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REE distributions in the black sands of Kavala coastal zone, northern Greece: mineralogical and geochemical characterization of beneficiation products

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Abstract: Black sands from the area of Loutra Eleftheron, Kavala, northern Greece, are known for their enrichment in rare earth element (REE) bearing minerals. This paper presents results from basic characterization tests of the naturally enriched in REE minerals sands in Kavala region trying to understand the heavy mineral distribution and their possible potential as a resource. For this purspose a combination of scanning electron microscopy (SEM), X-ray diffraction and ICP-MS analysis were employed to characterize the concentrates from laboratory grain size separation and magnetic separation (high intensity magnetic separators - HIMS). Characterization of the magnetic separation and grain size fractions showed that the magnetic fraction of the black sand is strongly enriched in the LREE, relative to the non-magnetic fraction ca. LEE were enriched by a factor of 1.62 relative to the bulk composition. Allanite is the major host mineral for LREE in the magnetic fraction. SEM/EDS and ICP-MS analysis of the different grain size fractions showed LREE enrichment in the fractions – 0,425 +0,212 mm, and a maximum enrichment in the - 0,425, + 0,300 mm. The maximum enrichment in achieved after magnetic separation of the grain size fractions. The information gathered can be used to identify the optimum fraction for REE recovery which is essential for the design of a beneficiation process.

Keywords: Rare Earth Elements (REE); black sands; EURARE; allanite; monazite; mineralogical characterization; geochemical characterization; magnetic separation; grain size fractions

1. Introduction

Heavy-mineral sands (or "black sands) are sedimentary deposits of dense minerals that accumulate in coastal environments, locally forming economic concentrations of the heavy minerals. They serve as a major source of titanium worldwide and, in some cases, show high accumulation in REE and Th [1]. Rare Earths have attracted considerable interest in recent years, in particular due to concerns over their sustainable supply for high efficiency electronics and energy technologies [2–5]. Previous exploration projects have shown that the most promising REE sources in Greece may be the secondary type deposits, such as placers and sea-floor sediments in the northern Aegean region and in particular the Strymon Bay and Kavala regions [6–8]. Geological prospecting by the Institute of Geology and Mineral Exploration (I.G.M.E) of Greece on the black sands in the broader area of Strymon bay started in 1980's and focused primarily on the natural enrichment in actinides (U-Th) and associated radioactivity in the on-shore and offshore zones of Loutra Eleftheron-Nea Peramos regions [6–7]. Geochemical and mineralogical studies indicate that the heavy minerals traced in the Kavala black sands, derive from the Symvolon and Kavala plutons, which are deformed granodioritic complexes of Miocene age [10–12]. Moreover the recently accomplished European project EURARE highlighted the significance of the blacks sand in Kavala region for REE recovery [9,14], as well as the secondary REE resources in Greece, such as the the bauxite residue (red mud) from the processing of Greek bauxites, as an REE source [5,8,9]. Preliminary results from the beneficiation test of black sands in the course of EURARE project showed also the high content of radionuclides that follows the high concentration of REE in the concentrates [9] .

Many new REE deposits are currently being developed to help meet the projections of future world demand, yet most of these developing deposits include rare earth bearing minerals for which there is limited processing knowledge. Currently exploited rare earth-bearing minerals worldwide are bastnäsite, monazite and xenotime. Other REE bearing minerals are rarely found in deposits of economic significance such as eudialyte, synchysite, samarskite, allanite, zircon, steenstrupine, cheralite, rhabdophane, apatite, florencite, fergusonite, loparite, perovskite, cerianite, and pyrochlore (Table 1) [13].

This paper presents new data on the characterization of the Kavala black sands and ore beneficiation products at laboratory scale, from research work undertaken by I.G.M.E, in the framework of EURARE project. The resultant magnetic property characterisation of different products at laboratory scale, is examined in order improve understanding of mineral behaviour through the different separation tests. This information is valuable in selecting the proper pre-concentration process. For this purpose scanning electron microscopy (SEM), X-ray diffraction analyis and inductively coupled plasma–mass spectrometry (ICP-MS) were used in combination, for the characterization of the raw materials.

Detailed sampling along a 10 km traverse line from Loutra Eleftheron to Nea Peramos, Kavala region, was conducted in the course of EURARE during the period of 2013-2015 (Figure 1, marked area). Preliminary beneficiation tests presented here focused on the naturally most enriched sample (No. 123). A composite sample was prepared after homogenization of all the samples collected and evaluation of beneficiation tests used this composite sample as a reference sample for mass balance calculations.

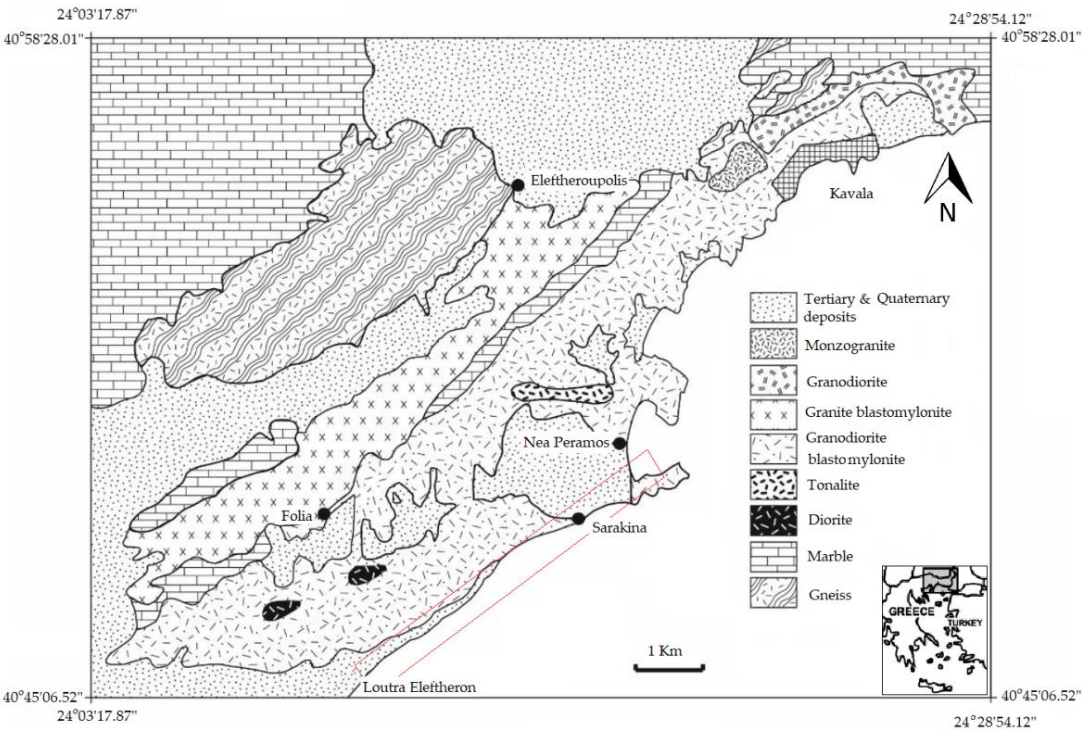


Figure 1. Geological map of the sampling are (red box) of Kavala region, Nea Peramos–Loutra Eleftheron coast (modified map after [12]). The large igneous body behind the coastline is Symvolon granite.

Table 1. Silicate REE bearing minerals. Adapted from [13; and references therein].

Mineral Name	Chemical forMula	Density (g/cm³)	Magnetic Properties	Weight % REO	ThO_2
Allanite (Ce)	$(Ce,Ca,Y)_2(Al,Fe^{2+},Fe^{3+})3(SiO_4)_3(OH)$	3.50-4.20	paramagnetic	3-51	0-3
Allanite (Y)	$(Y,Ce,Ca)_2(Al,Fe^{3+})_3(SiO_4)_3(OH)$	n/a	paramagnetic	3-51	0-3
Cerite (Ce)	$Ce_9Fe^{3+}(SiO_2)_6[(SiO_3)(OH)](OH)_3$	4.75	paramagnetic	-	-
Cheralite (Ce)	$(Ca,Ce,Th)(P,Si)O_4$	5.28	n/a	-	<30
Eudialyte	$Na_4(Ca,Ce)_2(Fe^{2+},Mn^{2+},Y)ZrSi_8O_{22}(OH,Cl)_2$	2.74-3.10	n/a	1-10	-
Gadolinite (Ce)	$(Ce,La,Nd,Y)_2Fe^{2+}Be_2Si_2O_{10}$	4.20	paramagnetic	-	-
Gadolinite (Y)	$Y_2Fe^{2+}Be_2Si_2O_{10}$	4.36-4.77	paramagnetic	-	-
Gerenite (Y)	$(Ca,Na)_2(Y,REE)_3Si_6O_{18}.2H_2O$	n/a	-	-	-
Hingganite (Ce)	$(Ce,Y)_2Be_2Si_2O_8(OH)_2$	4.82calc	-	-	-
Hingganite (Y)	$(Y,Yb,Er)_2Be_2Si_2O_8(OH)_2$	4.42-4.57	n/a	-	-
Hingganite (Yb)	$(Yb,Y)_2Be_2Si_2O_8(OH)_2$	4.83calc	n/a	-	-
Limoriite (Y)	$Y2(SiO_4)(CO_3)$	4.47	n/a	-	-
Kainosite (Y)	$Ca_2(Y,Ce)_2Si_4O_{12}(CO_3).H2O$	3.52	n/a	-	-
Rinkite (rinkolite)	$(Ca,Ce)_4Na(Na,Ca)_2Ti(Si_2O_7)2F_2(O,F)_2$	3.18-3.44	n/a	-	-
Sphene (titanite)	$(Ca,REE)TiSiO_5$	3.48-3.60	paramagnetic	<3	-
Steenstupine (Ce)	$Na_{14}Ce_6Mn_2Fe_2(Zr,Th)(Si_6O_{18})2(PO_4)7.3H_2O$	3.38-3.47	n/a	-	-
Thalenite (Y)	$Y_3Si_3O_{10}(F,OH)$	4.16	4.41	-	-
Thorite	$(Th,U)SiO_4$	6.63-7.20	paramagnetic	<3	-
Zircon	$(Zr,REE)SiO_4$	4.60-4.70	diamagnetic	-	0.1-0.8

2. Results

2.1. Mineralogical and Geochemical Characterization of the Bulk Samples

"Heavy minerals" are generally defined as dense minerals that have a specific gravity greater than 2.85 (Table 1)[1,13]. The heavy minerals of the sand samples show a wide range of Ti-rich, REE-bearing and U-Th-rich silicate minerals, identified by optical microscopy, SEM/EDS and XRD analysis. The heavy minerals contained in the Kavala black sands are the following, in order of abundance: mainly amphiboles (Mg-hornblende, K-pargasite), magnetite, titanite, allanite, hematite, ilmenite, rutile, epidote, zircon, thorite, monazite, cheralite, apatite, xenotime.

SEM/EDS semi-quantitative analysis of allanite indicated that total elemental concentration of LREE(La, Ce, Nd) range ca. from 6 wt% to 13 wt%. Back scattered electron images showed that most of the allanites exhibit zoning towards the marginal areas of the grain (Figure 2a,b,g). The chemical composition of the peripheral zones indicates replacement of the allanite with clinozoisite and epidote. Zoned allanites contain significant Th in the central part of the grain, ca. up to 2.5 wt% and they show metamict texture. This is documented by the abudant radiation lines in the structure of the grain displayed by this type of allanite which results from the destructive effects of its own radiation on the crystal lattice. (Figure 2 b, d).

The bulk chemical analysis of the Kavala black sands are normalized against the Post-Archean Australian shale composition (PAAS) [15] in order to identify possible geochemical anomaly and assess the degree of REE enrichment relative to an average upper crustal composition. The average rare earth element (REE) pattern of terrigenous sediment and especially shales, as opposed to chondrite, is widely accepted to reflect the upper continental crust [16]. This average composition is used in order to estimate the natural enrichment in the studied samples. REE normalized diagrams of Figure 3 show a distinct enrichment of the Kavala black sands relative to the PAAS (sedimentary upper crust equivalent) ca. up to 60 times. Sample No. 123 is further tested for its efficiency in benefication tests, because it is the most REE enriched sample (Table 2).

2.2. REE Distribution in the gRain Size Fractions

After grain size analysis all the grain size fractions were analysed for their trace element composition (Appendix 1, Table 1). A combination of SEM/EDS and ICP-MS achemical analysis of the different grain size fractions showed a LREE enrichment in the fractions – 0,425 +0,150 mm and a maximum enrichment in the - 0.355 + 0212 mm; the latter grain size corresponds to the "liberation" size of allanite which is confirmed by the microscopic observations (Figure 4, 5). The same trend of enrichment is observed both in the sample No. 123 and the composite sample, as shown in Figures 4 and 5, respectively.

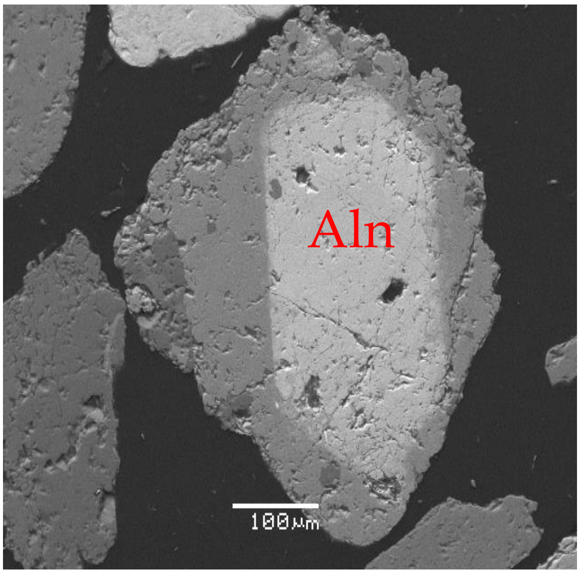
2.3. REE distribution in the magnetic fractions

Magnetic separation technique is a common separation step in rare earth mineral beneficiation to concentrate the desired paramagnetic REE bearing and is commonly used for monazite or xenotime [13,17]. The LREE tend to concentrate in the magnetic fraction because of their magnetic properties. Comparison between XRD spectra of the magnetic fraction and the bulk sample (No. 123) show a relative enrichment in magnesiohornblende, biotite, magnetite allanite and titanite. Magnetic separation was conducted on the various grain size fractions of the composite sample-Amixed aiming to test the maximum possible recovery of REE from the bulk sample. Chemical analysis (by ICP-MS) of the produced concentrates show that maximum REE concentration was achieved on the same grain size fractions with those shown in the grain size analysis, ca. fractions – 0,425 +0,300 (Figure 6).

The total recovery by magnetic separation test estimated from the different grain size separately, is 75–90% for La and Ce respectively, in the 20% of feed material (Figure 7).

Table 2. Total LREE and HREE and total REE composition of the different samples collected, in the course of EURARE project. Note sample No 123 is the most naturally enriched in REEs.

	ΣLREE	ΣHREE	ΣREE
No 115	622	33	655
No 116	852	43	895
No 117	1443	66	1509
No 117A	326	19	344
No 118	728	34	762
No 119	3587	128	3715
No 120	129	13	142
No 121	2082	98	2180
No 122	2285	107	2392
No 123	7826	296	8123
No 124	6810	261	7070
No 125	4669	189	4858
No 126	105	9	114
No 127	2311	70	2382
No 128	801	40	841
No 129	613	40	652



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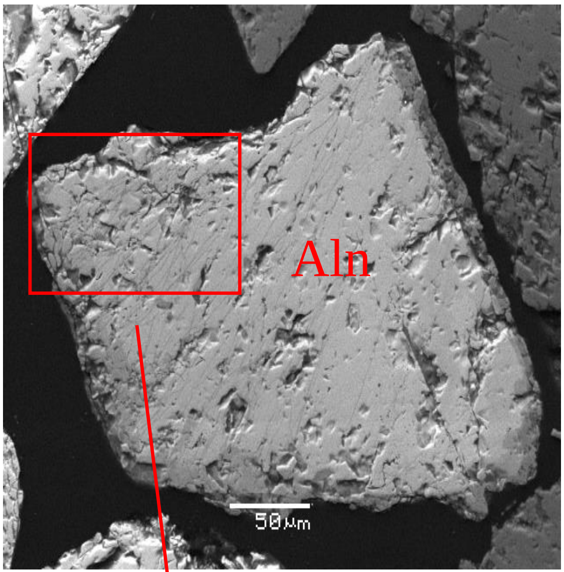

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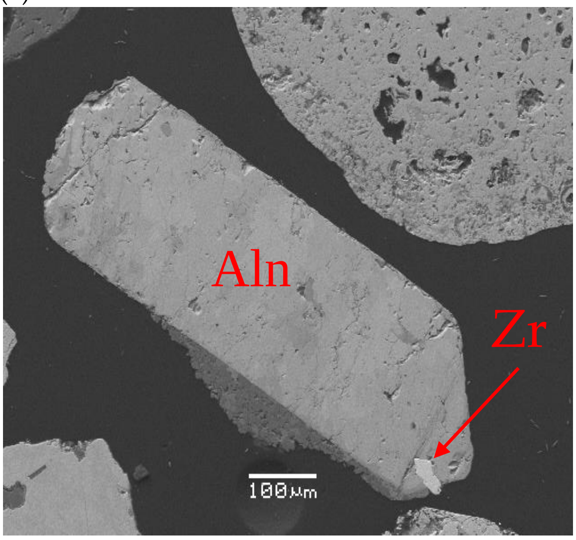

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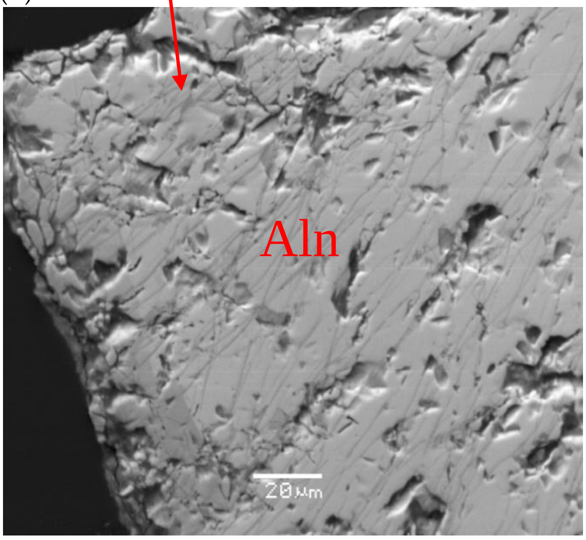

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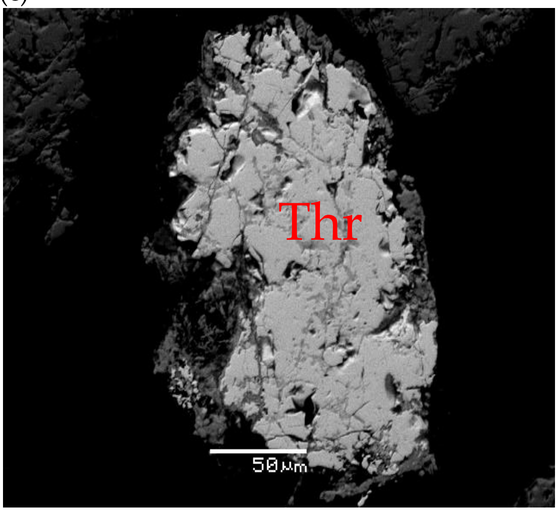

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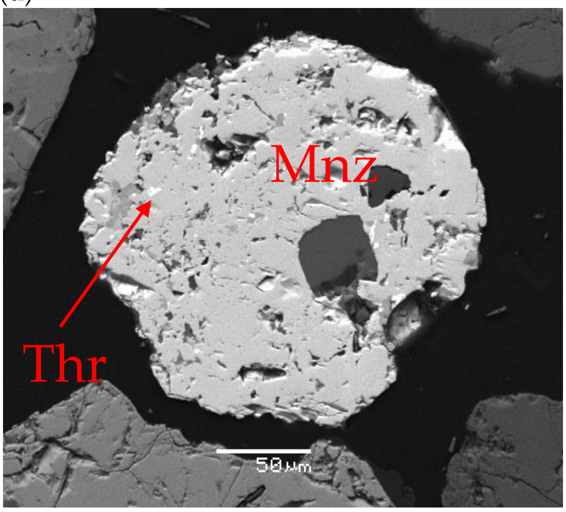

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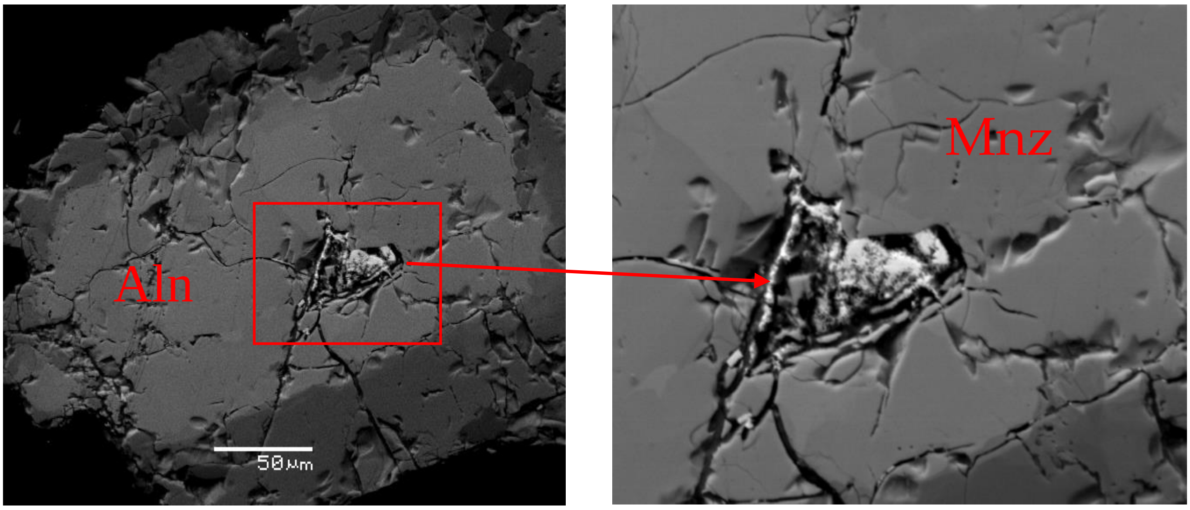

(g) (h)

Figure 2. Back scattered electron images from SEM of various REE-minerals and other heavy minerals of different grain size fractions. (**a**), (**b**) zoned allanite –(Ce) showing metamict structure (-0.425 mm to +0.212 mm), (**c**) allanite containing zircon inclusions from the magnetic fraction, (**d**) magnified area of the allanite grain in (**b**), (**e**) thorite weathered grain, darker zones are U depleted (**f**) monazite containing thorite inclusions, from the magnetic fraction (**g**) allanite containing inclusion of Ca-rich monazite (cheralite), shown in magnification in (**h**); Abbreviations: Aln-allanite, Zr-zircon, Mnz-monazite, Thr-thorite.

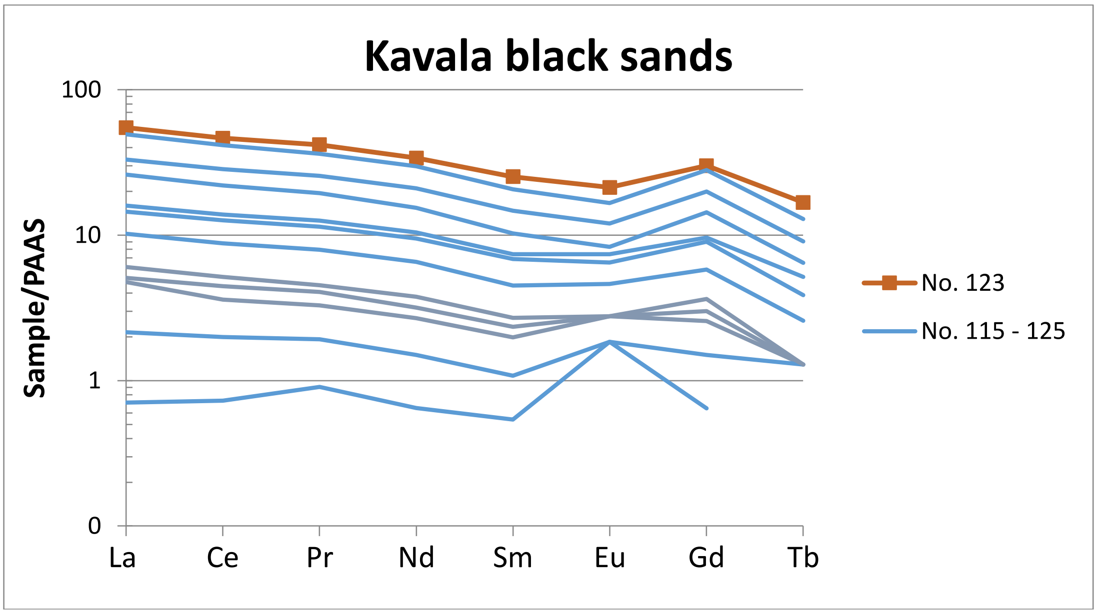

Figure 3. REE normalized composition of black sands and sample No 123 shown in different color. Normalized compositions against the standard composition of Post Archean Australian Shale by [15] as an equivalent sedimentary upper crust average.

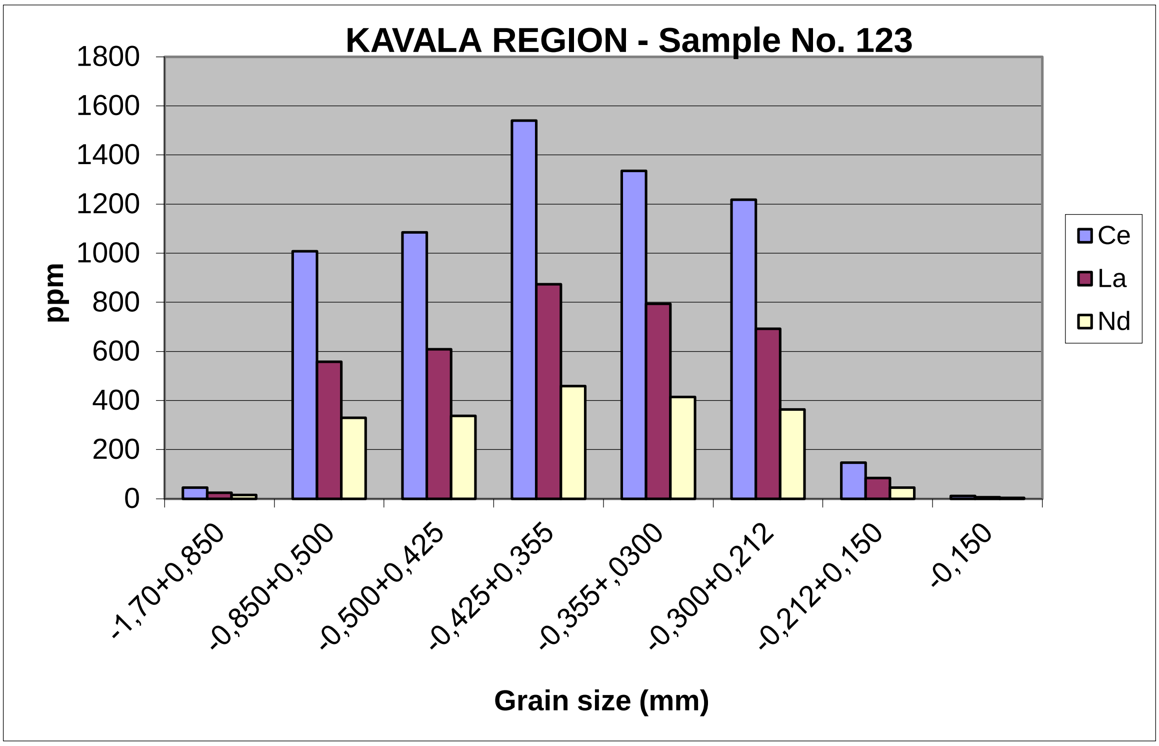

Figure 4. Distribution of LREEs in the various grain sizes of the naturally enriched sample (No. 123).

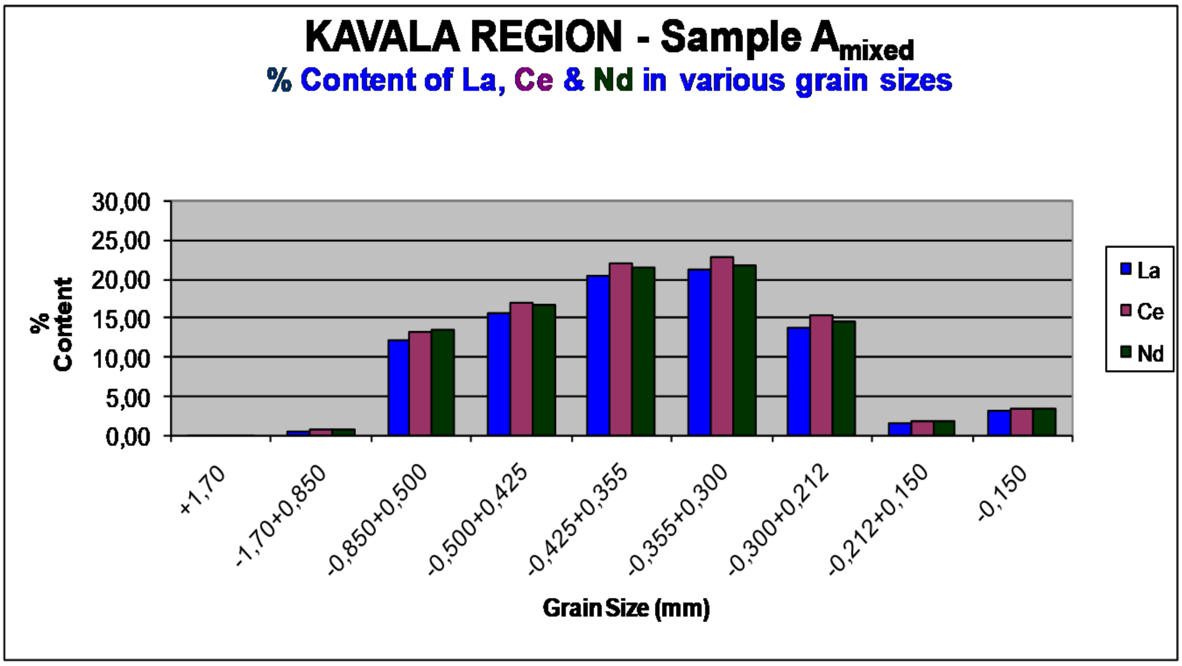

Figure 5. Distribution of LREEs in the various grain sizes of the composite sample (sample Amixed).

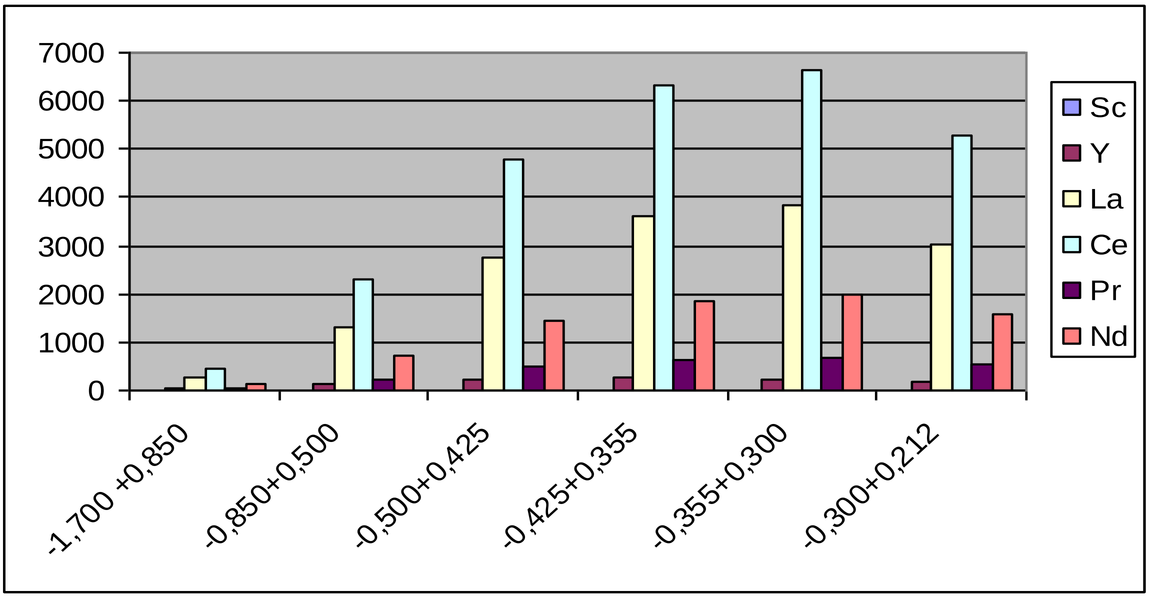

Figure 6. Distribution of LREEs in the magnetic fractions of the different grain sizes in the composite sample (Amixed).

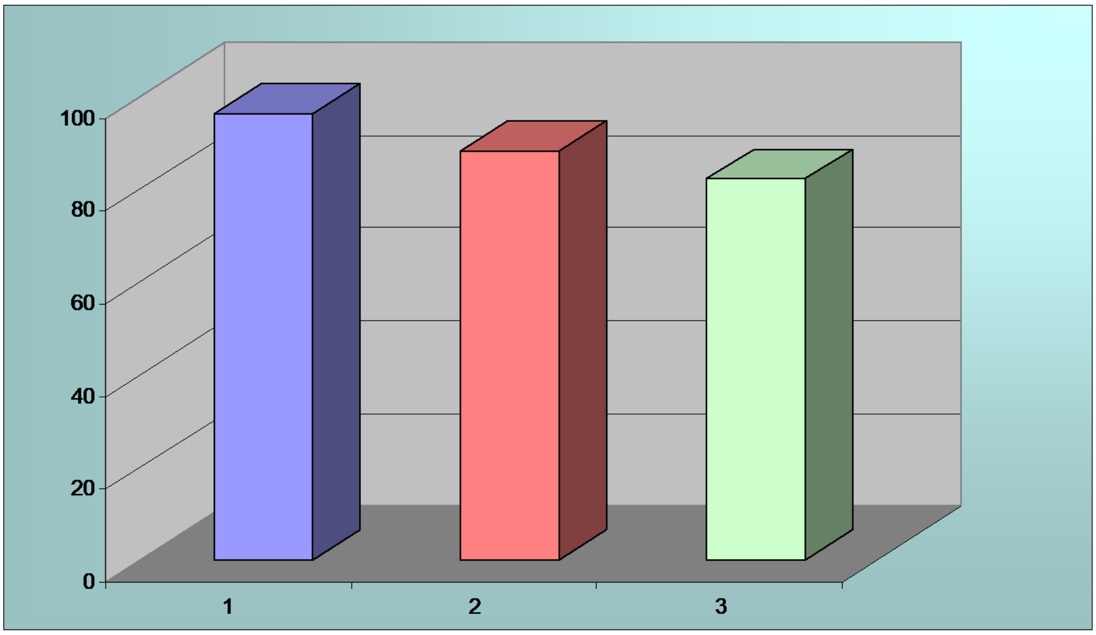

Figure 7. Recovery (in wt%) of La, Ce and Nd after magnetic separation (sample No .123).

4. Discussion

The beneficiation of the REE bearing minerals is a subject which requires a great deal of investigation to fill the knowledge gaps existing in the developing rare earth projects [13,17]. The only REE bearing minerals that are presently extracted on a commercial scale are bastnäsite, monazite, and xenotime [13]. Previous research papers described a series of physical separation processes employed to pre-concentrate rare earth minerals (REM) and reject iron oxide minerals from the magnetic fractions including, gravity, magnetic, electrostatic and flotation separation techniques [18] and references therein.

Magnetic separation of minerals is based on different behaviours of mineral particles when exposed to an applied magnetic field. The magnetic response of a material to an applied magnetic field is due to the presence of unpaired electrons which induce magnetic dipoles in the material.

These magnetic dipoles possess individual magnetic moments and the alignment of these magnetic moments with an applied magnetic field will produce a resultant magnetic force on the material when these moments are aligned by an externally applied magnetic field. The magnetisation of a material is a measure of the density of magnetic dipoles induced in the material [19].

Chemistry is the main factor that controls the magnetic susceptibility of mineral. Many iron-bearing minerals are either ferromagnetic or paramagnetic. Ferromagnetic refers to minerals strongly attracted to a magnet, like a piece of iron. The common ferromagnetic minerals include magnetite, maghemite, pyrrhotite, and pentlandite. Paramagnetic refers to minerals less magnetic than ferromagnetic [13]. Minerals containing rare earth elements are only moderately paramagnetic like allanite, monazite, bastnaesite and xenotime [19,20]. The main host mineral for LREEs in Kavala black sands is allanite-(Ce), commonly containing inclusions other REE-bearing phases such as thorite, apatite, zircon, monazite and cheralite. Therefore, REE concentration in the magnatic fraction is attributed to the allanite and monazite which were effieciently separated in the magnetic fraction. The magnetic separation on each grain size separately, improved significantly the total recovery of REE ca. achieved recoveries ranging from 75 – 90% and production of a concentrate with 1,5 wt% REE .

Further selective REE extraction from concentrate was tried by acid treatment, either leaching or acid baking followed by water leaching, conducted by I.G.M.E during EURARE project [14]. The acids used were HCl , H_2SO_4, or both. The results showed that rather low recoveries are possible. In direct acid leaching decreasing pulp density leads to increasing rare earth recovery whilst the opposite is observed in the recovery procedure with acid baking; an increasing pulp density at acid baking step at about 15% leads to an increasing recovery tendency of about 15-20%. The duration of acid baking test seems to have no effect on the recovery of rare earth elements.

5. Materials and Methods

5.1. Sampling

Detailed sampling along a 10 km traverse line from Loutra Eleftheron to Nea Peramos areas, Kavala region, was conducted in the course of EURARE during the period of 2013-2015 (Figure 1).

5.2. Preparation of Samples During Grain Size Analysis and Magnetic Separation

The beneficiation tests were conducted at the Department of Mineral Processing and Technology, I.G.M.E. From the sample No. 123 a representative subsample was prepared (958 gr) and the required amount separated through a splitter was submitted to the chemical analyses .Wet sieving method was performed to get the various grain size fractions namely: +1.7 mm; -1,7 +0.850 mm; -0,850 +0.500 mm;-0,500 +0.425 mm; -0,425 +0.355 mm;-0,355 +0.300 mm;-0,300 +0.212 mm; -0.212mm (Appendix A, Table 1).

In the course of wet sieving process we observed a change in the color moving onto smaller grain size fractions. The samples were placed in a dryer for 24 hours at 105 ºC. All the samples including the bulk sample with exception of sample No-2 (+1,7 mm) (due to its low quantity were dried and weighted amount of ~ 10 gr for the chemical analyses whereas 15 gr for the mineralogical analyses, from each grain size fraction was comminuted to -0,074μm.

In magnetic separation tests a test sample of 1640,51 gr was used. The magnet used, is an ERIEZ High Intensity Magnetic Separator (HIMS), of stable intensity (at 10 cycles). After the first separation stage, the two products were weighted (Appendix - Figure 1). A second stage of magnetic separation was performed on the already separated magnetic fraction to get the purest possible magnetic product (Appendix A–Figure 1).

5.3. Mineralogical Analysis

Microscopical investigations were carried out with a LEICA DM/LP microscope with reflected light and transmitted light mode as well. Mineralogical analysis was conducted by X-ray diffraction (Siemens D-5005) at the NKUA (Geology Dept.), using a Siemens D-5005 diffractometer with Cu K _ radiation. Magnetic fraction, non magnetic fraction and all the grain size fractions were finely ground in the appropriate size, placed in a sample holder and smeared uniformly onto a glass slide, assuring a flat upper surface. The resultant diffraction patterns were processed using EVA software by Bruker, to identify peaks and relate them to selected mineral phases present in the Kavala black sands samples.

5.4. SEM/EDS Analysis

Sand grains were mounted within a plug of epoxy resin and then polished grain-mount sections were prepared. Before SEM analysis, the thin section was covered with a thin veneer of carbon using a vacuum carbon coater.

Textural analysis and semi-quantitave elemental analysis of heavy minerals was undertaken using a JEOL JSM-5600 Scanning Electron Microscope (SEM) coupled to an energy dispersive X-ray spectrometer (EDS) of OXFORD LINK ISIS 300 (OXFORD INTRUMENTS), with software ZAF correction quantitative analysis, at the Department of Geology and Geoenvironment, NKUA, using secondary electron (SE) and backscatter electron (BSE) modes.

5.5. Chemical analysis

REE ore sample preparation as a first step includes digestion with aqua regia and HF (in order to solve dissolution problems in siliceous samples) in Teflon® containers and then the residue was chemically attacked with HCl and H_2O_2. The samples were preserved in 5% concentrated HCl. REEs were analysed by inductively coupled plasma – massspectrometry (ICP-MS) at I.G.M.E. The instrumental sensitivity of ICP-MS was measured by external calibration solutions with matrix correction [21].

6. Conclusions

Mineralogical analysis of the black sands from the shoreline of Kavala area, northern Greece allowed the following conclusions:

- Allanite-(Ce) is the major host mineral for light REE (LREE) whereas monazite, zircon and thorite are subordinate. Most of the allanites exhibit zoning, with the marginal areas of the grain showing strong depletion in REE. The chemical composition of the peripheral zones indicates replacement of the allanite with epidote. Metamict allanites are thorium enriched relative to the non-metamict allanites.

Geochemical characterization of the magnetic separation and grain size analysis allowed the following conclusions to be made:

- From the grain size analysis it is indicated that the smaller the grain size the higher the content of REE ; thus, a simple screening can achieve a satisfactory pre-beneficiation.
- Acombination of SEM/EDS, XRD and ICP-MS analysis of the different grain size fractions showed LREE enrichment in the fractions –0,425 +0,150 mm, and a maximum enrichment in the –0,425, + 0,300 mm. The latter grain size corresponds to the "liberation" size of allanite.
- A step wise magnetic separation improves the recovery of REE. This is indicated by applying magnetic separation on each grain size fraction.
- The increase in REE content is associated with the increase of thorium content in concentrates. This is attributed to the increased abundance of metamict allanites.

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Author Contributions: V.A. conceived and designed the experiments; V.A. and S.P performed the experiments; V.A. and C.S analyzed the data; K.P. conceived the broader research project and the participation of I.G.M.E in EURARE project; C.S., V.A and S.P. wrote the paper."

Abbreviations

The following abbreviations are used in this manuscript:
REE : Rare Earth Elements
LREE : Light Rare Eart Elements
HREE : Heavy Rare Earth Element
XRD: X-ray Diffreaction
SEM/EDS: Scanning electron microscopy/Energy dispersive spectroscopy
I.G.M.E: Institute of Geology and Mineral Exploration
PAAS: Post-Archean Australian Shale
EURARE: EU Rare Earth (project acronym)
REO: Rare Earth Oxide
ICP-MS: Inductively Coupled Plasma – Mass Spectrometry
HIMS: high intensity magnetic separators

Appendix A

Table 1. Grain size analysis and REE concentration (ppm) in the grain size fractions of sample No. 123

Sample No. 123	Grain size (mm)	Weight (gr)	Weight (%)	Cumulative weight	Weight passed (%)	La (ppm)	Ce (ppm)	Nd (ppm)	Th (ppm)
No.130	+1,70	14,24	0,89	14,24	0,89				
No 131	-1,70+0,850	100,04	6,26	114,28	7,15	246	452	151	89
No 132	-0,850+0,500	530,42	33,21	644,7	40,36	1052	1901	620	385
No 133	-0,500+0,425	218,94	13,71	863,64	54,07	2777	4954	1541	1250
No 134	-0,425+0,355	234,08	14,66	1097,72	68,73	3731	6580	1959	1700
No 135	-0,355+0,300	187,90	11,76	1285,62	80,49	4228	7105	2204	1755
No 136	-0,300+0,212	229,62	14,38	1515,24	94,87	3016	5301	1582	1505
No 137	-0,212+0,150	69,67	4,36	1584,91	99,23	1202	2110	648	641
No 138	-0,150	12,35	0,77	1597,26	100	503	902	289	287
	TOTAL	1597,26	100,00						

Table 2. Measurements of the mass fractions from magnetic separation test of sample No. 123

Sample No. 123	Weight (gr)	Mass Fraction wt %
123 Non Magnetic A	642,08	39,32
123 Non Magnetic B	87,18	5,34
123 Magnetic B	903,63	55,34
Total	1632,89	100
Loss	7,62	0,47

(a) (b)

Figure A1. Photos of magnetic separation products. (**a**) First stage separation of the magnetic and non magnetic product (**b**) Second stage separation of the magnetic product.

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