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MINERAL CHEMISTRY AND FORMATION OF AWARUITE AND HEAZLEWOODITE IN THE XEROLIVADO CHROME MINE, VOURINOS, GREECE

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Abstract

The Serpentinite between the chromite bodies 4 and 5 of Xerolivado mine (Vourinos, Greece), contains sparsely very small grains (<20μm) of awaruite ($Fe_{0.91}Cu_{0.06}Co_{0.03}Ni_3$), heazlewoodite ($Ni_{2.91}Fe_{0.06}S_2$), magnetite and Co-pentlandite ($Ni_{3.79}Fe_{2.98}Co_{2.38}S_8$). The olivine contains 0.40 wt% NiO and 6.91 wt% FeO, while the serpentine 0.18 wt% NiO and 3.02 wt% FeO. The Co-content of awaruite is 1.31 wt% and that of heazlewoodite 0.12 wt%. Heazlewoodite is a product of the primary Co-pentlandite reduction, resulting from the serpentinization of the ultramafic rock. The Ni content of awaruite is derived both from olivine and from Co-pentlandite. The reducing environment resulting from serpentinization and the low sulphur fugacity, favour the formation of awaruite, heazlewoodite and magnetite.

Keywords: *Pentlandite, olivine, serpentine, magnetite.*

Περίληψη

Ο σερπεντινίτης μεταξύ των χρωμιτικών σωμάτων 4 και 5 στο μεταλλείο Ξερολίβαδο (Βούρινος, Ελλάδα) περιέχει σποραδικούς πολύ μικρούς κόκκους (<20μm) αβαρουίτη ($Fe_{0,91}Cu_{0,06}Co_{0,03}Ni_3$), χεζλεγουδίτη ($Ni_{2,91}Fe_{0,06}S_2$), μαγνητίτη και Co-πεντλανδίτη ($Ni_{3,79}Fe_{2,98}Co_{2,38}S_8$). Ο ολιβίνης περιέχει 0,40 %κβ NiO και 6,91 %κβ FeO, ενώ ο σερπεντίνης 0,18 %κβ NiO και 3,02 %κβ FeO. Η περιεκτικότητα Co του αβαρουίτη είναι 1,31 %κβ και του χεζλεγουδίτη 0,12 %κβ. Ο χεζλεγουδίτης είναι ένα προϊόν της αναγωγής του πρωταρχικού Co-πεντλανδίτη, που προκύπτει από τη σερπεντινίωση του υπερβασικού πετρώματος. Το περιεχόμενο Ni στον αβαρουίτη προέρχεται τόσο από τον ολιβίνη και από τον Co-πεντλανδίτη. Το αναγωγικό περιβάλλον που προκύπτει από τη σερπεντινίωση και η χαμηλή μερική πίεση του θείου, ευνοούν τον σχηματισμό αβαρουίτη, χεζλεγουδίτη και μαγνητίτη.

Λέξεις κλειδιά: *Πεντλανδίτης, ολιβίνης, σερπεντίνης, μαγνητίτης.*

1. Introduction

The paragenesis and the chemical composition of the opaque minerals (e.g., sulphides, metal alloys) formed during serpentinization, depend on the initial chemical composition of the olivine and the oxygen and sulfur fugacities (fO_2 and fS_2). The Ni^{2+} commonly display preference in the M1 site of olivine, and the serpentinized olivine is proposed as the source of nickel (Brown, 1980; Filippidis and Annersten, 1981; Annersten *et al.*, 1982; Filippidis, 1982, 1985, 1991; Nord *et al.*, 1982; Deer *et al.*, 1997), whereas, the origin of the sulfur is attributed to the fluid phase that causes the serpentinization. The sulfur either exists in the fluid phase, or comes from sources outside of the ultramafic body and transferred by the fluid phase along with H_2O, CO_2 and Cl (Ashley, 1973; Groves and Keays, 1979; Groves *et al.*, 1979; Donaldson, 1981; Donaldson and Bromley, 1981; Seccombe *et al.*, 1981; Pasteris, 1984).

The “internal” sulfur, which originates from magmatic sulphides, immigrates during serpentinization (Shima and Naldrett, 1975; Donaldson, 1981; Seccombe *et al.*, 1981). Sulfur can occur under reducing conditions from these magmatic sulphides (e.g., pentlandite, pyrrhotite) with the process of desulfurization, producing H_2S, sulphides and alloys at temperatures of 365-445^{o}C. The produced H_2S, reacts with the metallic elements that are released during the serpentinization of the silicate minerals and Ni-Fe-sulphides are produced. Further serpentinization, can lead to the formation of violarite and/or millerite (Krishna Rao, 1964, Kanehira *et al.*, 1975).

The maximum thermal stability of pentlandite is at the temperature of 610^{o}C, however pentlandites frequently contain amounts of Co substituting Fe and Ni. The presence of Co raises the thermal stability of pentlandites (up to 630^{o}C) and the confining pressure reduces it to 425^{o}C. The maximum thermal stability of heazlewoodite is 556^{o}C, but metal deficiency lowers it to 524^{o}C The Ni content of awaruite and heazlewoodite is interpreted as being derived both from primary silicates and from a primary sulphide such as pentlandite; under reducing conditions pentlandite is desulphurized (Craig and Scott, 1974).

The present study investigates the mineral-chemistry and formation of awaruite (Ni-Fe alloy) and heazlewoodite, found in the serpentinite of the Xerolivado chrome mine, Vourinos, Greece.

2. Geologic setting

The Vourinos ophiolite complex is located in western Macedonia of northern Greece (Fig. 1). It covers an area of 400 km^2 dominated by mantle rocks and it constitutes a complete ophiolite sequence with a well-exposed petrologic moho (Grieco and Merlini, 2012). The crustal sequence consists of mafic and ultramafic cumulates, gabbro, dykes, pillow lavas and carbonate sediment cover (Liati *et al.*, 2004; Rassios and Moores, 2006). The age of the Vourinos oceanic crust was found to be 168.5±2.4 my and 172.9±3.9 my via U/Pb analyses of zircons within plagiogranite (Liati *et al.*, 2004). Mantle rocks are strongly depleted and dominated by harzburgite with abundant irregular chromitite-hosting dunite bodies (Saccani *et al.*, 2004; Bortolotti *et al.*, 2004; Grieco and Merlini, 2012). Some areas, several close to the eastern emplacement margin, are serpentinized (Margaras and Vacondios, 1996, Grieco and Merlini, 2012).

Many authors have worked on Vourinos geological and petrological/geochemical characteristics and evidence confirms the existence of multiple magma chambers and that the harzburgites represent mantle residue, remaining after a high degree of partial melting (Moores, 1969; Jackson *et al.*, 1975; Harkins *et al.*, 1980; Beccaluva *et al.*, 1984; Paraskevopoulos and Economou, 1986; Konstantopoulou and Economou-Eliopoulos, 1991). The chromite formation in dunite occurred at about 1300^{o}C with re-equilibration at about 600^{o}C (Rassios and Kostopoulos, 1990). The successive stages of the structural evolution and deformation of the chromite-hosting dunite bodies were: a) Dunite and chromite formation within the upper mantle, b) High-temperature plastic deformation resulting from mantle flow, c) Low-temperature plastic to semi-brittle deformation resulting in folding of dunite and chromite and d) Brittle deformation (faults and thrusts) displacing the dunites and chromite ore bodies (Ross *et al.*, 1980; Roberts, 1988; Konstantopoulou, 1993; Filippidis, 1996, 1997; Grieco and Merlini, 2012). Serpentinization processes controlled the final mineralogical composition of the rocks and resulted in the serpentinization of the former dunite and its alteration to serpentinite and/or serpentinized peridotite.

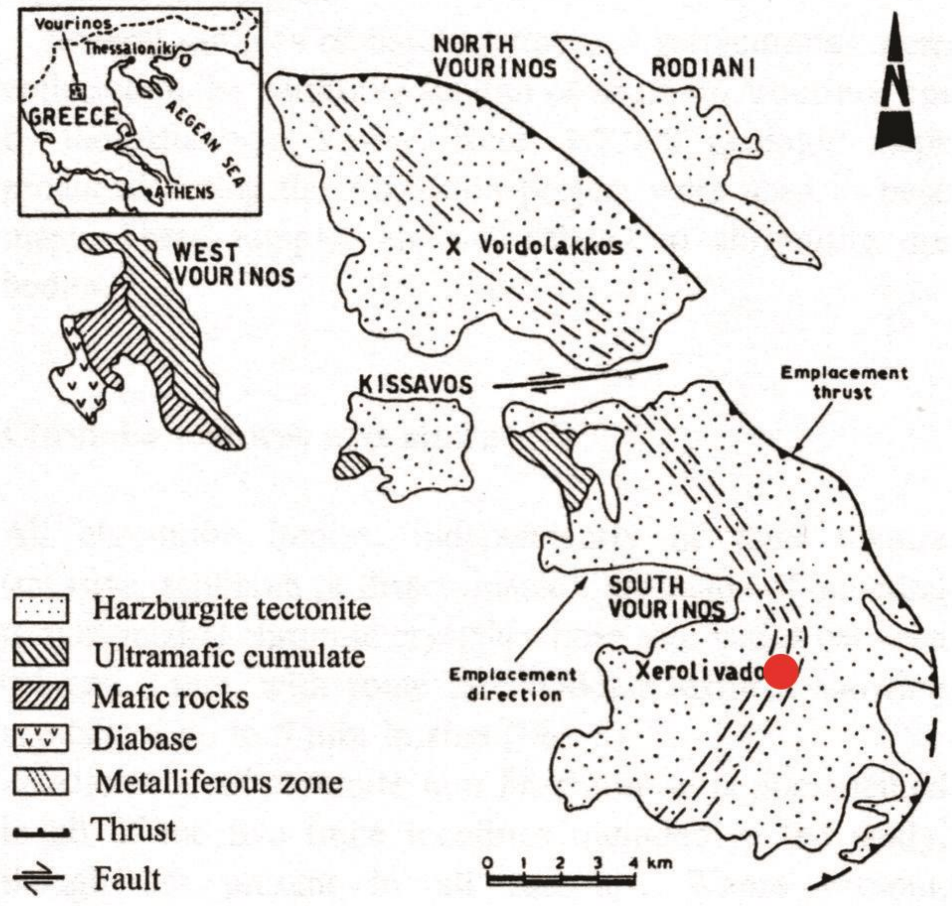


Figure 1 - Major petrologic units of the Vourinos ophiolite complex and location of the Xerolivado mine (red circle) (after Grivas *et al.*, 1993).

The largest dunite body of Vourinos occurs at Xerolivado locality (Fig. 1). It has an approximate surface exposure of 3 km^2 (3 x 1 km). Harzburgite tectonite hosts the dunite body but also outcrops within the dunite, occurring as elongated masses, with length up to 300 m, striking NE-SW (Apostolidis *et al.*, 1981; Roberts, 1988; Stamoulis, 1990; Filippidis, 1996, 1997). The Xerolivado chromite mine, hosted in the ultramafic body, is one of the world's largest alpine type chromite deposit, with a known potential of 6 million tons of schlieren ore averaging 22 modal percent chromite-schlieren chromitite bodies contain bands of schlieren ore, each being 1 to 15 cm thick, alternating with the ultramafic rock (Stamoulis, 1990; Filippidis, 1996).

Three main normal fault zones (F1, F2 and Fm) divide the Xerolivado mine into four sectors: the northern, the central, the southern and the southwestern (Fig. 2). These fault zones down throw the ultramafic body and the hosted chromitite bodies to the SW with horizontal and vertical dislocations (Stamoulis, 1990; Filippidis, 1996, 1997). The schlieren chromite bodies with thickness ranging between 1 and 12 m strike NE-SW and steeply dipping towards NW.

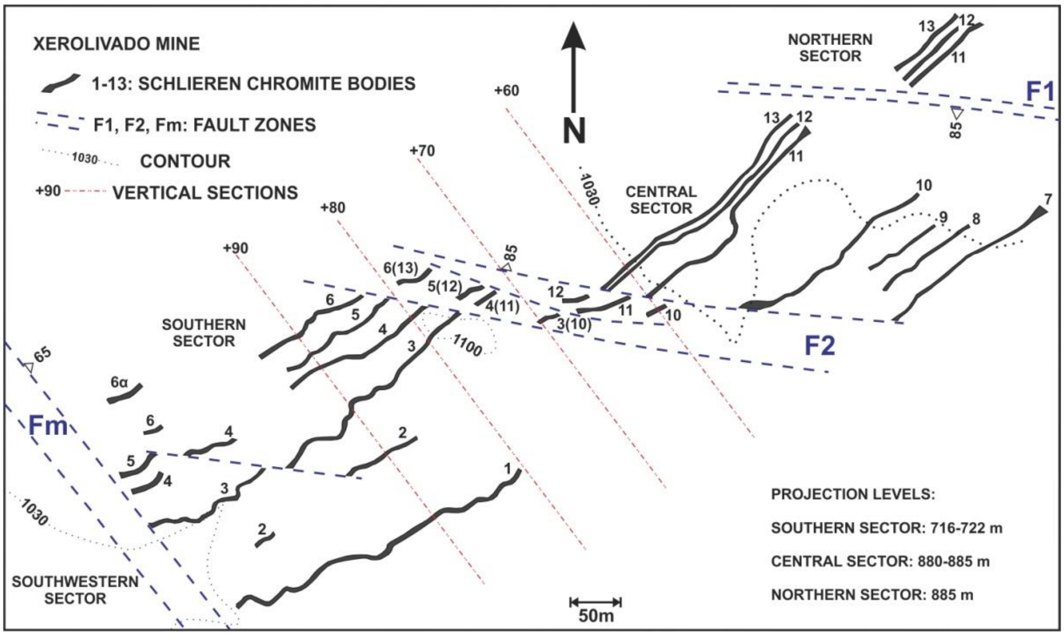


Figure 2 - Distribution and form of the schlieren chromite ore bodies of the Vourinos Xerolivado mine (modified after Filippidis, 1996).

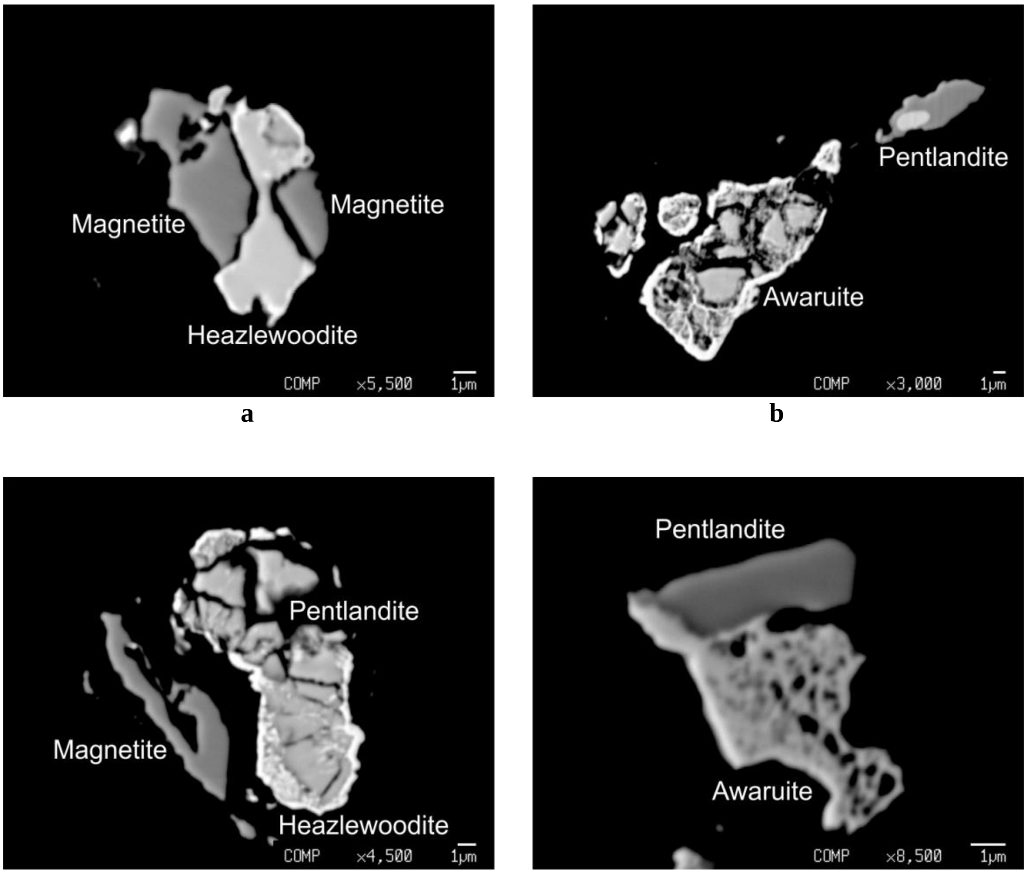
3. Materials and methods

The serpentinite samples were collected from the underground tunnels of the Xerolivado chromite mine, between chromite bodies 4 and 5 (Fig. 2). Thin and thin-polished sections were mounted from these samples and they were investigated by optical microscopy, scanning electron microscope and electron microprobe for their textures as well as their mineralogical and chemical composition.

Mineral chemistry of sulphides and metal alloys was determined with a JEOL 8200 electron microprobe at the University of Milan. For the analyses the system was operated using an accelerating voltage of 15 kV, a sample current on brass of 15 nA and a counting time of 20 s on the peaks and 10 s on background. A series of natural minerals were used as standards.

4. Results

The microscopic examination of the samples shows that they are dominated by the presence of serpentine. Modal analyses of the samples shows that presence of serpentine makes up more than 90% v/v of total silicates, thus all samples are characterized as serpentinites. Serpentine has a typical mesh texture, the position of the original fractures and grain boundaries of olivine are marked by a simple parting or by a string of magnetite, sulphides and metal alloys. Sulphides, magnetite and metal alloys grains are found disseminated in the serpentinite matrix having a relatively small size of no more than 20 μm (Fig. 3). Awaruite and heazlewoodite are also found substituting primary pentlandite (Fig. 3b, c and d). Chromite is also present in disseminated grains. Some chromite grains are altered to ferrochromite in spots on their rims.



a b

c d

Figure 3 - Microphotographs from scanning electron microscope (SEM) with back-scattered electron image (BSI) from Xerolivado serpeninites. a) Sample D4-5/717, magnetite (gray) and heazlewoodite (light gray), b) Sample D4/765, awaruite (light gray) and pentlandite (gray), c) Sample D4-5/738, magnetite (gray), pentlandite (light gray) and heazlewoodite (white rim), d) Sample D4-5/765, awaruite (light gray) and pentlandite (gray).

The chemical compositions of awaruite, heazlewoodite, and pentlandite are presented respectively in Tables 1, 2, and 3.

Awaruite contains on average 75.71 wt% Ni, 21.67 wt% Fe, 1.53 wt% Cu and 1.31 wt% Co (Table 1). Heazlewoodite contains 71.32 wt% Ni, 1.48 wt% Fe and 0.12 wt% Co (Table 2). Pentlandite contains 28.14 wt% Ni, 21.02 wt% Fe and 17.71 wt% Co (Table 3). Olivine present in the samples contains 0.40 wt% NiO and 6.91 wt% FeO, while serpentine contains 0.18 wt% NiO and 3.02 wt% FeO (Tzamos, unpublished PhD thesis).

Table 1 - Chemical composition (wt%) of Awaruite (Xerolivado mine serpentinite).

Sample	D4-5/717A	D4-5/717B	D4-5/738	C1/745A	C1/745B	C3/717B	Average
As	Bdl	0.03	Bdl	N/A	N/A	N/A	0.01
Sb	0.03	Bdl	Bdl	N/A	N/A	N/A	0.01
Co	0.95	1.06	1.91	N/A	N/A	N/A	1.31
Cu	1.44	3.63	1.29	0.93	1.52	0.35	1.53
Fe	22.17	21.45	16.38	24.74	20.18	25.10	21.67
Ni	74.65	73.42	80.13	74.76	77.52	73.76	75.71
Total	99.24	99.59	99.71	100.43	99.22	99.21	100.24
Structural formulae based on 3 (Ni)							
As	-	-	-	-	-	-	-
Sb	-	-	-	-	-	-	-
Co	0.04	0.04	0.07	0.00	0.00	0.00	0.03
Cu	0.05	0.14	0.04	0.03	0.05	0.01	0.06
Fe	0.94	0.92	0.64	1.04	0.82	1.07	0.91
Ni	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Total	4.03	4.10	3.75	4.07	3.87	4.08	4.00

Bdl: Below detection limit, N/A: not analyzed

Table 2 - Chemical composition (wt%) of Heazlewoodite (Xerolivado mine serpentinite).

Sample	D4-5/717A	D4-5/717B	D4-5/717C	D4/765	D4-5/738A	D4-5/738B	C1/745	C1/745	Average
As	Bdl	Bdl	Bdl	Bdl	0.02	0.02	N/A	N/A	0.01
Sb	Bdl	Bdl	Bdl	Bdl	0.04	Bdl	N/A	N/A	0.01
Co	0.06	0.14	0.12	0.04	0.27	0.10	N/A	N/A	0.12
Cu	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl
Fe	1.42	1.14	2.11	1.27	1.82	1.52	1.07	1.48	1.48
Ni	72.01	70.95	70.71	70.94	70.99	71.10	72.14	71.75	71.32
S	27.44	27.81	27.43	27.40	27.20	27.39	25.06	24.81	26.82
Total	100.93	100.04	100.37	99.65	100.34	100.13	98.27	98.04	99.76
Structural formulae based on 2 (S)									
As	-	-	-	-	-	-	-	-	-
Sb	-	-	-	-	-	-	-	-	-
Co	-	0.01	-	-	0.01	-	-	-	-
Cu	-	-	-	-	-	-	-	-	-
Fe	0.06	0.05	0.09	0.05	0.08	0.06	0.05	0.07	0.06
Ni	2.87	2.79	2.82	2.83	2.85	2.84	3.15	3.16	2.91
S	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Total	4.93	4.85	4.91	4.88	4.94	4.90	5.19	5.23	4.99

Bdl: Below detection limit, N/A: Not analyzed

Table 3 - Chemical composition (wt%) of Pentlandite (Xerolivado mine serpentinite).

Sample	D4-5/765A	D4-5/738	D4/765	D4-5/765B	Average
As	Bdl	Bdl	0.01	0.04	0.01
Sb	Bdl	Bdl	Bdl	0.08	0.02
Co	18.18	17.50	19.56	15.58	17.71
Cu	Bdl	0.02	Bdl	Bdl	0.01
Fe	21.70	22.57	22.10	17.70	21.02
Ni	26.09	27.97	23.34	35.17	28.14
S	33.30	31.56	34.33	30.52	32.43
Total	99.27	99.62	99.34	99.09	99.34
Structural formulae based on 8 (S)					
As	-	-	-	-	-
Sb	-	-	-	0.01	-
Co	2.38	2.41	2.48	2.22	2.38
Cu	-	-	-	-	-
Fe	2.99	3.28	2.96	2.66	2.98
Ni	3.42	3.87	2.97	5.03	3.79
S	8.00	8.00	8.00	8.00	8.00
Total	16.79	17.56	16.41	17.92	17.15

Bdl: Below detection limit

5. Discussion and conclusions

The chemical formulae of the studied opaque minerals are $Fe_{0.91}Cu_{0.06}Co_{0.03}Ni_3$ for awaruite, $Ni_{2.91}Fe_{0.06}S_2$ for heazlewoodite and $Ni_{3.79}Fe_{2.98}Co_{2.38}S_8$ for Co-pentlandite. In figures 4 and 5, the relative compositions of the studied mineral phases in Fe-(Ni+Co)-S and Fe-Ni-Co are shown respectively.

The formation of heazlewoodite, awaruite and magnetite as a result of the serpentinization is clearly shown by the rock texture, with disseminated small grains of the opaque minerals in the serpentinite, with the formation of rims of heazlewoodite (Fig. 3c) and awaruite (Fig. 3b) around Co-pentlandite and by even more severe substitution of Co-pentlandite grains from awaruite (Fig. 3d).

Nickel was contained in the original Mg-Fe olivine and the primary Co-pentlandite. The initial chemical composition of the (Mg,Fe,Ni) olivine, the reducing environment during serpentinization, the oxygen and sulfur fugacity (fO_2 and fS_2), controlled the formation and chemical composition of the heazlewoodite and the Ni-Fe alloy (awaruite). Heazlewoodite is a product of the primary Co-pentlandite reduction, resulting from the serpentinization of the ultramafic rock which contained traces of pentlandite (Craig and Scott, 1974; Brown, 1980; Filippidis and Annersten, 1981; Annersten *et al.*, 1982; Filippidis, 1982, 1985, 1991; Nord *et al.*, 1982; Deer *et al.*, 1997).

The serpentinization of (Mg,Fe,Ni) olivine and the alteration of primary Co-pentlandite, converted some of Ni and Fe into the serpentine, and some of Ni, Fe and Co into heazlewoodite and awaruite. At very low sulfur and oxygen fugacity to sulfur and oxygen free serpentinization system, awaruite and heazlewoodite were formed. Heazlewoodite, awaruite and magnetite were formed as a result of the serpentine and brucite being unable to incorporate as much Fe and Ni into their lattices as the original olivine. The Ni content of awaruite is derived both from primary olivine and from primary Co-pentlandite. The reducing environment resulting from serpentinization yields a low sulphur fugacity, which favour the formation of the reduced opaque assemblage heazlewoodite-awaruite-magnetite.

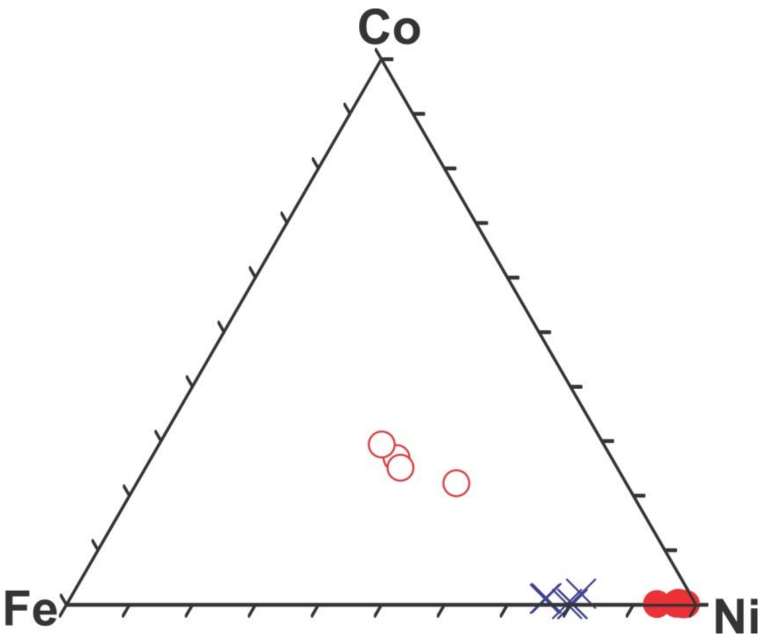


Figure 4 - Ternary diagram Fe-(Ni+Co)-S showing the relative compositions of the Xerolivado mine pentlandites (o), heazlewoodites (•) and awaruites (x).

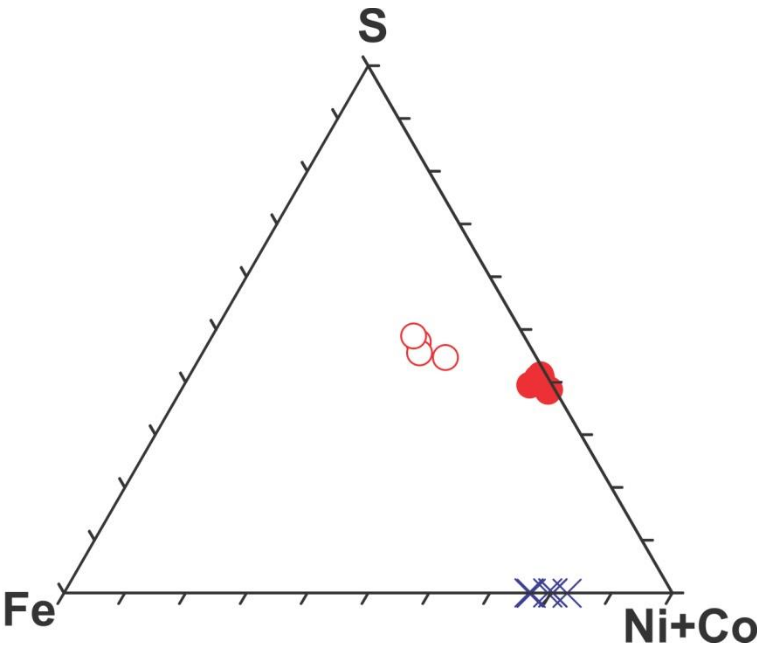


Figure 5 - Ternary diagram Fe-Ni-Co showing the relative compositions of the Xerolivado mine pentlandites (o), heazlewoodites (•) and awaruites (x).

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