15th International Congress of the Geological Society of Greece
Athens, 22-24 May, 2019 | Harokopio University of Athens, Greece
Bulletin of the Geological Society of Greece, Sp. Pub. 7 Ext. Abs. GSG2019-092

Actinides and Rare Earth Elements (REE) in Sedimentary Formations of Greece: A Review

I.T. Tzifas[1], P.N. Gamaletsos[2], A. Papadopoulos[3], A. Godelitsas[4], N. Kantiranis[3], P. Misaelides.[5], A. Filippidis[3]

(1) Institute of Earth Sciences, Heidelberg University, Im Neunheimer Feld 234, 69120 Heidelberg, Germany
ioannis.tzifas@geow.uni-heidelberg.de
(2) Department of Materials Engineering, KU Leuven, Kasteelpark Arenberg 44, 3001 Leuven, Belgium
(3) Department of Geology, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece
(4) Department of Geology & Geoenvironment, National & Kapodistrian University of Athens, Zografou 15784 Athens, Greece
(5) Department of Chemistry, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece

The rare earth elements (REEs) have been characterized by European Union (EU) as critical raw materials with a significant risk of supply due to their wide utilization in many new technological applications. The growing demand for REE has spiked the research initiatives on new potential REE resources in Europe and is also linked to the increasing exploitation efforts from various geological settings. Regarding on that fact, Greece could play an important role in REE market by targeting the potential evaluation of sedimentary formations such as bauxites, phosphorites, placers and laterites. The present study is providing a review based on the distribution and quantification of the REEs in various sedimentary formations of Greece and, specifically, in the black costal sands near Kavala granitoids, the bauxite deposit of Parnassos-Ghiona, the phosphate rocks of Epirus and, finally, the lateritic ores of Evia and Larymna. The uranium (U) and thorium (Th) content of these formations was also extensively investigated because of its close geochemical association with the REEs. In order to contribute to better understanding of the nature of REE and the above-mentioned actinides from micro- to nano-meter scale a number of analytical techniques were applied. In particular, electron microscopic techniques (SEM-EDS, EPMA, TEM/HRTEM) were combined with synchrotron radiation (SR)- methods (μ-XRF and μ-XANES) as well as with single-crystal XRD and ICP-MS/ LA-ICP-MS.

The allanite-bearing black coastal sands close to Kavala granitoids (N. Greece) have gained the attention displaying a total REE (ΣREE+Y) content ranging from 4010 to 10810 ppm, while Th was also enhanced (236-1205 ppm). The chemistry of the sand mineral components showed that the main Th- and REE- hosting phases were allanite and titanite and, to a lesser extent, monazite, zircon and apatite (Tzifas 2017 doctoral dissertation, Papadopoulos *et al*., 2016). In addition, chemical analyses of the magnetic and non-magnetic fractions of the sands exhibited higher Light REE (LREE: La-Gd) concentration in the latter (1908 ppm and 12470 ppm respectively) due to the relatively higher presence of the afore-mentioned REE-bearing minerals. Tzifas *et al*. (2017) also studied coastal sands of the volcanic island of Nisyros and found relative enrichment in High Field Strength Elements / HFSE (Nb, Ta) compared to actinides (namely U and Th) and REEs. The same authors interpreted this as combination of background geology (provenance) and mineralogical composition of the sands controlling the particular endowment in critical metals. Papadopoulos (2018) extensively studied the REE and actinide content in various coastal areas near granitoids revealing that in Mykonos and Naxos Islands the REE content was also enhanced (ΣREE: 64-9620 ppm and 74-4700 ppm respectively) and comparable with those of the ones of Kavala.

Greek bauxites from the Parnassos-Ghiona active mines studied by Gamaletsos *et al*. (2019) demonstrated an increased content in LREE (varying from 106 to 913 ppm) compared to the relatively lower content of the HREE (ΣHREE- from Tb to Lu including Y- varying between 45 and 179 ppm; ΣHREE = 95 ppm). The overall REE concentration (ΣREE + Y+Sc) varied from 192 to 1109 ppm. However, it should be pointed out that significant variations were observed between the Fe-depleted (avg. 268 ppm) and the Fe-rich bauxites (avg. 569 ppm). This differentiation of the REE concentration in Fe-rich bauxites can be attributed to the higher participation of (diagenetic and/or epigenetic) REE minerals, mainly LREE-fluorocarbonates as indicated by the SEM-EDS investigation. It is worthy to be mentioned that the REE-content of the Greek bauxite metallurgical residues / BR (also known as "red mud") seems to be remarkably increased by almost two times compared to that of the Parnassos-Ghiona bauxite parent material. The data presented by Gamaletsos *et al*. (2019) showed similar REE values compared to karst-type bauxites of the globe. The actinide content, and particularly of Th, is also relatively increased in the bauxites. The Fe-depleted samples contained up to 63 ppm Th whereas the corresponding content of the Fe-rich samples is lower (Gamaletsos *et al*., 2011; Gamaletsos *et al.*, 2016).

Organic-rich phosphatized limestones from Epirus region were found to present enhanced phosphorous content (27 wt.%) and natural uranium enrichment (647 ppm). Their relatively high ΣREE + Y content (56-280 ppm) can be linked, on the basis of the mineralogical and geochemical investigations, with the presence of carbonate-apatites and/or organic matter (Tzifas *et al.*, 2014). The REEs average concentration values were compared to those of phosphate deposits of other countries (i.e., Israel, Egypt, Tunisia) demonstrating that, regardless of the observed similar trends, the Epirus samples were not especially enriched.

Nickeliferous laterite ores from two typical central Greece deposits of Larymna and Evia (Samouhos *et al*., 2019), exhibited ΣREE = 774 ppm and 76 ppm respectively, while their clay fraction demonstrated significant enrichment in contrast to the initial ore (ΣREE = 1014 and 40 ppm, respectively). The scandium (Sc) concentrations found to present similar values in both mining areas (64 and 42 ppm, respectively). The mineralogical investigation of laterites indicated

that both materials contain crystalline hematite- and chlorite group phyllosilicates, whereas the Evia sample additionally illite. Transmission electron microscopy investigations revealed that laterite ores consisted of complex nanoscale aggregates of the above-mentioned phases.

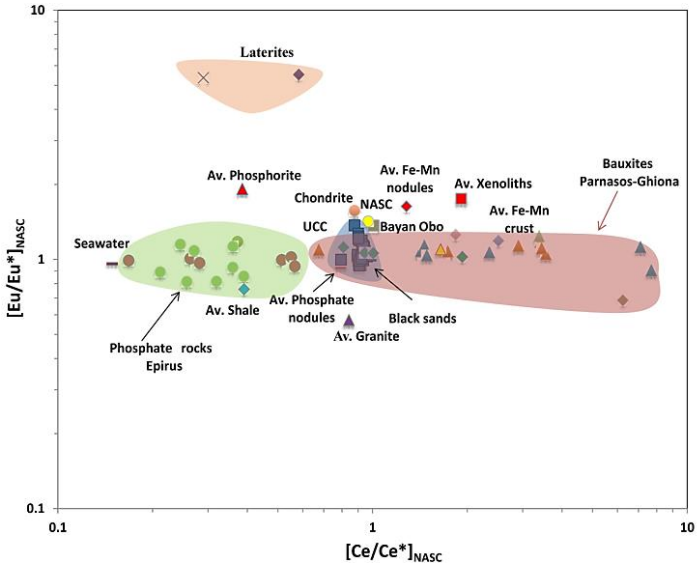

Figure 1. REE discrimination diagrams for bauxites, laterites, phosphates, black sands compared to various geological materials of the globe.

To the extent that Eu/Eu* - Ce/Ce* bivariate diagrams for sedimentary geomaterials provide information about their origin as Leybourne & Johannesson (2008) suggested, similar diagrams were constructed for the same reason in the case of bauxites, laterites, phosphorites and Kavala black sands. The average values of various geomaterials of the globe were also used for comparison (Fig. 1). The black sands showed that the samples are not located close to the field of the average granite as they were influenced from various geological processes. In the case of the bauxites, it is revealed that the Ce/Ce* ratios significantly varies. This fact might be attributed to the $Ce^{3+} \leftrightarrow Ce^{4+}$ and the LREE re-mobilization during the supergene/epigenetic processes. The lateritic samples exhibited high Eu/Eu* ratios as a matter of the fact that they do not exclusively originate in ultrabasic -ophiolitic- rocks as previously considered, while the organic-rich phosphatized limestones are not typical phosphorites, covering a rather large range as a result of the impact of surface waters.

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