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A Review on the Critical and Rare Metals Distribution throughout the Vertiskos Unit, N. Greece

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Abstract: The undisturbed supply of critical and rare metals is crucial for the robustness and sustainability of the advanced technological industry of the European Union (EU). Since 2008, several EU funded research projects have highlighted the domestic exploration and exploitation possibilities of some specific European regions. Throughout the SE Europe the Serbo-Macedonian metallogenic belt (SMMB) in northern Greece is highlighted as one of the most promising exploration targets. The Vertiskos Unit which forms the geological basement of the SMMB in Greece hosts several Oligocene-Miocene ore deposits and mineralization occurrences. Most of these ore mineralizations are reported being enriched in metals such as Sb, Bi, Te, Co, REEs and PGMs. Thus, in this paper we review the critical and rare metal endowment of these ore mineralizations in an effort to summarize and highlight the exploration potential of the region.

Keywords: critical and rare metals; rare earth elements; ore mineralization; Vertiskos Unit; Serbo-Macedonian metallogenic province; sustainable development; exploration

1. Introduction

One of the most crucial factors affecting the operations and the sustainability of the global economy is the undisturbed and steady supply of the high technological industry in critical and rare metals. This is expressed through a constant need and unrest to meet the industrial production supply demands and the technological needs of the societies of the advanced and advancing countries. During the beginning of the 21st century the importance of this relation is highlighted by the reshape of the traditional trading networks, under unstable political and economic environment [1]. Moreover throughout the advanced countries recently appeared a raging concern on the ethics of critical and rare metals exploitation, as well as an effort to support the supply demand with domestic production trying to achieve a certain level of self-sufficiency [1,2]. This, resulted in a thorough investigation through several research projects of the critical and rare metals exploration and exploitation potentials, as well as in the development of breakthrough technological applications such as the exploitation of industrial by-products (e.g., red mud) and the recycling of e-wastes [3–5]. Regarding the mining sector exploration geology is the key factor controlling the successful outcome of the investigation of the critical and rare metals potentials [6,7].

The European Union (EU) since 2008 has steadily support several EU funded research projects on the domestic exploration and the economic geology of all mineral resources as they are summarized at PERC code [8–11]. The critical and rare metals definitions are mainly derived from the technological, economic, dependency, and supply risk impact that they have on the modern high technological industry and not from the natural occurrence of these metals [12–14]. According to the EU Growth Commission as critical metals are mentioned the antimony (Sb), beryllium (Be), bismuth (Bi), cobalt (Co), gallium (Ga), germanium (Ge), hafnium (Hf), indium (In), niobium (Nb), scandium (Sc), tungsten (W), tantalum (Ta), the Heavy Rare Earth Elements (HREEs), the Light Rare Earth Elements (LREEs), and the Platinum Group Metals (PGMs) [15]. In addition, as critical natural mineral resources along with the above mentioned metals are mentioned the following: baryte, borate, coking coal, fluorspar, helium, magnesium, phosphorus, the natural graphite and rubber, the phosphate rocks, and the silicon metal [15]. In contrast to the critical metals, for the definition of rare metals the natural occurrence in technically and economically exploitable worthy concentrations and the monetary acquisition cost are mainly considered [14]. Thus, as rare metals are characterized the following: rhodium (Rd), platinum (Pt), palladium (Pl), iridium (Ir), osmium (Os), rhenium (Re), ruthenium (Ru), germanium (Ge), beryllium (Be), gallium (Ga), indium (In), tellurium (Te), mercury (Hg), bismuth (Bi), gold (Au), and silver (Ag) [7,16].

These metals have numerous industrial applications. Their use in alloys enhances the characteristics of the final products. They are used in the manufacture of diodes, infrared detectors, semiconductors, batteries, low friction metals, paints, ceramics, flame retardants, resistant super alloys, magnets, catalysts, liquid crystal displays, photovoltaic systems, wind turbines, flat panel displays, and hybrid and electric vehicles. Furthermore, most of them are also used in the military industry. Thus sometimes they are also called strategic metals, as they are used for example in jet fighter engines and space-based satellites [17].

The numerous ancient mining and metallurgical remains throughout northern Greece emphasize that from the beginning, since Early Bronze age, the ancient Greeks had realized the importance of the mineral wealth exploitation [18,19,21]. This activity continued up to the pre-industrial and industrial eras mainly by producing gold, silver, copper, lead, zinc and iron [21]. During the modern era the exploitation is restricted to lead, and zinc, however, significant possibilities have been recently raised for gold and copper exploitation and metallurgy [22–24].

Besides the well defined occurrence of base and precious metals throughout northern Greece, various critical and rare metals have been also reported so far [25–29]. Although several published researches highlight their presence, a more thorough study needs further and in detail examination of their distribution and correlation with the regional magmatism, the hydrothermal alterations, and ore geology. In this contribution we present briefly some recently published and literature data, mainly on Sb, W, Te, Bi, Co, Au, Ag, REEs (La, Ce, Gd), and PGMs (Pb, Pt, Ru, Ga) obtained from selected mineralizations (Vathi, Gerakario, Laodikino, Rizana, Stephania, Koronouda/Kilkis; Stanos, Chalkidiki/NE Chalkidiki) using ICP-MS bulk rock analyses. These data are combined with published information on the geology, mineralogy and geochemistry of several critical and rare metallic elements found in the Tertiary Serbo-Macedonian metallogenic belt in Greece. These data will contribute significantly to the knowledge about the mode of occurrence of critical metals in Vertiskos, for a possible future exploration and exploitation.

2. Geological and Metallogenic Overview

2.1. Geological Setting

The Tertiary Serbo-Macedonian metallogenic belt spreads across the center of the Balkan Peninsula following the Serbo-Macedonian Massif (SMM). It has an elongated and southeastwards curved shape. It is located to the west of the Late Cretaceous (Apuseni-Balkan) Banatite metallogenic belt and towards the south it borders to the east with the Rhodope metallogenic belt [30]. In northern Greece the Oligocene-Miocene Serbo-Macedonian metallogenic belt (SMMB), along with the

adjacent Rhodope metallogenic province, host the majority of the ore bearing intrusions and intrusion-related ore deposits of Greece (Figure 1) [22].

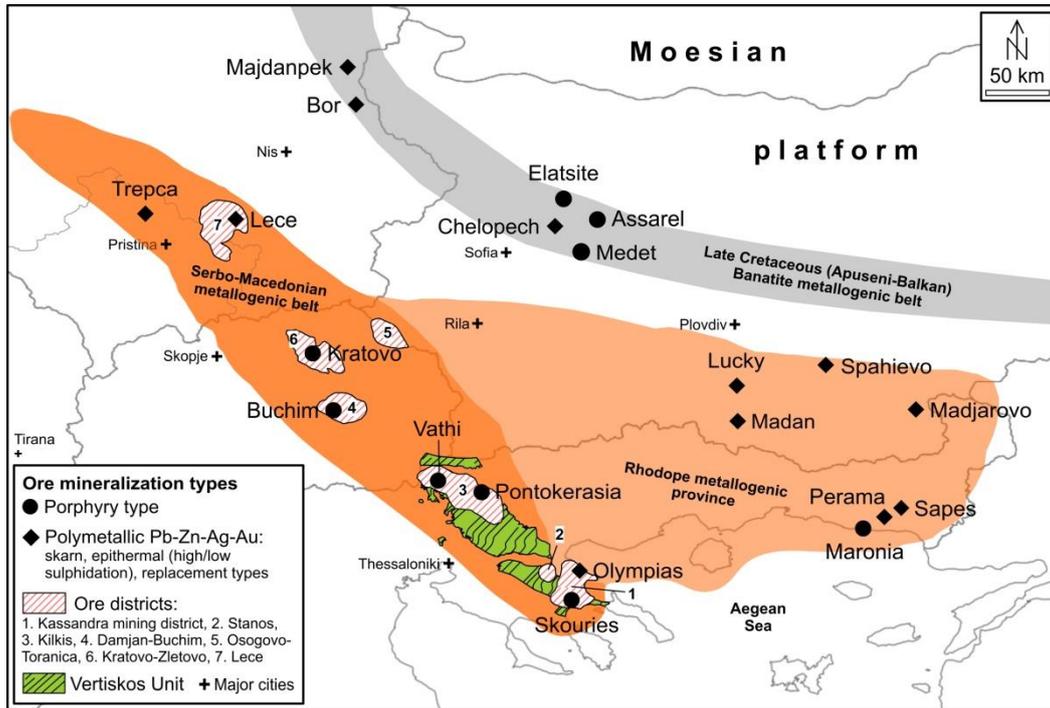


Figure 1. Schematic map showing the spatial development of the SMMB and the Rhodope metallogenic province across the SE Balkan Peninsula. The major ore districts of the SMMB are highlighted (modified after; [22,30,40,41]).

The metamorphic rocks of the Vertiskos Unit build up the largest part of the complex tectono-magmatic terrain of the SMM and consequently they form the geological background of the SMMB (Figure 1) [31–33]. The Vertiskos Unit borders to the east with the Kerdyllion Unit of the Rhodope Massif along the Kerdyllion low angle detachment fault zone [31], and to the west with the Units of the Circum Rhodope belt [34,35]. Back-arc crustal stretching and unroofing characterize the Cenozoic geotectonic evolution of the Vertiskos Unit [30,32]. These complex geotectonic processes favored the development of highly mineralized magmas and facilitated the intrusion of numerous magmatic rocks within the upper crust creating several ore mineralizations [22,23,25,33,36]. Initially, these metallogenic events were structurally controlled by Eocene-Oligocene detachment and supra-detachment faults which favored the magmatic and hydrothermal fluid circulation. Later on, during Oligocene-Miocene, shear zones and normal and strike-slip faults further enhanced this circulation [33,34]. During Pliocene-Holocene these structural mechanisms were evolved to the active tectonic regime [37].

2.2. Metal Endowment

The Vertiskos Unit hosts several porphyry, epithermal, skarn/carbonate replacement, and intrusion-related vein ore types which are hosted or associated with the Oligocene-Miocene intrusions [25] (Figure 2). Spatially these ore mineralizations are mainly distributed along NE Chalkidiki, to the south, and in the Kilkis region, to the north [25,38]. At the northern part of the Kilkis ore district are hosted mainly porphyry ore deposits (Figure 2a). Towards the south of the district are found mainly intrusion related ore mineralization and sparse Tertiary magmatic rocks (Figure 2b) [33]. The NE Chalkidiki region hosts the Kassandra mining district which spreads both at Vertiskos and Kerdyllion Units (Figure 2c). Carbonate replacement ore mineralization types

characterize the northern part of the district, while the southern part hosts mainly porphyry ore deposits [25,38].

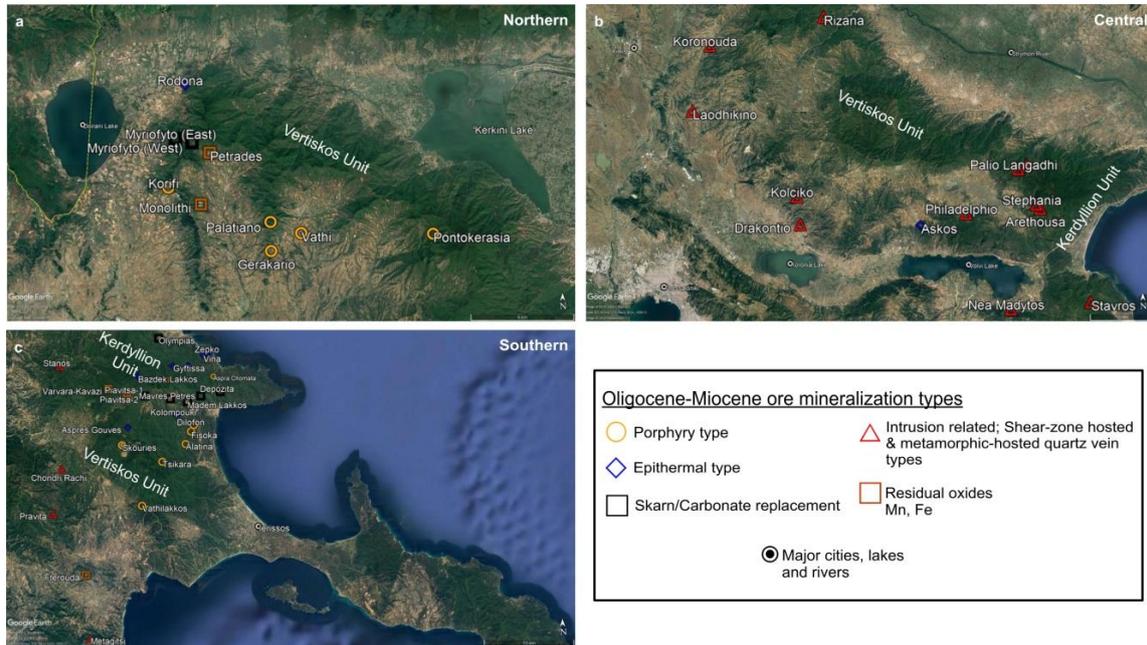


Figure 2. The spatial distribution of the ore mineralization types across the northern, central and the southern part of the Vertiskos Unit of the Serbo-Macedonian Metallogenic Belt in northern Greece. The ore deposits and ore mineralization occurrences of the adjacent Kerdyllion Unit are also displayed (modified after [25,40] and references therein).

Table 1 summarizes the metal endowment of the Vertiskos Unit. Most of these ore mineralizations were at the past or could be in the future primary targets for base (Cu, Pb, Zn, Fe, Mn) and precious metals (Au, Ag), while few of them consist exploration and exploitation targets at the moment (e.g., Fisoka, Skouries). It should be mentioned that since ancient times the southern part was subjected to significantly more extent exploration and exploitation activities.

By taking into consideration the most modern exploration techniques the northern part is a greenfield area, especially in respect to the critical and rare metals occurrences. In recent years, several authors have highlighted the critical and rare metals potential of selected Oligocene-Miocene ore bearing intrusions deposits in the Vertiskos Unit [22,25,28,39–42]. Nevertheless, the distribution and the relation of these metals with the ore minerals, the magmatic rocks, the regional tectonics and the hydrothermal alterations need a more thorough investigation.

3. Critical and Rare Metals throughout the Vertiskos Unit

The majority of the porphyry and intrusion related ore mineralization types across the Vertiskos Unit are enriched in critical and rare metals (Table 1). The enrichment for several of these ore mineralizations occurrences have been manifested by chemical analysis of whole-rock mineralized surface and core samples [39,40,42]. In addition, minor research has been done on the analysis of the mineral geochemistry of several ore mineralizations by using scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) [43,44]. However, the study of the mineral geochemistry by using electron probe micro analysis (EMPA) and laser ablation inductively coupled plasma mas spectrometry (LA-ICP-MS) is quite restricted to our knowledge. Relative examples are the recent geochemical studies of the Stanos shear-zone hosted Cu–Au–Bi–Te mineralization and Skouries Cu-Au-porphyry ore deposit [45,46].

Table 1. Characteristics of selected critical and rare metal bearing ore mineralization occurrences from the Vertiskos Unit.

Deposit Name	Ore & Mining Districts	Commodities	Mineralization Type	Deposit Style	Critical & Rare Metals	References
Vathi	Kilkis	Cu, Au, Ag, Fe, Mo, U	Porphyry	Sub-alk ¹ Cu-Au	W, Ga, Te, Bi, La, Ce, Nd, Gd, Au, Ag	[42]
Gerakario	Kilkis	Cu, Au	Porphyry	Sub-alk ¹ Cu-Au	Sb	[47,48]
Skouries	Kassandra	Cu, Au, Mo	Porphyry	Sub-alk ¹ Cu-Au	Pd, Pt, Ru, Te, Bi	[38,46,47]
Stanos	Stanos	Cu, Au, Ag, Bi, Te	Intrusion related		Au, Ag, Bi, Te	[45]
Laodikino	Kilkis	Cu, Au, Fe, As, Zn, Pb, Te, Co, Ni, Sb, Bi	Intrusion related	Shear-zone hosted &	Au, Te, Co, Sb, Bi	[44]
Rizana	Kilkis	Sb, W	Intrusion related	Metamorphic-hosted quartz vein	Sb, W	[49]
Stephania	Kilkis	Cu, Ag, Au, Bi, Te, Co, Ni, As	Intrusion related		Ag, Au, Bi, Te, Co	[25,45]
Koronouda	Kilkis	Cu, Au, Ag, Zn, Pb, Fe, As, Ni, Co, Sb, Te, Bi	Intrusion related		Au, Ag, Co, Sb, Te, Bi	[25,45]

¹ Sub-alk = Sub-alkaline.

Most of these ore mineralization occurrences lack accurate grades of measured and indicated reserves for base and precious metals, as they were never constitute an exploration target during 20th and 21st centuries. An exception is the Skouries Cu-Au porphyry deposit which contains measured and indicated resources of 289.3 Mt grading 0.58 g/t Au and 0.43% Cu [24]. Platinum and palladium contents from mineralized samples range respectively from 45 to 490 ppb and up to 3300 ppb and are mainly associated with chalcopyrite [39]. It should be mentioned that a light enrichment in PGMs is manifested also for other porphyry intrusions of the Vertiskos Unit (e.g., Pontokerasia, Fisoka) [39].

For the Vathi Cu-Au-Mo-U porphyry deposit old resources estimations based on shallow drillings suggested indicated resources of 15 Mt grading 0.8 g/t Au and 0.3% Cu [48]. A more recent study [40,42] showed that the highest critical and rare metals contents obtained from surface oxidized samples include up to: 6.996 ppm Au, 4.2 ppm Ag, 200 ppm W, 24.5 ppm Ga, 0.81 ppm In, 3 ppm Te, 22.06 ppm Bi, 500 ppm La, 715 ppm Ce, 211 ppm Nd, 13.67 ppm Gd. In addition, the highest contents which were also measured reach up to 9297 ppm Cu, 340.7 ppm Mo, 328.6 ppm U, 1399.48 ppm Pb, and 234 ppm Zn.

The ore mineralization at the Sb-bearing shear-zone hosted deposit of Rizana is hosted in quartz veins [25,49]. The mineralization spreads in an area covering approximately 30 km². During 1930s 2.3×10^{-6} kg of ore were exploited with more than 30% Sb, while the indicated reserves are over 5.0×10^{-7} kg with 30–35% Sb [25]. Wolframite is also found within the ore assemblage [49]. Stibnite also occurs at the Gerakario Cu-Au porphyry deposit hosted in peripheral, to the main porphyry intrusion, quartz veins [25]. These veins are crosscutting the adjacent gneisses and are attributed to an epithermal stage which followed the porphyry stage [25]. Probable reserves indicate 28 Mt of ore with 0.9 g/t Au and 0.4% Cu, but no data exist for the Sb reserves [48].

The Stanos, Laodikino, Stephania and Koronouda ore mineralization are hosted in metamorphic quartz veins within shear zones crosscutting the SMM gneisses. Although their mineralogical assemblages resemble those of other shear-zone hosted deposits worldwide, they do not belong to the orogenic gold type of ore deposits [45]. The regional metallogenic models, the salinity of the hydrothermal fluids, as well as the enrichment they share in common in chalcophile elements (e.g., Au, Bi, Te, Co), suggest that their genesis is related to buried magmatic intrusions.

A wide variety of Te-Bi-sulphosalts and tellurides are also mentioned in various mineralizations including bismuthinite, tellurobismuthite, aikinite, hessite, petzite, altaite, and sylvanite [25,43,44]. Although there are several other minor ore mineralizations enriched in Sb, Au, Ag, Bi, Co, Ni (e.g., Philadelphio, Nea Madytos, Kolchiko), there is a general lack of information on their spatial morphological characteristics and their reserves [25,43,45]. Finally, the REEs found in the coastal placer deposits of Chalkidiki highlight the enrichment of the magmatic rocks of the broader region in these metals [25].

4. Conclusions

The critical and rare metals are integral and the most significant components of the modern high technological industry. This is demonstrated by their numerous uses in industrial manufacturing.

Complex geotectonic and magmatic processes characterize the Tertiary metallogenic processes at the Vertiskos Unit in northern Greece [33]. These processes inherited a significant metal enrichment in base and precious, as well as in critical and rare metals [33]. The most significant ore mineralizations are found in Vathi, Gerakario, Skouries, Stanos, Laodikino, Rizana, Stephania, and Koronouda which are enriched in Sb, W, Te, Bi, Co, Au, Ag, REEs (La, Ce, Gd), and PGMs (Pb, Pt, Ru, Ga). Thus, this creates a future economic potential, and adds to the sustainability of the present and future exploration and exploitation projects in Northern Greece [21,24,47].

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