

# Rare Earth Elements in the Black Sands From Coastal Cliffs Sedimentary Deposits, of Aggelochori Area

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## Introduction

Coastal sands are a result of weathering of nearby rocks. The erosion and deposition can be a result of either the sea waves, or of the action of the local streams and rivers. Black coastal sands are a result of the action of sea waves that separate the heavy (black) from the light (white) minerals. The heavy fraction of the black sands is mainly consisted of titanite, rutile, monazite, xenotime, zircon, magnetite, illmenite and allanite. Sometimes, the concentration of such minerals allows their economic exploitation either for economic metals or Rare Earth Elements (REE). Some heavy minerals being resistant in chemical weathering are exclusively enriched in REEs, such as monazite, xenotime and allanite. The light fraction is consisted of common minerals like quartz, feldspars, calcite and other minerals found in the nearby rocks (Pohl, 2005; Ridley, 2013). Previous research has been done about the coastal black sands found in Greece. Most of them are focused at northern Greece (Pe and Panagos, 1979; Pergamalis et al., 2001; Papadopoulos et al., 2014; 2015; 2016; 2018; Tzifas et al., 2017). The study area belongs to the Axios Zone. Particularly, in the narrower area metamorphic rocks intruded by felsic igneous rocks and their sedimentary counter parts in the presence of Neogene – Quarternary formations are found (Filippidis et al., 1997 and references there in).

### Objectives

Filippidis et al. (1997) provided a mineralogical and radiological study of the studied sands. In this study, the main objectives are to provide additional mineralogical information. Moreover, the chemical content, exclusively focusing on the REEs is also studied in order to give the economic importance of these sands. The REE concentrations of the studied sands are compared to those of black sands exhibiting elevated REE contents from Kavala and Sithonia (Papadopoulos *et al.*, 2014; 2016). Finally, primary effort to study the source rocks of these sands is attempted by comparing the REE patterns of the black sands with the REE patterns of neighbouring granitic rocks (Fanos and Monopigado).

### Methods

Four samples (5 kg each) collected from a coastal slope at height of five meters above sea level at a distance of 30 meters from each other, in order to examine a horizon of black sand formed in the recent geological period. The samples have been washed with clean water to remove any shells and algae and dried at the oven at 50 degrees for 48 h. The 4, 2, 1, 0.063 mm sieves have been used to obtain the grain size distribution of the samples. For minerals separation, representative 15 - 20 g of the 1 - 0.063 mm of each sample have been selected. Hand magnet was used to remove magnetic. Afterwards, the magnetic (I >1.70 mA) and non-magnetic (I <1.70 mA) fractions have been obtained by using a magnetic separator. 0.5 g from each magnetic fraction was pulverized, in order to get the semi-quantitative mineralogical composition with P-XRD. Then, the sample being the most enriched in zircon (sample AGG-3) was selected for chemical analyses. In particular, the whole rock and the fractions >4, 4-2, 2-1, 1-0.063 mm as well as the magnetic and non-magnetic fractions of 1-0.063 mm grain size have been pulverized and analyzed for their major elements content with XRF and trace elements content by ICP-MS at MS Analytical laboratories, Canada.

### Results

According to Schlee (1973), samples AGG-1, 2, 4 are classified as gravels and sample AGG-3 as gravel sediment, indicating probable fluvial transport and deposition environment (Venetikidis, 2012). The main mineral constituents are quartz, feldspars and phyllo-silicates. Minor quantities of magnetite and titanite have been found. Traces of pyroxenes, amphiboles and dolomite as well as heavy minerals such as zircon, hematite and illmenite are present.

The  $\Sigma$ REE (ppm) of the samples was 75.14 for the whole rock (w.r.) and 99.66, 76.00, 54.72 and 73.46 for the fractions >4 mm, 4-2 mm, 2-1 mm and 1-0.063 mm respectively. For the magnetic separated samples, the I>1.70 fraction has 283.95 ppm while the I <1.70 fraction has 39.88 ppm.

The whole rock (w.r.) REE patterns, have been compared to the REE patterns of black sands from Kavala and Sithonia, displaying elevated REE concentrations (Papadopoulos *et al.*, 2014; 2016) (Fig. 1). In order to assume the source rock, the whole rock REE patterns are compared with those of local granitic rocks (Fanos and Monopigado) (Michail *et al.*, 2016 and references therein and Koroneos, 2009 respectively) (Fig. 2).

### Conclusions

Excluding several common silicates, like quartz and feldspars, the main REE bearing minerals are zircon and titanite. The **EREE** content of the studied samples are below but close to the average value of the Sithonia sands, but well below those of Kavala sands. The REE pattern of the w.r. is quite similar to those of Monopigado and Fanos granitoids. The presence of ultrastable detrital non opaque heavy minerals like zircon and titanite along with the unstable amphiboles and pyroxenes and the stable to moderate stable opaque heavy minerals hematite and ilmenite is suggestive for mineralogical immaturity and thus relatively limited sediment transportation. Furthermore, the absence of the characteristic pinkish feldspars of Fanos pluton, implies that the source rock of the studied sediment could possibly be the Monopidado pluton. Further investigation is imperative, in order to determine the source rock.



Figure 1. Comparison of the black sands (w.r.) REE pattern with those of (a) Sithonia and (b) Kavala



Figure 2. Comparison of the black sands (w.r.) REE pattern with the REE whole rock pattern from (a) Fanos and (b) Monopigado granitic rocks.

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