The Potential for REE and Associated Critical Metals in Coastal Sand (Placer) Deposits of Greece: A Review

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Abstract: The rare earth elements (REEs) are characterized by the European Union (EU) as critical raw materials with a significant risk of supply because of their broad utility in both traditional and emerging technological applications. The growing demand for REE has caused a flurry in the search for new REE deposits in Europe and elsewhere in the world, and is also linked to rising exploitation efforts in a variety of geological settings. To this end, Greece appears to be a promising candidate to become a leading EU country in terms of REE by virtue of its natural endowment in sedimentary heavy mineral deposits (placers) along its long coastline. The present review focuses on the distribution, abundance, and bulk geochemistry of REEs and other critical metals (Ta, Nb, Co) associated with placer deposits of Greece, and specifically with geologically young heavy mineral sand accumulations developed proximal to felsic plutonic source rocks. These deposits are also enriched in the actinides uranium (U) and thorium (Th), as both of these metals are typically associated with REE-rich minerals such as xenotime, monazite, thorite, allanite, and zircon. Previous studies have employed a variety of analytical techniques down to nano-meter scale with the aim to elucidate the mineralogy and distribution of REE and associated actinides in Greek beach placers. In view of this mineralogically-intensive background, the present review focuses chiefly on bulk geochemical characteristics of the same deposits and the variations thereof between two major geographical regions (northern Greece, southern Aegean) and across individual placer occurrences within them. In this framework, we present comprehensive compositional comparisons between the different deposits, highlighting the geological sub-environments wherein they occur, their distinctive sources and geochemical signatures, and their potential economic significance in terms of REE and other critical metal enrichments where applicable.

Keywords: rare earth elements (REE); actinides; Greece; coastal sands; geochemistry

1. Introduction

1.1. Rare Earth Element (REE) Applications and Global Demand

Rocks and ores containing high concentrations of REE and other critical metals (e.g. Co, Nb, Ta) are very important for technological and specialized metallurgical applications [1]. At present, the global demand is 100 million tons of rare earth oxides per year [2]. The estimated global reserves by USGS are approximately 110 million tons. Presently, the bulk (about 90%) of the REE production globally, is coming from the Bayan Obo deposit (Mongolia). Recycling REEs is expected to play a more important role in the near future [3,4]. However, as the demand is increasing, it will be very difficult to meet the global needs for REEs [5–7].

The increasing demand for REEs and critical metals worldwide (Figure 1), as well as their uneven global distribution and apparent scarcity (most large active mines are located in China) has led the EU to encourage research for new REE deposits [8,9]. The region of Scandinavia as well as Greenland, host the majority of prospective REE deposits in EU, but research for new REE-bearing potential deposits is also in progress in other EU countries. REE in beach placers, as well as in bauxites and laterites, has drawn interest for further detailed investigations [10–13]. Elevated content of light REE (LREE) (La, Ce) of at least fundamental scientific interest, has also been observed in other, more atypical settings, such as the porphyry Cu-Au system of Vathy in Kilkis, Greece [14]. Due to the increasing market demand and the limitations involved in recycling, natural REE deposits remain the primary REE source. REE deposits related to carbonatitic magmatism as well as ion-adsorption type deposits, are presently the most popular resources under production [15,16]. Therefore, research on new REE deposit types is becoming increasingly pertinent, with emphasis particularly on the viability of bauxites, phosphates, placers and clay deposits as promising REE resources [17–22]. It should be pointed out that although measured REE contents might appear economically attractive across a breadth of alternative deposit types, the feasibility of many of these may be hindered due to limitations with respect to current methodologies in metallurgical extraction. To this end, a number of studies focusing on resource feasibility have been published in recent years, such as the one of Gradeal et al. [23]
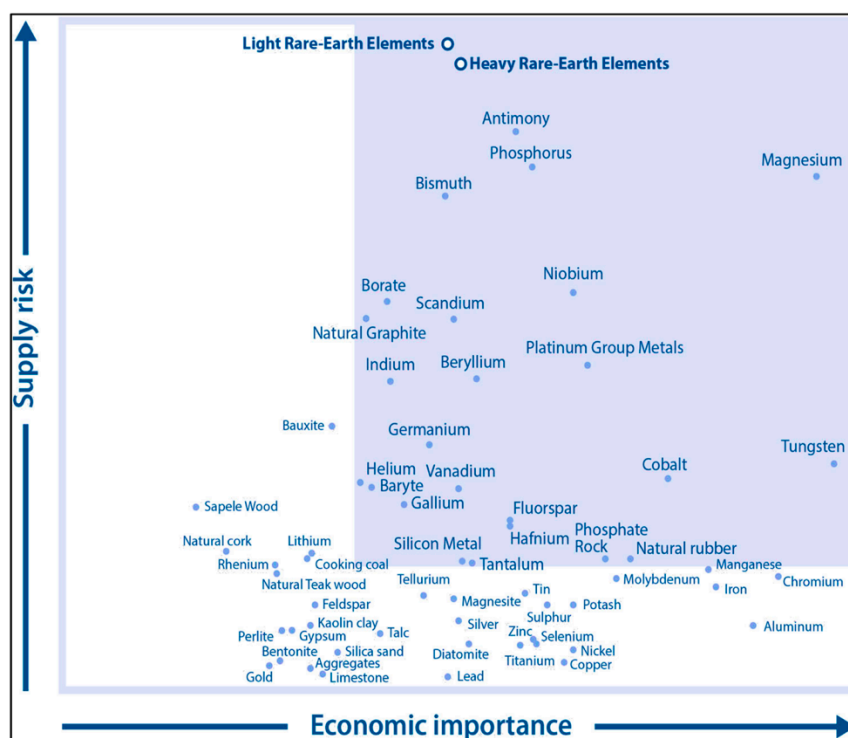

Figure 1. Diagram illustrating the critical metals according to EU reports [8] based on economic importance and supply risk (after Binnemans al. [22]).

1.2. REE-Bearing Phases and Radiological Implications

At present, the number of minerals considered to be REE carriers of economic potential is above 200 [24]. The same minerals contain significant amounts of the naturally radioactive elements U and Th, which share similar geochemical characteristics with the REEs [25]. This poses an obvious radiological risk [26], a topic which has already been discussed is previous studies with particular emphasis on the natural radioactivity emitted by beach placers in Greece [27–35] and references therein). Environmental and health concern is therefore at the center of the economics of REE deposits, thus calling for measures to limit harmful environmental and human impacts, e.g., [36].

At the same time, the intrinsic enrichment of REE deposits in radioactive minerals offers a powerful tool for the exploration of such deposits. It is therefore no surprise that radiometric methods as part of geophysical exploration campaigns, have facilitated the discovery of a number of new deposits across the world. Examples of such deposits are located primarily in the USA and Canada [37], India [38], Brazil [39], China [40], Iran [41] and Mexico [42–49], and less so in other countries [50].

1.3. Coastal Heavy Mineral Sands

Coastal heavy mineral sands, also widely referred to as "black sands" (due to their common enrichment in Fe-Ti oxides) or simply placers, are economic deposits of heavy minerals and have diverse economic interest as a result of a wide-ranging provenance control from one deposit to another. These deposits form as a result of processes of mechanical erosion, transport, hydrodynamic (or wind-driven in the case of aeolian transport) sorting and ultimately accumulation at suitable sites, leading to the preferential concentration of higher density minerals that are resistant to chemical weathering (such as ilmenite, zircon and monazite), relatively to lighter minerals [51–54].

Depending on source rock (provenance) characteristics, beach placers can be particularly enriched in REE and other critical metals (e.g., Co, Nb, Ta). The economic importance of these deposits is closely related to which exact minerals host the REE, and specifically to the ability to extract the REE from the host mineral structure [55]. India, W. Australia, S. Africa, and Madagascar are countries with the best-known commercial placer examples at present containing economic REE concentrations [56]. Monazite and xenotime are the most common REE-hosting minerals in these deposits, and these are minerals characterized by well-established metallurgical methodology for the extraction of REE from them [56–58]. India is the most important Th producer, through the exploitation of the monazite-rich beach placers of Orissa [59,60].

1.4. Placers of Greece

Although Greece is a relatively small country in terms of continental areal extent, it has a comparatively very long coastline. This renders it as one of the countries of highest prospectivity with respect to placer deposits in general. Consequently, several areas have been identified and investigated for their mineralogical and geochemical potential for heavy mineral sands, with particular reference to REE (Figure 2). A number of studies have been carried out on the coastal areas of Kavala [10,11,27,28,33,61,62], Touzla Cape (Aggelochori) [29] Sithonia Peninsula of Chalkidiki [30,31,35,63] and the area of Maronia in Samothrace (Northern Greece) [34]. The southern Aegean region and specifically the Atticocycladic belt is another area that has received increased research attention for its placer potential [64]. Beach placers from Nisyros island have also been investigated as an end-member case study of heavy mineral sands in a predominantly volcanic provenance. The remaining placer deposits mentioned above from northern Greece and the Atticocycladic belt, represent coastal sands derived mainly from the weathering of plutonic rocks [65].

All aforementioned studies have focused on beach sands that have apparently formed from the weathering of granitic rocks with recognized potential to contain elevated primary REE concentrations by comparison to average crust. The wealth of recent research activity on a substantial number of Greek placer occurrences (Figure 2), has prompted this integrated review based chiefly on their bulk geochemical characteristics. We, therefore, present here a comprehensive account of the REE, actinide, and associated critical metal potential of placer deposits of Greece, which is primarily based on previously published bulk mineralogical and geochemical data. We complement these with additional unpublished geochemical results for bulk trace element compositions of coastal heavy mineral sands from the Atticocycladic belt, along with similar new data from the Chalkidiki peninsula, namely the Aggelochori coastal region. We then summarize the salient mineralogical and geochemical signatures and economic potential of the various deposits covered. In the absence of quantitative reserve information available to us at the time this review was compiled, we have given consideration chiefly

to the primary controls in variations of REE concentration and, where applicable, of critical metals as well, for these apparently disparate occurrences from a geographical and geological viewpoint.
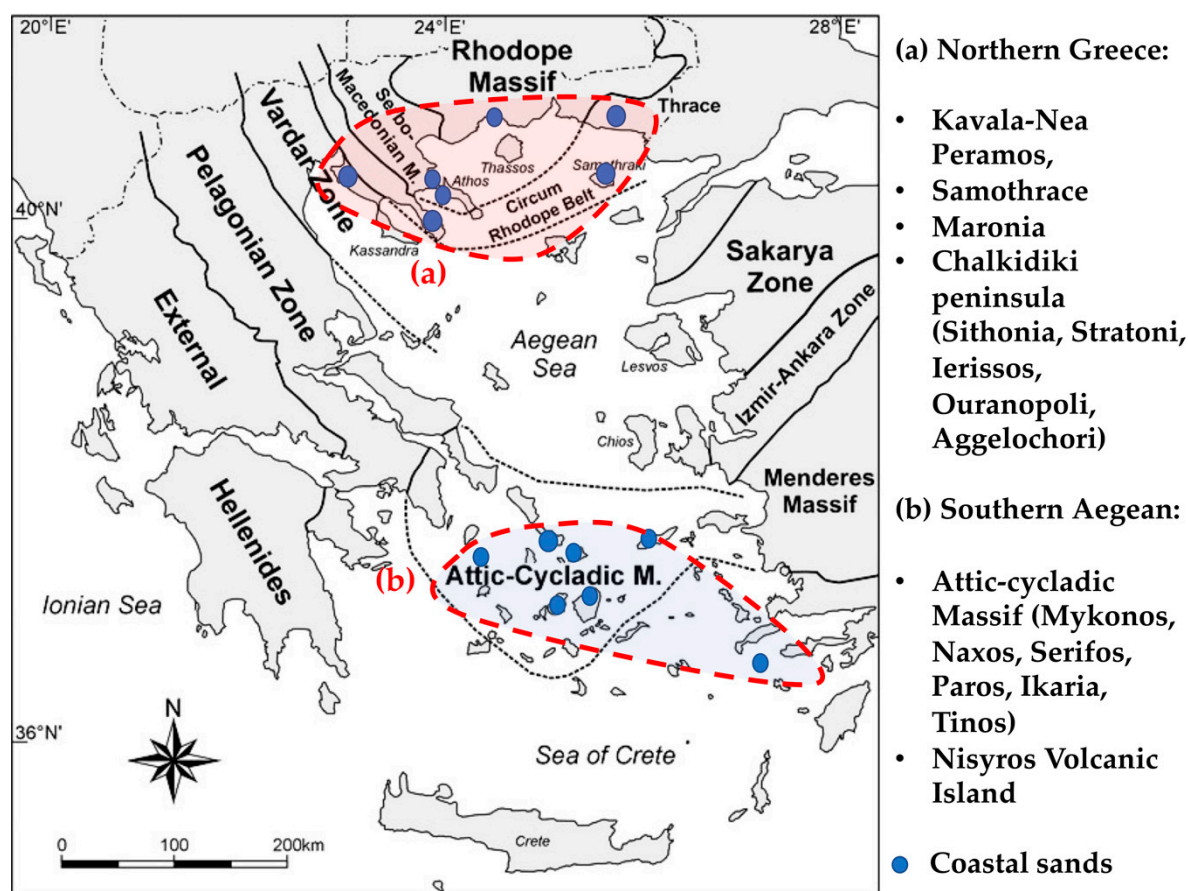

Figure 2. Geographic localities of Greece containing rare earth element (REE)-enriched beach sands as reviewed in this paper. Detailed maps for each of the localities displayed can be found in the Supplementary Materials.

For more in-depth geological information on each occurrence reviewed the reader is referred to the Supplementary Materials detailed maps and additional geological details, and to earlier publications specific to each locality revisited [27–35,61–65]. Through reviewing this substantial body of older and recent research, our ultimate goal with the present treatise is to provide a useful and timely first-order reference for academics and industry professionals alike, with a vested interest in the metallogenic potential of Greece with respect to REE.

2. Materials and Methods

As also described in the reviewed literature [27–35,61–65] samples of heavy mineral sands were collected both from surface exposures and from the immediately reachable subsurface thereof. Sampling was carried out against a chosen grid, the dimensions of which varied from one locality to the next, depending on the dimensions of each beach. A total of thirty-seven samples were taken from Kavala, thirty from Sithonia, one from Nisyros, twenty-eight from Atticocycladic zone, six from NE Chalkidiki, three from Samothraki, two from Maronia and one from Aggelochori.

Following comprehensive mineralogical determinations, bulk geochemical compositions of all materials presented in this review were determined by Inductively Coupled Plasma Optical Emission and Mass Spectrometry (ICP-OES and ICP-MS) using a PerkinElmer Sciex Elan 9000 equipment (Concord, Ontario, Canada) after $LiBO_2/LiB_4O_7$ fusion and HNO_3 digestion of 0.2 g of pulverized bulk

sand sample. Loss on ignition (LOI) was determined by heating the samples at 1000 °C. The total C- and S-contents have been determined by using a LECO carbon and sulfur analyzer. Bulk chemical analysis and LOI measurements were carried out at the ACME and ACT Labs (Canada) whereas heavy mineral separation (where applicable) was conducted at the Department of Geology, University of Thessaloniki. Further details on the analytical methodology used can be found in all previous publications that have also served as key sources for the information presented herein [27–35,61–65]. Analytical data are archived in the Supplementary Materials.

P-XRD analyses were conducted at ACTLABS, Ontario, Canada. A quantity of each pulverized sample was put into a standard holder. Quantitative identification of mineral phases were determined using the Rietveld method, which is based on the calculation of the full diffraction pattern from crystal structure information. The X-ray diffraction analysis was performed using a Panalytical instrument on a P source and an XRCE detector.

3. Results

3.1. Northern Greece: Kavala, Samothrace, Maronia

3.1.1. Kavala-Nea Peramos

The mineralogy and geochemistry of coastal sands west of the city of Kavala (Figure 2) has been a subject of research in many previous publications, due to their recognized potential for REE [10,11,27,33,61,62]. The most recent of these studies deals with the distribution characteristics of REE and Th [33]. Some indicative results of this work are illustrated in Figures 3 and 4. Mineralogically, the sands of Kavala are dominated by a variety of silicate minerals (quartz, feldspar, hornblende, epidote, titanite, garnet) along with iron oxides and hydroxides (magnetite, hematite). In association with these, small quantities of phosphate phases (apatite) and Ti-oxides (ilmenite) are mineral components of obvious economic interest [33]. The REE-rich epidote allanite (see also Figure 3) has been highlighted as the main REE-hosting phase, along with monazite, zircon, apatite, titanite and garnet (Figure 4). By contrast, zircon and monazite grains were found to be present mainly as inclusions in other mineral phases such as hornblende and allanite.

Following pre-treatment of the sands via magnetic separation, magnetic and non-magnetic fractions were obtained and analysed. Semi-quantitative estimates of modal mineral abundance using P-XRD revealed that the magnetic fraction contains 2–10% allanite and 4–16% titanite together with abundant iron oxides (magnetite and hematite). The non-magnetic fraction consisted mainly of tectosilicates, hornblende and titanite; in this fraction, allanite was present in substantial modal concentration, ranging from 12 to 20%. Minor quantities of mica and carbonate were also observed.
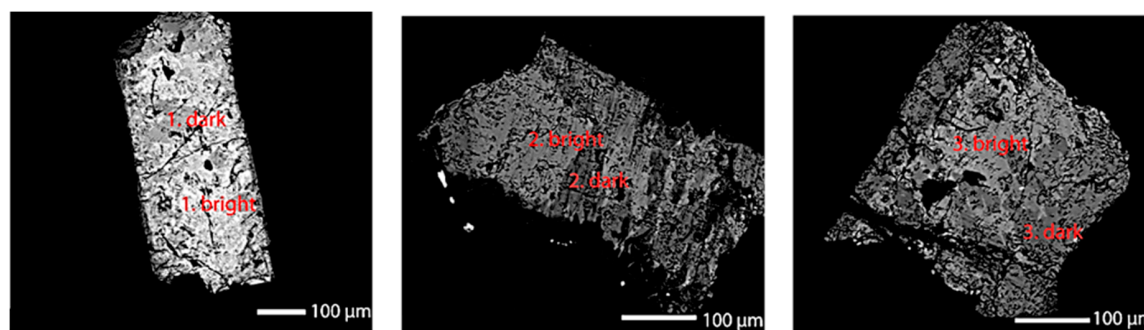

Figure 3. Various textural forms of allanite crystals from samples of heavy mineral sands from Kavala (modified from Tzifas et al. [33]).
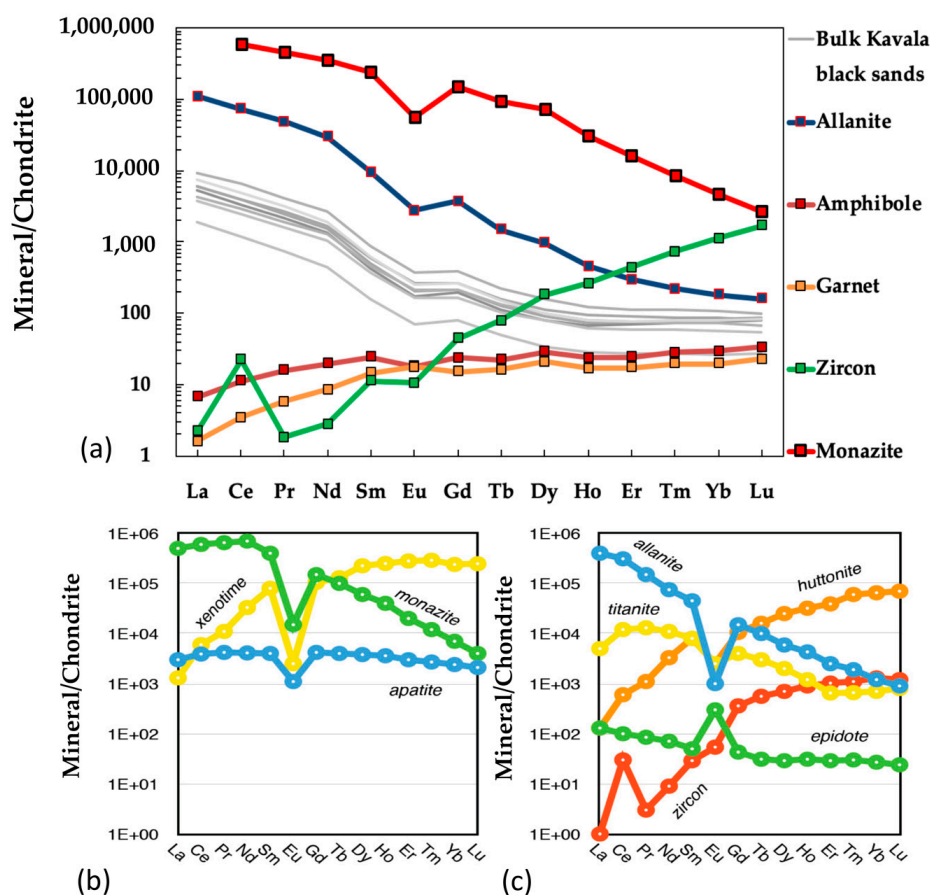
Figure 4. Chondrite-normalized REE patterns (upper) for the main U-, Th- and REE-bearing minerals (**a**) of coastal heavy minerals sands of Kavala region [33]. Chondrite-normalized REE patterns (lower) of accessory phosphates (**b**) and silicates (**c**) are from Bea [66]).

Combination of Electron Microprobe Analysis (EPMA) and Laser-Ablation Inductively Plasma Spectroscopy (LA-ICPMS) revealed that the ΣREE content of allanite was approximately 13 wt.%, with enhanced Th content ranging from 1135 to 1451 mg/kg. Allanite grains from Kavala sands are also enriched in other critical metals with most significant being V (392–399 mg/kg), Ga (401–458 mg/kg) and to a lesser extent Sc (64.5–94 mg/kg). Average uranium concentration is at 151 mg/kg.

An unidentified Ce-rich phosphate phase—most probably monazite or xenotime—was found to be present in Kavala black sands mainly as micron-sized (less than 10 μm) alteration selvages of allanite. The mineral records enrichment in LREE (8794 mg/kg) and to a lesser extent in HREE (814 mg/kg). Concentrations of the naturally radioactive elements Th and U were also significant (967 and 147 mg/kg). The same can be argued for the metals Y and Ga, which returned concentrations of 503 mg/kg and 4400 mg/kg respectively. The other phosphate phase present, namely apatite, accounts for a small fraction of REE and is also relatively enriched in LREE (1670 mg/kg) while the U (up to 23 mg/kg) and Th (21 mg/kg) contents are much lower than those of allanite and monazite.

Zircon is an additional REE-hosting phase, with relatively higher concentration in heavy REE (HREE) (253–890 mg/kg) compared to LREE (8–44 mg/kg). Corresponding U and Th concentrations range from 196 to 630 and 373 to 2310 mg/kg respectively. The increased presence of zircon accounts for the elevated concentration of Hf (8810–10,590 mg/kg), and to a lesser extent Sc (152–218 mg/kg) and Y (332–1259 mg/kg).

Titanite accounts for part of the REE budget in the Kavala sands, with higher LREE content (2180–1264 mg/kg) compared to the HREE one (378–2210 mg/kg). As expected in association with Ti-rich phases, the high-field strength elements Nb (396–2100 mg/kg) and Ta (6–91 mg/kg) showed

correspondingly enhanced concentrations, followed by lower abundances for V (512–841 mg/kg), U (78–833 mg/kg), Th (200–917 mg/kg) and Ga (9–42 mg/kg).

3.1.2. Maronia

The Maronia plutonic complex is the prevailing source for the homonymous heavy-mineral sand occurrences in N. Greece [34]. Three main rock groups have been distinguished here, ranging in compositions from basic to felsic. Basic rocks are effectively gabbros, intermediate compositions range from (quartz) monzonite to monzogabbro, whereas felsic rocks consist of granite and its porphyritic/aplitic equivalents. The gabbros show high alkali characteristics [67].

Upper Continental Crust (UCC) [68] normalized spidergrams (Figure 5) for representative heavy mineral sands from Maronia show relatively high abundances in High Field Strength Elements (HFSE: Hf, Zr, Ta, Nb), Light-Ion lithophile elements (LILE: Cs, Rb, Ba, K, Sr) and transition metals and metalloids (As, Sb, Sn, Zn, Cu, Mo, Co, and Pb). By comparison, REE concentrations are rather subdued and essentially plot on the UCC compositional line. This suggests that zircon and Ti-rich species in the sampled sands are more abundant by comparison to REE-rich phases such as phosphates. Enrichments in transition metals can readily be attributed to copper-molybdenum mineralization recorded in the felsic porphyries of the source complex [69].
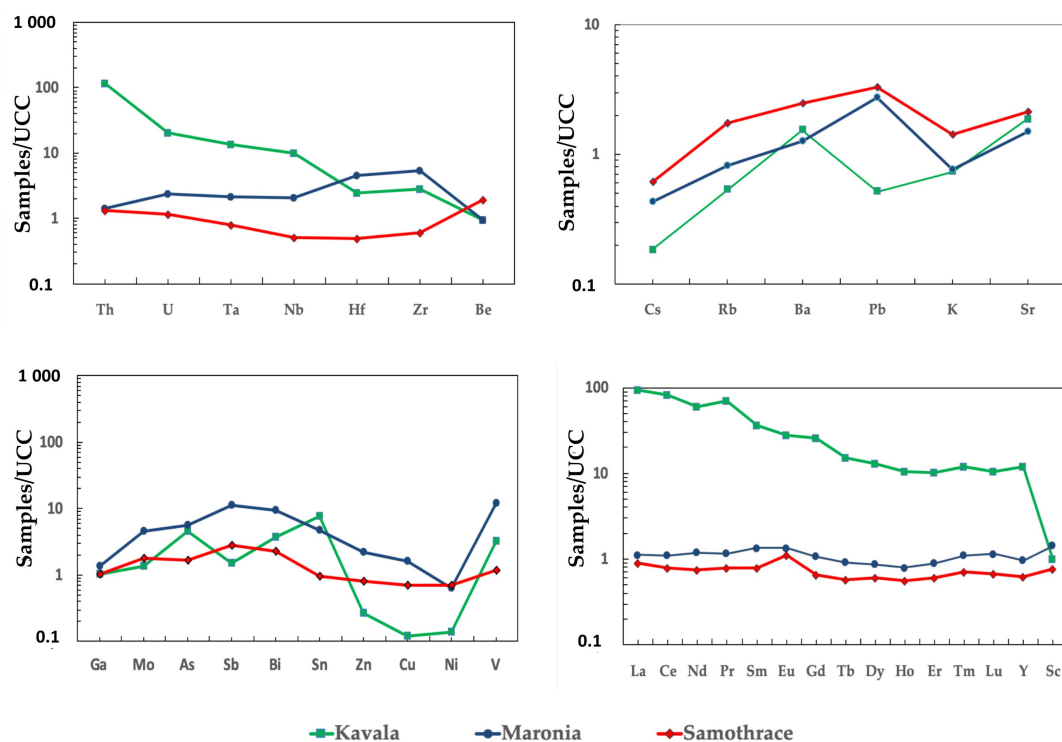

Figure 5. UCC-normalized compositional spidergrams for REE, HFSE, LILE, and transition metals of coastal sand deposits representing different localities of Northern Greece.

3.1.3. Samothrace

Heavy mineral sand samples from the island of Samothrace have been obtained in proximity to neighbouring plutons [34]. The Samothrace pluton is an intrusion composed of monzonites and granites. The mineral constituents of these rocks are quartz, feldspars, biotite, hornblende, magnetite, ilmenite, apatite, zircon, titanite, allanite and rutile. UCC-normalized spidergrams for the Samothrace coastal sands show concentrations above the upper crust average for LILE and transition metals and metalloids (As, Sb), while HFSE and REE concentrations are low and comparable to those from the Maronia locality above (Figure 5).

Chondrite-normalized REE diagrams (Figure 6) show the relatively higher endowment of the Kavala coastal sands as compared to both those of Samothrace and Maronia. Otherwise, the REE patterns have a similar and characteristic negative slope, suggesting a strong control on REE budgets by the mineral allanite, in spite of the erratic pattern for Eu. The muted REE abundances of the black sands at Samothrace and Maronia is thus interpreted as a result of higher dilution effects by the silicate mineral fraction of the sands which is dominated by quartz, feldspars and other relatively heavier silicates such as hornblende.
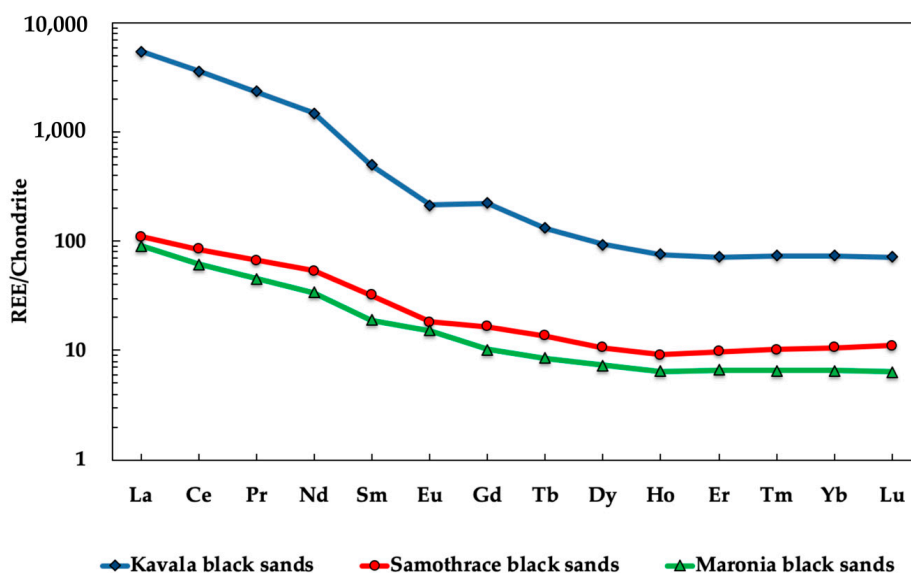

Figure 6. Chondrite-normalized REE patterns of coastal sands from N. Greece (Kavala, Maronia, and Samothrace).

3.2. Sourhern Aegean: Atticocycladic Coastal Zone

Mineralogical and geochemical data for the REE content and individual REE-bearing phases of coastal heavy mineral sands from the Atticocycladic coastal zone (Ikaria, Mykonos, Naxos, Serifos, Paros, Tinos; see Figure 2) were recently summarized by Papadopoulos et al. [64]. The surrounding source rocks bear an obvious effect on the mineralogical composition of these sands. These consist mainly of felsic plutonic rocks, metamorphic rocks of variable composition (e.g., gneiss, amphibolite) as well as clastic sediments, while in Tinos alone, meta-ophiolites are an additional lithological component of the local provenance. Coastal sand samples are significantly enriched in REE compared to their source provenance, with highest relative enrichments recorded in beaches of Mykonos. At one specific locality, the Panormos beach, abundances of ΣREE up to >9500 mg/kg have been determined [64].

UCC-normalized trace element spidergrams for different localities of the Atticocycladic zone are herein presented for the first time (Figure 7). Coastal sands from Mykonos show high abundances in REE compared to average crust, with an apparent negative slope in HREE distribution. Relative enrichment is also observed in actinide content (Th, U) as well as in other critical metals such as Ta, Nb and Bi. Moreover, metalloids (As, Sb) are also present in relatively elevated concentrations compared to other localities, possibly signifying the effects of hydrothermal activity at the area. The same applies to the LILE contents (Rb, Pb, Ba), especially Ba.
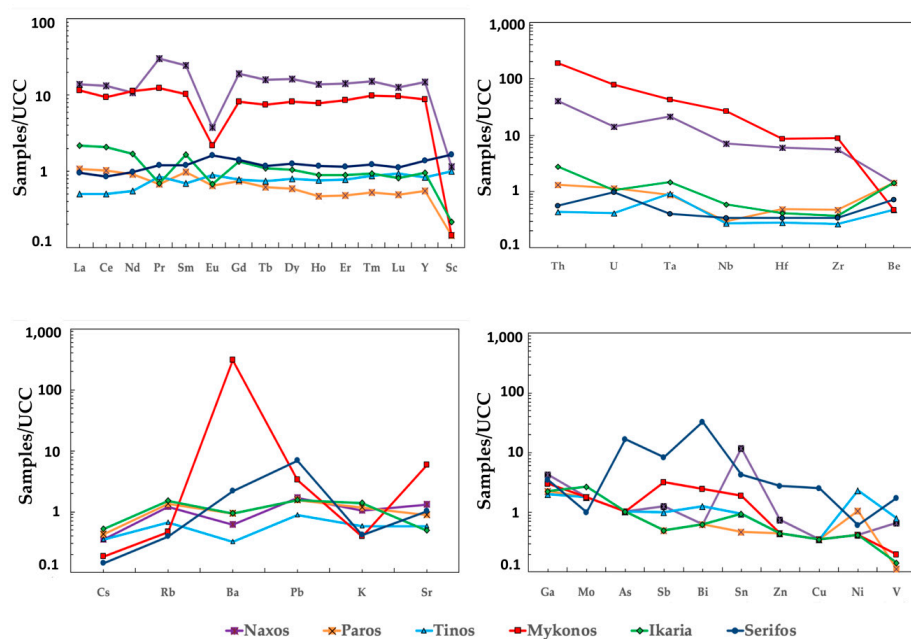
Figure 7. UCC-normalized spidergrams of coastal sands derived from different localities of the Atticocycladic zone (Mykonos, Serifos, Naxos, Tinos, Paros, Ikaria).

The coastal sands of Naxos also show enrichment in REE and actinides, comparable to that of Mykonos. However, the UCC-normalized spidergram for the Naxos sands (Figure 7) shows a flatter HREE pattern compared to that of Mykonos. Ta and Sc also illustrate a relative enrichment, while LILE and transition metals are depleted. Serifos is enriched in transition metals/metalloids (particularly Bi), depleted in LILE and HFSE, and with a flat REE pattern at abundances approximately double those of UCC (Figure 7). Coastal sands from Paros, Tinos and Ikaria show similarly flat REE patterns but much lower REE abundances compared to UCC, and therefore reveal little economic interest, at least with respect to the REE.

Chondrite-normalized diagrams of REE (Figure 8) for sand samples derived from the Atticocycladic zone show clear overall similarities in terms of the negative slope and presence of negative Eu anomalies. A slight difference lies in the somewhat flatter REE pattern for the Naxos sands, which thus display a relatively more enriched HREE budget than the other localities displayed (Figure 8). This is broadly reflected in absolute REE abundances too: Mykonos coastal sands have ΣREE contents ranging from 65–9620 mg/kg, at an average value of 1620 mg/kg. The LREE abundance accounts for much of that average (60–8770 mg/kg) compared to the HREE ones (7–910 mg/kg). By contrast, Naxos coastal sands have a ΣREE content between 74 and 4720 mg/kg at an average value of 1990 mg/kg. The LREE concentration at Naxos ranges from 55 to 1715 mg/kg, while the HREE one from 273 to 463 mg/kg.

According to Papadopoulos et al. [64], the geochemical comparison between the source rocks and the coastal sands of the Atticocycladic coastal zone show a clear source-to-sink control for the REE budgets (Figure 9). Among the heavy minerals present, allanite is the dominant REE-phase and thus controls the bulk REE signature. Xenotime, thorite, and monazite—being non-silicate minerals and thus relatively easier to extract REEs from their mineral structures—have also been identified, but they are found in relatively small concentrations (Figure 10). Allanite from both the source granitoids and coastal sands of Mykonos have similar characteristics (e.g., zonation and composition), confirming the source control. An igneous and metamorphic origin though is suggested for allanite that is present in the samples from Naxos [64].

In other areas such as Paros, Tinos, Serifos and Ikaria, the REE concentrations carry no obvious commercial appeal. More specifically, coastal sand samples from Serifos are dominated by REE-poor minerals such as epidote, garnet, and pyroxene, which are indicative of a metamorphic and/or metasomatic (skarn) origin. This metamorphic-derived fraction of heavy minerals dilutes the modal

abundance of allanite and thus the potential of the studied sands in REE. Samples from Tinos are likewise enriched in a similar suite of minerals (epidote, amphiboles and pyroxenes) that point to an origin largely from the meta-ophiolitic rocks of the area. These minerals are evidently also not associated with high REE concentrations.
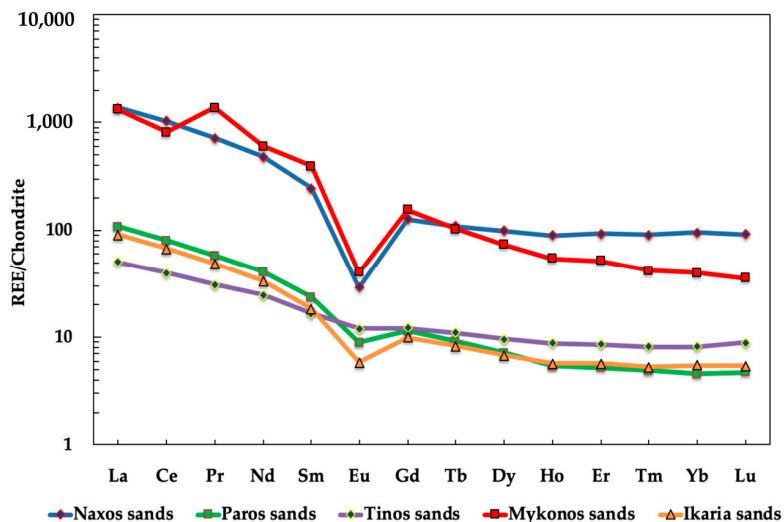

Figure 8. Chondrite-normalized patterns of REE for coastal sands derived from different localities in the Atticocycladic zone (Mykonos, Serifos, Naxos, Ikaria, Tinos, Paros).
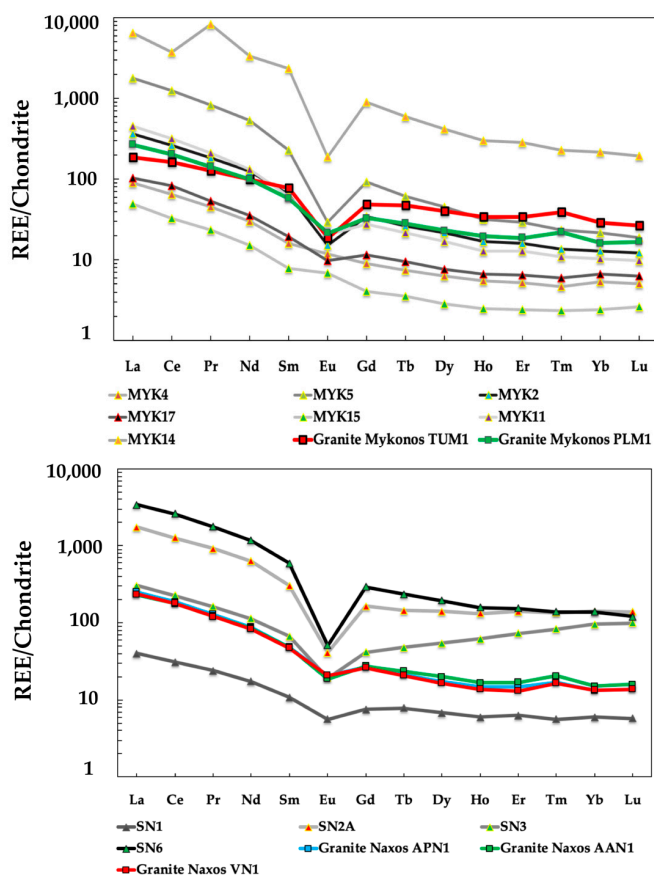

Figure 9. Chondrite REE patterns of Naxos and Mykonos coastal sands compared to the source rocks (Modified from Papadopoulos et al. [64]).
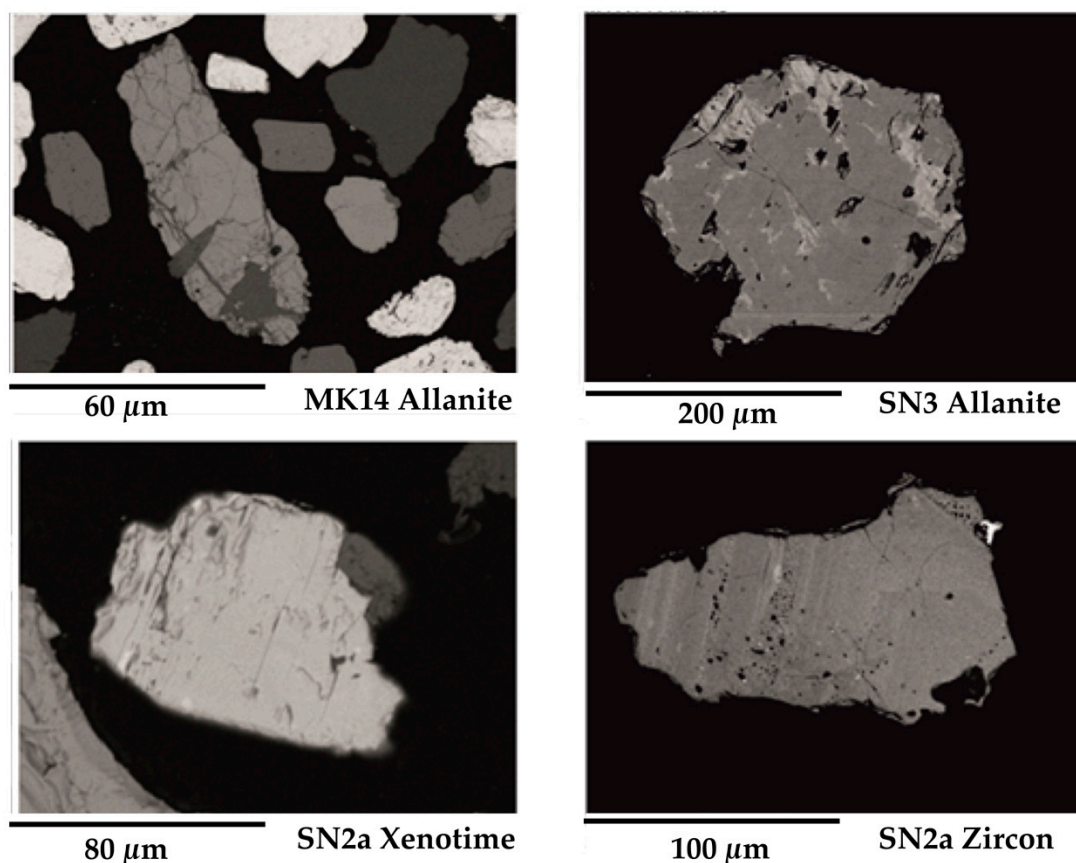
Figure 10. Back-scattered electron images of selected heavy mineral grains separated from coastal sands from the Atticicycladic zone [63].

3.3. Northern Greece: Chalkidiki Peninsula (Sithonia, Ierissos, Ouranoupoli, Stratoni, Aggelochori)

3.3.1. Sithonia

The coastal sand deposits from Sithonia in the Chalkidiki peninsula (Figure 2), have been studied extensively by Papadopoulos et al. [30,31,63]. The metamorphic basement of Sithonia is intruded by the Sithonia Plutonic Complex (SPC) which is the major source rock for these beach sands. The coastal heavy mineral sands have been found at the southeastern part of the Sithonia peninsula and they are associated with a hornblende-biotite granodiorite.

The coastal sands from Sithonia show relatively high REE content (15–6450 mg/kg) compared to the UCC (Figure 11). In particular, the LREE content ranges from 660 to 5810 mg/kg while the HREE content is much lower (3.1 to 9.8 mg/kg). Apart from the REE, other elements with notably elevated contents and thus potential economic interest are HFSE such as Nb (average 485 mg/kg) and Ta (average 39 mg/kg). Monazite, titanite, epidote, and allanite are the main mineral phases that influence significantly the REE and HFSE concentrations of the bulk sand samples studied (Figure 12). Monazite and allanite apparently control the LREE enrichment, while zircon accounts for a significant fraction of the HREE abundance. All above minerals are enriched > 3 orders of magnitude over the whole-rock samples in terms of REE. The same minerals also control the U and Th content of the beach sands.
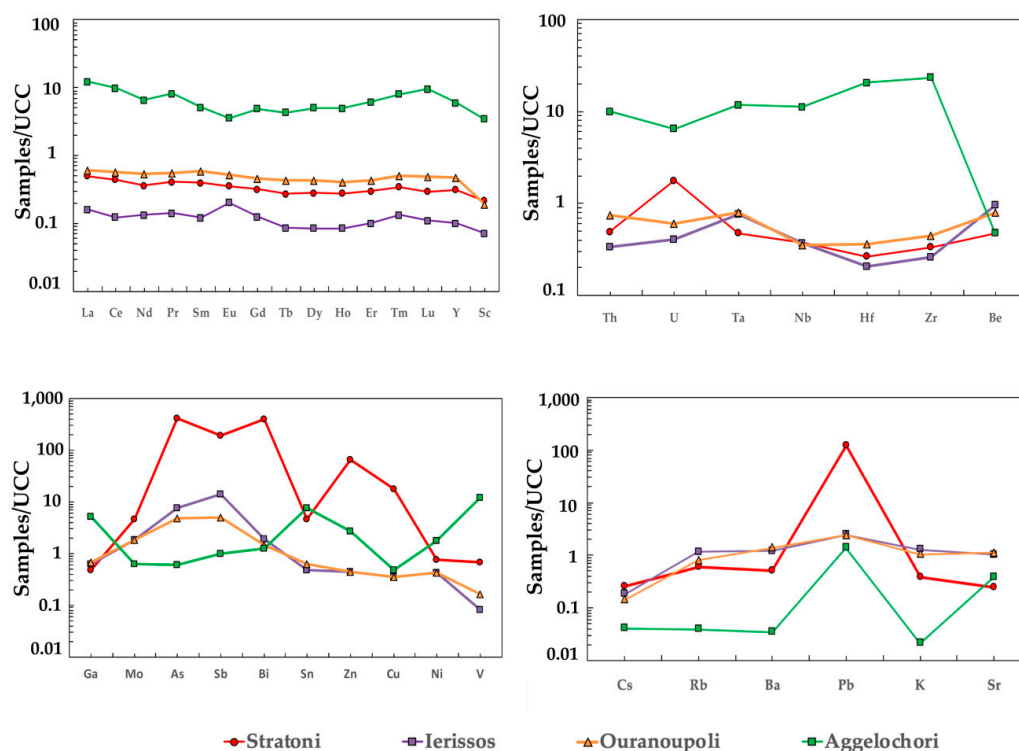
Figure 11. UCC-normalized spidergrams of coastal sands derived from different localities of Chalkidiki peninsula.
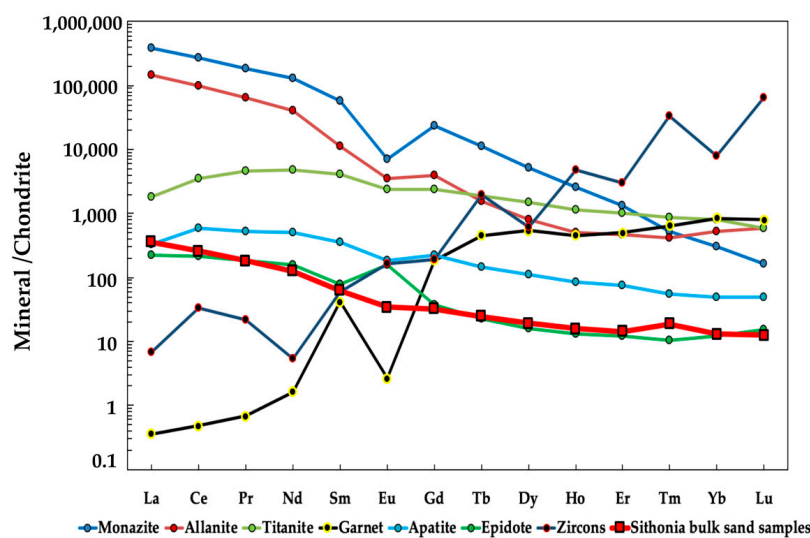

Figure 12. Chondrite-normalized patterns of the main mineral constituents of heavy mineral sands from the Sithonia coast [63].

3.3.2. Ierissos, Ouranoupoli, Stratoni

The localities of Stratoni, Ierissos and Ouranoupoli are located at NE Chalkidiki, which is characterized by an abundance of plutonic rocks in proximity to the shoreline. Samples from local beaches have been investigated by Papadopoulos et al. [35]. These three localities lie within the Greek part of the Serbo-Macedonian Massif (SMM), a series of metamorphosed rocks, being sub-divided to the upper Kerdylia and lower Vertiskos geotectonic units, mainly consisting of gneisses, amphibolites and marbles [70,71]. The SMM was intruded by granitoids in the Tertiary. The Stratoni granodiorite

intrusion (29 Ma) [71], was followed by porphyritic intrusions and is linked to magmatic hydrothermal activity and the occurrence of various associated ore deposits [72].

All three localities (Ierissos, Ouranoupoli and Stratoni) are characterized by coastal mineral sands with no appreciable REE enrichment relative to the UCC average (Figure 12). All studied samples are also depleted in LILE and HFSE, though Ierissos and Stratoni present significant enrichments in transition metals (As, Sb, Cu, Zn). The latter enrichments likely reflect the mineralized nature of the country rocks as indicated in the foregoing paragraph.

3.3.3. Aggelochori

The mineralogical investigation of coastal sands from Aggelochori showed that ilmenite, magnetite, garnet, zircon and rutile are the main mineral constituents [29]. Minor amounts of quartz, sphene, pyroxene, sillimanite, feldspar, biotite, hematite, tourmaline, chromite, niobian-rutile and pyrrhotite have been identified. Inclusions in ilmenite and magnetite of Nb-bearing rutile and pyrrhotite have also been recorded. The source rocks to these sands belong to the Axios zone of the Hellenides, which is mainly composed of gneisses, schists, amphibolites, carbonates, and igneous (mainly ultramafic) rocks of Mesozoic and Palaeozoic age [73]. Neogene and Quaternary formations which mainly consist of clays, sands, gravels, marls, sandstones, limestones and alluvial deposits [74], constitute the geologically youngest component of the provenance.

New geochemical data, specifically chondrite-normalised REE spidergrams, are presented here for the Aggelochori region (Figure 13). Average HREE (65 mg/kg) and LREE contents (1280 mg/kg) are elevated compared to the respective values for coastal sands from Chalkidiki peninsula. The increased HREE content manifested by the flat chondrite-normalised pattern by comparison to other samples from the local area (Chalkidiki peninsula), is attributed to the dominance of zircons and garnets in the heavy mineral fraction, along with abundant Ti-rich species. The coastal sands from Aggelochori are thus also enriched in HFSE such as Nb (134 mg/kg), Ta (10 mg/kg), Zr (4521 mg/kg), Hf (108 mg/kg) and Th (104 mg/kg). Additional elevated abundances are also recorded for the elements Co (80 mg/kg), V (1179 mg/kg), Ni (82 mg/kg), similarly attributable to the high Ti fraction of the sands.
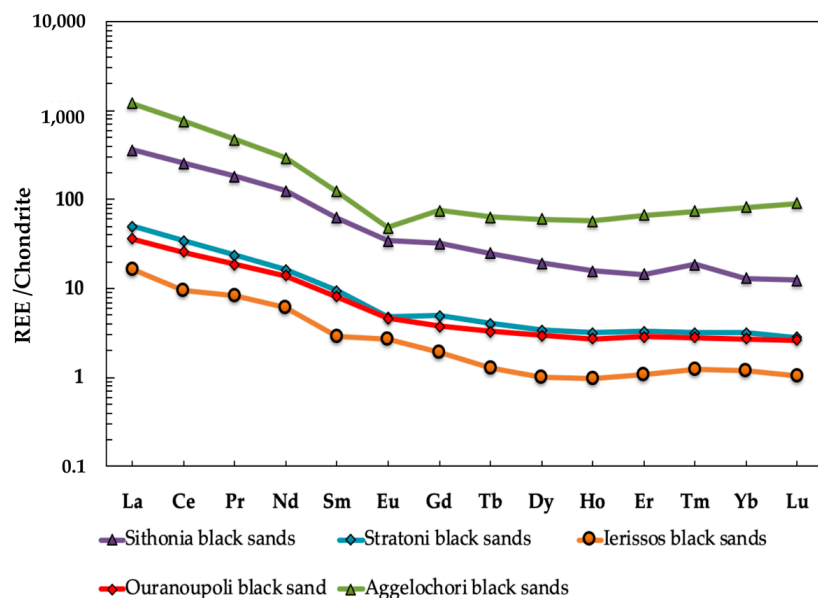

Figure 13. Chondrite-normalized diagram of REE of coastal sands derived from different regions of Chalkidiki peninsula.

3.4. Southern Aegean: Nisyros Volcanic Island

Beaches associated with volcanic terranes can also contain endowments in heavy minerals of potential economic interest [75]. The island of Nisyros belongs to the Hellenic Volcanic Arc and its heavy mineral sand deposits have been investigated for their strategic metal content [65]. The coastal sediments of Nisyros represent eroded and re-worked material fundamentally originating from Quaternary felsic volcanics.

Bulk chemical analysis of coastal sands of Nisyros compared to UCC [65] indicated enhanced content in Nb (245 mg/kg) and V (1920 mg/kg) while the metals Ta, Zr, Hf, Co, and Sn were also present in appreciable concentrations. The high modal abundance of Ti-rich phases (ilmenite, rutile) is responsible for the observed Nb and Ta budget while the abundant zircon controls the Zr and Hf contents. In contrast, relative depletions are observed in LILE and selected incompatible elements (e.g., K, Rb, Cs, Sr, Ba). Concerning REE content, chondrite-normalized patterns of bulk sands from Nisyros show that they are LREE-enriched (average: 190 mg/kg) by comparison to HREE (average: 20 mg/kg); yet, in terms of overall bulk REE content, they are characterized as of low potential (REE + Y = 240 mg/kg). A sample from the caldera referred as "fresh volcanic material" was also investigated and illustrated enrichment in transition metals and metalloids (Se, Bi, Hg, As, Pb), as well as in volatile components, while it was depleted in LILE. The REE content here is also very low (REE + Y = 96 mg/kg). It is therefore evident that the compositional data of the heavy mineral sands is consistent with the composition of the adjacent source rocks. In terms of overall heavy mineral budget, worth noting is the high abundance of ilmenite in the Nisyros sands, which controls the enhanced content in Nb and Ta, as further supported by μ-XRF results [65]. Enhanced concentrations in LREE, where present, are accounted for by mineral phases such as titanite and apatite.

4. Summary and Concluding Remarks

In this review, a selection of bulk geochemical and other representative data were presented from a number of heavy mineral sand occurrences located at various coastal locations of Greece. Quantitative grade and tonnage estimates for these occurrences were unfortunately not available to us at the time of compilation of this review. Our main objective was, therefore, to provide a comprehensive qualitative account of the different locations, in terms of REE and associated critical metals (mainly actinides: U, Th) and HFSE. Understanding the different geological environments of, and source controls for the formation of heavy mineral sand deposits in Greece is paramount for a sound assessment of these resources and the commodities they contain. It is hoped that this review will constitute an important starting reference for the evaluation of REE and other critical metals present in beach placer occurrences in Greece, leading possibly to future economic exploitation as this already happens for similar deposits globally.

The Greek coastal sand deposits of Kavala, Mykonos, and Sithonia, share a generally common assemblage of REE- and actinide-bearing minerals (e.g., allanite, monazite, titanite and zircon) while the Nisyros and Aggelochori localities have abundant Ti-rich phases. Monazite, xenotime and bastnaesite are typical REE-rich minerals currently mined for extraction of their REE content worldwide. Beach sand from Kavala and Mykonos, which present the higher REE concentrations out of the occurrences reviewed in this paper, have only minor modal monazite abundances, mainly as inclusions or micro-aggregates contained within other mineral hosts, thus contributing to a relatively low economic potential. Allanite, being the main REE-phase in both Kavala and Mykonos, is not currently exploited for its REE content anywhere globally, placing the future feasibility of these deposits in doubt. Further developments in REE metallurgy and beneficiation are therefore imperative in order to convert at least some of the occurrences presented in this paper, into viable economic resources.

The coastal sand deposits of Kavala, Sithonia, Mykonos, Naxos, Aggelochori, and Nisyros record variable relative enrichment in their concentrations of REE by comparison to average crust. As expected, associated critical metals (Nb, Ta, V), and particularly actinides (U, Th) are also found to be enriched in the same localities. The remaining areas reviewed (Maronia, Samothrace, Ierissos, Ouranoupoli) have

comparatively much lower concentrations in both REE and critical metals. In particular, the Kavala coastal area demonstrates the highest average content of REE and actinides, followed by Sithonia, Mykonos, and Naxos (Table 1).

Heavy mineral coastal sands from Sithonia exhibit elevated HFSE and REE contents, whereas those of Nisyros and Aggelochori have high HFSE (Nb and Ta) but relatively low REE. Coastal sands from Ierissos, Maronia, Serifos and Stratoni have enrichments in a broad suite of transition metals and metalloids, evidently associated with hydrothermally-affected and locally mineralized source rocks; otherwise, their contents in practically all critical metals are low.

Table 1. Summary of average REE concentrations (mg/kg) in placer deposits from Greece.

Coastal Sands		HREE	LREE	ΣREE
Kavala-Nea Peramos (37 samples)	Average	162	2318	2430
	Min	7	52	58
	Max	2310	10,508	10,879
	St.Dev.	351	2822	2940
Aggelochori (Tuzla Cape) (1 sample)		50	129	179
Nisyros (1 sample)		41	198	240
Ouranoupoli (3 sample)	Average	15	78	92.
	Min	7	25	31
	Max	26	143	170
	St.Dev	10.8	60.1	70.9
Stratoni (2 samples)	Average	10	59	69
	Min	7	48	54
	Max	13	71	84
	St.Dev.	4	16	21
Maronia (2 samples)	Average	7.8	110.6	118.3
	Mix	8	107	115
	Max	8	113	121
	St.Dev.	0.3	3.8	4.1
Sithonia (30 samples)	Average	47	439	487.
	Min	3	9	14
	Max	663	5811	6474
	St.Dev.	125	1100	1225
Samothrace (3 samples)	Average	180	1580	1761
	Min	3	9	14
	Max	663	5811	6474
	St.Dev.	9	30	28
Naxos (4 samples)	Average	273	1715	1988
	Min	20	55.2	74
	Max	463	4260	4724
	St.Dev.	206	1931	2118
Serifos (8 samples)	Average	39	159	197
	Min	22	92	114
	Max	68	363	432
	St.Dev.	33	242	275

Table 1. *Cont.*

Coastal Sands		HREE	LREE	ΣREE
Paros (1 sample)		18	138	154
Tinos (1 sample)		26	74	100
Mykonos (9 samples)	Average	140	1482	1623
	Min	7	5	64
	Max	912	8707	9620
	St.Dev.	291	2776	3065
Ikaria (6 samples)	Average	17	105	121
	Min	10	24	34
	Max	30	272	302
	St.Dev.	7	89	96

St.Dev.: Standard Deviation.

The mineralogical composition of the source rocks naturally exerts the primary control over the accumulation of mineral constituents at any coastline, and thus of their critical metal endowment. In the case of all the occurrences included in this treatise, felsic to intermediate igneous rocks were implicated almost in every instance as suitable sources for economic detrital REE accumulations. Contributions of metamorphic rocks are also demonstrated in the case of some localities from the Atticocycladic zone, as well as from Sithonia [63]. However, it is the subsequently complex sorting and reworking of the mineral constituents of interest through processes of erosion and transport, as already discussed by many authors and references therein [27,28,30,31,33,35,61–63], that dictates whether the economic elements will be found in a congruent or predictable distribution in the resultant heavy mineral accumulations [76].

Many new REE-bearing occurrences of economic potential, such as the placer deposits of Greece, are currently being investigated with the aim to help meet the projections of future world demand. In spite of the elevated REE grades for some of these deposits, limitations in current processing technology for REE-rich minerals such as allanite, which dominates Greek REE-rich placers, are major hindrances to their overall economic viability. The latter would be further compounded in cases of low tonnage/grade estimates (when available) for individual deposits, and most certainly by the associated environmental risks imparted by the accompanying enrichments in radioactive elements (actinides). These challenges must be added to the intrinsic difficulty in extracting and separating individual REE because of their similar ionic radii, and to the relative volatility of the REE market with respect to the fluctuating demand of individual elements over others [77]. We believe that future developments in extractive REE metallurgy may well be the most deciding factor in transforming presently uneconomic placer REE resources of Greece (and elsewhere) to viable ores for the domestic and global market.

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