Geochemical and Mineralogical Characteristics of Serpentinite and Carbonated Serpentinite: case of Magnesite (Bou Azzer inlier, Central Anti-Atlas, Morocco)

Mohamed Bhilisse[1*], Amina Wafik[1], Hassan Admou[1], Lhou Maacha[2], Marc Constantin[3]

1- Department of Geology. Faculty of Sciences-Semlalia, Cadi Ayyad University, Marrakesh, Morocco.
2- Managem Mining Company (SA), Twin Center, Casablanca, Morocco.
3- University of Laval, Quebec, Canada.

* Corresponding Author: mohamed.bhilisse@edu.uca.ma

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Abstract

Ultramafic rocks are essentially constituted by silicates of magnesium: forsterite, and/or Diopside-enstatite; who's the most common hydrothermal alteration are the serpentinization. To Bou Azzer, the serpentinisation affected almost all of the ultrabasic rocks. Among the phenomena bound to the serpentinisation observed on the ground, we distinguish the magnesium deposits (Carbonated serpentinite). These magnesian deposits correspond to veins taken in serpentinized peridotites either realizes the contact between serpentinites and ultrabasic and basic cumulats. These veins of some centimeters a few meters away from power concentrate essentially in the regions of Ait Ahmane, Ingujjem and Ambed and are formed by massive or brecciated magnesite or in cauliflower. The petrography ic and mineralogical studies of the deposits of magnesite of Bou Azzer, reveal mainly two different mechanisms: The replacement metasomatic in situ of the serpentine and the filling of fracture by circulation of a hydrothermal mineralizing fluid. A geochemical study of magnesites and serpentinites of Bou Azzer showed magnesite to be enriched in SiO_2, Al_2O_3, Fe_2O_3, MgO, MnO and Sr and depleted in Na_2O, P_2O_5, K_2O and CaO relative to the hosted serpentinite. It is suggested that the ascent of hydrothermal fluids rich in CO_2 pulls the change of the serpentine and the streaming of meteoric waters are at the origin of the magnesite. The latter gradually and partially replace the original serpentine, but occasionally total replacement occurs. Given the geological, structural, petrographic, and geochemical characteristics, the magnesite of Bou Azzer is of type Kraubath.

Keywords: Bou Azzer, Magnesite, Carbonated serpentinite, Serpentinisation, Kraubath.

1–Introduction

The Bou Azzer inlier of the Anti Atlas of Morocco represents a geological window into the proterozoic basement surrounded by a discordantly overlying infra-cambrien to paleozoic cover sequence. The serpentinization at Bou Azzer occured in two phases: i) a pseudomorphic oceanic serpentinisation materialized by the isotropic serpophite preserving the primary form of olivine crystals with needles antigorite fibro-struck orbrucite as inclusions in the serpentine; ii) and tectonic serpentinization during the obduction of ophiolite with lizardite and chrysotile as a common serpentine mineral products. Magnesite is a rare rock forming mineral occurring in different marine and non-marine geological settings due to the geochemical relations of silicon, iron and calcium. However, magnesite deposits have been formed since the

Archean either as carbonated ultramafic rocksor as sedimentary beds. Moreover, major magnesite deposits occur in the Precambrian, and thick magnesite dominated sequences are unknown in the Phanerozoic (Abu-Jaber and Kimberley 1992). Classification of magnesite deposits traditionally has been based on “types” based from Middle European localities (Pohl and Siegl 1986). Generally, the use of type deposits is unsatisfactory. Equally, the usage of crystallinity is problematic to classify magnesite deposits, distinguishing macroscopically into cryptocrystalline, fine-grained and coarse-crystalline (spary) magnesites (Abu-Jaber and Kimberley 1992). In fact, aprt from very minor, local exceptions there are only two types of magnésite deposits (Redlich, 1909):

i) The veitsch type, which characterized by sugary to coarse grained magnesite forming nearly monomineralic lenses within marine platform sediments.

ii) The kraubath type consisting of veins and stockworks of micro-crystalline magnesite hosted by dunite and peridotite.

We focused our work on field investigation by geological mapping and many cross-sections and sampling of Mechoui, Ambed, Inguijem and Ait Ahmane massives. Our laboratory investigation was based on petrographic, metallographic and geochemical studies. The present study made it possible to study the chemical and mineralogical characteristics of serpentinite and carbonated serpentinite. Our recent study on tectonite and serpentinization process and The Bou Azzer, focused on five selected areas from West to East: Bouffrokh, Mechoui (Mokhazni), Bou Azzer center, Ambed, Ait Abdallah and Ait Ahmane. In this work we mapped some serpentine massifs in order to determine any lateral or vertical variation to Bou Azzer inlier’s scale.

2- Geological setting

The Neoproterozoic central Anti-Atlas segment (800–580Ma) is a Pan-African suture zone separating the northern margin of the West African Craton (WAC) to the south from the Siroua-Saghro arc terranes to the north (Saquaque et al., 1989, 1992; Hefferan et al., 1992 ; Admou and Bouougri, 2002; Thomas et al., 2002; Bouougri, 2003).

In the Bou Azer-El Graara inlier, outcrop the oldest remnant formations (Blein *et al.*, 2014; Admou *et al.*, 2013; Soulaimani *et al.*, 2013 Chevremont *et al.*, 2013) which are:

- The Tachdamt-Bleïda Group suggested to be Upper Tonian – Lower Cryogenian (NP1-2) and composed of siltstones, quartzites, sandstones and basalts;
- The Tichibanine-Ben Lgrad Group, Lower Cryogenian (NP2i), composed of fine siltstones crosscutted by granitoids of Taghouni massif;
- The assif n’Bougmmane-Takroumt plutono-metamorphic complex, composed of orthogneisses, metamorphosed mafic rocks, and paragneisses attributed to Lower Cryogenian (NP2i). These metamorphic rocks are crosscutted by Upper Cryogenian (NP2s) granitoids;
- The Bou Azer–El Graara Group (ophiolitic complex) considered Upper Cryogenian (658 ± 9 Ma, Aït Ahmane sheet), composed of serpentinized mantellic peridotites, dykes of gabbros and dolerites, basalts and a volcano-sedimentary unit;
- Dioritic to granodioritic intrusions at the Cryogenian – Ediacaran limit (NP2-3), Bou Frokh and Bou Azer massifs, and the polyphased Taghouni massif;
- The Bou Lbarod–Iouraghene Group composed of ignimbrites and andesite of Lower Ediacaran age (NP3i), dated at 625 ± 8 Ma on the Aït Ahmane sheet. This magmatism is contemporaneous of the Tiddiline Group;

- The Tiddiline Group attributed to Lower Ediacaran (NP3i, 606 ± 4 Ma, Alougoum sheet) and composed of sandstones, siltstones and locally interlayered rhyolites;

The Ouarzazate Group attributed to Upper Ediacaran (NP3s, 566 ± 4 et 567 ± 5 Ma) composed essentially of ignimbritic pyroclastic flows, of dacitic to rhyolitic composition, associated with pyroclastic tuffs and brecciasand volcano-sedimentary deposits. The top of this group is characterized by andesitic flows interlayred with ignimbritic pyroclastic flows.

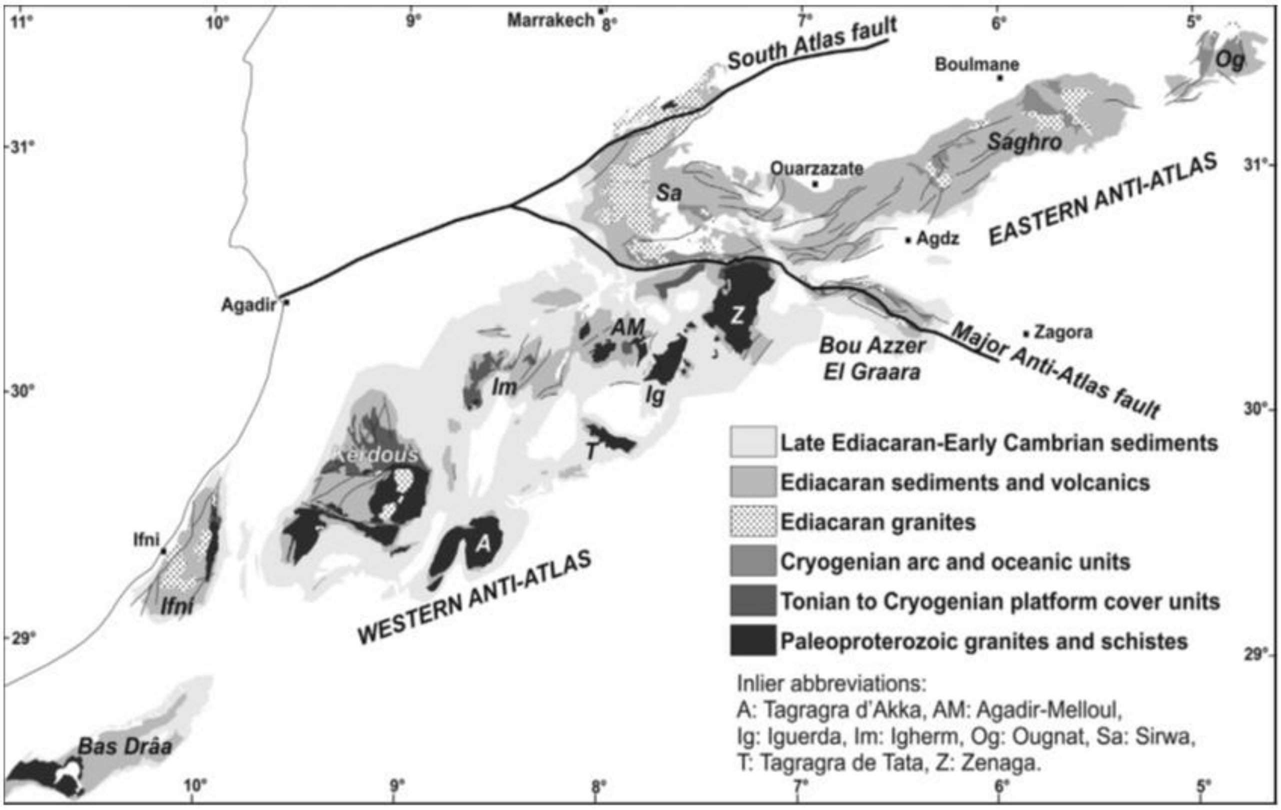

Figure 1) Simplified geological map of the Anti-Atlas showing the location of the Bou Azzer-El Graara inlier [modified from Walsh et al. (2002) and Gasquet et al. (2008)].

The Bou Azer – El Graara ophiolitic complex is composed of serpentinized peridotites, cross-cutted by basic and ultramafic dykes, basic and ultramafic cumulats, gabbros, basalts, a dyke complex and a volcano-sedimentary unit. This ophiolite occurs in tectonic slices. Located in the Bou Azzer-El Graara inlier, the Bou Azzer 'green rocks' were firstly considered as an intrusive serie (Jouravsky, 1952; Choubert, 1970). Routhier, 1963 was the first author to suggest the1occurrence of an ophiolitic complex which has then been confirmed by Leblanc in 1973 (Fig. 2). The ophiolitic complex is made up of serpentinized ultramafic rocks, meta gabbroic and meta basaltic units, with few outcrops of pelites and red cherts.Even if the whole complex has been dismembered, a complete ophiolitic sequence can be reconstructed. 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). Recently this ophiolite has been dated at 697± 8Ma by (El Hadi *et al*., 2010). A NE-SW cross section surveyed in the southern side of Aït Ahmane village shows the folding and faulting events that affected the different lithological units. A must see synclinal structure is noticeable near Jbel Oumagha (Fig. 3).

This Bou Azzer ophiolite contains several types of mineralization in both the mantle and the crustal sequence: The serpentinized mantle sequence is complete. It does not show Relic texture or deformation characterized and reveals the abundance of rock structure more or less homogeneous finely fibrous or shale. Some serpentinites are more or less Mg rich chlorite and talc (Leblanc, 1975; Wafik 2001). (Jouravsky, 1952) synthesis and (Leblanc, 1981) shows four types of occurrence:

- Network stringer at the heart of massive sepentine;
- vein bands heart massive serpentine;
- vein strips on the edges tectonised massive serpentine;

Banded rings on inclusions or serpentine wall rocks.

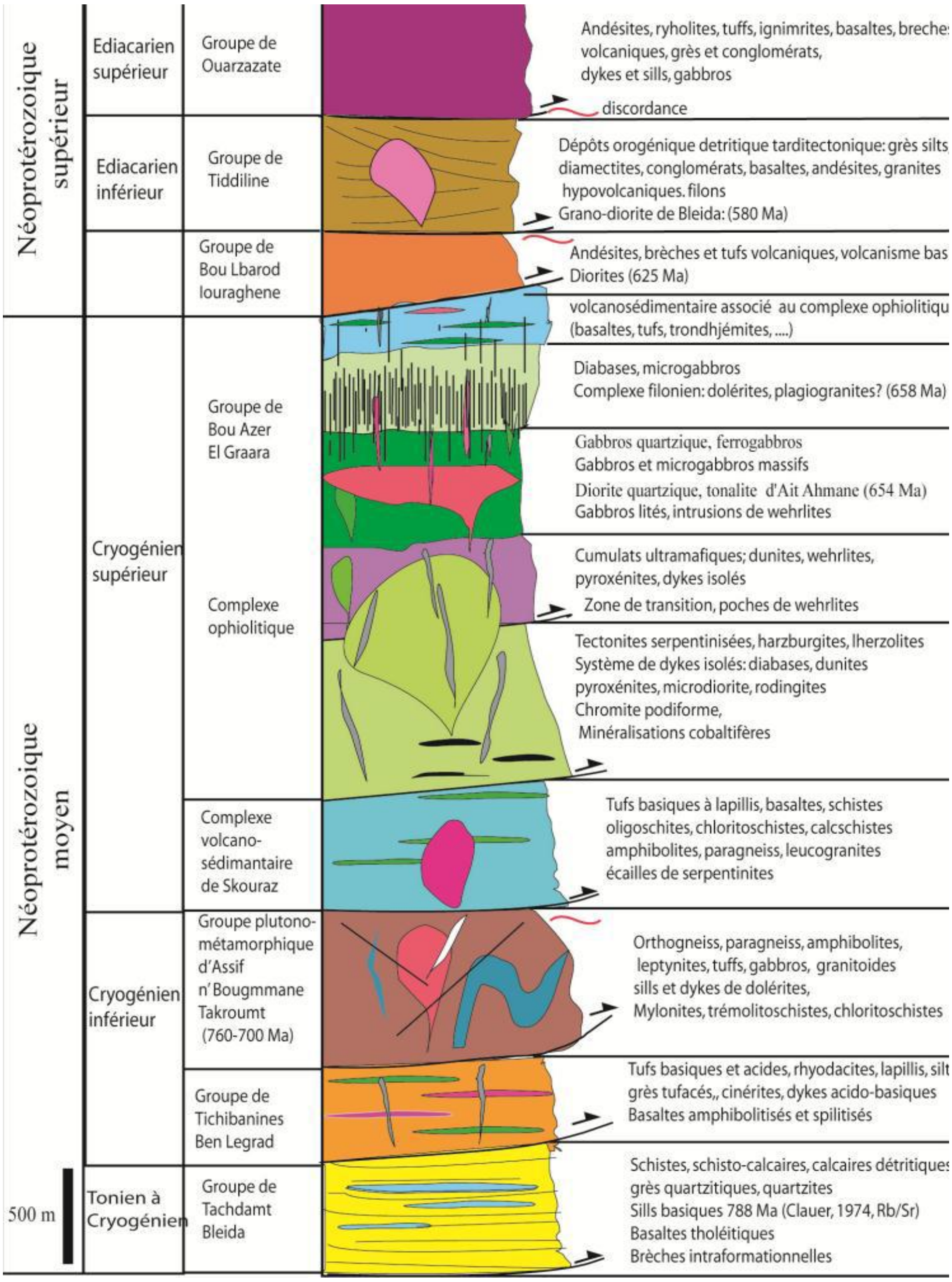

Figure 2) Synthetic log of the Bou Azzer ophiolite (Leblanc, 1973).

3- Serpentinisation in Bou Azzer

The serpentinization at Bou Azzer occured in two phases: a pseudomorphic oceanic serpentinisation materialized by the isotropic serpophite preserving the primary form of olivine crystals has affected in a homogeneous way the entire series, often with needles antigorite fibro-struck. Brucite is fairly frequent in the serpentinite of Bou Azzer, it is observed as inclusions in the serpentine; and tectonic continental serpentinisation during ophiolite's subduction and obduction with lizardite and chrysotile (Wafik, 2001).

We focused our work on field investigation by geological and numeric mapping and many cross-sections and sampling of Mechoui, Ambed, Inguijem and Ait Ahmane massives. Our laboratory investigation was based on petrographic, metallographic and geochemical studies.

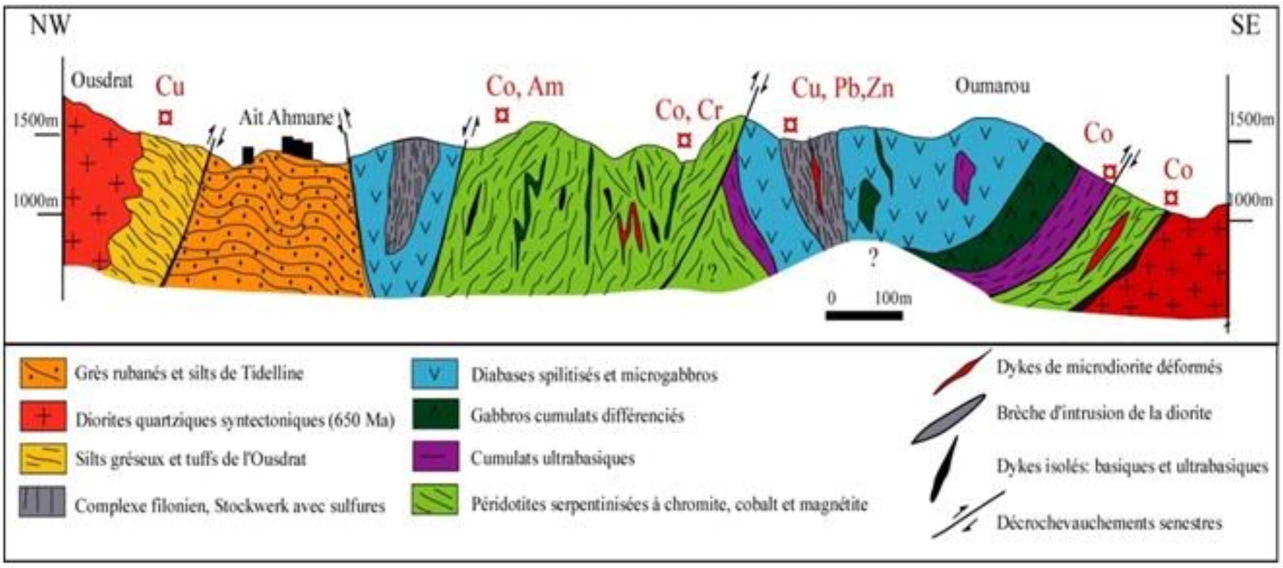

Figure 3) Structural relations of the lithological units of the Aït Ahmane ophiolite (Admou et al, 2013).

The three principal minerals of the serpentine group,chrysotile, antigorite and lizardite, have a very similarchemical composition, but significantly different structures. In fact, the single ideal chemical formula(OH) $3Mg_3[Si_2O_5$ (OH)] corresponds to several crystalstructures that represent different solutions for the minimizationof the mismatch between sheets of SiO4 tetrahedraland sheets of MgO_2 (OH) $_4$ octahedral. In lizardite,the resulting structure is planar, owing to shifts of theoctahedral and tetrahedral cations away from their idealpositions and to the limited Al-for-Si substitution in the tetrahedral sites.

We observed that serpentinization of ultramafic formations of bou Azzer ophiolites and current gradients are related to different level of deformation. Serpentinization is more developed and complex in more deformed areas, as senestrial faults and shear zones, that are mainly oriented N110° à 130°E. Sometimes N20°E N60°E faults has been observed. The lineation is mainly oriented N 65 à 70°. The main frequent paragenesis in this 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 into small thin veinlets and banded textures materializing the metasomatosis fronts. Some veins and dykes are fully transformed into giobertite and magnesite (Bhilisse *et al.*, 2013) as in the case of the massif Ambed and Ait Ahmane.In contact with dykes, the gabbroid and granitoid, the serpentines are transformed. The intrusive rocks also exhibit the impressions of metasomatic transformations contacts with serpentinite. They are materialized by fringes rodingites to vesuvianite and garnet on centimetric powers. In areas with high hydrothermal alteration, the serpentines are transformed into listwanites.

Several mineralizations types are associated with ophiolite of Bou Azzer (i) in transition area the nickel mineralization are scattered (ii) podiform chromite deposits and associated PGE

(iii) gold and palladium mineralization of Bleida Far West cashed by basic rocks of cumulates (vi) hydrothermal stockworks mineralizations of cobalt, nickel, arsenic and gold of Bou Azzer. The genesis of those mineralizations is result of both hydrothermal and tectono-magmatic processes.The results show that a primary paragenesis of magmatic origin with pentlandite, chromospinelle, and cobaltiferous and/or nickeliferous magnetite has been highlighted in Ambed massive where the serpentinization of ultramafic rocks is partial, and it is probably associated with Fe sulphides (pyrrhotite and/or pyrite). However, the mineralogical assemblages identified in Aghbar and Bou Azzer East massive where serpentinization is total are composed on secondary minerals of polydymite cobaltiferous, millerite cobaltiferous, orcelite and magnetite cobalti-nickeleferous. These mineralizations could come during serpentinization from mutation of a primary mineral pargenesis formed on olivine and pentlandite+pyrrhotite aggregates. For chromite mineralization, the Scanning Electron Microscope observations show a textural relationship between serpentine minerals and chromite crystals which reflect a precocious serpentinization setting on same time of chromite pods. The genesis of cobaltiferous hydrothermal mineralizations is basically related to the serpentinization process on both tectonophysical and chemical context (Bhilisse *et al.*, 2014). In chemical level, serpentinization control the mobility and leaching of nickel and cobalt exist in primary ultramafic minerals (olivine and pyroxene) which marked in arsenides, sulfides and iron oxides.

3.1- Serpentinite: Mineral components and textures

Serpentine minerals are phyllosilicates that contain up to 13 % water and form during the hydration of basic and ultrabasic rock.

Hydration commonly takes place in an ocen spreading context, thus documenting chemical exchanges between the oceans and solid earth (Alt and shanks, 2003).

Serpentine minerals, wich 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.

Our recent study on tectonite and serpentinization process and The Bou Azzer, focused on five selected areas from West to East: Bouffrokh, Mechoui (Mokhazni), Bou Azzer center, Ambed, Ait Abdallah and Ait Ahmane. In this work we mapped some serpentine massifs in order to determine any lateral or vertical variation to Bou Azzer inlier's scale. The field study has pointed out a gradient both horizontally and vertically. Therefore, the ultrabasic rocks of the western part of the buttonhole particularly at the level sector of 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 major Serpentinization stages the Bou Azzer Pan-African orogen are observed:

1) Pseudomorphic Precoce stage: materialized by the isotropic serpophite preserving the primary form of olivine crystals, often with needles antigorite. Brucite is fairly frequent, as micrometric inclusions in other serpentine minerals as antigorite and serpophite.
2) Tectonic Late stage: materialized by framework or parallel veins and fractures filled by chrysotile α and γ. These minerals are often crosscutting the antigorite, serpophite and brucite crystals. They are accompanied by opaques minerals. These opaque assemblages are associated with serpentinization process. Macroscopically and microscopically interstitial spaces and schistosity plans are underlined by thick laminas and veins of magnetite. Some sulfides as

pyrite and chalcopyrite are also filling this fractures.

These results lead us to assume that the precoce syn-rifting serpentinization of has affected homogeneously ultramafic rocks of Bou Azzer ophiolites and late tectonic serpentinization has affected heterogeneously ultramafic rocks of Bou Azzer ophiolites. This resulted in serpentinization's vertical and lateral gradients which are related to deformation gradient during panafrican ophiolite's subduction and obduction from East to West. This was accented by different erosion levels and massifs deepen. In areas with high hydrothermal alteration as Mechoui sector, serpentines have been transformed to listwenites. They have variable compositions of the metamorphic grade, with a full combination carbonate, breunnerite, quartz, magnetite and fuschite with relics of antigorite and chromospinelles.

In contact with gabbros granitoids dykes, serpentinites become chloritic with of asbestos with banded textures corresponding to advancing metasomatism's front. The intrusive rocks also exhibit the of metasomatic transformations contacts with serpentinite. They are materialized by centimetric rims of rodingite to vesuvianite and garnet. Some veins and dykes are fully transformed into giobertite and magnesite by supergene alteration of serpentinite like Ambed and Ait Ahmane massifs.

Our petrographic study 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) argued by XRD analysis (Fig. 4). The dominant serpentine mineral is antigorite (Fig. 5).

It was found that considerable amounts of lizardite and subordinate amounts of dolomite, calcite and magnesite are the components of the serpentinite.

The opaque minerals in serpentinites are represented mainly by chromite and magnetite. Small amounts of fine blebs and grains of scattered sulphides (pentlandite, polydymite cobaltiferous, and millerite cobaltiferous in serpentinites) were detected (Alansari, 2010; Bhilisse *et al.*, 2014).

Magnetite in serpentinite rocks is classifies genetically as primary and secondary types. Primary magnetites occur as fine to meduim euhedral to anhedral grains, secondray magnetite occurs in serpentinites rocks as parallel streaks and blades along the cleavage plans of pyroxene relics (Fig. 6). Magnetite in the altered bou azzer serpentinites occucs as disseminated and irregular skeletal primary grains, or as secondary ones, being the product of alteration of chromite. Magnetite is also in plans schistosity flux recovery by a second cleavage crenulation. The magnetite may also constitute the filling microcracks or edges arranged in gridded structures and also are present in isolated form relatively large (0.5 to 2 mm) crystals. The latter is usually a hole.

In conclusion, apart from the magnetite in large crystals, it is in most cases of magnetites, from the precipitation of iron in the content originally ferromagnesian primary minerals (olivine and pyroxene) dissolved in different phases of hydrothermal alteration (Fig. 7).

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 and Whittaker, 1977) classification of serpentinite textures. In the Ait ahmane rocks, the pseudomorphs are of the hourglass type (with unequal sectors and outlines of original olivine boundaries, see (Fig. 8) showing pene-trative fabric and mesh texture (as fine and dense fibrous lamellar aggregates after olivine. Besides, bastites, i.e. pseudomorphs after pyroxene, are observed in subordinate amounts.

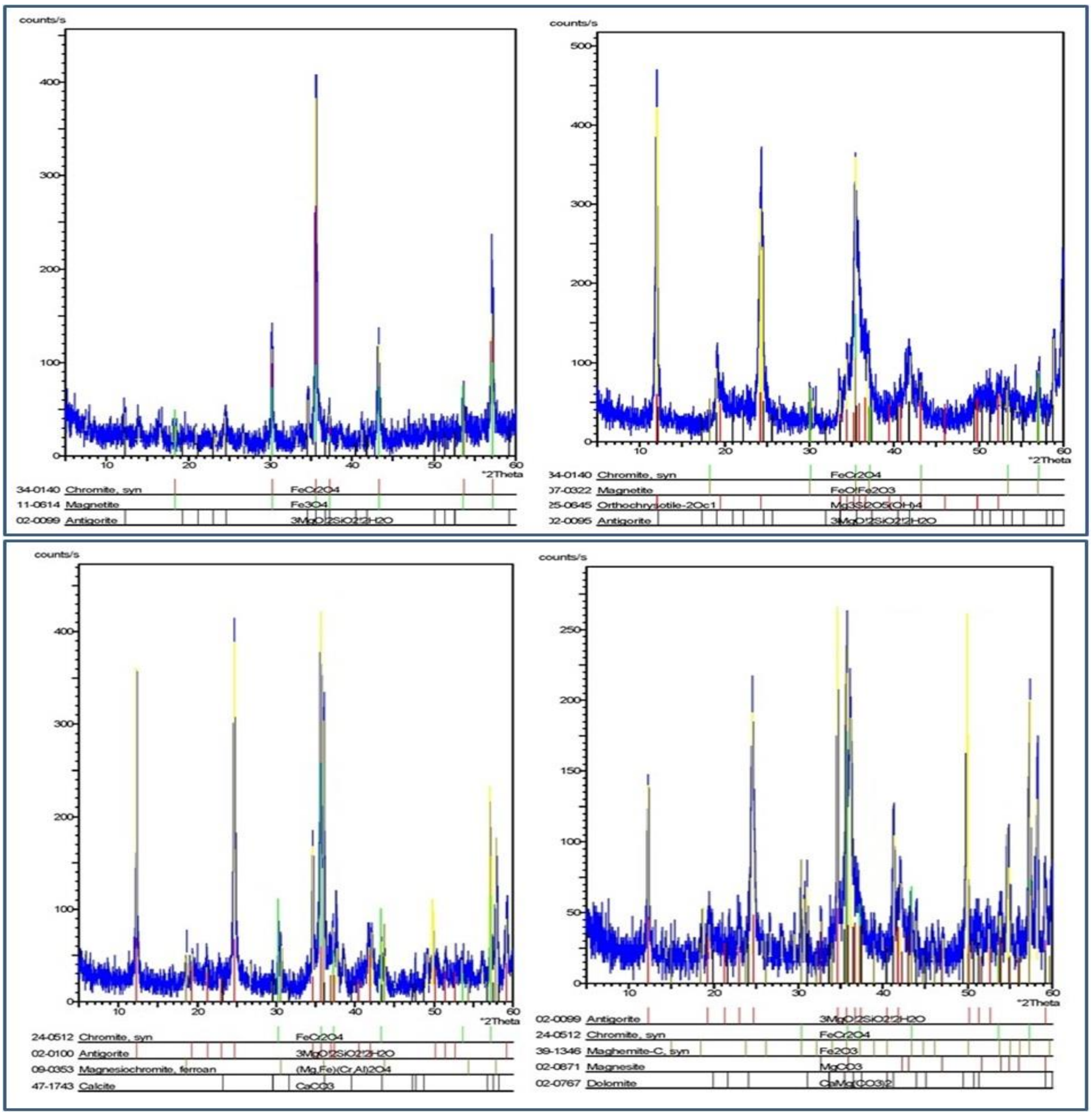

Figure 4) X-ray diffraction of serpentinite of Bou Azzer.

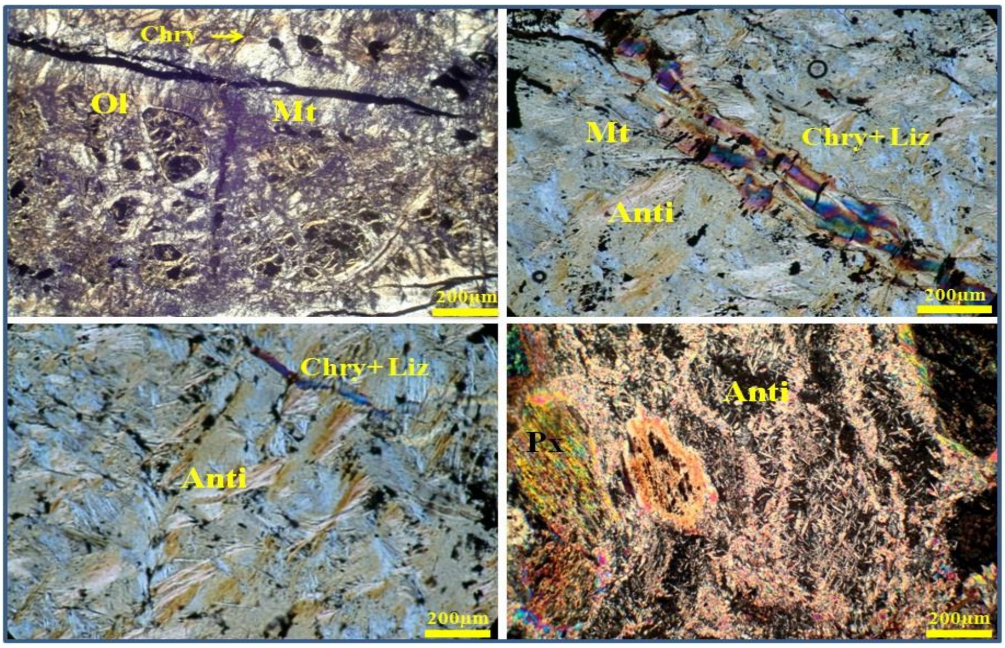

Figure 5) Photomicrographs of mineralogy of the serpentinite. Ol: olivine, Ant: antigorite, Liz: Lizardite, Chry: chrysotile, Mt: Magnetite.

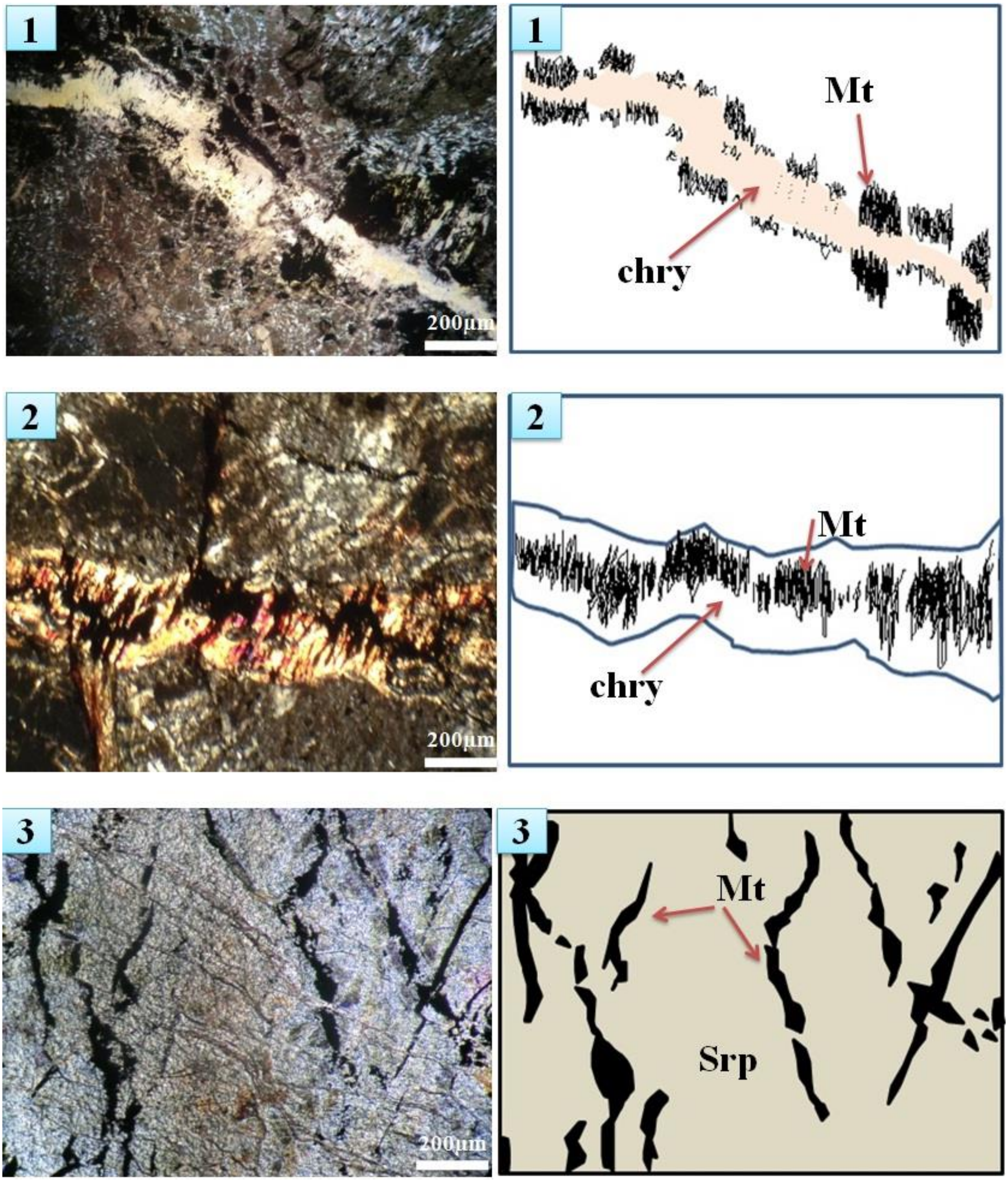

Figure 6) Photomicrographs of Opaque minerals in serpentinites and in altered serpentinites (1): magnetite borders chrysotile, (2):magnetite in chrysotile (3): Magnetite in serpentinites as disseminated) (chry: chrysotile, Mt: magnetite, Srp: serpentine).

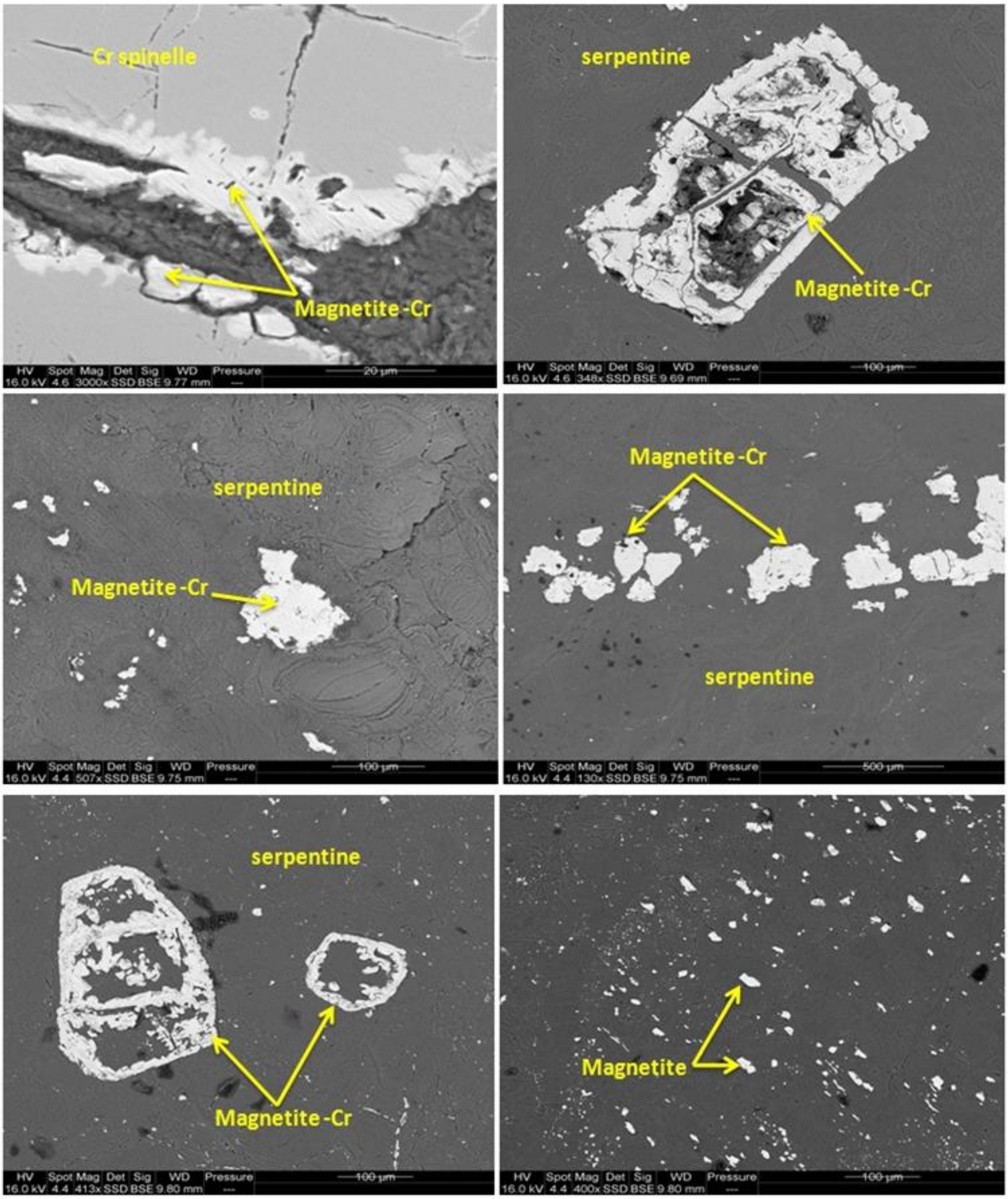

Figure 7) Photomicrographs by SEM: Types of magnetite.

On the other hand, pseudomorphic textures in serpentinites are represented by knitted (of interlocked perpendicular flakes and fibers parallel to the cleavage planes of original orthopyroxene) and bastite textures (Fig. 9) and sometimes by plumose texture and paillette texture. (Fig. 10)

In general, antigorite-lizardite serpentinites preserve pseudomorphic textures (Wicks and Whittaker, 1977; O'Hanley, 1996): i) bastites after clinopyroxene and ii) hourglass textures (Fig. 11). Theses textures can be interpreted as the result of low grade metamorphism.

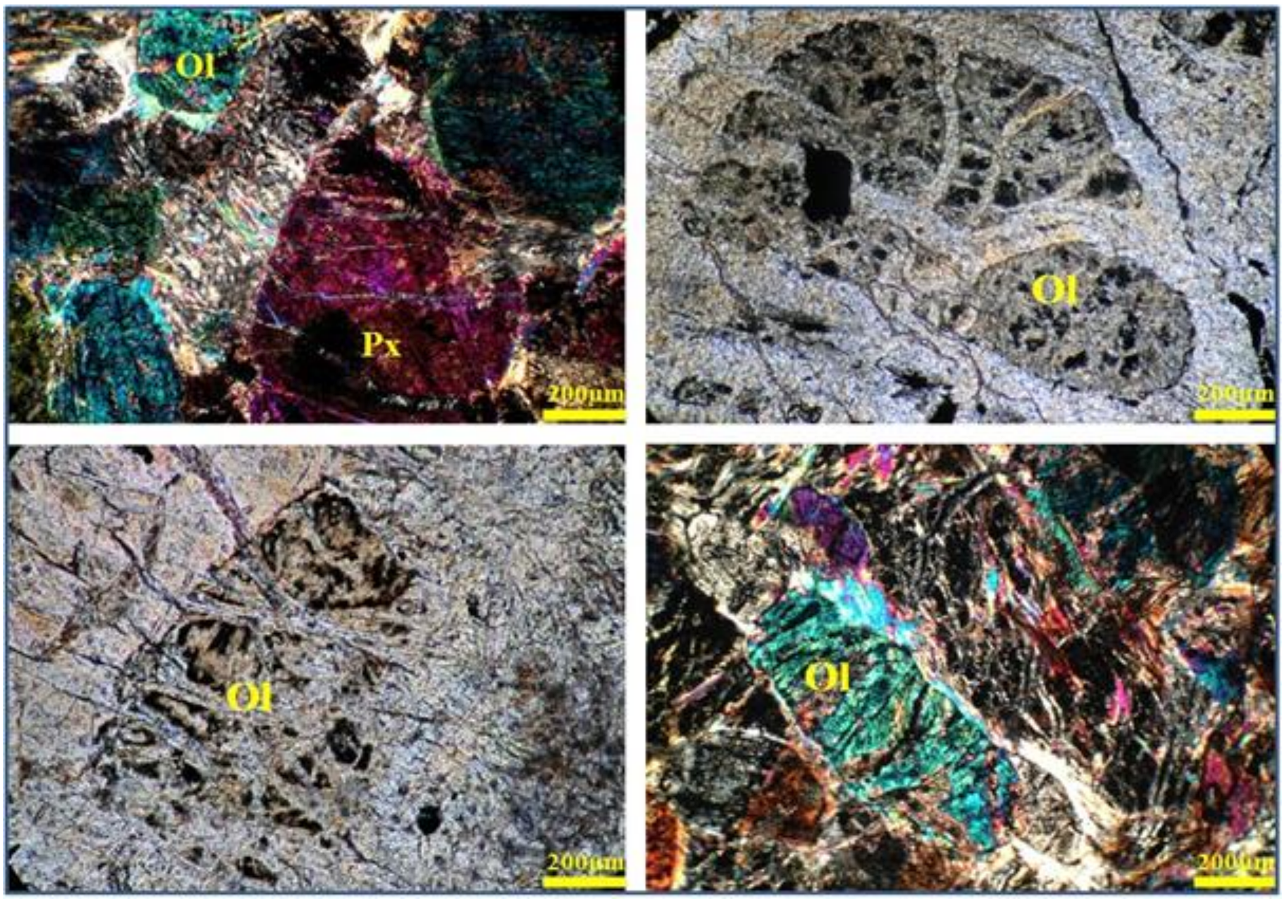

Figure 8) Textures in serpentinite rocks: mesh texture. Ol: olivine, Px: pyroxene.

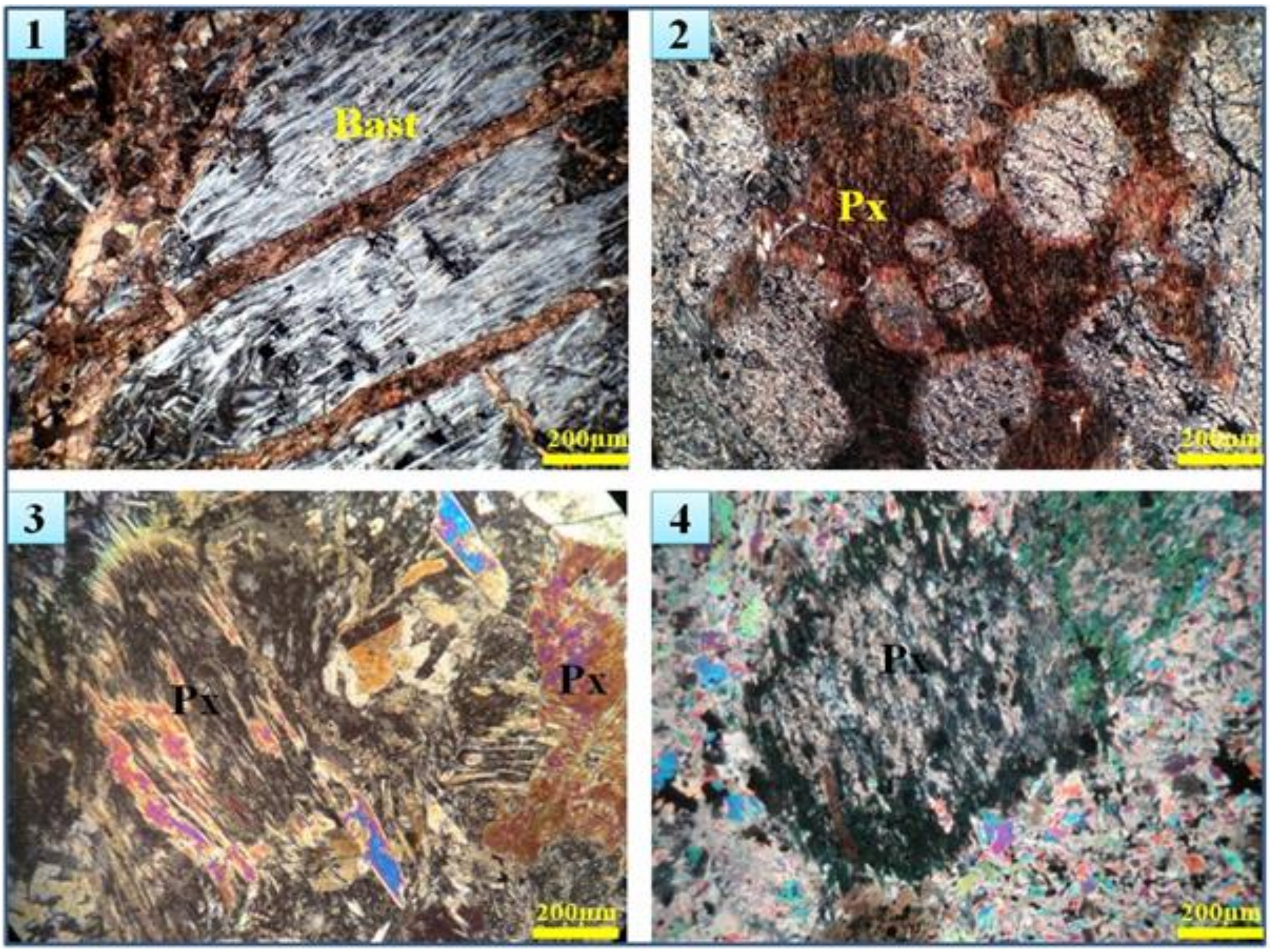

Figure 9) Textures in serpentinite rocks: bastite textures (Ol: olivine, Bast: bastite).

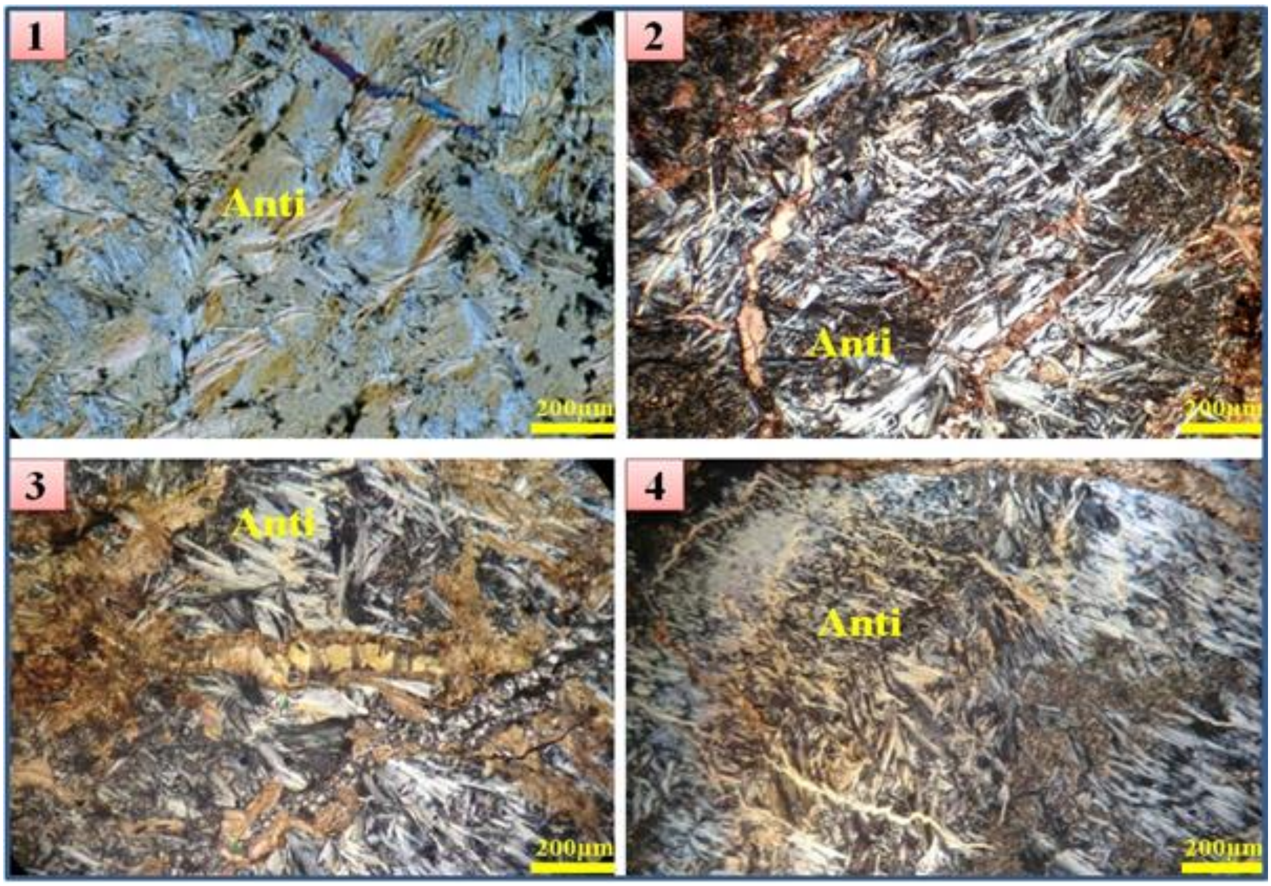

Figure 10) Textures in serpentinite rocks: plumose and paillette texture (Anti: antigorite).

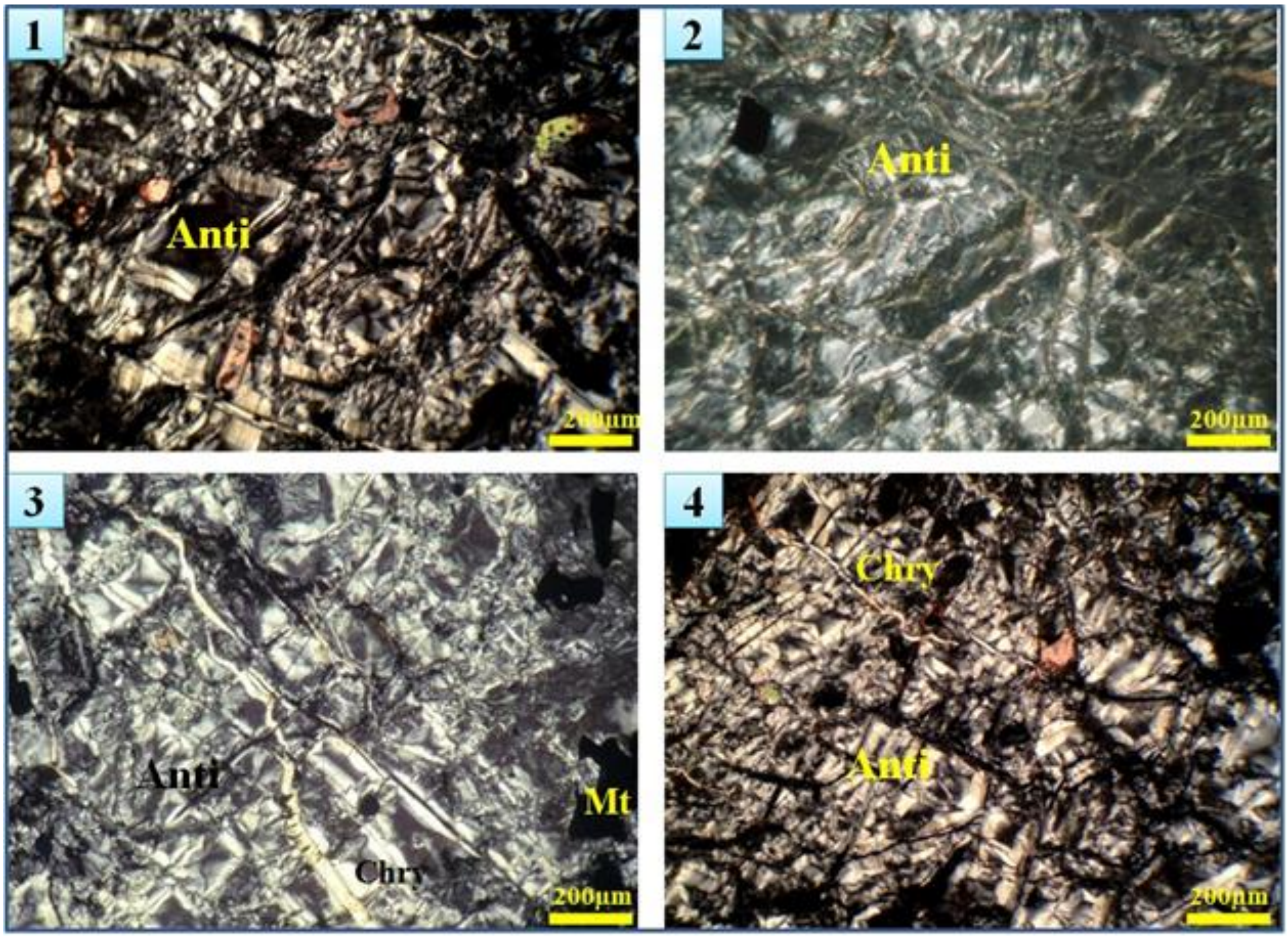

Figure 11) Textures in serpentinite: Pseudomorphic texture (hourglass texture). Anti: antigorite, Chry: chrysotile.

Moreover, experimental studies confirm that antigorite is the stable serpentine mineral under high-pressure conditions (Bromiley et pawley, 2003; Pardon-Navarta *et al.*, 2010; Reynar and wunder, 2006; Ulmer et Trommsdroff, 1995; wunder and Schreyer, 1997). Lizardite and chrysotile are the main varieties that are present in low-grade serpentinites from the oceanic lithosphere and from low-grade metamorphic ophiolites (Andréani *et al.*, 2007; Evans, 2004).

In the literature, it is typically proposed that the thermal stability field of antigorite and lizardite theoretically overlap between temperatures of 30 and 300 °C, while chrysotile is metastable (Evans, 2004).

Lizardite and antigorite coexist (or at least lizardite is not completely destabilized) between 320 and 390 °C for pressures greater than 9 Kbar (Schwartz *et al.*, 2013). It is noticeable that below 300 °C and 4 Kbar, antigorite is not observed. This observation contradict the phase diagram of O'Hanley 1996 in which antigorite appears at 250 °C at low pressures and suggests that antigorite crystallization is not only temperature dependent but also may be pressure dependent (Ulmer and Trommsdorff, 1995, Wunder and Schreyer, 1997).

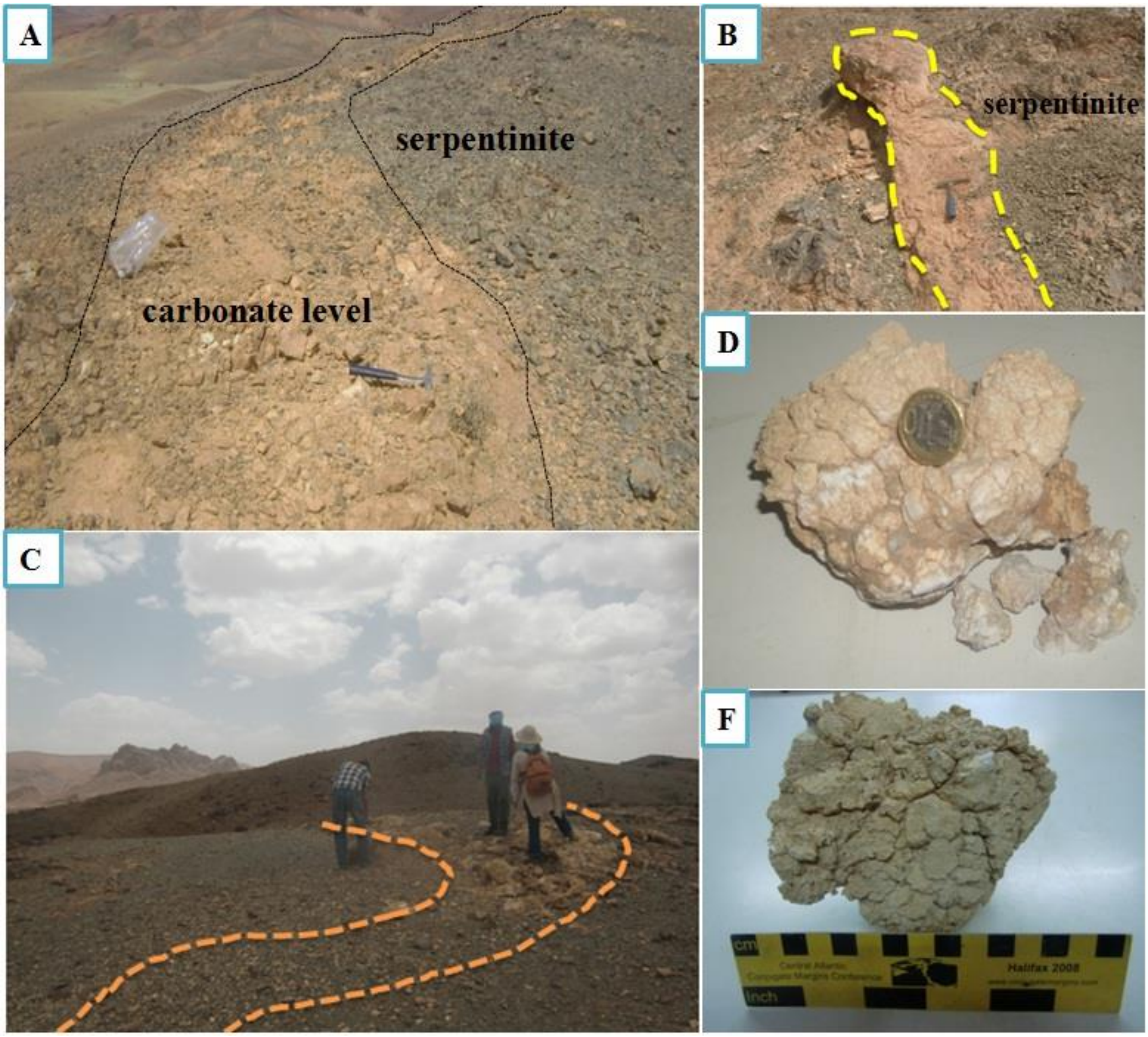

Figure 12) Magnesite veins in serpentinites of Bou Azzer (A, B and C: Magnesite in serpentinite, D: magnesite in cauliflower, F: magnesite brecciated).

Enhanced in situ carbonation of ultramafic rocks such as peridotites is currently considered to be a promising strategy for the mitigation of anthropogenic CO_2 emissions (Kelemen and

Matter, 2008). Peridotites may be suitable sites for CO_2 sequestration because they are globally abundant and primarily composed of silicate minerals that are rich in divalent cations (e.g., olivine: $(Mg,Fe)_2SiO_4$, orthopyroxene: (Mg,Fe) $2Si_2O_6$ and clinopyroxene: Ca $(Mg,Fe)Si_2O_6$).

Natural examples from both ocean floor and continental settings (e.g., ophiolite complexes) demonstrate that ultramafic rocks are reactive when in contact with CO_2 and may eventually transform into ophicarbonates (Trommsdorff and Evans, 1977; Trommsdorff *et al.*, 1980) or listwanites (Naldrett, 1966; Halls and Zhao, 1995; Hansen *et al.*, 2005). However, despite their Mg-rich nature, ultramafic rocks are often found in association with calcite rather than dolomite or magnesite.

4- Magnesite of Bou Azzer

4.1- Geology

The massif of Bou Azzer is recut by veins of magnesite of some centimeters a few meters away from power. These veins are more or less branched out and concentrate essentially in the regions of Ait Ahmane, Ingujem and of Ambed. These veins of magnesite sometimes contain enclaves and angular elements of serpentinites encaissantes. These veins are taken or in serpentinized peridotites either they realize the contact between serpentinites (Figs. 12A, B and C).

The massif of ultrabasic rocks is ingeneral, recut numerous breaks hemmed by serpentine and filled sometimes by the magnesite. This one is compact or brecciated in texture in cauliflower (Fig. 12 : D and F). The veins of magnesite the most important for Bou Azzer are located in the sector of Ait Ahmane, which is situated in the extremity of the mining district of Bou Azzer, in approximately 30 km in the mining center. This part of the buttonhole is characterized by the pile the most complete ophiolitic on the scale of the district with a wide development of the basic and ultrabasic terms.

As what is already indicated in the previous part, the veins of magnesite east of Bou Azzer are collected or in serpentinized peridotites either they realize the contact between serpentinites and ultrabasic and basic rocks. The formation of these veins is connected to the phenomenon of carbonatation of serpentinized peridotites, because the injection of the CO_2 in peridotites hosts gives birth of the magnesite, the silica and of small quantities of dolomite, under conditions of temperature of 200°C and of pressure PCO_2 from 130 to 180 bars (Hövelman *et al*. 2011; Diabitzias, 1980).

In brief, the formation of magnesite takes place by two essential stages:

Stage 1: transformation of olivine in serpentine:

$$3Mg_2SiO_4 + SiO_2 + 4H_2O \rightarrow 2Mg3Si_2O_5\ (OH)_4$$

Stage 2: transformation of serpentine in talc and magnesite:

$$2Mg_3Si_2O_5(OH)_4+3CO_2 \rightarrow Mg_3Si_4O_{10}(OH)_2+3MgCO_3+3H_2O$$

Magnesite veins and veinlets occur in the shear and fracture zones of serpentinites which are altered into soft, highly fractured, brown and reddish- brown rocks forming zones restricted to the selvages and inside the magnesite veins.

4.2- Structural setting

Magnesite veins and veinlets occur along shear and fracture zones of serpentinites which are altered into soft, highly fractured, brown and reddish brown rocks (Fig. 13). The contacts of the vein with host rocks are commonly sharp.

The deposit major direction of N20 to N110 marks an event filling shear zones. These structures are filled with carbonate, asbestos andoxides (magnetite) implying that the fluid is very rich in oxygen. The folded edges of asbestos fibers are a consequence of deformation along shearing, in whichthe filler is asbestos along the axis of the aperture, and the veins are parallel or perpendicular to the axis of extension. The whole association is traversed by fractures filled with calcite and magnetite (Fig. 14), and also cut bybasic dyks**.** Serpentinization is complicated due to intense deformation along senestrial faults and shear zones that is mainly oriented N110° to N130°. Sometimes N20° to N60° faults has been observed (Fig. 15). The lineation is mainly oriented N 65 to N70°. The main frequent paragenesis in this shear zones and faults is lizardite, chrysotile and asbestos with minor antigorite, chromitite and magnetite.

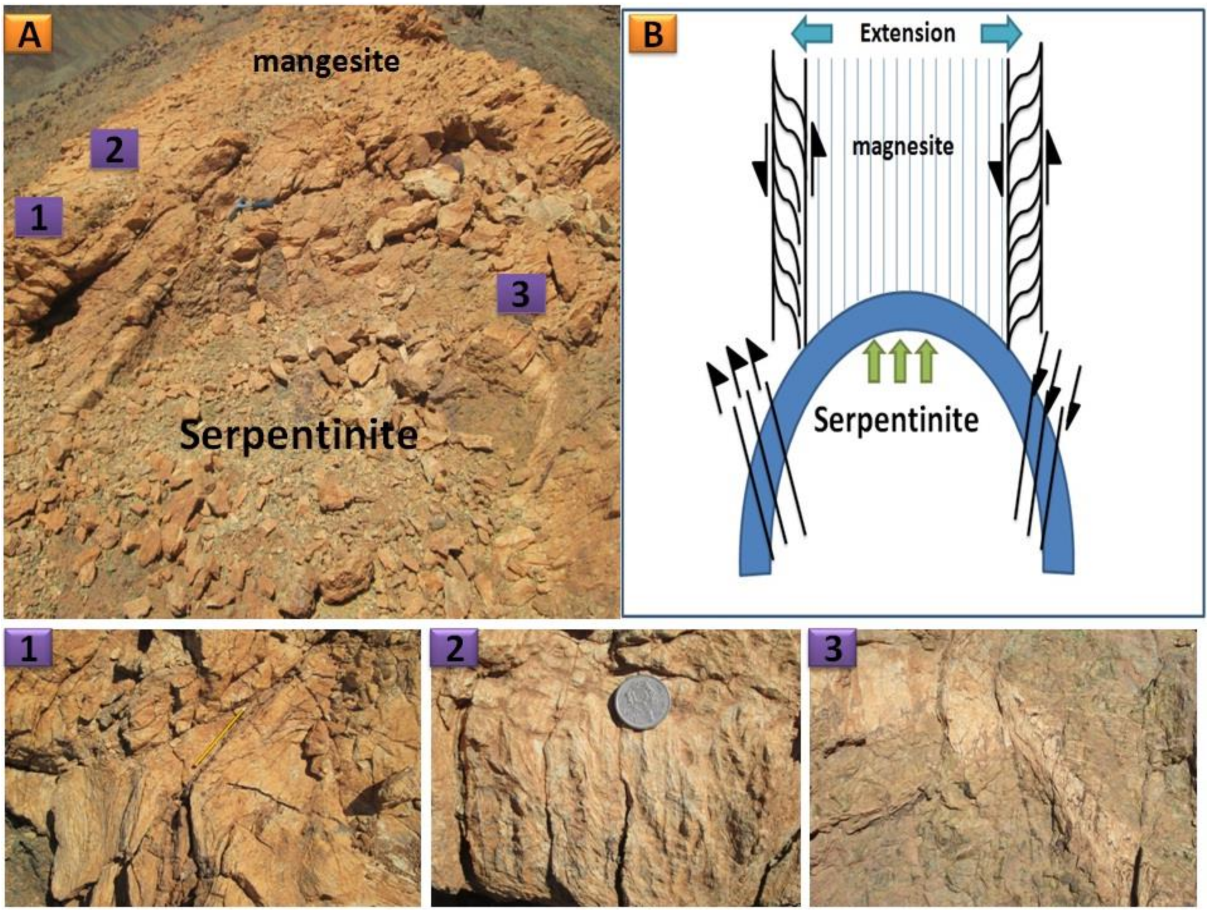

Figure 13) structural control of magnesite deposits.

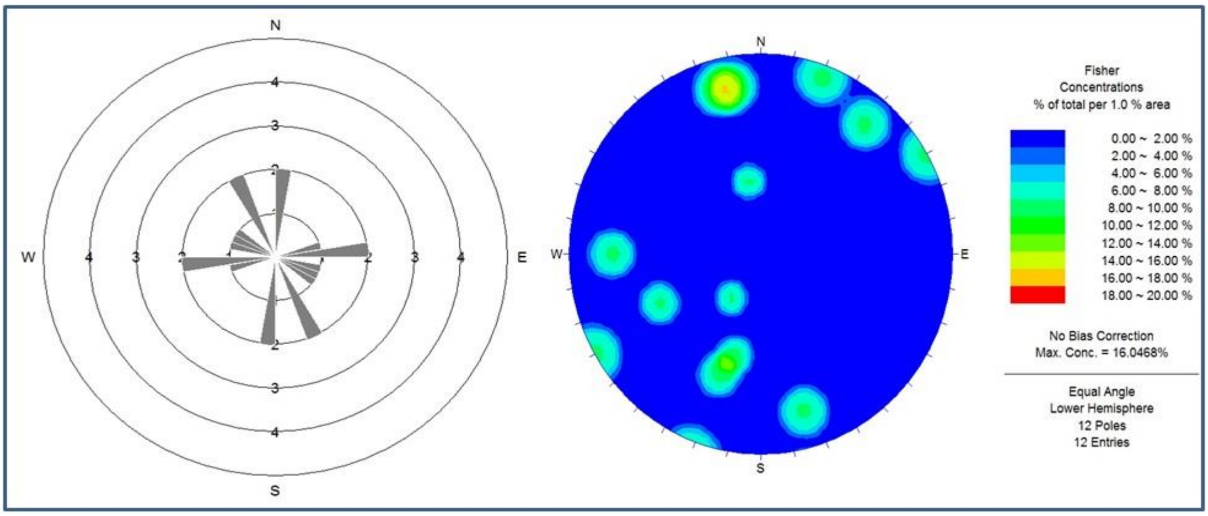

Figure 14) Stereograph of fractures rich on magnetite.

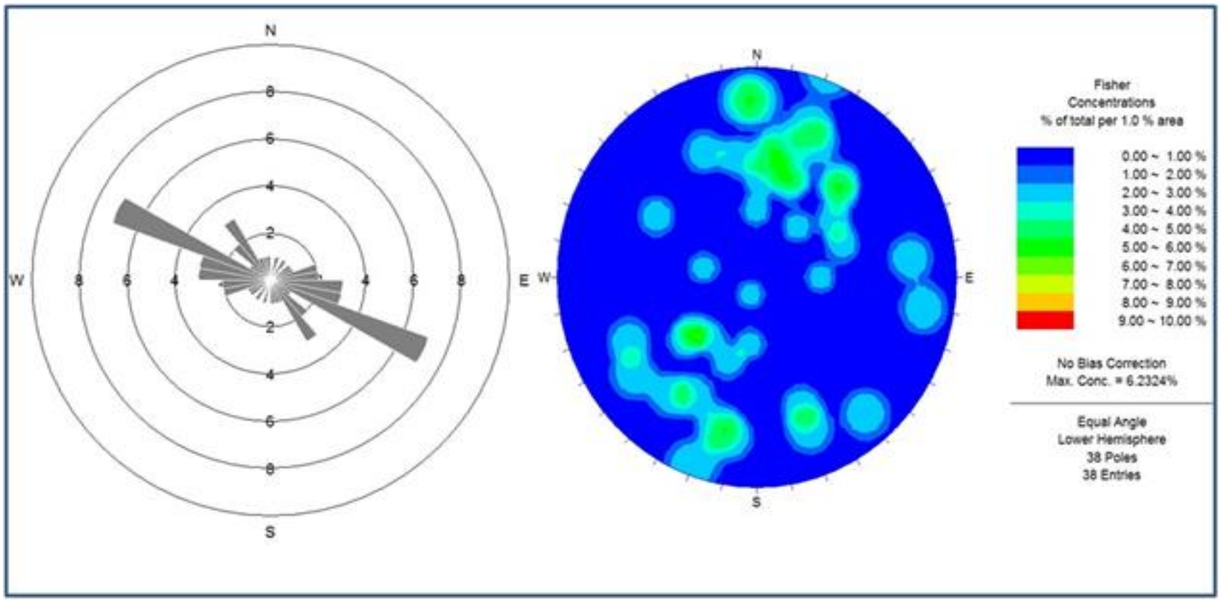

Figure 15) Stereograph of schistosity (S1).

4.3- Mineralogy

The petrographic study of the samples taken in the sectors of the study to Bou Azzer are characterized by minerals of magnesite crystallized at first by brown color and other whitish crystals stemming from a late fluid (Fig. 16) with veins filled by serpentinized minerals and sulphides very rare (chalcopyrite) in inclusion. The petrographic study of the magnesites of Bou Azzer showed the presence of the primary and secondary fluid inclusions (Lw-Vw-Sn) which accompanied the formation of mineral. These Inclusions let suggest that the formation of magnesite is connected to the circulation of salt fluids.

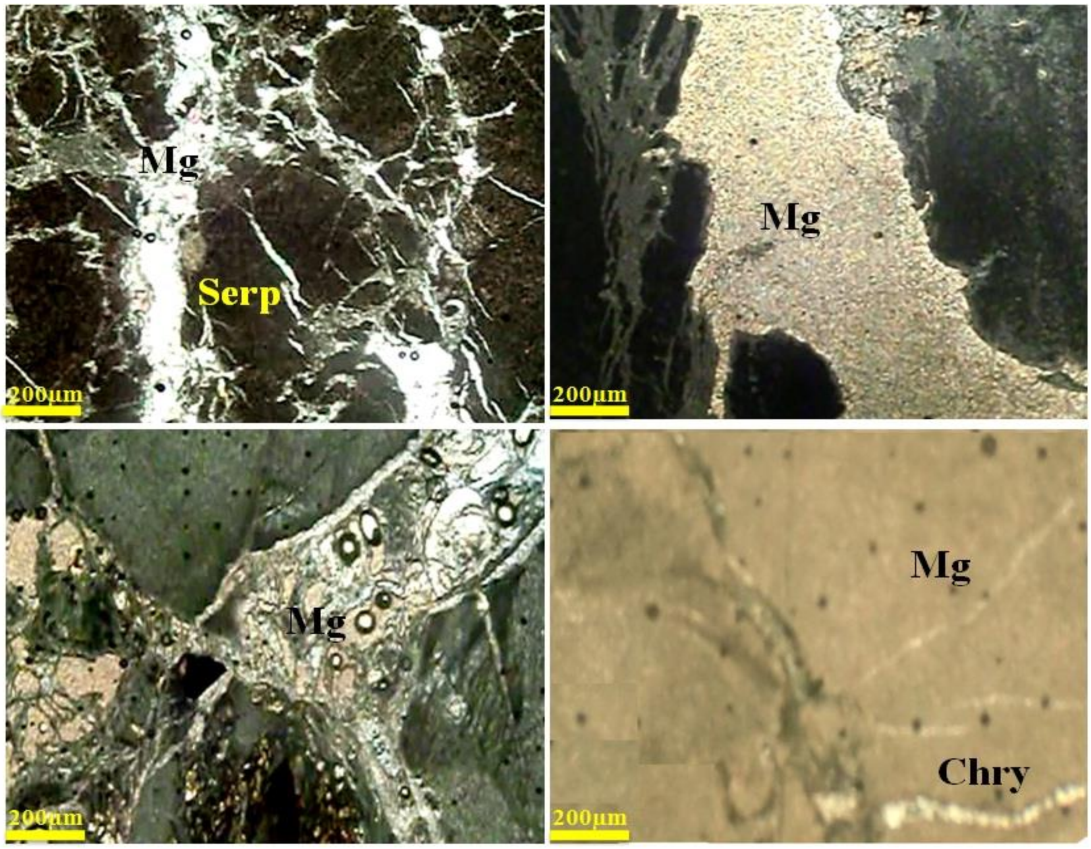

Figure 16) Photomicrographs of magnesite (Mg : magnesite, Chry : chrysotile).

These brines responsible for the implementation of the magnesite are characterized by primary fluid inclusions which accompanied the growth of the crystals of magnesite. Salts were later crossed by secondary fluid inclusions correspond globally to the superposition of several directions. According to the genetic classification of fluid inclusions, one distinguishes: Primary fluid Inclusions formed at the same time as the crystal host. They are trapped following the disturbances which occur during the growth of mineral. The secondary fluid Inclusions formed during episodes of fracturing of the crystal host enters the episodes of growth of the crystal.

4.4- Geochemical features

One of the major difficulties is to define the protolithe of every distorte altered rock. Protolithe was also chosen according to the criteria of ground with knowledges the relation between the deposits of magnesites and the serpentinite in our case. This choice was then verified by the method of (Grant, 1986) which is an application simplified by the method of (Gresen, 1967). It allows forcing the connection rock girl and taking them (source rock). It consists of a linear representation of the concentration of the elements of the rock A according to the concentration of elements in the rock B. This method allows finding motionless elements during deterioration. The latter form a line which passes by the origin, called isocone.

The geochemistry of the magnesian deposit is based on the major elements and on tracks at the end to characterize main correlations adopted between these elements and the possible scientific interpretations to explain the mobility of the chemical elements (Table 1), the enrichment and the leaching and the main changes during the transformation of serpentinites.

Table 1) concentrations of major elements (%) and trace (ppm) veins of magnesite and serpentinite

Element	Serpentinite	Magnesite
AL2O3	1,4	0,98
Cao	0,27	0,49
Cr2O3	0,28	0,2
Fe2O3	9,2	7,06
K2O	0,005	0,005
MgO	39,73	40,32
MnO	0,09	0,12
Na2O	0,005	0,005
P2O5	0,005	0,005
SiO2	42,67	45,82
TiO2	0,02	0,005
Zr	0,5	0,5
Y	0,5	0,5
Ba	17,29	73,14
Co	81,52	0,5
Cr	1544,64	55,24
Cu	9,63	4,78
Ni	2267,34	45,97
Pb	2,99	2,84
Sr	4,51	180,1

The transformation of theserpentinized peridotitewith magnesite was evaluated by the method of (Grant, 1986), the results show(Fig. 17):

• An enrichment of SiO_2; Al_2O_3; Fe_2O_3; MgO; MnO and Sr

• A leaching of Na_2O; P_2O_5; K_2O and CaO.

• The elements Zr; TiO_2 and Y are motionless.

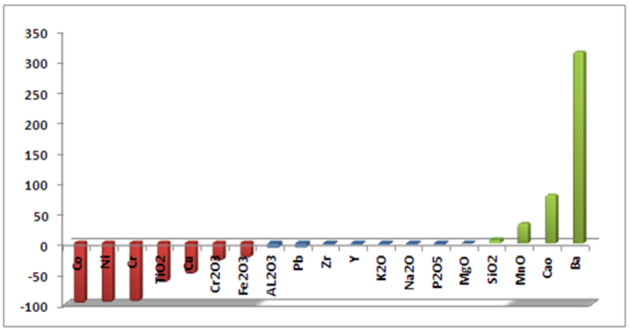

Figure 17) Composition-volume diagram (Gresens, 1967), applied to data from the Ait Ahmane index; gains and losses of elements are based on the volume factor, with g (serpentinites) = 2.8; and g (magnesite) = 3.

In order to study the phenomenon of magnesite formation in the area of Ait Ahmane, we sampled as well at the level of collecting it that at the level of the vein of magnesite. These samples were analyzed by ICP in the laboratory of «Stewart Geochemical and Essay " in Russia. The most used method is the one of (Gresens, 1969). This method implies (involves) that the chemical transformations are isovolumic or not isovolumic. It is expressed by the following equation when a protolithe A or a mineral A is transformed protolithe B there or mineral B.

$$Xn=fv\ (gB/gA)\ (CBn-CAn) \quad (1$$

- Xn: Is the profit (gain) or the loss undergone by element n.
- gB: Density of the rock or that of faded mineral (B).
- gA: Primary density of the rock or the mineral (A).
- CBn: Concentration of the element in the rock or the mineral (B).
- CAn: Concentration of the element in the rock or the primary mineral (A).
- Fv: The volume factor.

The fv gives an indication on the variation of volume, if fv> 1 this indicates that the reaction is accompanied by a profit (gain) of volume, whereas (while) if fv<1, the reaction is accompanied with a loss of volume, and if fv=1 the mineralogical transformation is isovolumic.
By applying this method to a sample of magnesite and another of the wall-rock, we deduct that the transformation of the serpentinite it magnesite is not only made by chemical loss of elements, but also by a relative loss of volume.
We recall that the carbonation is a final stage of alteration of the serpentinite; it results from the reaction to CO2 and H_2O by meteoric serpentinite (Pronost et al., 2012).
Variation of chemical elements in serpentinites to carbonated clusters (Fig. 18), according to the increase of weathering and carbonation of serpentinite to the cluster carbonated, we found:

- An increase of Co and As;
- A decrease of Ni.
- Thus the Co remains constant in the serpentinite and becomes significant in the cluster carbonated, while Ni decreased during carbonation serpentinite to become low in the cluster carbonated. So we can say that Ni is leached during carbonation of serpentinite and concentrated in other places away from carbonates.
- If the chemical elements such as Co and Ni are the same between serpentinite and carbonate cluster, it means they were not moving during carbonation.
- If the chemical elements are most important in the serpentinite in the cluster, it means they have been leached during carbonation.
- If, against the elements are most important in the cluster carbonated, it means they have

been enriched by the alteration that is to say carbonation of serpentinite.

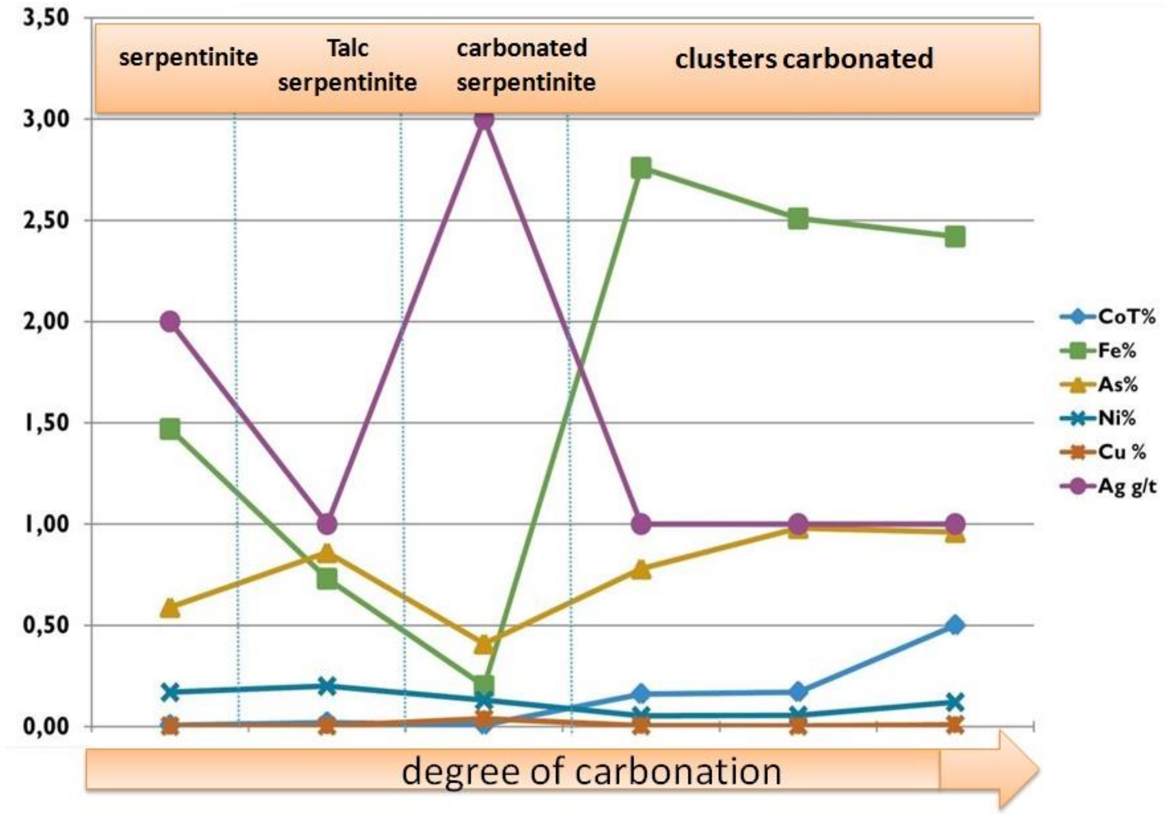

Figure 18) Variation of chemical elements serpentinites to carbonated clusters depending on degree of carbonation.

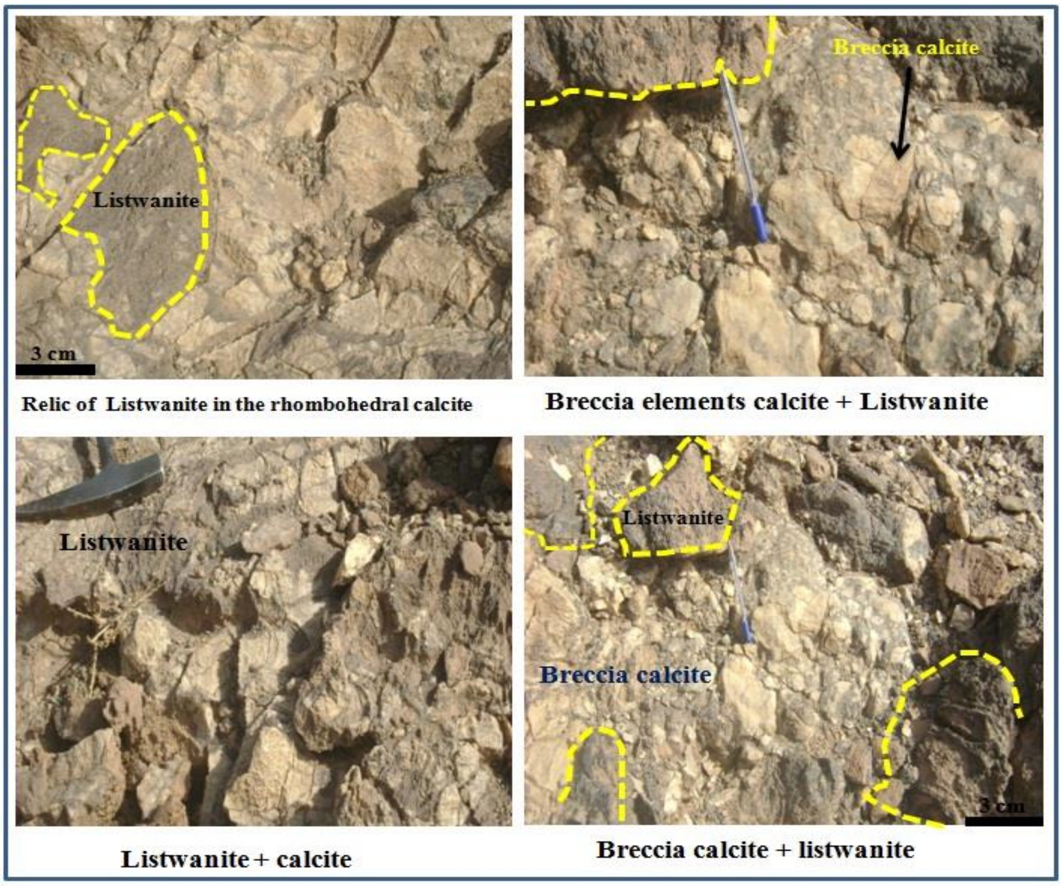

Figure 19) Photographs of listwanite.

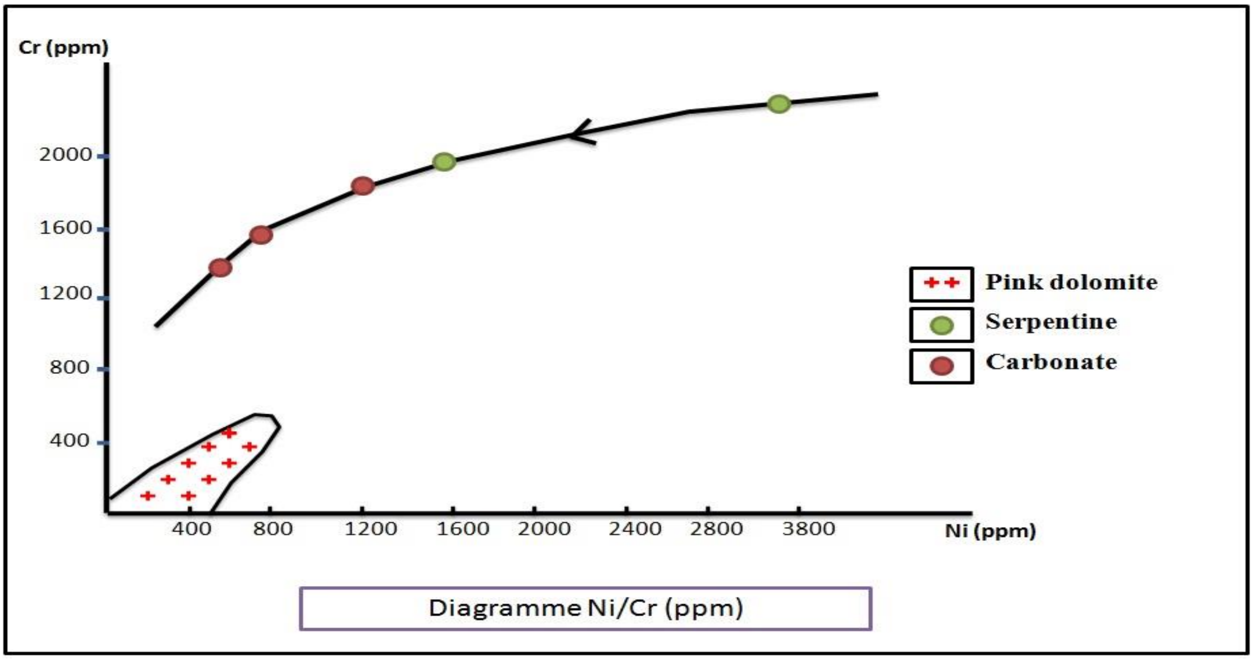

Figure 20) The behavior of nickel and chromium in the process of listwanitisation

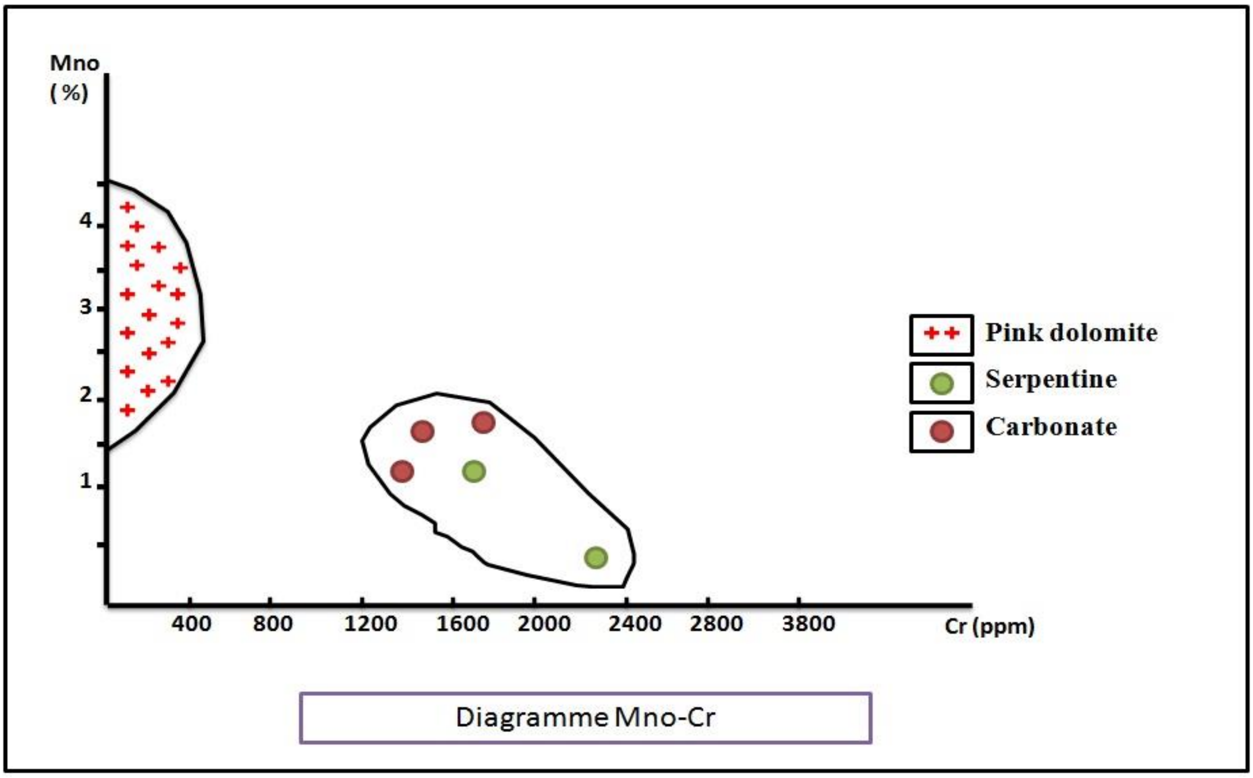

Figure 21) Classification by geochemical ratio Mn/Cr : listwanites and carbonates of the mineralizing event

Among the phenomena of carbonation also distinguishes in Bou Azzer "the listwanitization".

Listwanite is a terme long used by soviet geologists working in the goldfields of Russia (Goncharenko, 1970; Kulesheivich, 1984).

listwanite are associated with the major accidents preferentially athwartship. They are with the tectonic contacts of serpentine with the formations of the Precambrien III, intraserpentine, or in scales within the formations other than the serpentine.

These carbonated bodies are often linear and present progressive passages with serpentine (Fig. 19).

They have ribboned structures fossilizing thes tructures of serpentine in tectonized zones.

The succession characteristic of these formations includes (Maacha, 2013):

- Serpentine with talc
- Zones with talc and breunnerite.
- Zones with quartz and breunnerite.

The role of carbonates in the genesis of the cobaltiferous mineralizations tightens the interest of these results (profits) in the approach (initiative) of exploration of these types of deposit. The carbonates markers of mineralization (pink dolomite) are relatively rich in MnO and low in Ni and Cr. The listwanitization is accompanied by enrichment in Mno and a leaching out of Ni and Cr. (Figs. 20 and 21).

5- Discussion and conclusions

The analyses in total rocks of magnesites of Ait Ahmane (Bou Azzer- East) make it possible to underline the following points: The big variation of SiO_2, which shows low contents in the zone of reaction with serpentinites and intermediate values within magnesites. This variation could represent a leaching of SiO_2 in the zone of reaction of transformation.The contents in CaO show an inverse evolution of that of the SiO_2, the low values in CaO correspond to big values in SiO_2. This suggested that the fluid belongs to the reaction of transformation of serpentinite to magnesite the ascending fluid upward is very rich in CaO and becomes poor during the formation of magnesite but generally is impoverished in CaO.The highest contents of MgO coincide with the highest contents of SiO_2 on the other hand Al_2O_3 is less plentiful in the magnesite (rock richer in MgO), this is probably related to the rarity of minerals with strong content of Al_2O_3. P_2O_5 is leached rock by the hydrothermal fluid in the same terms as TiO_2. In general the geochemical results show that TiO_2 remains motionless during the process of deterioration.Elements of Cr, Co, Ni, and Cu generally show content raised in magnesite rich in Mg and low in that with low contents Fe. The less important contents of Zn and Cu can be justified by the existence of the traces of Fe, Cu sulphides and of Zn sulphides.

The masses of carbonates and carbonated serpentinite outcropping along the buttonhole including contact with serpentine diorites south and the north Adoudounien were classified in "listwanites." A rock with the process of implementation is closely related to serpentinization and constitutes the final stage. In the case of Bou Azzer, these formations are more a product of weathering per descenssum for major accidents. Work surveys and mining works have shown that all of these bodies do not extend in depth and present progressive alteration fronts both laterally and in depth.

The serpentimisation of ultrabasites took place before the Panafrican Phase B1 and continued during this phase (Leblanc, 1975).Serpentinite carbonation took place in two phases:

A first carbonation took place in connection with major accidents B2. Serpentine is then transformed into a shell of quartz and fuschite. The texture of the rock shows no preferred orientation could indicate deformation B1. However, this carbonation fossilises serpentine structures.

The second carbonation is evidenced by the development of iron-bearing carbonates. These are derived from the processing of litwanites and release of manganese.

The final stage of hydrothermal alteration is a third phase of carbonation which are associated arsenides. Carbonates include dolomite and calcite in well developed euhedral crystals. A magnesium chlorite rosette occupies the interstices.

Carbonation of serpentine is manifested through: i) Erosion serpentine minerals; ii) Their replacement by talc in an intermediate stage then; iii) The growth of calcite; iv) Some minerals such as magnetite are observed at all stages.

Descriptions of ground show that the magnesite associated with the serpentinites. Its origin, although supposed superfine by (Trescases, 1973) never was clearly shown. Many studies on the whole of the in ophiolite the worlddescribe the
formation of magnesite associated with the serpentinites (Griffis, 1972; Dabitzias, 1980; Pohl, 1990; Abu-Jaber and Kimberley, 1992; Zedef *et al*, 2000; Hansen *et al.*, 2007). This work shows that the magnesite deposits within the ultrabasic rocks are mainly formed by two different mechanisms: (1) the replacement metasomatic in situ of serpentine and (2) filling of fracture. By a mineralizing fluid In a case as in the other, the formation of magnesite is carried out according to the reaction:

$Mg_3Si_2O_5(OH)_4(s) + 3CO_2\ (g,\ aq) = 3MgCO_3\ (s) + 2SiO_2\ (aq) + H_2O\ (aq)$

Serpentine + CO_2 = Magnesite + Silica + Water

Thus, Bou Azzer the development of the magnesite veins is made with depends on the serpentinites, this hypothesis is argued as well,by the presence of irregular contacts between magnesite and their surrounding rock, that by the presence of peridotite enclaves. In Bou Azzer we can suppose that the streaming of meteoric waters or ascent of hydrothermal fluids rich in CO_2 involves the deterioration of the serpentine.

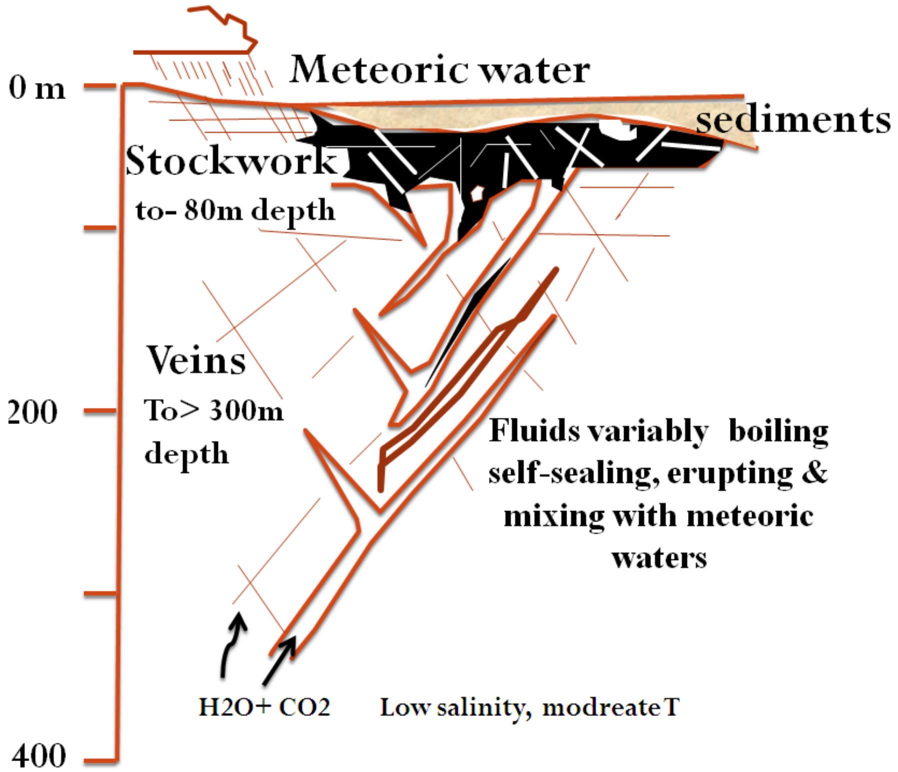

Figure 22) Kauubath type magnestie deposit modelled as a near surface epithermal system (Polh, 1990).

The resulting magnesite gradually occupies the place of serpentine original, until its total replacement. In this case, silica produced by in situ replacement of serpentine by magnesite only is crystallized very little on the spot (spot est un endroit ou place), suggesting its re-mobilization by the fluids. And this which shown by (Dabitzias, 1980). According to the classification of (Pohl, 1989; Redlich, 1909; Pohl, 1990; Dabitzias, 1980), the magnesite of Bou Azzer, we allot to type Kraubath's deposits (Fig. 22). This type is the veins of stockworks of massive white or in texture in cauliflower in grains is bound by the serpentine, the talc, the piolite, the geothite. These veins and stockwork are collected in ultramafic rocks. The model of installation of these deposits calls upon an origin of hydrothermal deterioration to which can join a supergene deterioration.

Listwanite appears on the base of Adoudounien. Their relations with other carbonated veins show their early character. Indeed, they are always reacting by veins Quartzo - carbonated cross-functional. The listwanitization is less partially posterior than Adoudounien and previous to the episode to mineralisator.

Besides, we raised figures of discordance between listwanite and shale and sandstone horizons of Adoudounien what brings to suppose that the process of change is synchronous in these deposits. In this case, the rise of plastic serpentine would be favored by the Infra-Cambrian distension and the change by the exogenous fluids charged with calcium.

Ultimately, we are in a process of deterioration supergene, which took place in several episodes and which played a role of receptacle the hydrothermal fluids. A geochemical study is based on whole rock analysis by ICP-MS of serpentinites to Bou Azzer. Mass balance, by using Greisens's method, Zr; TiO_2 and Y, defined by Grant's method as immobile elements, has been applied to calculation of tranferts water/rock. All the results pointed out very high mobility of most oxides and metallic elements. Some oxides and elements are enriched from the less serpentinized core to the fractured and faulted periphery as: SiO_2, Al_2O_3, Fe_2O_3, MgO,MnO and Sr, and others oxides and elements are leached as Na_2O, P_2O_5, K_2O and CaO. In the same time metal's transitions are leached from very deformed serpentinite. This is evidence that serpentinite is source of Bou Azzer nickel and cobalt arsenides occurrences, that has been deposed in faults and contact between serpentinite and intrusive massives. The combination between tectonic and serpentinisation controled the mobility and leaching of Ni and Co, that were components in substitution with Fe in primary ultramafic minerals olivine and pyroxene.

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