REE distribution in the black sands from the shore of Loutra Eleftheron, Kavala, northern Greece: mineralogical and geochemical characterization of fractions from grain size and magnetic separation analysis

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Introduction

Rare earth elements (REE) are critical metals used in advanced applications and are of high demand in the European Union (EU) [1–3]. Black sands from the shoreland area of Kavala (from Loutra Eleftheron to Nea Peramos), northern Greece, are known for their enrichment in rare earth element (REE) bearing minerals [4-6]. Previous research projects on the black sands in the area of interest conducted by the Institute of Geology and Mineral Exploration (I.G.M.E) of Greece initially focused on the natural enrichment of in actinides (U-Th) and associated radioactivity [4,5,7]. Geochemical and mineralogical studies indicate that the minerals traced in the Kavala black sands, derive from the Symvolon and Kavala plutons, which are deformed granodioritic complexes of Miocene age [8].

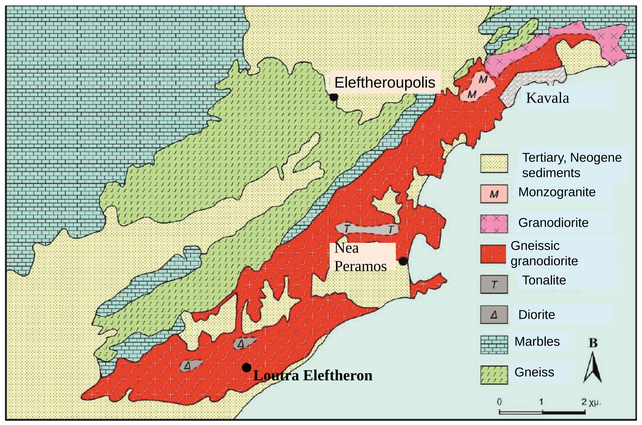

Figure 1. Geological map of Kavala pluton including the sampling sites (modified map after [9] Neiva et al. 1996)

Material and methods

Detailed sampling was conducted by I.G.M.E along the coastline of Loutra Eleftheron and Nea Peramos, Kavala region, in the course of EURARE project . Preliminary beneficiation tests focused on the sample #123 which shows the maximum natural enrichment in REE concentration compared with all the other samples.

Two different beneficiation techniques were performed on the bulk sample #123 at laboratory scale ca. grain size separation (wet sieving) and magnetic separation (High Intensity Magnetic Separators - HIMS), performed at the Laboratory of Beneficiation and Metallurgy of I.G.M.E.

In the course of wet sieving process we observed a change in the color as we moved onto smaller grain size fraction. After the first stage of the magnetic separation, the two products were weighted . A second stage of magnetic separation was performed on the already separated magnetic fraction to get the purest possible magnetic concentrate.

The products of beneficiation were characterized and compared using a combination of scanning electron microscopy –SEM/EDS and X-ray diffraction at the Geology Department, NKUA and ICP-MS analysis at I.G.M.E.

Results

I. Mineral identification

"Heavy minerals" are generally defined as dense minerals that have a specific gravity greater than 2.85 [10]. The heavy minerals of the sample 123 were identified by optical microscopy, SEM/EDS and XRD are the following in order of abundance :

Heavy minerals : amphibole (Mg-hornblende, pargasite), magnetite, rutile, zircon, titanite, ilmenite, allanite, epidote, monazite, xenotime and apatite.

Light minerals : quartz, feldspars , biotite, muscovite.

II. Mineralogical analysis of the magnetic fraction

- The REEs tend to concentrate in the magnetic fraction because of their magnetic properties.
- Allanite is the major host mineral for LREE, with Ce being the dominant rare earth element in its structure ca. allanite-(Ce).
- Back scattered electron images from SEM showed that most of the allanites exhibit zoning towards the marginal areas of the grain. The chemical composition of the peripheral zones indicates replacement of the allanite with zoisite and epidote.
- Metamict allanites are thorium enriched as shown by their disintegrated appearance and SEM/EDS analysis (Fig. 2b, d).
- XRD scan of the magnetic fraction compared to the scan of the bulk sample 123 shows a significant difference in the mineral phases. Minerals in the magnetic fraction include allanite, titanite, magnetite, rutile, magnesiohornblende and albite. Biotite and quartz are also present in smaller quantities. The bulk sample 123 contains mainly quartz, albite, microcline, anorthite, illite and muscovite. Potassium pargasite, titanite and hematite were traced too.

III. Mineralogical analysis of the grain size fractions

- A combination of SEM/EDS 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 - 0.355 + 0212 mm; the latter grain size corresponds to the "liberation" size of allanite.

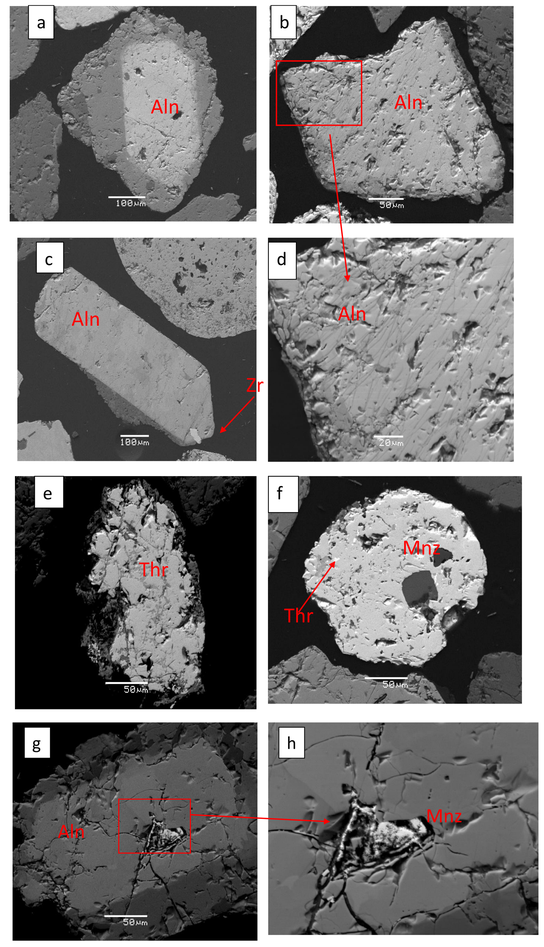

Figure 2. Back scattered electron images from SEM of dominant REE-minerals in different grain size fractions. (a), (b) zoned allanite (–Ce) showing metamict structure (-0.425 mm fraction), (-0.212), (c) allanite containing zircon inclusions from the magnetic fraction, (d) magnified area of the allanite grain in (b), (e) metamict weathered thorite 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.

IV. REE distribution in the different fractions

- The distribution of REEs between the bulk sample 123 and the magnetic fraction was studied based on chemical analysis of the respective samples (ICP-MS results) conducted by the Department of Analytical Laboratories at I.G.M.E.
- Chemical analysis of the magnetically separated fractions and the bulk sample 123 showed high enrichment in La and Ce in the magnetic fraction compared to the bulk sample and the non magnetic fraction (Figure 3).
- According to Figure 4(b), the initial bulk sample 123 and the magnetic fraction are enriched in LREE up to 100 times, relative to the PAAS composition (an average composition of the sedimentary upper crust). This clearly indicates the natural enrichment of the Kavala black sands, at ore grade. Further beneficiation of the bulk sample 123 by magnetic separation technique results in a enrichment of 1.6 times (Fig. 4a).

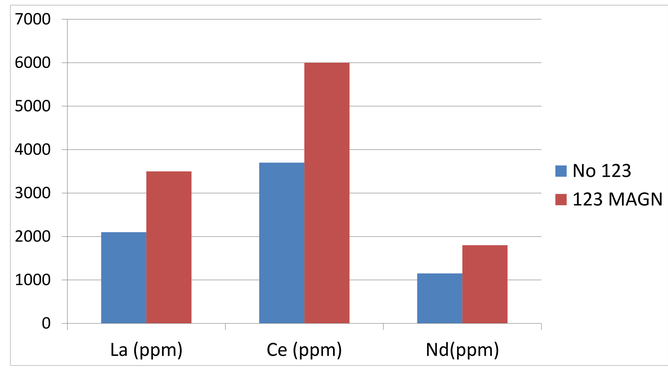

Figure 3. Distribution of La, Ce and Nd in the bulk sample #123 and the magnetic fraction.

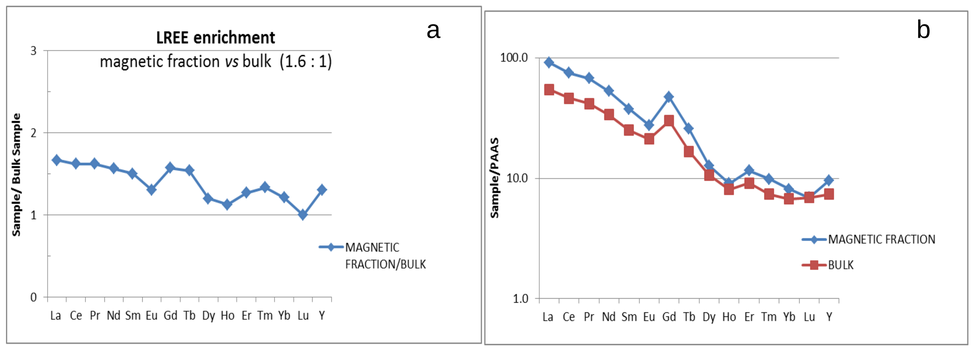

Figure 4. REE normalized composition of the magnetic fraction and the bulk sample 123. (a) Normalization of the magnetic fraction against the initial bulk REE composition shows an enrichment 1.6 times. (b) Normalized compositions against the standard composition of Post Archean Australian Shale (Taylor and McLennan 1985).

Conclusion

Mineralogical and geochemical analysis of the composite sample of black sands from the shoreline of Loutra Eleftheron-Nea Peramos, Kavala area, northern Greece allowed the following conclusions:

Mineralogical characteristics

- Allanite-(Ce) is the major host mineral for light REE (LREE) whereas monazite, zircon and thorite are subordinate. A rare type of Ca-monazite was identified as inclusion in allanite.
- Metamict allanites are common and are thorium enriched.

Beneficiation

Characterization of the magnetic separation and grain size fractions allowed the following conclusions to be made:

- The magnetic fraction is strongly enriched in the LREE, relative to the non-magnetic fraction, and is found 1.62 times higher than the bulk composition.
- A combination of SEM/EDS 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- 0,355, + 0,212 mm, the latter grain size corresponds to the "liberation" size of allanite.

Acknowledgments

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