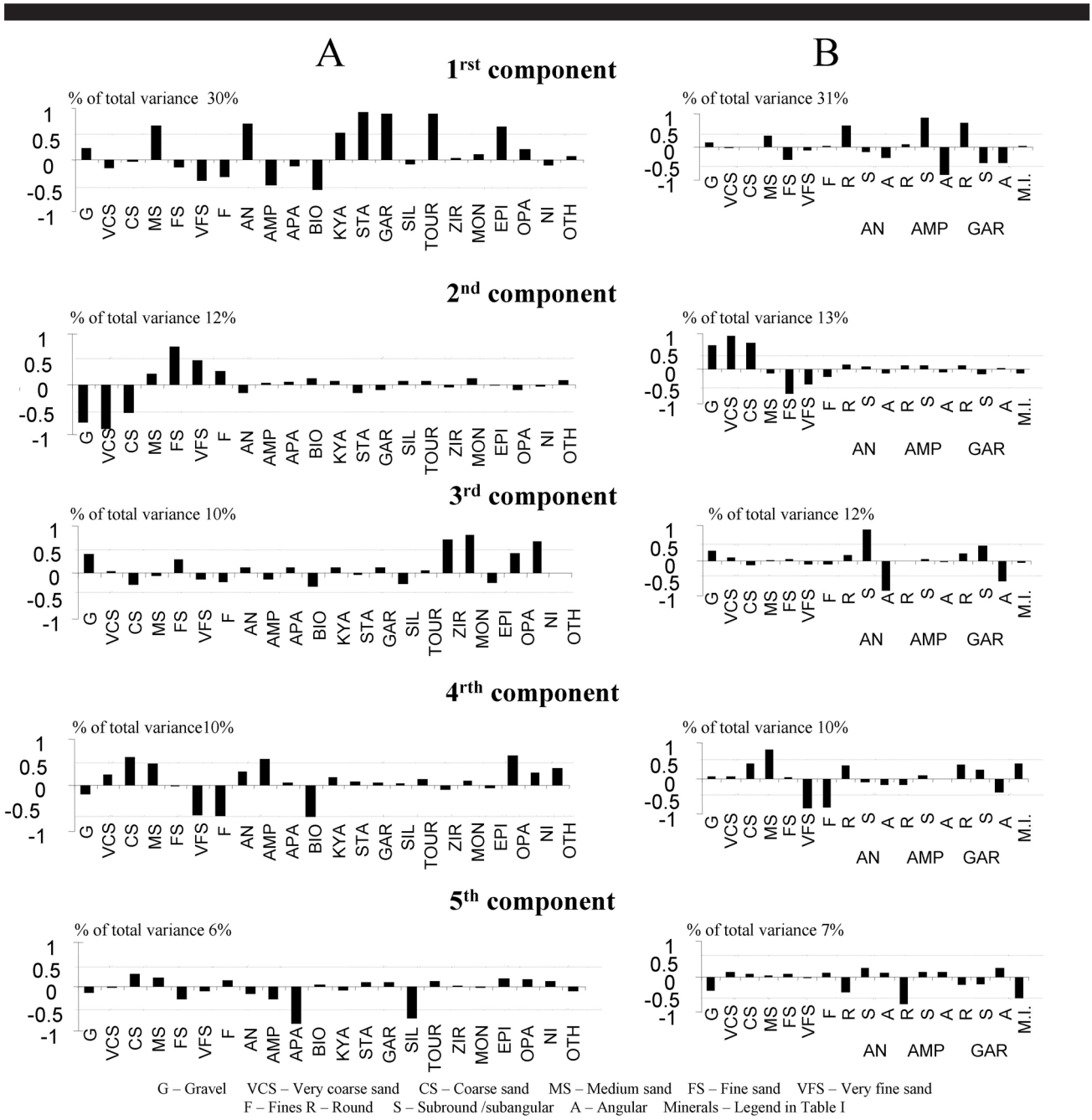

Figure 3. PCA analysis 1rst approach (A) and 2nd approach (B)Figure 3. PCA analysis 1rst approach (A) and 2nd approach (B).

In the second PCA approach (Figure 3B), the selected first 5 components explain almost 70% of the data variance. Component 1 relates the rounded minerals with medium sand (ϕ1-2), in opposition with the angular and sub-angular/sub-rounded minerals which are correlated to the finer fractions (ϕ2-3). The second component again shows the differences between coarse and fine sediments. The third component reflects the opposition between angular and sub rounded and rounded minerals. Component 4 and 5 are very similar. They relate the coarse sand with the rounded minerals and the M.I., in opposition to fine sand that is related to angular minerals.

DISCUSSION

Differences in sediment grain-sizes, the importance of which is readily seen from the use of the PCA analysis, can be used as a tool to understand the sedimentary processes. There is a strong opposition between coarse to medium sand (ϕ<-1 to 2) and fine sand to clay (ϕ 2 to >4). The grain size of sediment is closely related with the frequency of the mineral species.

In levels with finer sand, sandy mud and muddy sand (high FD/CD) the sediment is less mature (M.I. range between 3 and 4). The heavy mineral assemblage of these levels is composed by the less dense species, with platy and lamellar forms. The heavy minerals mean grain size is closer to the mean grain size of the entire sediment suggesting, suspended load transport (FRADIQUE and CASCALHO, 2003). According to DRAGO *et al.* (2002), these levels represent a brackish environment of low salinity with fluvial signature. Levels with medium to coarse sand have high M.I., low FD/CD index and much rounder, denser heavy minerals (such as garnet, zircon, tourmaline, andalusite, monazite and staurolite). The mean grain sizes of these minerals tend to be smaller than the mean grain-size of the total sediment, which may reflect bedload transport conditions (FRADIQUE and CASCALHO, 2003). These are the levels with the lowest terrigenous influence and high CM/DM as in SED4a and SED3 suggesting fluvial transport with littoral reworking.

In PCA (component 5, first approach) we can observe a high correlation between apatite, sillimanite (both euhedral) and medium to coarse sand fraction. The fine sediment analysis

reveals a high percentage of feldspars (lower levels of SED 1). The proximity of the bedrock, namely granites and gneisses, is responsible for these sediment characteristics.

CONCLUSIONS

The present work allowed the determination of different environments using sediment grain size and composition, both of the coarse and of the fine fractions, as well as the shape of the grains. Episodes of stronger fluvial influence (represented by the muddy sand-sandy mud levels) and of intensified marine influence (testified by the coarser levels with rounded and denser minerals) were identified. Such episodes can also be deduced from the mineralogical indexes that were computed.

ACKNOWLEDGEMENTS

This work is a DISEPLA contribution and was undertaken as a part of the project ENVI-CHANGES-PLE/12/00 funded by Fundação para a Ciência e a Tecnologia (Portugal).

We would like to thank Fernando de Magalhães, Rui Taborda, Raul Fonseca and Conceição Freitas for the useful and constructive advices given which undoubtedly led to a fruitful outcome of this work.

LITERATURE CITED

BARAHONA, E., 1974. *Arcillas de ladrillería de la provincia de Granada: evaluación de algunos ensayos de materias primas*. Ph.D. Thesis, Granada Univ., Spain, 398pp.

CALLAHAN, J., 1987. A non-toxic heavy liquid and inexpensive filters for separation of mineral grains. *Journal of Sedimentary Petrology,* 57, 765-766

DAVIS, J.C., 1986. *Statistics and data analysis in geology*. John William and Sons, New York, 664 p.

DRAGO, T.; NAUGHTON, F.; MORENO, J.; ROCHA, F.; CACHÃO, M.; SANCHEZ GÕNI, M. F.; OLIVEIRA, A.; CASCALHO, J.; FATELA, F.; FREITAS, C. and ANDRADE, C., 2002. Geological Record of Environmental Changes in the Douro Estuary (NW Portugal) since the Late Glacial. *Proceedings of the 6th Littoral 2002 International Symposium*, (Porto, Portugal), volume 3, pp. 341-346

DRAGO, T.; FREITAS, C.; CACHÃO, M.; MORENO, J.; CASCALHO, J.; OLIVEIRA, A.; NAUGHTON, F.; FRADIQUE, C.; SILVEIRA, T.; FATELA, F.; 2003. Douro estuary sedimentary record and sea level rise evolution in the last 14 000 years. *Proceedings of the 4th Symposium on the Iberian Atlantic Margin,* (Vigo, Spain), *Thalassas* 19(2a), pp.101-103

DRYDEN, A. L. JR., 1931. Accuracy in percentage representation of heavy mineral frequencies. *Proc. Natl. Acad. Sci. USA*, 17, 233-238

FLEMMING, B.W., 2000 A revised textural classification of gravel-free muddy sediments on the basis of ternary diagrams. *Cont. Shelf Research*, 20, pp.1125-1137

FRADIQUE, C. And CASCALHO, J.,2003. Heavy mineral data in deducing the sedimentary processes in Douro estuary, Portugal. *Proceedings of the 4th Symposium on the Iberian Atlantic Margin,* (Vigo, Spain), *Thalassas* 19(2b), pp.49-50

KOMAR, P. D., 1989. Physical processes of waves and currents and the formation of marine placers. *Reviews in Aquatic Sciences*, 1(3), 393-423.

MELLINGER, R. M., 1979. Quantitative X-ray diffraction analysis of clay minerals. An evaluation. *Saskatchewan Research Council, Canada, SRC Report* G-79: 1-46

MORTON, A. C. and HALLSWORTH, C. R., 1999. Processes controlling of heavy mineral assemblages in sandstones. *Sedimentary Geology*, 124, 3-29.

PEVEAR, D.R. and MUMPTON, D.R., 1989. *Quantitative mineral analysis of clays*. CMS Workshop Lectures, 1. The Clay minerals Society, Colorado (USA).

POWERS, M.C., 1953. A new roundness scale for sedimentary particles, *Journal of Sedimentary Petrology*, 23, 526-577

SCHULTZ, L.G., 1964. Quantitative interpretation of mineralogical composition from X-ray and chemical data for the Pierre Shale. *United States Geological Survey Professional Paper* 391-C,1-31.

THOREZ, J., 1976. *Practical identification of clay minerals*. G. Lelotte. Bruxelles. 99p.

VIDINHA, J.M., ROCHA, F. ANDRADE, C. and GOMES, C., 1998. Mineralogical characterization of the fine fraction of the beach and dune sediments situated between Espinho and Torreira (Portugal). Geostatistical approach. *Cuaternario y Geomorfología*, 12 (3-4), 49-56.