Mineralogical and Geochemical Constraints On the Origin of Mafic–Ultramafic-Hosted Sulphides: The Pindos Ophiolite Complex

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Abstract: Sulphide ores hosted in deeper parts of ophiolite complexes may be related to either primary magmatic processes or links to hydrothermal alteration and metal remobilization into hydrothermal systems. The Pindos ophiolite complex was selected for the present study because it hosts both Cyprus-type sulphides (Kondro Hill) and Fe–Cu–Co–Zn sulphides associated with magnetite (Perivoli-Tsoumes) within gabbro, close to its tectonic contact with serpentinized harzburgite, and thus offers the opportunity to delineate constraints controlling their origin. Massive Cyprus-type sulphides characterized by relatively high Zn, Se, Au, Hg, and Sb content are composed of pyrite, chalcopyrite, bornite, and in lesser amounts covellite, siegenite, sphalerite, selenide-clausthalite, telluride-melonite, and occasionally tennantite–tetrahedrite. Massive Fe–Cu–Co–Zn-type sulphides associated with magnetite occur in a matrix of calcite and an unknown (Fe,Mg) silicate, resembling Mg–hisingerite within a deformed/metamorphosed ophiolite zone. The texture and mineralogical characteristics of this sulphide-magnetite ore suggest formation during a multistage evolution of the ophiolite complex. Sulphides (pyrrhotite, chalcopyrite, bornite, and sphalerite) associated with magnetite, at deeper parts of the Pindos (Tsoumes), exhibit relatively high Cu/(Cu + Ni) and Pt/(Pt + Pd), and low Ni/Co ratios, suggesting either no magmatic origin or a complete transformation of a preexisting magmatic assemblages. Differences recorded in the geochemical characteristics, such as higher Zn, Se, Mo, Au, Ag, Hg, and Sb and lower Ni contents in the Pindos compared to the Othrys sulphides, may reflect inheritance of a primary magmatic signature.

Keywords: sulphides; ophiolites; ultramafic; selenium; gold; Pindos

1. Introduction

Traditionally, the sulphide mineralization associated with ophiolite complexes is that of Cyprus-type volcanogenic massive sulphide (VMS) deposits. They may be derived from the interaction of evolved seawater with mafic country rocks, under greenschist facies metamorphic conditions and subsequent precipitation on and near the seafloor, when ore-forming fluids are mixed with cold seawater [1–5]. They are associated with basaltic volcanic rocks and are important sources of base and trace metals (Co, Sn, Se, Mn, Cd, In, Bi, Te, Ga, and Ge) [1]. Massive sulphide deposits have been described in the Main Uralian Fault Zone (Ivanovka and Ishkinino deposits), southern Urals; they are mafic–ultramafic-hosted VMS deposits and show mineralogical, compositional, and textural
analyses with present-day counterparts on ultramafic-rich substrates [6]. Recently, an unusual association of magnetite with sulphides of Cyprus-type VMS deposit was described in Ortaklar, hosted in the Koçali Complex, Turkey, which is part of the Tethyan Metallogenic Belt [7]. Additionally, the largest magnetite deposit in a series of apatite and sulphide-free magnetite orebodies hosted in serpentinites of Cogne ophiolites, in the Western Alps, Italy, is characterized by typical hydrothermal compositions [8].

Although the Fe–Cu–Ni–Co-sulphide mineralization was initially considered an unusual type in ophiolite complexes, several occurrences have been located, like those in pyroxenite cumulates of the Oregon ophiolite [9], in dunites associated with chromitites of the Acoje ophiolite, Philippines [10], in layered gabbros of the Oman ophiolite [11], in dunites of the upper mantle–crust transition zone of the Bulqiza (Ceruja, Krasta), Albania ophiolite [12], Shetland (Unst), UK ophiolite [13], and the Moa-Baracoa ophiolitic massif (Cuba) [14]. On the basis of magmatic texture features and steep positive chondrite-normalized Platinum-Group Elements (PGE) patterns, sulphide mineralization of that type has been interpreted as reflecting the immiscible segregation of sulphide melts [9,13,14]. Moreover, the occurrence of Fe–Ni–Cu–Zn-sulphide mineralization (with dominant minerals pyrrhotite, chalcopyrite, and minor pentlandite) in mantle serpentinized peridotites and mafic to ultramafic rocks of ophiolite complexes of Limassol, Cyprus, Othrys (Eretria) in Greece, Pindos (Tsoumes) ophiolite and elsewhere has been the topic of research for extensive studies [15–20]. On the other hand, texture and geochemical characteristics, including PGE contents, and a very low partition coefficient for Ni and Fe between olivine and sulphides are inconsistent with sulphides having an equilibrium with Ni-rich host rocks at magmatic temperature [16,18]. Although the initial magmatic origin is not precluded, present characteristics of the highly transformed ore at the Eretria (Othrys) area may indicate that the magmatic features have been lost or that metals were released from the host rocks by a low-level hydrothermal circulation process [16]. Fe–Cu–Zn–Co–Ni mineralization is also reported in seafloor VMS deposits from modern oceans (as well as in their possible analogues on several ophiolites on land, e.g., Urals) indicating that these deposits can be formed by purely hydrothermal processes [19].

Despite the extensive literature data on a diverse array of sulphide mineralizations, sulphide ores hosted in mafic–ultramafic ophiolitic rocks are characterized by structure as well as mineralogical and geochemical features, suggesting either magmatic origin or links to serpentinitization processes and metal remobilization from primary minerals into hydrothermal systems. The present study is focused on some new SEM/EDS and geochemical data on Cyprus-type and Fe–Cu–Co–Zn-type sulphides hosted in deeper parts of the Pindos ophiolite complex, aiming to improve our understanding of the factors controlling trace element incorporation into sulphide minerals and their origin.

2. Materials and Methods

2.1. Mineral Chemistry

Polished sections (20 samples) from sulphide ores were carbon-coated and examined by a scanning electron microscope (SEM) using energy-dispersive spectroscopy (EDS). The SEM images and EDS analyses were carried out at the University of Athens (NKUA, Athens, Greece), using a JEOL JSM 5600 scanning electron microscope (Tokyo, Japan), equipped with the ISIS 300 OXFORD automated energy-dispersive analysis system (Oxford, UK) under the following operating conditions: accelerating voltage 20 kV, beam current 0.5 nA, time of measurement (dead time) 50 s, and beam diameter 1–2 μm. The following X-ray lines were used: FeKα, NiKα, CoKα, CuKα, CrKα, AlKα, TiKα, CaKα, SiKα, MnKα, and MgKα. Standards used were pure metals for the elements Cr, Mn, Mo, Ni, Co, Zn, V, and Ti, as well as Si and MgO for Mg and Al2O3 for Al.

2.2. Whole Rock Analysis

The studied sulphide samples were massive and disseminated mineralizations, derived from large (weighing approximately 2 kg) samples, which is necessary to obtain statistical representative
trace element distribution in sulphide ores. They were crushed and pulverized in an agate mortar. Major and minor/trace elements were determined at the SGS Global—Minerals Division Geochemistry Services Analytical Laboratories Ltd., Vancouver, BC, Canada. The samples were dissolved using sodium peroxide fusion, combined Inductively Coupled Plasma and Atomic Emission Spectrometry, ICP-AES and Mass Spectrometry, ICP-MS (Package GE_ICP91A50). On the basis of the quality control report provided by Analytical Labs, the results of the reference material analysis in comparison to expected values, and the results from the multistage analysis of certain samples, showed an accuracy and a precision of the method in good agreement with the international standard (<10%).

3. A Brief Outline of Characteristics for the Studied Sulphides

The Pindos ophiolite complex, of Middle to Upper Jurassic age, is located in the northeastern part of Greece (49° N, 21° E), lies tectonically over Eocene flysch of the Pindos zone, and contains a spectrum of lavas from Mid-Ocean Ridge, MOR basalts through island arc tholeiites (IATs) to boninite series volcanics (BSVs) [21–23]. Two tectonically distinct ophiolitic units can be distinguished: (a) the upper unit (Dramala Complex), including mantle harzburgites, and (b) a lower unit, including volcanic and subvolcanic sequences at the Aspropotamos Complex (Figure 1). This complex consists of a structurally dismembered sequence of ultramafic and mafic cumulate ophiolitic rocks, including gabbros, which is locally underlain by sheets of serpentinite [21,22]. Sulphide mineralization in the Pindos ophiolite complex is located near the Aspropotamos dismembered ophiolite unit, belonging to the lower ophiolitic unit of the complex and includes the following.

A volcanic and subvolcanic sequence composed mainly of basaltal and basaltic andesite pillow lavas ranging from high to low Ti affinity [20–24]. The different magmatic groups may have been derived from different mantle sources and/or various degrees of partial melting [20–24]. Massive Cyprus-type sulphide ore occurrences in the form of small lenses (maximum 4 × 40 m), are located in an abandoned mine, at the Kondro Hill, very close to the village of Perivoli (Figure 1). The estimated ore potential is about 10,000 tons with an average 6.6 wt.% Cu and 9.4 wt.% Zn [25]. They occur on the top of diabase (massive or pillow lavas) and are directly overlain by metalliferous (Fe-Mn-oxide-bearing sediments). Due to the tectonic disruption of the Aspropotamos unit, the spatial association between massive and stockwork disseminated mineralization is unclear.

Several sub-vertical veins of quartz with veinlets and a brecciated pipe-shaped diabase dike (stockwork ore zone) have been described in the Neropriona area of the Aspropotamos unit, Kondro Hill, with disseminations of pyrite + chalcopyrite, and dominant mineral-altered plagioclase and clinopyroxene, penninite, kaolinite, quartz, epidote, and calcite [20,25–27]. Small irregular to lens-like occurrences (4 × 1.5 m) of massive Fe–Cu–Zn–Co-type sulphide mineralization associated with magnetite are exposed at the Perivoli (Tsoumes) Hill (Figure 1). These are hosted within gabbro, close to its contact with serpentinitized harzburgite [20,25], consisting of pyrrhotite, pyrite, chalcopyrite, and sphalerite associated with magnetite. The contact between ore and hosting rock is not sharp, appearing as irregular nets of veinlets. Rounded fragments of highly altered rock and massive fragments of sulphide ore are broadly parallel to the shear plane of a thrust fault.
4. Mineralogical Features

4.1. Cyprus-Type Sulphides

The massive ore is mainly composed of pyrite, chalcopyrite, bornite, and in lesser amounts covellite, siegenite, sphalerite, and claushtalite, while pyrrhotite is lacking (Figure 2). Chalcopyrite, bornite, and sphalerite occur in at least two different generations. Pyrite grains vary from euhedral to subhedral and rarely framboidal. Textural relationships indicate that early pyrite, commonly occurring as large crystals but often exhibiting dissolution, is extensively penetrated and replaced by fine-grained chalcopyrite, bornite, and sphalerite in a matrix of quartz (Figure 2). Copper-bearing sphalerite, with up to 3.6 wt.% Fe, 4.2 wt.% Cu, and 1.7 wt.% Bi, occurs within pyrite crystals and/or cements minor chalcopyrite and pyrite (Figure 2b,e,f; Table 1). Pyrite is extensively replaced by intergrowths between chalcopyrite, bornite, and Fe-poor sphalerite (Figure 2b,d; Figure 3) and occasionally contains Co (Table 1). Fine-grained intergrowths of framboidal or colloform pyrite-borne, occurs in a matrix of quartz (Figure 2g,h). Fine-grained chalcopyrite or bornite are often found in cross-cutting veins, hosting selenides (mainly claushtalite, PbSe) (Table 1), the telluride mineral melonite (NiTe₂), gold, galena, and barite [26]. Furthermore, present investigation reveals the formation of aggregates of secondary minerals, occurring as characteristic crusts on bornite surfaces (Figure 2i–l). These minerals are present-day grown minerals, on the surface of polished sections of sulphide ore, exposed to air, under room conditions (20–25 °C) and moderate air humidity (atmospheric water). Gold, as inclusions in chalcopyrite reaching a maximum size of 20 μm with Ag contents of up to 9 wt.%, is a rare component of the ores [26]. Additionally, we observed the presence of submicroscopic gold, i.e., <1 μm and thus invisible under an optical microscope, in grains of pyrite, chalcopyrite, and bornite, that increases with decreasing crystal size, reaching contents up to 7.7 ppm Au in pyrite, 8.8 ppm Au in very fine intergrowths between pyrite and sphalerite, and 17.3 ppm Au in fine intergrowths between pyrite and bornite [20].
| Mineral       | Pyrite | Sphalerite | Chalcopyrite | Bornite |
|--------------|--------|------------|--------------|---------|
| Fe           | 44.6   | 43.7       | 42.8         | 41.0    |
| Cu           | n.d.   | 0.5        | 2.1          | 4.1     |
| Zn           | n.d.   | n.d.       | 57.7         | 99.4    |
| Co           | n.d.   | 1.2        | n.d.         | 1.2     |
| Bi           | n.d.   | n.d.       | n.d.         | 1.2     |
| Se           | n.d.   | n.d.       | n.d.         | n.d.    |
| S            | 54.1   | 53.9       | 53.9         | 53.9    |
| Total        | 99.9   | 99.3       | 99.3         | 99.9    |

Cont

| Mineral       | Pyrite | Sphalerite | Chalcopyrite | Bornite |
|--------------|--------|------------|--------------|---------|
| Fe           | 3.8    | 3.2        | 2.2          | 2.1     |
| Cu           | 70.8   | 70.6       | 71.1         | 71.1    |
| Zn           | n.d.   | n.d.       | 82.4         | 76.2    |
| Se           | n.d.   | n.d.       | n.d.         | 21.6    |
| Co           | n.d.   | n.d.       | n.d.         | n.d.    |
| Bi           | n.d.   | n.d.       | n.d.         | n.d.    |
| Se           | n.d.   | n.d.       | n.d.         | n.d.    |
| S            | 24.5   | 21.6       | 23.9         | 26.2    |
| Total        | 99.4   | 100.0      | 99.4         | 100.7   |

Cont

| Sulphides associated with Magnetite | Tsumes |
|-----------------------------------|--------|
| Pyrrhotite | Pyrite | Chalcopyrite | Sphalerite |
|-----------|--------|--------------|------------|
| Fe        | 61.0   | 58.9         | 59.7       |
| Cu        | n.d.   | n.d.         | 31.4       |
| Zn        | n.d.   | n.d.         | 2.3        |
| Bi        | n.d.   | n.d.         | 1.4        |
| S         | 39.4   | 39.8         | 40         |
| Total     | 100.4  | 100.6        | 99.7       |
Figure 2. Backscattered electron (BSE) images representative of various morphological forms and textures of pyrite associated with chalcopyrite and sphalerite in a matrix of quartz (a–d); euhedral pyrite displaying erosion and replacement by chalcopyrite–sphalerite intergrowths (b); a close intergrowth between pyrite and bornite (d,e); selenides (clausthalite) as inclusions within bornite (f); fine-grained intergrowths of framboidal or colloform pyrite-bornite, in a matrix of quartz (g,h); replacement of bornite by neo-formed intergrowths of Cu minerals (i–l), which are Cu-enriched and Fe-depleted (Table 1). Scale bar: 200 μm (a); 50 μm (b,f,g,i); 20 μm (e); 10 μm (c,d,h,j,k,l). Abbreviations: py = pyrite; cp = chalcopyrite; sph = sphalerite; bn = bornite; PbSe = clausthalite; qz = quartz; f.py = framboidal forms of pyrite with tiny inclusions of Cu minerals; ge-sp = intergrowths of neo-formed Cu minerals with composition corresponding to geerite and spionkopite.
4.2. Breccia Pipe

Disseminated pyrite, minor chalcopyrite, and sphalerite occur mostly in vesicles filled by quartz, kaolinite, chlorite, and epidote, within brecciated pipe-form diabase (a discharge pathway) underlying the Kondro massive ore [27]. Samples (n = 10) of pyrite separates from the diabase breccia have shown a limited range for $\delta^{34}$S values from +1.0 to +1.5‰ [27].

4.3. Massive Fe–Cu–Co–Zn-Type Sulphides Associated with Magnetite

The sulphide ore is mainly composed of pyrrhotite, while pyrite, chalcopyrite, sphalerite, malachite, and azurite are present in lesser amounts. Pure magnetite, often forming a network texture, is associated with sulphides, either as massive ore with inclusions of sulphides (chalcopyrite, pyrite, and pyrrhotite), or as individual grains dispersed within sulphide ore (Figure 4). A characteristic feature of magnetite is its elongated and curved form and its textural relationship with the sulphides. Pyrrhotite, which is the most abundant sulphide, is followed by chalcopyrite and sphalerite, all showing an irregular contact with the magnetite, that often occurs surrounding sulphides (Figure 4a–c). Additionally, a salient feature is the occurrence of an (Fe/Mg) phyllosilicate associated with sphalerite, chalcopyrite, and magnetite (Figure 4d–f; Figure 5).
Figure 4. Backscattered electron (BSE) images showing intergrowths between pyrrhotite, sphalerite, and magnetite in a matrix of calcite (a); elongated curved crystals of magnetite and inclusions within pyrrhotite (b); intergrowths between pyrrhotite, sphalerite, chalcopyrite, and magnetite in a matrix of calcite (c); magnetite associated with sphalerite in a matrix of calcite and (Fe,Mg) silicate (d); sphalerite adjacent to chalcopyrite with inclusions of (Fe,Mg) silicate (e); transitional contact between chalcopyrite and sphalerite and their intergrowths with magnetite (f). Scale bar: 100 μm (a,c,d); 50 μm (b); 20 μm (e); 10 μm (f). Symbols: cal = calcite; Fe-Mg-Si = (Fe,Mg) silicate, and as in Figure 2.
Figure 5. Backscattered electron (BSE) images showing intergrowths of pyrrhotite, pyrite, chalcopyrite, and sphalerite in a matrix of calcite and an unknown (Fe–Mg) silicate (a), Table 2; single scanning for S (b), Fe (c), Cu(d), and Zn (e). Scale bar for b, c, d as in 5a (50 μm). Symbols, as in Figures 2 and 4.

|       | tsoumes (Fe,Mg)-silicate | Laramie Complex [28] | Hisingerite |
|-------|--------------------------|----------------------|-------------|
| SiO2  | 35                       | 33.2                 | 42.7        | 37.8        |
| Al2O3 | 0.9                      | 1.1                  | 1.2         | 0.03        |
| Cr2O3 | n.d.                     | n.d.                 | 0.03        | 0.04        |
| Fe2O3 | 42.3                     | 43.2                 | 35.83       | 46.94       |
| MnO   | n.d.                     | n.d.                 | 0.15        | 0.49        |
| MgO   | 11.9                     | 12.1                 | 7.46        | 2.15        |
| NiO   | n.d.                     | n.d.                 | 0.05        | 0.01        |
| CaO   | n.d.                     | n.d.                 | 0.81        | 0.39        |
| Total | 90.1                     | 89.6                 | 88.22       | 87.85       |
5. Geochemical Characteristics of Sulphides

Massive sulphide ores from the Kondro Hill exhibit uncommon high contents in Au (up to 3.6 ppm), Ag (up to 56 ppm), Se (up to 1900 ppm), Co (up to 2200 ppm), Mo (up to 370 ppm), Hg (up to 280 ppm), Sb (up to 10 ppm), and As up to 150 ppm, which are much higher than those in the Fe–Cu–Zn–Co-type sulphide hosted in ultramafic parts of the complex, along a shearing zone, close to a contact with gabbros (Table 3), as well as within brecciated pipe-form diabase (a discharge pathway) underlying the Kondro massive ore [20]. Major and minor elements, such as Fe, Cu, and Zn, are hosted in sulphides (pyrrhotite and pyrite, chalcopyrite, bornite, and epigenetic high Cu minerals, and sphalerite, respectively). Magnetite and Fe silicates (Tables 1 and 2), selenides, tellurides, gold, galena, and barite are occasionally present, but Mo-bearing minerals were not identified.

Major and trace elements in massive sulphide ores of Cyprus- and Fe–Cu–Co–Zn-type sulphides from the Pindos ophiolite complex, along with those from comparable ophiolites such as the Othrys and Troodos ophiolite complexes [29–33], are plotted in Figure 6. Although there are overlapping fields, it seems likely that the Pindos sulphides can be distinguished by their higher Zn (Figure 6a,c) and Co (Figure 6b) contents (Figure 6). The highest Se contents were recorded in the Pindos and the Apliki ores (Cyprus) accompanied by Cu and Au contents (Figure 6d,e). A positive trend is also clear between Cu and As (Figure 6f).

Table 3. Geochemical characteristics of sulphide ores hosted in the Pindos, Othrys, and Troodos ophiolites. Data: present study [20].

| Location       | wt % | wt % | wt % | ppm          |
|----------------|------|------|------|--------------|
|                | Fe   | Cu   | Zn   | Co | Ni | Mo | Se | As | Au | Ag | Hg | Sb | Cu/(Cu + Ni) | Ni/Co | Pt/(Pt + Pd) |
| Pindos         |      |      |      |    |    |    |    |    |    |    |    |    |              |       |             |
|                | 26.9 | 6.9  | 2.9  | 1400 | 20 | 50 | 170 | 140 | 1.1 | 56 | 40 | 9.5 | >0.99        | 0.014 | __           |
|                | 21.2 | 6.1  | 2.6  | 1250 | 32 | 80 | 400 | 150 | 1.3 | 34 | 70 | 7.1 | >0.99        | 0.026 | __           |
|                | 26.5 | 16.4 | 3.2  | 600  | 12 | 310| 1500| 90  | 3.3 | 38 | 170| 8.1 | >0.99        | 0.02  | __           |
|                | 22.5 | 10.1 | 9.8  | 500  | 11 | 40 | 1900| 64  | 3.6 | 32 | 280| 10 | >0.99        | 0.022 | __           |
| Kondro Massive ore |    |      |      |      |    |    |    |    |    |    |    |    |              |       |             |
|                | 11.9 | 25.4 | 1.1  | 2200 | 27 | 80 | 850 | 40  | 3.2 | 39 | 60 | 2.1 | >0.99        | 0.012 | __           |
|                | 20.8 | 7.2  | 2.2  | 910  | 110| 91 | 350 | 140 | 3   | 35 | 48 | 6.6 | >0.99        | 0.12  | __           |
|                | 9.5  | 18.9 | 1    | 870  | 60 | 76 | 1100| 10  | 2.1 | 40 | 128| 1.3 | >0.99        | 0.07  | __           |
|                | 26.4 | 11.6 | 8.3  | 280  | 8  | 36 | 1900| 64  | 1.9 | 38 | 280| 10 | >0.99        | 0.028 | __           |
|                | 23.2 | 8.1  | 2.5  | 1000 | 13 | 370| 1400| 200 | 1.9 | 48 | 168| 1.4 | >0.99        | 0.013 | __           |
| Aspropotamos   |      |      |      |      |    |    |    |    |    |    |    |    |              |       |             |
| Disseminated   | 7.1  | 0.006| 0.007| 27   | <5 | <5 | <5  | 25  | 0.018| <1 | <1 | <1 | 0.3 | __           | __    | 0.95         |
| Diabase breccia| 6.9  | 0.007| 0.009| 15   | <5 | <5 | <5  | 25  | 0.025| <1 | <1 | <1 | 0.6 | __           | __    | 0.97         |
|                | 49.8 | 1.8  | 0.4  | 600  | 9  | 80 | 130 | 20  | 0.15 | 6 | 10 | 1 | >0.99        | 0.015 | 0.12         |
|                | 33.4 | 2.5  | 0.12 | 1100 | 12 | 150| 350 | 27  | 0.14 | 7 | 30 | 0.8 | >0.99        | 0.01  | 0.87         |
|                | 31.2 | 1.4  | 0.11 | 540  | 8  | 70 | 95  | 20  | 0.11 | 8 | 11 | 0.9 | >0.99        | 0.015 | 0.22         |
|                | 30.3 | 1.7  | 0.1  | 520  | 7  | 58 | 41  | 11  | 0.03 | 5 | 16 | 0.4 | >0.99        | 0.013 | 0.87         |
| Othrys         | 39.4 | 3.3  | 0.02 | 2300 | 2400| 40 | 6   | 2   | 0.01 | <1 | 1  | 0.2 | 0.93        | 1.04  | 0.99         |
|                | 35.9 | 0.44 | 0.12 | 400  | 3700| 30 | 7   | <5  | 0.02 | <1 | 0.3 | 0.2 | 0.49        | 12.33 | 0.6          |
| Eretria        | 37.4 | 0.89 | 0.01 | 2000 | 2500| 46 | 8   | <5  | 0.01 | <1 | 0.6 | 0.2 | 0.78        | 1.25  | 0.86         |
| Cyprus         | 38.8 | 1.8  | 0.12 | 1500 | 12000| 40 | 35  | 47  | 3.5 | 2.1 | 2  | 18 | 0.6 | 8             | __    | __           |
| Limassol       | 43.5 | 1.74 | 0.03 | 1800 | 17100| 610 | 5   | 12800| 8.2 | 8.2 | <1 | 73 | 0.5 | 9.5           | __    | __           |
|                | 43.8 | 3.8  | 0.34 | 2300 | 1400| 70 | 110 | 190 | 4.5 | 4.5 | <1 | 10 | 0.96        | 0.61  | __           |
Symbol _:_ Pt contents < 10 ppb.
Figure 6. Plots of major and trace elements of Cyprus-type (labeled as Cy) sulphide ores and Fe-Cu ± Co ± Zn sulphides hosted in ultramafic rocks (labeled as ultram.) from the Pindos (P), Othrys, and Troodos ophiolite complexes. Although there are overlapping fields, the ores from the Pindos can be distinguished for the presence of ores with higher Zn (a,c) and Co (b) contents in Cyprus-type ores. The highest Se contents are recorded in the Pindos and the Apliki ores (Cyprus) accompanied by Cu and Au contents (d,e). A positive trend is also clear between Au and As (f). Data: Table 3; [3,7,16,18,20,29,30].

6. Discussion

6.1. A Comparison between Magmatic Sulphides and Those Hosted in Mafic–Ultramafic Ophiolites

It has been well established that the formation of magmatic deposits is related to the segregation of sulphide melts by immiscibility from basaltic magmas, which are able to collect precious metals (PGE, Ag, Au) as well as other chalcophile elements (Se, Te, Bi, Pb, As, Sb) because of their high partition coefficient (D_{sulphide melt/silicate melt}) [34,35]. The compositions of the magmatic ores may be mainly controlled by (a) the metal abundances of the mantle source and the degree of partial melting [36,37], (b) the degree of fractional crystallization and potential crustal contamination during magma ascent [38], and (c) interactions with magmatic-hydrothermal or metamorphic-hydrothermal fluids [39–41]. Compositional data obtained from a large number of magmatic sulphide deposits [42] show clear differences from the Fe–Cu ± Co ± Zn ± Ni-sulphide mineralization hosted in ophiolite complexes.

The unusual Fe–Cu–Ni–Co type of sulphides hosted in mafic–ultramafic ophiolitic rocks is characterized by varying structural, mineralogical, and geochemical features, which are not of magmatic origin. Sulphides hosted in the magmatic sequence of ophiolite complexes [9–14] have been interpreted as reflecting the immiscible segregation of sulphide melts, which they exhibit magmatic texture features and steep positive chondrite-normalized PGE patterns [9–14]. However, the Pindos (Tsoumes) Fe–Cu–Co–Zn-sulphides, consisting mainly of pyrrhotite, chalcopyrite, bornite, and sphalerite and hosted within gabbro, close to its tectonic contact with serpentinized harzburgite, differ compared to the Othrys (Eretria) sulphides, which are located at the peripheries of podiform chrome bodies hosted in serpentinized harzburgite and consist of pyrrhotite, chalcopyrite, and minor Co-pentlandite. Furthermore, the Pindos massive sulphides differ from those in the serpentinitized rocks of the Limassol Forest (Troodos), which are composed dominantly of troilite, maucherite, pentlandite, chalcopyrite, bornite, vallerite, magnetite, minor sphalerite, graphite, molybdenite, and gold. In addition, the sulphides in the Limassol Forest contain much higher Au and As, up to 8 and 62 ppm, respectively [15,18], compared to the Pindos sulphides (Table 3). Despite the above differences between the Pindos, Othrys, and Limassol sulphides, they are all characterized by higher Cu/(Cu+Ni) ratios (>0.99, 0.5–0.93, and 0.2–0.96, respectively) compared to most magmatic deposits, having Cu/(Cu+Ni) ratios ranging from 0.05 to 0.14 [42]. In addition, the Ni/Co ratio in magmatic deposits typically ranges from 15 to 50 [42], whereas the range of Ni/Co ratio is 1.0–12 for the Eretria, 0.6–14 for the Limassol, and 0.01–0.02 for the Pindos (Tsoumes) samples (Table 3).

Model calculations have shown that the relatively high Co tenor and low Ni/Co cannot be explained by an earlier phase of fractional crystallization or sulphide segregation [43]. Thus, the higher Ni and Co contents in sulphide occurrences associated with chromitite bodies in the Othrys (Eretria) peridotites may suggest re-mobilization of Fe, Co, and Ni during hydrothermal alteration of peridotite in the presence of aqueous H₂S, and precipitation of Ni–Co–Fe sulphides [44,45]. The presence of graphite-like material in chromitites associated with sulphides from the Othrys complex, along shear zones that served as fluid pathways through the chromitites [46,47], may support the mobilization and re-precipitation of Fe–Ni–Co sulphides. Furthermore, the occurrence of phosphides such as Ni–V–Co phosphide [48], Mo₃Ni₃P₄₋ₓ [49], NiVP [50], and the associated sulphide V₅S₈ [51] in chromitite concentrates from the Othrys ophiolite are consistent with extremely low fO₂ (reducing environment) during serpentinization [51] and re-precipitation of sulphides.
Intergrowths between sulphides and magnetite often forming curved crystals, which reflect a simultaneous deposition, coupled with the occurrence of calcite and an unknown (Fe,Mg) silicate (Figure 4d–f) resembling Mg–hisingerite [52] may provide evidence for the conditions of the Pindos sulphide deposition. Such a (Fe,Mg) silicate is unusual compared to the common presence of Mg-enriched serpentinite in other ophiolite complexes. It seems to be comparable with the secondary phyllosilicates described in altered ferroan metaperidotite (“Oxide Body”), from the Laramie Complex (Laramie city, WY, USA), and serpentinites containing the Si-free minerals, such as brucite and NiFe alloy (awaruite). Such secondary phyllosilicates contain approximately equal amounts of end-members of the serpentine [(Mg,Fe₂⁺)₅Si₃O₉(OH)₄] and hisingerite [Fe³⁺₂Si₂O₇(OH)₂nH₂O] [28]. The substitution of Fe³⁺ ions into the serpentine structure is crystallographically favorable because of the smaller ionic radius of Fe³⁺ compared to that of Mg²⁺ [53]. Moreover, based on a thermodynamic model for hydrothermal alteration in the Fe-silicate system, it has been shown that the formation of serpentine–hisingerite solid solutions after primary olivine may occur at elevated $\Delta \mu_{\text{Fe}_2\text{O}_3}$ and low $\Delta \mu_{\text{H}_2\text{O}}$ at low temperatures (about 200 °C) [28]. In addition, it has been suggested that H₂ production is associated with Fe(III) incorporation into serpentine (or magnetite) [54–56].

The association of magnetite with sulphides from the Pindos (Tsoumes) resembles an unusual association of magnetite with sulphides of Cyprus-type ophiolite-hosted VMS deposit in Ortaklar, located in the Koçali Complex, Turkey [7]. They are similar in terms of the deposition order, as suggested by the observed textural relationships: Fe-sulphide (pyrrhotite or pyrite) → chalcopyrite → sphalerite and subsequently magnetite (Figure 4; [7]) and the Cu, Zn, Pb, and Au-Ag contents [7]. Such temporal relationships among the primary ore minerals have been attributed to the evolution of ore-forming fluids. Specifically, increasing oxygen fugacity ($f_{\text{O}_2}$) and pH would deplete sulphide (H₂S) and facilitate the magnetite precipitation in the hydrothermal fluids [7]. In addition, the Pindos sulphides exhibit similarities with the Cogne magnetite deposit (Western Alps, Italy), which is the largest in a series of apatite and sulphide-free magnetite orebodies that are hosted in serpentinites belonging to western Alpine ophiolitic units [8]. The authors applying thermodynamic modelling of fluid–rock interactions concluded that fractionation processes such as phase separation were critical to generate hydrothermal fluids capable of precipitating large amounts of magnetite in various types of ultramafic host rocks [8]. Although variable textures described in the large Cogne magnetite deposit differ from those in the Pindos magnetite ore, the trace element content of magnetite from the Cogne deposit, characterized by high Mg and Mn and low Cr, Ti, and V [8], is comparable to those in the Pindos magnetite separates [57]. Additionally, Fe–Cu–Zn–Co–Ni mineralization has been reported in seafloor VMS deposits from modern oceans, as well as in their potential analogues on several ophiolite complexes, as exemplified in the Urals, supporting the origin of such deposits by hydrothermal processes [19]. Moreover, hydrothermal products including Cu–Zn–(Co)–rich massive sulphides, hosted in ultramafic rocks at the Rainbow (Mid-Atlantic Ridge), exhibit structure, mineralogy, and bulk rock chemistry similar to those found in mafic volcanic-hosted massive sulphide deposits [58].

In general, the main factors controlling metal associations in seafloor massive sulphide (SMS) deposits may be the temperature of deposition, seafloor spreading rate and r/w ratio, and zone refining [59]. The authors emphasized the significance of the final depositional conditions and evolution of mound and vent structures rather than the original geochemistry of the hydrothermal fluid; the composition of the substrate may become relevant in subseafloor mineralization, where sulphides are precipitated by the reaction of ascending hydrothermal fluids with substrate host rocks [59]. Individual deposits may show a mixture of geochemical signatures, which may be related to mafic and ultramafic rocks [19,58]. Assuming that the leaching of elements from substrate rocks is influenced by the structure of the oceanic lithosphere and by the nature of the hydrothermal convection (spreading rate), some specific geochemical features, such as Au enrichment, Au/Ag and Co/Ni ratios, may be related to the nature of the substrate, the presence of a magmatic influx of volatiles and metals, the morphology of vent structures, the ridge spreading rate, or a combination of these factors [19,58,59]. Although the observed textural and mineralogical features (Figures 3–5) are inconsistent with an origin of the sulphides at magmatic temperatures, the recorded differences,
such as the higher Zn, Se, Mo, Au, Ag, Hg, and Sb and lower Ni contents in the Pindos compared to the Othrys sulphides (Table 3; Figure 6), may reflect inheritance of a primary magmatic signature.

6.2. Genetic Significance of Trace Elements

The massive Cyprus-type sulphides from the Kondro Hill are characterized by elevated Zn, Co, Se, Au, As, Ag, Mo, and Sb content (Table 1) compared to those of the Othrys and most of the Troodos sulphide ores (Figure 6). Apart from the major elements, namely Fe, Cu, and Zn, hosted in pyrite, chalcopyrite, bornite, and sphalerite, Au occurs as submicroscopic particles (<1 μm) in grains of As-bearing pyrite, chalcopyrite, and bornite [20,26]. Selenium and Te are found as individual fine minerals, such as selenides (clausthalite) and tellurides (melonite) in Cu minerals (Figure 2f; [26]). Although Se can be easily dissolved as a solid solution in high-temperature chalcopyrite [58], the presence of clausthalite in a late generation of fine-grained chalcopyrite–sphalerite intergrowths, penetrating into an earlier stage ore, may indicate re-distribution of Se. A late growth of clausthalite is also supported by the occurrence of clausthalite and tellurides filling cracks in pyrite and Cu minerals [26]. Furthermore, on the basis of thermodynamic calculations, it has been demonstrated that the presence of selenides in the oxidation zones of sulphide ores of Uralian VMS deposits is related to their stability under oxidizing conditions [60]. Molybdenite or other visible Mo minerals in the Pindos and Othrys sulphides have not yet been reported. It has been established that Mo displays siderophile, chalcophile, and lithophile behavior, depending on the composition of the system (including fO2 and fS2), temperature, and pressure [61]. Further research is required to define the potential presence of invisible Mo minerals (less than 1 μ) in the Pindos sulphide-magnetite ores.

6.3. Stability of Sulphides

A salient feature of the sulphide minerals is a varying stability. The occurrence of euhedral pyrite crystals, in contrast to microcrystalline unhedral Cu and Zn sulphides (Figure 2), may indicate that pyrite was more stable during subsequent modification of the orebody. Although early large crystals of pyrite may be replaced by chalcopyrite or bornite and Fe-poor sphalerite intergrowths (Figure 2), the formation of cruciform aggregates of secondary minerals occurs only on bornite surfaces (Figure 2i–l), probably reflecting a difference in their stability. The preferential leaching of Cu and Zn sulphide phases and the neo-formation of high Cu sulphides on bornite in contrast to neighboring pyrite may be the result of a preferred dissolution of Cu sulphides over pyrite, due to differing surface potentials [62]. It has been suggested that bornite with sulfur in excess (x-bornite) is stable at high temperature [62]. The authors of this study show that if the so-called sulfur-rich bornites are annealed at lower temperature, chalcopyrite or chalcopyrite and digenite exsolve, depending on the annealing temperature and composition. In addition to this exsolution, a new phase forms below approximately 140 °C, which is referred to as x-bornite, and it is a metastable phase. Although x-bornite is a metastable phase, the presented data (Figure 2i–l; Table 1) may confirm that x-bornite can remain for a long time in natural environments, and epigenetic minerals, with a stoichiometry resembling geerite or spionkopite [63,64], can be formed under environmental conditions in a short time.

7. Conclusions

The compilation of the mineralogical, geochemical, and mineral chemistry data from the sulphide occurrences hosted in the Pindos ophiolite complex and those from other ophiolites lead us to the following conclusions:

- Elevated contents of Au as invisible submicroscopic Au in pyrite and Cu minerals in the Pindos sulphides may reflect main collectors of Au at the time of the sulphide mineralization.
- The occurrence of clausthalite (PbSe) and fine-grained gold in chalcopyrite–bornite–sphalerite intergrowths of a subsequent stage mineralization in the Pindos sulphides indicates their remobilization/re-deposition.
- Sulphides (pyrrhotite, chalcopyrite, bornite, and sphalerite) associated with magnetite, at deeper parts of the Pindos (Tsoumes), exhibit Cu/(Cu+Ni), Ni/Co, and Pt/(Pt+Pd) ratios,
suggesting either no magmatic origin or a complete transformation of a preexisting magmatic assemblages.

- Textural features and the presence of the (Fe/Mg) phyllosilicate resembling Mg–hisingerite, and calcite in the matrix of the Pindos sulphides, suggest precipitation of the sulphide-magnetite ore at the deeper levels from a Fe-rich and alkaline ore-forming system.
- The preferential leaching of Fe and S and neo-formed high Cu sulphides on bornite, in contrast to neighboring pyrite, may be the result of a preferred dissolution of Cu sulphides over pyrite, confirming literature data on differing surface potentials between those sulphides.
- Assuming that trace elements in epigenetic minerals are derived from the decomposition of primary minerals, and coupled with the higher Zn, Se, Mo, Au, Ag, Hg, and Sb and lower Ni contents in the Pindos compared to the Othrys sulphides, this may reflect inheritance of a primary magmatic signature.

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