Graphite, Sheelite and Cassiterite Mineralized Skarns of Frag Al Ma, Sidi Bou Othmane District, Jebilet, Morocco

Amina Wafik1,4, Nouamane El Aouad1,2, Youssef Daafi3, Abdelfattah El Mostadi4, Yahia Boukhriss4, Abellah Mouttaqi5 and Hassan Admou3

1 Dynamic of la Lithosphere & Genese of Ressources, Faculty of Sciences Semlalia, Cadi Ayyad Marrakech University, Morocco
2 FourEtude 3S, Marrakech, Morocco
3 Group Office Chérifien des Phosphates (OCP) Youssoufia Morocco
4 Faculty of Sciences, University Chouaib Doukali, EL Jadida, Morocco
5 Office national des hydrocarbures et des Mines (ONHYM). Rabat - Morocco

* Correspondence: wafik@uca.ac.ma

Abstract
Sidi Bou Othmane region in the Central Jebilet is formed by a Devonian schistose series. The polyphase Hercynian deformation in this area is characterised by penetrative, subvertical, symmetamorphic schistosity (S1), accompanied by folding. Syntectonic granitic intrusions, hidden in the Sidi Bou Othmane region, is marked by a contact of metamorphism, which responsible for the replacement phenomena observed essentially in the limestones of the region which are transformed into graphitic Sn-W exoskarns. Syntectonic, skarnification is polyphase: (i) prograde stage (T= 500-750°C) : with graphite, garnets, idocrase, pyroxene, wollastonite, quartz, scheelite and molybdenite, crossed by a network of successive veins (garnet, idocrase, wollastonite, quartz and calcite; (ii) retrograde stage (T= 400-500°C): with garnet, idocrase, pyroxene wollastonite, quartz, calcite, epidote scheelite and cassiterite; (iii) hydrothermal alteration stage (T ≤400°C) : with sericite and clay accompanied by abundant scheelite and cassiterite, favoured by the high oxidation rate. Therefore, they would have formed in a reduced environment, in relation to large batholiths or stocks of quartz diorites and/or granites in syn, late- to post-orogenic to anorogenic contexts, in the absence of any cogenetic volcanism. The economic mineralisation of graphite was formed mainly during prograde stage, under reducing conditions. It was formed by devolatilization of a bituminous origin linked to the reef limestones and organic matter, trapped in the shales according to the following reaction:

\[ CH_4 + CO_2 \rightarrow 2H_2O + C_2 \]

Keywords: Skarns; Graphite; Sidi Bou Othmane; Morocco

1. Introduction

The word Skarn is an Old Swedish mining term. It originally refers to archaeological layers. Today, this term can be grouped into two main classifications (Phan, 1969; Bartholomé, 1970; Zharikov, 1970; Einaudi et al., 1981)
1. The skarns resulting from the metamorphic recrystallization of carbonate rocks following metasomatosis, under the effect of gradients of chemical potential of the various elements presented in the protolithic rock and leading to the formation of "calc-silicate bands" (Thompson, 1975).

2. The "infiltration metasomatic skarns" by the percolation of hydrothermal solutions, under the action of fluid pressure gradients, causes the replacement of carbonate levels whether it is in contact or not with magmatic intrusions (Fonteilles, 1978).

This study focuses on the Sidi Bou Othmane's skarns, located about 30 km north of the Marrakech city, in the central Jebilet massif (Fig. 1).

From geological perspective, the Jebilets are a metallic province of Hercynian age, known from vein deposits, Volcanogenic massive sulphide-type mineralization and pyrometasomatic deposits or skarns. These replacement deposits would result from a paleogeothermal system related to the emplacement of Hercynian granitoid stocks (Fig. 2) in relation to the polyphase tectonic-magmatic history.

![Fig. 1. The geographical location of Sidi Bou Othmane region (Google Earth)](image)

Metallogenically, several mineral deposits have been described in metamorphic limestones in the Sidi Bou Othmane area. They include 1) graphite zones with scheelite and cassiterite (Huvelin, 1977; Ramboz and Bastoul, 1985; Bastoul, 1992; El Mostadi, 1992; El Mostadi et al., 2001) 2) the lithiniferous pegmatite veins which consist of quartz, muscovite, plagioclase, perthite orthoclase, tourmaline and accessory minerals (garnet, apatite, epidote, vesuvianite, iron and manganese phosphates, niobite, andalusite, beryl and cassiterite) (Permingeat, 1952; Huvelin, 1977). 3) The Bir-Nhas zinciferous veins (Pb-Zn) are oriented globally in E-W. They belong to a vast fracture field with quartz-carbonate fillings (Huvelin, 1977).
2. History

The exploitation of the graphite deposits of the central Jebilets was made convenient by easy access, the proximity of both the national road and the railroad. The deposit of Frag Al Ma, district of Sidi Bou Othmane is located in the northern part of the Central Jebilets, about 25 km north of Marrakech and 20 km north of Oued Tensift, where the road intersects the railway to Casablanca.

The first research permit, covering the remote mineralized zone, was granted to V. Sellès on March 5, 1921; However, the first research works carried out by the Société des Mines de Rouina took place between 1924 and 1929. In 1929 the processing plant was erected and production was started, reaching 1800 tons in 1930.

The Mining Society of Gundafa took a share in The company Mines et Graphite (SMG), providing technical assistance.

The total exploitation period of the deposit lasted from 1929 to 1953, i.e. 24 years, with a total production of about 8700 tons of graphite concentrate with 45% carbon, which was used for the manufacture of batteries, lubricants, refractories, pencils and others...

The last reserves estimated and evaluated by Bolze, 1960 in Huvelin (1977) amount to 525,000 tons, without excluding additional possibilities with Fig.2.

Fig.2. Map of the different Graphite deposits of Sidi Bou Othmane.

- Louis research: Is located to the SSW of the locality of Sidi Bou Othmane. The mineralized zone of Louis corresponds to a graphitic garnet at the top of a less transformed limestone, this rich band has been exploited by trenching (Huvelin, 1977).
- Delmar Research: Located SW of Sidi Bou Othmane. It is a mineralized zone of graphitic grenatites that was working before the war and resumed from 1950 on 250m of extension and 4 to 10 m of thickness (Huvelin, 1977).
- Frag-Al-Ma: The graphite deposit of Frag El Ma, meaning watershed, located SSW of the village of Sidi Bou Othmane. The graphite zone in metamorphic limestones, have a length ranging from a few meters to several hundred meters; their thickness generally does not exceed one to two tens of meters (Huvelin, 1977).
- Berger research: located SE of the locality of Sidi Bou Othmane. It is a mineralized zone, outcropping over about fifty meters with a depth of 6 to 10m, has been exploited in part by a depth of 6 to 8 m (Huvelin, 1977).
- Exploitation of the hill 607 and research 210: is located south of Sidi Bou Othmane City. A thousand tons of 45% graphite were extracted (Huvelin, 1977).
- Koudiat Abboud: is located south of Sidi Bou Othmane corresponds to a graphite-bearing granatite in the vicinity of a less transformed limestone.
- Douar Lamhazil is located south of Sidi Bou Othmane. This rich band has been exploited by trenches.
- In the area of Douar Mansour: small scrapings were made.

Early work on these deposits highlighted several features and has revealed information on the components of mineralising fluids (Permingeat, 1951; Huvelin, 1977; Ramboz, 1988; Bastoul, 1992; El Mostadi, 1992). However, many questions remain unanswered, including possible mechanisms for selective graphite enrichment. We attempt to contribute to the discussion in this paper by presenting preliminary geological, mineralogical and geochemical data. We take into account the current classification of Einaudi and Burt (1982) on analogous deposits, this type of mineralisation and related modelling, and its propensity to develop on a regional scale.

3. The Geological Context of Sidi Bou Othmane Area

The area of Sidi Bou Othmane is located in the Hercynian massif of the Central Jebilet (Fig. 3). This region is supposed to be a transition zone between the Sarhlef Unit in the West and the Kharrouba Unit in the East. It is characterized by two sets defined by Huvelin (1977), called Sarhlef schists and Kharrouba flysch, subdivided for structural reasons, into several units tectonically superimposed from West to East: the Bou Gader unit, the Skhirat unit, the Abda unit and the Sarhlef unit (Sougy, 1976; Poutchkovsky, 1978; Muller et al., 1979).

The Frag-Al-Ma graphite is hosted in the Upper Devonian metamorphic limestones of the Sidi Bou Othmane area (Fig. 4). The limestones were transformed into cipolins and tactites in contact with granite. The graphite, which would come from the metamorphism of bitumens initially contained in the sediment, is irregularly distributed in the mass of metamorphic limestones (Fig. 5). Graphite ores have a variable boron content (Huvelin, 1977). The reserves following the graphite-enriched zones are indeed limited; however, the edges of the metamorphic limestones offer large reserves (several hundred thousand tons) with a low graphite content (more than 12%), with the advantage of the scarcity of sulfides, which makes it possible to avoid the penalty of sulfur and copper (Permingeat, 1957 in Huvelin, 1977).
Fig. 3. Geological map of the Sidi Bou Othmane region (modified from Delchini et al., 2018).
3.1. Metamorphism

According to previous researches (Huvelin, 1977; El Hassani, 1980), two types of metamorphism are distinguished: regional metamorphism and contact metamorphism.

The regional or epizonal dynamic metamorphism emphasized by the preferential orientation of quartz, muscovite and biotite (Huvelin, 1977; Bordonaro, 1983; Bernard et al., 1988). The minerals resulting from this metamorphism are sericite, chlorite, quartz, epidote and biotite which appears sporadically characterize the green schist domain (Huvelin, 1977; Bordonaro, 1983). In a recent study, Delchini et al. (2016) was able to highlight the existence of a garnet-staurolite paragenesis, typical of
amphibolite facies attached to the M2 regional metamorphic phase, at pressure and temperature conditions of 4-5 Kbar and 560 - 585°C respectively.

The contact metamorphism is expressed by the development of non-oriented andalusite and cordierite spots characteristic of low pressure metamorphism in the metapelites and on the other hand calcium silicates which develop in the metamorphic limestones (Marbles). The paragenesis of the contact metamorphism suggests that the plutons were emplaced less than 2.2 kbar corresponding to a maximum depth of 8 km (Bouloton, 1992).

**Fig. 5.** A) Sarhlef shale with sandstone-pelitic alternation. B) Spotted shale, in the halo of contact metamorphism near the magmatic intrusion.

### 3.2. Deformation in the Sidi Bou Othmane Region

The Sidi Bou Othmane region has undergone polyphase Hercynian deformation, characterized by the formation of ductile and brittle structures that are related to several phases. Bordonaro (1983) described five phases of deformation in the Jebilet (D0, D1, D2, D3 and D4), while Delchini et al. (2018) distinguishes 5 phases (D0, D1, D2 polyphase (a, b, c)):

- D0 antschist deformation with large radius of curvature folds oriented E-W, related to the syn-sedimentary slip sheets of the eastern Jebilet;
- The D1 deformation is marked by a synschistose folding of average direction N30 with axial plane slightly sloping in the East and straightened in the West, it is regional syn-metamorphism;
- The D2 deformation (D2a) coincides with the paroxysm of the deformation and metamorphism; it is characterized by folds and shears taking up the D1 structures;
The D3 deformation (D2b) is characterized by a N110 to N150 crenulation schistosity sloping towards the NE and very localized thrusting towards the West. These structures are observed mainly in the west of the Sidi Bou Othmane area;

- The D4 deformation (D2c), is represented by two sets of conjugated N70 dextral and N135 sinistral decoupling. Chevron folds and fold bands are also observable.

The deformation in the Sidi Bou Othmane area is very intense. It is marked by folds, generally sloping towards the west (45° to 85°) and a penetrative axial plane flow schistosity (Huvelin, 1977; El Mostadi, 1992) and this study.

The regional metamorphism transformed the limestones of the Sidi Bou Othmane area into marble. The stretching lineation shows a generally SW dip in the eastern part of the region, then becomes NE in the western part. This indicates that the movement is conjugate in both NE and NW directions. In the Marrakech senestial shear zone, the movement of material is NW, as the stretching lineation dip is SW.

Brittle structures affect all the previous structures. They are sinister or dexter strike-slip faults with quartz-carbonate filling.

3.3. The Granitoids of the Jebilets

The Central Jebilets are engaged in ductile shearing along a 10 km corridor around the N-S Sidi Bou Othmane-Marrakech axis, and cut by syntectonic granites. All the granitic plutons (Bramram-Tabouchent-Bamega and Oulad Ouaslam) outcrop south of the axis of the shear zone in the Sidi Bou Othmane region (30 km north of Marrakech City) (Huvelin, 1972; Lagarde and Choukroune, 1982). Two groups of granitoids have been distinguished: granodiorites and leucogranites in which the latter intersected the former (Huvelin, 1972; Saquaque, 1985; Chemsseddoha, 1986; Bensalah, 1989) (Fig. 3).

The granodiorites are peraluminous and calc-alkaline affinity dated to around 330 Ma (Mrini et al., 1992), although recent dating suggests older ages (up to 358 Ma (Delchini et al., 2018). They are composed of large crystals of potassium feldspar and biotite, plagioclase, and automorphic crystals of cordierite and andalusite that show characteristics of primary minerals of magmatic origin (Lagarde, 1987).

Leucogranites are intrusive in the granodiorite and are younger with an age of 295±15 Ma obtained by Rb-Sr dating (Mrini et al., 1992). They are observed in the vicinity of the Bamega and Tabouchent granites. These leucogranites are two-mica granites, affected by late-magmatic phenomena; tourmalisation and muscovitisation (Lagarde, 1987).

Although the contact metamorphism is well developed in the region of Sidi Bou Othmane, granites do not outcrop. The evidence of their presence remain the veins of pegmatite, enclaves of granite in microdiorites (Huvelin, 1977); however, their presence is highlighted by geophysical prospection (Fig. 6) (Wafik et al., In progress). The allochemical contact metamorphism following with circulations of late magma fluids subsequently transformed these marbles into graphite, scheelite and cassiterite mineralized Skarn (Permingeat, 1951; Huvelin, 1972; Bastoul, 1992; El Mostadi, 1992).

In these contact zones, bands of high graphite content (up to 85%) are locally encountered. Their thickness sometimes reaches a few decimeters, but in the longitudinal direction they are very irregular and they disappear more or less quickly. They are found as well at Frag El Ma, Louis' research, Koudiat Abboud, 210's research, Berger's research and Delmar's research. Massive skarns are more abundant than banded skarns.

The skarns of Sidi Bou Othmane are the result of transformation of marbles under the effect of the circulation of fluids. The limestones and graphitic shales in the region could not evolve in a closed system for oxygen, because of their abnormally high iron oxidation rates. Due to the large thermal gradient and high permeability created by ductile deformation, a flow of oxidizing fluids occurred in the
region (Ramboz and Bastoul, 1985) that is thought to have been responsible for the formation of tin and tungsten oxides.

**Fig. 6.** Interpretative geological E-W cross-sections through the central Jebilet massif (completed from Dechini 2018). For localization.

### 4. Materials and Methods

This study is based on mapping, field observations, petrographic and metallographic studies. The field work allowed us to observe and describe the different lithological facies (limestones, schists, pegmatites veins, microdiorite veins and late quartz-carbonate veins). This work was carried out using the following maps:

- Geological map of Jebilet at 1/200 000 (Huvelin, 1972).
- Geological and mineralization map of Central Jebilet at 1/100 000 (Huvelin, 1972).

The results obtained both in the field and in the laboratory will allow us to complete the geological and mineralization map of Central Jebilet at 1/100 000 (Huvelin, 1972) (Fig. 1), using GIS software for data processing.

In the laboratory 17 polished thin sections were made from the samples collected in the field. A mineralogical characterization with transmitted light microscope of the mineral phases mineralization and gangue in the DLGR laboratory; a quantitative analysis with scanning electron microscope (SEM) and a characterization in Raman microspectrometry were carried out in the center of analysis and characterization (CAC) of the Cadi Ayyad University. The petrographic and metallographic study of these slides allowed us to approach the genetic history of the skarns of Sidi Bou Othmane and to establish a genetic model.

Materials and Methods should be described with sufficient details to allow others to replicate and build on published results. Please note that publication of your manuscript implicates that you must make all materials, data, computer code, and protocols associated with the publication available to readers. Please disclose at the submission stage any restrictions on the availability of materials or
information. New methods and protocols should be described in detail while well-established methods can be briefly described and appropriately cited.

Materials and Methods should be described with sufficient details to allow others to replicate and build on published results. Please note that publication of your manuscript implicates that you must make all materials, data, computer code, and protocols associated with the publication available to readers. Please disclose at the submission stage any restrictions on the availability of materials or information. New methods and protocols should be described in detail while well-established methods can be briefly described and appropriately cited.

Research manuscripts reporting large datasets that are deposited in a publicly available database should specify where the data have been deposited and provide the relevant accession numbers. If the accession numbers have not yet been obtained at the time of submission, please state that they will be provided during review. They must be provided prior to publication.

Interventionary studies involving animals or humans, and other studies require ethical approval must list the authority that provided approval and the corresponding ethical approval code.

5. Results

5.1. Petrography of the Graphitic Skarns of Sidi Bou Othmane

The allochemical contact metamorphism following with circulations of late magma fluids subsequently transformed these marbles into graphite mineralized skarns and cassiterite occurrences (Permingeat, 1951; Huvelin, 1977; Bastoul, 1992; El Mostadi, 1992). Graphite occurs in irregularly distributed pockets in the metamorphic limestones; However, it is preferentially concentrated in the contact zone with the schists (Fig. 8). They are constituted by graphitic greenschists that are located at the contact between the marbles and the metashales. The mineral association consists of garnet, graphite, vesuvianite, quartz, calcite, epidote, wollastonite, molybdenite, scheelite, traces of chalcopyrite and pyrite. Crystallization is polyphase with a matrix of garnet, graphite, pyroxene, quartz, epidote and calcite, intersected by veins of garnet, potassium feldspar, quartz, vesuvianite, pyroxene and calcite.

5.2. Petrogenesis of the Skarns and Associated Mineralization

The observations of the different skarns in the field, completed by the petrographic study, allowed to highlight three phases of formation: (i) a prograde phase during which the calcium silicates of the skarns were formed is related to which is subdivided into two stages; an early stage with garnet, pyroxene, graphite, and a fissural stage with wollastonite, feldspar; (ii) a retrograde phase with epidote, quartz, and calcite; (iii) a hydrothermal alteration phase with sericite, clay, and quartz.

5.2.1. Phase 1: Prograde

The prograde phase in the Sidi Bou Othmane skarns is characterized by two stages of calcic silicate formation (garnet, vesuvianite, pyroxene and wollastonite).

• Early prograde stage

This stage is observed in massive, banded and veined skarns (Fig.7). It results in the formation of garnet, vesuvianite, pyroxenes and wollastonite. This stage is responsible for the formation of all the skarns in the region from limestones metamorphosed into calcic silicate marbles. It shows a succession of metasomatic zones from marbles to greenschists.
• Fissural prograde stage
   It corresponds to a fissural stage where the circulation of fluids gave rise to veins filled essentially with garnet, vesuvianite, pyroxene, wollastonite, potassium feldspar, quartz, epidote and calcite. These veins are present in mineralized skarns and absent in marbles and metapelites. This stage is associated with scheelite mineralization that is often observed in veinlets that largely cut the graphitic granatites (Fig. 7).

5.2.2. Phase 2: Retrograde
   This phase is characterized by intense retrograde transformations of stage 1A minerals (garnet, graphite with rare scheelite, and wollastonite) partially of stage 1B minerals (garnet, graphite, vesuvianite with veins of schellige). The importance of these transformations decreases from wollastonite, to garnet and vesuvianite, whereas pyroxenes do not seem to be affected by these transformations (Fig. 8). Scheelite is observed in this stage and is characterized by the presence of grains associated with large epidote, calcite and quartz crystals.

5.2.3. Phase 3: Late hydrothermal alteration
   The hydrothermal alteration phase is marked by the appearance of sericite, clays (chlorite) and by an oxidation of sulfides into hematite. It is also marked by the richness of scheelite. The W is rich in hydrothermalized rocks (with calcite and clay minerals), it is present in 1.59 wt.%. These results were mentioned by El Mostadi (1992). The hydrothermal alteration phase is marked by the presence of cassiterite (El Mostadi, 1992). Cassiterite is associated with scheelite and retrograde phase minerals (quartz, epidote and calcite).
   The minerals of this phase (garnet, vesuvianite and wollastonite) are often found in association with graphite. This explain why there is a synchronous formation between the calcic silicate minerals and the graphite.

5.3. Deformation
   The mineralized body is crossed by several veins of different directions; E-W, N-S and NE-SW, filled with calcite, wollastonite, quartz, epidote and coarse garnet. These veins materialize zones of fluid circulation, corresponding to the fissural stage. The field study showed a more or less heterogeneous deformation, materialized by boudinage, shearing or folding of the veins crossing the skarns. The ductile deformation is linked to a sinister shear zone with folding of the veins. The analysis of the deformation in the Frag Al Ma orebody showed that it underwent a downshearing movement marked by oblique and vertical striations, overlapping lenses, folded veins with notching folds and ripping steps. Indeed, the mineralized body is also cut by pre-atlasic veins similar to those of Bir N'Has.
Fig. 7. Photos of the different deformations of the Sidi Bou Othman skarns. A: massive Skarns, B and C: banded Skarns, D: contact between skarn ans schistes, E: breccias zone, F: folded Skarn.

5.4. Petrographic study

Some lenses are entirely transformed into tactites. These are constituted of garnet (grossular) to which calcite, diopside, idocrase and wollastonite are added. The textures change from conglomeratic to banded to brecciated (Fig. 8 A, B, C, D).

Garnet is by far the dominant mineral, occurring as more or less fractured automorphic crystals (Fig. 8) and filled with contemporaneous minerals mainly pyroxene, quartz, epidote (Fig. 8 A, B, C, D). Often the garnet crystals are zoned and contain graphite rims (Fig. 8 A-G). The whole is crossed by potassium feldspar (Fig. 10 E) and scheelite (Fig. 8 F) of the fissural stage. Hydrothermal alteration is shown by the replacement of the primary minerals by sericite and clays (Fig. 8 H).
Fig. 8. Microphotograph of skarns at transmitted light polarised; (A and B) massive graphitic skarn; (C and D) conglomeratic texture; E, F and G with pyroxene garnets, epidote, wollastonite and feldspar veinlets of fissural stage and scheelite. (H) Corrosion of garnet, vesuvianite by sericite and alteration stage clays. (Ep : Epidote, Gr: Graphite, Grs: garnets, Px : Pyroxene, Src :Sericite, Sch: Scheelite).

Scanning electron microscopy (SEM) of the massive skarns shows a highly enriched carbon composition (Fig. 9 A-C).
The analysis by Raman spectroscopy, gives a graphite with characteristics reminiscent of graphite oxides, amorphous graphite or even damaged graphene. This would be related to the crystallization temperature and the metamorphic degree (Fig. 9).

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>62.25</td>
<td>73.60</td>
</tr>
<tr>
<td>O</td>
<td>19.95</td>
<td>17.71</td>
</tr>
<tr>
<td>Fe</td>
<td>1.81</td>
<td>0.46</td>
</tr>
<tr>
<td>Mg</td>
<td>1.72</td>
<td>1.01</td>
</tr>
<tr>
<td>Al</td>
<td>0.37</td>
<td>0.19</td>
</tr>
<tr>
<td>Si</td>
<td>13.90</td>
<td>7.03</td>
</tr>
</tbody>
</table>

Fig. 9. Scanning electron microscope (SEM) and Raman microspectrometry analysis of Frag al Ma (FAM) massive skarns. A: SEM photograph; B: Quantitative chemical composition; C: analytical spectrum; D: Raman spectroscopy investigation of characteristics closer to damaged graphene and amorphous graphite or graphite oxides of (FAM) skarns.
6. Discussions

The Sidi Bou Othmane unit is considered as a transitional zone between two major structural units, the Central Jebilet and the Eastern Jebilet. The structural characteristics of the Sidi Bou Othmane area are manifested by the presence of a subvertical penetrative schistosity $S_1$ and by the evolution of the style of the folded structures with anisopic short-side and long-side folds, compatible with a sinister shear (Lagarde and Choukroune, 1982), which result from a WNW-ESE to NW-SE horizontal shortening (Lagarde and Choukroune, 1982; Le Corre, and Bouloton, 1987; Delchini et al., 2016).

The Sidi Bou Othmane region was the site of a contact metamorphism, which was superimposed on the regional metamorphism. This metamorphism is induced by hidden intrusions to which the pegmatite veins outcropping in the region are related, which would be the northern extension or

---

**Fig. 10.** Paragenetic mineral sequence of the Sidi Bou Othmane skarns.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Prograde phase</th>
<th>Retrograde phase</th>
<th>Hydrothermal alteration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Massive, banded</td>
<td>Veins</td>
<td></td>
</tr>
<tr>
<td>Graphite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Garnet</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vesuvianite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyroxene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wollastonite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sphene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potassium feldspar</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scheelite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molybdenite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Epidote</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnetite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sericite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clays</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
equivalent of the syn-tectonic calc-alkaline granodiorites (Tabouchnt, Bramram, Bamega) dated at ca. 330 Ma (Mrini et al., 1992). Although recent dating suggests older ages (up to 358 Ma, Delchini et al., 2018); crosscut by peraluminous leucogranites dated at ca. 300 Ma (Mrini et al., 1992).

The contact metamorphism is marked by the development of mottled schists (with andalusite and cordierite) in the metapelites and the transformation of limestones into marbles and the circulation of fluids responsible for the skarns genesis.

The skarns of Sidi Bou, show a dominance of grossular garnets, pyroxene with idocrase, rarely wollastonite, with early economic concentrations in graphite, at the contact between the limestone blocks and the shales, during the prograde phase. Garnet, epidote, quartz and calcite fillings are accompanied by scheelite (CaWO3 ) and cassiterite (SnO2 ) characterize the retrograde phase (El Mostadi, 1992) and this study.

Graphite is irregularly distributed in the mass of the skarns, however, it is mostly concentrated in the massive skarns, then in the banded and veined skarns and lastly in the calcic silicate marbles. It also occurs in the contact zone with the metapelites, along the transverse faults. In these contact zones, graphite occurs locally in subvertical bands, oriented NNE, in very high grade (up to 80 wt%). The graphite bands can reach a few decimeters to a few meters in thickness but the longitudinal extension is very variable. The skarns also contain occurrences of scheelite and cassiterite (Permingeat, 1952; P. Huvelin, 1977; El Mostadi, 1992). Hydrothermal circulation synchronous with the emplacement of granitoids is at the origin of reactions between limestone and fluids on the one hand and between gaseous species during devolatilization of hydrocarbons from sedimentary rocks (shale and limestone) on the other hand, during the prograde phase of contact metamorphism (Huvelin and Permingeat, 1980; Bastoul, 1992; El Mostadi, 1992).

Graphite is irregularly distributed in the mass of the skarns, however, it is mostly concentrated in the massive skarns, then in the banded and veined skarns and lastly in the calcic silicate marbles. It also occurs in the contact zone with the metapelites, along the transverse faults. In these contact zones, graphite occurs locally in subvertical bands, oriented NNE, in very high grade (up to 80 wt%). The graphite bands can reach a few decimeters to a few meters in thickness but the longitudinal extension is very variable. The skarns also contain occurrences of scheelite and cassiterite (Permingeat, 1952; P. Huvelin, 1977; El Mostadi, 1992). Hydrothermal circulation synchronous with the emplacement of granitoids is at the origin of reactions between limestone and fluids on the one hand and between gaseous species during devolatilization of hydrocarbons from sedimentary rocks (shale and limestone) on the other hand, during the prograde phase of contact metamorphism (Huvelin and Permingeat, 1980; Bastoul, 1992; El Mostadi, 1992).

According to Meinert et al. (2005), the skarn type deposits present a polyphase setting with three main stages which are usually very largely superimposed:

- The thermometamorphic stage corresponds to the emplacement of the intrusion and the dehydration of the host rock, with expulsion of fluids. It is an isochemical process which transforms limestones into marbles;
- The prograde metasomatic stage corresponds to an early metasomatosis with contribution of iron, manganese and aluminium at high temperature (500 to 600 °C) by the magmatic fluids released by the pluton. At this stage, typical anhydrous metamorphic silicates appear by reaction with the host rocks: pyroxenes (diopside-hedenbergite), garnet (andradite-grossular), clinozoisite, titanite, wollastonite, vesuvianite, and calcite and biotite. In the case of the tungsten skarns, fine deposits of low-grade disseminated scheelite (0.01 wt% CaWO3 ) may appear as early as this episode. This corroborates with our observations at Sidi Bou Othmane and confirms the results of previous work at Frag Al Ma (El Mostadi, 1992). Indeed, studies on thermicity on Jebilet by Raman spectroscopy (Delchini et al., 2018), defined a temperature of 613°C on calcite, 616°C on garnet and 623°C on pyroxene. This study revealed temperatures ranging from 599 to 635°C, in garnets from a single sample. This mineralogical assemblage at ± Garnets ± Vesuvianite ± Pyroxene ± Wollastonite is typical of crystallization conditions in the amphibolite facies, with temperatures ranging from about 550°C to 674°C around these intrusions (Delchini, 2018).
- The retrograde hydrothermal stage reflects the invasion of the system by lower temperature fluids (300-450°C). This influx of water causes partial hydrolysis of the minerals from the prograde stage and intrusive rocks, leading to the appearance of numerous hydrated minerals, including amphiboles (actinolite), hornblende, and tremolite), epidote, talc, chlorites, and sometimes sercite and montmorillonite clays, in addition to quartz and calcite. The nature of the retrograde minerals depends on the state of oxidation and sulfidation of the hydrothermal fluids. This corroborates with our observations at Sidi Bou Othmane and confirms the results of previous work at Frag Al Ma (El Mostadi, 1992). This is also the essential stage of sulphide deposition: the ore can then be enriched to a mineable
grade. Thermicity studies on the Jebilet by Raman spectroscopy (Delchini, 2018), also revealed lower temperatures up to 304°C, which were interpreted as related to late alteration in our study.

6.1. Spatio-Temporal Zonation

Within the igneous metamorphic aureole one can distinguish, wholly or partially from the intrusion to the intact limestones.

The increase in the temperature released by the granitic pluton would have catalyzed the interactions and the chemical exchanges between the magmatic body and the carbonate casing. Three types of skarns are distinguished, massive, banded and veined skarns.

Some of the minerals in the tactites can be considered as geothermometers:

- Wollastonite begins to form between 660 and 800°C; andradite garnet would form at a temperature below 800°C. Generally speaking, according to Bathman in Routhier (1969), pyrometasomatic phenomena are located in a temperature range between 400 and 800°C.

- The minerals present in the different paragenesis of the Frag El Ma graphite deposit are among others: garnet, quartz, epidote, wollastonite, allowed us to conclude that it is an exoskarns.

All the mineralogical observations allow us to trace the pressure and temperature conditions of the fluid responsible for the formation of the skarns. The presence of wollastonite suggests a minimum temperature of 580-600°C (Taylor, Liou and 1978, 1978; Hui, et al., 1994; Grammatikopoulos and Clark, 2006). The presence of fresh cordierite, andalusite and biotite in the schists, in contact with the granite, suggests a formation temperature above the reaction curve: muscovite + quartz = alumina silicates + orthoclase + H2O, in the andalusite field, i.e., a temperature range between 620 and 650°C. These results are in agreement with those of El Mostadi (1992). The paragenesis of the contact metamorphism suggests that the plutons were emplaced at least at 2.2 kbar corresponding to a maximum depth of 8 Km (Boulton, 1992). Based on the crystallinity of the graphite, El Mostadi (1992) estimated the crystallization temperature ≥ 480°C.

The presence of sphene in the skarns is reported by other works that show that these sphenes contain tin (0.65 to 0.7 wt% Sn) and high contents in fluorine (1.3 to 1.4 wt%). The enrichment in tin and fluorine could be an indication that the skarns are closer to a granitic intrusion. Indeed, there are numerous veins of cassiterite and niobio-tantalate pegmatites in the Delmar search (El Mostadi, 1992).

6.2. Genetic Interpretation

As summarized by Einaudi et al. (1981), low-sulfide skarns tend to be associated with the more reduced Type S or ilmenite-series magmas and Type I or magnetite-series magmas of the intermediate depth environments, whereas high-sulfide oxidized skarns tend to be associated with the more oxidized Type I magmas of the hypabyssal environment.

Oxygen fugacity depends on both the nature of the magma and the reduction capacity of the rocks, influenced, for example, by the presence of graphite. The reduced skarns, rich in Fe2+ and Mn2+, show pyroxene and prograde grossular, and a retrograde stage with biotite, plagioclase, magnetite and pyrrhotite. They include most of the tungstiferous skarns, sometimes with molybdenum, stanniferous, ferriferous, zinciferous, and most of the gold rich skarns. The Fe3+-rich oxidized skarns show abundant garnets (andradite) and diopside in the prograde stage, and a retrograde assemblage of epidote, chlorite, calcite, quartz and pyrite. Oxidized skarns include most copper-bearing skarns, some tungstiferous and gold-bearing skarns.

The Frag El Ma pyrometasomatic deposit was formed by the replacement of metamorphic limestone by garnet, pyroxene, graphite, idocrase, wollastonite and epidote skarns (Fig. 13). They were formed by thermochemical diffusion processes between the pluton and the metamorphosed limestone, which will release calcium that reacts directly with silica released by the underlying magma body, to
form calcium silicates. The most dominant skarns are graphitic garnetites more or less enriched in pyroxene, idocrase, wollastonite, epidote with more or less important concentrations in molybdenite, wolframite, scheelite, chalcopyrite, pyrite and fluorite. The emplacement of this mineralization is related to an aureole of contact metamorphism, caused by Hercynian granitic intrusions. The increase in temperature released by the granitic pluton, would have catalyzed the interactions and chemical changes between the magmatic body which contaminates the casing with silicate elements ($\text{SiO}_2$, $\text{Al}_2\text{O}_3$), and the limestone lenses which will release calcium, responsible for the setting of the gangue minerals.

The capricious distribution of graphite in the metamorphic limestones, its preferential concentration in the contacts with the shales and certain breaks, require great mobility of the carbonaceous material and would plead in favor of a bituminous origin linked to the reef limestones (permigeeat, in Raguin, 1954) - Following the degradation of carbonates, the released CO2 could be trapped and form graphite. Recently, the genesis and source of graphite have been elucidated by Bastoul et al. (1993), according to the following reaction:

$$\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{H}_2\text{O} + \text{C}_2$$

The source of carbon that constitutes graphite is related to organic matter, trapped in the shales that has undergone degassing and decomposition related to the cracking of the matter during the contact metamorphism caused by the intrusion, which enters into reaction with carbon dioxide derived from carbonates, according to the following model the formation of graphite could be explained according to three steps (Prograde, retrograde and hydrothermal alteration) (Fig. 11).
Fig. 11. Explanatory diagram of the formation of graphitic skarns of Sidi Bou Othmane, this diagram is conducted in this study using the results of previous work (El Mostadi, 1992; Bastoul et al., 1993).
Fig. 12. explanatory diagram of the main processes leading to the formation of the graphitic skarns of Sidi Bou Othmane. This scheme is carried out in this study using the results of previous work (Bastoul et al., 1993)

6.3. Classification of Skarns in Frag Al Ma

Skarns are generally sources of Fe, Cu, Zn, W, Mo and other metals, as well as other industrial substances. Skarns can be subdivided according to several criteria. For example, a distinction is made between exoskarn and endoskarn, which were originally used at metasomatic carbonate replacements, which may also refer to the location of the skarn relative to the causal pluton (external or internal). The terms exoskarn and endoskarn are used to indicate a sedimentary or igneous protolith, respectively. If the classification of Einaudi and Burt, (1982) is adopted, the Frag Al Ma skarns correspond to exoskarns.
Other criteria are also used, depending on the nature of the replaced carbonate rocks. Magnesian, manganic, and calcareous skarns can be used to describe the dominant composition of the resulting protolith and skarn minerals. These terms may be combined, as in the case of a magnesian exoskarn, which contains a forsterite-diopside-phlogopite skarn formed from dolomite. In the case of Frag Al Ma, the skarns developed at the expense of the limestones, which corroborates with the observations of Huvelin (1977) and El Mostadi (1992).

According to the classification of Jébrak and Marcoux (2008), based on the types of metals, the Frag Al Ma deposit belongs to the Mo skarns type, as it presents the mineralogy of garnet, Idocrase and Wollastonite which are calc-silicate minerals and also molybdenite, scheelite and chalcopyrite which are the main economic minerals of Mo skarns type deposits.

Variation in garnet and pyroxene composition is also discussed in the classification section (Burt, 1982) and review articles by Burt 1972a and b, 1974, 1977) Shimazaki, (1980), Einaudi et al. (1981), and Einaudi and Burt (1982). Skarn deposits are generally classified on the basis of dominant economic metal (Einaudi and Burt, 1982). Einaudi and Burt, (1982) distinguish five categories: i) Fe, ii) W, iii) Cu, iv) Zn-Pb, and v) Sn, while Meinert et al. (2005) identified seven categories, adding molybdenum and gold skarns. The latter is distinguished from the copper-gold skarns by high grades (5 to 15 g/t Au), a detrital limestone host, and especially by a link with reduced dioritic and granodioritic magmas.

Chemical analysis by electron microprobe of pyroxenes from marbles and skarns El Mostadi (1992) indicate a salitic to ferrosilitic composition, while those of garnets indicate a dominance of the grossular pole, with an evolution between the early stage IA to the stage IB.

The comparison of garnets and pyroxene from Frag Al Ma, with the data of (Einaudi et al., 1981; Einaudi, 1982 and references therein), Comparison of the garnet and pyroxene from Frag Al Ma, with the data of (Einaudi, 1982 and references therein), shows the garnet indicates Sn skarns and the pyroxene suggests W skarns, Fe skarns and Zn-Pb skarns, this evolution could be interpreted as an evolution in the field continuum from Sn skarn to W skarn to (Zn-Pb). This corroborates with the mineralogical observations in this study. They would be skarns belonging to both classes 2, 4 and 5 of Einaudi and Burt (1982). Therefore, they would have formed in a reduced environment, in relation to large batholiths or stocks of quartz diorites and/or granites in syn, late- to post-orogenic to anorogenic contexts, in the absence of any cogenetic volcanism.

7. Conclusions

The Sidi Bou Othmane skarns are enclosed in a schistose series of Upper Devonian age. They are marked by the presence of two types of mineralizations which are formed under different conditions and according to successive stages. The presence of contact metamorphism has transformed the marbles.

In skarns, as a result of metasomatic exchanges that result in the circulation of acid fluids between the granitic intrusion and the underlying carbonate host, the skarnification took place in three distinct phases:

- The prograde phase corresponds to the formation of calcium silicate minerals and the formation of graphite. During this phase, the environment is very reductive, within which the formation of calcium silicates and graphite is in equilibrium. This corroborates with previous work of El Mostadi (1992). The latter indicates that the pyroxene has the composition of salite-ferrosalite and that the garnet has essentially the composition of grossular.
- The retrograde phase corresponds to a stage of retromorphosis of the first phase minerals with the formation of scheelite and cassiterite in an environment that has become more oxidizing. It is accompanied by the disappearance of graphite.
The alteration phase: the skarns underwent hydrothermalism that paved the way for the oxidation of pyrite and chalcopyrite sulfides into covellite, hematite and magnetite, and the formation of sericite and clays. Scheelite is more abundant during this phase.

- The mineralized skarns of the Sidi Bou Othmane area are characterized by the dominance of grossular garnet and the scarcity of wollastonite, with the high economic concentration of graphite (estimated reserves of 525000 tons), with presence of cassiterite and scheelite. This potential is not exhaustive, moreover, the geophysical prospection in progress highlighted other resources in the course of valorization.

Acknowledgements

The authors would like to thank the reviewers and the editor for comments that greatly improved the manuscript.

References


