Minerals **2012**, *2*, 300-317; doi:10.3390/min2040300

OPEN ACCESS

minerals

ISSN 2075-163X
www.mdpi.com/journal/minerals

Review

Geological, Mineralogical and Geochemical Aspects for Critical and Rare Metals in Greece

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Received: 4 September 2012; in revised form: 9 October 2012 / Accepted: 10 October 2012 / Published: 19 October 2012

Abstract: The European Union (EU) is highly dependent on critical and rare metals which are very important for a sustainable development. However, European industry is not able to cover its demands from native sources and it imports commodities from third countries. Greece is one of the EU countries with the most potential for supplying these strategic metallic raw materials in the future, since it hosts a large number of ore deposits. The epithermal- and porphyry-type deposits and the reduced intrusion related systems of the Serbomacedonian and the Rhodope metallogenic provinces in Northeastern Greece are promising targets for a future exploitation and exploration in Sb, Te, Mo, Re, Ga, In, REE and PGE. Greece is the leading producer of Ni and Al in the EU from laterites and bauxites of central and northern Greece. These deposits also contain significant amounts of Co or REE which should be considered in the future plans of the processing industries. REE are found in high contents at the placer deposits between Chalkidiki and Kavala (North Greece) and elevated PGE concentrations are associated with the chromitites of northwestern Greece. Therefore, the mineral wealth of Greece can contribute significantly to a sustainable and a competitive economy of Europe.

Keywords: critical metals; rare metals; rare earth elements; sustainable development; Greece

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1. Introduction

Raw materials, particularly metals, are very important for sustainable functioning, since they are essential for the high-tech products such as electrical and electronic devices, photovoltaic systems, batteries, catalysts, optical fiber cables, synthetic fuels, *etc*. European industry needs sufficient access to certain mineral raw materials for the sound functioning of the EU's economy. However, the European Union (EU) is highly dependent on imports from third countries of strategically important metals, which are considered to be critical because of their economic value, the high supply risks affected by market distortions and the continuously decrease of their availability. An expert group under the auspices of the European Commission published in 2010, a list of 14 metal raw materials which are considered to be "critical" for the future sustainable development of EU: antimony, beryllium, cobalt, fluorine, gallium, germanium, graphite, indium, magnesium, niobium, platinum group metals, rare earths, tantalum and tungsten [1]. Due to their low concentrations in earth's crust, the critical metals are produced as by-products of other metals which are mined.

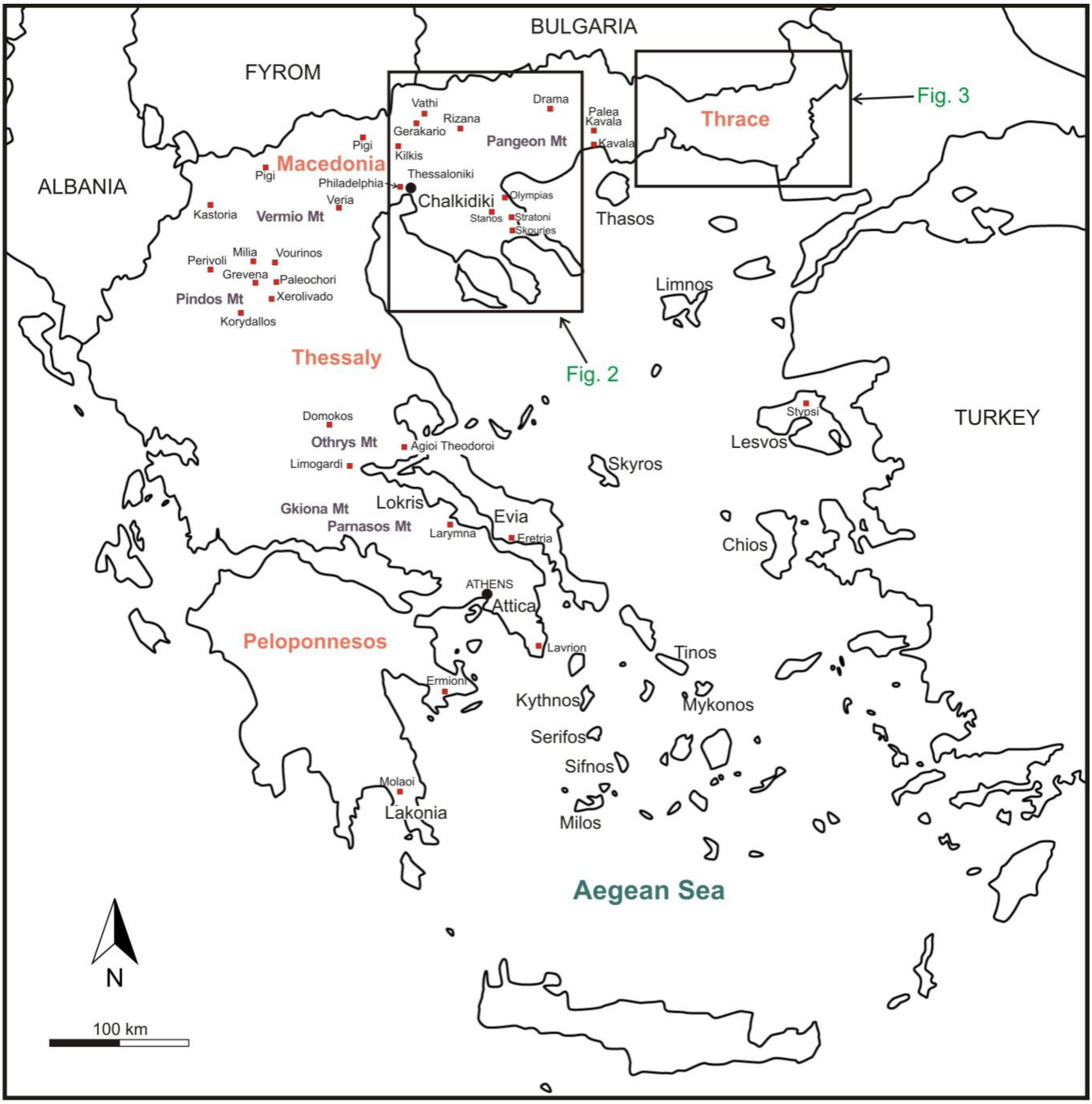
During the last years issues concerning the EU policy on securing raw material supplies by improving resource efficiency and recycling, have been high on the political agenda. In November 2008 the new European policy entitled: "The Initiative for raw materials to meet critical needs for growth and employment in Europe" was adopted and promulgated by the EU [2]. This initiative refers to the need of the EU to follow a comprehensive policy for ensuring access to mineral raw materials in order to enhance competitiveness and to achieve the Lisbon partnership for growth and employment.

The EU has many ore mineral deposits, even if their exploration and extraction are facing increased competition for different land uses and a highly protected environment, as well as several limitations in access to these deposits. Greece is one of the most significant metallogenic provinces of EU hosting a large number of ore deposits, which may provide an essential mineral wealth, including critical metals.

Mining has been part of the Greek civilization since prehistoric times, when Greeks began extracting non-metallic minerals and metals for use. Ancient underground mines and ruins of metallurgical furnaces throughout Greece are witnesses of the intense exploitation of the metallic mineral resources, mainly gold, silver, copper, lead and iron. Especially during the Classical and Hellenistic times, famous mining centers operated in Lavrion (Attica), Sifnos and Milos Islands (Aegean sea), Pangeon Mt, Palea Kavala, Chalkidiki and Thasos Island (northern Greece) (Figure 1).

In the last 70 years significant mining operations in Greece have focused on nickel, aluminum, chromium and iron-manganese deposits, as well as lead-zinc-(±Cu, ±Au, ±Ag) sulfide occurrences. However, several of these operations have been stopped in the last years due to various reasons. Recent investigations, especially in northern Greece (Macedonia and western Thrace), have revealed new prospects of gold-silver, copper, molybdenum-rhenium, antimony, tungsten and tellurium ore mineralization. According to [3] the total value of the indicated metallic mineral reserves of Greece exceeds €72 billion. It should be mentioned that Greece is the only country in the EU with large deposits of manganese, chromite, aluminum and nickel. It is the leading producing country in the EU for aluminum (from bauxite) and nickel (from laterite). Significant production of magnesium (from magnesite) is also reported. Greece has a comparative advantage in relation to other European countries due to the presence of a significant mineral wealth.

Figure 1. Map of Greece with the distribution of the most significant ore deposits. The ore deposits of Thrace are displayed in Figure 3.



In the last decades, the metal mining industry of Greece operated far below its productive capacity, with an exception of bauxite and laterite. This was affected also by the relatively reduced industrial activities, the long distance from the central European markets which restricted the export potential of the country, and the lack of considerable investments.

In this contribution we present briefly some new data, mainly on Te, In, La and Ce obtained from selected mineralizations (Pagoni Rachi, Perama Hill, Pangeon Mt., Pefka, Vathi/Kilkis) using ICP-MS bulk rock analyses in ACME Laboratories, of Canada. These data are combined with published information on the geology, mineralogy and geochemistry of several critical and rare metallic elements found in Greece, being necessary for the future sustainable development of the EU. We focus mainly on the less investigated metals Sb, Co, Te, Re, Mo, Ga, Ge, In, REE and Platinum Group Elements, because for other commodities like Mn, Cr, Ni, Al and Mg, there is a broad knowledge and experience with mining in Greece. These data will contribute significantly to the knowledge about the presence of critical metals in specific regions of Greece, for a possible future exploration and exploitation.

2. Geological Overview and Various Ore Deposit Styles in Greece

Geological setting of Greece consists of various elongated geotectonic terrains which represent successive episodes of oceanic riftings, spreadings, subductions and collisions in the region of Neotethys, known as Hellenide orogen [4]. The evolution of the Neotethys Ocean and the related lithosphere plates caused magmatic processes which led to the formation of considerable ore mineralizations.

Large magmatic Cr-(±PGE) deposits (Vourinos, Xerolivado, Milia, Korydallos/Pindos, Eretria, Domokos/Othrys, Chalkidiki and eastern Thessaly) (Table 1) are related with Mesozoic ophiolitic chains along the Pindos and Vardar ocean sutured zones. Ni-Fe laterites (Lokris, Evia, Kastoria) and Al bauxites (Parnassos Mt, Gkiona Mt) are also associated with these ophiolites, although most of these deposits are allochthonous, being incorporated among various karstified limestones due to the subsequent sedimentary processes. Only few, mostly uneconomic, VMS-type mineralizations (Table 1) are also in close association with the Mesozoic ophiolitic sequences within meta-volcanosedimentary rocks of basic affinity. They are mainly of Cu-pyrite Cyprus-, Kuroko Zn-Pb-Ag- and Fe-Cu-Ni-Co-type, forming stratabound and stratiform ore bodies in Xylagani (Thrace), in Vermio (Veria), in Perivoli (Pindos), in Agioi Theodoroi, Limogardi (Othrys), Eretria (Evia) and in Ermioni and Molaoi/Lakonia (Peloponnesos) (Table 1, Figure 1).

Significant precious and base metal sulfide ore deposits are widespread in Attic-Cycladic ore belt (south Evia, Sifnos, Mykonos, Tinos, Kythnos), along the South Aegean Active Volcanic Arc (Milos) and in Attica (Lavrion), of Lower Pliocene to Miocene age [5]. However, the most promising regions for future critical- and rare-metal exploration projects are the Serbomacedonian and Rhodope metallogenic provinces (Figure 2 and 3), in northeastern Greece [6]. These provinces include skarn-(Kimmeria/Xanthi), carbonate-replacement-(Olympias, Stratoni/NE Chalkidki), reduced intrusion-related-(Palea Kavala), epithermal (Perama Hill, Mavrokoryfi, Kassiteres, Sapes, Agios Philippos/Kirki, Pefka/Evros) and porphyry-(Pagoni Rachi/Kirki, Kassiteres-Sapes, Maronia, Skouries/Chalkidiki, Vathi and Gerakario/Kilkis) deposit styles, as well as placer gold occurrences and supergene fault/karst-controlled manganese oxides (Drama, NE Chalkidiki) and gold-bearing iron oxides (Palea Kavala, Thasos) [6,7]. These deposits are characterized by Pb, Zn, Sb, Bi, Cu and Mo ores with, less commonly, economic concentrations of Fe and Sn. They also include minor Au, Ag, PGE, Te, U, W, Re and As occurrences [7].

Table 1. Characteristics of critical- and rare metal-bearing mineralization in Greece (data sources in text).

Mineralization-type	Province	Area	Main metals	Critical and rare metals
Magmatic Cr-(±PGE)	Pindos	Vourinos	Cr	PGE
	Pindos	Xerolivado	Cr	PGE
	Pindos	Milia	Cr	PGE (Os, Ir, Ru)
	Pindos	Korydallos	Cr	PGE (Pt, Pd, Ru, Rh)
	Evia	Eretria	Cr	–
	Othrys	Domokos	Cr	–
	Thessaloniki	Triadi-Vassilika	Cr	PGE
	Chalkidiki	Vavdos	Cr	PGE
	Chalkidiki	Gerakini-Ormylia	Cr	PGE
	Eastern Thessaly	Kallipefki, Agia	Cr	–
	Aegean sea	Skyros	Cr	PGE (Ru)
	Veria	Vermio	Cr	PGE (Os, Ir, Ru, Rh, Pt, Pd)
VMS (Cyprus- and Kuroko-type)	Thrace	Xylagani	Cu, Fe, Au	–
	Serres	Lagadi	Cu, Fe	Co
	Veria	Vermio	Fe, Cu, Ni, Co	Co
	Kilkis	Polykastro	Pb, Zn, Ag	In, Ge, Ga
	Pindos	Perivoli	Fe, Cu	Co
	Othrys	Agioi Theodoroi	Fe, Cu, Ni, Co	Co
	Othrys	Limogardi	Fe, Cu, Ni, Co	Co
	Peloponnesos	Ermioni	Cu, Fe	Co
	Peloponnesos	Molaoi/Lakonia	Zn, Pb, Ag	In, Ge, Ga
Ni-Fe laterites	Lokris	Larymna	Ni, Fe	Co
	Evia		Ni, Fe	Co
	Kastoria	Ieropigi	Ni, Fe	Co
	Grevena	Paleochori	Ni, Fe	Co
	Veria	Vermio	Ni, Fe	Co
Al bauxites	Parnassos		Al	REE
	Gkiona		Al	REE
Shear-zone related	Chalkidiki	Stanos	Cu, Au, Bi, Mo	Te
	Lachanas	Rizana	Sb, W	Sb
	Thessaloniki	Philadelphia	Sb, Fe, Au	Sb
Carbonate replacement	Chalkidiki	Olympias	Pb, Zn, Au, Ag	In, Ge, Ga
	Chalkidiki	Stratoni	Pb, Zn, Ag	Te
	Xanthi	Thermes	Pb, Zn, Ag	In, Ge, Ga
	Attica	Kamariza/Lavrion	Pb, Zn, Ag, Au	In
Reduced intrusion-hosted	Kilkis	Pigi	Mo	W
	Thrace	Kimmeria/Xanthi	Fe, Cu, Mo, Bi	W
	Kavala	Palea Kavala	Au, Bi	Te
	Kavala-Drama	Pangeon Mt	Au, Bi	Te
	Attica	Plaka/Lavrion	Cu, Pb, Zn	Ga, REE (La, Ce)

Table 1. *Cont.*

Mineralization-type	Province	Area	Main metals	Critical and rare metals
Epithermal	Thrace	Perama Hill	Cu, As, Au, Bi	Te
		Mavrokoryfi	Cu, Sb, Ag, Au	Te
		St. Demetrios/Sapes	Cu, As, Au, Ag	Te
		St. Barbara/ Kassiteres	Cu, Au, Ag	Te
		Agios Philippos/Kirki	Pb, As, Cu, Ag, Bi	In, Ga, Ge
		Pefka/Evros	Cu, As, Ag, Au	Te, In,
		Kalotycho	Fe, Cu	–
		Kallyntirion	Pb, Zn, Cu, Au, Ag	Sb
	Aegean Sea	Tinos Island	Cu, Pb, Au, Ag	Te
		Limnos Island	Pb, Zn, Cu, Au, Ag	Te
Porphyry	Thrace	Pagoni Rachi/Kirki	Cu, Au, Mo	Te, Re
		Konos/Sapes	Cu, Au, Mo	Te, Re
		Maronia	Cu, Au, Mo	Re
		Myli/Esymi	Cu, Au, Mo	–
		Melitena	Cu, Mo	Re
	Chalkidiki	Skouries	Cu, Au, Mo	PGE (Pd, Pt)
	Kilkis	Vathi	Cu, Au, Mo	REE (La, Ce)
		Gerakario	Cu, Au	Sb
	Attica	Plaka/Lavrion	Mo	W
	Aegean Sea	Sardes/Limnos Island	Mo	–
		Fakos/Limnos Island	Cu, Mo	–
		Stypsi/Lesvos Island	Mo, Bi	–
Supergene fault /karst-controlled Mn-oxides	Drama		Mn	–
	NE Chalkidki		Mn	–
Fe-oxides	Kavala	Palea Kavala	Au	–
	Thasos		Au	–
Sediment-hosted, placers	Veria	Vegora	P	Ga
	Aegean Sea	Chios Island	–	Sb
	Chalkidiki-Kavala	Coastal zone	–	REE (Ce, La, Nd, Pr)

The Serbomacedonian and Rhodope metamorphic massifs comprise the crystalline basement of the Alpine orogenic belt in the Balkan peninsula and consist of amphibolite facies metamorphic rocks of continental and oceanic origin (Figure 2 and 3). They demonstrate a structural record of a late Mesozoic deformation episode overprinted by an early Cenozoic extensional deformation [8].

The deposits of the Serbomacedonian and Rhodope metallogenic provinces were formed during the final stage of the Tertiary orogenic collapse, which led to the formation of widespread Oligocene-Miocene silicic to intermediate magmatism [7,9–11]. This magmatism, considered to be part of the Cretaceous to Miocene Alpine-Balkan-Carpathian-Dinaride orogen [11], resulted from subduction and collision of the Pelagonian and Apulian microcontinents, detached from Africa in Triassic, with the European plate [12]. Slab detachment and/or roll-back was the principal mechanism, which resulted in the local ascent of asthenospheric mantle into the metasomatized mantle lithosphere and to magma generation [9,13]. Magmas were intruded to shallow depths along deep seated detachment faults, forming mafic to intermediate mantle-derived plutonic, subvolcanic and volcanic rocks of calc-alkaline, high-K calc-alkaline and shoshonitic to ultra-potassic (lamprophyric) affinities.

Figure 2. Simplified geological map of the Serbomacedonian metallogenic province in Greece, displaying the major ore deposits and prospects.

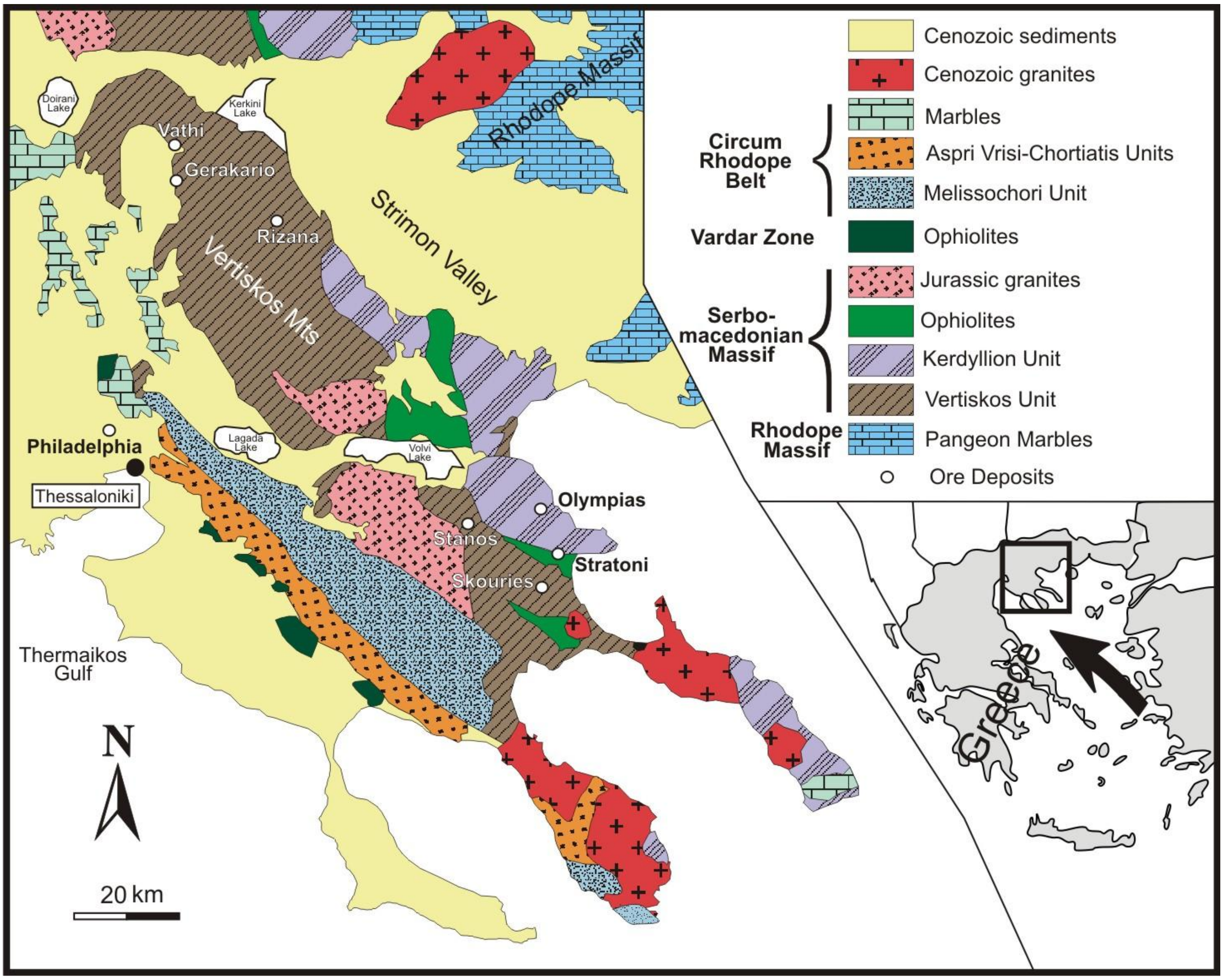
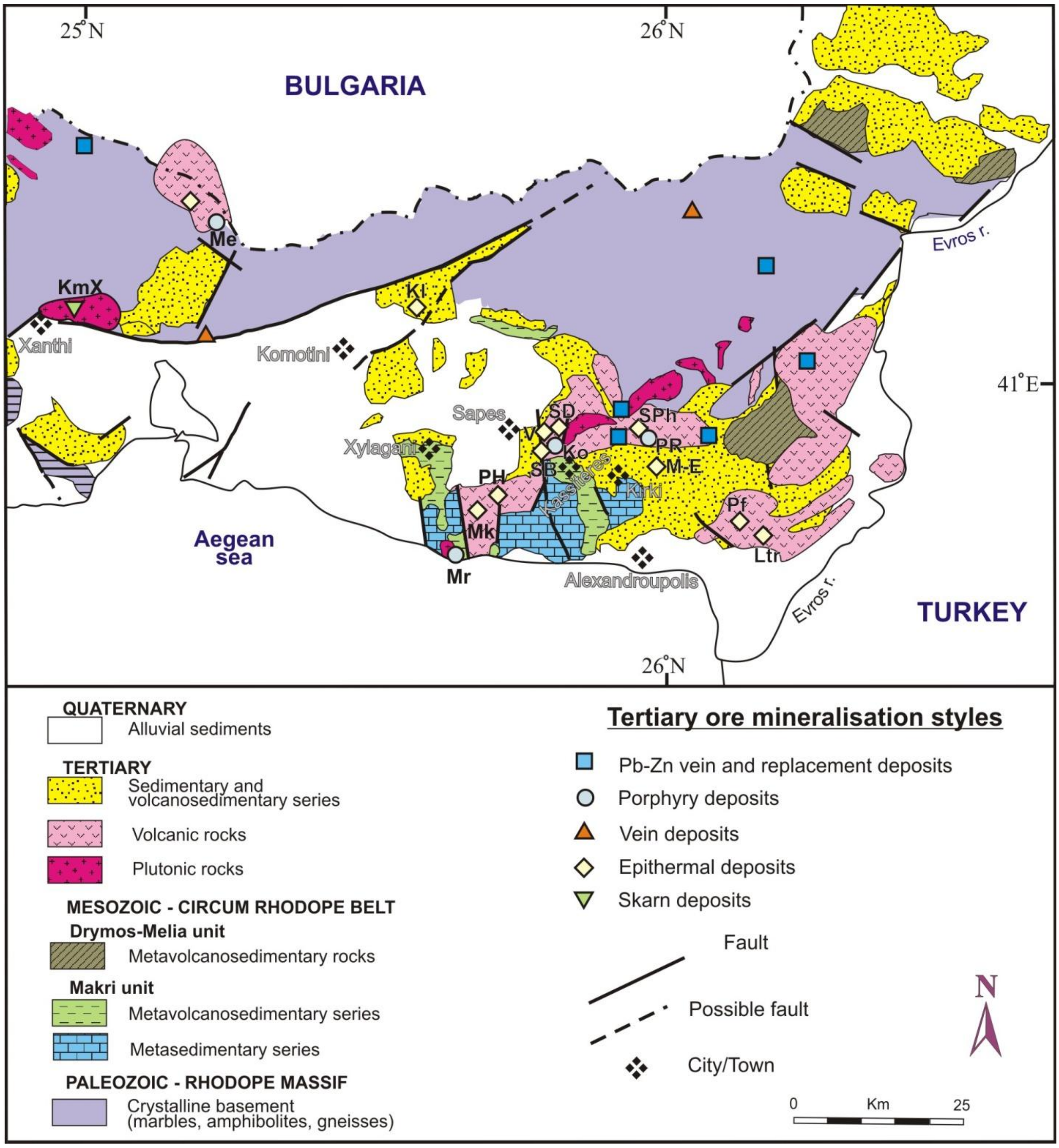


Figure 3. Simplified geological map of the Rhodope metallogenic province in Greece displaying the major Tertiary ore deposits and prospects [6,7 with modifications]. KmX: Kimmeria/Xanthi; Me: Melitena; Mr: Maronia; Ko: Konos/Sapes; SB: St. Barbara/Kassiteres; SD: St. Demetrios/Sapes; V: Viper; PH: Perama Hill; Mk: Mavrokoryfi; PR: Pagoni Rachi/Kirki; SPh: Agios Philippos/Kirki; Pf: Pefka; Ltr: Loutros; Kl: Kallyntirion; M-E: Myli/Esymi.



3. Critical and Rare Metals in Greece

3.1. Antimony (Sb)

Antimony is used for a number of industrial applications, as diodes and infrared detectors in the semiconductor manufacturing. It is alloyed with lead to increase its hardness. Antimony compounds are used in batteries, low friction metals, paints, ceramics, glass and pottery, as flame retardants in adhesives, plastics, rubber and textiles. Stibnite (Sb_2S_3) is the predominant ore mineral of antimony. China supplies over 75% of the total world production and in 2010 introduced quantitative and export licensing restrictions. Therefore antimony was recently placed in the highest risk category for future supply disruption.

In Greece, antimony is found in quartz veins mainly in the form of stibnite. One of the most important Sb occurrences is the low-sulfidation epithermal system of Kallyntirion prospect at the Rhodope metallogenic province (Figure 3), also including Pb, Zn, Cu, Au and Ag. Another significant stibnite mineralization is the shear zone-related Rizana/Lachanas deposit, Serbomacedonian province, which is related to sheeted quartz veins crosscutting gneisses and amphibolites. The mineralization is spread over an area 10 km long and 2–4 km wide, and is potential for future exploitation. In the years 1931–1938 mining operations produced 2.3×10^{-6} kg of ore consisting more than 30% Sb [14]. The estimated reserves are over 5.0×10^{-7} kg with 30%–35% Sb, in addition to small tungsten concentrations, associated with wolframite [14]. According to [15] the chemical analyses of enriched samples from Rizana/Lachanas revealed Sb content between 71.73 and 83.87 wt % (average 75.77 wt %). Other stibnite occurrences with relatively low Sb contents are located in Philadelphia/Thessaloniki, Chios Island and Gerakario/Kilkis [14].

Except from stibnite, antimony is also incorporated in numerous sulfosalts (tetrahedrite, famatinite, chalcostibite, zinkenite, bournonite, boulangerite) which are common in porphyry-, epithermal- and intrusion-related systems at the Rhodope metallogenic province, such as in Maronia, Pagoni Rachi/Kirki, Agios Philippos/Kirki, Mavrokoryfi, Pefka, Perama Hill, Sapes, Kapsalina/Thasos, Pangeon Mt. In some cases mineralized samples contain over 0.2 wt % Sb [6,7,16,17]. In addition, the galena concentrates from Lavrion, Attica, contain from 0.3 to 0.7 wt % Sb [18].

3.2. Cobalt (Co)

Cobalt has been used for a long time as a pigment in glass and porcelain industry. Recently it was classified as one of the critical metals due to its unique applications in lithium ion batteries, in resistant superalloys, in green-energy systems and in magnets [19]. Globally, cobalt is mined as a by-product of copper and nickel deposits in the Republic of the Congo-DRC (40%), in Zambia (20%), in Canada, in Australia, in Cuba, *etc*. China imports large amounts of cobalt (almost all the DRC’s production) in order to produce refined cobalt which is exported to the USA and the EU.

Greece is the major nickel supplier in EU and produces 2%–3% of the world total Ni. Nickel is mined from the laterite deposits in Lokris, Evia and Kastoria and is recovered by pyrometallurgical methods. These Fe-Ni laterites, which also contain cobalt, are mainly allochthonous and are associated with Mesozoic ophiolites. They are intercalated in Mesozoic limestones and show multistage transportation and re-deposition, responsible for a post-sedimentary redistribution of metals, resulting in Mn, Co, Ni-rich zones [20,21]. Chemical composition of different laterite occurrences in Greece shows that cobalt is mainly concentrated in the Fe-Ni-rich zones, demonstrating elevated contents which reach 0.10% in Paleochori, Grevena, 0.14% in Vermio, 0.16% in Kastoria and 0.22% in Lokris [20–22]. Co in these deposits is concentrated mainly in the mineral asbolane [22]. The metallurgical process of the Greek laterites in Larymna by LARCO, which produces Fe-Ni alloy, does not allow any Co recovering, which can be separated by hydrometallurgical treatment [23]. Consequently, Greece remains a potential region to supply the EU with significant amounts of cobalt in the future.

It should be also mentioned here that the non-economic sulfide ores hosted in the ophiolite complexes in Greece, including Cyprus-type and Fe-Cu-Ni-Co type, at Pindos and Othrys contain up to 2300 ppm Co [24].

3.3. Tellurium (Te)

Tellurium, a relatively rare metalloid, is used in manufacturing alloys and semiconductors, as well in vulcanizing rubber and in catalysts for petroleum. In alloys it improves properties like ductility and tensile strength or increase the durability and flexibility. It is added to lead to decrease the corrosive action of sulfuric acid in batteries and to improve the lead's strength and hardness. It is also used in making various types of detectors. Compounds made of Te, Cd and Hg, are excellent infrared sensitive semiconductors [25]. The use of high-purity tellurium enhances the effectiveness of the solar cell electric power generations and is very promising for future applications. Tellurium is extensively used as a coloring agent in ceramics and glasses. It is also used as a gasoline additive to reduce engine knocks in automobiles.

Almost all tellurium currently produced is obtained as a by-product of copper refining. It is estimated that the Cu deposits globally contain approximately 2.2×10^{-7} kg of tellurium reserves worldwide [25]. However, the high-grade ores are being exhausted and this may result in limitations in future tellurium supply.

In Greece tellurium is a common constituent of Cu-Au epithermal high-intermediate sulfidation type mineralizations (St. Barbara/Kassiteres, St. Demetrios/Sapes, Perama Hill, Mavrokoryfi, Pefka) and spatially associated porphyry Cu-Mo systems (Pagoni Rachi/Kirki, Konos/Sapes), in intrusion-related Au-Bi-Te systems (Palea Kavala, Pangeon Mt) of Oligocene-Miocene age at the Rhodope province, as well as in Limnos and Tinos Islands, Aegean sea (Fakos porphyry-epithermal- and Panormos intrusion-related Cu-Au-Te prospects respectively) [7,26–28]. Tellurium in these prospects is incorporated in various telluride phases, such as hessite, stützite, petzite, altaite, sylvanite, melonite, calaverite, coloradoite and tetradymite, as well as in the sulfosalt goldfieldite (tetrahedrite-group). In rare cases native tellurium is present in minor concentrations (Pefka, Tinos, Palea Kavala). The tellurium content in the mineralized samples is variable and is related with the distribution of Te-bearing minerals. According to new chemical analyses, provided here for the first time, the richest samples contain up to 40 ppm in Pagoni Rachi, 45 ppm in Perama Hill, 60 ppm in Pangeon Mt, and >1000 ppm in Pefka. Comparing with other potential Te-rich ore deposits worldwide (Boliden mining company will produce Te from the Kankberg gold mine, Sweden, with reserves of 2.8 Mt which contains 186 ppm Te in average [29]), the Pefka area is the most promising prospect for future Te exploration and exploitation in Greece.

The source rocks of the tellurides in northeastern Greek mineralizations are mantle-derived calc-alkaline (Thrace) to shoshonitic (Limnos) subvolcanic intrusions. Magmas were likely enriched in Te as a result of previous subduction of Te-bearing sediments [7].

3.4. Rhenium (Re) and Molybdenum (Mo)

Rhenium is very resistant against corrosion and is used in high-temperature superalloys for jet engines and industrial gas turbine engines. It improves the properties of tungsten and alloys in X-ray sources and in thermocouples to measure temperatures up to 2200 °C. Rhenium is also used in filaments, in chemical catalysts at petroleum industry, in space craft thrusters, in electrical contacts, in coatings, in flash lamps for photography. Radioactive rhenium is used in prevention and treatment of restenosis and liver cancer.

Molybdenum has various applications in the construction of grade and stainless steel, in chemicals such as lubricants, in the manufacturing of tool and high-speed steels, in the manufacture industry of cast iron and molybdenum metals, as well as in super alloys.

The world's highest grade molybdenum-rhenium deposit is located in Merlin at the Mount Dore ore prospect, consisting mainly of molybdenite, with minor chalcopyrite and pyrite, and is hosted within a series of altered carbonaceous metapelites and phyllites [30]. The mineralization exceeds over 1 km in length and is up to 40 m thick, to approximately 550 m from the surface. The current resources average 0.6% Mo and 10 ppm Re.

Molybdenite occurs mainly in three mineralization styles in Greece [31]: (1) Porphyry Cu-Mo and Mo ± Cu (Pagoni Rachi/Kirki, Ktismata/Maronia, Myli/Esymi, Konos/Sapes, Skouries/Chalkidiki, Melitena, Sardes/Limnos, Fakos/Limnos, Stypsi/Lesvos); (2) Reduced intrusion-hosted Mo-W systems (Kimmeria/Xanthi, Pigi/Kilkis, PlakaP/Lavrion, Serifos Island); (3) Shear zone related Cu-Au-Bi-Mo (Stanos/Chalkidiki).

A small molybdenite production was operated in Pigi in 1940–1944 with variable Mo grade, from 0.3% to 1.3% (rarely up to 10%) with an average of 0.6%–0.7% [14]. There is not any estimation about the current Mo reserves.

The porphyry Cu-Mo and Mo ±-Cu prospects of Pagoni Rachi, Maronia and Melitena, in western Thrace contain molybdenite with high to ultrahigh Re content (reaching 4.7 wt %), which are the highest concentrations of Re-in-molybdenites ever measured [31–33]. The microprobe analyses demonstrate that there is a positive correlation between Mo and Re supporting the concept that Re substitutes for Mo in the structure of molybdenite. Moreover, the very rare mineral rheniite (ReS_2) is found in the porphyry systems of the Pagoni Rachi and Konos/Sapes prospects [31,33].

Rheniite and high-Re molybdenite in these deposits precipitated under oxidizing conditions and from relatively acid hydrothermal solutions. The extremely high contents of rhenium in molybdenite at the Greek porphyry prospects could be explained by a rhenium release from the asthenospheric mantle wedge by subduction-related fluids and melts [33]. The Re-enrichment in the western Thrace molybdenites, suggest that this region should be a potential target for future Re- and Mo exploration and exploitation.

3.5. Gallium (Ga), Germanium (Ge) and Indium (In)

The rare metals gallium, germanium and indium are the most important commodities in the high-technology society, essential for electronic components. They are critical metals for the efficiency of utilization of recourses that are used and consumed in the order of millions of tones [34]. Moreover, germanium has major applications in optical materials and indium in liquid crystal displays (LCD). Presently gallium is produced as a by-product of bauxite processing and from the zinc processing residues, although the largest reserves are associated with phosphate ores [19]. Germanium and indium are recovered during the zinc production process.

The epithermal polymetallic veins of the Rhodope province are the most promising ore types for Ga, Ge and In exploitation in Greece. The Agios Philippos mine at Kirki, western Thrace, is a polymetallic vein deposit with intermediate-high sulfidation epithermal affinities and contains an unusual mineralogy consisting of several Pb-As-Cu-Bi-Sn sulfosalts. It is hosted within Eocene sediments and displays spatial relationships to Upper Oligocene rhyolite porphyry exposed at the northern part of the mining area. Wurtzite is the dominant Zn-ore mineral in Agios Philippos, along with sphalerite, and is found in the form of veinlets and granular masses. It contains considerable amounts of In (reaching 3.5 wt %) and Ga (reaching 1.6 wt %), whereas Ge is present in smaller amount (below 0.3 wt %) [35].

In Pefka/Evros the high-intermediate sulfidation epithermal mineralization is related to quartz veins hosted within andesitic and dacitic volcanic rocks. Bulk ore analyses (present study) revealed relatively high In content (up to 675 ppm), whereas Ga and Ge are low (max 17 ppm and 16 ppm respectively). Another potential deposit for future Ga exploration is the Lavrion intrusion-related deposit, especially the Pb-Zn-Cu bearing granitic dikes from Plaka deposit, where Ga reaches 326 ppm [36].

Relatively lower contents of In are indicated for the Lavrion carbonate-replacement ore bodies where sphalerite concentrates contain up to 43 ppm and the bulk Cu-pyritic ores up to 72 ppm [18]. The Polykastro/Kilkis and Molaoi/Peloponessos (Kuroko-type) and the Thermes/Xanthi and Olympias/Chalkidiki (carbonate-replacement) deposits should be also evaluated for their In, Ge and Ga potential [3].

Phosphate ores represent the largest reserves of several million tons, generally with a low Ga-content of 0.01%–0.1% [19]. The Neogene phosphate deposits of Greece contain low Ga content in general. The highest concentrations have been referred in the Vegora lacustrine basins of Vegora (Vegora-Komnina), 40 km northwest from Veria, where Ga in the phosphatic rocks reaches 15.9 ppm [37], and they cannot be considered as potential sources for future exploitation.

3.6. Rare Earth Elements (REE)

The demand for rare earth elements (REE) has been increased in the last years due to their applications in a wide range of consumer products such as automotive catalytic converters, photovoltaic systems, wind turbines, flat panel displays (cell phones, screen TVs, computers, portable DVDs), permanent magnets, hybrid and electric vehicles. They are also strategic raw materials with important defense uses in jet fighter engines, space-based satellites and communication systems. China controls approximately 95% of the global supply of rare earths and recently imposed quotas on exports in order to preserve its resources for domestic consumption. This has caused concerns in the EU, USA and Japanese markets regarding future REE supplies.

Recently it was announced that by 2013 USA will be able to meet a majority of its demands from North American sources [38]. European industry imports more than 90% of its REE needs and consumes about 30% of the global annual production [38]. The abandoned mines in Greece could relieve European industry problems [39] and this is in accordance with the recent investigation results in several areas of Greece.

Significant reserves of REE are found in the placer deposits along the coast of Northeastern Greece between the peninsula of Chalkidiki and Kavala, with 240 km coastal length [40–42]. Geochemical investigations revealed up to 8000 ppm in REE with 93.5% consisting of the light REE mainly Ce, La, Nd and Pr, with allanite being the main REE-bearing mineral phase [40]. It is very probable that the primary sources of these LREE bearing placers are located at the nearby Kavala or Pangeon Mt. intrusion-related systems. Recently, one metallurgical scoria from old smelting furnaces (possibly from Ottoman period) at the Pangeon Mt., revealed 6171 ppm La, 10,883 ppm Ce, 1062 ppm Pr, 3249 ppm Nd, 334 ppm Sm and 214 ppm Eu [43]. Further geological and geochemical research could help locate the extremely high LREE-enriched source rocks, possibly on Pangeon Mt. It should be however mentioned that the heavy REE are the more highly sought after in the world industry.

Of major importance for future REE exploration-exploitation can also be considered the bauxite deposits of Parnasos Mt, with REE contents reaching 6300 ppm [3], the Pb-Zn-Cu bearing granitic dikes from Plaka deposit in Lavrion with 428 ppm La and 976 ppm Ce [36], and the porphyry Cu-Au system of Vathi/Kilkis with relatively high content of La (500 ppm) and Ce (715 ppm) [this study].

3.7. Platinum Group Elements (PGE)

An increased worldwide usage of platinum group elements (PGE = Pt, Os, Ir, Pd, Ru, Rh) has been observed during the last decades, due to their unique physical and chemical properties that make them critical to many emerging technologies. Consequently they have become essential commodities and are considered as strategic metals because of their specialized applications in chemical, petroleum, high-tech, electrical, medical, and aerospace industries [19]. They also have important uses in environmentally related technologies, such as automobile catalytic converters and fuel cells. The global reserves of PGE are mainly concentrated in South Africa, followed by Russia and Canada, where they are by-products of nickel processing [19].

In Greece there are two target mineralization groups that contain elevated PGE grades: Porphyry-type deposits and chromite ores. A significant Pd-Pt enrichment has been determined in the Skouries porphyry Cu-Au deposit of NE Chalkidiki peninsula, in the copper ore, as well as and in the flotation concentrates [44,45]. The Pd content in the mineralized samples (stockwork veinlets from the potassic alteration and from the oxidation zones) ranges from 45 to 490 ppb and up to 3300 ppb in chalcopyrite concentrates, suggesting that Pd (in the form of the telluride merenskyite) is mainly associated with chalcopyrite [44]. The leaching process of the final concentrate (21 wt % Cu, 22 ppm Au, 2.4 ppm Pd, 0.04 ppm Pt) resulted in the recovery of 96.6% Au, 97.7% Pd and 100% Pt [45]. Since the intended investment in the Skouries deposit focuses on gold and copper mining and metallurgy, the recovery of Pd and Pt has a positive economic potential for a future sustainable development.

The second target mineralization group for PGE exploration in Greece is associated with the ophiolites of Veria, Pindos and Skyros Island. High PGE concentrations, reaching 25 ppm total PGE's (Os = 7400, Ir = 6020, Ru = 9700, Rh = 310, Pt = 760, Pd = 750, all in ppb) were determined in chromitites hosted in the Veria ophiolites, northern Greece [46,47]. These elevated PGE contents are associated with a great number (>100) of different PGM grains, mainly Os-Ru-Ir-Fe alloys, reaching 1 mm in size [47]. They are concentrated along a shear zone of strongly brecciated chromite ore. In Korydallos area, Pindos the PGE-mineralization is associated with several PGM grains (Pd-Cu alloys, sperrylite, Pt-Fe-Ni alloys, naldrettite, bismuthotelluride, native Au, *etc.*) [48]. The total PGE + Au content in the chromitites with low Cr# chromian spinel is 28 ppm (Pt = 17100, Pd = 7860, Ru = 2100, Rh = 1140, all in ppb) among the highest ever measured in ophiolitic chromitites worldwide, and the highest ever mentioned for chromitites from Greece [48]. It is assumed that a sulfur bearing melt played an important role in scavenging the PGE + Au content of the silicate magma from which chromian spinel had already started to crystallize [48].

The ophiolitic complexes of Thessaloniki (Triadi, Vassilika) and Chalkidiki (Vavdos, Gerakini-Ormylia) contain relatively low PGE contents (<0.5 ppm) and so they are not of economic significance [49].

4. Conclusions

The Serbomacedonian and Rhodope metallogenic districts in Greece (Figure 2 and 3) are among the richest ore provinces in Europe, and can be an exploration target in the near future, especially for critical and rare metals. The epithermal- and porphyry-type mineralizations, and the reduced intrusion-related systems of Northeastern Greece could produce Sb, Te, Mo, Re, Ga, In and PGE as by-products, along with base metals, Au and Ag, if the mining and extractive activities will start. In addition, laterites and bauxites of central and northern Greece which are mined for Ni and Al respectively, contain significant amounts of Co or REE and the processing industries should focus on the probability for a future exploitation. The chromitites of northwestern Greece contain significant concentrations of PGE, whereas the coastal sediments between Chalkidiki and Kavala are characterized by REE geochemical anomalies which may be related with the Kavala and Pangeon Mt reduced intrusion-related system, although this has to be clarified.

The mineral wealth of Greece can provide solutions to the challenge of a sustainable and a competitive economy. The rational exploitation of the ore deposits will offer significant developmental benefits and it will enable Greece to strengthen its global role in the mining industry. A new mining policy must focus on the more effective exploitation of the mineral resources, the improvement of the environmental performance, the safe operation of the mines and the accidents prevention, the mining waste management and the recycling process. However, when considering the exploitation of critical and rare metals, we have to keep in mind that this process is long, entails a high risk and requires large investments.

Acknowledgments

Special thanks are due to Basilios Tsikouras and two anonymous reviewers for carefully reviewing the manuscript and for their constructive comments and suggestions, resulting in significant improvement of this paper.

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