

New insights into mineralogy and geochemistry of allanite-bearing Mediterranean coastal sands from Northern Greece

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ABSTRACT

Allanite-bearing black coastal sands of Kavala (N. Greece) were studied using a combination of single-crystal XRD, EMPA, μ -XRF, bulk ICP-MS, LA-ICP-MS, μ -XANES and γ -ray spectrometry. The sands are rich in REE (Σ REE + Y: 4010 to 10,810 mg/kg), Th (236–1205 mg/kg) and other critical metals such as Nb, Ta and Co. The main REE- and Th-hosts are allanite and titanite. The allanite unit cell parameters were calculated whereas its formula was found to be $(\text{REE}_{0.470}\text{Ca}_{1.499}\text{Th}_{0.031})(\text{Ti}_{0.031}\text{Fe}^{+3}_{1.089}\text{Al}_{1.880})(\text{Si}_{2.906}\text{Al}_{0.094}\text{O}_{12})(\text{OH})$. The μ -XANES spectra showed that LREE are present in trivalent oxidation state. Analyses of the non-magnetic sand fractions showed higher LREE (12,470 mg/kg) due to accumulation of allanite. The materials showed elevated radioactivity ranging from 885 ± 13 to 3467 ± 20 Bq/kg. The obtained results provide new insights on the provenance of the sands, the abundance of REE, Th, and other immobile elements, and offer new clues for potential exploration and exploitation.

1. Introduction

1.1. REE applications and global market

The rare earth elements (REE) are a group of 17 chemically similar elements with a wide range of industrial uses and applications. The European Commission (EC) has characterized REEs as critical materials with a significant risk of supply (EU Commission, 2014; Sustainability, 2017). Currently, approximately 90% of the world's REE production is coming from the Bayan Obo and Maoniuping deposit (Xie et al., 2016). However, the demand for these elements is continuously growing due to their extended utilization in many new technological applications (Hatch, 2012; Massari and Ruberti, 2013). The recycling of scrap consumer electronics and technical industrial components will increasingly contribute to REE supply in the future (Binnemans et al., 2013) but is

unlikely to be able to meet the continuously increasing demand (Du and Graedel, 2011). The active deposits in Mongolia are mainly associated with carbonatite magmatism and to a lesser extent with ion-adsorption type deposits (Hoshino et al., 2012 and 2016). Renewed research initiatives on new potential REE resources are thus deemed necessary, and are also connected to increasing exploitation efforts for bauxites, phosphates, placer and clay deposits (Goodenough et al., 2016; Gamaletsos et al., 2018a).

Currently, more than 200 minerals have been recognized as essential REE-carriers (Eggert et al., 2016). REE-hosting phases commonly contain significant concentrations of Th and U, implying a close geochemical association between REEs and actinides (Jaireth et al., 2014; Gamaletsos et al., 2018b). This association is of considerable environmental concern in terms of exploitation. The presence of radioactive elements in REE-bearing minerals also plays an essential role in the

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detection of new deposits, as radiometric methods significantly contribute to the geophysical exploration of heavy mineral sands. High background radiation areas associated with such deposits have been found in the United States and Canada (NCRP, 1987), India (Mohanty et al., 2004 and references therein), Brazil (Paschoa, 2000 and references therein), China (Wei and Sugahara, 2000 and references therein), Iran (Ghiassi-nejad et al., 2002) and other countries (UNSCEAR, 2000). At the same time, there is an obvious need of implementing safety measures for the protection of personnel and the environment during mining and disposal of tailings. Barakos et al., 2015 focused their work on the procedures that should take place during underground REE mining and the measures to be taken to limit gaseous radioactive emissions, especially from radon and thorium. Additionally, beach sands have been extensively studied in Mexico by Armstrong-Altrin et al., (2012, 2014, 2015, 2017), Tapia-Fernandez et al., (2017) and Hernandez-Hinojosa et al., (2018) to infer the provenance based on the REE geochemistry.

1.2. Coastal heavy mineral-rich sands

Coastal heavy mineral sands (commonly referred to as “black sands”) can host economic accumulations of heavy metals (“placer” deposits) and offer a potential for future exploitation. Placer deposits form as a result of erosional and subsequent sedimentary processes, which lead to preferential deposition of potentially exploitable concentrations of high-density minerals, such as monazite and other REE-bearing minerals (Orris and Grauch, 2002; Castor and Hedrick, 2006). These mineral grains are resistant to chemical weathering and their accumulation in coastal areas is due to differential density-induced segregation. The economic importance of coastal sands with respect to REEs depends on their extractability and concentration in the mineral hosts (Vanecek, 1994). The majority of the commercial placer deposits are located in sands along coastlines. Indicative examples are deposits in India, W. Australia, S. Africa, Madagascar (Sengupta and Van Gosen, 2016) and Mexico (Armstrong-Altrin, 2009; Armstrong-Altrin et al., 2018). Monazite and xenotime are commonly found in elevated content in these types of deposits and they raise special interest because of their established beneficiation methodology and specifically the availability of metallurgical techniques for the optimum REE- and Th- extraction from these minerals (Sengupta and Van Gosen, 2016; Castor and Hedrick, 2006; Jackson and Christiansen, 1993; Jordens et al., 2013). Important examples of monazite recovery from coastal sands are those of Australia, Brazil and India. In particular, the presence of significant monazite concentrations in coastal sands of India (Orissa and Tamilnadu) placed this country in a leading position of global thorium production (Mohanty et al., 2003a, b).

1.3. Previous studies regarding coastal sands in Greece

Previous studies in Greece mainly concerned the geochemistry of heavy mineral sands of the coastal area west of Kavala (Pergamalis et al., 2001; Tsirambides and Filippidis, 2012; Papadopoulos et al., 2015, 2016a; Aggelatou et al., 2018), but also from the Touzla cape (Aggeloxori) close to the city of Thessaloniki (Filippidis et al., 1997) the Sithonia Peninsula coasts of Chalkidiki (Papadopoulos et al., 2014, 2015a and 2015b) and in the Atticocycladic zone (Papadopoulos et al., 2016b; Papadopoulos, 2018). Recently, Tzifas et al., (2017) studied coastal sands of the volcanic island of Nisyros and found relative enrichment in High Field Strength Elements (Nb, Ta) compared to actinides and REE elements. The same authors interpreted this as combination of background geology (provenance) and mineralogical composition of the sands controlling the particular endowment in HFSE. On the contrary, previous works in the coastal area between the peninsula of Chalkidiki and Kavala (240 km length) indicated significant reserves of REE contained in placer deposits (Eliopoulos et al., 2014). Papadopoulos et al., (2015) also published the results of

radioactivity measurements in this coastal area showing increased activity of ^{238}U -series (14–1710 Bq/kg), ^{232}Th -series (26–4547 Bq/kg) and ^{40}K (194–1307 Bq/kg). Furthermore, geochemical investigations revealed up to 8000 mg/kg of REEs with 93.5% of them consisting of the light ones, mainly Ce, La and Nd. Allanite was mentioned to be the main REE-host (Pergamalis et al., 2001; Melfos and Voudouris, 2012 and references therein; Papadopoulos et al., 2016a), however, detailed characterization of the economic importance of heavy minerals was never carried out prior to the present study.

1.4. Objectives of the present study

Knowledge of the REE-, Th- and U-bearing phases has key implications for the economic viability of the said placer deposits and the potential environmental impact of their beneficiation. The objective of the present work was to investigate the Th-, U- and REE- contents and mineralogy of the black sands rich in heavy minerals located in N. Greece and particularly in the shore line between Chalkidiki peninsula and Kavala bay. In order to fulfill the objective, we used the combination of various techniques like microscopic, spectroscopic, ICP-MS, and radiation based techniques. As mentioned earlier and based on previous studies, this area has been considered as a potential REE resource. Little is hitherto known about the abundance and mineralogical distribution of REEs and actinides in the black sands this area.

2. Geological setting of the kavala area

The Kavala pluton intruded in the metamorphic rocks of the Lower Tectonic Unit of the Rhodope Massif along a SW-NE direction (Fig. 1). The pluton is composed of I-type, calc-alkaline granitic rocks (Neiva et al., 1996). Tertiary and mainly Quaternary deposits, in the form of un-consolidated accumulations of alluvial origin and variable granulometric composition (gravels, pebbles, sand, clays and silts) are sourced from these plutonic rocks. The clastic material appears of poor to moderate sorting and generally poor rounding. The dominant igneous rock type is a medium to coarse-grained, hornblende-biotite granodiorite, with numerous enclaves of dioritic to tonalitic composition. Aplitic veins are also present. Coarse-grained granodiorite is present only in the NE part of the pluton. The granodiorite appears light to dark colored and is characterized by a gneissic texture due to syn- and post- magmatic tectonic activity. Small occurrences of biotite-hornblende tonalite and biotite monzogranite are also present (Kokkinakis, 1977; Neiva et al., 1996; Papadopoulos, 2011). Tourmaline-rich veins and breccias occur within the Lower part of the Kavala pluton (Xydous et al., 2016).

The mineral constituents of the Kavala plutonic rocks are quartz, feldspars, biotite, hornblende, titanite, allanite, zircon, monazite and apatite (Neiva et al., 1996). The quartz modal abundance ranges from 21 to 33%, feldspars from 63 to 70%, biotite and hornblende from 3 to 8% each, whereas total accessory minerals do not exceed each the value of 0.5% (Papadopoulos, 2011).

A Rb-Sr whole-rock age of 18 Ma was interpreted as the age of mylonitization (Kyriakopoulos et al., 1989). On the other hand, according to Dinter et al., (1995) the emplacement and mylonitization of the Kavala pluton took place at about 21–22 Ma ago (U-Pb and Ar-Ar dating on titanite and mylonitic hornblende respectively). K-Ar biotite ages of 15.5 ± 0.5 and 17.8 ± 0.8 Ma (Dinter et al., 1995) and Rb-Sr biotite ages of 14–16 Ma (Kyriakopoulos et al., 1989) were interpreted as reset metamorphic ages. Dinter and Royden (1993) considered these ages as cooling ages related to the emergence of the Rhodope metamorphic core complex in the footwall of the Strymon Valley detachment. This detachment is corroborated by Ar-Ar biotite and K-feldspar ages ranging from 11.1 ± 0.2 to 15.5 ± 0.3 Ma at the central part of the pluton (Dinter et al., 1995). The tectonic setting of the emplacement of the pluton has been linked to the post-collisional collapse of the Hellenic orogeny (Dinter et al., 1995; Koukouvelas and Pe-Piper, 1991;

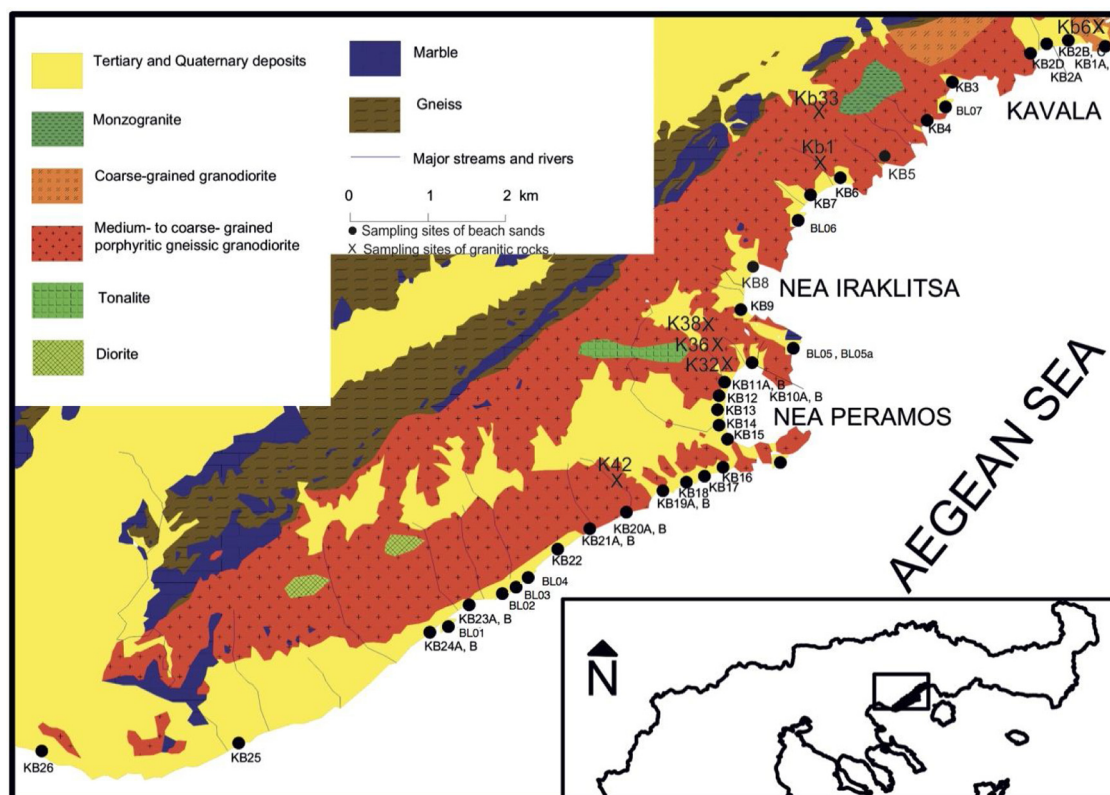


Fig. 1. Modified geological map of the Kavala area with the sampling locations (BL01–BL07), along with those from the recent research work of Papadopoulos et al., (2015).

Jones et al., 1992; Christofides et al., 1998; Kiliyas and Mountrakis, 1998).

3. Materials and methods

3.1. Sampling and mineral separation

Black sand samples (BL01–BL07) were collected along the coast of NE Greece between the peninsula of Chalkidiki and Kavala (close to outcrops of the Kavala pluton; Fig. 1). Eight sampling locations were selected for mineralogical and geochemical study. It should be pointed out that black sand concentrations were the highest near alluvial deposits derived from the river beds. Typically, the black sands alternate in the field with typical light-colored sands devoid of obvious heavy mineral enrichment (Fig. 2a–c).

One representative sample was used for standard separation methods. After washing with warm water and drying, removal of the coarse biological (mainly skeletal) material was achieved by sieving. Magnetic separation of the bulk samples was performed to further processing using a Franz magnetic separator (current < 0.4 A at forward and side slope of 15° and 25°). The chemical composition of the magnetic and non-magnetic fraction was determined by inductively-coupled plasma – mass spectrometry (ICP-MS). Subsequently, the magnetite was removed using a hand magnet, whereas the heavy mineral separation was carried out in four steps in order to obtain the concentrates of different mineral phases. In the first step, heavy liquid separation was performed using 80% sodium polytungstate (LST Fastfloat, density: 2.8 kg/m³) in order to eliminate quartz and feldspars. This step was followed by magnetic separation of the > 2.8 kg/m³ fraction by means of a Frantz magnetic separator. The non-magnetic fraction was further processed by pure methylene iodide (density: 3.3 kg/m³). The main heavy mineral phases separated using a picking tool under binocular microscope and were identified using scanning

electron microscopy-energy dispersive spectroscopy (SEM-EDS).

3.2. Gamma-ray measurements

The natural radioactivity of the samples was measured by high-resolution gamma-ray spectrometry using a reverse electrode germanium detector (REGE) (CANBERRA Instr. efficiency 23%, energy resolution 2.1 keV for the 1332 keV ⁶⁰Co γ-radiation). The detector was shielded by a low background lead shield (model Canberra 747E). A standard computer-based gamma spectrometry set-up (E.G & G. MAESTRO) was used for the accumulation and processing of the spectrometry data.

The ⁴⁰K ($T_{1/2}$: 1.252×10^9 years) activity of the samples was determined using its 1461 keV γ-rays. The ²³²Th (14.01×10^9 years) content was calculated as the weighted mean value of ²²⁸Ra ($T_{1/2}$: 5.75 years) using the 911, 968 and 338 keV, γ-rays emitted by ²²⁸Ac ($T_{1/2}$: 6.13 h) and ²²⁸Th ($T_{1/2}$: 1.91 years), measured through its decay products in equilibrium ²¹²Pb ($T_{1/2}$: 10.14 h), ²¹²Bi ($T_{1/2}$: 60.15 min/25.0 min) and ²⁰⁸Tl ($T_{1/2}$: 3.05 min). Determination of ²²⁶Ra ($T_{1/2}$: 1600 years) was based on measurement of its decay product ²²²Rn ($T_{1/2}$: 3.82 days) in equilibrium. As mentioned in the introduction, ²²⁶Ra is a ²³⁸U decay product and member of the uranium radioactive series ($A = 4n + 2$) in nature. For the establishment of the ²²⁶Ra–²²²Rn equilibrium, the samples were hermetically closed in containers for 25 days. A small quantity (ca. 2%) of powdered active carbon (particle size < 400 μm) was mixed with the sample in order to increase the ²²²Rn retention (Gaul and Underhill, 2005).

3.3. Mineralogical characterization

The mineralogical characterization was performed on thin sections and hand-picked grains under a binocular microscope, using a combination of standard optical microscopy; powder X-ray Diffraction (PXRD) using a Siemens D5005 diffractometer; and SEM-EDS using a

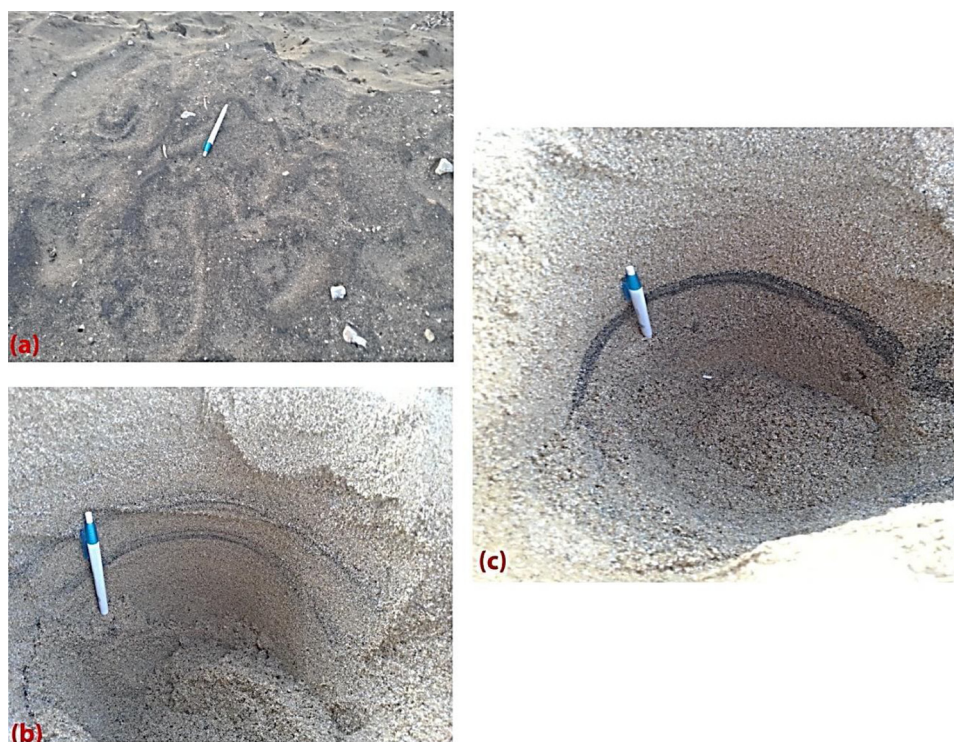


Fig. 2. Sampling locations showing the presence of coastal black sands.

Table 1

REE-content of the magnetic and non-magnetic sand fractions.

Element	Magnetic fraction (mg/kg)	Non-magnetic fraction (mg/kg)	UCC (Rudnick and Gao, 2003) (mg/kg)
La	557.8	3522.4	31
Ce	938.8	6140.6	63
Pr	93.7	616.9	7.1
Nd	287.3	1958.8	27
Sm	30.4	231.0	4.7
Eu	5.2	37.3	1
Gd	20.5	152.4	4
Tb	2.2	17.0	0.7
Dy	11.0	83.2	3.9
Ho	2.0	14.1	0.83
Er	6.1	40.3	2.3
Tm	1.0	6.0	0.3
Yb	7.5	38.3	2
Lu	1.5	5.8	0.31
ΣLREE	1908.0	12469.6	132.8
ΣHREE	56.9	394.5	15.34
ΣREE	1964.9	12864.1	148.14
Y	60.2	421.2	21
ΣREE + Y	2025.1	13285.3	169.14
ΣREE + Y	0.2 wt. %	1.3 wt. %	0.017 wt. %

JEOL JSM-5600 equipped with an Oxford EDS micro-analyzer. The chemical characterization of mineral separates was performed by a JEOL JXA-8230 Superprobe Electron Probe Microanalyzer at the Department of Petrology and Metalogenesis of the Institute of Geosciences and Sciences of the Paulista State University (Brasil). The energy dispersive spectra were acquired with a silicon drift detector with energy resolution at FWHM of 129 eV for Mn-K α , whereas wavelength dispersive spectroscopy (WDS) qualitative scans were performed with LDE1, TAP, PETL and LIFH crystals and dwell time of 60 ms in position steps of 50 μ m. The analyses were performed using acceleration of 15–20 kV and beam current of 10–20 nA.

For the P-XRD measurements, a portion of the individual pulverized

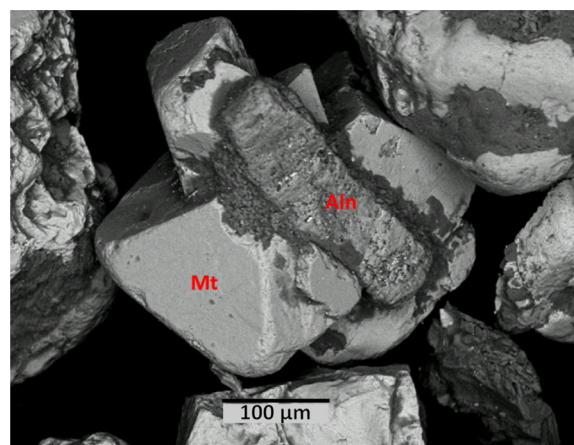


Fig. 3. SEM microphotographs showing aggregate of magnetite and allanite.

samples was loaded into a standard holder. The quantities of the crystalline mineral phases were determined using the Rietveld method (Will, 2006). The X-ray diffraction analysis was performed by a Panalytical X'Pert Pro diffractometer, equipped with a Cu X-ray source and an X' Celerator detector (measurement parameters: 40 kV and 40 mA; range 5–70 deg 2 θ ; step size 0.017 deg 2 θ ; time per step 50.165 s; fixed divergence slit, angle 0.50; sample rotation 1 rev/sec).

Micro-X-ray fluorescence (μ -XRF) measurements were performed in order to determine, with high resolution, the distribution of the sample constituents. For the scanning μ -XRF measurements a customized model of an ARTAX portable spectrometer (Bruker Nano GmbH) was utilized.

3.4. Geochemical characterization

The bulk chemical composition of eight (8) samples (BL01–BL07) was determined by Inductively Coupled Plasma Optical Emission and Mass Spectrometry (ICP-OES and ICP-MS) using a PerkinElmer Sciex

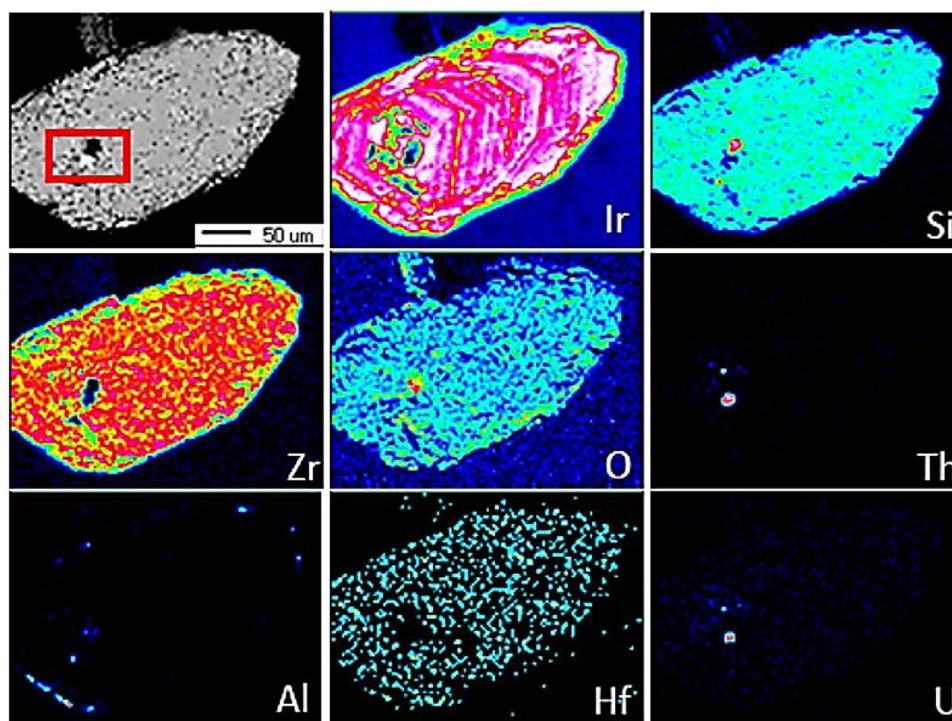


Fig. 4. Elemental mapping of zircon using EMPA (Supplementary material; Table 4). Note the thorite inclusion present.

Elan 9000 equipment after $\text{LiBO}_2/\text{LiB}_4\text{O}_7$ fusion and HNO_3 digestion of 0.2 g of sample. The loss on ignition (LOI) was quantified by heating the samples at 1000 °C. The total C- and S-content was measured using a LECO Carbon and Sulfur analyzer. The bulk chemical analysis and LOI measurements took place in ACME Labs (Vancouver, Canada) whereas the heavy mineral separation took place at the Institute of Earth Sciences of the University of Heidelberg (Germany).

Laser Ablation ICP-MS (LA-ICP-MS) analyses were performed at the Department of Earth Sciences, University of Perugia (Italy). The ICP-MS system used was a Thermo Scientific iCAPQ (Thermo Fisher Scientific) connected to a Teledyne Photon Machine G3 laser ablation unit. Detection limits for the REEs were 0.003 mg/g (Petrelli et al., 2016).

3.4.1. Synchrotron radiation (μ -XRF and -XANES) measurements

Synchrotron radiation (SR) micro-X-ray Fluorescence (SR μ -XRF) and X-ray absorption near-edge structure (μ -XANES) spectra were recorded using powders and polished sections at the SUL-X beamline of the Institute for Photon Science and Synchrotron Radiation (KIT, Germany). The target area of the thin polished section of allanite crystals to be analyzed by μ -XRF was selected by optical microscopy. Four allanite sample grains embedded polished sections were also examined for REE by SR-XRF after excitation by X-rays of 7 keV energy (just below the Fe K-edge).

XANES data were also obtained for the grains of REE-bearing sample. The intensities of the LREE- and Th- fluorescence emission lines excited by 17.5 keV X-rays were simultaneously recorded by a 7-element Si(Li) solid state detector. On areas with elevated REE concentrations XANES spectra for La, Ce, Nd and Pr were also recorded. Moreover, the CeL_3 XANES spectrum of the sample was compared to Ce^{+3} and Ce^{+4} references spectra. PrL_3 XANES spectra are difficult to be measured due to the fact that the $\text{LaL}_{\beta 1}$ and $\text{LaL}_{\beta 4}$ emission lines coincide with the $\text{PrL}_{\alpha 1}$ ones. The NdL_3 XANES spectrum suffers from the CeL_2 edge (6164 eV), which is very close to the NdL_3 one (6208 eV).

4. Results

4.1. Bulk geochemical analysis

The bulk chemical analyses of the Kavalas' coastal black sands exhibit variations in major and trace element concentrations (Supplementary material). The samples show wide range in the SiO_2 concentration (12.7 to 69.3 wt.%), while the Fe_2O_3 content varies from 5.7 to 76.3 wt.%. The latter is reflected in the corresponding modal variations in magnetic, Fe-rich opaque phases (mainly magnetite and ilmenite). The Al_2O_3 content varies from 3.3 to 12 wt.%, while CaO (2.9 to 5.3 wt.%), TiO_2 (0.62 to 2.25 wt.%), Na_2O (0.45 to 2.49 wt.%), MnO (0.07–0.38 wt.%) and P_2O_5 (0.1 to 0.16 wt.%) occur in much lower concentrations. The LREE content of the sands is higher compared to the upper continental crust (UCC; Rudnick and Gao, 2003) and ranges from 1946 to 10,506 mg/kg, while the HREE one is significantly lower (87–370 mg/kg). Thorium (Th), which is a hazardous radioactive element, has an average bulk concentration of 716 mg/kg (236 to 1204 mg/kg), whereas an average of 42 mg/kg was observed for U. Concerning other economically important metals, vanadium (V) and niobium (Nb) show concentration ranges from 342 to 835 and 26 to 118 mg/kg respectively. Other metals such as Hf (8–54 mg/kg), Ta (3–10 mg/kg) and Ga (2–18 mg/kg), were also present in lower concentrations.

The one-stage magnetic separation of the representative sample which used for further investigation led to artificial enrichment of the non-magnetic fraction in the majority of trace elements (including REE and actinides) compared to the magnetic one, except for vanadium. Consequently, the $\Sigma\text{REE} + \text{Y}$ content (Table 1) for the non-magnetic fraction was found to be 13,286 mg/kg (1.3 wt. %), whereas the corresponding value for the magnetic fraction was 2025 mg/kg (0.2 wt. %). Finally, the thorium concentration in the non-magnetic and magnetic fraction was respectively 1600 and 258 mg/kg.

4.2. Gamma-ray spectroscopic measurements

The activities of the radionuclides belonging to the ^{232}Th decay

Table 2
Chemical analysis of the black coastal sands' mineral constituents by LA-ICP-MS values (mg/kg).

Mineral/ Element →	Fe	Ti	Ca	Mn	Be	Cs	Li	V	Sc	Co	Ni	Cr	Ba	Sr
Allanite	91500	3040	97400	6367	0.2	0.03	1.1	392.2	94	8.9	2.5	47.1	1.4	313.1
Allanite	92200	4150	89700	6180	0.3	0.1	3.2	399	64.5	11.5	4.3	14.7	3.5	287.1
Apatite	595	35	–	1078	–	–	0.5	5.86	0.3	0.2	0.7	–	0.1	364.8
Monazite	17	37.5	–	0.9	–	–	5.1	–	–	–	–	–	0.6	33.5
Zircon	17.8	732	–	–	–	–	0.1	0.2	203.2	–	–	–	0.3	0.2
Zircon	5300	732	83	33.9	0.3	0.2	1.4	9.7	136.7	1.2	1.1	–	1.3	1.21
Titanite	5990	187600	200800	1021	–	0.04	0.3	643	11.02	0.1	0.3	1366	0.3	55.8
Titanite	8030	143400	147100	1230	0.1	0.02	0.4	640	9.6	0.3	0.6	10.9	5.2	64.6
Garnet	139400	7370	96900	8130	10.2	0.03	16.8	376	90.3	39.2	18.2	38.6	234.7	86.9
Amphibole	134100	4457	89100	7950	7.5	–	13.9	323.9	70.3	39.2	19.1	7.5	30.4	54.7
Amphibole	166800	23.2	12,640	31330	–	–	5.2	24.6	121	20.1	0.6	71.3	–	0.03
Feldspar	599	13.9	34360	8.1	7.93	–	0.85	0.72	16.8	–	–	–	65.3	1538
Epidote	123100	1310	223200	12300	–	0.101	–	75.3	8.5	12.0	4.6	–	0.5	0.61
Epidote	106600	1333	241400	5980	–	0.79	0.65	96.2	8.6	10.7	4.8	3.86	5	1.6
Mineral/ Element →	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Allanite	35100	63900	6150	20330	2208	248.9	1150	90.6	313.4	42	80	8.46	48.2	6.6
Allanite	44870	77200	7130	22440	2182	233	1107	81.4	272.6	36.1	69.7	7.29	41.5	5.47
Apatite	290.7	782	102.5	469	95.2	15.52	93.1	12.3	68.7	15	41.9	6.1	42.5	7.1
Monazite	–	559400	63500	256500	56100	4875	46250	5511	21500	2589	3950	299.8	1171	100.6
Zircon	0.005	24.7	0.028	0.66	1.9	0.7	12.1	4.3	52.2	20	92	20	189	39.4
Titanite	0.52	18.8	0.3	1.98	3.4	1.9	19.6	6.8	79	31.9	162	40	427	96
Titanite	298.4	1076	152.4	651	122.6	36.2	104	14.9	88.6	19.1	57.4	9.6	73.8	11.6
Garnet	862	3730	655	3220	719	143.8	527	70.5	377	71.4	185	26.4	171	22.1
Amphibole	3.35	16.8	3.8	25.1	10.5	2.4	13.9	2.4	16.6	3.8	11.9	2	15	2.65
Amphibole	0.59	3.3	0.8	6.1	3.3	1.5	4.64	0.9	6.4	1.5	4.3	0.7	4.9	0.9
Feldspar	0.001	–	0.005	0.11	0.6	0.3	5.63	3.3	40.6	11.1	33.1	5.2	42.3	7.3
Epidote	0.04	0.09	–	–	–	0.09	–	–	–	–	0.01	–	–	–
Epidote	0.04	0.8	0.5	6.88	3.8	2.7	3.7	0.6	2.8	0.53	1.4	0.2	1.9	0.3
Rutile	0.01	1.7	0.9	7.43	2.5	1.3	2.6	0.5	2.6	0.52	1.6	0.3	2.1	0.4
Mineral/ Element →	Cu	Ga	Rb	Zr	Nb	Pb	Ta	Th	U	Hf	Y			
Allanite	–	401.1	0.23	8.3	0.1	46.1	0.05	14,510	158.9	0.74	1069			
Allanite	0.5	458.6	1.5	8.6	0.2	36.4	0.05	11,350	103.6	0.68	886			
Apatite	–	5.34	–	0.3	0.01	4.4	0.01	21.04	22.83	0.04	465			
Monazite	–	4401	2.5	1.44	0.09	155.9	1.7	96,700	14,720	11.6	50,280			
Zircon	–	0.1	0.1	388000	4.4	5.8	1.9	196	373	9680	609			
Zircon	8.5	1.13	1.8	366000	7.7	5.1	2	630	2310	8450	1250			
Titanite	12.5	9.84	0.35	696	396	3.4	6.33	199.7	833	28.5	573			
Titanite	8.69	29.8	0.25	640	988	19.3	91.4	605	253	37.8	1940			
Garnet	1.75	36.9	7.7	2540	16.8	9.6	0.5	3.8	13.7	57	108.8			
Amphibole	–	37.9	10.3	14.73	6.7	6.5	0.06	0.005	0.025	1.2	42.4			
Amphibole	–	7.13	–	6.4	–	–	0.01	0.002	0.013	0.2	316.1			
Feldspar	–	24.1	0.4	0.07	–	48.3	–	–	–	–	0.04			
Epidote	–	29.0	0.24	37.1	0.97	–	0.14	0.14	3.28	1.8	18.6			
Epidote	–	27.2	1.4	46.1	4.9	0.9	0.6	0.35	6.27	1.8	16.5			

series of the individual samples showed elevated values ranging from 178.2 to 3467 Bq/kg. The ^{238}U decay series showed lower values ranging from 170.3 to 478 Bq/kg while the ^{40}K activities ranged from 114.5 to 729 Bq/kg. The ^{232}Th -, ^{238}U -series as well as of the ^{40}K activity values (in Bq/kg) of the individual samples along with their respective calculated standard deviation ($\pm \sigma$) are given in supplementary material (Table 1). ^{40}K represents another important source of natural radioactivity, associated with K, with significantly different geochemical characteristics. However, in heavy minerals-enriched sands it is not present in high concentrations (Papadopoulos et al., 2016a). The determined activity values are in good agreement with similar results published elsewhere (Papadopoulos et al., 2016b).

4.3. Mineralogical investigation of the bulk black sand

The results of the mineralogical investigation showed that the sands mainly consist of silicate minerals, Fe-oxides (magnetite, hematite) and, to a lesser extent, of phosphate phases and Ti-oxides (ilmenite, rutile).

Quartz, feldspars, micas (biotite, muscovite), hornblende and epidote (zoisite), are the modally dominant phases, while REE-rich epidote (allanite), clinopyroxene, Mn-garnet (spessartine) and sphene (titanite) are present in lesser concentrations. Zircon, rutile and thorite appeared as inclusions in many of the above-mentioned minerals, especially in allanite and biotite. Quartz, K-feldspar and plagioclase grains present partial evidence for conversion to micas whereas the biotite (mostly subhedral to anhedral) is locally chloritized. The orthoclase, microcline and plagioclase grains vary in size, and in many of these grains granophyric or perthitic texture is also displayed. Lithic fragments of granodiorite, monzogranite and granite ($> 200\mu\text{m}$) are also observed along with the mineral phases. The phosphate minerals are represented by apatite and monazite. Monazite appears in rather low concentrations and is mainly associated with allanite as an alteration product thereof.

Semi-quantitative estimates of mineral abundance via P-XRD measurements of the magnetic fraction of the black sands (Supplementary material; Fig. 1) primarily point out to magnetite (16–68 %), and hematite (9–30 %) as main constituents, while allanite (2–10 %), titanite

Table 3

Distribution of cations in T, M1, M2, M3, A1, A2 sites of various crystals allanite crystals. The figure of the allanite crystals with the spot analyses used for EPMA can be found in the supplementary material.

	1.dark	1.bright	2.dark	2.bright	3.dark	3.bright	4.dark	4.bright
Si	2.928	2.874	2.874	2.893	2.933	2.936	2.924	2.885
Al	0.072	0.126	0.126	0.107	0.067	0.064	0.076	0.115
T site	3	3	3	3	3	3	3	3
Al	1.02	1.003	1.016	1.009	0.982	1.001	0.998	1.001
M1 site	1.02	1.003	1.016	1.009	0.982	1.001	0.998	1.001
Al	1	1	1	1	1	1	1	1
M2 site	1	1	1	1	1	1	1	1
Fe2	0	0	0	0	0	0.037	0.017	0.019
Mn3	0.007	0	0.015	0.01	0	0	0	0
Fe3	1.012	1.079	1.062	1.145	1.058	1.056	1.047	1.126
Ti	0.031	0.044	0.024	0.035	0.027	0.044	0.016	0.045
M3 site	1	1	1	1	1	1	1	1
M site	3.02	3.003	3.016	3.009	2.982	3.001	2.998	3.001
Mn2	0.006	0	0	0.006	0.016	0	0	0
Fe2	0	0	0	0	0.015	0	0	0
Ca	0.994	1	1	0.994	0.969	1	1	1
A1 site	1	1	1	1	1	1	1	1
Ca	0.475	0.379	0.579	0.456	0.551	0.381	0.705	0.394
REE	0.478	0.564	0.397	0.502	0.457	0.576	0.281	0.572
Y	0.002	0.002	0.003	0.002	0.004	0.002	0.001	0.003
A2 site	0.955	0.945	0.979	0.96	1.012	0.959	0.987	0.969
A site	1.955	1.945	1.979	1.96	2.012	1.959	1.987	1.969
Σ charge cation	25.561	25.591	25.384	25.567	25.479	25.602	25.237	25.539
	5.dark	5.bright	6.bright	7.bright	1	2	3	4
Si	2.954	2.980	2.908	2.859	2.948	2.855	2.917	2.897
Al	0.046	0.020	0.092	0.141	0.052	0.145	0.083	0.103
T site	3	3	3	3	3	3	3	3
Al	0.973	1.01	1.003	1.029	1.003	1.016	1.026	1.008
M1 site	0.973	1.01	1.003	1.029	1.003	1.016	1.026	1.008
Al	1	1	1	1	1	1	1	1
M2 site	1	1	1	1	1	1	1	1
Fe2	0.041	0	0	0	0	0	0	0
Mn3	0	0.008	0.005	0.029	0.003	0.016	0.025	0.009
Fe3	0.987	1.188	1.083	1.156	0.894	1.185	1.053	1.104
Ti	0.03	0.048	0.043	0.029	0.004	0.026	0.035	0.028
M3 site	1	1	1	1	1	1	1	1
M site	2.973	3.01	3.003	3.029	3.003	3.016	3.026	3.008
Mn2	0.026	0	0.036	0.025	0.016	0	0	0.004
Fe2	0.027	0	0	0	0	0	0	0
Ca	0.947	1	0.964	0.975	0.984	1	1	0.996
A1 site	1	1	1	1	1	1	1	1
Ca	0.572	0.372	0.422	0.519	0.959	0.467	0.455	0.535
REE	0.448	0.58	0.565	0.474	0.052	0.5	0.509	0.442
Y	0.002	0.003	0.001	0.006	0.003	0.002	0.003	0.004
A2 site	1.022	0.955	0.988	0.999	1.014	0.969	0.967	0.981
A site	2.022	1.955	1.988	1.999	2.014	1.969	1.967	1.981
Σ charge cation	25.476	25.727	25.698	25.561	25.052	25.489	25.604	25.453

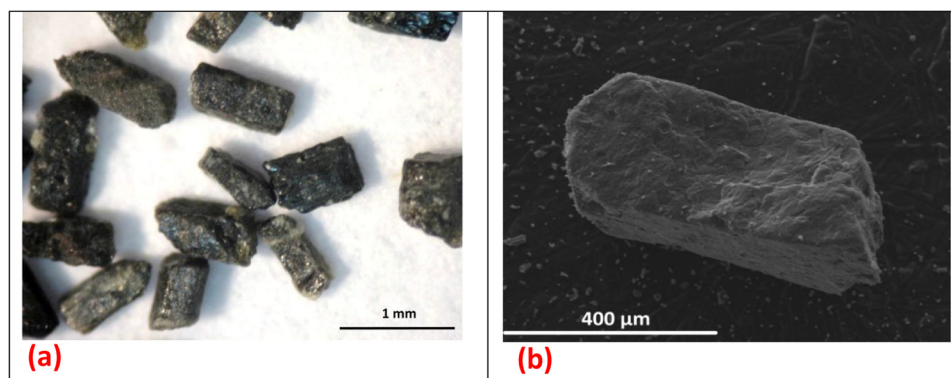


Fig. 5. (a) Allanite crystals observed by binocular microscope (b) backscattered image (BSE) of a single allanite crystal.

(4–16 %) and hornblende (23–40 %) are also present in significant contents. The non-magnetic fraction of the heavy minerals mainly consists of quartz (8–39 %), K-feldspar (8–21 %), plagioclase (9–30 %), hornblende (16–40 %), allanite (12–20 %) and titanite (3–28 %). The

latter was observed in both fractions because of its weak magnetic susceptibility. Small amounts of mica and calcite are also observed. The PXRD patterns of both the magnetic and non-magnetic fractions confirm the presence of magnetite, a fact also suggested by the aggregates

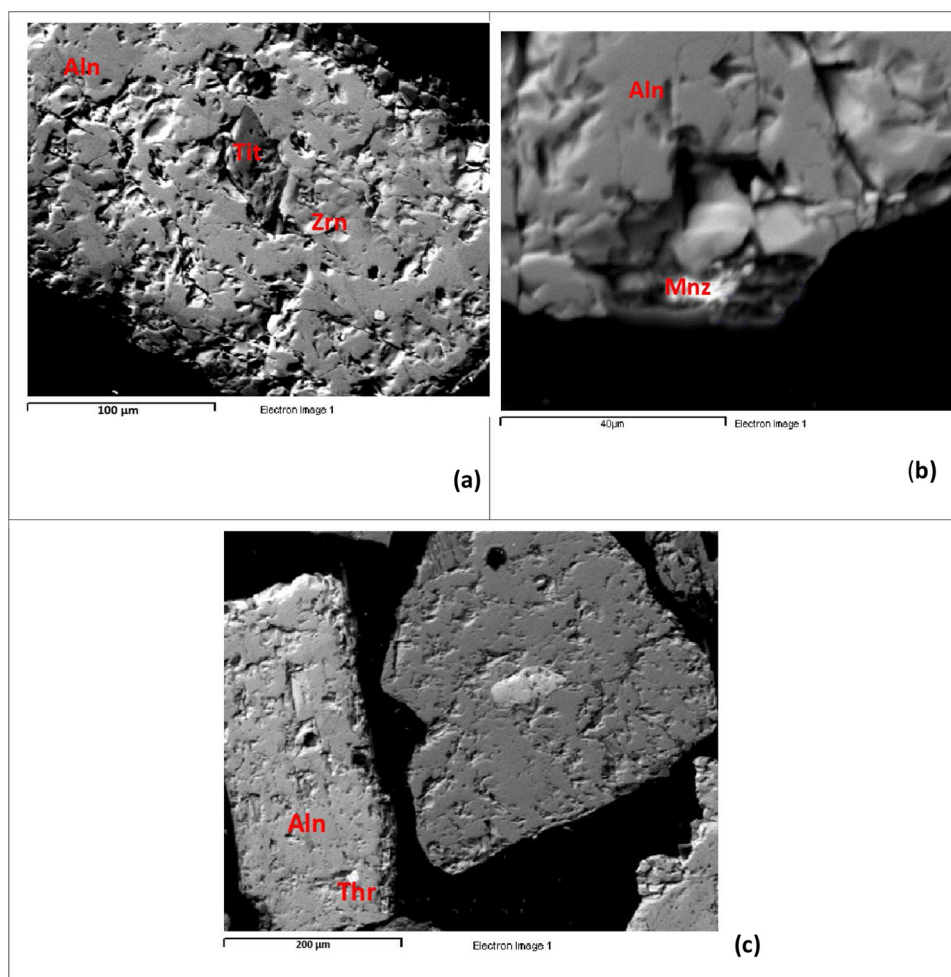


Fig. 6. (a) BSE image of allanite (Aln) crystal. The crystal contains also titanite (Tit) and zircon (Zrn) inclusions (b) Monazite inclusions or/and micro-/sub-micro mineral aggregates were probably derived from the breakdown of allanite (c) Thorite inclusion in allanite crystal.

that occur between the Fe-oxide and other minerals such as allanite (Fig. 3).

Zircon and titanite are two further abundant REE- and Th-bearing phases of the studied sands targeted by EMPA. According to microprobe element maps of Th- and U-silicate phases, thorite or uranotorite possibly occur as inclusions in zircon (Fig. 4 and Fig. 6c).

4.4. Trace element distribution in mineral phases of the black coastal sands

LA-ICP-MS analyses of individual mineral grains of the coastal black sand are shown in Table 2. The REE-bearing mineral allanite (Σ REE content 12.96 wt. %) in the coastal black sands is enriched in Th (11350–14510 mg/kg), V (392–399 mg/kg), Ga (401–458 mg/kg) and U (151 mg/kg). The concentrations of Sc (64.5–94 mg/kg) may also be regarded as significant due to the fact that this metal belongs, among others, to the group of the economically critical metals (EU Commission, 2014).

Zircon grains present higher concentration in HREE (253–890 mg/kg) compared to the LREE (8–44 mg/kg). U- and Th-concentration in the same grains ranges from 196 to 630 and 373 to 2310 mg/kg respectively. As expected, the Hf concentration is high (8810–10590 mg/kg), and the same can be argued to a lesser extent for Sc (152–218 mg/kg) and Y (332–1259 mg/kg) concentrations.

Titanite grains contained elevated Nb (396–2100 mg/kg), U (78–833 mg/kg), Th (200–917 mg/kg), V (512–841 mg/kg) and to a lesser extent Ta (6–91 mg/kg) and Ga (9–42 mg/kg). The LREE budget of the titanite ranges from 2180 mg/kg to 12,640 mg/kg, while the

HREE appear in lower concentration (378–2210 mg/kg). Additionally, EPMA analysis of titanite crystals showed that the Σ REE content of titanite crystals ranges from 1 to 2.6 wt.%, while their Th concentration ranges from 0.03 to 0.08 wt. % (Supplementary Table 3).

The mineral phase with the highest REE content but with scarce presence in the black sands was a Ce-rich phosphate phase – most probably monazite – with 879,400 mg/kg LREE and 81,371 mg/kg HREE. The Th- and U- concentrations were also high (96,700 and 14,720 mg/kg), while Y and Ga 50,280 mg/kg and 4400 mg/kg respectively.

The other phosphate mineral observed in the coastal black sands, namely apatite, incorporates REE (particularly LREE: 1670 mg/kg), but in much lower quantities compared to xenotime or monazite. U (up to 23 mg/kg) and Th (21 mg/kg), are in comparatively much lower concentrations than those in Th-rich minerals like allanite and monazite.

Finally, garnets show low concentration in REE (average HREE: 48 mg/kg and LREE: 9 mg/kg) compared to the other mineral components of the sand, while the U content ranges from 3 to 20 mg/kg and the Ga one between 30 and 41 mg/kg.

4.5. The composition of allanite detected by SEM-EDS, EPMA, single-crystal XRD, μ -XRF, SR μ -XRF and μ -XANES

Allanite, the most common Th- and REE- mineral phase in the studied coastal black sands, is of great importance because of its abundance and its REE enrichment. For this reason, allanite was extensively investigated by a combination of microscopic, spectroscopic and

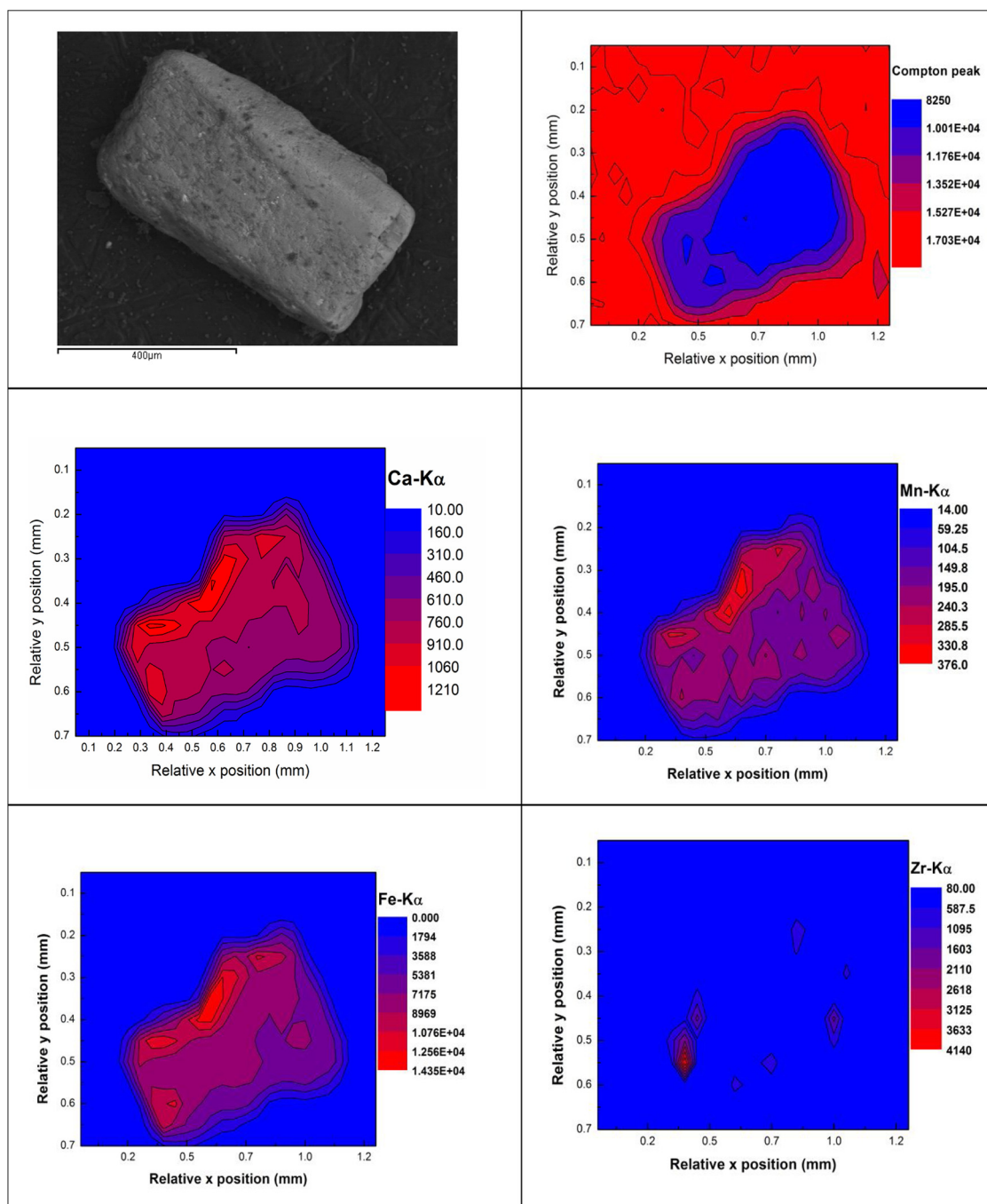


Fig. 7. Major element (Fe, Ca and Mn) and Zr μ -XRF elemental maps in an allanite crystal.

synchrotron radiation-based techniques within the frame of this study. Allanite belongs to the epidote group of minerals (Gieré and Sorensen, 2004) and can be described by the general formula $A_2M_3(SiO_4)(Si_2O_7)O(OH)$. According to Orlandi and Pasero (2006), the monoclinic epidotes, which display a great chemical variability, can be divided into two subgroups, which are distinguished on the basis of the dominant cation at the A2 site: the allanite subgroup ($A2 = REE$) and the epidote subgroup ($A2 \neq REE$). Allanite occurs in the form of euhedral to subhedral crystals, tabular to prismatic, black in color with vitreous luster, while its physical appearance varies from fresh to intensely altered (Fig. 5 (a, b)). SEM-EDS revealed the presence of inclusions or/and micro-/sub-micro mineral aggregates in allanite crystal such as monazite, titanite and zircon (Fig. 6a-c)

μ -XRF measurements were performed in order to obtain detailed

information about the chemical composition of selected allanite crystals from the sand. Specifically, elemental maps, based on μ -XRF data were produced visualizing the spatial distribution of the individual elements within the different mineral components of the sand. In addition to the spatial distribution of the characteristic fingerprint X-rays, the intensity distribution of the Compton scattering of the exciting anode tube characteristic X-rays ($Rh-K_{\alpha}$) served to identify the crystal boundaries being preferentially enhanced due to the presence of epoxy resin (Haschke et al., 2012). The element mapping of a representative allanite crystal showed the presence, in notable concentrations, of La, Ce, Nd and Y as well as of Th along with Ca, Mn and Fe. Sr and Zr were also associated with the allanite crystals (Fig. 7 and Fig. 8).

Electron microprobe analysis of the allanite crystals (Supplementary Table 2) yielded the following representative empirical formula based

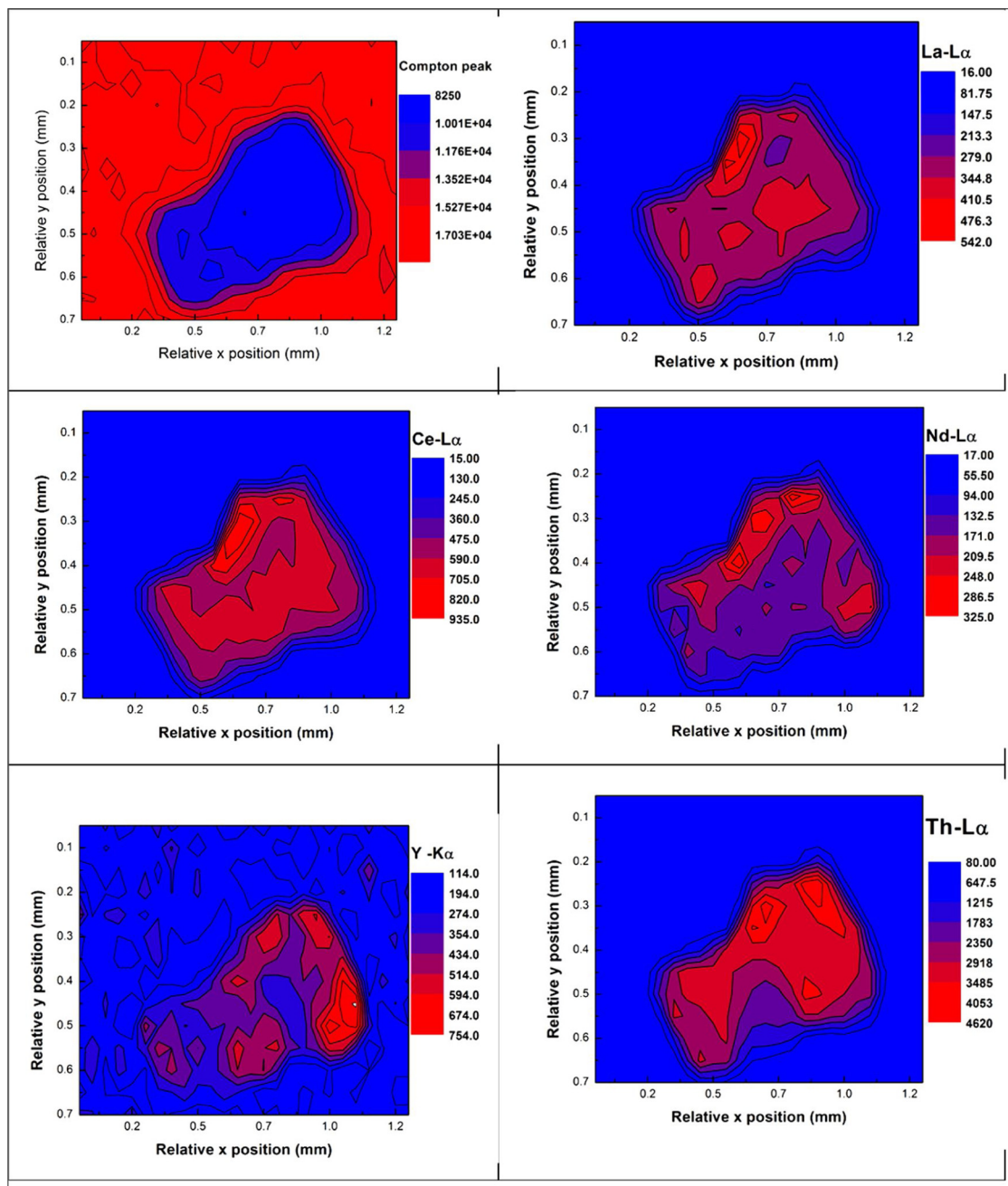


Fig. 8. LREE + Y and Th μ -XRF elemental maps in an allanite crystal from the Kavala black coastal sands.

on their composition: $(\text{REE}_{0.470}\text{Ca}_{1.499}\text{Th}_{0.031})(\text{Ti}_{0.031}^{4+}\text{Fe}_{1.089}\text{Al}_{1.880})(\text{Si}_{2.906}\text{Al}_{0.094}\text{O}_{12})(\text{OH})$. In this formula $\text{REE}_{0.470}$ represents the sum of the individual lanthanides ($\text{La}_{0.136}$, $\text{Ce}_{0.236}$, $\text{Pr}_{0.021}$, $\text{Nd}_{0.069}$, $\text{Sm}_{0.006}$, $\text{Y}_{0.003}$). Allanites as it was mentioned above consisted of brighter and darker zones in some cases and in other cases they appear as homogenous crystals in BSE images (Fig. 9). The brighter part compared to the darker areas of allanites showed higher enrichment in REE and Th.

The $\Sigma\text{REE} + \text{Y}$ content in allanites ranged from 8.9 to 17.2 wt. %. The brighter parts of the crystals showed higher values compared to the darker ones. The Th content was also elevated (0.80–2.53 wt. %) in contrast to the U which was considerably lower (0.02–0.11 wt. %).

An unaltered allanite crystal, without visible inclusions with size $0.28 \times 0.19 \times 0.16$ mm, was selected to be used for crystal refinements by single-crystal XRD. The unit cell parameters of allanite from Kavala coastal placer deposit, were (in Å) $a = 8.8878$, $b = 5.6928$, $c = 10.1164$ and $V = 463.65 \text{ Å}^3$. The system and the space group of the crystal were

monoclinic and $P2_1/m$, respectively.

The structure of allanite after the refinements is presented in Fig. 10. The structure consists of two sets of edge-sharing octahedra chain -the M sites-, which are set parallel to $[010]$. One of them is a composite chain consisting of M(1) octahedra with greatly distorted M(3) sites attached on alternate sides along its length. The M(2) octahedra usually are occupied only by Al (Dollase, 1971, 1973). Calculations of the cation distribution in the allanite crystal structure based on the EMPA microanalysis (Table 3) also revealed that the M1 and M2 octahedra were mainly occupied by Al^{+3} , while the M2 site is shared with Fe^{+3} , Mn^{+3} and in some cases Ti^{+4} and Fe^{+2} . The chains are cross-linked by two types of tetrahedral sites (T) pairs of Si_2O_7 groups. Al^{+3} is also possible to be involved, in small extend, in T sites along with Si. The A(1) and A(2) sites reside between the chains and the cross-links. A(1) site is occupied by Ca and 9-fold coordinated, as in other epidote-group minerals, but the coordination polyhedron is less regular than in

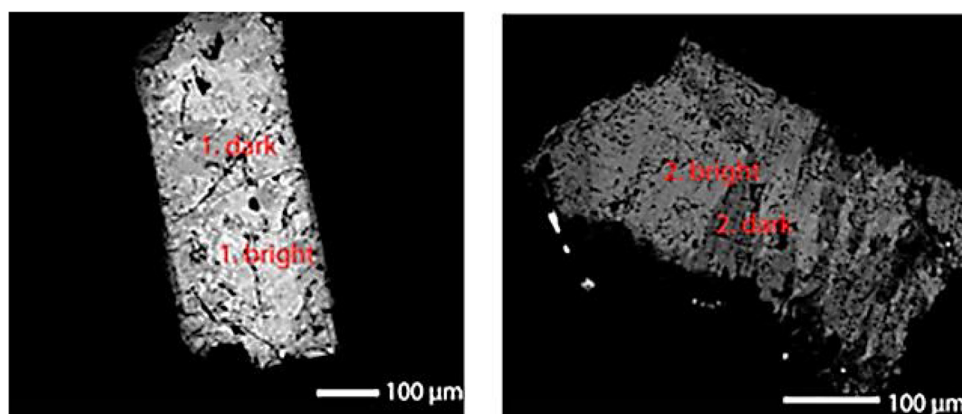


Fig. 9. BSE images of allanite crystals showing the existence of bright and dark areas.

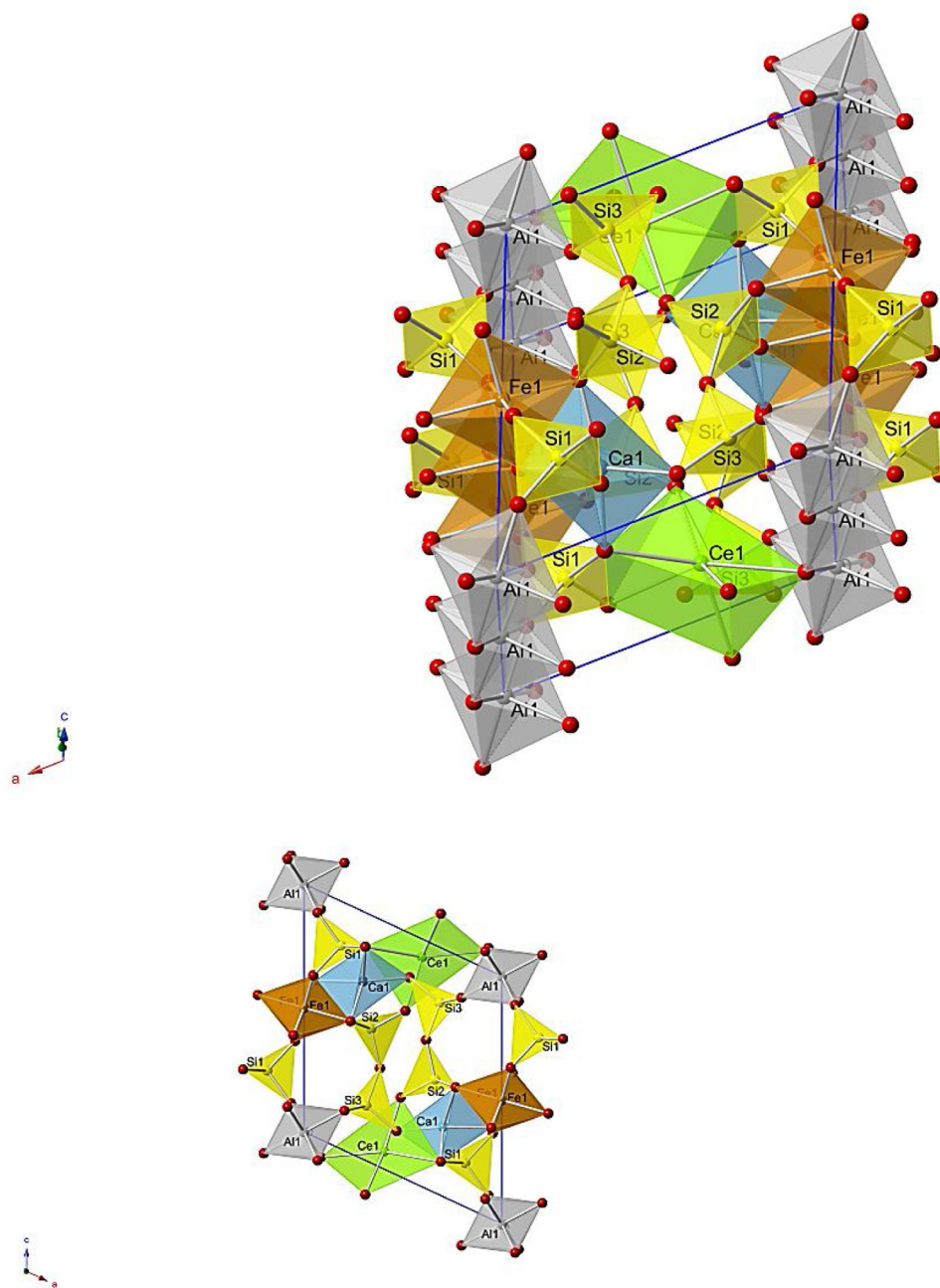


Fig. 10. Crystal structure and unit cell of allanite from the Kavallas' black coastal sand.

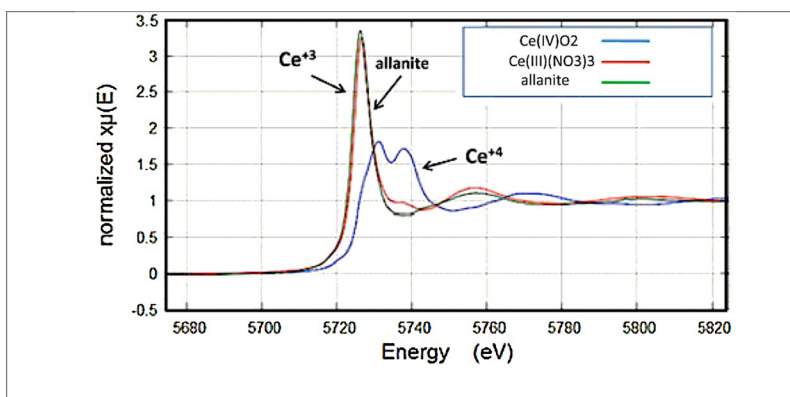


Fig. 11. CeL₃ XANES spectrum of an allanite grain compared with Ce(IV)O₂ (blue) and Ce(III)(NO₃)₃ (red) spectra. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

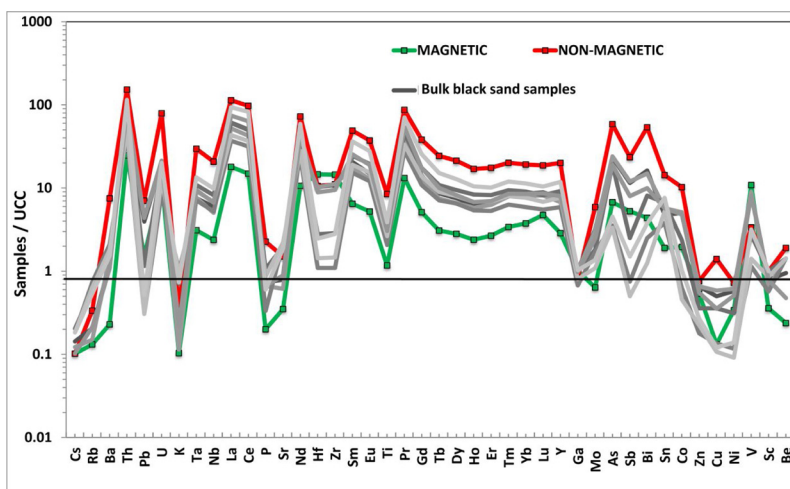


Fig. 12. UCC-normalized trace element spidergram of the coastal black sands samples.

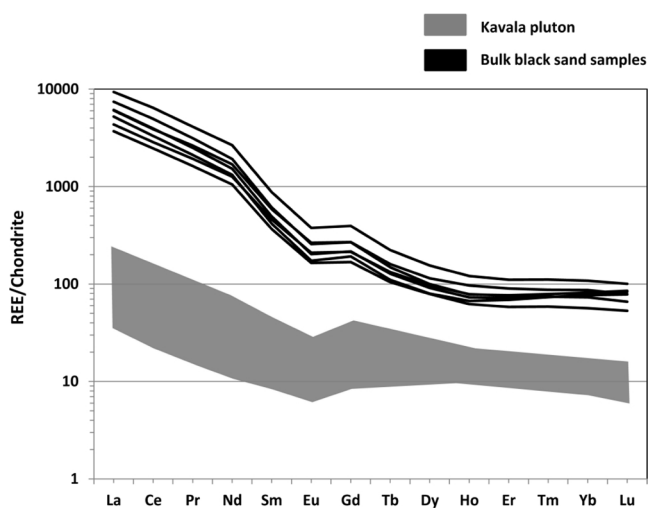
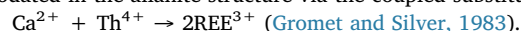


Fig. 13. Chondrite normalized diagram for the black coastal sands compared to the Kavala pluton (Neiva et al., 1996).

epidote. The A(2) site is 11-fold coordinated in allanite and contains the REE³⁺ (Dollase, 1971). In the case of the allanite under investigation, the trivalent REEs typically occupy the A(2) sites along with Ca⁺² and Y. Ca⁺² was the main cation in A(1) site but in some cases the divalent Mn⁺² and Fe⁺² could also get involved. Details concerning the atomic coordinate and distances are presented in supplementary material

(Supplementary Table 5 and Table 6).

Concerning Th, trace to minor amounts of the element has been observed to occupy A-sites of the allanite structure (e.g., [Gieré and Zirconolite, 1986](#)). A parallel set of substitutions to those for Th could also be formulated for U^{4+} ([Oberli et al., 2004](#)). Thorium is accommodated in the allanite structure via the coupled substitution:



4.5.1. Synchrotron μ -XANES study of LREE in allanite

XANES spectra of allanite crystals were obtained at the LaL_3 edge, using the $\text{LaL}\alpha_1$ fluorescence emission. Lanthanum occurs in natural inorganic compounds in 3+ oxidation state and only in some synthetic complexes in the 2+ state. Hence, it was assumed that La in allanite is fundamentally trivalent. The analysis of the La L_3 -Edge XANES spectra published in the literature (Asakura et al., 2014a) for different compounds (e.g., La_4PdO_7 , La_2CuO_4 , LaCuSrO_4 , LaFeSrO_4 , LaSrAlO_4 , LaCoO_3 , and LaAlO_3) showed one slightly asymmetric and strong white line at around 5490 eV. This observation was in good agreement with the results of LaL_3 XANES spectra of allanite (Supplementary material; Fig. 3a). These peaks can be assigned to electric transition from $2p_{3/2}$ to 5d state (Asakura et al., 2014a). The PrL_3 XANES spectra are difficult to measure because of the La $L_{\beta 1,4}$ emission lines coinciding with the $\text{PrL}\alpha_1$ emission used for recording the Pr L_3 XANES spectra. A second attempt has been made using the $\text{PrL}\beta_2$ emission line to record the PrL_3 edge. The $\text{PrL}\beta_2$ emission has lower intensity than the $\text{PrL}\alpha_1$ one leading to a spectrum with increased interference. The $L_{\beta 2}$ also coincides with other lines like the $L_{\gamma 1}$ one. This is the reason why the LaL_2 edge is still visible in the spectrum (Supplementary material; Fig. 3b). Both Pr spectra in

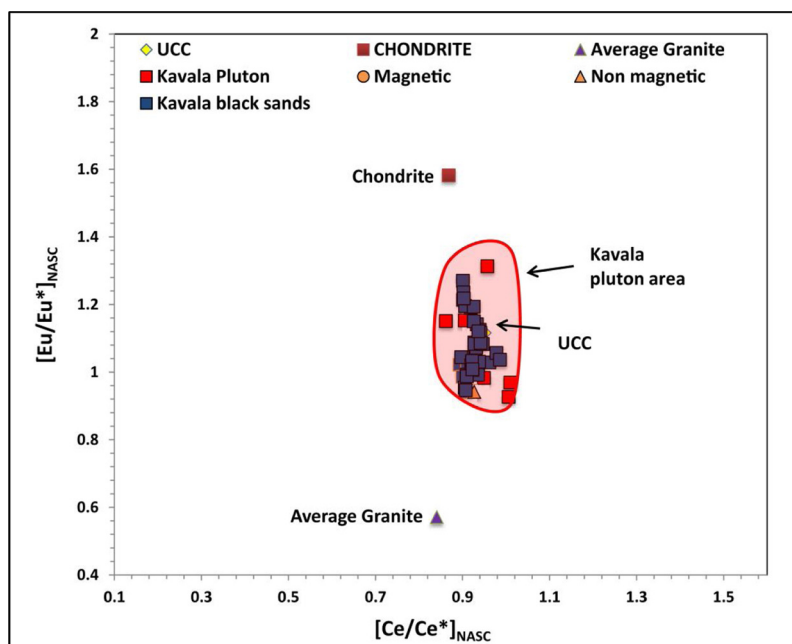


Fig. 14. REE discrimination diagrams for coastal black sands and Kavala plutonic rocks.

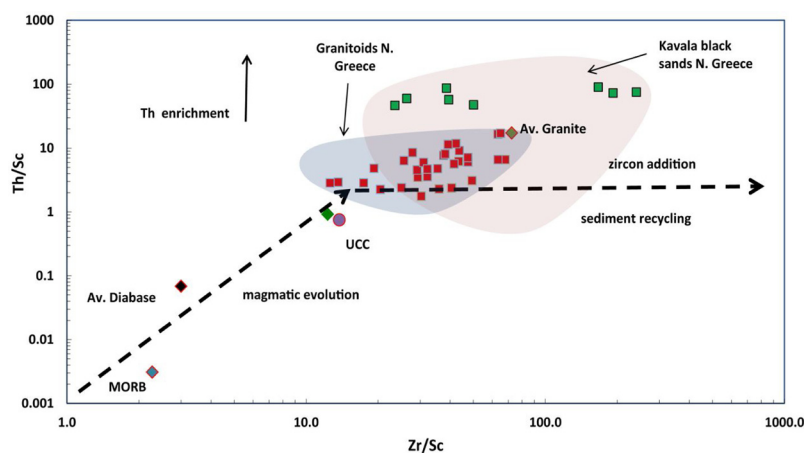


Fig. 15. Plots of Th/Sc vs. Zr/Sc for the black coastal sands and granitoids from N. Greece (Jones et al., 1992).

allanite crystals showed only one intense peak at 5970 eV, which originates from PrL_{3+} with f^2 configuration (Niu et al., 2014). PrL_{3+} -edge and PrL_{1+} -edge XANES spectra of praseodymium oxides NbPrO_4 , AlSrPrO_4 , NiSrPrO_4 , VPrO_4 , CoPrO_3 , CuPr_2O_4 , and SrPrCoO_4 have already been reported in the literature (Asakura et al., 2014a). All PrL_{3+} -edge XANES spectra showed an almost symmetric and featureless white line at ca. 5970 eV. There was no apparent difference among them. The CeL_2 edge (6164 eV) overlaps with NdL_3 edge (6208 eV). The two edges are located rather close. The NdL_3 -edge originates (Supplementary material; Fig. 3c) from the transition of the excited 2p electrons to the unoccupied 5d energy levels. The spectra begin to rise from the photon energy of 6192 eV and have a maximum at 6215.25 eV (Ozkendir, 2016).

In addition, XANES spectra were obtained at the CeL_3 edge (Fig. 11) using the $\text{CeL}_{\alpha 1}$ fluorescence emission. Two scans were performed at slightly different positions on the sample, because Ce is highly redox-sensitive in the beam. The CeL_3 XANES data were compared with Ce^{3+} ($\text{Ce}(\text{NO}_3)_3$) and Ce^{4+} (CeO_2) references spectra and showed that the Ce was accommodated in the allanite crystals of the Kavala black sands as Ce^{3+} (Fig. 11). CeL_3 -edge XANES spectra taken for Ce^{4+} using as reference material CeO_2 demonstrated a twin peak appearing at 5731

and 5738 eV (s. also Zhang et al., 2004). The trivalent Ce showed an intense white-line peak appearing at 5726.7 eV in the allanite spectrum (s. also Niu et al., 2014). The shape of CeL_3 XANES edge of trivalent cerium compounds is completely different, with a single strong white line feature and no secondary peaks (Luches et al., 2013).

5. Discussion

5.1. Provenance of allanite-bearing coastal black sands

UCC-normalized (Rudnick and Gao, 2003) spidergrams of the bulk Kavala black coastal sands (Fig. 12) showed distinct geochemical signals for minor actinides (Th, U) and REEs (mainly LREE). Although the main objective of this paper was to study the REE and actinide content, it is worthy to mention that notable values were also found for the High Field Strength Elements (HFSE) such as Nb, Ta, Hf, and V. On the contrary according to the same spidergrams the samples are depleted in Large Ion Lithophile Elements (LILE) (e.g., K, Rb, Cs, Sr, Ba) except for Ba which shows a positive peak.

The non-magnetic and magnetic sand fractions were also plotted in UCC-normalized spidergram for comparison. The non-magnetic fraction

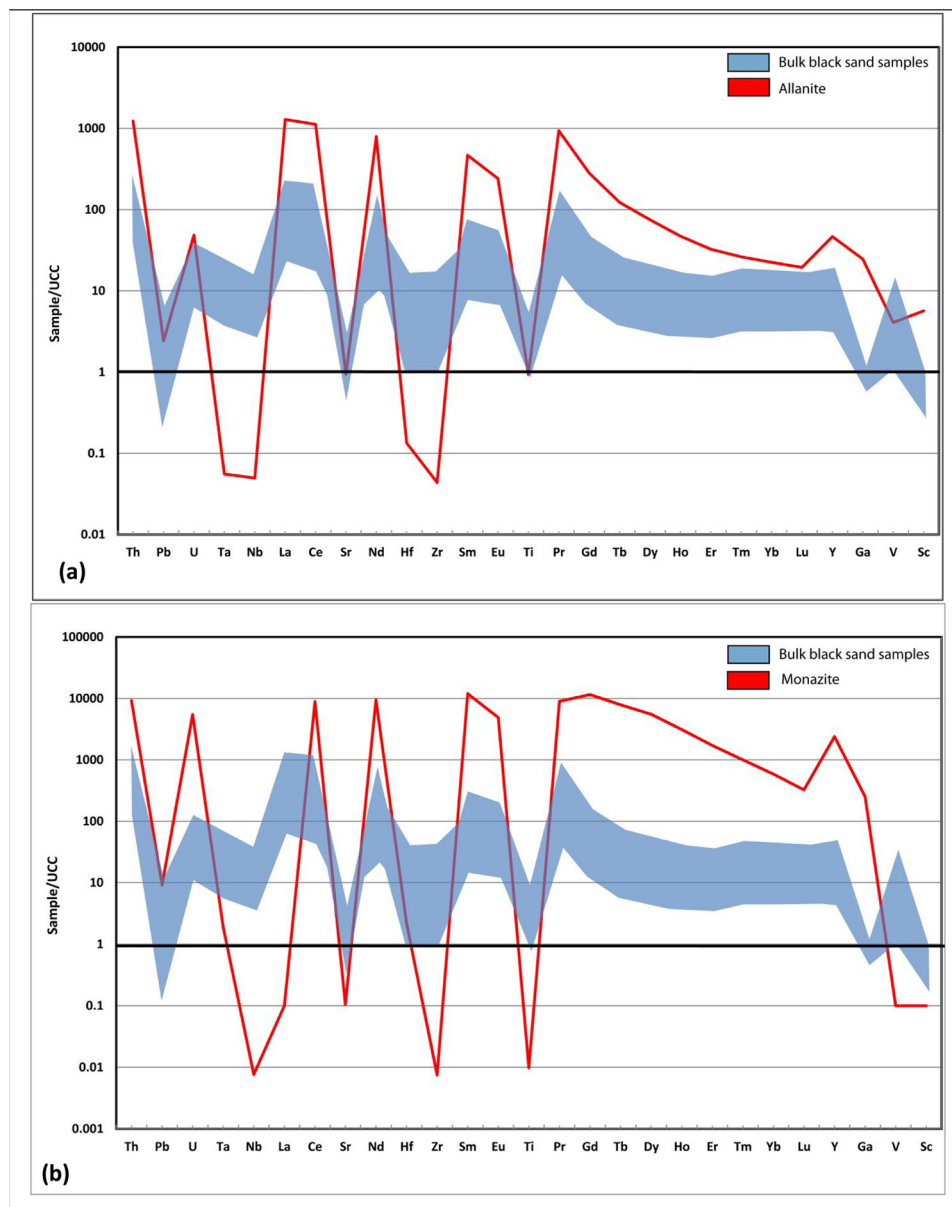


Fig. 16. UCC-normalized patterns for minerals of the black coastal sands in contrast to the bulk samples.

is clearly more enriched in REE and Th due to the fact that minerals such as monazite, apatite, zircon and the high allanite content are contained in this fraction. The diagrams nonetheless show that both fractions exhibit similar patterns, apart from specific trace elements such as V and Cu.

The REE chondrite-normalized patterns (Boynton, 1985) of the bulk coastal black sands (Fig. 13) show considerable enrichment in LREE yet much lower HREE concentration resulting in a generally negative slope and distinct negative Eu anomaly. Leybourne and Johannesson (2008) studied stream sediments and argued that the existence of mafic rocks as provenance will generally account for distinct negative Eu anomalies in the ensuing heavy mineral detritus, owing to crystal fractionation of feldspars in the original mafic melt. For that reason, we have included in the same diagram (Fig. 13) data for the neighboring granitoid bodies of Kavala. The REE chondrite-normalized patterns clearly indicate a strong similarity between the neighboring plutons and the allanite-bearing coastal black sands.

Leybourne and Johannesson (2008) demonstrated, using Eu/Eu^* - Ce/Ce^* bivariate diagrams for sedimentary geological materials, that these ratios provide information about the origin of the materials. In the

present study, the Eu/Eu^* - Ce/Ce^* bivariate diagrams (Fig. 14) constructed for the Kavala black sands showed ratios similar to those of the Kavala pluton. The corresponding values plotted for the magnetic and non-magnetic fractions also showed that they originate from the Kavala pluton region. The Kavala sand samples thus seem to be closely associated with Kavala pluton samples. This argument is strengthened by the identification of the same mineral components in the sand and in Kavala plutonic rocks previously reported in the literature (Neiva et al., 1996). Apart from the mineral phases in common, similarities in textural and mineralogical characteristics of Kavala plutonic rocks were observed in the fractions contained in the coastal black sands.

Th/Sc vs. Zr/Sc ratio plots for the Kavala black sands and granitoids of N. Greece are given in Fig. 15. The Th/Sc vs. Zr/Sc plots can reflect sedimentary sorting and recycling (McLennan et al., 1993; Asiedu et al., 2000; Ramos-Vázquez et al., 2017, 2018). The first-cycle sediments show a simple positive correlation, whereas the additionally recycled ones a more rapid increase in Zr/Sc than in Th/Sc, which is a feature that it can be observed in samples of the black sand.

The black sands have evidently been subjected to sorting, as reflected by the enhanced Zr/Sc and Th/Sc ratios by comparison with the

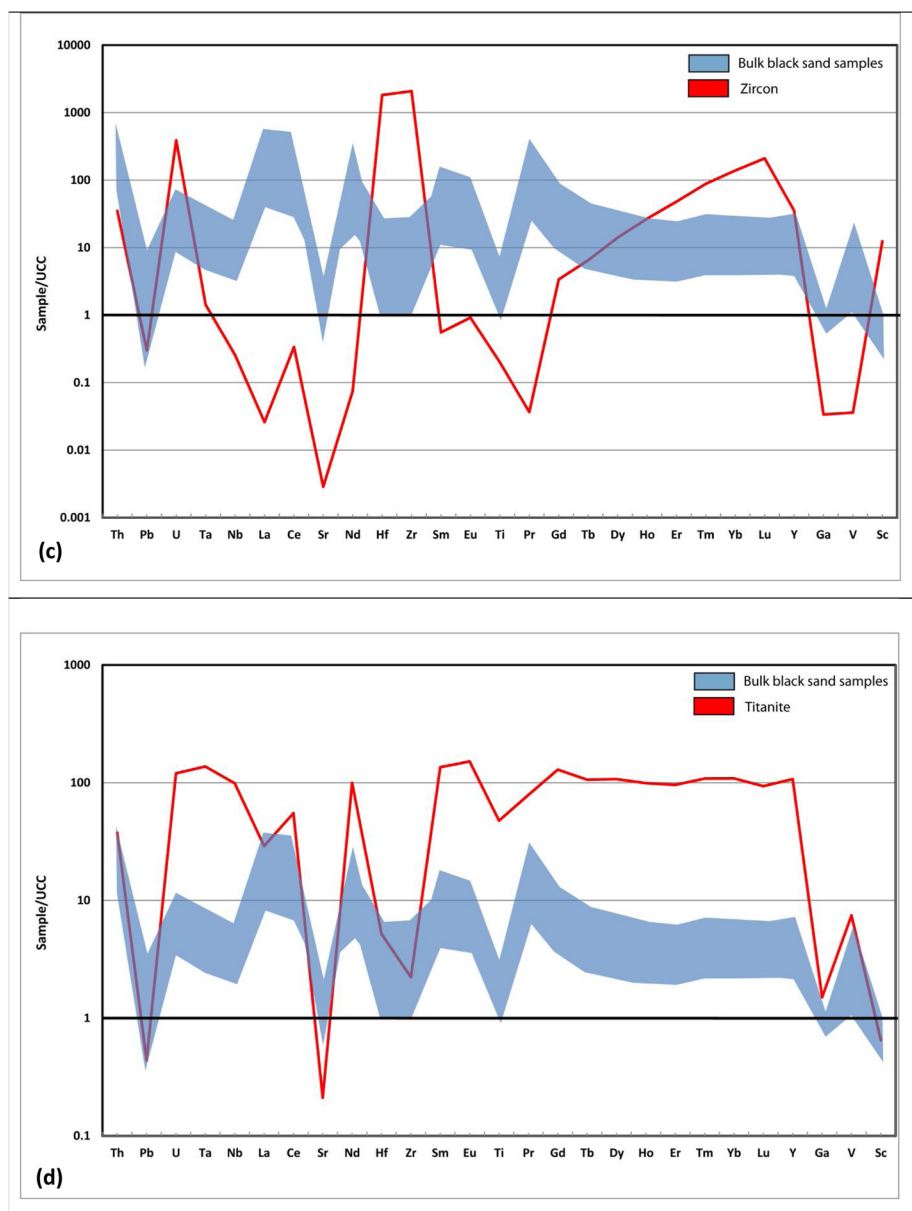


Fig. 16. (continued)

granitoids from the broader region of Kavala. The Kavala sand samples specifically showed that they have been subjected to sediment recycling and were enriched in Th and Zr relative to the granitoids. The coastal black sands originated from the natural erosion processes of the neighboring rocks of the Kavala pluton, which can also be considered as the main source. More discrimination diagrams (La/Th vs Hf and Th/Ni vs Zr/Ni) and ternary diagram (La-Th-Sc) for the coastal black sands can be found in the supplementary material (Figs. 4–7).

5.2. REE and actinide budget in the allanite-bearing black coastal sands

Based on the LA-ICPMS results, the LREE content is expected to be controlled mainly by the presence of allanite, monazite, apatite and titanite, while the HREE would be attributed to the presence of zircon. Concerning Th and U, allanite, zircon, titanite and monazite are the main minerals responsible for the corresponding concentration peaks. UCC-normalized spidergrams were also used for the comparison of the chemical composition between the different mineral constituents of the sand and the bulk samples (Fig. 16 a–h).

UCC-normalized diagrams of the REE- bearing minerals compared to the

bulk coastal sands.

5.2.1. Allanite

Allanite is demonstrably the main REE- and actinide-bearing mineral phase of the studied sands (ranging 10–20 %). The UCC-normalized allanite pattern (Fig. 16a) illustrates that it is one of the main controlling constituents for the REE-, Th- and U- budget in the black sands. The ability of allanite to accommodate REE- and actinides in its structure along with the possible substitutions of U, Th and REEs has been described by several authors in the literature (Cressey and Steel, 1988; Gieré and Sorensen, 2004). Particularly, Th has been observed as a minor to trace constituent in allanites (e.g., Bea, 1996; Wood and Ricketts, 2000; Oberli et al., 2004; Gregory et al., 2007) in contrast to U, which is typically present but in comparatively much lower concentrations (e.g. Oberli et al., 2004). This also applies to the allanite grains of the Kavala black sands, where the average Th and U content was found to be 12,900 and 131 mg/kg respectively. Microprobe analysis of the mineral demonstrates that it is characterized by zoning, probably with zoisite/clinozoisite, indicating that these grains were progressively zoned from allanite cores to REE-rich epidote and, finally,

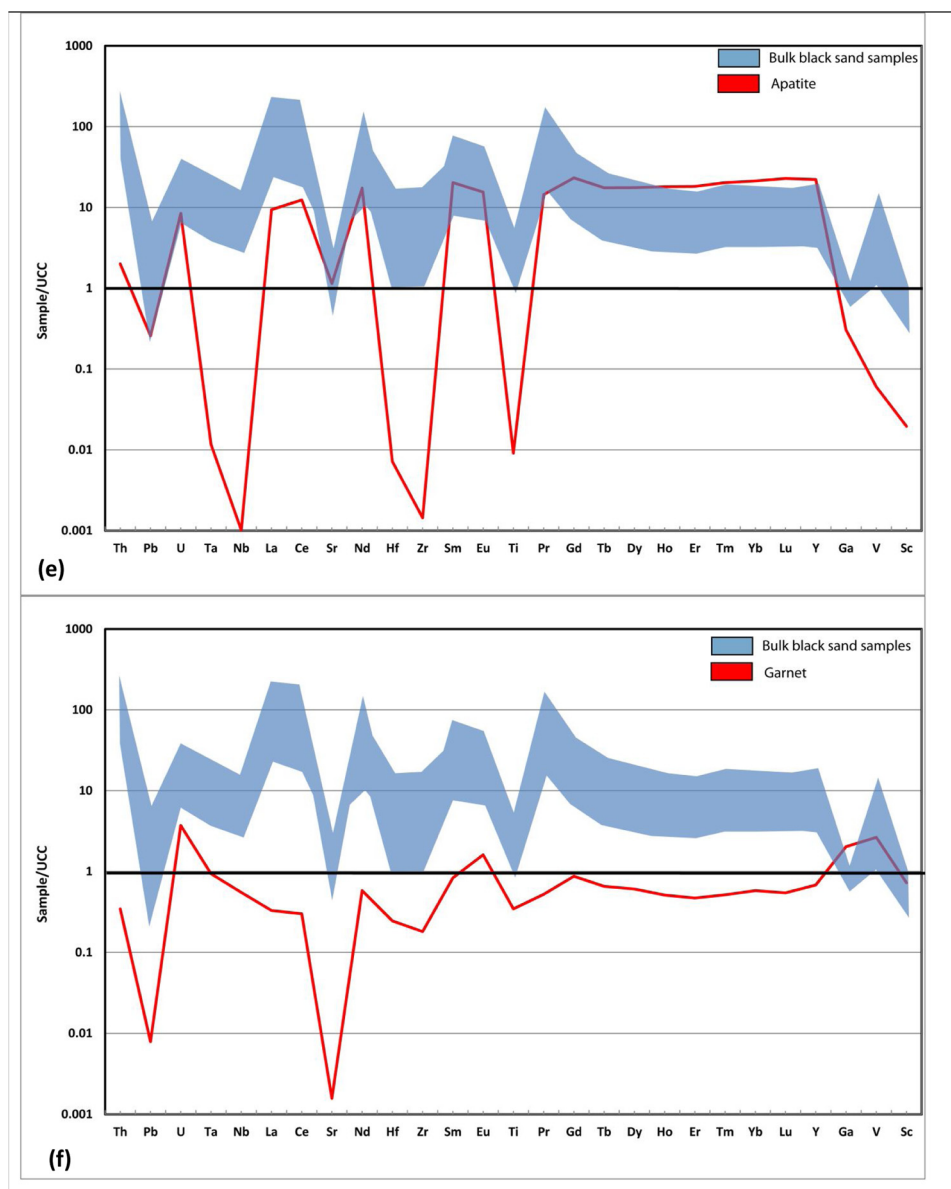


Fig. 16. (continued)

to epidote rims (e.g. Oberli et al., 2004). Such zoning likely reflects the progressive depletion of LREE in the host magma caused by crystallization (Romer and Siegesmund, 2003; Gieré and Sorensen, 2004). By contrast, rare co-existing monazite appears to be an alteration product of allanite. Moreover, REEs and Th show that they do not have homogenous distribution in the allanite, a fact that probably is based on metamictization. Apart from the afore-mentioned trace elements, allanite is also enriched in Ga and Sc compared to the bulk sand samples.

Th and REE were rather inhomogeneously distributed in the allanite crystals further supporting the assumption of their alteration origin. Linear correlations exported by the μ -XRF measurements evidenced that the La is mainly associated with Ce and less with the Th (Fig. 17). REE-bearing inclusions could possibly exist in the allanite crystals because of the presence of REE- and Th- accumulations observed in particular micro-regions of the elemental maps. Yttrium was also mostly accumulated in specific locations in the crystal. On the other hand, Ca, Fe and Mn clearly demonstrated a very good correlation. It is worth to mention that the distribution of Zr in the crystals could indicate that this element was not accommodated in the allanite crystal structure but occurred as zircon inclusion.

5.2.2. Monazite

Scarce alteration monazite in allanite crystals favors the accommodation of LREE (La to Eu; Förster and Harlov, 1999). UCC-normalized monazite (Fig. 16b) from the black sands exhibit positive anomalies for the REE (including Y), Th and U. The incorporation of trivalent actinides in the LnPO_4 monazite structure can take place through the direct substitution of REE by actinides (e.g. Dacheux et al., 2013).

5.2.3. Zircon

UCC-normalized pattern for zircons (Fig. 16c) derived from the black sands show positive geochemical anomalies for the HREE – including Y, Hf, U and Th. They are particularly enriched in Y and heavy lanthanides compared to the light and middle ones, a fact that it has also been described in the literature by other authors (Hanchar et al., 2001; Hoskin and Schaltegger, 2003; Finch and Hanchar, 2003).

5.2.4. Titanite

The LA-ICPMS results show that titanite contains high concentrations of a variety of trace elements including REE, actinides and HFSE, such as Nb and Ta. The total budget of the REE in titanites is expectedly much less related to other mineral components of the sand such as

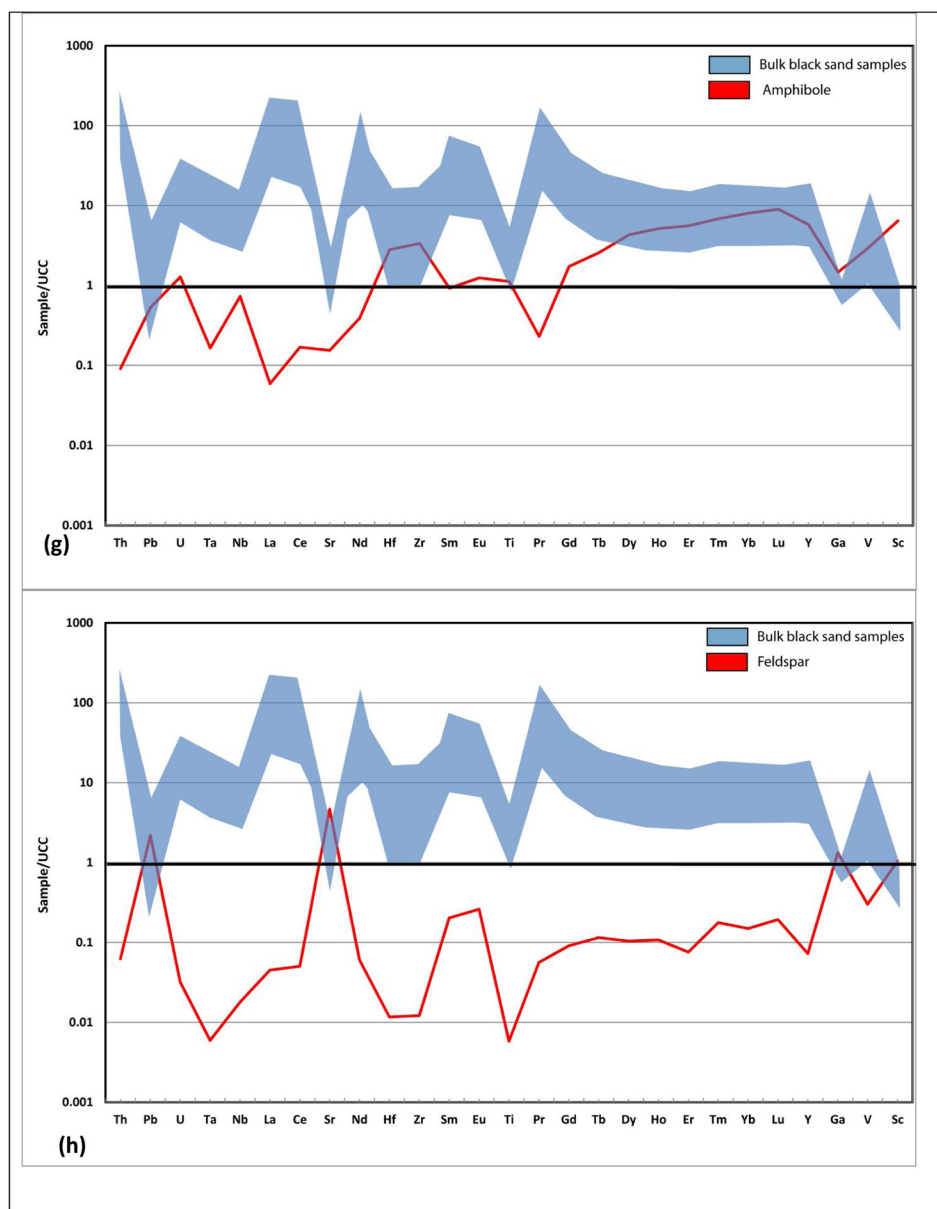


Fig. 16. (continued)

allanite and monazite. However, titanite is a modally dominant phase in the black sand, ranging from 4 to as high as 28 wt. %. It should be mentioned that titanite was observed in both magnetic and non-magnetic fractions due to the unavoidable mineral intergrowths in micro-scale. Hence it plays a significant role in controlling the total REE budget. In addition, titanite contains considerable concentrations of U and Th (Meinhold, 2010). Ta and Nb also represent elements that are typically accommodated in minerals such as the titanite, and this fact is manifested in the UCC normalized diagram for titanite (Fig. 16d). Finally, a distinct positive geochemical anomaly could be observed for V in the spidergram.

5.2.5. Apatite

The crystal structure and chemistry of apatite favors the substitution of many trace elements including Na, Mg, Mn, Fe, Sr, Y, Ba, REEs, Pb, Th, and U (Hughes and Rakovan, 2000; Rakovan and Hughes, 2002). In the case of apatite derived from the black sands, the UCC-normalized spidergram (Fig. 16e) illustrates a positive peak in REEs concentration along with a weaker one for Th and U. The other trace elements do not exhibit significant accumulation related to the bulk sand samples.

5.2.6. Garnet

Garnets, like apatite, have minor presence in the sands due to the fact that they were not detectable by XRD (< 3%). The UCC-normalized diagram (Fig. 16f) exhibits slight positive anomalies for U, Eu, V and Ga. However, with the exception of Ga, the other elements are present in trivial concentration against the bulk chemical analysis. Apart from zircon, the presence of garnet was also expected to contribute to the elevated HREE values (Grew et al., 2013) however, the LREE content in the black sands was slightly higher than the HREE one.

5.2.7. Amphiboles

UCC-normalized diagram for amphiboles (Fig. 16g), which are quite abundant in the sand, shows slightly positive anomalies for Hf, Zr and HREE, while the Sc concentration is also enhanced compared to the bulk sand.

5.2.8. Feldspars

Finally, the abundant feldspars in the sand samples represent their main light-colored mineral phase. As demonstrated in the UCC-spidergram (Fig. 16h), the only notable concentration peak imparted by the

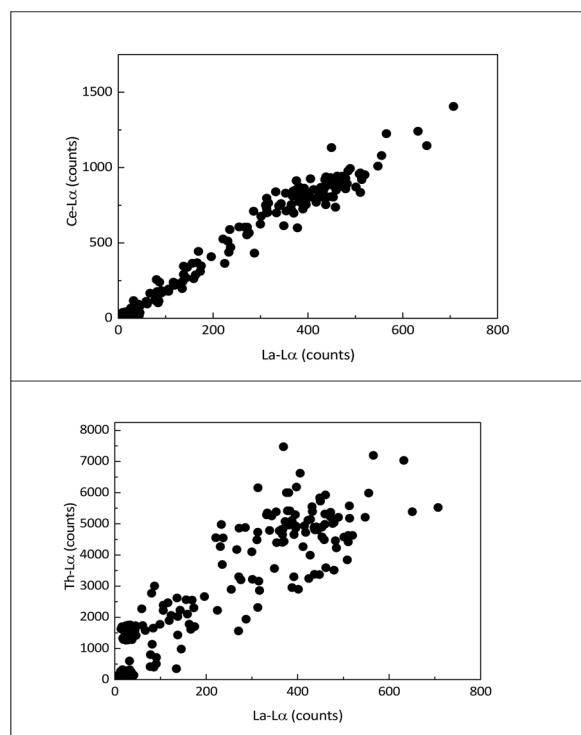


Fig. 17. Linear correlation of Ce La vs La La vs Th La vs La La in allanite crystal exported by μ -XRF.

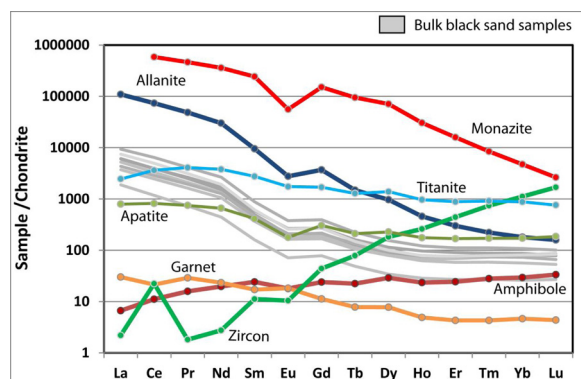


Fig. 18. REE-normalized patterns for the main U- Th- and REE-bearing minerals of the black coastal sand from Kavala region.

feldspars is that of Sr. In all other respects, it has a minor contribution to the total elemental budget, including the REEs and actinides.

Chondrite-normalized diagrams of the REE-bearing minerals compared to the bulk coastal black sands

Chondrite-normalized diagrams were constructed for the different mineral components and were compared with the bulk samples. The pattern of allanite shows a broadly linear negative slope with a small negative Eu anomaly (Fig. 18). Titanite, by contrast, shows a broadly flat pattern with slightly higher LREE relative to HREE and a distinct convex upward “hump” between La and Eu. Zircon shows a contrasting chondrite-normalized REE behavior by comparison with allanite. The zircon REE-spidergram has elevated content in normalized HREE (408–766 mg/kg) related to the LREE, resulting in a clear positive slope with a large positive Ce anomaly. The latter may be attributed to the predominantly magmatic origin of the grains. The high enrichment in HREE in zircon grains (Fig. 18), may thus exert a key control over the overall HREE budget in the bulk sand samples, subject to modal relationships. The grains of garnet and to a lesser extent, those of

amphiboles showed great variability in REE patterns indicating a possibly non-unique origin of these minerals. The epidotes and garnets had almost identical REE patterns (Fig. 18). The trend of the REE chondrite-normalized pattern of the same phase compares more closely to published results for monazite than those for xenotime (Förster, 2001; Xu et al., 2017). As indicated earlier though, monazite was observed mainly as inclusion in allanite, a feature that impeded separation and confident identification from the bulk sample.

Arguably, the key observation pertaining to the REE patterns displayed in Fig. 18 is the similarity in the pattern of the back sand with those of allanite, titanite and monazite. The bulk coastal black sands appear to be specifically enriched in LREE compared to HREE, in a fashion that qualitatively and rather convincingly agrees with the REE patterns of the aforementioned mineral phases. An obvious conclusion that can thus be extracted from Fig. 18 is that these three minerals – with allanite arguably the modally most important of the three in this instance – account for the REE budget of the investigated sands. Dilution of the REE budget by quartz and feldspar would then result in the muted REE abundances of the black sands by comparison to the pure end-member mineral phases.

5.3. Implications for further exploration

Whereas bulk chemical analysis showed significant enrichment in $\Sigma\text{REE} + \text{Y}$ (10,880 mg/kg), it is worth mentioning that there are many factors impacting the prospect of future exploitation of the studied placer deposit. First and foremost, the Th content in the black sands is relatively high (1200 mg/kg) which was enriched by over 30% (1600 mg/kg) through a single stage magnetic separation procedure. The positive correlation between La and Th content was revealed also from the discrimination diagram La vs Th, which can be found in the supplementary material (Fig. 7). Moreover, the radioactivity levels were enhanced especially for the samples that show the higher REE content. For instance, sample BL05 shows $\Sigma\text{REE} = 10,880$ mg/kg and the activity from ^{232}Th decay series was 3500 Bq/kg. In case of future exploitation, the high radioactivity level should therefore be carefully considered. The close connection between lanthanides and actinides requires particular attention and close monitoring during extraction. The rare earth element industry has to take into consideration all of the rare earth-specific criteria that can arise from economic and environmental issues, which may affect the REE mining processing (Barakos et al., 2015).

The presence of the coastal black sands does not cover large expanses of the Kavala coastal area of circa 240 km length. Instead, heavy mineral concentrations are mostly accumulated as alluvial deposits proximal to river mouths intercalated with layers of broadly non-mineralized light-colored mineral sands dominated by feldspars and quartz. In light of previous studies of a larger number of similar black sand samples derived from the same coastal area Papadopoulos et al. (2016a) showed that the ΣREE ranged from 58 to 7250 mg/kg, which is certainly a much more subdued concentration range by comparison to the results of the present study (2035–10880 mg/kg). This suggests that the samples used in this work represent localized and highly concentrated occurrences of black sands of enhanced economic potential.

The magnetic separation of the samples led to the enrichment of the non-magnetic fraction for the majority of the trace elements (including REE and actinides) related to the magnetic one. Hence, the $\Sigma\text{REE} + \text{Y}$ content for the non-magnetic fraction was 13,286 mg/kg (1.3 wt. %), while the magnetic one 2025 mg/kg (0.2 wt. %). REEs were found in both the magnetic and non-magnetic fractions, and this can be explained by the fact that the magnetic minerals (essentially magnetite) form aggregates with non-magnetic species such as allanites, thus curtailing efficient physical separation of the individual mineral species.

According to the REE chondrite-normalized patterns and the bivariate diagrams of the Eu/Eu^* - Ce/Ce^* shown earlier, the Kavala black sands display a source association with the neighboring Kavala plutonic

rocks. Previous studies of the Kavala pluton (Neiva et al., 1996) did not reveal commercially significant REE concentrations, thus the main interest from a REE perspective is essentially focused on the black sands only. Concerning the individual mineral constituents of the black sand, only monazite has been used so far for REEs extraction from economic deposits elsewhere. However, in the particular case of the Kavala coastal sands monazite is scarce (under 3%). Moreover, it mainly appears as inclusion in other mineral constituents such as allanite, and its crystal size appears to be small, on average < 10 µm. The mineral allanite, the most abundant REE-bearing phase of the sand, also exhibits high Th content. There is one particular study which deals with the recovery of lanthanides, uranium, thorium and zirconium from allanite by extraction chromatography using impregnated chromosorb (Gupta et al., 2013). The results of this study show that the lanthanides and the Th can be recovered from allanite at levels as high as 95%. In this case, this procedure of REE extraction could be applied in the black sands studied, however one should take under consideration the total cost involved in applying this specific methodology, in combination with the relative purity of the allanite crystals themselves. The performed mineralogical investigations revealed that allanite shows variable degrees of alteration, zonation and in many case inclusions, such as monazite, zircon and apatite. In the cases of apatite, titanite and zircon, there are few experimental studies dealing with their REE extractability potential (Pereira and Bilal, 2012; Hoshino et al., 2012) and, therefore, they are not further considered in this study.

6. Conclusions

The Kavala black coastal sands showed significant enrichment in REE particularly in LREE and lower actinides. Combination of mineralogical and LA-ICPMS techniques demonstrated that allanite, zircons, monazite, apatite and titanites are the main hosting phases, which are responsible for the enrichment. Th and U illustrated also enhanced concentration and were mainly observed in the REE-enriched phases.

The REEs were found in both the magnetic and non-magnetic fractions. This can be attributed to the fact that allanite grains form aggregates with other mineral phases such as magnetite. This observation places serious challenges with regard to the separation and recovery of the REE-rich minerals under investigation.

Eu/Eu* - Ce/Ce* bivariate diagrams combined with our mineralogical investigations showed that the black sands must have originated from felsic plutonic rocks around Kavala. Whereas the coastal zone of Kavala is up to 240 km long, the REE potential is accentuated only locally in alluvial accumulations near river mouths, where the black heavy mineral-rich sands alternate with silicate-rich non-mineralized sands.

Monazite is the only mineral used in several cases for REE extraction. However, in the case of Kavala beach sands, monazite participates in small concentrations mainly as fine inclusions in allanite (< 10 µm), indicating its low economic importance.

Allanite is the most abundant phase enriched in REEs in the Kavala coastal black sands. However, this phase has never been used for REE extraction on commercial scale. Important additional drawbacks are its high alteration leading to the formation of new phases (e.g., monazite and thorite) and its relatively high Th content.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.chemer.2019.05.002>.

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