Journal of Tethys: Vol. 3, No. 3, 216–236 *ISSN: 2345–2471 ©2015*

The Co, Ni, Cr and S mineralisations during serpentinization process in the Bou Azzer ore deposits (Anti-Atlas, Morocco)

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Received: 10 February 2015 / Accepted: 10 August 2015 / Published online: 01 September 2015

Abstract

The serpentinization of the harzburgitic mantle section of the Bou Azzer Neoproterozoic ophiolite is studied by field mapping, structural observations, optical micrography, SEM and X-ray diffractometry, and relationships with Co, Ni, Cr and sulphides minerals are discussed. Serpentinization occurred in two major steps with, i) intra-oceanic pseudomorphic serpentinization materialized by the isotropic serpophite often associated with antigorite fibres preserving the primary form of olivine crystals, and ii) tectonic serpentinization with lizardite and chrysotile crystallisation during ophiolite obduction and deformation in relation with synkinematic granitoid intrusions (ca. 650-635 Ma). Brucite is fairly frequent as inclusions in the serpentine aggregates. The serpentinization processes led to the remobilization of S, Fe, Ni and Co included in the primary magmatic assemblage. The sulfide assemblage varies with the degree of serpentinization, with from low to high degrees: pentlandite + pyrrhotite + pentlandite + heazlewoodite (godlevskite); pentlandite + polydymite (or violarite); pentlandite + millerite, and polydymite + millerite. The presence of orcelite, the only stable Ni arsenide during serpentinization, reflects conditions of high activity of Ni and low activity of Fe in the fluids involved in serpentinization. The relative frequency of maucherite underlines the importance of arsenic in mantle-sourced fluids. The values of the arsenic activity could locally be as high as that of sulfur to form an immiscible As-rich liquid, which is the origin of As-rich paragenesis of high temperature.

Keywords: Bou Azzer, Ophiolite, Serpentinization, Pseudomorphic, Morocco.

1- Introduction

Serpentinites basically form through peridotite hydration in varied structural settings such as oceanic ridges (Miyashiro *et al*., 1969; Alt and Shanks, 2003), ophiolites (Coleman, 1971; Coleman and Keist, 1971), transform fracture zones (Skelton and Jakobsson, 2007), passive margins (Sibuet *et al*., 2007), subduction zones (Ranero *et al*, 2003, Ewans and Hawkins, 2003) or kimberlite intrusions (Dawson, 1980). They are composed essentially of antigorite, chrysotile and lizardite with sub-ordinate amounts of carbonates, chromite, magnetite, magnesite, talc, tremolite and chlorite. Antigorite is the most common mineral and occurs as flaky crystals or interpenetrating and interlocking elongate plates. Sometimes, the antigorite flakes and blades are arranged in roughly parallel aggregates. Chrysotile occurs as cross-fiber veinlets traversing the antigorite matrix, which indicates its late crystallization under static conditions. Lizardite occurs as fine aggregates or as isotropic irregular plates. Brucite that forms during early serpentinization of olivine further reacts with SiO2-rich fluids and forms lizardite, leading to the lack of brucite in these serpentinized peridotites. Besides causing changes of rheology and density of mantle rocks (Escarti *et al*, 1997), serpentinization also influences other characteristic petrophysical properties such as magnetic susceptibility and seismic velocities (Ranero *et al*, 2003, Bach *et al*, 2006). Serpentinization also is believed to play an important role in geochemical budgets of the oceans (Tampson and Melson, 1970, Snow and Dick, 1995) and may have important consequences for microbial processes (Kelley *et al*, 2001, Holm and Charlon, 2001).

Of particular importance for economic geology is the fact that serpentinization is accompanied by the early individualisation of Co, Ni and Cr minerals. In the present paper we consider the case of the Neoproterozoic serpentinites from the Bou Azzer inlier of the Central Anti-Atlas (Morocco). The mantle section of the Bou Azzer ophiolite is dominated by totally serpentinized harzburgite (Leblanc, 1975). Less abundant dunite occurs as lenses and bands within harzburgite. Small-scale chromitite pods, pyroxenite dykes and late-stage wehrlite intrusions also occur. This mantle section is characterized by its high degree of serpentinization, and chrysotile asbestos has been exploited, especially along the borders of a dialogite (rhodochrosite) body (Leblanc and Billaud, 1982). Late hydrothermal alteration has transformed serpentinite to chloritic facies with thin veinlets of asbestos and banded textures materializing the metasomatic fronts. This article describes the geological, petrological, mineralogical and textural characteristics of the Bou Azzer serpentinites, in order to define the behavior of nickel, cobalt, chrome and sulfur during serpentinization process.

2- Geological background

The Bou Azzer- El Graara erosional inlier, along with the Siroua inlier to the west (Fig. 1) exposes a Pan-African suture zone along the Anti-Atlas Major Fault (Choubert, 1947), which divides the Precambrian terrains of the Anti-Atlas Mountains into two distinct areas (Choubert, 1963), i.e., 1) Paleoproterozoic to Tonian metamorphic and magmatic terranes south west of the Anti-Atlas Major Fault, belonging to the External Zone of the Pan-African Belt, and 2) Tonian to Cryogenian-Early Ediacaran terranes north-east of the fault, belonging to the Internal Zones of the belt (Gasquet *et al*., 2008).

In the External Zone (e.g. Kerdous and Zenaga inliers), the ~1100-800 Ma Lkest-Taghdout Group consists of Neoproterozoic limestone and quartzite platform deposits These deposits overlie unconformably Paleoproterozoic schists and granites belonging to the northern margin of the West African Craton.In the Bou Azzer suture zone (Fig. 2), the 770-760 Ma Tichibanine-BenLgrad Group consists of meta-volcanic and meta-sedimentary deposits attributed to an intra-oceanic volcanic arc (Soulaimani *et al*., 2013). The Assif n'Bougmmane-Takroumt or Igrane-Bou Azzer metamorphic complex is composed of gneisses, amphibolites and mica-schists. This arc complex is intruded by basic rocks and granites. Recent datings yielded ages of 755±9 Ma for the orthogneiss protholiths and 695±5 Ma for two-mica leucogranites (D'Lemos *et al*., 2006; El Hadi *et al*., 2010; Admou *et al*., 2013). The Bou Azzer-Aït Ahmane dismembered meta-ophiolite complex (Leblanc, 1975) consists of a mantle section of ultrabasic tectonites extending mostly to the west and by a crustal section of gabbroic and basaltic units extending to the east of the inlier. These metamorphic oceanic units are intruded by synkinematic intrusions dated at ca. 650-635 Ma (e.g. Ait Ahmane, Ousdrat, Bou

Offroh), and by post-tectonic intrusions of upper Neoproterozoic age, including the 586 Ma-old Bleida granodiorite. The Bou Azzer 'green rocks' were firstly considered as an intrusive series (Jouravsky, 1952; Choubert, 1970). Routhier (1963) was the first author to suggest the occurrence of an ophiolitic complex, which was then confirmed by Leblanc (1973). Several studies have been conducted on this complex (Leblanc, 1975; Leblanc et Lancelot, 1980; Saquaque, 1992; El Hadi, 1988; Hilal, 1991; Admou, 1989; Naidoo *et al*., 1991; Bodinier *et al*., 1984; Soulaimani *et al*., 2006). Recently this ophiolite has been dated at 697±8 Ma (El Hadi *et al*., 2010). A NE-SW cross-section surveyed in the southern side of Aït Ahmane village shows the deformational events that affected the different lithological units. A synclinal structure is notice able at Jbel Oumagha (Admou *et al*., 2013; Bhilisse *et al*., 2014).

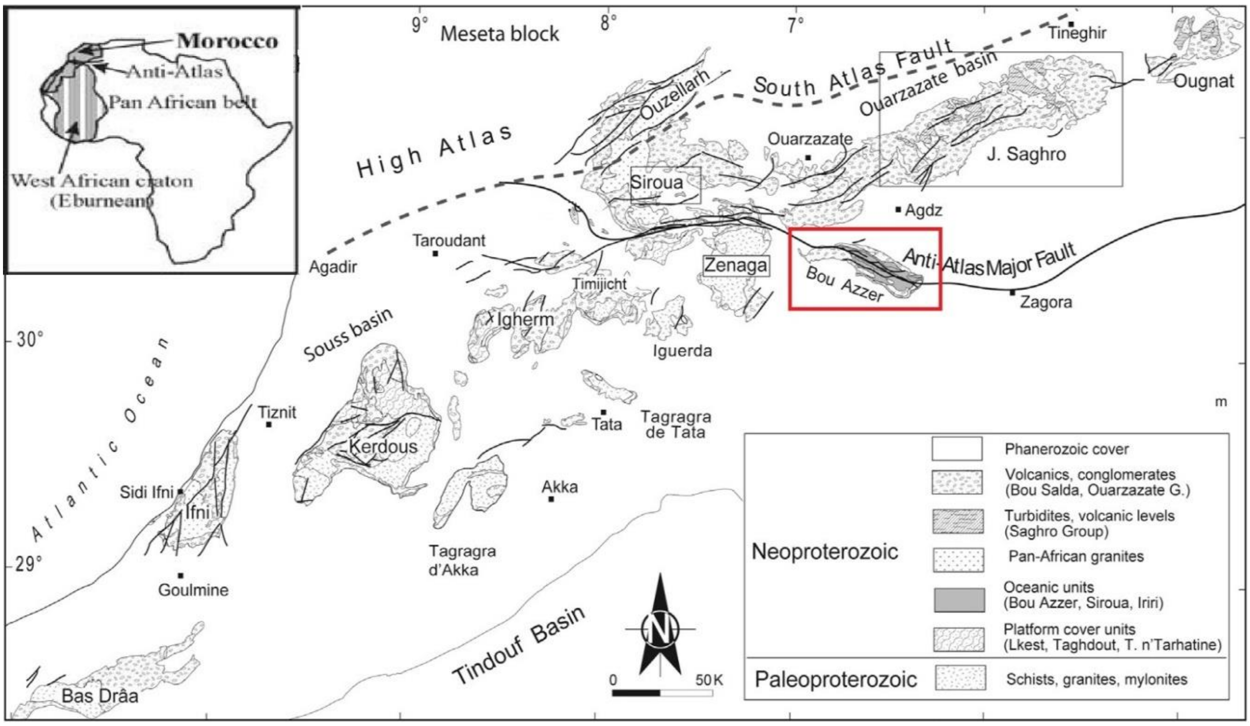

Figure 1) Generalized tectonic map of Anti-Atlas Mountains inliers (adapted from Gasquet et al., 2008).

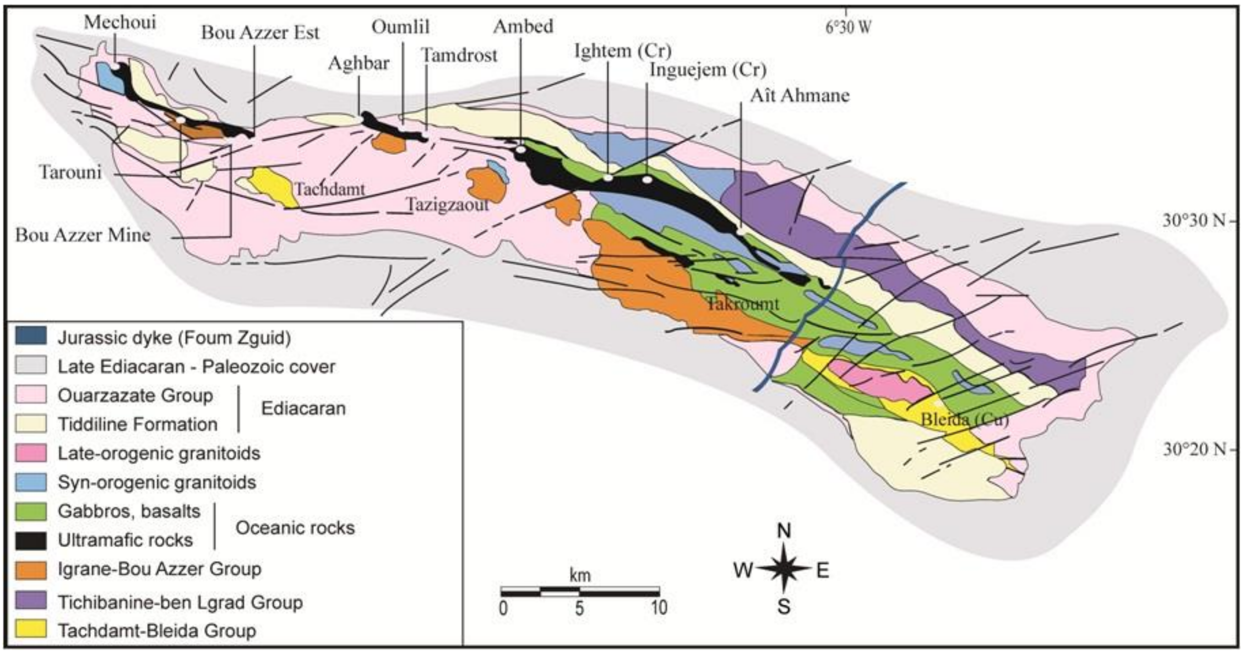

Figure 2) Geological map of the Bou Azzer–El Graara inlier (Oberthür et al., 2009).

The Bou Azzer ophiolite contains several types of mineralisation in both the mantle and the crustal sequence: The serpentinized mantle sequence does not show relict texture or deformation structures. Some serpentinites contain Mg-rich chlorite and talc (Leblanc, 1975). The mantle section of Bou Azzer ophiolite is dominated by totally serpentinized harzburgite, but dunite also occurs as lenses and bands within harzburgite as well as small-scale chromitite pods, pyroxenite dykes and late-stage wehrlite intrusions.

3- Materials and methods

Our study focused on five selected areas, from west to east: Bou Offroh, Mechoui (Mokhazni), Bou Azzer Center, Ambed, Ait Abdallah and Ait Ahmane (Fig. 2). During this work we mapped parts of the serpentine massifs in order to determine any lateral or vertical variation at Bou Azzer inlier scale.

Samples were studied in thin sections under the metallographic microscope, by scanning electronic microscope (SEM) and X-ray diffractometry using Managem Center facilities.

3.1- Field data

The field study unraveled a gradient of serpentinization both horizontal and vertical. The ultrabasites of the western part of the inlier (particularly at Bou Offroh) are completely serpentinized while the process of serpentinization is partial at Ambed and almost absent in some eastern areas as Ait Ahmane and Ait Abdellah.

Two serpentinization stages can be distinguished at Bou Azzer (Bhilisse *et al*, 2014), 1) an early “pseudomorphic stage” materialized by the isotropic serpophite preserving the primary form of olivine crystals, often with antigorite needles. Brucite is fairly frequent as micrometric inclusions in serpentine minerals as antigorite and serpophite; and 2) a late, “tectonic stage” materialized by veins filled by chrysotile α and γ often crosscutting the antigorite, serpophite and brucite crystals. They are accompanied by opaque minerals. Macroscopically and microscopically interstitial spaces and schistosity planes are underlined by thick laminas and veins of magnetite. Some sulfides as pyrite and chalcopyrite are also filling this fractures. We observed that the serpentinization of ultramafic formations is related to different level of deformation. Serpentinization is more developed and complex in more deformed areas where sinistral faults and shear zones are observed (mainly oriented N110-N130, but sometimes N20°E to N60°E). The lineation is mainly oriented N 65–N70. The main paragenesis in the shear zones and faults is lizardite and chrysotile and asbestos with minor antigorite and chromitite and magnetite. Late hydrothermal alteration has transformed serpentinite to chloritic facies with asbestos in thin veinlets and banded textures representing the metasomatic fronts. Some veins and dykes are fully transformed into giobertite and magnesite, as in the case of the Ambed and Ait Ahmane massifs. In contact with gabbroid and granitoid dykes, the serpentines are transformed. The intrusive rocks also exhibit evidence of metasomatic transformations along their contacts with the serpentinites. In areas of high hydrothermal alteration, the serpentines are transformed into listwenites (Maacha, 2013).

3.2- Petrography and textures

Serpentine minerals are phyllosilicates that contain up to 13 % water and form during the hydration of basic and ultrabasic rock. Serpentine minerals, which have the simplified structure formulae $(Mg, Fe^{2+})\ 3Si_2O_5(OH)_4$, are made of superposed 1:1 alternating tetrahedral and octahedral sheets. The different spatial arrangements of these layers result in three main serpentine minerals, lizardite, chrysotile and antigorite.

The chemistry of serpentine is relatively simple, but common substitutions can include aluminum for silicon in tetrahedral coordination and aluminum and either ferrous or ferric iron for octahedrally coordinated magnesium (Deer *et al*. 1966; Wicks and Plant 1979; Trommsdorf and Evans 1972; Frost 1975; Worden *et al*. 1991; O'Hanley and Dyar 1993). The compositions of serpentine replacing olivine and pyroxenes in the same rock differ (O'Hanley 1996), although with advancing serpentine recrystallisation the differences in compositions diminish (O'Hanley 1996). The petrographic study of the Bou Azzer samples show that the antigorite-lizardite serpentinites contain the mineral assemblage: antigorite - lizardite – chrysotile - diopsidic - clinopyroxene - chlorite - magnetite - ferrian chromite ± brucite and carbonated minerals (calcite, dolomite and magnesite). The dominant serpentine mineral is antigorite (Fig. 3).

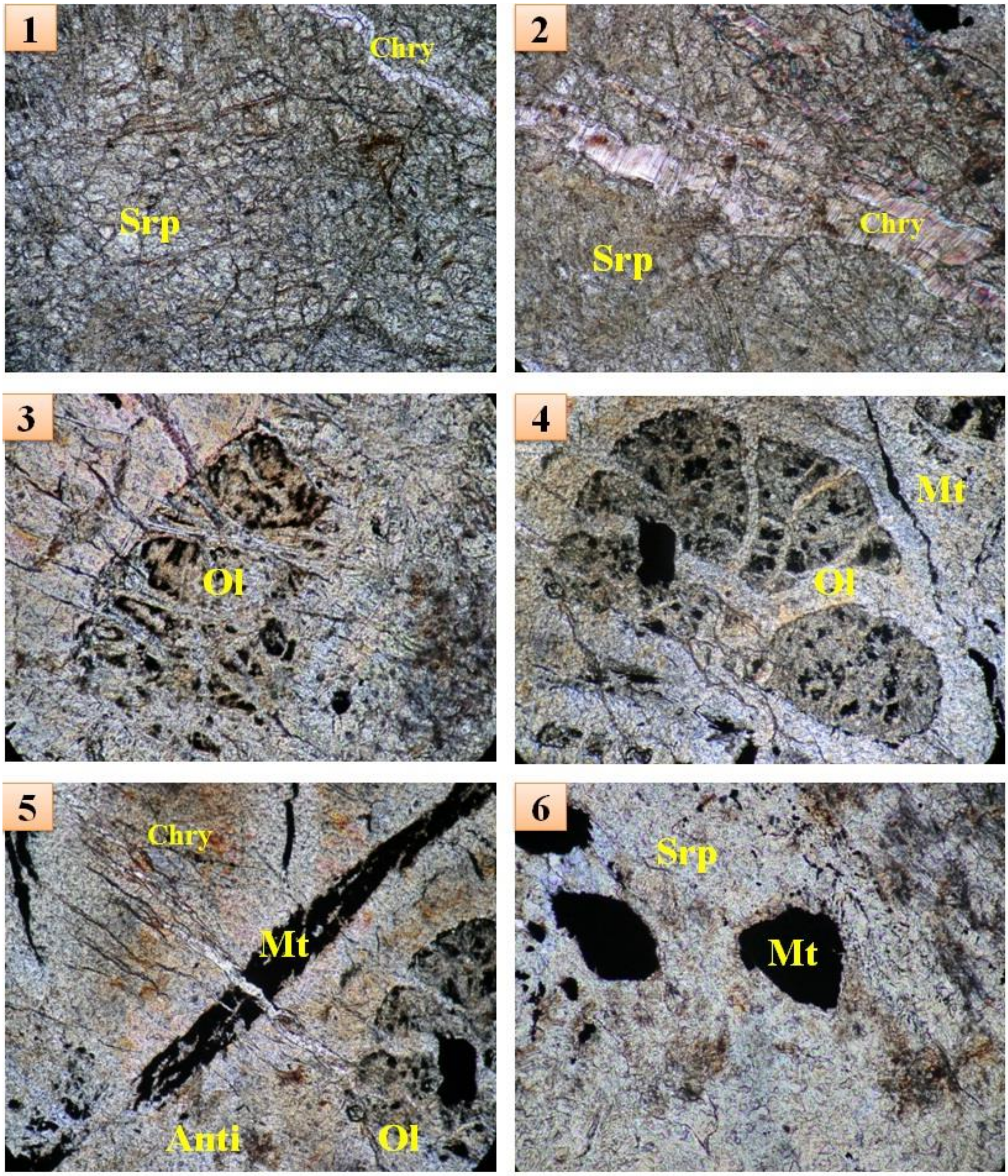

Figure 3) Photomicrographs of serpentine minerals in serpentinites and in altered serpentinites. (Ol: olivine, Srp: Serpentine, Ant: Antigorite, Chry: chrysotile, Mt: Magnetite).

The opaque minerals in serpentinites are represented mainly by chromite and magnetite. Small amounts of fine blebs and grains of scattered sulphides (pentlandite, cobaltiferous polydymite, and cobaltiferous millerite) were detected (Alansari, 2010). Magnetite in serpentinite rocks is classified genetically as primary and secondary types. Primary magnetites occur as fine to medium euhedral to anhedral grains, whereas secondary magnetite forms parallel streaks and blades along the cleavage planes of pyroxene relics. Magnetite in the altered Bou Azzer serpentinites occurs as disseminated and irregular skeletal primary grains, or as secondary ones, being the product of alteration of chromite.

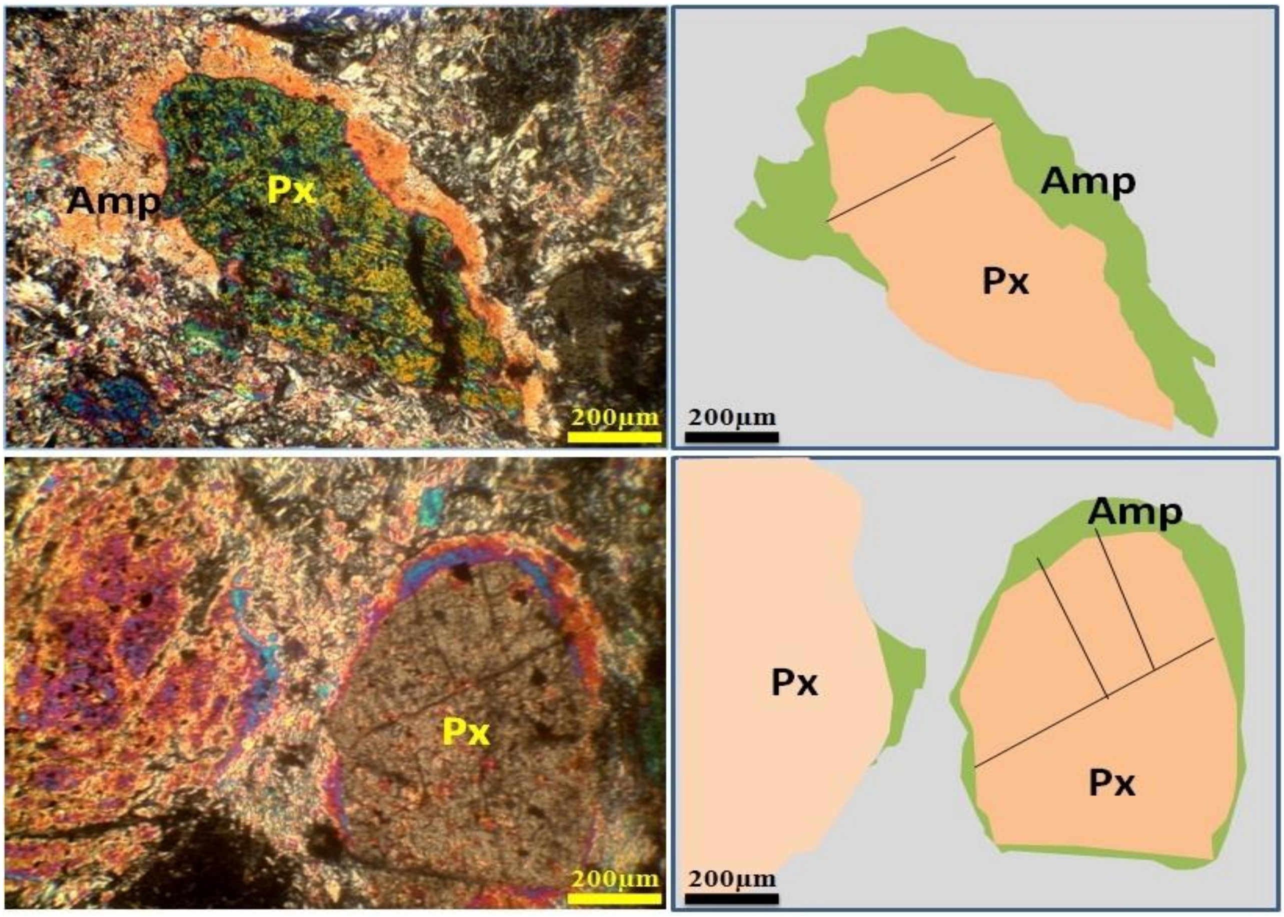

Figure 4) Photomicrographs of phenomene of ouralitisation (Px: pyroxene, Amp: Amphibole.

On the basis of microscopic studies we have identified three different types of veins which fill open tension fractures in the area, and consist of antigorite, lizardite and chrysotile in chronological order. These veins contain subordinate amounts of secondary magnetite and sulfides (mainly pyrite and chalcopyrite). Brucite is quite common, it occurs as inclusions in serpentine. Opaque assemblages are related to serpentinization. Indeed the Bou Azzer and Ait Ahmane serpentinites are generally dominated by antigorite, with the interstitial spaces and schistosity planes highlighted by thick laminae of macroscopic magnetite. Chrysotile veins are well developed since the rocks lie in a strongly sheared area.

The development of antigorite started with pyroxene pseudomorphose and the formation of bastite through the nucleation of very fine fibres of antigorite, which gradually spread in the form of sheets. This passage is marked a fine textural evolution of a raw mesh structure to mesh sheet structure. Antigorite occupies progressively any penetrative way in the rock and finally exhibits a very large flake texture interspersed by chrysotile veins and carbonates.

In the Bou Azzer ultrabasites, pyroxene ouralitisation is recorded by large rims of fibrous tremolite, likely developed before serpentinization (Fig. 4). We found that serpentinization of talc, chlorite and phlogopite also produces bastite indistinguishable from those after chain silicates. O'hara (1967) has expanded the term bastite to include talc pseudomorphs after pyroxene, but this adds an unfortunate complication to the terminology and is not recommended. The opaque minerals in the serpentinites are represented mainly by chromite and magnetite.

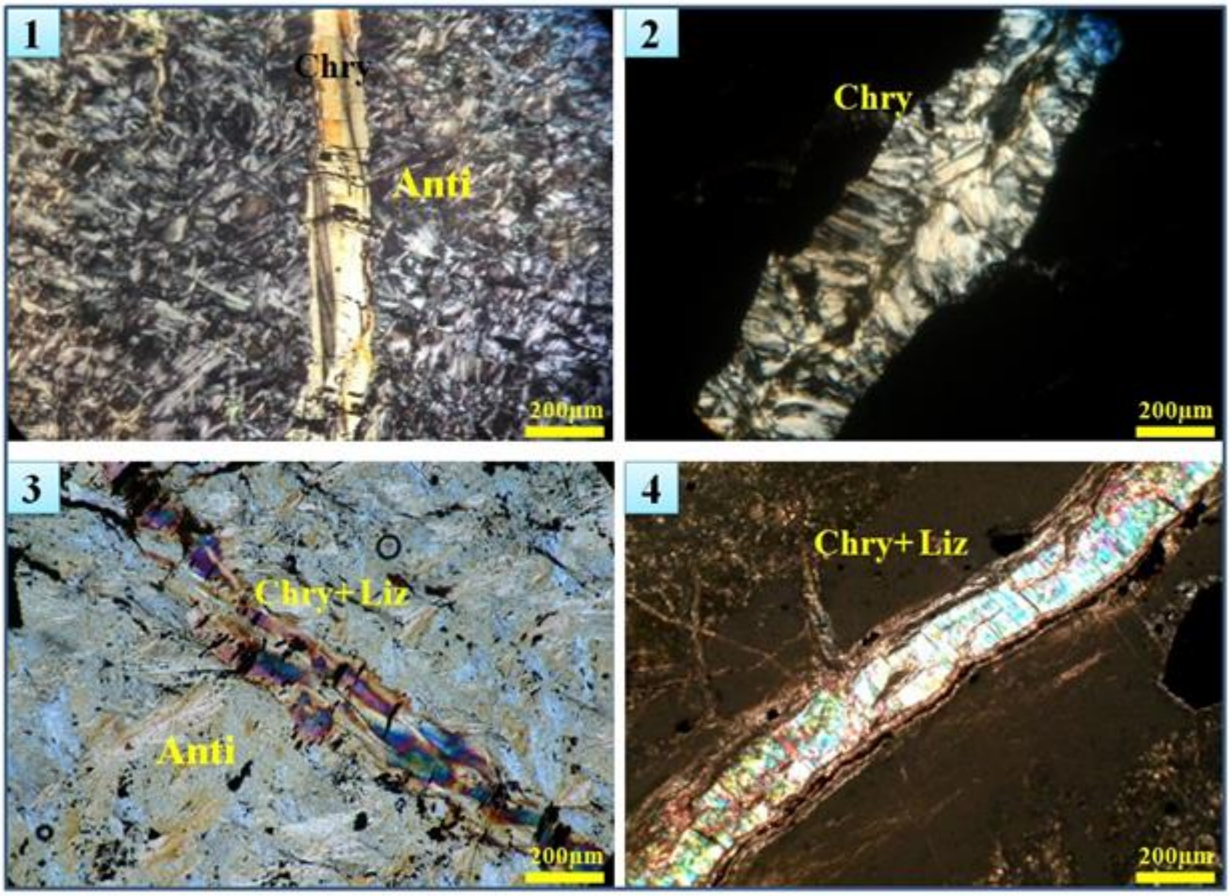

Figure 5) Textures in serpentinite rocks: fibrous textures (Anti: Antigorite, Chry: chrysotile, Liz: Lizardite).

Microscopically, the serpentinite rocks preserved the habits of grains and original textures of both olivines and orthopyroxenes, indicating harzburgite composition of parent rocks. Based on Wicks (1969) and Wicks and Whittaker (1977) classification of serpentinite textures, the Bou Azzer serpentinites represent mainly pseudomorphic types. In the serpentinite rocks, the pseudomorphs are of the hourglass type (with unequal sectors and outlines of original olivine boundaries, showing penetrative fabric and mesh texture (as fine and dense fibrous lamellar aggregates after olivine). Besides, bastites pseudomorphs after pyroxene are observed in subordinate amounts. On the other hand, pseudomorphic textures in Bou Azzer serpentinites are represented by knitted (or interlocked perpendicular flakes and fibers parallel to the cleavage planes of original orthopyroxene) and bastite textures, and sometimes by plumose texture. Textures in the altered serpentinite country rocks at Bou Azzer are non pseudomorphic (represented by penetrative fabric serrate veins of lizardite and carbonate grains enclosing pseudomorph relics of hourglass polygons among them). The recrystallization of pseudomorphic into non pseudomorphic serpentinites resulted in the replacement of the bastite textures by the interlocking ones. Moreover, rare mesh pseudomorphs seem to have been stretched and oriented. The parallel oriented lamellae begin to have been slightly brownish- stained and enriched in carbonate veinlets forming serrate veins texture. The orientation and recrystallization of pseudomorphic mesh and bastite textures are extensively developed in highly altered serpentinites.

This fibrous texture (Fig. 5) where the grains are interlaced shows birefringence colors unusually high compared to other serpentine minerals, ranging from yellow to pink. Serpentine with intermediate texture consists of a mixture of pseudomorphic, recrystallized and isotropic serpentine. Mixtures of pseudomorphic and recrystallized textures are characterized by serpentine grains with pseudomorphic rims and clusters entrapped within the center, or by an assemblage of pseudomorphic and recrystallized serpentine. The other type has a conventional pseudomorphic texture, but serpentine is isotropic instead of presenting the usual hourglass texture. This type of serpentinite is intersected by a network of serpentine veins ranging from low to dense. It has a massive and foliated structure in the shear zones.

4- Serpentinization and sulfide mineralization

4.1- Nickel, Cobalt and Iron

A variety of Fe-Ni-Co sulfides occur in moderately to completely serpentinized rocks of the Bou Azzer massives. The assemblages vary with the degree of serpentinization, from pyrrhotite-pentlandite assemblage to pentlandite-violarite, pentlandite-violarite-heazlewoodite-godlevskite assemblages, to pentlandite-violarite-millirite and violarite-millirite assemblage. The following opaque minerals have been found in minor to trace amounts: magnetite, pyrrhotite, pentlandite, chromite, heazlewoodite, godlevskite, chalcopyrite, cobaltite and nickeline in decreasing order of abundance. Serpentinization of olivine yields an excess of magnesium and iron, which are normally accommodated in brucite and magnetite. Magnetite is abondant in serpentine and some chromite grains in serpentine have a magnetite rim. Pyrrhotite–pentlandite-magnetite aggregates are commonly accompanied by minor chalcopyrite and rarely traces of cobaltite and nickeline. Pentlandite aggregates are invariably associated with minor magnetite and rarely with a trace of godlevskite. Godlevskite is included in heazlewoodite grains.

Pentlandite (between 40.46 wt% Ni and 41.55 wt% Ni) was progressively replaced by heazlewoodite, nickeliferous silicate hydroxide of Fe, Cr, Mg and Ca (5.16 wt% Ni and 26.49 wt% Ni), nickeliferous silicate hydroxicarbonates of Fe, Mn and Ca (5.21 wt% Ni) (Fig. 6) and magnetite with increasing degree of serpentinization. The pentlandite analyzed by SEM show a Ni/Fe ratio between 1.62 and 1.73. These values are much higher than normal value 1.00. These values are also markedly superior to those of pentlandite which co-exists with the Ni-Fe phase as awaruite (Ni_3Fe).

The mineralogical assemblages identified in the Bou Azzer units where serpentinization is important are composed of secondary minerals of cobaltiferous polydymite, cobaltiferous millerite, orcelite and cobalti-nickeleferous magnetite (Fig. 7). These mineralisations could come during serpentinization from mutation of a primary mineral paragenesis formed of olivine and pentlandite + pyrrhotite aggregates.

The intimate association between cobaltiferous polydymite and magnetite aggregates may result from replacement of magmatic mineral aggregates with pentlandite and pyrrhotite during the serpentinization process. The serpentinization of ultramafic rocks led to the remobilization of S, Fe, Ni and Co included in the primary magmatic assemblage. The sulfide assemblage varies with the degree of serpentinization: pentlandite+ pyrrhotite + pentlandite + heazlewoodite godlevskite , the later stages, pentlandite + polydymite (or violarite), pentlandite + millerite and polydymite+ polydymite + millerite. Mackinawite associated with pentlandite and pyrrhotite is rare and resulted from the desulfurization of magmatic sulfides by release of hydrogen.

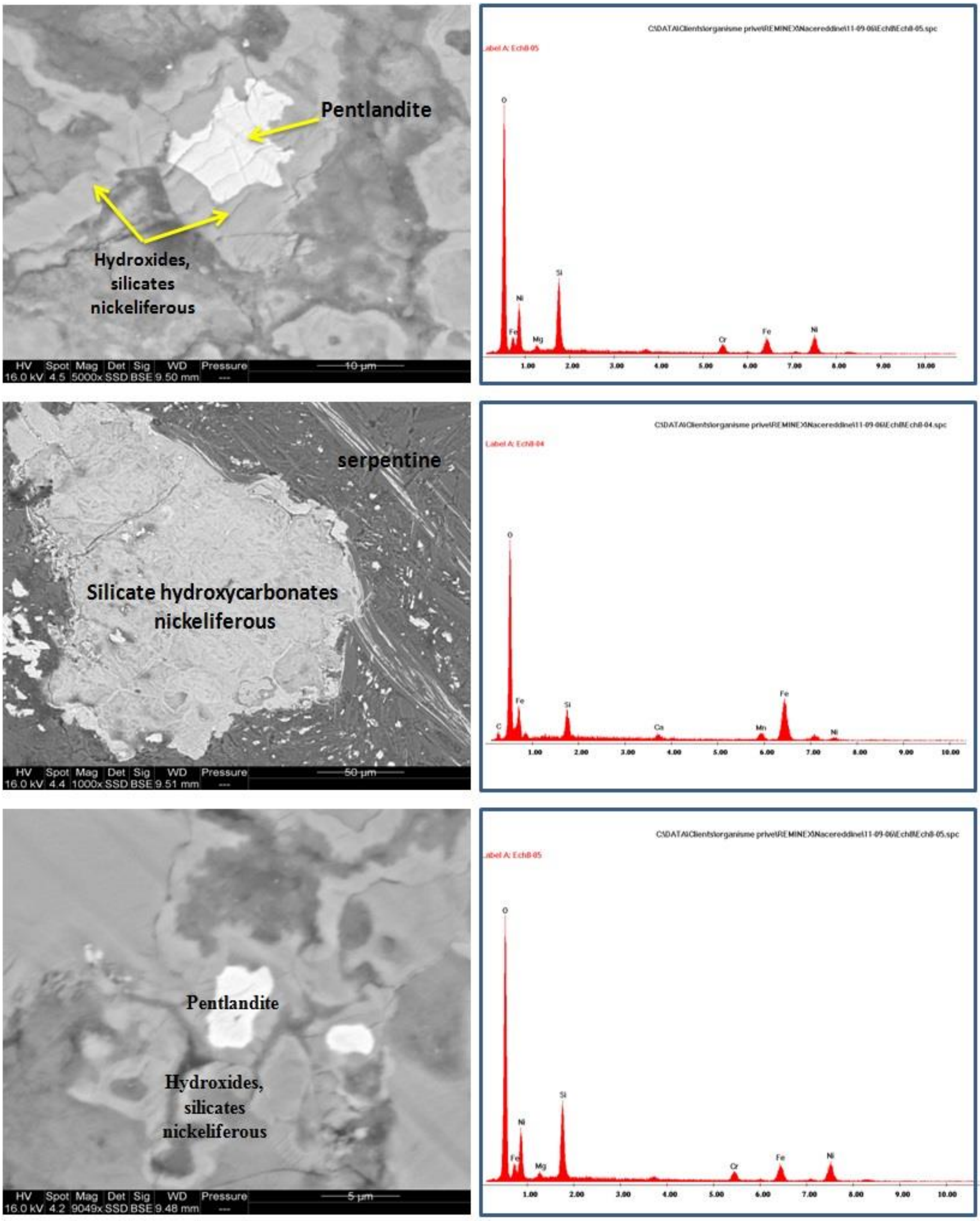

Figure 6) Petrographic and mineralogical characterization of nickel in serpentinite (left): The relationship between Pentlandite (sulfur of nickel) and nickeliferous silicate hydroxides of Fe, Cr, Mg and Ca. Pentlandite and nickeliferous silicates hydroxicarbonates of Fe, Mn and Ca. (right): spectrum for each type of nickel sulphide (Alansari, 2010).

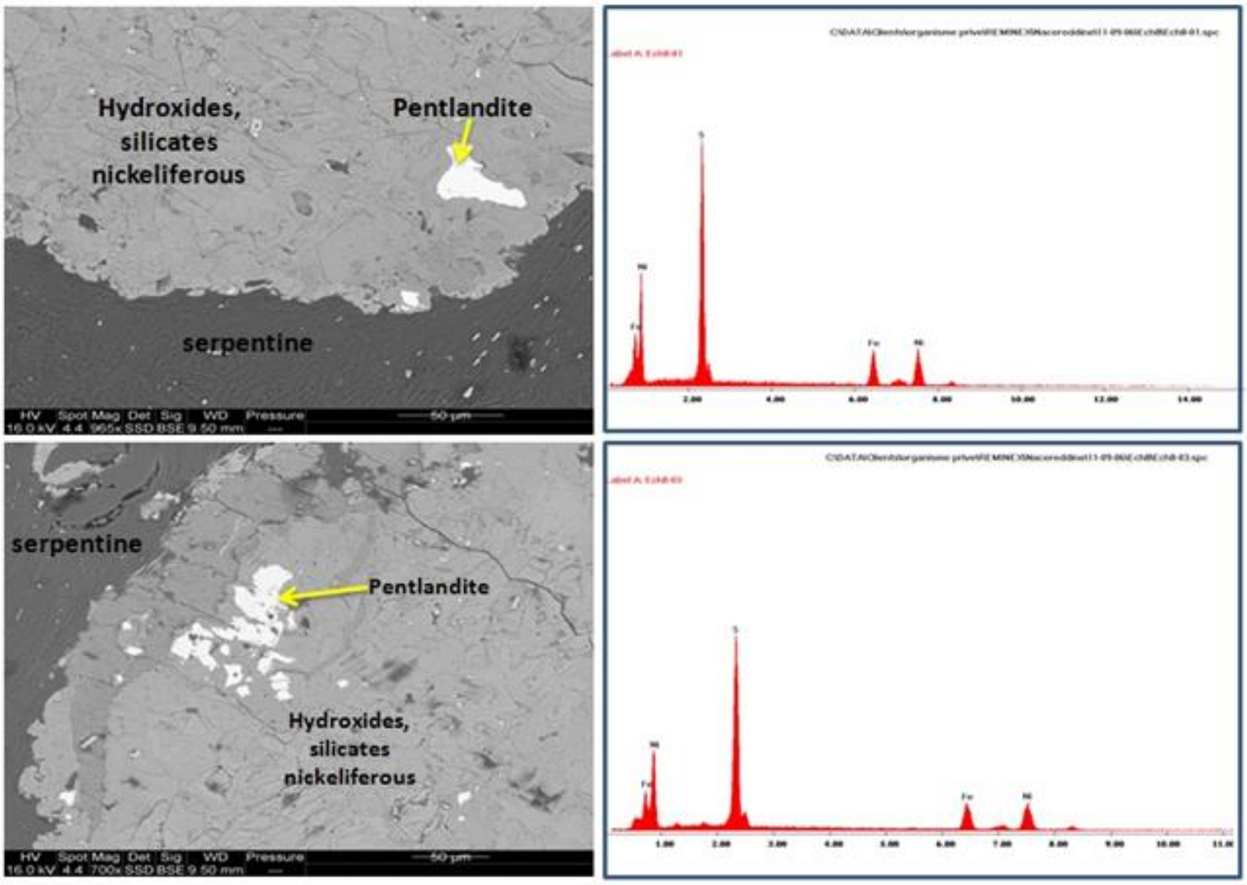

Figure 6) continued.

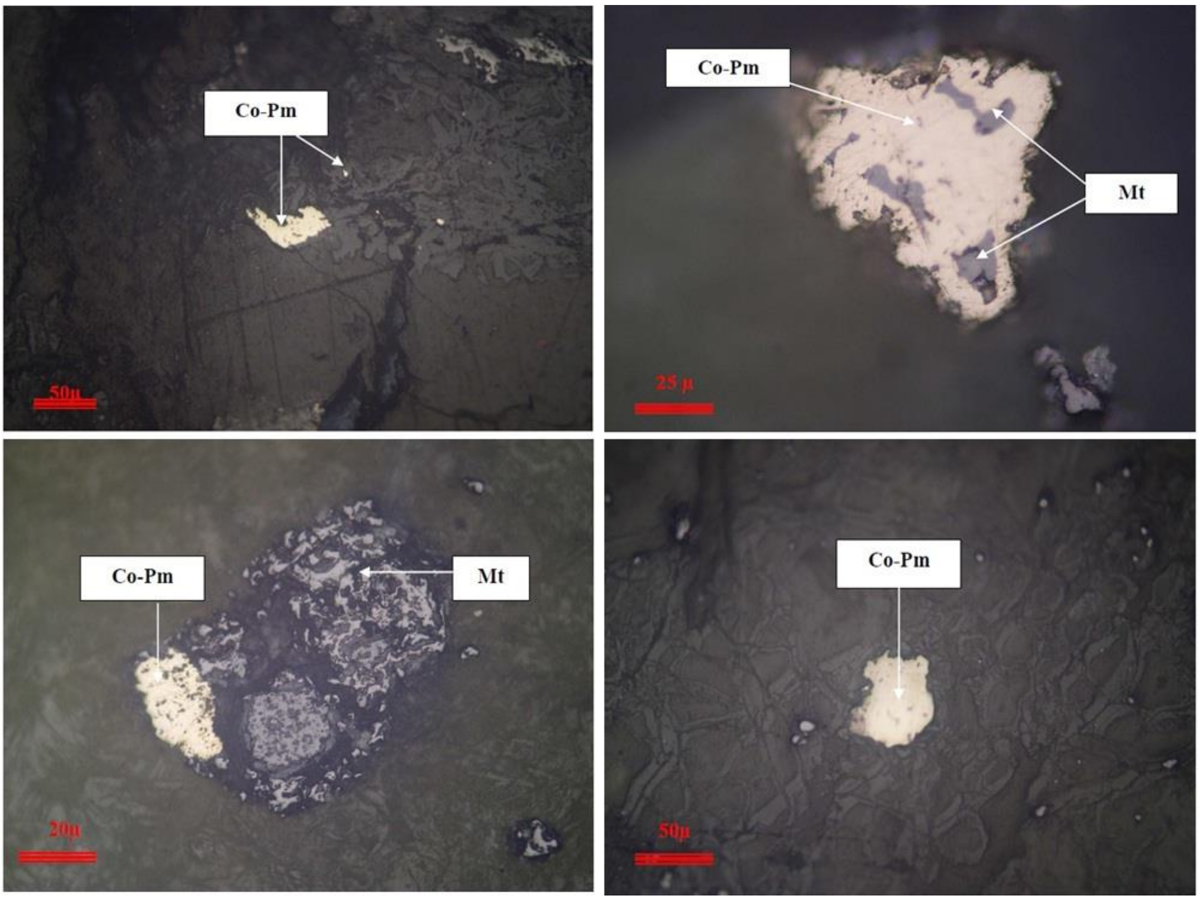

Figure 7) Photomicrography of the mineralogical assemblages identified in Bou Azzer massive where serpentinization is total (Co-Pm: polydymite cobaltiferous, Mt: millerite cobaltiferous; Alansari, 2010).

In contrast, the more Ni-rich pentlandite-heazlewoodite (godlevskite) magnetite aggregates of the Bou Azzer body appear to have formed from metals and sulfur that originated from both dissolution of magmatic sulfides and hydration of olivine. The modes of occurrence of sulfide (-magnetite) suggest that metals and sulfur originate from both olivine and probably preexisting magmatic sulfides moved only a short distance and precipitated in the present sites contemporaneously with serpentinization or somewhat later. In the rock body, sulfide veins and veinlets that formed at a later stage (violarite-millerite aggregates) coexist with a smaller quantity of magnetite than sulfide masses that formed at an earlier stage (pentlandite - heazlewoodite - godlevskite aggregates; Fig. 8).

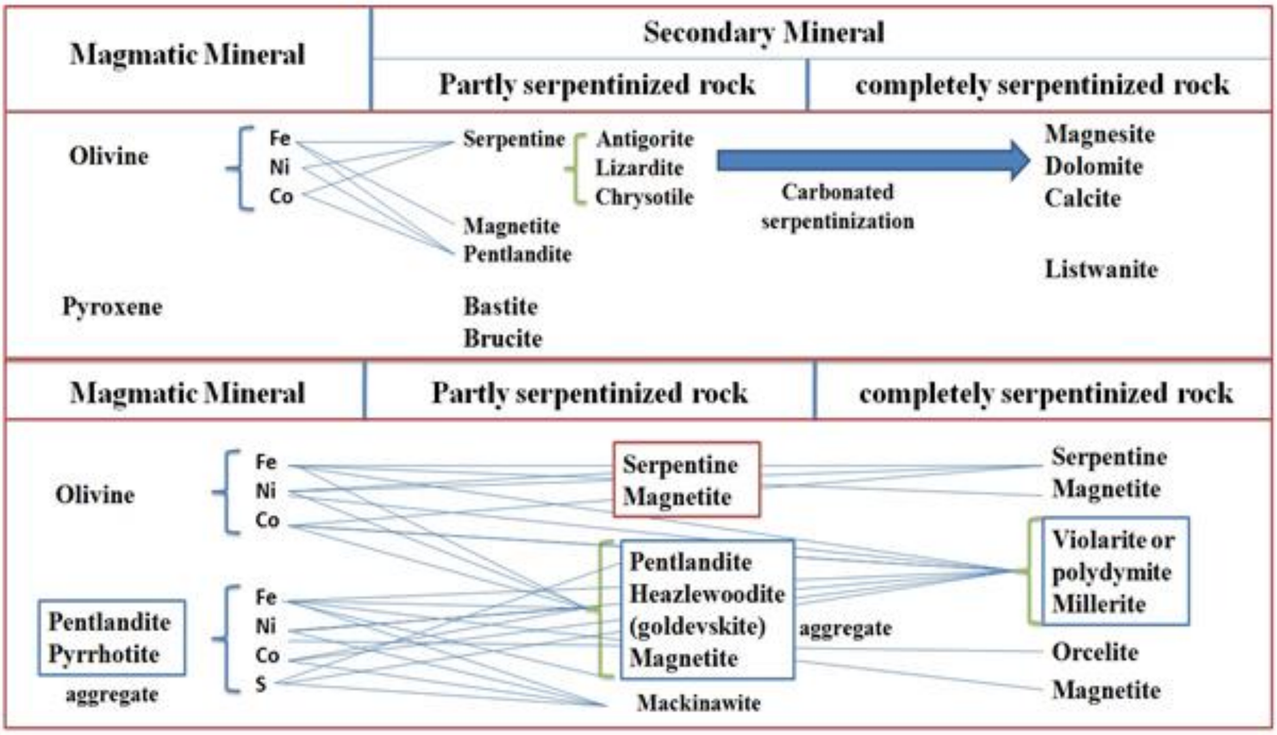

Figure 8) Behavior of Co, Ni, and S during serpentinization process in Bou Azzer ultramafic rocks.

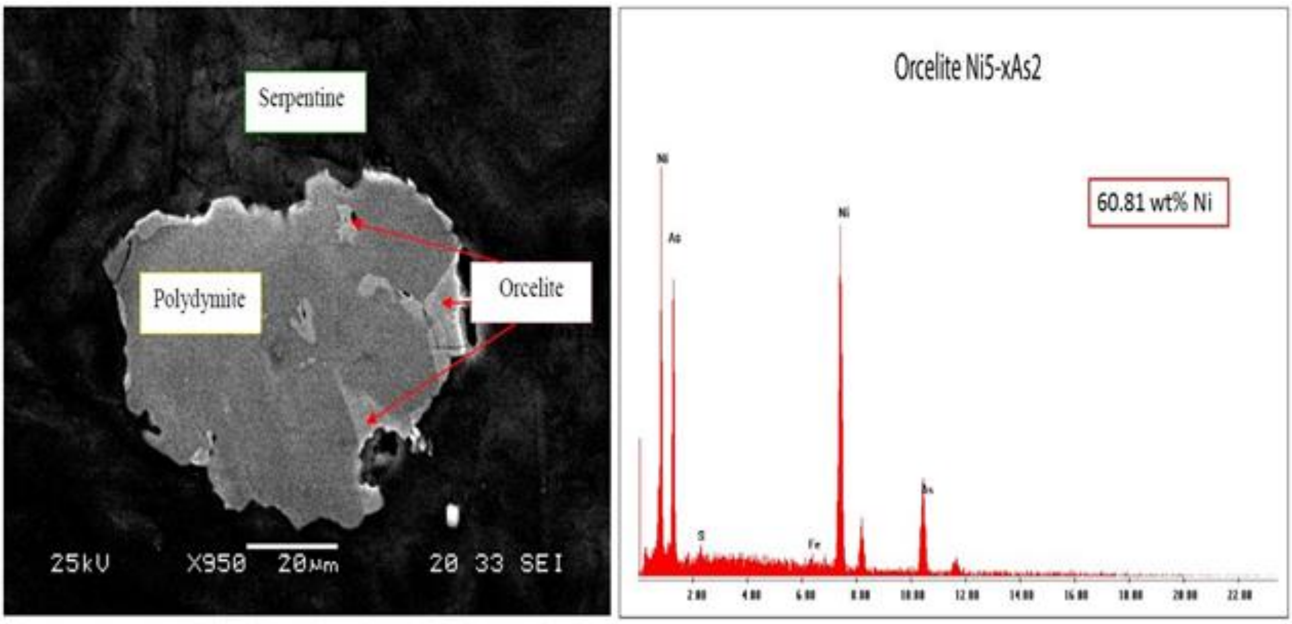

Figure 9) Photomicrography of orcelite, the only stable Nickel arsenide during serpentinization (left) and X-ray spectrum (right).

The presence of orcelite, the only stable Ni arsenide during serpentinization, reflects conditions of high activity of Ni and low activity of Fe in the fluids involved in serpentinization (Fig. 9). The relative frequency of maucherite underlines the importance of arsenic in mantle-sourced fluids. The values of the arsenic activity could locally be as high as that of sulfur to form an immiscible As-rich liquid, which is the origin of As-rich high temperature paragenesis.

4.2- Chrome and its Oxides

In the Bou Azzer serpentinites, primary minerals are completely replaced by serpentine minerals. The only visible primary minerals are relics of chromite spinels emphasizing the magmatic foliation of tectonites. The spinel grains are themselves altered along their borders by ferritochromite, magnetite and stichtite (hydrated carbonate-hydroxide of Mg and Cr) (Fig. 10) and in some specimens stichtite surrounds relict grains of Cr-rich spinel; in others stichtite has completely replaced euhedral or subhedral chromites.

Serpentinization has been accompanied by the formation of magnesioferrite and also in some cases by the alteration of chromite into magnesiochromite. Chalcopyrite, millerite, bravoite and other Ni-Co alloys are also observed in the center of serpentine minerals. Magnetite ($Fe^{+2}Fe_2^{+3}O_4$) and magnesioferrite ($Mg^{+2}Fe_2^{+3}O_4$) are common. They form coronitic alteration around the chromite and magnesiochromite and underline cleavage and shear planes within tectonites, reflecting their secondary appearance. They are associated with a coeval serpentine. Iron necessary for the formation of these two minerals is probably related to serpentinization. The textural relationships observed by SEM between the serpentine minerals and crystals chromites show a synchronous, early serpentinization with the chromite pods setting (Fig. 11).

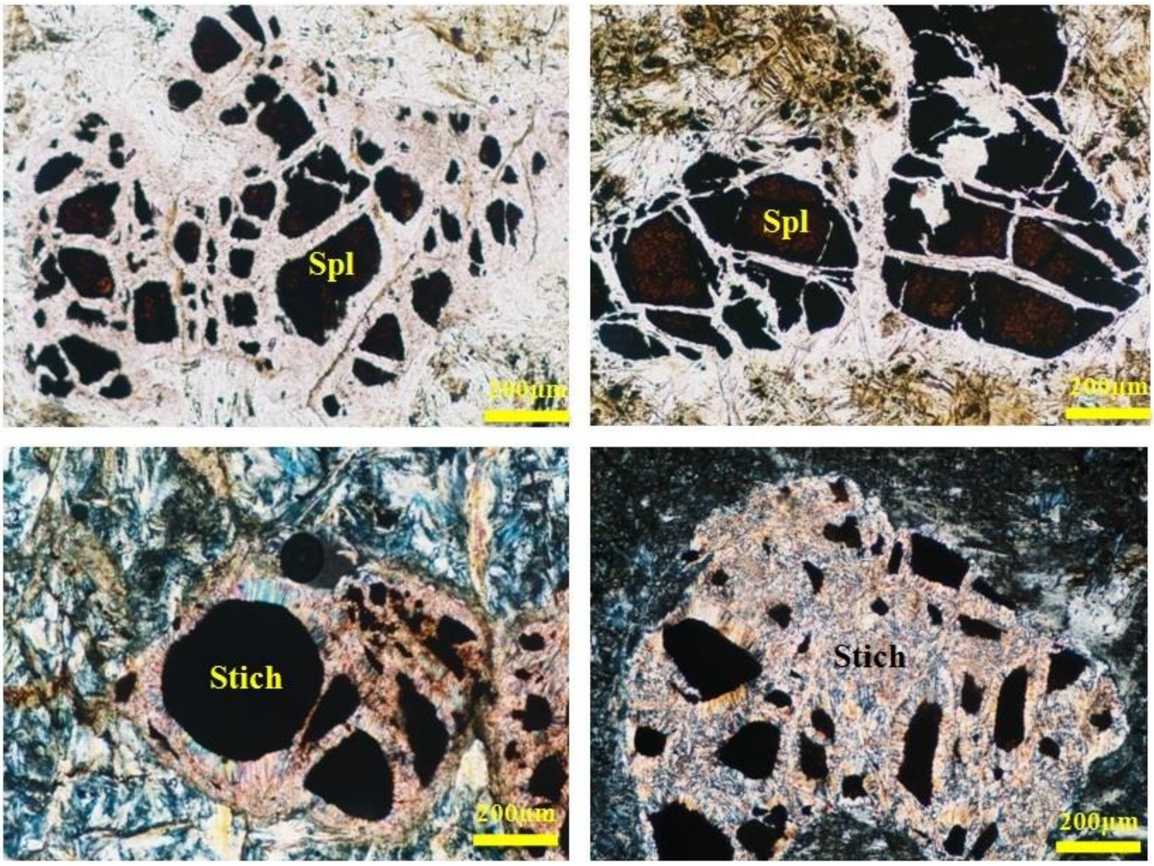

Figure 10) Photomicrography of Cr-spinels altered along their borders by magnetite and stichtite (hydrated carbonate-hydroxide of Mg and Cr). (stich: stichtite, spl: spinel) (Alansari, 2010).

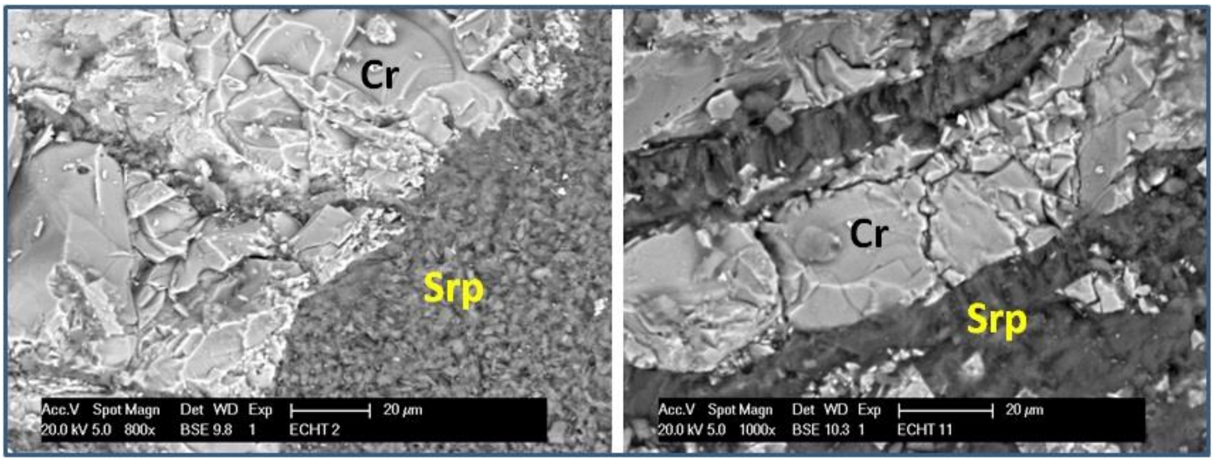

Figure 11) The SEM pictures of the textural relationships between the serpentine minerals and chromite crystals show a synchronous early serpentinization with the chromite pods setting.

4.3- Oxides of Mg, Cr, Fe, Mn, Ba, Ca and Al

Chromium is also present in the oxy-hydroxides of Mg and Fe present in chromite patches whose edges are marked by the development of calcite. Calcite and psilomelane can constitute the infilling of microcracks through the serpentine (Fig. 12). Oxides of Al and oxides of Mn, Ba and Ca also are distinguished (Fig. 13).

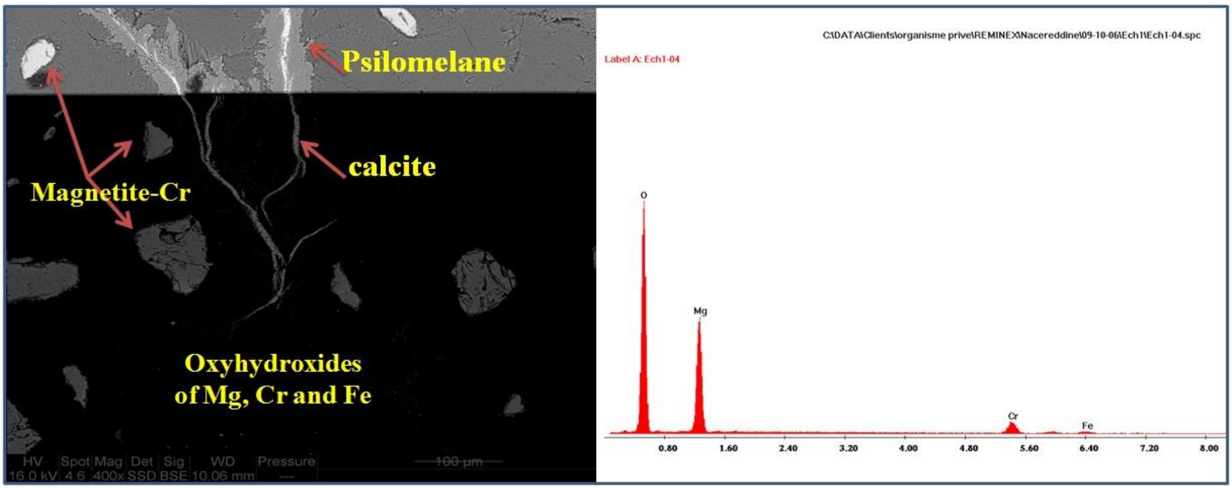

Figure.12) Calcite and psilomelane can constitute the infilling of microcracks through the serpentine.

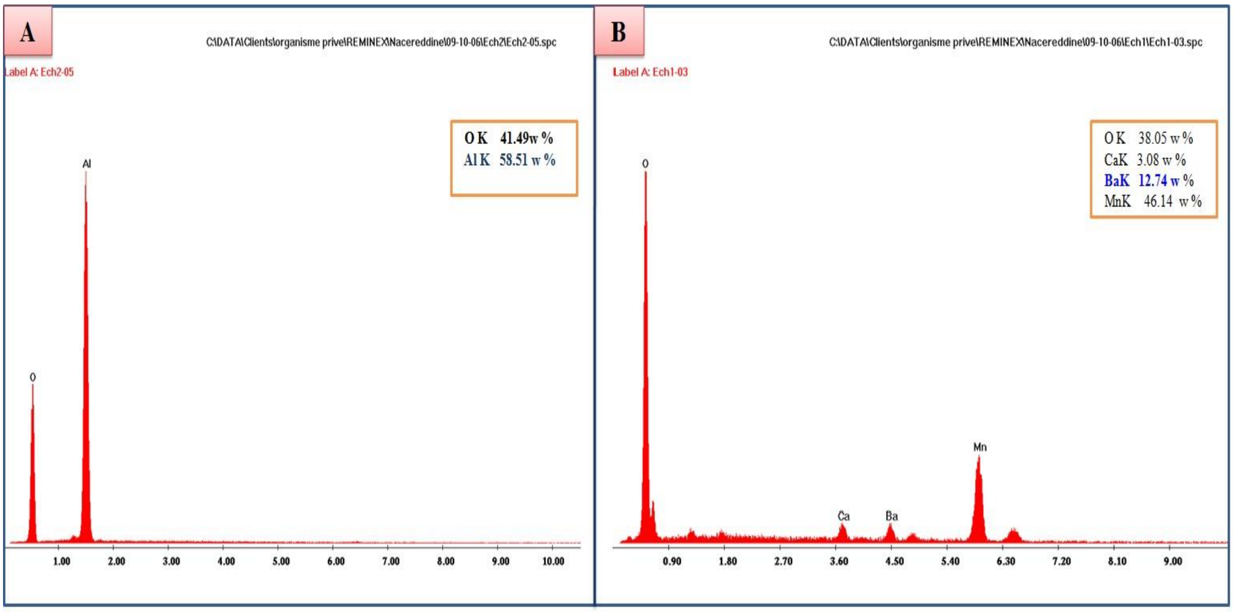

Figure 13) Spectrum shows the presence of A): Oxides of Al, B): Oxides of Mn, Ba and Ca.

4.4- Magnetite

Magnetite occurs as fine grained crystals dispersed in the matrix or concentrated in the serpentine mesh of olivine relics. Magnetite is also concentrated in the new recrystallized serpentine structures. Based on our petrographic study there are several generations of magnetite. The first generation occurs in the core of mesh structures (e.g. olivine) and in the cleavages and bastite boundaries (e.g. pyroxene). The second generationoccurs at the mesh borders as fibrous and octahedral magnetite. Likewise, the magnetite veins are sometimes underlined with chrysotile fibers perpendicular to the walls and sometimes magnetite surrounds and enters the chromite grains, chrysotile and even carbonates. In a later stage, the magnetite may appear as millimetric to centimetric octahedral crystals intersecting the serpentine and stock works crosscutting the serpentine structure (Fig. 14-1). Some magnetite occurs along planes of metamorphic foliation intersected by a cleavage crenulation (Figs.14-2 and 3). Occasionally, magnetite may constitute the filling of microcracks or isolated, relatively large crystals (Fig. 14-4). Some spinels are corroded and replaced by silicate of Cr, Fe and Mg (Fig. 15).

In conclusion, apart from the large magnetite crystals, in most cases magnetites orioginate from the precipitation of iron originally included in the primary ferromagnesian minerals (olivine and pyroxene) and dissolved during the different phases of hydrothermal alteration.

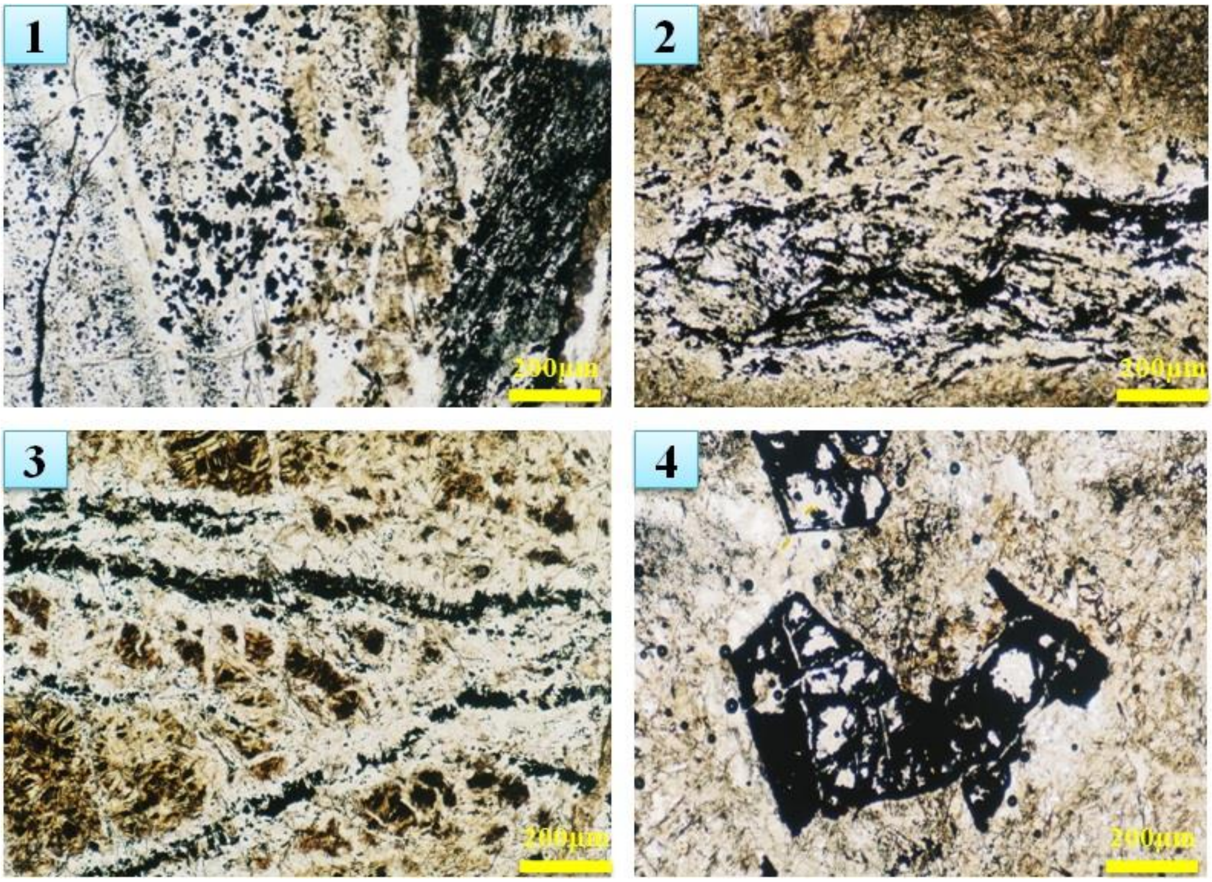

Figure 14) Photomicrographs of opaque minerals in serpentinites and the various aspects of magnetite.

Compared to other serpentine massifs, those of Bou Azzer are poor in native metals and sulfides. The relative abundance of nickel in magnetite can be linked to the poor concentrations of sulfide and ferronickel awaruite-type in serpentine (Ramdohr, 1967), and this according to the partial pressure of oxygen during serpentinization. Peridotites contained high levels of metallic elements and relatively low in sulfur, which correspond to the black serpentine rich in Cu, Ni, Co and As. Serpentinization, whether complete or partial, is always accompanied by the release of iron which crystallized as hematite or magnetite.

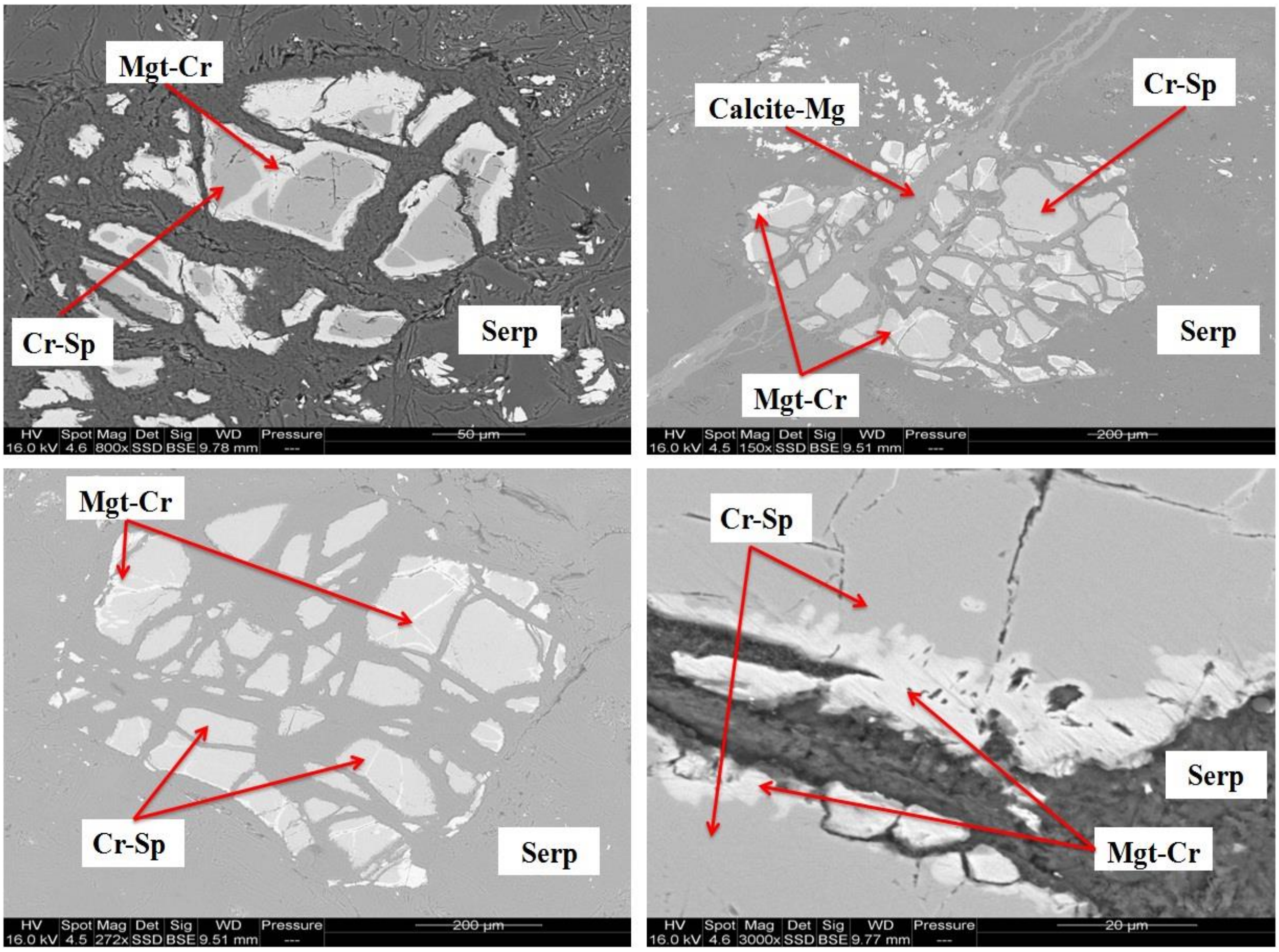

Figure 15) Photomicrograph by SEM of magnetite: Spinel corroded and replaced by silicate of Cr, Fe, Mg. Note that the fragments of spinel are crosscut by microcracks filled by chromiferous magnetite. (Cr-Sp: chromiferous spinel; Serp: serpentine; Mgt-Cr: chromiferous magnetite; calcite-Mg: magnesium-rich calcite)(Alansari, 2008).

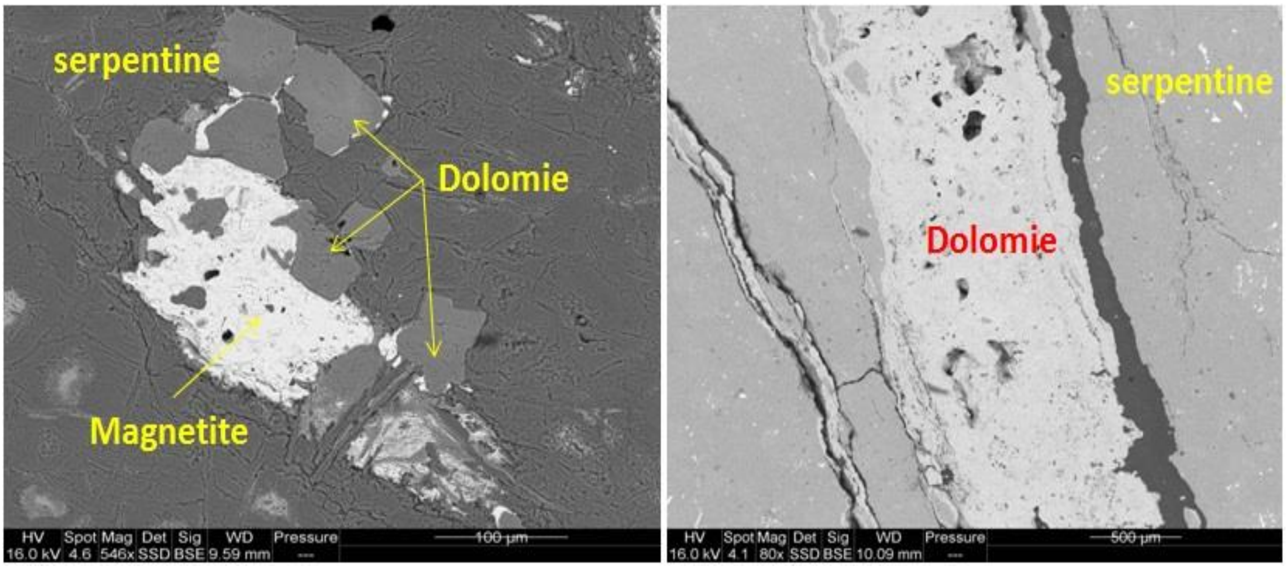

Figure.16) Photomicrographs of carbonated minerals in serpentinite (Alansari, 2010).

4.5- Calcite and dolomite

Carbonate, identified as magnesite generally occupies the smooth fractures that develop characteristically in serpentine. It form fibers and occasionally some empty rhombohedral crystals. They can mingle with chrysotile and antigorite and even form veins of fibrous carbonates. These minerals are characteristic of carbonate serpentinization, they appear in abundance in Ait Ahmane and Ambed areas (east of Bou Azzer). Dolomite is rare. It is found in crevices or in grains and more or less corroded magnetite (Fig. 16). Finally, there are contact reactions between serpentine and other rocks.

5- Discussion

5.1- Movement of metals and sulfur

Remobilization during serpentinization occurs when elements like Fe, Co and Ni are released from primary silicates and incorporated in the newly formed serpentine and magnetite or, in the presence of aqueous H2S, precipitate as Ni–Co–Fe sulfides (Gülaçar and Delaloye, 1976; Shiga, 1987; Alt and Shanks, 2003).

At Bou Azzer, the breakdown of Ni-bearing olivine produced Ni-bearing serpentine mesh whereas the hydration of Cr and Al-bearing pyroxene resulted in Al and Cr-rich serpentine bastite. Bastite is the only form of pseudomorphic serpentine that prevails in the sulfide-bearing serpentinites, even when other pseudomorphic textures (mesh and hourglass) have been overprinted.

In some ultramafic bodies, serpentinization occurred as an essentially isochemical process (Coleman and Keith, 1971) without any apparent change of major components Si, Mg and Fe nor of minor components Cr, Al and Ni (Donaldson, 1981).Accordingly we consider Al and Cr in Bou Azzer serpentine as originating from the former clinopyroxene and chromite components rather than introduced from external sources through the hydrous fluids responsible for serpentinization. It is likely that serpentine composition, especially its minor constituents, depend not only on the parental olivine composition, but also on mineralogy and modal composition of the original rock. The relationship between the degree of serpentinization and the composition of the sulfide aggregates illustrates that Fe content of the sulfide aggregates is reduced with progressing serpentinization. In contrast, Ni is strongly enriched with increasing serpentinization. Cobalt content varies in accordance with nickel. Sulfur content is characterized by a gradual depletion with initial serpentinization and an increase in completely serpentinized rocks.

5.2- Chronology

The serpentinization of the Bou Azzer ultrabasites took place before the Pan-African collision (“phase B1”, Leblanc, 1975), currently dated at ca. 650-635 Ma (Samson *et al*., 2004; El Hadi *et al*., 2010; Walsh *et al*., 2012; Soulaimani *et al*., 2013) and continued during this phase (). Serpentinization drives the fluid to hyperalkalinity and causes the system to become highly reducing (O’Hanley, 1996). Serpentinization can involve both replacement of minerals and direct precipitation from fluids (Andréani *et al*., 2004). Serpentinization reactions can occur at either constant volume with removal of Mg and Si (Thayer, 1966, 1967; Evans, 2004) or with volume increase under isochemical conditions (Hostetler *et al*, 1966; Page, 1967; Coleman, 1971).The abundance of magnetite in different stages of serpentinization and extreme scarcity of native forms of iron or nickel sulfide in serpentine indicate a high oxygen fugacity during serpentinization. Mineralogical study of serpentinite samples in deformed areas shows the direct link between tectonic stress intensity and the abundance of chrysotile. In summary, the serpentine pseudomorphs after olivine and pyroxene typically formed in the ocean during the mantle exhumation, while recrystallized serpentine formed by replacement of previous varieties during the obduction and subsequent tectonic processes, although the formation of recrystallized serpentine in the ocean cannot be excluded.

6- Conclusion

The process of serpentinization produces characteristic structures that record the history of mineralogic changes and structural deformation associated with volumetric expansion and strain. Although in many cases the process can lead to complete replacement of the original mineralogy, the types of pseudomorphism (mesh texture after olivine and bastite after pyroxenes) permit determination of the original rock type and even the pre-serpentinization deformational structures.

The continuous removal of iron from aggregates of magmatic sulfides to from magnetite, as well as the uptake of nickel and cobalt from olivine, account for the progressive formation of relatively Ni and Co enriched sulfide aggregates. As previously discussed, sulfur released through the decomposition of magmatic sulfides contributed to the formation of additional sulfides in conjunction with metals released from olivine, and remainder, if present, may have formed S_2 or H_2S. The gradual depletion of secondary sulfides in sulfur during serpentinization is likely attributed to an increase in total metals, due to predominance of the incorporated nickel and cobalt over the removed iron, or to the generation of S_2 or H_2S (Shiga,1987). The combination of petrological, metallogenic studies in the studied area allowed us to confirm that the ultramafic rocks of Bou Azzer contained primary magmatic Ni-Co mineralisation, whose evidence is still preserved in the chromites. The mineralisations have then been subjected to two main episodes of serpentinization during which the early mineralisations were remobilized and concentrated, i.e. (i) an early episode during oceanic rifting/extension, and (ii) a second episode coeval with the Pan-African continental collision. The subsequent emplacement of late to post Pan-African diorite and quartz-diorite intrusions triggered hydrothermal systems that would have again concentrated cobalt in the serpentinites. It seems therefore that the Co metal stock of Bou Azzer is the result of at least three post primary mineralisation stages of alteration. The values of the arsenic activity could locally be as high as that of sulfur to form an immiscible As-rich liquid, which is the origin of As-rich high temperature paragenesis.

Acknowledgments:

The present work was financially supported by the Bou Azzer-CTT Mining Company.

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