

METASOMATIC ZONING, MINERALIZATIONS AND GENESIS OF Cu, Zn AND Mo AZEGOUR SKARNS (WESTERN HIGH ATLAS, MOROCCO)

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Abstract: The Cu, Zn, Mo and W deposit of Azegour is located on the north side of the western High Atlas. Deposition of mineralizations is associated to the hydrothermal transformations that affected carbonated bars of the Palaeozoic series during the intrusion of the calc-alkaline hyperaluminous granite of Azegour. The type of the hydrothermal transformations recorded in the carbonated bars is controlled by the lithological nature of the protolith and is closely confined with the volcanic and volcanoclastic levels. At least five paragenetic stages of skarn formation and ore deposition have been recognized: Stage I: clinopyroxene; stage II: wollastonite ± vesuvianite; stage III: garnet; stage IV: quartz ± potassium feldspar ± calcite ± sulphides ± molybdenite ± cassiterite ± scheelite ± fluorite ± accessory minerals (apatite, zircon, sphene) and stage V: amphibole ± calcite ± chlorite ± muscovite ± epidote ± sulphides. Two mineralizations stages can be distinguished. The first stage essentially of sulphides and sulfoarsenides (Cu, Pb, Zn, As and Ag) was mainly observed in volcanic and volcanoclastic rocks in contact with the dolomitic marble. These mineralizations are previous to the metamorphic and structural events having affected the Azegour area. The second stage of mineralization (Mo, W and Sn) observed in the skarnified marble of granitic metamorphic aureole is associated to a hydrothermal metamorphism produced by an acidic fluid arising from the granitic pluton. The temperature deposition of mineralization during the ultimate prograde stage is lower than that required for the grenatites formation which approaches 640°C.

Keywords: skarn, mineralization, metasomatic, Azegour, High-Atlas, Morocco, Cu, Zn, Mo and W deposit.

1. INTRODUCTION

The skarn deposits of Azegour belong to the pyrometasomatic metallogenic province linked with the Hercynian granites of Morocco. It was exploited for the first time, in 1921, for copper and thereafter for molybdenum between 1930 and 1946 with an annual average of 200t/j of concentrate with 85% of MoS₂. The reserves were estimated at 1.4 to 1.5 ore Mt with 0.2 to 0.7% MoS₂, 2 Mt of ore with 0.4% WO₃ and 1 Mt of ore with 1.4 to 2.8% Cu. The exploitation works ceased in 1972 but the increases of metal courses in these last years contributed to undertake researches on the site in the perspective of the next reopening of the mine.

Excepted the Permingeat (1957) works that allowed to characterize the geological formations enclosing the skarns of Azegour and the hydrothermal transformations associated, all other

recent works are focused on the geochemical and geodynamic signature of the plutonic and volcanic magmatism of the sector (Charlot et al., 1967, El Amrani, 1987; Ait Ayad et al., (2000); Mrini et al., 1992 and Amenzou & Badra, 1996).

This paper provides a characterization of the various hydrothermal stages contributing to the formation of the Azegour skarns with the aim of tracing the spatiotemporal evolution of these transformations and the associated mineralizations.

2. GEOLOGICAL SETTING

The skarn deposit of Azegour belongs to the paleozoic block in the north side of the western High Atlas. It is located about 60 km in the SW of Marrakesh city and about 20 km in the SW of the Amizmiz village (Fig. 1).

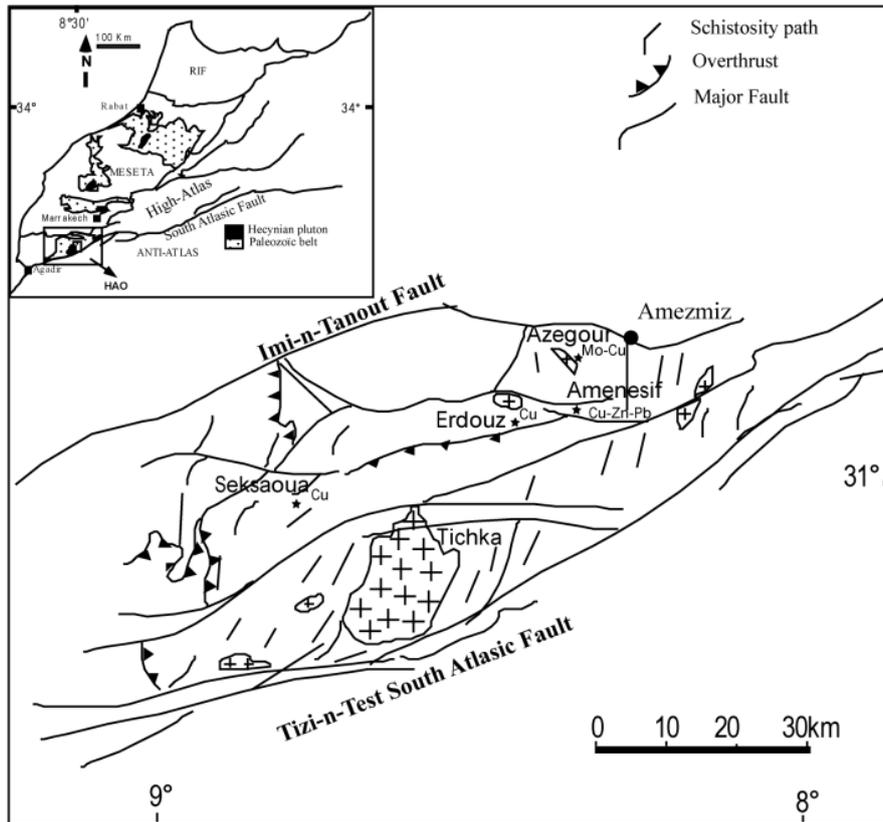


Figure 1. Structural outline of western high-Atlas and studied area localisation.

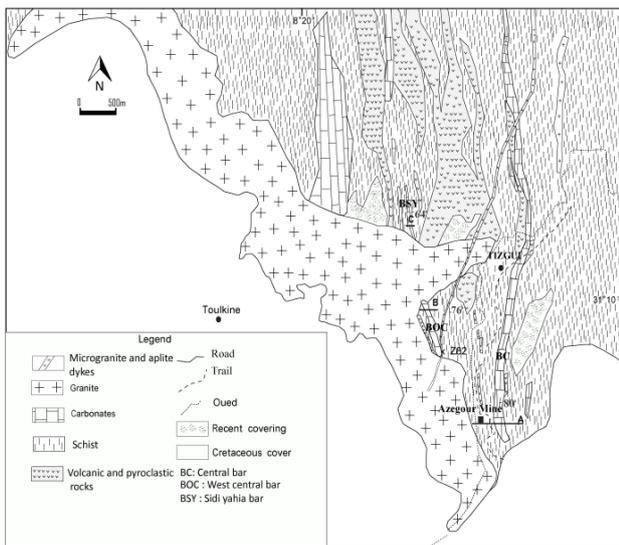


Figure 2. Geological map simplified of the studied area (after Permingeat, 1957, modified).

The regional geology is marked by a lower paleozoic volcano-sedimentary series which are unconformably overlain by the Cretaceous-tertiary sub-atlasic series. The paleozoic series are intruded by tardi-Hercynian granites represented mainly by the Tichka and the Azegour ones. The mine of Azegour is developed in the metamorphic aureole of the granite in the SE of the intrusion (Fig. 2).

2.1. Volcano-sedimentary series

The lower Cambrian lithostratigraphic series begins with a thick (approximately 40 m) lava flow and of pyroclastites, covered by a gresio-pelitic series (120 m) with interbedded volcanic and pyroclastic rocks, overlain by limestone bars and lenses (70 m) inter-layered with thin pelitic, volcanic and pyroclastic bands or lenses, then covered by an andesitic flow (50 m) inter-layered with pelitic and volcanic lies. The middle Cambrian is essentially composed of sandstone and pelite (Permingeat, 1957; and Badra et al. 1992). This lithostratigraphic succession is very similar to that of the nearby mining areas of Amensif and Tighardine where similar hydrothermal transformations to those of Azegour were described.

2.2. Igneous rocks

The volcanic activity in the area of Azegour is essentially represented by lava flows of plurimetric thickness. It begins with dark fine basaltic rocks of microlithic aphanitic or porphyric texture with phenocrysts of plagioclase and ferro-magnesian, generally retromorphosed. Relatively acidic rocks of andesitic and dacitic type with phenocrysts of quartz and alkaline feldspar can be occurring.

These lavas were classified by Ouazzani et al., (1998) in three types: 1) back arc basins basalts

depleted in the most incompatible elements; 2) andesites weakly to moderately enrich in incompatible elements and 3) dacites resulting from the differentiation of andesites.

This magmatic activity is linked to a volcanic arc context, previously to the Cambrian extension. The analyses realised in this work (Table 1) are rather in favour of a continental intra-plate tholeiite widely described in the lower Moroccan Cambrian (Badra et al., 1992, Piqué et al., 1995; Ouali et al., 2000).

The pink granite of Azegour outcrops on a band, directed NW-SE, of about 7 km long and 1 km

wide. It shows a constant mineralogical composition formed by quartz (40%), perthitic orthose and microcline (43%), acidic plagioclase type of albite-oligoclase (16%) and of biotite often chloritized (1%). Accessories are the apatite, the sphene, the zircon and the iron oxides. From a chemical point of view, it is a potassic alkaline hyperaluminous granite ($1.18 < A/CNK < 1.269$; [A/CNK is the molar ratio $Al_2O_3 / (CaO + Na_2O + K_2O)$]) showing a rather constant chemical composition (77% SiO₂, 5% K₂O, 2,5% Na₂O, CaO<0.5%, MgO<0.1% and Fe₂O₃* <1.2%).

Table 1. Chemical analyses of granitoids and volcanic rocks from Azegour

| Sample | Z61 | Z95 | Z90 | Z86 | Z87 | Z99 | Z88 | Z89 | Z92 | Z82 | Z100 |
|--------------------------------|---------|----------|--------|---------|---------|---------|--------|--------|--------|--------|-----------|
| Type | basalte | andesite | dacite | granite | granite | granite | aplite | aplite | aplite | aplite | pegmatite |
| SiO ₂ | 40,19 | 45,67 | 61,97 | 78,28 | 76,49 | 77,11 | 77,35 | 76,93 | 78,01 | 76,59 | 77,41 |
| TiO ₂ | 2,59 | 1,69 | 0,72 | 0,09 | 0,08 | 0,11 | 0,07 | 0,14 | 0,09 | 0,11 | 0,08 |
| Al ₂ O ₃ | 17,77 | 15,93 | 15,11 | 11,51 | 11,79 | 12,32 | 12,34 | 12,13 | 12,50 | 12,28 | 12,74 |
| Fe ₂ O ₃ | 13,44 | 9,79 | 4,94 | 0,33 | 1,19 | 0,55 | 0,76 | 0,22 | 0,66 | 0,63 | 0,85 |
| MnO | 0,15 | 0,12 | 0,08 | 0,01 | 0,07 | 0,01 | 0,02 | 0,01 | 0,03 | 0,02 | 0,01 |
| CaO | 8,22 | 12,03 | 4,15 | 0,27 | 0,24 | 0,30 | 0,34 | 0,37 | 0,27 | 0,69 | 0,34 |
| MgO | 8,28 | 7,34 | 1,84 | 0,04 | 0,07 | 0,09 | 0,06 | 0,07 | 0,03 | 0,11 | 0,07 |
| Na ₂ O | 1,19 | 2,60 | 2,10 | 2,48 | 2,12 | 2,52 | 2,65 | 2,57 | 2,47 | 2,42 | 3,01 |
| K ₂ O | 4,05 | 1,19 | 3,39 | 4,75 | 5,74 | 5,18 | 5,15 | 4,86 | 4,91 | 5,21 | 4,53 |
| P ₂ O ₅ | 0,42 | 0,18 | 0,28 | 0,01 | 0,01 | 0,01 | 0,01 | 0,01 | 0,02 | 0,01 | 0,01 |
| LOI | 2,10 | 1,20 | 5,36 | 0,44 | 0,68 | 0,54 | 0,56 | 0,48 | 0,87 | 0,41 | 0,48 |
| Total | 95,88 | 96,36 | 94,30 | 97,75 | 97,79 | 98,19 | 98,73 | 97,31 | 98,96 | 98,05 | 99,04 |
| A/CNK | 0,84 | 0,59 | 1,04 | 1,19 | 1,16 | 1,20 | 1,17 | 1,19 | 1,27 | 1,13 | 1,22 |
| Ni | 135,40 | 69,20 | 9,23 | 4,52 | 5,71 | 5,04 | 5,64 | 5,76 | 4,85 | 5,20 | 7,09 |
| Cu | 34,40 | 17,96 | 22,70 | 14,06 | 15,26 | 5,24 | 30,66 | 4,14 | 102,60 | 18,53 | 6,29 |
| Zn | 171,10 | 144,70 | 93,10 | 9,03 | 121,90 | 13,50 | 18,70 | 14,60 | 263,50 | 72,80 | 12,74 |
| Sc | 32,12 | 26,59 | 8,37 | 2,38 | 2,30 | 1,73 | 4,91 | 1,38 | 1,93 | 1,62 | 2,56 |
| Ga | 26,00 | 16,60 | 20,10 | 18,00 | 18,80 | 18,30 | 27,60 | 16,60 | 20,30 | 19,90 | 26,40 |
| Rb | 195,40 | 25,30 | 95,30 | 198,90 | 212,80 | 194,90 | 210,00 | 180,10 | 182,10 | 134,40 | 201,20 |
| Sr | 990,70 | 318,30 | 164,10 | 21,60 | 24,20 | 38,90 | 19,00 | 44,70 | 22,40 | 35,50 | 17,40 |
| Li | 186,10 | 45,99 | 67,07 | 8,29 | 10,01 | 11,79 | 5,83 | 16,36 | 5,67 | 25,77 | 15,70 |
| Y | 33,14 | 23,59 | 24,98 | 5,24 | 10,56 | 8,93 | 11,19 | 9,31 | 9,07 | 20,07 | 9,00 |
| Zr | 286,70 | 144,10 | 330,40 | 65,20 | 68,40 | 78,80 | 75,70 | 121,00 | 81,00 | 94,50 | 87,20 |
| Nb | 12,91 | 5,06 | 14,90 | 23,20 | 25,10 | 19,10 | 71,40 | 17,90 | 24,80 | 30,10 | 34,60 |
| Pb | 18,60 | 42,10 | 9,70 | 8,20 | 106,70 | 8,10 | 27,90 | 19,90 | 118,50 | 47,30 | 13,00 |
| Th | 4,11 | 1,69 | 9,17 | 27,37 | 32,78 | 23,52 | 20,21 | 32,10 | 34,30 | 37,74 | 29,20 |
| U | 0,00 | 0,20 | 2,40 | 5,20 | 3,80 | 3,20 | 9,30 | 6,10 | 8,60 | 13,80 | 7,10 |
| Ba | 1294,00 | 180,20 | 958,00 | 165,70 | 484,00 | 224,80 | 307,90 | 289,80 | 160,10 | 178,40 | 98,52 |
| Co | 20,77 | 22,21 | 7,57 | 0,00 | 0,63 | 0,13 | 0,08 | 0,00 | 1,80 | 1,98 | 1,47 |
| Cr | 227,50 | 115,80 | 16,00 | 2,00 | 2,56 | 2,86 | 3,50 | 4,93 | 2,25 | 5,22 | 7,16 |
| V | 273,10 | 185,20 | 63,38 | 1,04 | 6,10 | 3,57 | 3,05 | 2,45 | 3,17 | 3,56 | 2,45 |
| La | 27,85 | 7,07 | 42,89 | 14,51 | 25,58 | 23,64 | 19,54 | 17,83 | 14,46 | 32,50 | 16,88 |
| Ce | 72,64 | 22,65 | 82,45 | 28,86 | 38,88 | 41,08 | 37,46 | 35,53 | 28,40 | 60,43 | 26,47 |
| Eu | 3,06 | 1,88 | 1,53 | 0,03 | 0,22 | 0,14 | 0,02 | 0,28 | 0,02 | 0,21 | 0,02 |
| Nd | 39,14 | 10,82 | 34,46 | 2,65 | 9,28 | 8,51 | 4,84 | 7,47 | 4,07 | 15,45 | 4,37 |
| Yb | 3,41 | 2,67 | 2,70 | 1,05 | 1,96 | 1,79 | 2,48 | 1,76 | 2,01 | 3,02 | 2,69 |
| Nb/Y | 0,39 | 0,21 | 0,60 | 4,43 | 2,38 | 2,14 | 6,38 | 1,92 | 2,73 | 1,50 | 3,85 |
| La/Yb | 8,17 | 2,65 | 15,88 | 13,87 | 13,06 | 13,18 | 7,88 | 10,11 | 7,19 | 10,75 | 6,27 |

It is affiliated to calc-alkaline orogenic granites according to the diagrams of Pearce et al., (1984) and Thiéblemont & Cabanis (1990) (Fig. 3 and Table 1). These results are in accordance with the previous geochemical studies (El Amrani, 1987 and Mrini et al., 1992) and with the typological studies of zircon (Amenzou & Badra, 1996).

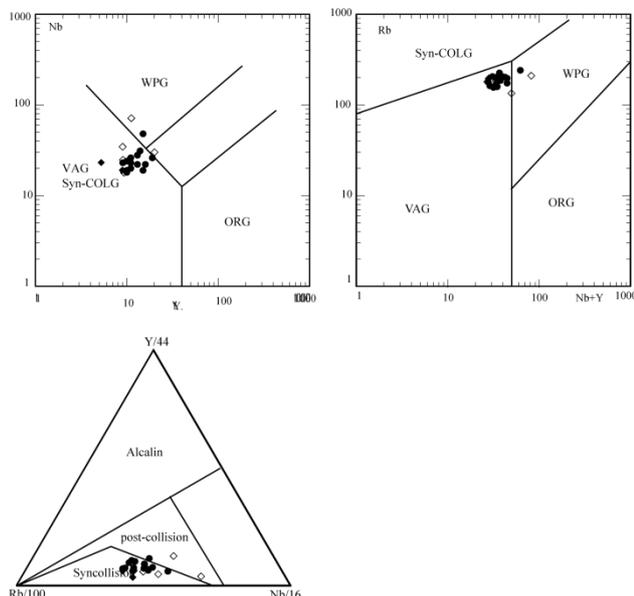


Figure 3. Distribution of Azegour granites in Nb vs Y and Rb vs Nb+Y diagram's from Pearce et al., (1984) and (Rb/100) vs (Y/44)-(Nb/16) diagram's from Thiéblemont and Cabanis (1990). ORG: Oceanic Ridge Granite; VAG: Volcanic Arc Granite; WPG: Within Plate Granite and SynCOLG: Syn-collision granite. Filled diamond: granite, empty diamond: aplite and microgranite and filled circle: granite analysed from Ait Ayad et al., (2000).

The peraluminous character of the granite, its strong content in silica, the ratio $K_2O / Na_2O > 1$, its modal and normative composition (muscovite and ilmenite) suggest a crustal origin (S-type granite) according to the classification of Chappell & White (1974) and Raymond (1995). The same affinity can be shown on the variations diagrams of the figure 4 where the Azegour granites plot in or close to the field of molybdenum granites defined by (Chowdhury & Lentz, 2011).

The granite intrusion is controlled by the Hercynian lithospheric faulting (Lagarde et al., 1990). According to Ait Ayad et al., (2000), the granite is intruded in a tension fracture related to dextral shear Hercynian movements along N70°E direction. The Rb/Sr dating rock attributes a Permian age (271 ± 3 Ma) to this granite (Mrini et al., 1992).

The granite is accompanied with a dyke cortege including microgranites, pegmatites and aplites. The pegmatites, essentially of quartzo-feldspathic composition, also appear as decimetric pockets form in

the granite. The aplite veins are located inside the granite but also in the host schist and sandstone. The most important one extend over several tens meters (60 m approximately) in the SE of the granitic massif. This aplite has the peculiarity to be rich in sphene, allanite and zircon (sample Z82). From a chemical point of view, this aplite is particularly rich in Y, Th, U, La, Ce and Yb (Table 1).

2.3. Tectonic and metamorphism

The paleozoic series of Azegour records two Hercynian phases of deformation (Ait Ayad et al., 2000). A first submeridian deformation phase, predating the granite intrusion, and correspond to the Hercynian major event known in the Moroccan paleozoic massifs. A second phase, post-granite intrusion, is marked by folds N140°E and shear senestral N70°E.

A thermal metamorphism related to the granite intrusion, overlaps the general metamorphism of low grade which affects the paleozoic series of Azegour. The thermal metamorphism develops a metamorphic aureole of about 1.5 km in the host rocks (Permingeat, 1957). It appears in the schist by the formation of cordierite spotted schist, cordierite-biotite knotted micaceous schist and sometimes andalousite and rare cordierite-biotite hornfels. The thermal metamorphism induces recrystallization of carbonate to variant degree (cipolin) with dolomite always as major phase and diopside, humite, green spinelle and occasionally scapolite. Other minerals present are quartz, muscovite, and a rare ilmenite, and pyrite. Hydrothermal transformations (skarnification) overlap this purely thermal early stage and lead to the formation of pyroxenites, wollastonites, grenatites, accompanied with Cu, Zn, Mo and W mineralizations.

3. SKARN MINERALOGY AND PARAGENESIS

The Cambrian series at Azegour contains four main lens-shaped carbonated bars with variable size, distributed east westward as follows: the central bar which has been the object of old exploitation for copper and molybdenum, the western central bar, the bar of sidi Yahia and that of Toulkine situated further west. The present work carries on the central bar, western central bar and that of Sidi Yahia which record the maximum of hydrothermal transformations.

In detail, the studied carbonated bars show a heterogeneous composition going from pure dolomite, with a few clastes of quartz, to the dolomites with pelitic, volcanic and pyroclastic

fractions. These latter appear as millimetric to centimetric lenses interstratified within the dolomites or as centimetric to decimetric beds inter-layered within the dolomites. The type of the hydrothermales transformations recorded in the carbonated bars is controlled by the lithologic nature of the protolith and is closely confined with the volcanic and volcanoclastic levels (Fig. 4, A, B, and D).

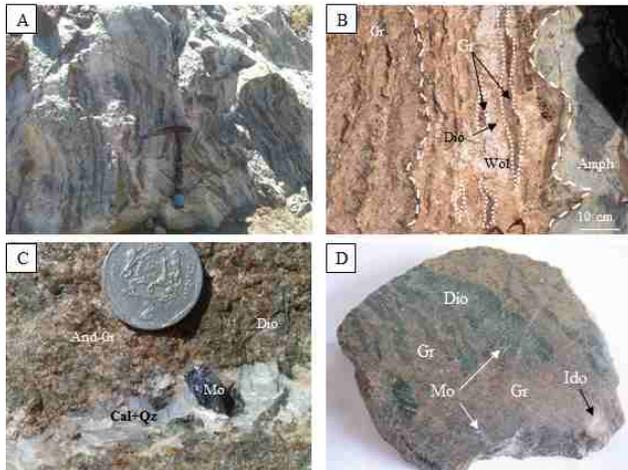


Figure 4. Macroscopic texture example of Azegour skarns: A: banded marble not transformed; B example of transformation in the contact of volcanic rocks. To note the clear zone reaction to the contact of dark volcanic rock; the grossular with relics of wollastonite and diopside; C: quartz, calcite, molybdenite vein recutting the grandite with relics of diopside; D: banded diopside and grossular skarn. Note the molybdenite disseminated in grossular. Gr: grossular, Dio: diopside, Wol: wollastonite, Amph: volcanic rock, Grd: grandite (mixed andradite-grossular garnet), Mo: molybdenite, Cal: calcite and Qz: quartz.

Petrographical and mineralogical textures allow recognizing at least five hydrothermal stages. Early minerals are largely anhydrous, whereas later ones are predominantly hydrous:

Stage I: clinopyroxene

Stage II: wollastonite ± vesuvianite

Stage III: garnet

Stage IV: quartz ± potassium feldspar ± calcite ± sulphides ± molybdenite ± cassiterite ± scheelite ± fluorine ± accessory minerals (apatite, zircon, titanite)

Stage V: amphibole ± calcite ± chlorite ± muscovite ± epidote ± sulphides.

The textural feature also indicates that later hydrous minerals have developed largely by pervasive and diffusive replacement of prograde earlier minerals and to a minor extent by filling vugs, veins and fissures.

These transformations draw a well-defined zoning which repeats at the level of every skarnified bar or carbonated lens. So, from granite (proximal

zone) towards the host (distal zone), we describe: pyroxenites → Wollastonite ± vesuvianite → Grenatite → Quartz ± potassium feldspar ± mineralizations. To these prograde transformations can succeed retrograde transformations inducing the formation of amphibole, epidote and chlorite.

Paragenetic studies based on macro- and micro-textures show that skarn at Azegour follows the prediction of metasomatic zoning theory according to Korzhinsky (1970) and reflects changes in fluid dynamics (diffusion vs. advection), fluid chemistry (pH), P, T and host rock composition. These transformations are similar to those described in other W, Sn and/or Mo skarn type in Morocco (Aissa et al., 1995), in Romania (Ciobanu & Cook, 2004), in USA (Gaspar et al., 2008) and in Australia (Singoyi & Zaw, 2000).

A comprehensive description of the skarn mineral paragenesis is given below and the paragenetic stages are listed in table 2.

Table 2. Paragenetic relationships of Azegour skarns. Evidence used for the paragenetic relation includes micro textural and macro textural data.

| Mineral | Stage | | | | | |
|---------------|-------|---|----|-----|----|---|
| | 0 | I | II | III | IV | V |
| Humite | | — | | | | |
| Amphibole | | — | | | | — |
| Spinel | | — | | | | |
| Clinopyroxene | — | | | | | |
| Wollastonite | | | — | — | | |
| Vesuvianite | | | — | — | — | |
| Grossulaire | | | — | — | | |
| Andradite | | | — | — | | |
| Grandite | | | | — | — | — |
| Quartz | | | | — | — | — |
| K-feldspar | | | | — | — | — |
| Apatite | | | | | — | — |
| Zirconolite | | | | | — | — |
| Amphibole | | | | | | — |
| Calcite | | | | | | — |
| Chlorite | | | | | | — |
| epidote | | | | | | — |
| Molybdenite | | | | | — | — |
| Chalcopyrite | — | — | | | — | — |
| Scheelite | | | | | — | — |
| Cassiterite | | | | | — | — |
| Fluorite | | | | | — | — |
| Pyrite | — | — | | | — | — |
| Sphalerite | — | — | | | — | — |
| Arsenopyrite | | | | | — | — |
| Galena | — | — | | | — | — |
| Grey copper | | | | | | — |
| Silver | | | | | | — |
| Marcasite | | | | | | — |
| Magnetite | | | | | | — |
| hematite | | | | | | — |

3.1. Clinopyroxenites

The clinopyroxenites at Azegour skarn are of diopside and hedenbergite type with few intermediate terms. The diopside is green to pale green color and is more widespread than the dark green hedenbergite (Fig. 4 C and D).

The grain size of clinopyroxene is constant in the same sample but variable from one sample to another. The average crystals size is about 0.1 to 1 mm across but some clinopyroxene may be up to 4 mm long. The clinopyroxene grains commonly occur as shattered short prismatic or anhedral crystals and may exhibit granoblastic textures. They form a rhythmic banded textures of 0.5 to 5 cm strength parallel to the host bending rock. The contact is diffuse and progressive with the healthy marble on one side and with the wollastonite and/or the garnet on the other side (Fig. 5 C). Clinopyroxenite often contains isolated crystals of garnet that display corroded edges. The fine-grained clinopyroxene may be found as relict inclusions in later mineral phases, such as vesuvianite, wollastonite and garnet. The clinopyroxene may be partially or completely altered to actinote and/or hornblende, chlorite, calcite, quartz and iron oxydes.

The clinopyroxenite stage is not generally accompanied with mineralization except for some transected later cracks and veins of pyrite, chalcopryite and iron oxides.

3.2. Wollastonite

Wollastonites appears as white bands or lenses of centimetric to a few meters thick (2 m). Crystals with lamellar intergrowth can reach 3 cm in size. The wollastonite is associated with the brown vesuvianite, without corroded rims, with variable proportions. It develops on the clinopyroxene which can be reduced to small microscopic crystals relicts within wollastonite (Fig. 4 B and 5 B). We have never observed a wollastonite developing directly on the marble. The contact between garnets and wollastonites is diffuse and progressive and garnets as isolated crystals or polycrystalline clusters can appear within wollastonites (Fig. 4).

From a chemical point of view, the wollastonite is pure with some traces of Mn and Fe. The retrograde event stage induces the transformation of the wollastonite to calcite + quartz or clayey products.

3.3. Vesuvianite

The vesuvianite is less abundant than the wollastonite. It appears as brownish individual crystals

with less than millimeter in size, associated or not to the wollastonite (Fig. 5 B and D). It develops directly on the marble or on the clinopyroxenite. In this last case relict inclusions of diopside are observed there.

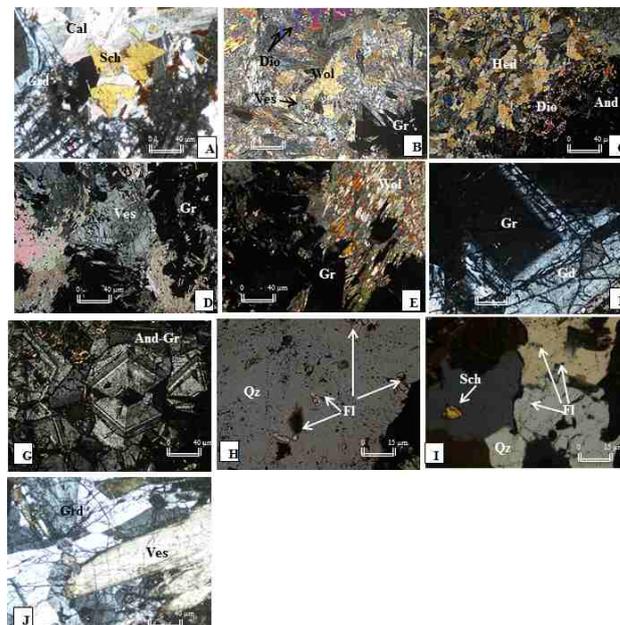


Figure 5. Some images of hydrothermal stage from Azegour skarns. A: scheelite with calcite in geode of grandite; B: grossular developing on wollastonite and vesuvianite with relicts of diopside; C: grossular developing on diopside; D: grossular developing on marble with vesuvianite; E: grossular developing on wollastonite; F: garnet with grossular core and grandite border; G: zoning and twins in grandite; H: fluorite associated with quartz; I: fluorite and scheelite in quartz and J: association vesuvianite-grandite. Sch: scheelite, Cal: calcite, Dio: diopside, Hed: Hedenbergite, Wol: wollastonite, Ves: vesuvianite, Gr: grossular, And: andradite, Grd: grandite (mixte anisotropic andradite-grossular garnet), Fl: fluorite.

Another vesuvianite variety, relatively iron rich than the previous one, green colour was observed. It is euhedral lamellar shape, centimetric size and have a sharpe contours with the garnet which seems precocious than this vesuvianite (Fig. 5 J).

The development of the wollastonite \pm vesuvianite stage seems controlled by the lithological nature of the protolith. Indeed, in the more or less pure calcic marble, this stage is very developed. On the other hand, in the impure marble (with pelitic fraction), garnates develops directly on clinopyroxenites or on marble without intermediate stage of wollastonite \pm vesuvianite.

3.4. Grenatites

The garnatite facies are widespread and represent the major period of skarn formation and ore deposition at Azegour. It forms bands which can

reach 3 m strength and an extension of about ten meters. They form dense geodic rocks filled with quartz and calcite (Fig. 4 C). Crystals can be centimeteric in size and are generally idiomorphous forming very characteristic coarse-grained rocks. Grenatites commonly replaces early clinopyroxenes, wollastonites and/or vesuvianite (Fig. 5 B, C, D, E). There is no sharpe front between the transformations but a mixed zones where isolated garnets grain grow on clinopyroxenes, wollastonite and/or vesuvianite. The crystal size of garnets grows gradually towards grenatites. Grenatites is always found at the distal side of the transformations. However, this zonality (clinopyroxenites → wollastonite ± vesuvianite → Grenatite) can sometimes repeat on both sides of the grenatite.

According to the color and to the chemical composition, estimated from the MEB, three types of garnets can be distinguished:

- 1- isotropic brown to orange garnet of grossular type;
- 2- isotropic dark green garnet of andradite type;
- 3- anisotropic yellowish green grandite garnet of intermediate composition between garnets 1 and 2; this garnet can be polysynthetic twinning with development of lamellae perpendicular to crystal face of the crystal and show characteristic oscillatory zoning (Fig. 5 G).

The compositions of garnets 1 and 2 often evolve towards the garnet 3 forming a characteristic isotropic and euhedral cores with sharp contacts to later anisotropic overgrowths (Fig. 5 F). In the grandite garnets 3, the border of the crystal is more anisotropic than the core. Similar garnets to garnets 3 were described and interpreted as a simply crystal growth features (Akizuki, 1984); a modifications of preexisting garnets as a result of externally induced local strain (Ciobanu & Cook, 2004) either as early retrograde shock-induced features related to high fluid pressure; changes in fluid pressure can lead to chemical disequilibrium (Ciobanu & Cook, 2004).

At Azegour area, we notice that the grossular (garnet1) prevails in the distal zone, the andradite in the proximal zone particularly in skarns developed in the immediate contact of the granite in the West central carbonated bar. In the intermediate zone we sometimes find the andradite, sometimes the grossular. Also we note that the iron rich vesuvianite is associated only with the grandite garnet (garnet 3).

The development of the garnet directly on clinopyroxenes or on wollastonite involves mobility of the alumina at least on a local scale.

3.5. Quartz and K-feldspar

It represents the ultimate prograde stage where the quartz associated or not to K-feldspar fills geodic spaces in garnets. They can also appear as transected later cracks or anastomosed veins in the garnets (Photo C, Fig. 5). This stage is particularly developed nearby the contact of the granite intrusion. The quartz ± K-feldspar stage is associated with the Mo, Cu, F, W, Sn, Zn and Pb mineralizations deposit. The holders minerals (molybdenite, chalcopyrite, fluorite, scheelite, cassiterite, sphalerite and galena) are commonly associated or even in inclusion in the quartz (Fig. 5 H and I).

Other rare minerals, of variable distribution, like native silver, grey copper, apatite, sphene and zirconolite are also associated to this ultimate stage.

4. ORE DEPOSIT

In the Azegour area, the economic mineralizations are represented mainly by local concentration of chalcopyrite and molybdenite associated with scheelite, sphalerite, galena and pyrite. Trace minerals were also observed. It's about grey copper and silver. Some bismuth, uranium and beryllium minerals were also described by Permingeat (1957).

The skarn mineralizations occur as irregularly shaped clusters, pods or thin lenticular bands following compositional banding. They are most often linked to grenatites. The present works show that these ore lenses are often associated with metasomatized carbonate and the associated volcanic and volcanoclastic rocks. The textural relationships between mineralization and hydrothermal stages suggest a late emplacement of mineralization relative to the garnet stage.

Molybdenite occurs as isolated or grouped lamellas, often twinned and kinked (Photo A, Fig. 6). In all the samples observed, molybdenite appears alone or sometimes associated with iron oxides and hydroxides. Very rarely, fibrous molybdenite is associated with pyrite and chalcopyrite (Fig. 6 B, C and D). In some skarn samples, molybdenite occurs as fine fibers associated with quartz and calcite, plugging cracks and fractures affecting garnets and vesuvianite. Molybdenite is always observed in association with vesuvianite and grenatites. In volcanic and volcanoclastic rocks molybdenite was rarely observed.

Chalcopyrite represents the second phase after molybdenite in term of abundance. It occurs as isolated crystals or as fine blebs or ribbon occupying molybdenite cleavage (Fig. 6 B). These

micrometric to millimetric crystals and ribbons of chalcopyrite most often overlap clinopyroxenites, vesuvianite and grenatites. Locally, chalcopyrite is present as large flies associated with quartz-feldspar and / or calcite and / or chlorite. Most often, chalcopyrite occupies with quartz and calcite geodic spaces in garnets (Photo D, Fig. 6 D). Locally, chalcopyrite with pyrite form thin ribbons parallel to grenatites layers, reflecting the importance of late remobilization related to regional deformation. The most important concentration of chalcopyrite appears in tuffaceous and volcanic rocks. In these rocks, chalcopyrite appears as millimetric to centimetric bands sometimes containing fine droplets (10-20 microns) of grey copper locally associated with native silver. Locally, chalcopyrite holds some sphalerite inclusions (20-150 microns).

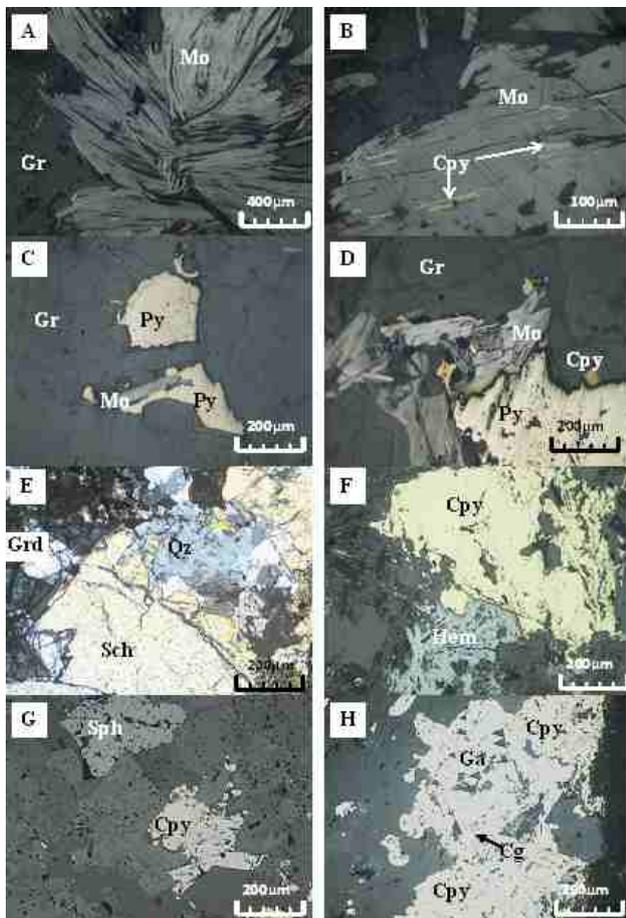


Figure 6. Some images of Azegour mineralization. A: lamellar masses of molybdenite (Mo) in geodes of grossular (Gr); B: Chalcopyrite (Cpy) occupying cleavage plans of molybdenite (Mo); C: association pyrite (Py) – molybdenite (Mo) in geodes of grossular garnet (Gr); D: Pyrite-chalcopyrite-molybdenite in grossular; (E) Association scheelite (Sch)-quartz (Qz) in grandite garnet (Grd); (F) Hematite (Hem) developing on Chalcopyrite (Cpy); (G et H) Polymetallic Mineralization (sphalerite (Sph)-chalcopyrite (Cpy)-galena (Ga)-grey copper (Cg) and silver) disseminated in volcanic facies.

Scheelite has been observed as isolated crystals or grouped masses. Its size sometimes exceeds the millimeter. In some samples scheelite occurs as, anhedral to euhedral isolated crystals or grouped masses screening the grandite garnet. It is most often isolated or associated with late quartz and calcite (Fig. 5 A and I and Fig. 6 E). Generally, scheelite characterizes the quartz stage. The presence of scheelite in association with this type of garnet is in accordance with Zharikov (1970) and Shimazaki (1977) works.

Fluorite appears as micrometric individual euhedral crystals, sometimes associated to scheelite. Generally fluorite is included in quartz (Fig. 5 H and I).

Cassiterite was rarely observed as anhedral crystals, locally cracked and fractured. It is generally associated with quartz and zirconolite in grenatites.

Pyrite is ubiquitous in the skarnified carbonate and associated volcanic and volcanoclastic rocks. It appears as individual euhedral to subhedral crystals or as clusters in the groundmass. Pyrite crystals vary in size (20 microns to more than one millimeter) and exhibit a variety of textures reflecting a metamorphic growth. It is generally disseminated in rocks characterizing the metamorphic halo. These pyrites are often transformed into marcasite. Locally, pyrite is corroded by magnetite and hematite. In some samples, pyrite appears occupying with chalcopyrite the cleavage plans of molybdenite and / or the boundaries between molybdenite crystals (Fig. 6 C and D).

Sphalerite is moderately represented in Azegour deposit. It has been observed sporadically at the metamorphic halo. The largest concentrations of sphalerite were found in carbonated tuff adjacent to grenatites. These sphalerites occur most often in modest size ranges (50 to 300 microns) and are locally rich in exsolution of chalcopyrite (Photo G, Fig. 7). In some samples, sphalerites are usually crowned with chalcopyrite. Two generations of sphalerite, sometimes combined in a single sample, were identified: (i) iron-rich sphalerite with reddish internal reflections (ii) a second generation (low iron content) showing yellow to greenish-brown internal reflections.

Arsenopyrite is rarely observed. It is generally fine-grained (20 to 150 μm) and exhibits euhedral shape. The arsenopyrite grows on the sphalerite – chalcopyrite assemblage.

Galena is rare in the deposit comparatively to the other sulphides minerals. It was observed either as fine inclusions in sphalerite and either as large bands associated with chalcopyrite, grey copper and silver (Fig. 6 H).

Marcasite is represented by clusters and aggregates often intergrown with, or rimming, pyrite and chalcopyrite. Locally, pyrite and marcasite are altered to hematite, goethite and lepidocrocite.

5. SYNTHESIS AND CONCLUSIONS

The present work on the Azegour deposit enhances a typical mineralogical and metallogenic evolution of skarn-type deposits known and described worldwide (Tornos et al., (2000); Tornos et al., (2008); Singoyi & Zaw (2000); Meinert et al., (2005); Chowdhury & Lentz (2011); Liu et al., (2012) and Bo Wan et al., (2013). At the scale of Morocco, the Azegour skarn deposit is the only one which shows high concentrations of molybdenum and copper. Statistical studies of skarns worldwide (Bo Wan et al., 2013) indicate that this wealth of Mo and Cu is related to the calc-alkaline nature of the associated granites. Also, Azegour granite presents a peraluminous character with alumina saturation index similar to granitoids associated to Mo skarns. Granitoids associated with other types of skarns are rather intermediate between metaaluminous and peraluminous granites (Meinert, 1995).

Five hydrothermal stages have been recognized; four with prograde character whose ultimate mineralizing stage is quartz \pm feldspar. These prograde stages would be the consequence of deep circulation of hot fluids. According to Chowdhury & Lentz (2011), the presence of hedenbergite–diopside in the skarns indicates a temperature of about 500°C to 600°C. For Taylor & Liou (1978), the formation of wollastonite requires temperatures of 580 - 600°C. These temperatures are lower than those prevailing during the emplacement of the granite. According to Ait Ayad et al., (2000), Azegour granite is emplaced at pressures of 2 to 2.5 kbar corresponding to temperatures of 630-660°C, considering an average geotherm of 30°C/km.

The grossular assembly indicates low CO₂ concentrations (Le Anderson, 1981 and Deer et al., 1993). The reactions of hydrothermal transformations hedenbergite-wollastonite-garnet, described above, which we can materialize by the three reactions quartz + calcite = wollastonite + CO₂; hedenbergite + calcite + 1/O₂ = andradite + quartz + CO₂ and hedenbergite + wollastonite = andradite + quartz, indicate a temperature of about 640°C and a molar fraction X_{CO₂} ~ 0.3 (Taylor & Liou, 1978). These conditions correspond to the Azegour garnetites formation. The relatively high X_{CO₂} value is attributed to the presence of carbonates in the hydrothermal paragenesis of Azegour. The estimated temperatures (640°C) and magnetite-hematite association observed

in the Azegour skarn mineral assemblages suggest a condition of oxygen fugacity between -12.5 and -16 (Taylor & Liou, 1978).

According to Watanabe & Arima (1989), the formation of vesuvianite and other ferro-magnesium silicates would be conditioned by volatile linked to granitic magma. The formation of fluorite in Mo skarn is conditioned by a reduced environment (Meinert 1993 Meinert et al., 2005). In the Azegour area, the fluorite formation in the ultimate prograde stage with quartz \pm K feldspar, as well as the presence of some amount of F (detected by MEB) in vesuvianite are in favor of a rather high concentration in this element. This high content of F would have favored the formation of a late vesuvianite associated with the grandite.

The early skarn mineral which characterize prograde stage are entirely or partially replaced by later hydrated minerals such as epidote, amphibole \pm quartz, muscovite and chlorite which characterize the retrograde stage. These hydrous minerals are formed from lower temperature, low pH magmatic fluids or variable salinity (high to low) fluids (Singoyi & Zaw, 2000; Meinert et al., 2003). For Einaudi et al., (1981); Kwak (1987); Meinert (1993); Tornos et al., (2000); Singoyi & Zaw (2000) and Meinert et al., (2005), these minerals are the result of the inflow of cooler surficial waters that invade the hydrothermal system after the crystallization of the pluton.

In the Azegour deposit, many of skarnified and mineralized zones are centred on volcanic contacts, indicating that hydrothermal fluids flowed up along those contacts and subsequently out along faults, stratigraphic contacts, and zones of brecciation. The same association between volcanic-exhalative deposit and skarn has been described in the Altay mountains (southern China) by Liu et al., (2012).

In detail, the distribution of skarnified zones shows that the changes are very important in the immediate contact of the granite pluton (central western bar) and reflect the direct effect of the granitic intrusion, whereas moving eastward (middle bar), changes do not seem to be directly related to the granite. Indeed, the strongly metasomatized and skarnified zones appears in intact limestone bands. This implies that hydrothermal emanations causing these changes are related to fluid circulation driven by lithologic contacts and / or deep faults in relation with hidden apophyses.

The ore deposit of Azegour is characterized by two distinct paragenetic assemblages:

(i) A polymetallic assemblage with chalcopyrite, sphalerite, galena, grey copper, pyrite, arsenopyrite and native silver associated with quartz. This assemblage which characterizes mainly

volcanic and volcanoclastic facies, was also observed in a recrystallized carbonate without hydrothermal transformations. This leads us to conclude that this type of mineralization is independent with skarnification phenomena. The mineralogical and textural characteristics of this assemblage indicate that it appears to be widespread across the entire western High Atlas. It remembers especially those described in the areas around the Amensif and Tighardine deposits.

(ii) An assemblage with molybdenite, scheelite, cassiterite and fluorite associated with pyrite, chalcopyrite, magnetite and hematite in relation with skarnification caused by the emplacement of the granite.

The precipitation of scheelite in the terminal anhydrous prograde skarn stage with quartz \pm K-feldspar is similar to that described on the scheelite skarn of King Island (Kwak & Tan, 1981) and those of the southern Cordillera (Newberry & Einaudi, 1981). Petrographic and mineralogical investigations imply that the chemical environment favourable for scheelite deposition is limited to one in which ferrous iron-bearing grossular (grandite) is stable. Zharikov (1970) interpreted this to require acidic skarn-forming fluids, whereas Shimazaki (1977) suggested, instead, highly reduced environments characterized by oxidation states below the pyrrhotite–pyrite–magnetite buffer. According to Tornos et al., (2008), fluids would only precipitate scheelite and REE when reacting with the carbonatic rocks, which increased the pH and the $a\text{Ca}^{2+}/(a\text{H}^+)^2$.

As discussed above we can conclude that the precipitation of Azegour ore deposit can be divided in two distinct stages, separated in time and space. The first stage with sulphides and sulfarsenides (Cu, Pb, Zn, As, Ag) occurs mainly in volcanic and volcanoclastic rocks in contact with the dolomitic marbles. The mineralization appears precocious to structural and metamorphic events that affected the Azegour area. The local enrichment of copper, lead and zinc observed in volcanic and volcanoclastic rocks as well as intact marble, indicate the effect of local remobilization and reconcentration of preexisting mineralization in relation with metamorphism event. The second stage of mineralization with Mo, W, F and Sn observed in skarnified marble of granitic metamorphic aureole is related to a hydrothermal metamorphism produced by an acidic fluid arising from the granite pluton.

The scheelite-fluorite association supposes a reduced environment. The deposit of mineralization during quartz \pm K-feldspar ultimate prograde stage supposes a lower temperature conditions than that required for the formation of grenatites which

approaches 640°C.

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