

THE POTENTIAL OF RARE EARTH ELEMENTS IN GREECE

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Abstract

The Rare Earth Elements (REE) in Greece occur in a number of environments and are found in igneous, sedimentary, or metamorphic rocks of different ages. Enrichments in the REE can be divided into two classes: primary types, generally formed by igneous or hydrothermal processes; and secondary types, in which the REE have been further concentrated from a primary enrichment through sedimentary processes or weathering. Primary types are typically veins, layers or zones of REE enrichment within the bedrock; secondary types may include weathered horizons such as laterites/bauxites, placers, and sea-floor sediments. Secondary types are economically the most important types in Greece.

Introduction

The rare-earth elements have unique and diverse chemical, magnetic and luminescence properties that make them strategically important in a number of high-technology industries. Dramatically increasing prices for the REE reflect the expanding range of applications and the narrow global supply base. Consequently, the REE are increasingly becoming more attractive commodity targets for the minerals industry (Hoatson et al. 2011)

The most promising REE sources in Greece may be supergene Al and Ni deposits (i.e. bauxites and laterites) and sands with heavy minerals that have been identified along the coastal area of NE Greece. Collected samples from coastal sands consist mainly of micro-sized mineral crystals derived fundamentally from neighboring granitoid rocks. Microscopic and microanalytical work showed the presence of REE-hosting silicates (allanite, zircon, sphene, thorite) and phosphates (monazite, xenotime, apatite). Bulk chemical analyses conducted by ICP-MS confirmed elevated concentration of REE (Σ REE: 46 – 7195 ppm) and particularly LREE (Σ LREE: 40 – 6920 ppm). Relevant research, being carried out is expected to contribute in the investigation of other geological materials of Greece (granites and granitic pegmatites) assumed to show a considerable REE potential.

1. REE mineralization types in Greece

1.1 REEs in laterite/Bauxite

Greece is the only EU country with extensive but low-grade nickel laterites. The Greek laterites are unique in the world in that they are sedimentary and have originated by transport and sedimentation of laterite-derived material, generated by weathering of ultramafic rocks, on karstic Triassic –Jurassic limestones or on ultramafic ophiolitic rocks (Valeton et al. 1987, Eliopoulos and Economou-Eliopoulos 2000). The multistage transportation and re-deposition of the laterite ore is well documented by the presence of a conglomerate composed mostly of rounded-elongated saprolite and silicified saprolite. The post-sedimentary redistribution of metals resulting in changes of the mineralogical composition of laterites is demonstrated by the presence of asbolane and Mn, Co, Ni-rich zones in the lowest parts of the Aghios Ioannis (Nissi). Nissi is characterized by both nickel and bauxitic laterites with very high values, up to 6440 ppm Σ REE, along with enrichment in Mn, Ni and Co within the lowermost part of laterite and footwall limestone of the Nissi deposit. Such enrichment in both light and heavy REE and the presence of authigenic REE minerals bastnäsite, hydroxylcarbonate-(Nd) and hydroxylcarbonate-(La) are consistent with a downward mobilization of REE and concentration at the footwall limestone like in the majority of karstic bauxite deposits with authigenic REE minerals (Maksimovic and Panto 1991). Another important laterite deposit in Greece is located in Lokrida (Marmeiko). The deposit is hosted by Upper Jurassic-Lower Cretaceous limestone and contains bastnäsite and monazite as REE-bearing minerals. Among the main factors controlling the REE content in laterites are the composition of the rock source, the duration of the lateralization process, the size of the ore bodies, the distance of the transportation, the pH and Eh conditions (Economou-Eliopoulos et al., 1997).

The Parnassos-Ghiona geotectonic zone, including the major bauxite deposits of Greece in the mountains of Parnassos, Elikonas, Kalidromon and Iti, is part of the Mediterranean karst bauxite belt. These deposits are hosted within carbonate rocks and have different ages. Three bauxite horizons, B1, B2 and B3, can be distinguished (from the oldest to the youngest), which are intercalated with shallow-water limestone, within an Upper Jurassic to Middle Cretaceous sequence of the Parnassos-Ghiona zone (Fig. 1). Bauxite occurrences hosted within Upper Eocene limestone are well known in the areas of Nafpaktos, Smerna and Pylos of western Greece (Papastavrou 1986; Laskou 1991, 2003). Typical bauxite ore is characterized by pelitomorphic (fine-grained), ooidic (pisoliths and/or oolites) and clastic textures and by dark red to red-brown colour. The pelitomorphic texture predominates, whereas clastic varieties are comparatively minor. However, there is a significant proportion (approximately 30 % volume) of yellow and grey to whitish bauxites, associated with

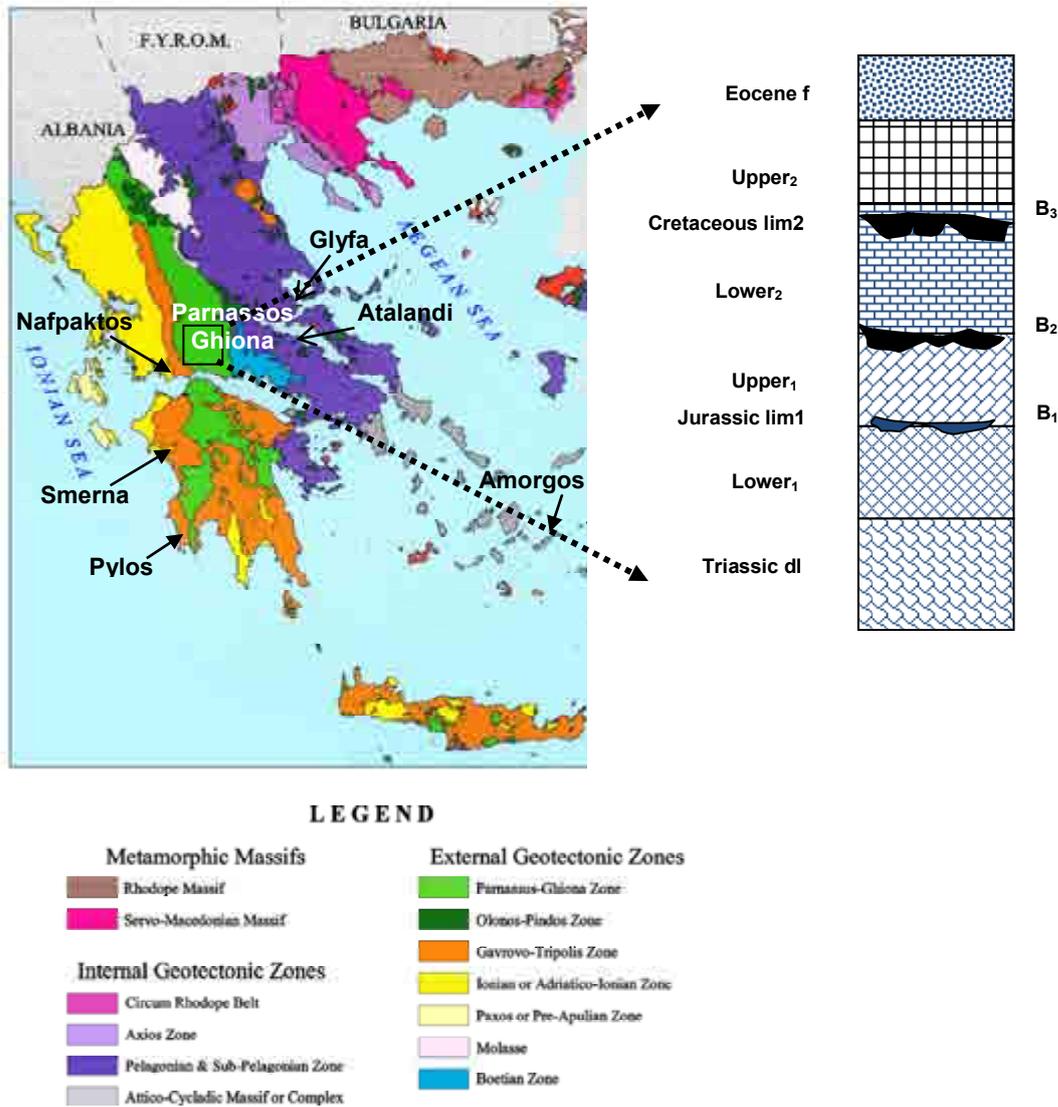


Figure 1: Fig. 1 Structural zones of the Hellenides (after Moudrakis 1992). Location map and stratigraphic column of the Parnassos-Ghiona bauxite deposits. Symbols: dl = dolomitic limestone; lim1 = grey (Lower) and dark colored (Upper) Jurassic limestone; lim2 = limestone; f = flysch, overlain by Quaternary conglomerates; B1 = First bauxite horizon, B2 = Second bauxite horizon, B3 = Third bauxite horizon

right-stipping E-W striking faults (Mariolakos et al.1997; Laskou and Economou-Eliopoulos 2007). The bauxite ores are mainly composed of the AlOOH polymorphs boehmite and diaspore with lesser amounts of gibbsite ($Al_2O_3 \cdot 3H_2O$), goethite or/and hematite, anatase and rutile. Kaolinite, illite and pyrite are common in thrust-fault affected parts of the deposits, whereas chamosite, quartz and zircon are present in lesser amounts.

Bauxite ore samples show a wide variation in their trace-element composition, especially in the content of light REE (LREE). The Σ LREE content is positively correlated

with Al_2O_3 ($r=0.61$), as well as with P_2O_5 and Y. The Fe_2O_3 content correlates negatively with the REE content, whilst there is a positive correlation between the Fe_2O_3 value and the light to heavy REE (LREE/HRE) ratio. The $\Sigma\text{LREE}/\Sigma\text{HREE}$ ratio ranges from 5.5 (Pylos) to 25.3 (Smerna). Special attention has been given to bauxite deposits of the middle and upper bauxite horizon at the Parnassos Mountain. More specifically, representative bauxite samples from the Prossorema were collected from two profiles with alternating beds of pisolithic and fine-grained structure and from the Frussia area, covering a horizon of 4 m to 7 m in thickness. The average ΣREE value is 2,270 ppm (Laskou 1991; Laskou and Andreou 2003). Moreover, the recorded values are higher in the Prossorema profiles compared to the Frussia one. High La, Nd and Y contents have also been recorded by Valetton et al. (1987) in black crusts near the footwall contact of the B2 horizon of the Parnassos-Ghiona deposit. The highest degree of REE (LREE or/and HREE) enrichment is noted in gray or red samples with a lower Fe_2O_3 content, higher LOI-values, and higher concentration in MnO in the samples of each profile. According to Vlasov, (1966), the rare earth elements accumulated together with iron and manganese oxides. The chondrite normalized (Taylor et al. 1981) REE-patterns of the analyzed samples (average values) from three bauxite profiles show a similar trend (Fig. 2).

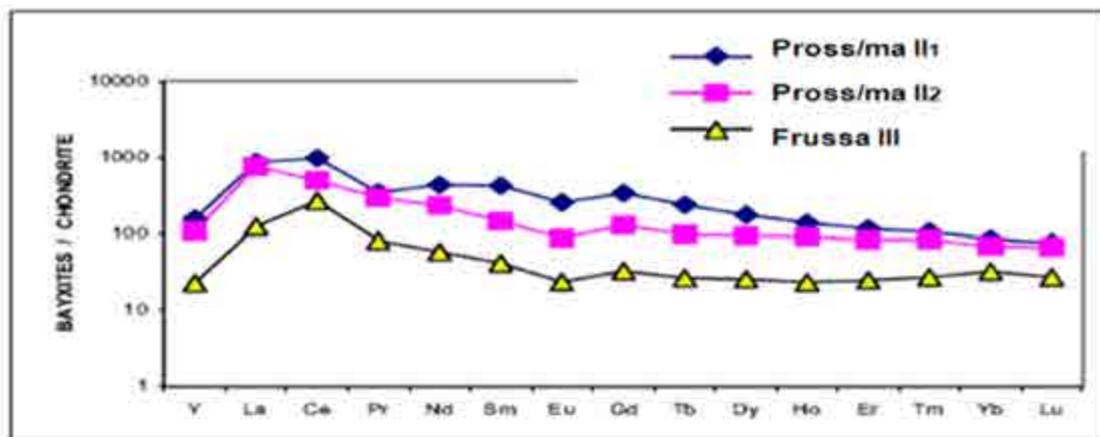


Figure 2: Chondrite-normalized REE-patterns (average values) for bauxite from certain deposits of the Parnassos-Ghiona M. (chondrite values from Taylor et al. (1981))

The determined REE bearing minerals are detrital rhabdophane-Ce, florencite-Ce, churchite and xenotime (Laskou and Andreou, 2003). Similar detrital REE minerals are also accumulated in the Hungarian bauxite deposits (Bardossy et al., 1976). The concentration of REE in bauxite deposits is controlled by their initial content in the parent rocks, by diagenetic or epigenetic modifications, by the influence of circulating waters and underlying barriers of limestone (Laskou and Andreou 2003).

1.2 REEs in black sands

REEs in black sands are found in the Nea Peramos and Strymonikos Gulf areas in northern Greece (Fig. 3) derived from the plutonic rocks of the area mainly the Kavala and Symvolon plutons.

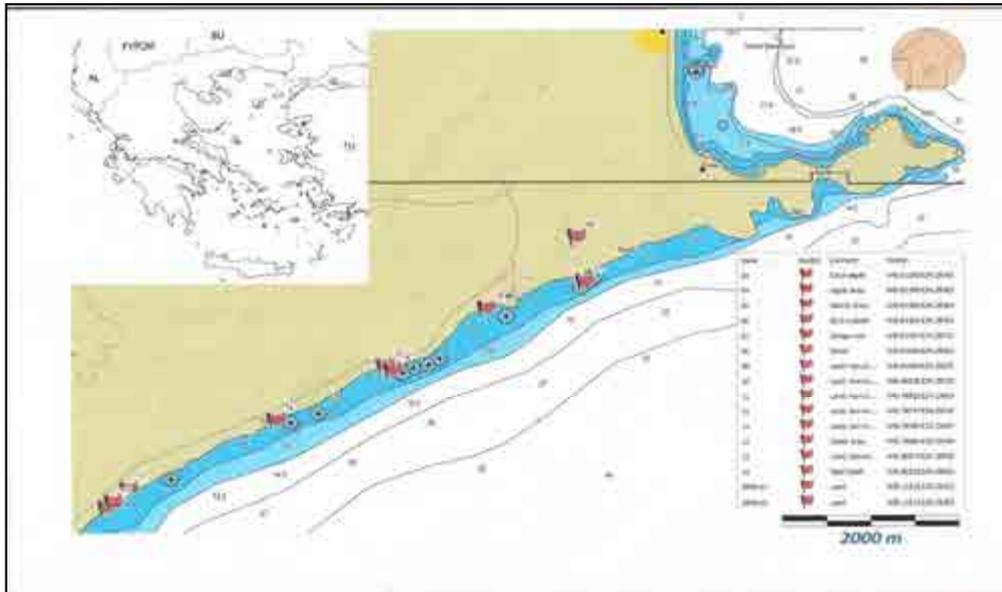


Figure 3: Nea Peramos and Strymonikos Gulf area with sampling locations

The area geologically belongs to the lower tectonic unit of the Rhodope Massif (Pangeon Carbonate Platform), comprise massive marbles, micaceous gneisses, mica schists, calc-silicate schists, and amphibolites and was metamorphosed to the upper greenschist-lower amphibolite facies. Plutonic rocks, most commonly monzonite and granodiorite with lesser amounts of gabbro, are also widespread in the Rhodope Massif, although they are most common in the eastern and central parts. The Kavala pluton is dominantly composed of amphibole-biotite granodiorite with subordinate amounts of diorite, tonalite, monzogranite, and monzodiorite. It is medium- to coarse-grained and consists largely of quartz, plagioclase, K-feldspar, amphibole, and biotite, with lesser amounts of titanite, allanite, apatite, zircon, and epidote (Neiva et al., 1996). Based on textural characteristics epidote is inferred to be of magmatic origin. Mineralogically the black sands are consisting of quartz, feldspars (sanidine, microcline, albite), micas (biotite, muscovite and paragonite), titanite, epidote (zoisite and allanite), hornblende, ilmenite, monazite, xenotime, zircon, and apatite. The REE-bearing minerals are monazite, allanite, titanite, uraninite, zircon, and apatite. Chemical analyses in representative black sand samples showed elevated values of La (930ppm), Ce (992 ppm), Nd (318), Y (55) and Pr (98). Chondrite normalized patterns of samples from the Symvolon granodiorite (Fig. 4a) and patterns of samples from black sands (Fig. 4b) are similar.

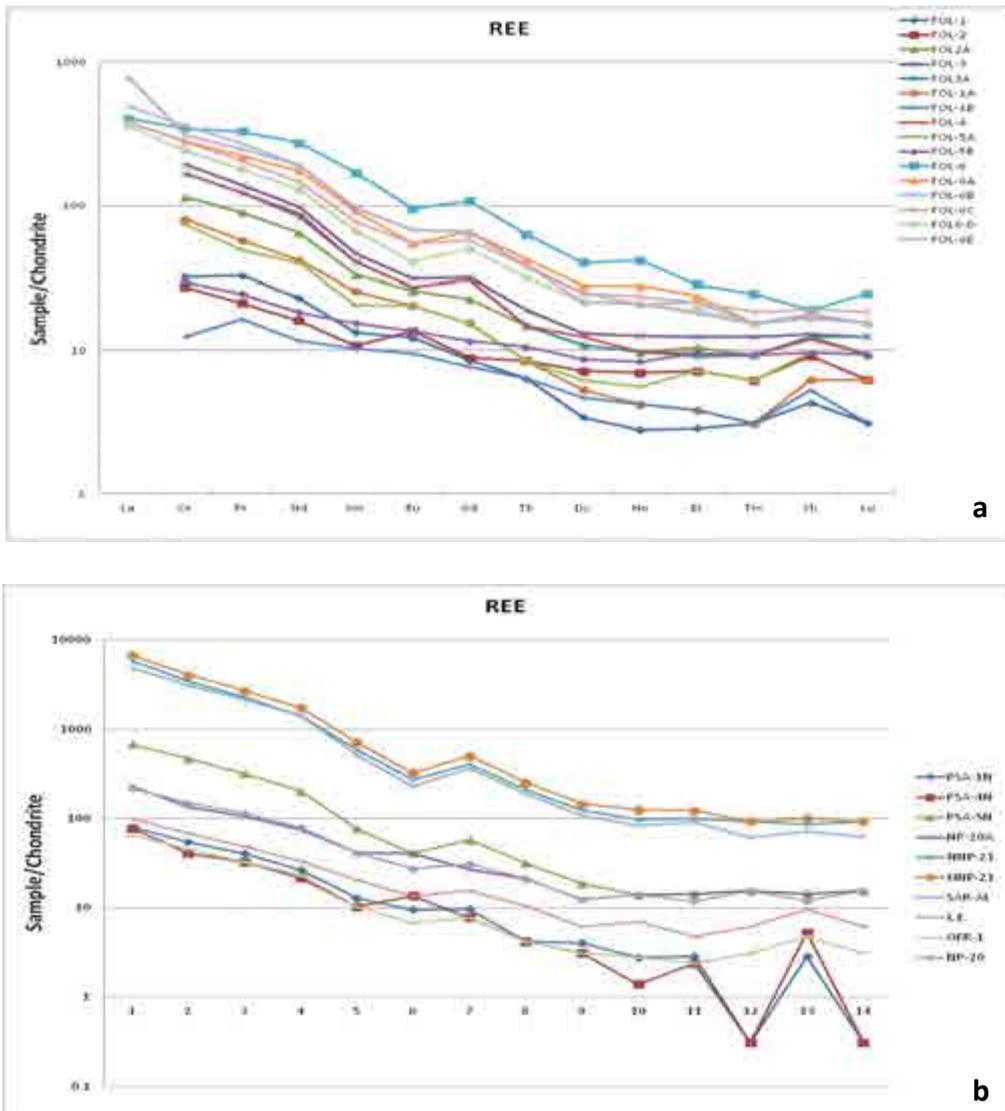


Figure 4: Chondrite-normalized REE-patterns (average values) for samples from the Symvolon granite (a) and black sands (b) from Nea Peramos.

1.3 REEs in granites and granitic pegmatites

This type of mineralisation occurs in a number of granite intrusions in Greece with the most important one being the **Samothrace granite**. The area of interest covers the SW part of the island comprised of altered volcanic rocks of trachytic and dacitic composition with porphyritic texture. REE-bearing minerals are allanite, titanite and zircon. Allanite occurs as elongated crystals in the mass of the rock, with a length which reaches 1mm, while the average size ranging from 0, 4 mm to 0,5mm (**Fig. 5**). Chemical analysis of allanite crystals showed increased contents of cerium (Ce) and other elements of the group of rare earth elements (La, Nd). The proportion of rare earth elements in allanite crystals can even reach 20%.

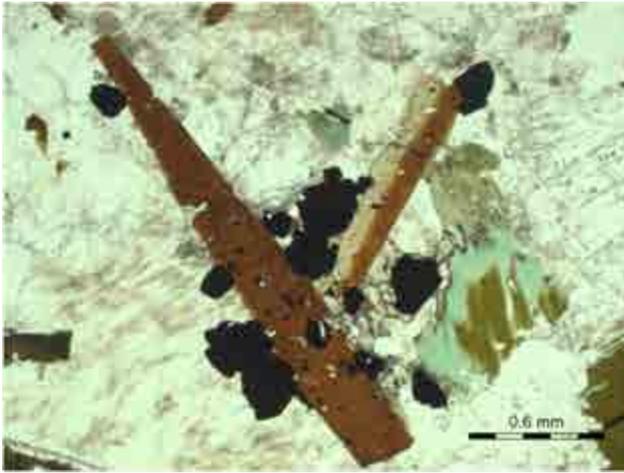


Figure 5: Alanite crystals from the peripheral K-rich granodiorite of Samothrace Island, Greece.

Highly deformed and metamorphosed rocks of the dismembered ophiolite complex of the Ano Vyrini area, Eastern Rhodope, are hosting REE minerals, such as allanite, monazite, zircon, xenotime, titanite and apatite. These rock types are hosted in shear zones and are characterized as ultra-mylonites and ultra-cataclasites. Their thickness is up to 10m and they follow the dip and strike of the ultrabasic body. Their formation is related to the thrust movement of the ophiolitic rocks that occupy an area of 95km². Xenotime crystals contain Σ REO (Y, Nd, Sm, Tb Dy, Y) up to 59,23% and monazite crystals Σ REO (La, Ce, Nd, Sm) up to 56,64%.

1.4 REEs in phosphorites

Extensive beds of phosphate limestones occur in the middle Ionian zone in Western Greece. They were formed during the Lower Senonian and are contemporaneous to the limestone deposition. These limestones are distinguished in laminated phosphatized and organic-rich phosphatized ones. REE content is generally low in both types. However, the organic-rich material type exhibits higher REE contents and the Σ REE is 195.5 ppm, whereas for the laminated type the Σ REE is 34.5ppm. REE-bearing mineral is apatite for the laminated type and the organic-rich material for the second (Tzifas et al., 2014).

Summary and Conclusions

REE in Greece are associated with igneous, sedimentary, and metamorphic rocks in a wide range of geological environments. Elevated concentrations of these elements have been documented in heavy-mineral sand deposits (beach and offshore marine), laterite/bauxite deposits, (per)alkaline igneous rocks, and granitic pegmatites. The distribution and concentration of REE in these deposits are influenced by various rock-forming processes, including enrichment in magmatic or hydrothermal fluids,

separation into mineral species and precipitation, and subsequent redistribution and concentration through weathering and other surface processes.

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