

Article



Evolution of Ore-Forming Fluids at Azegour Mo-Cu-W Skarn Deposit, Western High Atlas, Morocco: Evidence from Mineral Chemistry and Fluid Inclusions

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Abstract: The Azegour Mo-Cu-W skarn deposit, located on the northern side of the Western High Atlas, occurs in lower Cambrian volcanic and sedimentary rocks. The mineralizations are linked to the hydrothermal alterations that affected carbonated layers of the lower Cambrian age during the intrusion of the calc-alkaline hyperaluminous Azegour granite. Four stages of the skarn and ore mineral deposition have been identified as follows. Firstly, (i) the early prograde stage and (ii) the late prograde stage. These prograde stages are characterized by anhydrous minerals (wollastonite, garnets, and pyroxenes) associated with scheelite mineralization. Based on mineral chemistry studies, the early prograde stage is dominated by andradite (Ad72.81-97.07) and diopside (Di_{61.80-50.08}) indicating an oxidized skarn; on the other hand, the late prograde stage is characterized by a high portion of grossular ($Gr_{66,88-93,72}$) and hedenbergite ($Hd_{50,49-86,73}$) with a small ratio of almandine (Alm_{2.84-34.99}), indicating "strongly reduced" or "moderately reduced" conditions with low $f(O_2)$. The next two stages are (iii) the early retrograde stage and (iv) the late retrograde stage, which contain hydrous minerals (vesuvianite, epidote, chlorite, muscovite, and amphibole) associated with sulfide. Fluid inclusions from pyroxene and quartz (prograde skarn stage) display high homogenization temperatures and high to low salinities (468.3 to >600 °C; 2.1 to >73.9 wt% NaCl equiv.). The boiling process formed major scheelite mineralization during prograde skarn development from dominated hydrothermal magmatic fluid solutions. By contrast, fluid inclusions associated with calcite-quartz-sulfide (retrograde skarn stage) record lower homogenization temperatures and low salinities (160 to 358 °C; 2.0 to 11.9 wt% NaCl equiv.). The distribution of the major inclusions types from the two paragenetic stages are along the trend line of fluids mixing in the salinity-homogenization temperature (magmatic water), illustrating the genesis of ore-forming fluid by mixing with fluids of low temperatures and salinities (metamorphic and meteoric waters).

Keywords: Azegour; skarn; petro-geochemistry; paragenetic stages; mineralization; fluid inclusions

1. Introduction

Skarn deposits are abundant, variable, and economically important. They are a principal global source of tungsten, a significant source of copper, and an important source of iron, molybdenum, zinc, and gold [1,2]. Typically, skarn deposits form through metasomatism processes at or near the contact zones between predominantly carbonate-rich rocks and magmatic intrusions or within carbonate veins along faults or fractures [3]. These deposits are commonly characterized by two distinct alteration stages defined by the sequential



Citation: El Khalile, A.; Aissa, M.; Touil, A.; Hibti, M.; Loudaoued, I.; Bilal, E. Evolution of Ore-Forming Fluids at Azegour Mo-Cu-W Skarn Deposit, Western High Atlas, Morocco: Evidence from Mineral Chemistry and Fluid Inclusions. *Minerals* **2023**, *13*, 1537. https:// doi.org/10.3390/min13121537

Academic Editor: Nuo Li

Received: 9 October 2023 Revised: 20 November 2023 Accepted: 7 December 2023 Published: 11 December 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). precipitation of calc-silicate minerals: (1) early prograde assemblage (wollastonite, garnet, and pyroxene) and (2) later retrograde assemblage (vesuvianite, epidote, chlorite, and amphibole). Significant variations in composition, from core to rim within a zoned crystal, reflect the chemical and physical changes in the medium where the crystals grew. Thus, an analysis of the intracrystalline zonation of metasomatic minerals may provide a more or less continuous record of the processes taking place during the evolution of metasomatic transformations [4–12]. Fluid inclusions trapped in hydrothermal minerals can store important information about the physicochemical conditions of the ore fluids in ancient mineralization systems [13,14].

Moroccan skarns are generally associated with late Hercynian granitoids. In the province of the central Paleozoic massif of the western Meseta, they exhibit pneumatolytic mineralizations, such as Sn-W-B, in the El Hammam skarns [15–19] or stratiform tungsten skarns in Jbel Aouam [20–26].

In the Hercynian Jebilet region, this category is represented by the Sidi Bou Othmane skarns [27–31]. Finally, in the Western High Atlas, the pyrometasomatic deposit at Azegour for W-Cu-Mo [32–41] and the Amensif polymetallic Cu-Pb-Zn skarn deposit [42–44] can be found.

Furthermore, the Western Moroccan High Atlas Mountains host ore deposits and prospects of significant economic value. The Guedmiwa metallogenic district, situated in the northern range of the Western High Atlas, encompasses base and precious metal mineralization, including the Assif El Mal Pb-Zn-(Cu-Ag) vein deposit [45], the Erdouz Ag-Zn-Pb vein deposit [46], and the Seksaoua Cu syngenetic deposit [47].

The Azegour skarn deposit is one of several base and precious metal deposits hosted within the Palaeozoic formations on the northern side of the Western High Atlas. Previous studies on the Azegour skarn deposit primarily focused on geological descriptions, petrography, the geochemistry of igneous rocks associated with mineralized skarns, and the geochronology of the Mo-Cu-W mineralization.

This contribution presents the stages of evolution, paragenetic minerals, mineral chemistry, and the first investigation of skarn-hosted fluid inclusions from the Azegour skarn deposit. Our objective is to provide insights into the fluid evolution of the Azegour skarn deposit, which can be applied to enhance our understanding of the mechanisms involved in ore deposit genesis.

2. Geological Setting

The regional geology of the Azegour area is marked by a lower Cambrian volcanosedimentary series consisting of lava flow and pyroclastites, which are sandstone-mudstone rocks interlayered with volcanic and pyroclastic rocks. It also consists of limestone bars and lenses interbedded with thin pelitic, volcanic, and pyroclastic bands or lenses, as well as andesitic flow in intercalation with pelite and volcanic lies [34]. The middle Cambrian is essentially composed of sandstone and pelite [39,48]. The Cambrian sequences are unconformably overlain by the Cretaceous-Tertiary sub-atlanic formations. The magmatic activity of Azegour is linked to its volcanic arc context, and previously to the Cambrian extension. According to [34], this magmatic activity is a continental intra-plate tholeiite, as widely described in the lower Moroccan Cambrian [44,48–52]. During the magmatism of late Hercynian orogeny, small plutons of granite, granodiorite, including the intrusive rocks of Azegour, and other felsic rocks were formed. The Azegour pink granite outcrop has an elongated form and extends NNW-SSE (Figure 1); it is about 7 km long and 1 km wide, representing a stock that is inclined to the southeast. This Azegour intrusion has a Permian Rb-Sr age (271 \pm 3 Ma) [53]. From a chemical point of view, the granite is a K-calc-alkaline hyperaluminous granite of crustal origin (S-type granite) [34]. The calc-alkaline granites of Azegour are associated with the molybdenum granite type [34].



Figure 1. (a) Structural domains of Morocco and location of the Western High Atlas domain (black quare). (b) Simplified geological map of the Western High Atlas. The red square shows the study area in the Moroccan sketch (modified from [54]).

The Azegour Cu-Mo-W skarn deposit, situated approximately 60 km southwest of Marrakech city and about 20 km southwest of the Amizmiz village, represents one of the numerous base and precious metal deposits hosted in the Palaeozoic formations on the northern side of the Western High Atlas.

The lower Cambrian lithostratigraphic series begins with a thick (approximately 40 m) lava flow and pyroclastites, covered by a greso-pelitic series (120 m) with interbedded volcanic and pyroclastic rocks. All of these are overlain by limestone bars and lenses (70 m) with intercalations of thin pelitic, volcanic, and pyroclastic bands or lenses. These

volcano–carbonate formations are covered by an andesitic flow (50 m) inter-layered with pelitic and volcanic lies. The middle Cambrian is essentially composed of sandstone and pelite formations [39,48] (Figure 2). This lithostratigraphic succession is very similar to that of the nearby mining areas of Amensif, where similar hydrothermal transformations to those of Azegour were described [44,55]. The paleozoic series of Azegour records two Hercynian deformation phases [56]. A first submeridian deformation phase predates the granite intrusion, and corresponds to the 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.



Figure 2. Geological map of Azegour area; the Lower Cambrian volcano–sedimentary series are cut by Hercynian granites [34].

3. Sampling and Analytical Methods

The samples collected from the different outcrops (granite, marble, skarn or ores) provided the material for the mineralogical and petrographic study in the study area. A total of 240 samples were collected from the surface and from cores within mineralized intercepts for the purpose of conducting petrography, mineralogy, and metallography. Identifying all mineral phases, including opaque minerals, required using SEM (Scanning Electron Microscope) imagery and microanalysis.

Mineralogical descriptions were performed on both hand specimens, thin, and thick sections using an Olympus BX41 metallographic microscope with transmitted and reflected light. Subsequently, minerals were studied using a scanning electron microscope (SEM), and ten polished sections were examined using a Philips XL30 instrument equipped with SE, BSE, and EDX detectors at the Reminex Research Center and Laboratory (Marrakech). The operating conditions included an accelerating voltage of 20 to 30 kV, a beam current of 20 nA, and count times of 20 sat.

The granite samples were analyzed using an ICP-AES (Inductive Coupled Plasma Atomic Emission Spectrometry Activa–Horiba Jobin Yvon Spectrometer) in the Geosciences and Environment Department of the National School of Mines in Saint Etienne, France.

The major oxide composition of minerals was determined using an electron microprobe (EPMA) device. The EPM analysis of polished and carbon-coated thin sections was conducted with the JXA-8230 electron microprobe at the Geosciences and Environment Department of the National School of Mines in Saint Etienne.

A detailed examination of fluid inclusions trapped within clinopyroxene, garnet, quartz, and calcite crystals was conducted on 35 doubly polished thick sections (150–200 μ m). From this selection, ten thick sections were chosen for microthermometric analysis. The microthermometric analyses were performed using a LINKAM THMSG 600 heating-freezing stage (ranging from -180 °C to +600 °C), mounted on an Olympus BX41 microscope, at the Mineral Resource and Energy Laboratory of the Geology Department of the Faculty of Sciences in Meknes.

4. Results

4.1. Petrography and Geochemistry of the Azegour Intrusion

The pink granite of the Permian Azegour outcrops on a band, directed NW-SE, that is about 7 km long and 1 km wide [35,39,40,53]. Before the geochemical analyses, all the samples were petrographically investigated. This showed a constant mineralogical composition formed by quartz (40%), perthitic potassic feldspar (orthose and microcline) (43%), sodic plagioclase type of albite–oligoclase (16%), and biotite that was often chloritized (1%). The accessories are apatite, sphene, zircon, and iron oxides.

Major and trace element analyses were performed on the granite samples to reveal the relations with the geochemistry of Azegour granite and its relationships with the skarn types and their metal contents. 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 relatively constant chemical composition (77% SiO₂, 5% K₂O, 2.5% Na₂O, CaO < 0.5%, MgO < 0.1% and Fe₂O₃ < 1.2%) (Figure 3a,b), and corresponding to the S-type granite (Figure 4b) related to volcanic arc context (Figure 3c,d). For this purpose, representative samples were collected from the granite's unaffected outcrops via hydrothermal alteration, and the results are given in Table 1. In the element variation diagrams (Figure 4), the major and trace element contents of the Azegour pluton were compared to the average values of the granitoids associated with the different skarns [3,57]. The major element and trace contents of the Azegour pluton are generally comparable to those of the Mo skarn granitoids.



Figure 3. Harker diagrams and trace-element contents for the Azegour granitoid and comparison with world skarn granitoids [3] (a) K_2O vs. SiO_2 , (b) K_2O + Na_2O vs. SiO_2 , (c) Fe_2O_3 + CaO + Na_2O/K_2O ratio vs. SiO_2 , (d) MgO vs. SiO_2 (e) A/NK vs. A/CNK, (f) Rb vs. Sc, (g) V vs. Ni, and (h) Rb/Sr vs. Zr. (A/NK: Al/(Na + K); A/CNK: Al/(Ca + Na + K)). (Black circles corresponds to composition of skarn-related granitoids [3]).



Figure 4. Plots illustrating the chemistry of the Azegour granite: (a) SiO_2 versus K_2O diagram (after [58,59]); (b) aluminum-based classification on molar A/NK versus A/CNK diagram [60]; (c,d) distribution of the granitoid samples on the Nb–Y and Rb–(Y + Nb) trace element diagrams used for discriminating the tectonic settings of granites and comparison with the [61] (WPG: within plate granitoids, ORG: ocean ridge granitoids, VAG: volcanic arc granitoids, syn- and post-collision).

Table 1. Major oxide (wt%) and trace element (ppm) contents of the samples from the Azegour granitoid.

Sample No.	Z-86	Z-87	Z-99	Z-88	Z-89	Z-92	Z-82	Z-100					
	Major oxide (wt%)												
SiO ₂	78.28	76.49	77.11	77.35	76.93	78.01	76.59	77.41					
TiO ₂	0.09	0.08	0.11	0.07	0.14	0.09	0.11	0.08					
AL_2O_3	11.51	11.79	12.32	12.34	12.13	12.5	12.28	12.74					
$Fe_2O_3(t)$	0.33	1.19	0.55	0.76	0.22	0.66	0.63	0.85					
MnO	0.01	0.07	0.01	0.02	0.01	0.03	0.02	0.01					
CaO	0.27	0.24	0.3	0.34	0.37	0.27	0.69	0.34					
MgO	0.04	0.07	0.09	0.06	0.07	0.03	0.11	0.07					
Na ₂ O	2.48	2.12	2.52	2.65	2.57	2.47	2.42	3.01					
K ₂ O	4.75	5.74	5.18	5.15	4.86	4.91	5.21	4.53					
P_2O_5	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01					
LOI	0.44	0.68	0.54	0.56	0.48	0.87	0.41	0.48					
Total	97.75	97.79	98.19	98.73	97.31	98.96	98.05	99.04					

Sample No.	Z-86	Z-87	Z-99	Z-88	Z-89	Z-92	Z-82	Z-100
			Trac	e elements (pp	m)			
Ni	4.52	5.71	5.04	5.64	5.76	4.85	5.2	7.09
Cu	14.06	15.26	5.24	30.66	4.14	102.6	18.53	6.29
Zn	9.03	121.9	13.5	18.7	14.6	263.5	72.8	12.74
Sc	2.38	2.3	1.73	4.91	1.38	1.93	1.62	2.56
Ga	18	18.8	18.3	27.6	16.6	20.3	19.9	26.4
Rb	198.9	212.8	194.9	210	180.1	182.1	134.4	201.2
Sr	21.6	24.2	38.9	19	44.7	22.4	35.5	17.4
Li	8.29	10.01	11.79	5.83	16.36	5.67	25.77	15.7
Y	5.24	10.56	8.93	11.19	9.31	9.07	20.07	9
Zr	65.2	68.4	78.8	75.7	121	81	94.5	87.2
Nb	23.2	25.1	19.1	71.4	17.9	24.8	30.1	34.6
Pb	8.2	106.7	8.1	27.9	19.9	118.5	47.3	13
Th	27.37	32.78	23.52	20.21	32.1	34.3	37.74	29.2
U	5.2	3.8	3.2	9.3	6.1	8.6	13.8	7.1
Ba	165.7	484	224.8	307.9	289.8	160.1	178.4	98.52
Co	bdl	0.63	0.13	0.08	bdl	1.8	1.98	1.47
Cr	2	2.56	2.86	3.5	4.93	2.25	5.22	7.16
V	1.04	6.1	3.57	3.05	2.45	3.17	3.56	2.45
La	14.51	25.58	23.64	19.54	17.83	14.46	32.5	16.88
Ce	28.86	38.88	41.08	37.46	35.53	28.4	60.43	26.47
Eu	0.03	0.22	0.14	0.02	0.28	0.02	0.21	0.02
Nd	2.65	9.28	8.51	4.84	7.47	4.07	15.45	4.37
Yb	1.05	1.96	1.79	2.48	1.76	2.01	3.02	2.69
Nb/Y	4.43	2.38	2.14	6.38	1.92	2.73	1.5	3.85
La/Yb	13.87	13.06	13.18	7.88	10.11	7.19	10.75	6.27
A/CNK	1.19	1.16	1.2	1.17	1.19	1.27	1.13	1.22

Table 1. Cont.

4.2. Mineral Assemblage and Zonation of the Skarn

Skarn metasomatic development manifests in an intense replacement of the carbonated bars of the Cambrian series during the intrusion Permian granite. The mineralization genesis is associated with the hydrothermal transformations that affected carbonated bars. In detail, the studied carbonated bars show a heterogeneous composition, varying from pure calcite to calcite-dolomite (Cal + Dol), with a few clasts of quartz, to dolomites with pelitic, volcanic, and pyroclastic fractions (Figure 5b). Mineralogy is the key to recognizing and defining skarns. The new minerals are typically coarse-grained crystals that grow over and replace the carbonate-rich rock (exoskarn). The skarnified zones are oriented N-S parallel to the general direction of the carbonated bars exposed in ribbons or lenses (Figure 6). Wollastonite and/or pyroxene develops directly on the marble. The contact between garnetites and wollastonitites is diffuse and progressive, and garnets as isolated crystals or polycrystalline clusters can appear within wollastonitites (Figure 5c,d). Zoned garnet is replaced by pyroxene (Figure 5e). Calcite and chlorite are the main alteration products, while interstitial quartz and calcite are also observed. Pores and fractures of garnet are filled with quartz, calcite, and K-feldspar crystals (Figure 5f,g). The geometry and the zonation of the skarn in Azegour are shown in Figure 6. The skarn exhibits a banded structure, the internal planar structures of the skarn are defined by alternating bands: bands of garnet-rich skarn, bands of wollastonitite or bands of garnet-rich wollastonitite (Table 2).



Figure 5. Photographs of representative skarns from the Azegour deposit: (**a**) photograph showing west central carbonated bar; (**b**) marble not transformed; (**c**) diffuse front of garnetite development on wollastonite; (**d**) contact between garnetites and wollastonities is progressive with garnets in isolated crystals or polycrystalline; (**e**) garnet and pyroxene with molybdenite; (**f**) quartz vein recutting the garnet; (**g**) texture example with garnet, potassium feldspar, calcite, and epidote minerals. (Wo: Wollastonite; Grt: Garnet; Px: Pyroxene; Mol: Molybdenite; Qz: Quartz; Kfs: Potassic feldspar; Cal: Calcite; Ep: Epidote).



Figure 6. Mineral zonation of calcic skarn in the west central carbonated bar.

Table 2. Petrographic characteristics of skarn zones in the Azegour skarn deposit. Cal, calcite; Dol, dolomite; Sp, Spinel; Scp, scapolite; Ph, phlogopite; Wo, wollastonite; Grt, garnet; Grs, grossular; Anr, andradite; Ves, vesuvianite; Px, pyroxene; Di, diopside; Hd, hedenbergite; Sch, scheelite; Qz, quartz; Kfs, K-feldspar; Pl(Ab), plagioclase (albite); Amp, amphibole; Ep, epidote; Chl, chlorite; Ms, muscovite; Pect, pectolite; Hem, hematite; Oli, Oligiste.

Rock Type	Sample No.	Mineral Facies	Mineral Assemblage	Characteristic Properties
Marble	Z1A,Z5A,Z5B,Z5B2,Z22,Z64, Z59,Z84,Z103,Z111,Z112	Cal + Dol	$\begin{array}{l} \text{Cal} + \text{Dol} \pm \text{Px} \ \text{(Di)} \pm \\ \text{Sp} \pm \text{Scp} \pm \text{Ph} \end{array}$	Marble show a heterogeneous composition, varying from pure calcite to calcite dolomite (Cc + Dt), with a few clasts of quartz, to dolomites with pelitic, volcanic and pyroclastic fractions.
	Z6A3,Z6AB,Z6B1,Z6B3,Z7A2, Z7B1,Z7B2,Z8A,Z8B,Z32A, Z35C,Z53,Z69,Z60	Wo-Grt zone	Wo + Grt (Grs-Adr) \pm Px (Di-Hd) \pm Qz \pm Cal \pm Amp \pm Sch \pm Ves	Wollastonite developing directly on the marble. The contact between grenatites and wollastonitites is diffuse and progressive and garnets as isolated crystals or polycristalline clusters can appear within wollastonitites.
Skarn	ZA2,Z4C1,Z4C2,Z9,Z9B,Z10, Z11A,Z11B,Z12B,Z13,Z14A, Z14B,Z17,Z18A,A19,Z21B, Z23A,Z23B,Z24A,Z24B,Z25A, Z25B,Z37A,Z37B,Z41A,Z41B, Z61,Z70,Z78,Z79,Z102,Z110, Z114,Z125B	Grt zone	$\begin{array}{c} & \text{Grt} \left(\text{Grs-Adr} \right) + \text{Px} \\ (\text{Di-Hd}) \pm \text{Sch} \pm \text{Ves} \pm \\ & \text{Sph} \pm \text{Qz} \pm \text{Cal} \pm \text{Kfs} \\ & \pm \text{Pl} \left(\text{Ab} \right) \pm \text{Amp} \pm \text{Ep} \\ & \pm \text{Chl} \pm \text{Ms} \pm \text{Pect} \pm \\ & \text{Sulphides} \pm \text{Hem} \pm \text{Oli} \end{array}$	Zoned garnet is replaced by pyroxene. Calcite and chlorite are the main alteration products and interstitial quartz and calcite are observed. Pores and fractures of garnet are filled with quartz, calcite and k-feldspar crystals.

4.3. Mineral Chemistry of Pyroxene and Garnet

The mineralogical composition, including refractory pyroxene and garnet, provides valuable information for identifying skarn-related mineralization types. Garnet and pyroxene are found in almost all skarn types and exhibit significant compositional variations [1,62,63]. Skarn deposits have been classified based on the composition of pyroxene and garnet due to the correlations between the compositions of these minerals and the associated metals [3]. The structural formulae of garnet and pyroxene were calculated using MinPlot [64].

4.3.1. Pyroxene

A chemical analysis of pyroxene from the various skarn zones of Azegour, given in Table 3 and plotted in Figure 7, shows that they are predominantly of hedenbergite $(Hd_{50.49-86.73}Di_{12.22-48.22}Joh_{0.69-2.40})$ and diopside $(Hd_{35.74-48.57}Di_{61.80-50.08}Joh_{1.34-2.46})$ composition. Oscillatory zoning was noted in some of the pyroxenes from the center toward the edge during the microscopy studies (Figure 8d). The outermost rim consists of fine oscillatory zoning. The images reveal the rhythmical variation in pyroxene compositions from core to rim.

Table 3. Representative results of electron microprobe analysis of pyroxenes from Azegour skarn zones. (bdl: below detection limits).

Sample No.	Z7B2A	Z7B2B	Z6B1A	Z6B1B	Z6B1C	Z7B2	Z54	Z20A	Z20B	Z18A	Z18B	Z4C1A	Z4C1B	Z49A	Z49B
(wt %)															
SiO ₂	53.04	51.19	50.60	49.94	49.72	49.71	52.19	51.13	50.60	49.72	49.71	51.13	50.60	50.13	50.57
TiO ₂	0.13	0.58	0.88	0.97	0.90	0.79	0.17	0.56	0.47	0.50	0.59	0.24	0.36	0.37	0.25
Al_2O_3	0.64	2.35	3.18	3.46	3.71	3.42	0.65	2.59	2.18	1.71	1.42	0.99	0.82	1.53	1.82
FeO	6.55	9.98	9.26	9.35	10.28	11.14	11.91	12.42	13.93	16.38	16.14	18.42	18.42	19.93	18.92
MnO	0.44	0.25	0.26	0.23	0.29	0.17	0.49	0.24	0.26	0.39	0.17	0.24	0.24	0.24	0.24
MgO	14.06	11.91	11.93	11.73	11.35	10.80	10.98	8.72	7.36	7.35	7.80	4.72	4.96	3.72	3.96
CaO	24.65	24.11	24.05	23.79	23.55	23.36	24.11	24.02	24.05	23.55	23.36	23.02	23.65	22.60	22.98
Na ₂ O	0.35	0.42	0.49	0.47	0.45	0.39	0.24	0.35	0.39	0.45	0.39	0.25	0.29	0.85	0.65
K ₂ O	bdl	bdl	bdl	0.02	0.02	bdl	bdl	0.01	bdl	0.02	bdl	0.01	0.01	0.01	0.01
Total	99.86	100.79	100.65	99.96	100.27	99.78	100.74	100.04	99.24	100.07	99.58	99.02	99.35	99.38	99.40
Cations of	n the bas	is of 6 o	xygen at	oms											
Si	3.74	3.69	3.66	3.65	3.65	3.66	3.74	3.72	3.73	3.68	3.71	3.79	3.77	3.76	3.77
Ti	bdl	0.01	0.01	0.01	0.01	0.01	bdl	0.01	0.01	0.01	0.01	bdl	bdl	0.01	bdl
Al ^(IV)	0.01	0.05	0.06	0.07	0.07	0.07	0.01	0.05	0.04	0.03	0.03	0.02	0.02	0.03	0.04
Al ^(VI)	0.02	0.07	0.09	0.10	0.11	0.10	0.02	0.08	0.06	0.05	0.04	0.03	0.02	0.05	0.05
Fe ²⁺	0.20	0.31	0.29	0.29	0.32	0.35	0.38	0.40	0.45	0.53	0.53	0.61	0.61	0.66	0.62
Fe ³⁺	0.09	0.14	0.13	0.13	0.14	0.16	0.17	0.17	0.19	0.23	0.22	0.26	0.26	0.38	0.36
Mn	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Mg	0.35	0.30	0.30	0.29	0.28	0.27	0.28	0.22	0.18	0.18	0.20	0.12	0.12	0.09	0.10
Ca	1.42	1.41	1.41	1.40	1.39	1.39	1.42	1.42	1.44	1.43	1.42	1.41	1.44	1.40	1.41
Na	0.01	0.01	0.01	0.01	0.01	0.01	bdl	0.01	0.01	0.01	0.01	bdl	0.01	0.01	0.01
K	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
% Di	61.80	48.22	50.08	49.33	46.03	42.99	41.29	35.10	28.24	25.41	26.86	16.12	16.78	12.22	13.56
% Hd	35.74	50.49	48.57	49.49	52.51	56.21	56.31	63.61	70.36	73.20	72.45	82.79	82.14	86.73	85.34
% Jo	2.46	1.29	1.34	1.18	1.46	0.80	2.40	1.29	1.40	1.38	0.69	1.09	1.08	1.05	1.10

The electron microprobe analysis of the pyroxenes are plotted within the hedenbergite– diopside–johannsenite ternary diagram (Figure 7). These data show that the pyroxenes have a predominantly hedenbergitic to diopsidic composition. The pyroxene resembles that from Mo, W, Sn, and Cu skarns [3,65].



Figure 7. Jo-Di-Hd ternary diagram showing the compositional variations of pyroxene from the Azegour. End members are Di, diopside; Hd, hedenbergite; and Jo, johannsenite [66] (The green circles correspond to the pyroxene compositions from our study).

4.3.2. Garnet

Three major generations of garnets are identified within the Azegour deposit based on textural and optical characteristics. (i) Type I: Euhedral and isotropic garnets with $(Ad_{72.81-97.07})$ represent the early prograde phase (Table 4). They appear dark in BSE (Backscattered Electron) images and are later replaced by oscillatory zoned garnets. (ii) Type II: Euhedral and anisotropic garnets (andradite–grossular) (Figure 7a–c). Oscillatory zoned garnets exhibit corresponding chemical zoning and are common in the study area. They appear brighter in BSE images. Many coarse garnet crystals display zoning textures under cross-polarized light, with some characterized by an Al-rich core and Fe-rich rim (Figure 7b,c). (iii) Type III: Euhedral and anisotropic garnets often exhibit dodecahedral twinning and are predominantly grossular ($Gr_{66.88-93.72}$) with a significant portion of almandine ($Alm_{2.84-34.99}$) (Figure 7d). Garnet types can vary in different metal deposits [3]. The garnet components in the Azegour deposit plot within the field typical of skarn Zn, Cu, Mo, Sn, and W deposits can be seen worldwide (Figure 9).

Table 4. Representative results of electron microprobe analyses of garnets from Azegour skarn zones.(bdl: below detection limits).

Sample no.	Z54A	Z54B	Z48A	Z48B	Z4A	Z4B	Z9A	Z9B	Z6B1A	Z6B1B	Z7B2A	Z7B2C	ZT7	ZT8	ZT9	ZT10
(wt %)																
SiO ₂	42.40	40.43	39.85	38.85	44.43	38.54	38.45	37.96	38.09	38.01	36.84	36.72	35.26	35.26	34.36	34.93
TiO ₂	0.56	0.68	0.01	bdl	0.05	0.26	0.12	0.04	bdl	bdl	0.87	bdl	bdl	bdl	bdl	0.01
Al_2O_3	17.89	19.21	21.74	28.99	13.29	15.01	25.07	26.27	24.39	23.06	16.06	17.28	1.30	0.49	0.52	4.88
FeO	5.13	3.09	10.97	5.44	11.38	9.58	9.83	8.88	11.44	11.85	3.25	2.82	29.14	29.83	30.67	26.54
MnO	0.13	0.12	bdl	0.18	0.23	0.32	0.04	0.26	0.02	0.10	bdl	bdl	0.39	0.35	0.29	0.35
MgO	0.66	0.60	0.45	0.12	0.01	0.06	0.05	0.03	0.03	0.04	3.46	3.29	0.07	0.10	0.03	0.14
CaO	27.67	36.49	20.48	24.23	35.06	36.27	23.91	23.11	23.28	23.42	36.24	36.32	33.33	32.48	33.64	31.22
Na ₂ O	0.34	bdl	0.03	bdl	0.02	bdl	bdl	0.01	0.01	0.02	0.02	0.01	0.32	0.51	0.27	0.21
K ₂ O	0.23	0.02	0.08	0.01	0.01	bdl	bdl	bdl	0.01	0.01	0.02	bdl	bdl	bdl	bdl	bdl
Cr_2O_3	bdl	0.01	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Total	95.01	100.65	93.63	97.83	104.48	100.04	97.47	96.57	97.27	96.52	96.76	96.44	99.81	99.13	99.79	99.07

Table 4. Cont.

Sample no.	Z54A	Z54B	Z48A	Z48B	Z4A	Z4B	Z9A	Z9B	Z6B1A	Z6B1B	Z7B2A	Z7B2C	ZT7	ZT8	ZT9	ZT10
Cations on the basis of 12 oxygen atoms																
Si	3.33	3.04	3.13	2.80	3.27	2.99	2.91	2.86	2.92	2.97	2.92	2.91	2.96	3.00	2.91	2.94
Al (IV)	bdl	bdl	bdl	0.20	bdl	0.01	0.09	0.14	0.08	0.03	0.08	0.09	0.04	bdl	0.06	0.06
Al (VI)	1.66	1.71	2.05	2.37	1.18	1.40	2.19	2.26	2.16	2.11	1.43	1.54	0.10	0.05	bdl	0.46
Ti	0.03	0.04	bdl	bdl	bdl	0.02	0.01	bdl	bdl	bdl	0.05	bdl	bdl	bdl	bdl	bdl
Cr	bdl															
Fe ³⁺	bdl	0.19	bdl	bdl	0.47	0.51	bdl	bdl	bdl	bdl	0.22	0.19	1.58	1.62	1.68	1.30
Fe ²⁺	0.37	0.01	0.96	0.79	0.23	0.11	0.88	0.89	0.94	0.92	bdl	bdl	0.47	0.51	0.49	0.57
Mn	0.01	0.01	bdl	0.01	0.01	0.02	bdl	0.02	bdl	0.01	bdl	bdl	0.03	0.03	0.02	0.02
Mg	0.08	0.07	0.05	0.01	bdl	0.01	0.01	bdl	bdl	0.01	0.41	0.39	0.01	0.01	bdl	0.02
Ca	2.33	2.94	1.72	1.87	2.77	3.02	1.94	1.87	1.91	1.96	3.08	3.09	3.00	2.96	3.06	2.82
Total	7.81	7.99	7.91	8.06	7.94	8.08	8.02	8.04	8.02	8.00	8.19	8.20	8.19	8.17	8.22	8.19
% And	bdl	9.82	bdl	bdl	29.08	27.12	bdl	bdl	bdl	bdl	12.57	10.39	92.44	97.07	97.02	72.81
% Gro	93.72	87.51	63.06	69.63	70.27	71.91	68.67	67.14	66.88	67.76	71.55	75.23	6.13	1.41	2.03	25.58
% Alm	2.84	bdl	34.99	29.46	bdl	bdl	31.03	32.11	32.97	31.82	bdl	bdl	bdl	bdl	bdl	bdl
% Pyr	3.10	2.36	1.95	0.49	0.04	0.23	0.20	0.14	0.12	0.18	15.89	14.37	0.33	0.50	0.15	0.68
% Spe	0.34	0.28	bdl	0.42	0.60	0.74	0.10	0.61	0.03	0.24	bdl	bdl	1.10	1.02	0.81	0.93



Figure 8. BSE images of garnet and pyroxene from the Azegour Mo-Cu-W skarn deposit. Photomicrographs of typical samples in the Azegour deposit: (**a**) intergrowth and oscillatory zoned garnet associated with pyroxene from the Azegour deposit. Bright regions are characterized by relatively andraditic composition compared to dark regions. Core of garnet is Fe-rich, after crystallization through which the Al-rich garnet formed; (**b**) the zoned coarse garnet crystal associated with pyroxene (hedenbergite) and lamellar of molybdenite between garnet and pyroxene; (**c**) oscillatory zoning patterns in garnet is associated with pyroxene (hedenbergite) and is replaced by calcite; (**d**) garnet (grossular) is pervasively modified by retrograde chlorite, calcite, zoned pyroxene grains generally consisting of a homogeneous core (diopside), and oscillatory zoned rims (hedenbergite). (Grt: Garnet; Grs: Grossular; Adr: Andradite; Px: Pyroxene; Mol: Molybdenite; Cal: Calcite; Chl: Chlorite).



Figure 9. Sp + Alm-Gr-Ad ternary diagram for garnets from the Azegour [66] (The orange hexagons corresponds to the garnet compositions from our study).

4.4. Metasomatic Alteration and Mineralization

In the Azegour deposit, both anhydrous and hydrous calc-silicates were formed during two distinct metasomatic stages, first the prograde stage and then the retrograde stage. Such a sequence is typical of skarns worldwide [1,3,67–69]. Revealing the paragenesis pattern in the deposit can provide valuable information about metasomatic alteration and ore-forming processes. Paragenetic studies, based on macro- and microtextures, indicate that the formation of the Azegour skarn occurred in several distinct stages. Four stages of skarn and ore mineral deposition are recognized: (i) the early prograde stage consists of the dominant mineral assemblage of wollastonite, diopside, andradite, and grandite. Subsequent skarn stages often overprint this stage. (ii) The late prograde stage consists of an assemblage of hedenbergite, johannsenite, grossular, and scheelite. (iii) The early retrograde stage consists of an assemblage of vesuvianite, quartz, K-feldspar, albite, calcite, amphibole, epidote, molybdenite, chalcopyrite, and pyrite. (iv) The late retrograde stage is characterized by an assemblage of calcite, dolomite, chalcopyrite, pyrite, hematite, and marcasite.

Early prograde stage: Wollastonite \pm and radite \pm grandite \pm diopside

This stage occurred when the granitic magma reacted with the carbonate bars, resulting in their isochemical metamorphism into approximately homogeneous limestones and metasomatized horns. Based on the optical characteristics of mineral assemblages and structures, wollastonite and/or pyroxene (diopside) develop directly on the marble, which is composed of calcite and dolomite (Figure 10a). In this stage, two generations of garnet have been identified within the deposit. Type I (andradite) is a first-generation (Figure 10c,e) anhedral, completely isotropic mineral with numerous fractures; it develops directly on coarse fan-shaped wollastonite, and sometimes exhibits zonal anisotropy along the rim. Type II (Grandite) is anisotropic with low birefringence and sector twinning (Figure 11b). The abundance of ferriferous garnets, as well as the deficiency of subcalcic garnets and hedenbergite, indicate oxidized skarns [70]. The development of twinning suggests that the growth of Type II was slow [71]. From a chemical point of view, the wollastonite is pure with some traces of Mn and Fe. They are partially replaced by diopside (Figure 10b,d). All garnets are usually replaced by the later-formed minerals, just before the late prograde stage begins, and the garnet commonly replaces early diopside ((Figure 10c) and (Figure 11e)).



Figure 10. Photomicrographs showing textural and optical characteristics of prograde skarn mineral assemblages from the Azegour skarn deposit: (**a**) calcite and dolomite are carbonate minerals in marble, associated with pyrite; (**b**) aggregates of long columnar wollastonite crystals, intergrown with pyroxene (diopside); (**c**) pyroxene (diopside) and vesuvianite–mg replacing the core and rim of zoned garnet (andradite); (**d**) scheelite disseminated in pyroxene (diopside) and wollastonite; (**e**) euhedral isotropic garnet I (andradite), partially showing anisotropy along the rims (Grossular). The fracture-filling mineral within garnet is calcite. (Wo: Wollastonite; Grt: Garnet; Di: Diopside; Ves: Vesuvianite; Kfs: Potassic feldspar; Cal: Calcite; Dol: Dolomite; Sch: Scheelite; Py: Pyrite).



Figure 11. Photomicrographs showing textural and optical characteristics of retrograde skarn mineral assemblages from the Azegour skarn deposit. (a) Mg-rich vesuvianite developing on pyroxene (diopside); (b) Fe-rich vesuvianite growing on garnet (grossular); (c) amphiblole replacing pyroxene eventually crosscut by the late anhydrite of the quartz–calcite–sulfide (chalcopyrite), calcite vein-filling texture including garnet inclusions; (d) pores and fractures of garnet (grossular) are filled with quartz, calcite, and K-feldspar crystals, albite, and sphene; (e) garnet (andradite) and pyroxene (diopside) while matrix mineral is calcite, muscovite, and opaque minerals included in the altered pyroxene; (f) pores of garnet (grossular) and Fe-rich vesuvianite are filled with fluorite and molybdenite. (Grt: Garnet; Ves-Mg: Magnesian Vesuvianite; Ves-Fe: Ferriferous Vesuvianite; Di: Diopside; Amp: Amphibole; Qz: Quartz; Ccp: Chalcopyrite; Mol: Molybdenite; Sph: Sphene; Ab: Albite; Kfs: Potassic feldspar; Cal: Calcite; Ms: Muscovite; Sul: Sulfide; Flr: Fluorite).

Late prograde stage: hedenbergite \pm johannsenite \pm grossular \pm scheelite

This stage is dominated by hedenbergite and grossular, with a subordinate amount of scheelite and johannsenite. The high hedenbergite and grossularite compositions in the late prograde stage, with a significant portion of subcalcic garnet as almandine, indicate "strongly reduced" or "moderately reduced" conditions [70,72]. The garnet tends to be grossular and clinopyroxene tends to be hedenbergite and johannsenite in composition. The presence of grossular suggests low CO₂ concentrations [73,74]. No sulfides and/or oxides are formed during this stage. Grossular occurred in the skarn zone as medium to coarse-grained and anhedral to euhedral crystals.

Early retrograde stage: Vesuvianite \pm quartz \pm k-feldspar \pm albite \pm calcite \pm amphibole, epidote \pm molybdenite \pm chlocopyrite \pm pyrite

The early retrograde is marked by the deposition of alteration minerals. Two types of vesuvianite were observed: a brownish variety rich in Mg, without corroded rims (Figure 11a) and with variable proportions. It formed as the replacement product of wollastonite, diopside and garnet (andradite), and a greenish variety rich in Fe, which has a euhedral lamellar shape with sharp contours and appears to be younger than the associated garnet (grossular) (Figure 11b,f).

The early retrograde stage: characterized by the alteration of early higher temperature minerals and the crystallization of texturally later minerals, such as amphibole, quartz, and calcite. This is evident from their relicts increasingly replacing garnet and pyroxene (Figure 11c,e). The epidote crystals grew inside or around garnet crystals and also coexist as patchy aggregates with K-feldspar, plagioclase (albite), calcite, and sulfides. K-feldspar is especially well developed and is genetically associated with silicification (Figure 11c–e). Amphibole is the most common alteration mineral in the Azegour altered host rocks, resulting from the alteration of pyroxene. The minerals formed during the early retrograde stage are widespread and represent the major period of ore deposition. The mineralization is characterized by the precipitation of the Mo- and Cu-bearing mineral assemblage. The ore structures include disseminated, massive, stockwork, veinlet, and speckled textures (Figure 12). Typical ore textures are euhedral to subhedral granular, metasomatic relic texture, and molybdenite is the principal mineral at Azegour and has mainly developed during this stage. Molybdenite occurs as isolated or grouped lamellae, often twinned and kinked, and is associated with quartz, calcite, and K-feldspar, plugging cracks and fractures affecting garnets and vesuvianite (Figure 12a,b). Chalcopyrite represents the second most abundant mineral after molybdenite. It occurs as isolated crystals, fine blebs or ribbons occupying molybdenite cleavage (Figure 12b). Chalcopyrite holds some sphalerite inclusions and galena (Figure 12d), with chalcopyrite developing on bornite (Figure 12c). Fluorite appears as micrometric individual euhedral crystals, sometimes included in quartz. Titanite is found as discrete grains in the interstices of K-feldspar and quartz, suggesting a hydrothermal origin (Figure 12d,f). Arsenopyrite is rarely observed, generally fine-grained (20 to 150 μ m), and exhibits a euhedral shape. Arsenopyrite grows on the sphalerite– chalcopyrite assemblage (Figure 12d). Galena is relatively rare in the deposit compared to the other sulfide minerals. It was observed either as fine inclusions in sphalerite or as large bands associated with chalcopyrite and grey copper (Figure 12d,e).

Late retrograde stage: calcite \pm dolomite \pm chalcopyrite \pm pyrite \pm hematite \pm magnetite \pm marcasite

The late retrograde stage commonly partially replaced earlier stages. Calcite typically occurs as veins or veinlets that traverse the early retrograde stage and earlier mineral assemblages. Hematite develops in magnetite as exsolution lamellae and replacement phases (Figure 12f). Chalcopyrite, along with pyrite, forms thin ribbons parallel to garnetites layers, reflecting the importance of the late remobilization related to regional deformation. Pyrite is corroded by magnetite and hematite. Hematite is relatively more abundant and may form massive bodies. Marcasite is represented by clusters and aggregates often intergrown with or rimming pyrite and chalcopyrite. Sulfides are relatively scarce in this



stage. Locally, chalcopyrite and pyrite fill the interstitial sites and fractures, suggesting that they represent a late retrograde stage of skarn formation.

Figure 12. Some images from Azegour mineralization paragenesis. (**a**) Lamellar masses of molybdenite interstices between garnet and pyroxene; (**b**) chalcopyrite occupying cleavage plans of molybdenite; (**c**) chalcopyrite developing on bornite; (**d**) galena and sphalerite cut across chalcopyrite, including arsenopyrite in chalcopyrite; (**e**) gray copper developing on chalcopyrite; (**f**) interstitial magnetite was replaced by the hematite. (Grt: Garnet; Cpx: Clinopyroxene; Mol: Molybdenite; Ccp: Chalcopyrite; Br: Bornite; Sp: Sphalerite; Gn: Galena; Ars: Arsenopyrite; Qz: Quartz; Gray-Cu: Gray copper; Mag: Magnetite; Hem: Hematite).

The four stages of skarn and ore deposition are summarized in the paragenetic table (Figure 13).

	<u>C</u> ,	Metasomatic alteration and mineralization							
	Stage	Prograde	stage	Retrog	rade stage				
	Substage	Early	Late	Early	Late				
	Temperature	> 600 to 560 °C	560 to 400 °C	400 to	o <150 °C				
	Wollastonite								
	Diopside		-						
	Hedenbergite	_							
	Johannsenite								
	Andradite								
	Grandite								
	Grossular								
	Vesuvianite-(Mg)		-						
	Vesuvianite-(Fe)				-				
	Spinel								
	Scapolite								
	Humite								
	Phlogopite								
	Apatite								
	Quartz								
	Calcite								
S	Albite								
ra	K-feldspar								
Je	Amphibole								
Лin	Epidote								
2	Sphene				-				
	Muscovite								
	Chlorite								
	Pectolite								
	Fluorite								
	Scheelite								
	Molybdenite		_						
	Chalcopyrite								
	Bornite								
	Gray copper								
	Sphalerite								
	Arsenopyrite								
	Galena								
	Pyrite								
	Magnetite								
	Hematite								
	Marcasite								
			Time		<u>`</u>				
		Abundant	Loc	al	– – Trace				

Figure 13. Mineral paragenesis and ore assemblages in the skarn zones of the Azegour skarn deposit.

4.5. Fluid Inclusions Petrography and Microthermometry

4.5.1. Petrography and Classification of Fluid Inclusions

The fluid inclusion properties of the Azegour skarn deposit were investigated in garnet, pyroxene, quartz, and calcite samples obtained from both prograde and retrograde skarns. Primary and secondary fluid inclusions (FIs) were differentiated based on the criteria outlined by Roedder [75]. This study exclusively focused on the analysis of primary FIs. Based on the phases present at room temperature and microthermometric behavior, three types of primary FIs were identified: (i) liquid-rich two-phase FIs (L); (ii) vapor-rich FIs (V) have a gas/liquid ration >65%; and (iii) halite-bearing multiphase FIs (S) typically contain more daughter minerals on their ores.

The L-type FIs are abundant in all of paragenetic stages, ranging from 5 to 35 μ m in diameter. They exhibit ellipsoidal or irregular shapes in garnet, pyroxene, and quartz and rectangular shapes when observed in calcite. These inclusions are typically located along the growth zones of both the early and late stages, and they are characterized by the vapor phase comprising 5 to 40 vol.%. The L-type fluid inclusions commonly coexist with S and V types within fluid inclusion assemblages in both the prograde and retrograde skarn (Figure 14a,d,g,h).

The V-type FIs are characterized by their higher vapor ratios (RV) than the liquid phase (RV > 65%). They typically range in size from 5 to 15 μ m and exhibit elliptical and circular shapes. These inclusions are homogenized to the vapor phase and are commonly found along the growth zones of both early and late-stage quartz crystals. They may occur individually or cluster together and can coexist with the S-type and L-type fluid inclusions (Figure 14c,h).

These S-type FIs are frequently hosted within garnet, pyroxene, and quartz. They typically consist of one or more solid daughter minerals, an aqueous phase, and a vapor bubble. These inclusions exhibit irregular to negative crystal shapes and are commonly $5-35 \mu m$ in diameter. The daughter minerals often take on regular cuboid or quadrilateral shapes. Notably, pyroxene inclusions of this type tend to contain a significant abundance of solids. What distinguishes these inclusions is their high salinity, as evidenced by the presence of up to five solid daughter minerals (Figure 14f). These solid materials' morphology and optical properties suggest that the cube-shaped daughter mineral is halite, the most prevalent solid found in these fluid inclusions. Other daughter minerals include sylvite, which has more rounded edges, and certain transparent mineral daughters, that do not fully dissolve before reaching the temperature limit of the stage. (Ts > 600 °C), are observed (Figure 14b,c,e,f,h).

4.5.2. Microthermometry

In this study, a total of 111 primary fluid inclusions from various minerals and different mineralization stages were measured. These included 59 L-type inclusions, 42 S-type inclusions, and 10 V-type inclusions. The data for V-type inclusions are relatively scarce compared to the other types, primarily because this type has an indistinct phase boundary, making it challenging to observe phase transformations during the cooling and heating processes. All the data are summarized in Table 5.

Prograde Skarn Stage

Primary FIAs in garnet, pyroxene, and early quartz were selected for microthermometric measurements. L- and S-type inclusions are the most abundant, almost occupying up to 90% of all FIs. It is evident that L-type inclusions coexist with S-type inclusions within any FIAs of minerals in this stage. The eutectic temperature (Te) of all the inclusion types was between -57.2 and -30.6 °C, indicating a low eutectic due to the presence of salts other than NaCl and KCl, such as CalCl₂ or FeCl₂ [76].

L-type inclusions are observed in pyroxene, garnet, and quartz. Homogenizations to the liquid phase with gas disappearing were performed and the values are in the range of 390 °C to 460 °C for pyroxene, >600 °C for garnet, and 223 °C to >600 °C for quartz

(Table 5, Figure 15). According the temperature of final ice melting (Tm-ice), salinity values correspond to 9.7–15.2 wt% NaCl equiv. for pyroxene, 12.0–32.8 wt% NaCl equiv. for garnet, and 15.0–17.5 wt% NaCl equiv. for quartz [77].

The V-type inclusions measured in quartz of the prograde skarn exhibited ice melting temperatures of -7.2 to -1.2 °C, equivalent to salinities between 2.1 and 10.7 wt% NaCl equiv. The final homogenization temperatures ranged from 500 to >600 °C. Vapor bubbles occupied more than 95% in terms of volume ratio, and the phase boundary was hard to observe at around 550 °C. In many of these primary FIAs, V-type inclusions coexisted with S-type inclusions within the same FIA, suggesting boiling during entrapment (Table 5; Figure 15).



Figure 14. Photomicrographs of representative fluid inclusions in the Azegour skarn deposit. (**a**) A fluid inclusion assemblage including L inclusions in the garnet of the prograde skarn stage; (**b**) a typical S-type inclusion containing multiple daughter minerals in the garnet of the prograde skarn stage; (**c**) coexistence of V- and S-type in garnet; (**d**) L-type inclusions in pyroxene of the prograde skarn stage; (**e**) a typical S-type inclusion containing multiple daughter minerals in pyroxene of the prograde skarn stage; (**f**) S-type inclusion containing multiple daughter minerals in pyroxene of the prograde skarn stage; (**f**) S-type multisolid in pyroxene of the prograde skarn; (**g**) L-type inclusions in quartz of the prograde skarn stage; (**h**) coexistence of L-, V-, and S-type inclusions in quartz of the retrograde skarn stage; (**i**) L-type inclusions in calcite of the retrograde skarn stage and secondary fluid inclusions of the late calcite of the retrograde skarn.

Host Mineral	FI Type	Size (µm)	Eutectic Temperature Te (°C)	Ice-melting Temperature Tm (°C)	Halite Dissolution Temperature Td (°C)	Final Homoge- nization Temperature Th (°C)	Salinity (wt% NaCl Equivalent)
Pyroxene	L	10-30	-59.0 to -40.0	−11.2 to −6.4		390 to 460	9.7-15.2
(n = 16)	S	10-40	-78.5 to -40.0	-38.1 to -18.1	>600	>600	>73.9
Garnet	L	10–15	-84.5 to -46.5	-36.0 to -8.3		>600	12.0-32.8
(n = 19)	S	10-25	-84.2 to -46.5	-35.5 to -19.3	580 to >600	535 to >600	64.7->73.9
	L ₁	10–30	-53.0 to -45.0	-13.7 to -11.4		>600	15.4–17.5
Quartz	L ₂	10-30	-53.0 to -46.0	-13.7 to -11.4		223 to 246	15.0-16.6
(n = 48)	V	5-20	-51.3 to -35.3	-7.2 to -1.2		468.3 to >600	2.1 - 10.7
	S	15–30	-66.0 to -45.0	−31.6 to −8.2	>600	>600	>73.9
Calcite (n = 28)	L	10–15	-55.3 to -30.6	-0.6 to -8.5		160 to 358	2.0–11.9

Table 5. Summary of microthermometric data of fluid inclusions from different host minerals andstages in the Azegour skarn deposit.

The S-type inclusions in pyroxene, garnet, and quartz from the prograde skarn are represented by homogenization temperatures of 535 to >600, respectively (Table 5; Figure 15) and the corresponding salinities are 64.7 to >37.9 wt% NaCl equiv. The halite dissolution temperatures of these inclusions are higher than the vapor disappearance temperatures, and the daughter minerals also did not dissolve when reaching the final homogenization temperature.

Fluid inclusion studies in pre-ore pyroxene and garnet suggest that the initial hydrothermal solutions were characterized by notably high temperatures and salinity, resembling the composition of magmatic fluids [78–80]. Fluid inclusion studies of S-type and V-type inclusions within the same FIA in garnet and quartz were associated with scheelite mineralization, suggesting boiling during entrapment.

Retrograde Skarn Stage

FIAs in retrograde skarn (quartz and calcite) are characterized by a dominance of L-type inclusions. These inclusions consist of both liquid and vapor phases (L + V), with the vapor phase being volumetrically smaller (RV < 10%) than the liquid phase. During heating, L-type inclusions homogenize into a single liquid phase via vapor disappearance. Quartz and calcite are represented by low homogenization temperatures of 223 to 246 °C and 160 to 358 °C in the liquid phase, respectively (Table 5; Figure 15). According to the temperature of final ice melting (Tm-ice), salinity values correspond to 15.0–16.6 wt% NaCl equiv. for quartz and calcite associated with sulfide mineralization suggest that the ore-forming fluids during the retrograde stage were a mixture of magmatic and meteoric waters with a temporal increase in meteoric water content [1,81–83].





5. Discussion

5.1. Relationship between Skarn Type and the Granitoid Geochemistry

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 [84] 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 an alumina saturation index similar to the granitoids associated with Mo skarns. Granitoids associated with other types of skarns are rather intermediate between meta-aluminous and peraluminous granites. Based on Sr and Nd data from references [65], the Azegour granite is derived from a crustal-mantle source with a strong contribution from the mantle, similar to the Lyangar W-Mo and Koitash W-Mo skarn deposits [85,86]. The abundance of fluorite and Mo mineralization in the retrograde stage constitutes a significant indication of mineral deposits in the post-collisional to within-plate environment in response to asthenospheric mantle uplift. The exsolution of magmatic hydrothermal metalliferous fluids can be attributed to either a concealed Permian magma or the Azegour granite. Indirectly, the metals were derived from the mantle, as inferred from fluid-rock interactions between the ore-forming fluids and the carbonate host rock; these interactions strongly imply a relationship between these rocks. The high values of δ^{34} S measured at the Azegour skarn fall outside the field values indicating a mainly magmatic origin of sulfur in the skarn deposits [37]. Metals could also originate from these rocks, serving as additional potential sources. These conclusions are in agreement with the findings of references [34,37,42–45]. The Mo, Cu, and W deposit at Azegour in the Western High Atlas range exhibits numerous similarities with skarn deposits in Morocco (Central Morcocco and Jebilet region); they are all spatially associated with the emplacement of post-tectonic granites with ages ranging from 340 to 270 million years [87]. The Azegour deposit remains the only one with significant molybdenum concentrations (molybdenite) without any mineralogical expression of tin. This absence of tin may be attributed either to the low tin content in the source (granitic magma, host rock) or to the absence of favorable conditions for tin entrapment. The mineral assemblages and textural features of the Azegour skarn deposit are similar to those of other skarn deposits around the world; the major scheelite mineralization was formed during prograde skarn development from hydrothermal solutions dominated by magmatic fluids, and from scheelite deposition by the boiling process, as is also common in other tungsten skarn deposits such as those of King Island W [88], Nuri Cu-W-Mo [12], Kensu W-Mo [89], and Pampa de Olaen W [90]. The deposition of molybdenite in the retrograde stage is favored by reduced conditions, an increase in fS_2 , and a decrease in temperature [85,86]. According to [91], molybdenite typically precipitates at 440–360 °C, characterizing the retrograde stage.

5.2. Fluid Evolution and Mineralization Process

The mineralogical and fluid inclusion data of the Azegour skarn provide information on the type and evolution of the fluid regime in contact with the magma-carbonate rock, as well as on the temperatures of skarn formation. Petrography and microthermometry show that the homogenization temperatures and salinity of the prograde skarn are higher than retrograde skarn inclusions. In the diagram of homogenization temperature versus salinity (Figure 16), fluid inclusions associated with garnet, pyroxene, and quartz (prograde skarn stage) display high homogenization temperatures and high to low salinities (468.3 to >600 °C; 2.1 to >73.9 wt% NaCl equiv.). The major scheelite mineralization was formed during the prograde skarn development from hydrothermal solutions dominated by magmatic fluids during the boiling process. Microthermometric data indicate that boiling occurred at a temperature between 468.3 and >600 °C. After boiling, the coexisting multiphase and vapor-rich fluid inclusions showing fluid immiscibility were formed by the direct separation of the fluids from a crystallizing magma (e.g., [92]). By contrast, fluid inclusions associated with quartz-calcite-sulfide (retrograde skarn stage) record lower homogenization temperatures and low salinities (160 to 358 °C; 1.1 to 12.3 wt% NaCl equiv.). The distribution of two types of inclusions is along the trend line of fluid mixing

at the salinity–homogenization temperature (magmatic fluid), which illustrates that the ore-forming fluid took place by mixing with fluids of low temperatures and salinities (metamorphic and meteoric fluids). The different stages of hydrothermal evolution are shown in Figure 17.



Figure 16. Homogenization temperature–salinity diagram of primary fluid inclusions from different host minerals. Showing characteristics of fluid evolution in the Azegour skarn deposit.



Figure 17. Schematic genetic model showing paragenetic succussions and formation temperatures of the Azegour mineralized skarn in relation to interpreted fluid (modified from [83,93]). It also shows possible skarn formation temperatures. Qz: quartz; Kfs: K-feldspar; Pl: plagioclase; Bt: Biotite; Cal: calcite; Dol: Dolomite; Wo: wollastonite; Grt: garnet; Px:pyroxene; Sch: scheelite; Ves: vesuvianite; Amp: amphibole; Ep: epidote; Ccp: chalcopyrite; Mol: molybdenite, Py: pyrite; Mag: magnetite; Ms: muscovite; Chl: chlorite.

6. Conclusions

Based on geology, mineralogy, and fluid inclusion studies in the Azegour Mo-Cu-W deposit, the following conclusions can be drawn.

- (i) The ore deposition resulted from the interplay between fluids and the carbonate host rock. By examining mineralogical and geological characteristics, we can classify the Azegour deposit as a proximal skarn system, closely linked with the Permian granitic intrusion (Azegour granite) in terms of spatial correlation. The major and trace element contents of the Azegour pluton are generally comparable to those of the Mo skarn granitoids.
- (ii) The skarnification processes and their evolutionary trend can be divided into four stages: (Early prograde stage → Late prograde stage → Early retrograde stage → Late retrograde stage). The sulfide mineralizations are developed mainly during the retrograde phases. They exhibit an early prograde phase with dominant assemblage minerals of wollastonite, diopside, andradite, and grandite; this stage appears relatively "oxidized", transitioning to late prograde and retrograde stages, principally with grossular, hedenbergite, and hydrous silicates, respectively, which are termed "reduced" and confirmed by the presence of a small portion of subcalcic garnet (almandine) and johannsenite. These anomalies potentially signify changes in the oxygen fugacities and temperatures of the fluids involved in the mineralization process.
- (iii) Microthermometric data indicate a trend of decreasing temperatures and salinities from the early to late stages for both mineralization episodes. Fluid boiling is considered the main reason for tungsten mineralization in the prograde stage. Sulfide ores are formed as a result of the interaction/mixing between magmatic hydrothermal fluids with high temperatures and salinities released from the Azegour granite and an external fluid component, which is composed of metamorphic and meteoric fluid and characterized by low temperatures and salinities.

Author Contributions: Conceptualization, A.E.K. and M.A.; methodology, A.E.K., M.A., A.T., M.H., I.L. and E.B.; software, A.E.K. and I.L.; validation, A.E.K., M.A. and A.T.; formal analysis, A.E.K., M.A., A.T., M.H. and I.L.; investigation, A.E.K. and M.A.; resources, A.E.K., M.A. and A.T.; data curation, A.E.K. and M.A.; writing—original draft preparation, A.E.K., M.A. and I.L.; writing—review and editing, A.E.K., M.A., A.T., M.H. and E.B.; visualization, A.E.K.; supervision, A.E.K., M.A. and A.T.; project administration, A.E.K., M.A. and A.T.; funding acquisition, A.E.K., M.A., A.T. and E.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Data supporting the findings of this study are available upon request from the first author (Abdessamed El Khalile, email: a.elkhalile@edu.umi.ac.ma).

Conflicts of Interest: The authors declare no conflict of interest.

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