

Review

On the Origin of New and Rare Minerals Discovered in the Othrys and Vermion Ophiolites, Greece: An Overview

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Abstract: In this contribution we review the mineralogical characteristics of five new and rare minerals discovered in the Othrys and Vermion ophiolites located in Greece, with the aim to better understand their origin. Three new minerals, namely tsikourasite $\text{Mo}_3\text{Ni}_2\text{P}_{(1+x)}$ ($x < 0.25$), grammatikopouosite NiVP and eliopoulosite V_7S_8 , were found in the chromitite from the Agios Stefanos deposit, whereas arsenotučekite $\text{Ni}_{18}\text{Sb}_3\text{AsS}_{16}$ was discovered in the Eretria (Tsangli) chromium mine, located in the Othrys ophiolite complex. The formation of the new phosphides tsikourasite and grammatikopouosite and the sulfide eliopoulosite from Agios Stefanos took place after the precipitation of the host chromitite. Very likely, they formed at lower pressure in an extremely low $f\text{O}_2$ and reducing environment during the serpentinization that affected the host ophiolite. The origin of arsenotučekite in chromitites coexisting with Fe–Ni–Cu-sulfide mineralization and magnetite at the Eretria (Tsangli) mine, is believed to be related to a circulating hydrothermal system. The most salient feature of theophrastrate $\text{Ni}(\text{OH})_2$ and associated unnamed $(\text{Ni},\text{Co},\text{Mn})(\text{OH})_2$ with a varying compositional range and a concentrating development, as successive thin layers, composed by fine fibrous crystals. The extremely tiny crystals of these hydroxides and the spatial association of mixed layers of Ni-silicides with theophrastrate may reflect the significant role of the interaction process between adjacent layers on the observed structural features. The scarcity in nature of the new minerals reviewed in this paper is probably due to the required extreme physical-chemical conditions, which are rarely precipitated.

Keywords: arsenotučekite; eliopoulosite; grammatikopouosite; tsikourasite; theophrastrate; origin; ophiolites; Greece



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1. Introduction

Special attention has been paid to synthetic double or polymetallic phosphides including NiCoP and FeNiP , due to their low price and easy access, as a hot topic in photocatalysis [1,2]. Natural phosphides, i.e., minerals containing phosphorus in a redox state lower than zero, are very uncommon minerals. Very few have been reported in terrestrial occurrences. They are mainly found associated with chromitites [3–9]. Small grains, approximately 15 μm across, with an approximately composition $(\text{Ni},\text{Fe})_5\text{P}$, were first noted in two chromite deposits hosted in the mantle peridotite of the Alapaesk ophiolite, Russia, and the Gerakini-Ormylia ophiolite, Greece [6]. Additionally, unnamed phosphides of Ni, Co, V, Mo, and one sulfide of vanadium were described in the abandoned chromite mine of Agios Stefanos of the Othrys ophiolite complex in Greece [4,5]. These were unexpected discoveries that raised questions concerning the environment of their formation. In this article, we present a review of the new minerals discovered in the Greek ophiolites of Othrys and Vermion. We describe their mineralogical characteristics and evaluate relevant mineralogical data from the literature. Our aim is to constrain their field of stability and the conditions of their formation.

2. Review of our Mineralogical Discoveries

Recently, three new mineral species, tsikourasite, $\text{Mo}_3\text{Ni}_2\text{P}_{(1+x)}$ ($x < 0.25$) [7]; eliopoulosite, V_7S_8 [8]; and grammatikopoulosite, NiVP [9], found in the chromite mine of Agios Stefanos (Figure 1), were approved by the Commission of New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA) (IMA 2018–156, 2019–090 and 2019–96, respectively). In addition, we defined arsenotučekite, $\text{Ni}_{18}\text{Sb}_3\text{AsS}_{16}$, discovered in the abandoned Eretria (Tsangli) chromium mine, located in the eastern portion of the Othrys ophiolite complex (Figure 1). It was approved as IMA 2019–135 [10]. Theophrastite, $\text{Ni}(\text{OH})_2$, was discovered in a small occurrence of metamorphosed Fe–Ni laterite in the Vermion ophiolite (Figure 1). It also was approved as a new mineral (IMA 1980–59). Theophrastite is named after Theophrastus (ca. 371–286 BCE), a Greek philosopher and mineralogist and author in 315 BC of the first mineralogy textbook [11]. Theophrastite is commonly associated with hydroxides, such as $(\text{Co,Mn,Ni})(\text{OH})_2$ and silicate minerals (mostly Ni-rich serpentine), garnet, vesuvianite and magnetite, all cross-cutting earlier deformed assemblages, suggesting a common origin in space [12]. Recently, theophrastite was described in association with aggregates of hydroxylated nickel carbonates, such as zaraitite $[\text{Ni}_3\text{CO}_3(\text{OH})_4 \cdot 4\text{H}_2\text{O}]$, otwayite $[\text{Ni}_2\text{CO}_3(\text{OH})_2 \cdot \text{H}_2\text{O}]$, nullaginite $[\text{Ni}_2\text{CO}_3(\text{OH})_2]$ and hellyerite $[\text{NiCO}_3 \cdot 6\text{H}_2\text{O}]$ aggregates in partially serpentinized dunite at Fujiwara, in the Sanbagawa metamorphic belt of high-pressure intermediate type, Japan [13]. This assemblage was described in a composite grain composed of millerite, heazlewoodite, awaruite and magnetite, suggesting that the constituent minerals probably formed together with during low-temperature alteration or the weathering of serpentinites and related nickel-rich ores [13]. The occurrence of the minerals tsikourasite, eliopoulosite and grammatikopoulosite in the same sample points to their formation in the same strongly reducing environment. Possible environments are: (i) low-temperature alteration of chromitite during the serpentinization process; (ii) high-temperature reaction of the chromitites with reducing fluids at a mantle depth; (iii) a lightning strike at the site of discovery or (iv) a meteorite impact [7–9]. The probability of intercepting a fragment of a meteorite or a fulgurite in the Othrys ophiolite during our sampling of the chromitite seems very unlikely, despite the fact that V-bearing sulfides and phosphides are common in meteorites [3,14]. The origin of the above new minerals discovered in Greek chromitites is not fully understood, although the presence of a highly reducing fluids containing dissolved H_2 derived from the reduction of H_2O during serpentinization has been suggested [4–6]. A low-temperature process (serpentinization, alteration or weathering) was proposed to explain the precipitation of phosphides in ophiolitic chromitite [4–6].

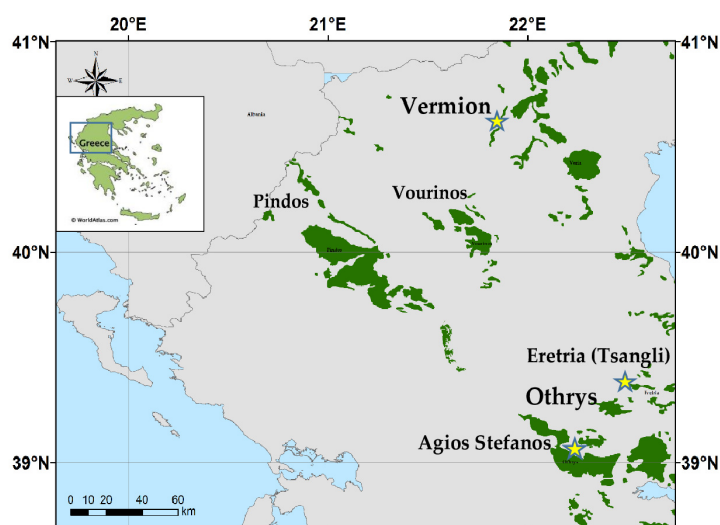


Figure 1. Location of the major ophiolites in central-north Greece, including Vermion and Othrys complexes, showing the deposits in which the new minerals have been discovered (yellow stars).

3. Characterization of the New Minerals

The new minerals overviewed in this contribution were analyzed in several laboratories using different techniques. Details for the physical and optical properties, chemistry, X-ray powder diffraction data, of the new minerals along with a brief description of the methodologies used are available in the relevant publications [4–11].

All rare minerals in the Othrys ophiolite complex were discovered in heavy mineral concentrates from approximately 10 kg massive chromitite, which were obtained in the laboratories of SGS Mineral Services, Canada, using the technique described by Ifandi et al. [4], Zaccarini et al. [5,7,10] and Bindi et al. [8,9]. Polished sections of heavy minerals were investigated using a JEOL JXA-8200 electron microprobe, installed in the E. F. Stumpfl laboratory, Leoben University, Austria, operating in WDS (wavelength dispersive spectrometry) mode. Major and minor elements were determined at 20 kV accelerating voltage and 10 nA beam current, with 20 s as counting time for the peak and 10 s for the backgrounds. The beam diameter was about 1 µm. The same instrument was used to obtain the back-scattered electron (BSE) images, as reported by Zaccarini et al. [5,7,10] and Bindi et al. [8,9]. Single-crystal X-ray data were obtained in the laboratory of the University of Florence, Italy, using an Oxford Diffraction Xcalibur diffractometer equipped with an Oxford Diffraction CCD detector with graphite-monochromatized MoK α radiation ($\lambda = 0.71073$ Å) on crystal fragments hand-picked from polished sections under a reflected light microscope [5–10].

Polished thin sections of metamorphosed Ni laterite were investigated using a reflected light microscope and a scanning electron microscope (SEM), at the University of Göttingen, Germany, using an ARL-SEMO electron microprobe. Analytical conditions were 15 kV accelerating voltage, 150 nA beam current. X-ray diffraction data for theophraustite, were obtained using a polycrystalline sample scanned with a Philips diffractometer used with a monochromator line 104 CuK α radiation, at the University of Göttingen, Germany, Ni filter, Si internal standard. Details for the physical and optical properties, chemistry and X-ray powder diffraction data of the above new minerals are available in relevant publications [4–11].

4. Geological Outline and Brief Description of the Mineralization

4.1. Geology of Othrys and Vermion Ophiolites

The dismembered Othrys ophiolite complex is a component of the Upper Jurassic to Lower Cretaceous Tethyan ophiolite belt, which includes the Pindos and Vourinos complexes (Figure 1). These ophiolites are characterized by petrological and geochemical features typical of both Mid-Ocean Ridge (MOR) and Supra-Subduction Zone (SSZ)-type associations (fore-arc and back-arc ridges) and have been a topic of extensive investigation in previous publications [15–17].

The Othrys ophiolite includes tectonically separated chromite deposits, namely Eretria (Tsangli), Domokos and Agios Stefanos (Figure 1) [18,19]. Tsikourasite, eliopoulosite and grammatikopoulosite have been found in massive chromitite hosted in the mantle sequence (plagioclase lherzolite, harzburgite, and minor harzburgite-dunite) at the abandoned mine of Agios Stefanos (Figure 1). It is located at the contact between mantle tectonite and crustal sequence that is intruded by several dykes of gabbro [4–9].

The Vermion ophiolite, Upper Jurassic–Lower Cretaceous in age, is mainly composed of mantle peridotites consisting of harzburgite, dunite, and orthopyroxene-bearing dunite, and, to a lesser extent, of crustal magmatic rocks (pyroxenites and gabbros) outcropping along the eastern margin of the so called Pelagonian massif [15–25]. Small (1 m $\times$ 15 m) lens-like of redeposited Fe–Ni occurrences, metamorphosed to amphibolite facies are found in the Vermion ophiolite, which are overlain by Cretaceous limestones [26,27]. Due to intense tectonism, the Fe–Ni laterite occurrences may be entirely enclosed within serpentinized harzburgites [27,28].

4.2. Products of Mineralization in the Othrys and Vermion Ophiolites

Arsenotučekite was found in the Eretria (Tsangli) chromite deposit, in which the mineralization led to spherical, lenticular or irregular bodies, variable in size. The host rock is a moderately depleted harzburgite and no systematic relation exists between the distribution or size of the orebodies to the size of host masses [18,19]. A salient feature of the Eretria (Tsangli) mineralization is the occurrence of massive Fe–Ni–Cu-sulfides, consisting of pyrrhotite, chalcopyrite and minor Co-bearing pentlandite, at the peripheral parts of the podiform chromite bodies in association with magnetite, hosted in serpentinized harzburgites [18,19].

In addition, at the Agoriani area, located about 8 km west of Domokos in the western part of the Othrys complex, irregularly shaped dikes and veins of gabbro and gabbroic intrude the plagioclase lherzolite. In this area, the presence of an unusual apatite-magnetite occurrence found along a shear zone at the contact between lherzolite and a relatively large (50 × 250 m) of fine-grained body of gabbro, was documented [20,21]. The chromite composition of the Othrys ophiolite chromitites that host the new minerals has been classified as magnesiochromite, although its composition shows a wide variation [4–10]. The contents (wt.%) of the major oxides are the following: Cr₂O₃ 44.96–51.64, Al₂O₃ 14.18–20.78, Fe₂O₃ 6.72–9.26, MgO 13.34–16.84 and FeO 8.3–13.31. The amounts (wt.%) of the trace elements are comprised in the following ranges: MnO 0.33–0.6, TiO₂ 0.03–0.23, V₂O₃ 0.04–0.3, NiO 0.07–0.24 and ZnO up to 0.07 [4–10]. The Cr stable isotope data in all chromitite samples from the Othrys complex have shown slightly positive $\delta^{53}\text{Cr}$ values (average + 0.043 ± 0.03‰) [25].

In addition, the platinum-group element (PGE) and gold content in chromitites from the Othrys complex is low, being invariably less than 500 ppb [22]. Nevertheless, several platinum-group minerals (PGM), such as laurite (Ru,Os)S₂, erlichmanite (Os,Ru)S₂, irarsite IrAsS, platarsite PtAsS, hollingworthite RhAsS, merenskyite (Pd,Pt)(Te,Bi)₂, cooperite-braggite (Pt,Pd,Ni)S, Pd–Cu–Pt alloys, Ru–Os–Ir–Ni alloys and Pd–Sb–Cu phases, have been identified [23,24].

The sulfide mineralization associated with magnetite and chromite in the Eretria area contains an average (recalculated to metal content in 100% sulfide) of 0.55 wt.% Ni, 5.15 wt.% Cu, 0.29 wt.% Co and much lower PGE content compared to that of magmatic sulfides [18,19,22]. A characteristic feature of the unusual magnetite-apatite mineralization in the Agoriani area is the large size (up to 3 cm) of the apatite crystals and the presence of abundant liquid-rich fluid inclusions in apatite [20,21].

The main characteristic feature of the mineralization associated with a dismembered, serpentinized harzburgite of Vermion ophiolite is the small size of a former Fe–Ni laterite occurrences, affected by intense tectonic activity, which has created the overthrusting, foliation and lineation of minerals [27,28]. The compact Fe–Ni-laterite ore is characterized by relatively high Mn, Co and Ni content and the lack of a pisolitic–oolitic texture, with magnetite being the major mineral, whereas chromite, (Mn,Co,Fe,Ni)-hydroxides and Ni-silicates are present in lesser amounts [27,28].

5. Mineralogical Aspects of the New Phases Discovered in Othrys and Vermion Ophiolites

5.1. Othrys

The new minerals of Agios Stefanos mine consist of two phosphides, namely tsikourasite, Mo₃Ni₂P_(1+x) (x is <0.25); grammatikopoulosite, NiVP; and the sulfide eliopoulosite, V₇S₈, the ninth known mineral containing V and S as major components [7–9]. Tsikourasite contains an appreciable amount of V (14.13 wt.%), Co (7.59 wt.%) and grammatikopoulosite Co (16.46 wt.%) and Mo (16.39 wt.%). Iron is low in tsikourasite (1.18 wt.%) and somewhat higher in grammatikopoulosite (3.83 wt.%). Eliopoulosite contains very little Fe, Ni, Co and Mo, all well below the 2 wt.% [7–9].

Tsikourasite, grammatikopoulosite and eliopoulosite occur as tiny crystals varying in size from 1 to 80 µm, forming single-phase crystals (Figure 2A,B) or being part of complex grains (Figure 2C–F) in a spatial association with other natural phases, such as nickel-

phosphide, Ni-bearing allabogdanite and barringerite, awaruite, chromite, pentlandite, millerite, quartz, chlorite, serpentine and epoxy [4–9].

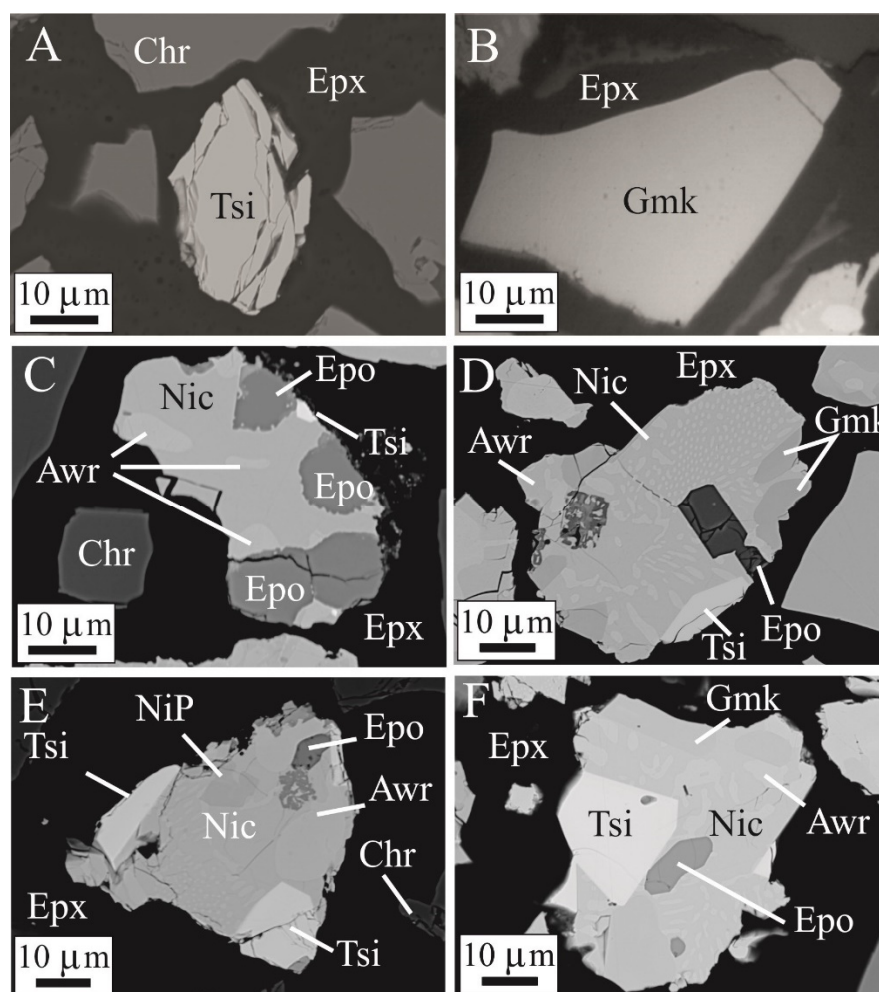


Figure 2. BSE images showing the new minerals found in the Agios Stefanos mine. Single-phase grains of tsikourasite (A) and grammatikopouosite (B) and composite grains containing tsikourasite, grammatikopouosite and eliopouosite (C–F). Symbols: Tsi = tsikourasite, Gmk = grammatikopouosite, Epo = eliopouosite, Awr = awaruite, Nic = nickelphosphide, Chr = chromite, Epx = epoxy. Images modified after Zaccarini et al. [7]; Bindi et al. [8,9].

Tsikourasite, grammatikopouosite and eliopouosite occur as tiny crystals varying in size from 1 to 80 µm, forming single-phase crystals (Figure 2A,B) or being part of complex grains (Figure 2C–F) in a spatial association with other natural phases, such as nickelphosphide ($(\text{Ni,Fe})_3\text{P}$), melliniite ($(\text{Ni,Fe})_4\text{P}$), awaruite $\text{Ni}_2\text{Fe-Ni}_3\text{Fe}$, chromite FeCr_2O_4 , pentlandite $(\text{Fe,Ni})_9\text{S}_8$, millerite NiS , quartz SiO_2 , chlorite $(\text{Mg,Fe})_5\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$ and serpentine $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$, [4–9]. Two minerals characterized by the ideal formulae Ni_2P , probably transjordanite, and V_2P have been also analyzed [4]. Despite their tiny size, fractures along a direction is occasionally present in few grains (Figure 2A). Some grains show a microstructure composed of regularly oriented microparticles that suggests a decomposition of a solid solution (Figure 2D–F).

The available crystallographic data show that tsikourasite is cubic, grammatikopouosite is orthorhombic and eliopouosite is trigonal [7–9].

Arsenotučekite, $\text{Ni}_{18}\text{Sb}_3\text{AsS}_{16}$, was the only new mineral discovered in the Eretria (Tsangli) chromium mine and corresponds to the As-dominant tučekite $\text{Ni}_9\text{Sb}_2\text{S}_8$ [10]. It forms anhedral to subhedral grains varying in size from 5 µm to rarely up to about 100 µm. It occurs as single phase grain (Figure 3A) or is associated with pentlandite, breithauptite

NiSb, gersdorffite NiAsS and chlorite (Figure 3B–D) [10]. Arsenotučekite forms irregular rims that partly replace pentlandite and gersdorffite (Figure 3C,D). According to the crystallographic data, arsenotučekite is tetragonal and is considered as a superstructure of tučekite, resulting from the ordering of Sb and As [10].

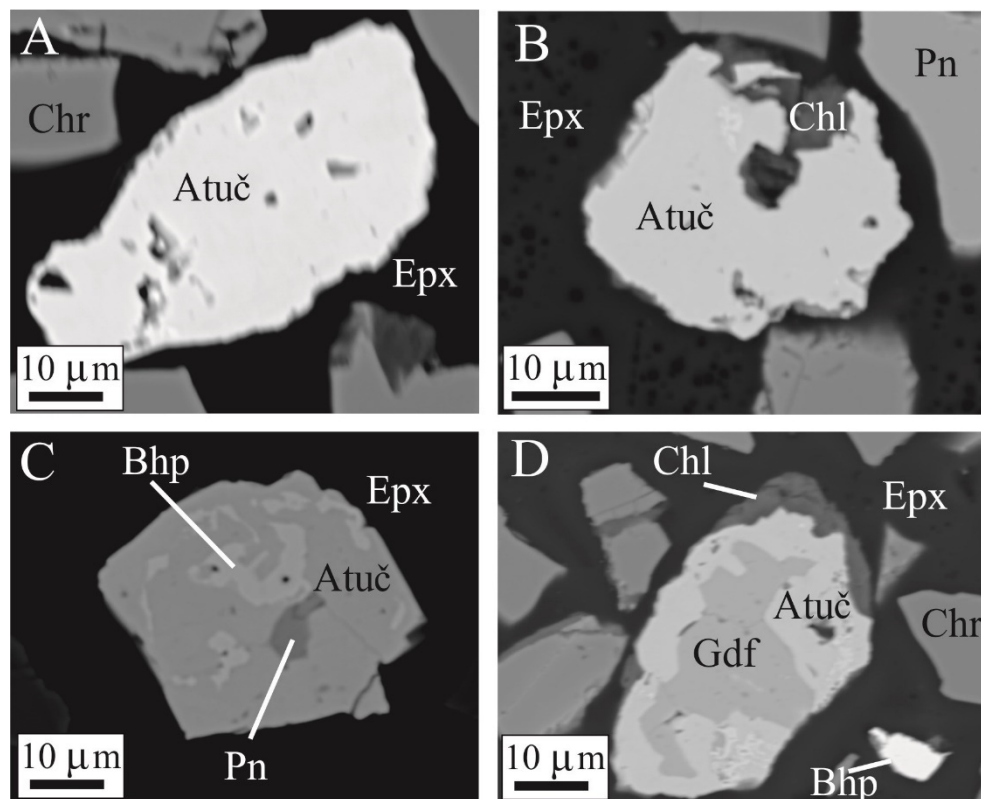


Figure 3. BSE images showing arsenotučekite discovered in the Eretria (Tsangli) chromium mine. Single-phase grains (A,B), and composite grains consist of arsenotučekite, breithauptite, pentlandite and gersdorffite (C,D). Arsenotučekite in contact with chlorite is shown in (B,D). Symbols: Atuč = arsenotučekite, Pn = pentlandite, Bhp = breithauptite, Gdf = gersdorffite, Chr = chromite, Epx = epoxy. The photos (A–C) are taken by Zaccarini et al. [10].

5.2. Vermion

Magnetite is the main mineral of the ore in the Vermion ophiolite. Chromite is minor and occur either with a cataclastic texture cemented by magnetite or as zoned chromite grains with a gradual increase of Mn, Co and Zn outwards of the chromite. These elements attain the greatest values at the periphery of chromite cores and in the ferrian-chromite, reaching values up to 13.0, 4.1 and 2.1 wt.%, respectively; they drop off to negligible values in magnetite [27,28]. Abundant silicate minerals (garnets, vesuvianite, chlorite serpentine and talc), calcite and small amounts of sulfides (mostly millerite, chalcopyrite and pyrite) are also present. Nickel is mainly hosted in chlorite, serpentine and in theophrastrite, a new mineral that contains up to 80 wt.% of NiO [11,12]. The BSE images from Fe-Ni-laterites at Vermion show a multistage evolution accompanied by a multistage redistribution of Ni, Co and Mn among (Ni-Co-Mn)-hydroxides and Ni-silicates (Figures 4–6). Detailed images show the presence of tiny laths of Ni(OH)₂ (Figure 4D,E) and Ni-silicides exhibiting a wide compositional variation (Figures 4 and 5B,D).

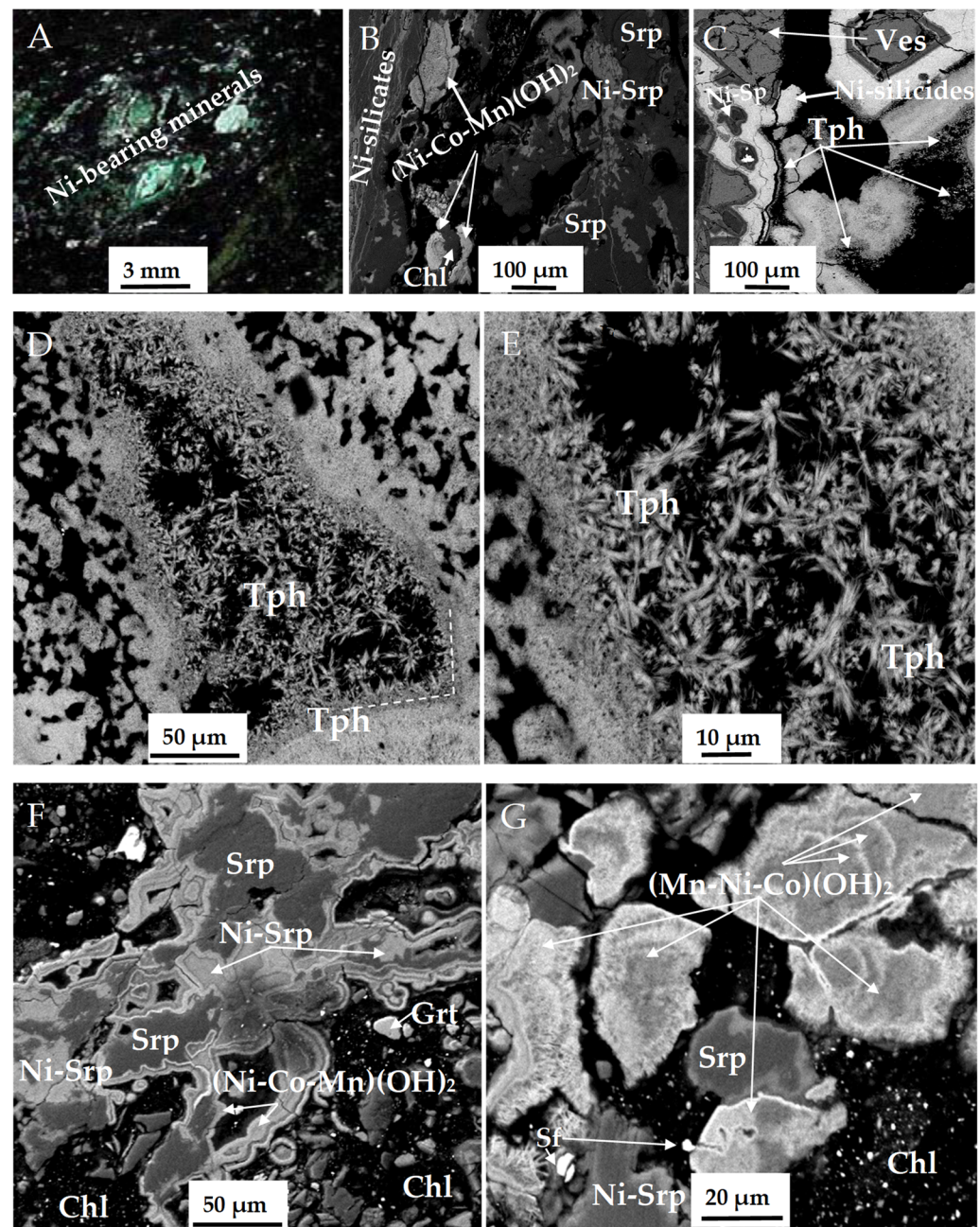


Figure 4. Photomicrograph (A) of the metamorphosed Fe-Ni-laterite ore from the area of Vermion Mt., showing a green association of theophrastite with (Co, Mn, Ni)-hydroxides and Ni-silicates. BSE images (B–G) showing textural relationship between Ni-Si-silicates and Ni-silicides covering fragmented crystals of vesuvianite (B); (Co, Mn, Ni)- solid solutions exhibiting concentrating development, whereas serpentine cross-cut all previous formations (C); early stage of tiny theophrastite crystals exhibiting a special association with Ni-silicides (C,D); close-up image of theophrastite (E). Texture relationships between serpentine, Ni-serpentine and (Ni-Co-Mn)-hydroxides reflecting the potential sequence of their formation (F,G). Symbols: Tph = theophrastite; Ves = vesuvianite; Srp = serpentine; Chl = chlorite; Grt = garnet; Sf = sulfides. Photos taken from Economou-Eliopoulos et al. [12].

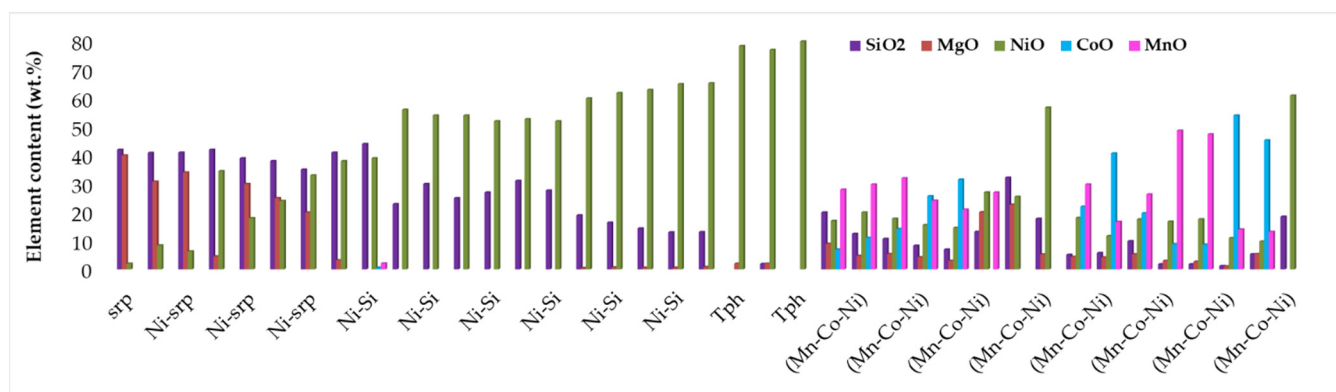


Figure 5. Variation in the SiO_2 , MgO , NiO , CoO and MnO contents, in serpentine (srp), Ni-serpentine (Ni-srp), Ni-silicides (Ni-Si) and (Mn, Co-Ni)-hydroxides, hosted in metamorphosed Ni-laterite samples from Vermion ophiolite. Symbols: as in Figure 3. Data source: present study and Economou-Eliopoulos and Eliopoulos [12].

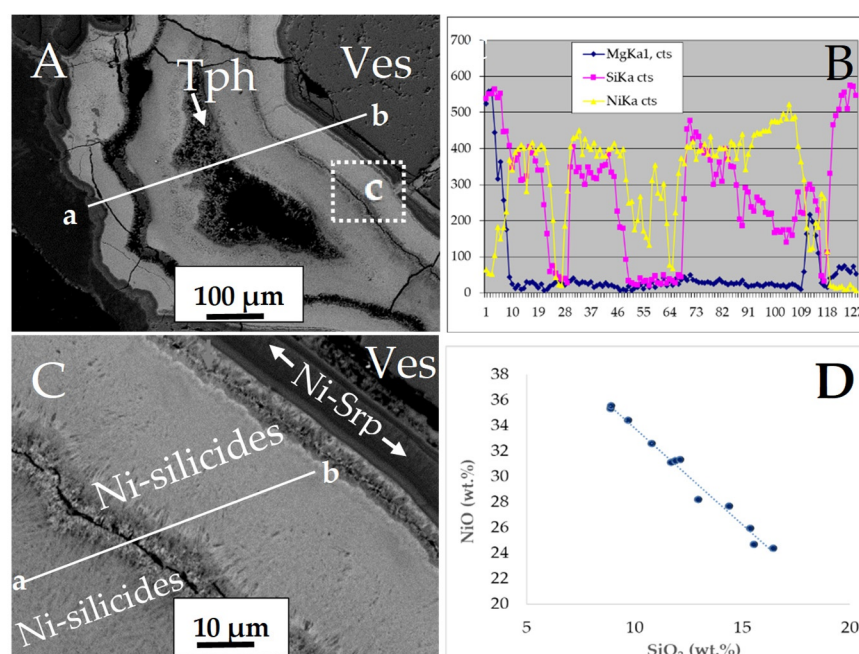


Figure 6. BSE images showing the concentrating development of Ni-silicides and Ni-silicates covering fragmented crystal of vesuvianite (A); scan along a–b of a (BSE)-image showing a wide variation of major elements Si, Ni and Mg, with the presence of Ni only at an early stage of theophrastrite precipitation (B); close-up image of silicides (C); plots of NiO versus SiO_2 (wt.%) in the compositions of silicides (D). Data source: present work and Economou-Eliopoulos and Eliopoulos [12].

In general, Ni is mainly hosted Ni-rich serpentine and theophrastrite (Figure 5) and in less extent into chlorite and serpentine, all cross-cutting earlier (Ni-Co-Mn)-hydroxides with a centering development and a wide compositional variation (Figure 6). The (Co,Mn,Ni)-hydroxides showing a centering development and a wide compositional variation and are crosscut often by serpentine and Ni-serpentine veins (Figures 4B and 7A), which clearly postdate the precipitation of the hydroxides.

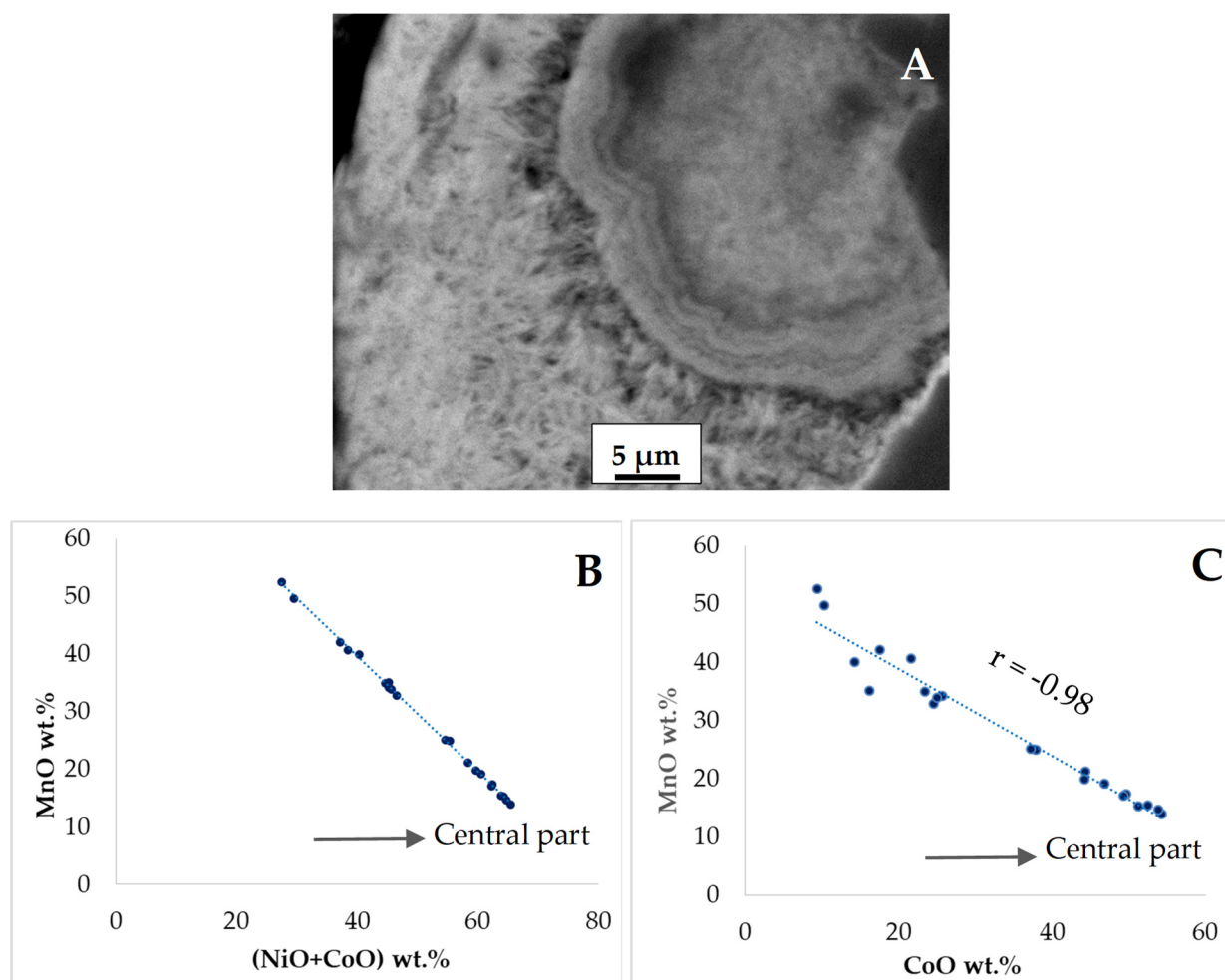


Figure 7. BSE image of (Co-Ni-Mn)-hydroxides showing the concentrating development as successive thin (a few to tens of μm) layers, composed of fine fibrous crystals (A); plots of MnO versus (NiO+CoO) (wt.%) (B) and CoO (wt.%) (C), exhibiting a wide compositional variation, with increasing MnO content outward and maximum CoO content at the central parts (C). Data source: present work and Economou-Eliopoulos and Eliopoulos [12].

6. Discussion

One can assume that chromitite, sulfides and magnetite ores as well as their host ultramafic rocks at the Agios Stefanos and Eretria (Tsangli) area are parts of a wider regional system, including the Agoriani area, all belonging to the Othrys ophiolite complex (Figure 1). The source of the components and geochemical processes controlling the formation of the new minerals discovered at Agios Stefanos and Eretria (Tsangli) may be considered in the framework of the whole regional system.

6.1. Potential Sources of the Components for the New Minerals from Othrys Chromitites

Cobalt, P, Ni Fe, Mo, V, As, Sb and S are the major constituents of the four new minerals discovered in the Othrys ophiolite [7–10,29]. Mineralized assemblages in the area, including the host chromitites, the small occurrences of massive (Fe–Ni–Cu–Co) sulfides at Eretria (Tsangli) [19,29] and the unusual occurrences of massive magnetite associated with apatite at Agoriani [20,21], can all be considered as potential sources of the elements in the new minerals. In addition, the sulfides of Eretria (Tsangli) are enriched in Mo, up to 40 mg/kg Mo [30]. Additionally, magnetite concentrates from the massive Eretrian occurrences of magnetite associated with (Fe–Ni–Cu)-sulfides and chromite contain average 1820 mg/kg V, while those from the Agoriani 640 mg/kg V [29].

With respect to the origin of the unusual mineralization in the Othrys ophiolite complex the geochemical characteristics, including PGE content, flat chondrite-normalized PGE-patterns, and very low partition coefficients for Ni and Fe between olivine and (Fe–Ni–Cu)-sulfides, are inconsistent with sulfides crystallized at a magmatic temperature; rather they are derived from a hydrothermal system circulation [19].

The characteristic features of the unusual magnetite-apatite mineralization in the Agoriani area, such as the large size (up to 3 cm) of the apatite crystals, the lack of fluorine (<20 ppm F) in the apatite, the presence of abundant liquid-rich fluid inclusions in apatite and the absence of ilmenite, indicate that a hydrothermal system played an essential role in the formation of these deposits [20,21].

In addition, the stable isotopes of oxygen for magnetite from Eretria (Tsangli), expressed as $\delta^{18}\text{O}_{\text{SMOW}}$ values per mil (differences to Standard Mean Ocean Water), is -2.2‰ [31], which is analogous to the $\delta^{18}\text{O}_{\text{SMOW}}$ values (-3.8‰ to -3.2‰) measured for magnetite from the apatite-bearing magnetite orebodies of Agoriani, formed probably at a temperature of $\sim 300\text{ °C}$ [20,21]. Therefore, the components of the new minerals located in chromitites of Agios Stefanos and Eretria (Tsangli) may be derived from the wider regional system during the multistage evolution of the Othrys ophiolite complex.

6.2. Origin of the New Minerals at Agios Stefanos

The lack of the new phosphides as inclusions in chromite is consistent with a formation postdating that of minerals stabilized at high temperature (chromite). Their co-existence with minerals facilitated by an extremely low $f\text{O}_2$ (reducing environment) in Gerakini-Ormylia (Greece), and Alapaevsk (Russia) suggests that they may have crystallized during the serpentinization process at a low temperature [6]. This assumption is supported by the finding of a Ni-phosphide in the serpentine matrix of the Alapaevsk chromitite [32]. Moreover, it has been demonstrated that among serpentinite, peridotite, chromitite, gabbro, rodingite and basalt in Greece, only the chromitites from the Othrys complex host considerable amounts of abiotic methane [33]. These authors suggested that the CH_4 formation occurred at temperatures below 150 °C via the Sabatier reaction during the serpentinization process, which provides further evidence that reducing conditions can be removed at a low temperature alteration of mantle-derived rocks [33]. In addition, recently, gaseous and matrix-bound phosphine (PH_3) has been found at well-known methane-emitting sites, such as Louisiana and Florida, in the U.S. [34], as well as in terrestrial and marshy wetlands and sediments [34–36].

Chromitite bodies formed in the mantle wedge of a SSZ environments, such as those associated with the Othrys ophiolite complex [26,36,37], can be fluxed by melts/fluids released from the subducting slab during their protracted multistage evolution [38,39]. The evaluation of the role of various soil sediment conditions (pH, redox, temperature, organic matter content, etc.) on the production and emission of phosphine (PH_3) and other reduced insoluble phosphorus compounds (metal phosphides) may be an important component in wetlands [40]. Additionally, phosphorus associated with organic matter buried in ocean sediment may represent a significant flux, during the subduction of marine sediments and uplift, but available information is still limited [34]. Moreover, on the basis of experimental data the reaction of the phosphidation is strongly endothermic and can only proceed by increasing the overall temperature [40].

Several natural phosphides have been described in three localities surroundings the Dead Sea, all belonging to a pyrometamorphic formation, known as a “Mottled Zone” [3]. According to these authors this Mottled Zone is a suite of chalky-marly sediments that underwent extensive and repetitive high-temperature ($500\text{--}1500\text{ °C}$) and low-pressure metamorphic events. Although the exact origin of Hatrurim Formation is still a matter of debate, two approaches have been suggested: (a) the primary materials adjacent to the Mottled Zone were bituminous sedimentary marls and chalks and (b) the high temperature was a result of a firing of hydrocarbons (preferentially methane) from mud volcano explosions initiated by tectonic activity at the Dead Sea transform fault [3]. The origin of reducing

conditions and high temperature required for the transformation of oxides and phosphates to phosphides have been explained in the context of the origin of the Mottled Zone [3,41]. This observation suggest that the phosphides found in the Dead Sea and those discovered in the Othrys ophiolite formed in a reducing environment but at different temperatures.

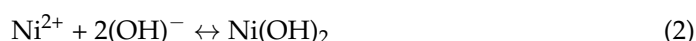
6.3. Origin of Theophrastite

The occurrence of theophrastite $\text{Ni}(\text{OH})_2$ and $(\text{Ni},\text{Co},\text{Mn})(\text{OH})_2$ in nature is extremely rare. The thermodynamic stable form $\beta\text{-Ni}(\text{OH})_2$ in nature is isostructural to brucite, $\text{Mg}(\text{OH})_2$, like several other $\text{M}(\text{OH})_2$ hydroxides, including the metals Mn, Fe, Co [11,29,42]. The texture relationships of the theophrastite with co-existing minerals from the Vermion ophiolite (Figures 4 and 6) coupled with experimental data from the literature suggest a formation from Ni-bearing solutions at low temperature (between 80 °C and 115 °C), in an alkaline environment and under moderately oxidizing conditions [12]. Theophrastite has been described in chromitite specimens from the Hagdale Quarry, Unst, Shetland Islands, Scotland, but it is Mg-bearing and occurs associated with a very poorly crystalline Ni-containing mixed hydroxide of the pyroaurite type or zaraitite. X-ray powder diffraction data show a shift in d spacing toward brucite compared with pure $\text{Ni}(\text{OH})_2$ [43]. Additionally, theophrastite described in the nickel ores of the Lord Brassey mine (Heazlewood ophiolitic ultramafic complex), Tasmania, Australia, is not pure $\text{Ni}(\text{OH})_2$; it is a mixed with poorly crystalline pyroaurite and is associated with zaraitite within vein cutting massive magnetite-chromite ore hosted in serpentinite [44]. Additionally, theophrastite associated with the hydroxyl nickel carbonates zaraitite, otwayite, nullaginite and hellyerite aggregates within partially serpentinized dunite from Fujiwara, the Sanbagawa metamorphic belt, Japan, differs compared to that from the Vermion Mt in terms of its composition and the associated ores [15].

Regarding the known α - and $\beta\text{-Ni}(\text{OH})_2$ [45], the β -phase material, that is isostructural with brucite, $\text{Mg}(\text{OH})_2$ [45], occurs naturally as the mineral theophrastite [11,45]. The substitutions of the Ni in the structure of the $\beta\text{-Ni}(\text{OH})_2$ by Mg, Co and other metals causes only a slight modification of the unit-cell parameters, for example the interplanar spacing, c , which is decreased with increasing Co content [46,47]. Dissociation at pH 7 is extensive, and the surface for Mn-hydroxides has a strong negative charge, whereas under very acid conditions an excess of H^+ is adsorbed to the surface, and it has a positive charge [48]. Thus, at sufficiently high pH, the hydroxide anion concentration exceeds the solubility limit and hexagonal $\text{Ni}(\text{OH})_2$ can be formed to the more perfectly crystalline β -phase at temperatures near or above the boiling point of water [48]. In addition, the amount of adsorbed Co is dependent on the pH in the surrounding fluids, the energy of bonding (equilibrium constant), the activity of Co^{2+} ions and the number or density of adsorption sites [49,50]. Based on the activation energy derived from the Arrhenius equations for Ni sorption on clay mineral ($E_a = 93 \text{ kJ mol}^{-1}$) and theophrastite (124 kJ mol^{-1}), it has been suggested that the Ni sorption was surface-controlled, and it can be inferred that although metal precipitation reactions often occur in the natural environment, the rate of these reactions depends strongly on the temperature [51].

The structure of $\text{Ni}(\text{OH})_2$ comprises a hexagonal close packing of OH^- ions with an alternate layers of octahedral sites occupied by Ni^{2+} ions resulting in a stacking of charge-neutral layers having the composition $\text{Ni}(\text{OH})_2$ [52]. The NiS formed in alkaline solutions is slightly sulfur insufficient, which is balanced by the incorporation of a hydroxyl group. This may increase the effect of water bonding on the structure of the material and is consistent with the observation of the increase in theophrastite-like $\text{Ni}(\text{OH})_2$ in materials from alkaline conditions [53].

The dominant reaction of the two competing reactions:



depends on the kinetics and thermodynamics of the two reactions under certain conditions [53]. The nickel sulfide precipitation is therefore expected to be much faster than that of theophrastrite in this system. However, this does not necessarily mean that the two species exist as two discrete phases. The incorporation of foreign anions into β -Ni(OH)₂ materials is far less common because adjacent layers are close-packed. Furthermore, foreign anions are quickly removed owing to the conversion of α - to β -Ni(OH)₂ [47].

The replacement of serpentine by Ni-bearing serpentine is common (Figure 3B). The increasing Ni/Mg ratios' involvement in the exchange reactions (Figures 4 and 6) seem to be consistent with calculated data indicating that at equilibrium in this reaction, Ni is much more stable in serpentine, whereas Mg²⁺ is removed by the solution [54]. The repeated cycles of dissolution and precipitation of silica and the progressive silicification in laterites may be linked to the preferred release of Mg and Ni in phyllosilicates and the development of silica-rich surfaces [55]. The common occurrence of the (Ni,Co,Mn)(OH)₂ with a concentrating development as successive thin layers, composed of fine fibrous crystals (Figures 3B and 6A), is accompanied by Ni-Si compounds showing a wide variation in their proportion (Figure 4). The presence of the Ni-silicates (Figures 4 and 6A) is consistent with extensive studies on the binary system Ni-Si shown that the sequence of the phase formation depends on the thermodynamics of the system, local availability of oxygen and the concentration of the reacting species at the growth interface [56,57].

7. Conclusions

The combination of the available data on texture relationships, mineralogical assemblage and the mineral chemistry of the new minerals from Othrys and Vermion ophiolites indicates that their genesis is linked with postmagmatic events and that their scarcity may be related to the required extreme physical-chemical conditions necessary for their precipitation, which can rarely be achieved in nature.

Although the components of the new minerals are available in the ore-forming systems in both the Othrys and Vermion ophiolites, the strongly reducing environment and relatively higher temperature required for the formation and stability of the new minerals from the Othrys differ from those for theophrastrite, forming concentrated precipitations at very low temperatures and under moderate oxidizing conditions.

The spatial association of mixed layers of Ni-silicides with the extremely tiny crystals of Ni(OH)₂ and (Ni,Co,Mn)-hydroxides at Vermion may reflect their metastability, which has a significant impact on the reaction products and the observed structural features.

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